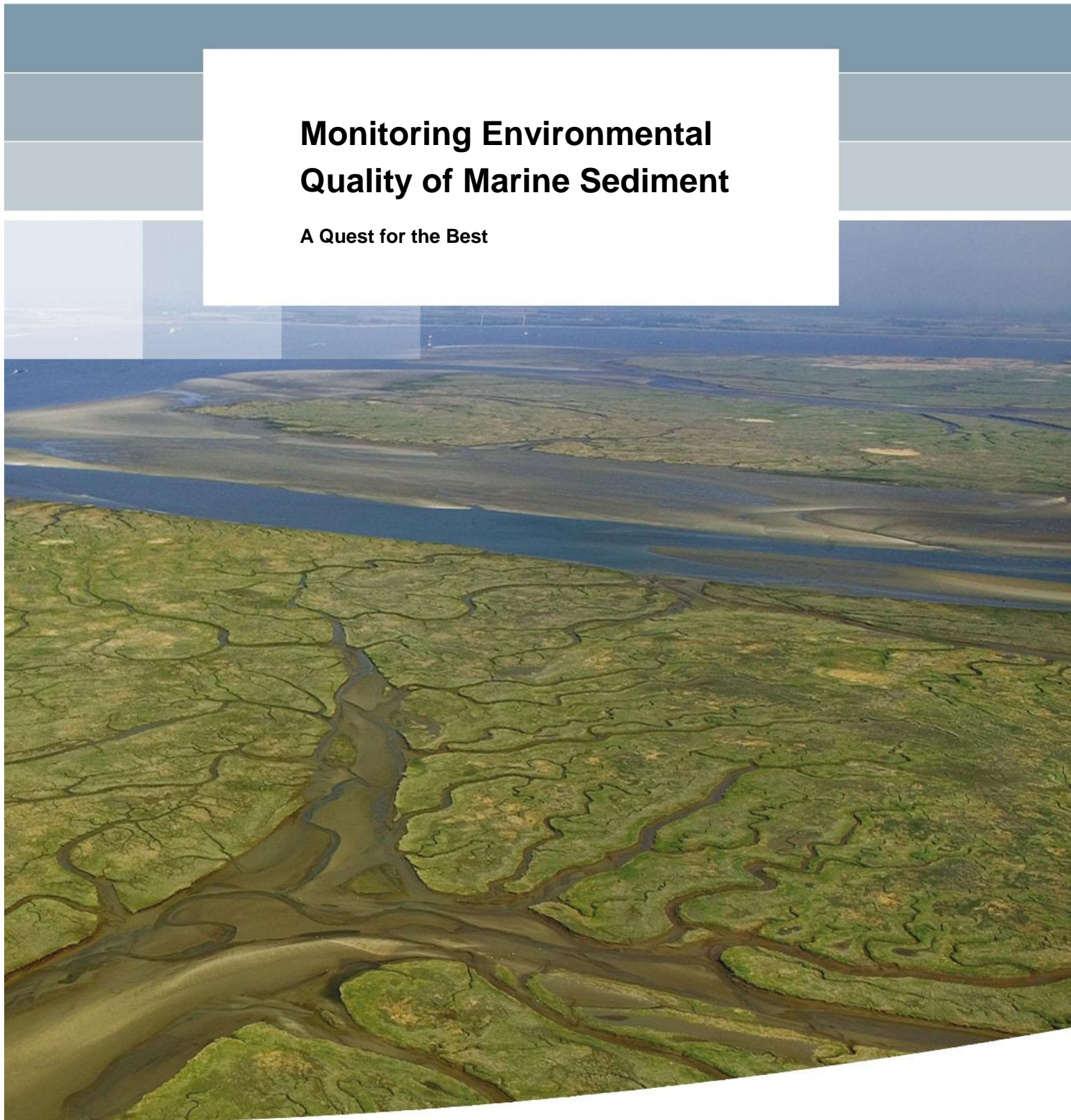Deltares
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Monitoring Environmental Quality of Marine Sediment

A Quest for the Best

Monitoring Environmental Quality of Marine Sediment

A Quest for the Best

Foppe Smedes

1209377-004

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Title
Monitoring Environmental Quality of Marine Sediment

Client	**Project**	**Reference**	**Pages**
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Water, Verkeer en Leefomgeving
Marcel Kotte
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Keywords
Equilibrium partitioning, marine sediment, hydrophobic contaminants, passive sampling, environmental quality assessment

Summary
The Netherlands has an obligation to OSPAR, and in future the MSFD, to monitor contaminants in sediments. Up till now, concentrations are determined in the particle fraction less than 63 µm, based on the fact that the contaminants of concern are concentrated in the clay and/or the organic carbon that is dominantly collected in the fine fraction. Sieved fractions <63 µm also have a more similar sample composition than total sediments improving comparability required for temporal and spatial trend monitoring. However, the properties of the sample still vary because of differences in the nature of clay minerals and organic carbon in terms of affinity for contaminants. This, together with the relative high costs associated with the laborious sieving procedures, implies the method is not the ideal approach.

In this report the possibilities are explored for improved and more efficient methods that could also be accepted as a standard in Europe. An evaluation of the present monitoring approaches revealed that robust monitoring with measured concentrations that are comparable in time and space can only be achieved if the sampled matrix has defined and constant properties; a requirement that cannot be met by any environmental matrix or compartment. A "constant sample" is only obtained by utilising an artificial "matrix" with defined and stable properties that is left to equilibrate with the environment or an environmental sample, i.e. the principle of passive sampling. Requirements for passive sampling methods in terms of sensitivity are derived from assessment criteria by conversion to corresponding concentrations in water (as freely dissolved) and material passive samplers are made from. Further the required properties of materials and approaches that need to be critically considered were discussed.

Using the requirements set for passive sampling in sediment a wide range sampling materials and methods were explored followed by a discussion that narrowed down to the applications of samplers as a coating at the inside of a bottle. The basic principle of these methods is that after adding sediment to the coated bottle under light agitation a rapid equilibration between the sediment and coating (sampler) takes place. Measured concentrations can be converted to freely dissolved or lipid basis and as such used in assessments. Further development of this simple application has the highest potential. A recognised risk is abrasion of the coating when coarse sediments are applied.

A proposal for the first development includes optimising the coating for resistance to abrasion and a trial sampling with sediments samples representing the Dutch monitoring area. Passive sampling is much less laborious than sieving fractions <63 µm but presently only applies to hydrophobic organic contaminants. Until a similar method is developed for metals sieving should continue but only one tenth of sample amounts are required. In EU, ICES and OSPAR the potential of passive sampling is recognised and the last chapter elaborates on the steps towards implementation of passive sampling methods in sediment and the progress made. Preparation of guidelines required for implementation is already part of the terms of reference of the ICES working groups.

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Title
Monitoring Environmental Quality of Marine
Sediment

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Rijkswaterstaat		1209377-004		1209377-004-ZKS-0001		57	
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Contents

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1 Summary and recommendations

1.1 Preface
This report provides an overview of the presently common methods for determining spatial and temporal trends of contaminating substances in sediment and especially its applicability for marine sediments and gives a way forward for the best available methodology. This summary includes the outcome of the evaluations and discussions and is combined with the conclusions and recommendations. At the same time it is also a reading guide for the document referring to the relevant chapters that deal with the subjects in more detail. This approach was chosen because the level of detail in the evaluation and discussion may not be relevant for all readers.

1.2 Introduction
For the spatial and trend monitoring of sediment quality under OSPAR, sediment samples are sieved and in the obtained particle fraction smaller than 63 µm concentrations are measured of the organic compounds, namely PCBs, PAHs, tributyltin, PBDEs, HCB, HCBD, and the metals Hg, Cd, Pb. Concentrations of substances are then further normalised to a set sediment composition (2.5% organic carbon or 5% Aluminium). Normalisation is a pragmatic approach that has always been under debate and applied in the absence of a better method. In addition the sieving procedure is very time consuming (and thus expensive), especially for sandy samples. The above aspects were the reason to explore alternative methods for monitoring the quality of sediment. This included equilibrium passive sampling (ex-situ sampling in the laboratory and in-situ field exposure), non-exhaustive extraction and/or kinetic methods.

1.3 Basis for quality assessment
The equilibrium partitioning theory is the basis for quality assessment but it has its imperfections as it is not able to correct properly for variability in properties of environmental matrices (Chapter 3). To obtain monitoring results that represent the environmental quality and are comparable in time and space it is necessary to measure the target substances in a constant homogeneous matrix with stable and well defined properties (3.3). Clearly, that does not apply to any natural matrix in the environment. Water contains a variable amount of suspended particulate material, biota comprises of different phases that vary with environmental and physiological conditions, and the composition of sediment is varying from sand to clay. Isolating the fine fraction of particles from sediment by sieving largely reduces the physical variability but differences in the nature of the material, i.e. organic carbon, remain and concentrations therein will only to a limited extent be proportional to the exposure level that aquatic or benthic organisms experience. When an artificial "matrix" with stable and well defined properties is equilibrated with the environment, the concentrations of chemical substances therein allow for an accurate comparison of contaminant levels in time and space. This is essentially what partition based passive sampling methods aim for.

1.4 Equilibrium partitioning and passive sampling
Passive sampling methods connect seamless to the equilibrium partitioning theory as they enable to express and compare contaminant levels in different compartments using the same basis and scale, namely the equilibrium concentration in the sampler material. This equilibrium concentration can subsequently be converted to a freely dissolved concentration, or alternatively to an equivalent concentration in a (synthetic) model lipid, typically present in adipose tissue of aquatic organisms. Both, pure water and model lipid, are defined matrices

and chemical concentrations in these matrices are proportional to chemical activity (i.e. the ratio between chemical concentration in the matrix and the matrix uptake capacity). The principle of the equilibrium passive sampling approach is outlined in chapter 4. For spatial and trend monitoring using a passive sampler having constant composition the concentrations obtained therein after equilibration with sediment could be used directly for quality assessments. However, for international comparability and quality assessments conversion to freely dissolved concentration in water or an agreed model lipid is preferred as levels in water and lipid are easily understood and accepted by the community.

1.5 Objectives and requirements

The assessment concentrations listed in MSFD Task Group 8 Report 2009 are used to set the level of sensitivity an alternative method should have. For sediment and biota the report lists background concentrations (BC); background assessment concentrations (BAC), environmental assessment concentrations (EAC) and an environmental range-low (ERL) which is the USA EPA version of the EAC. Equilibrium partitioning is used to convert these assessment criteria to corresponding freely dissolved concentrations and concentrations that a passive sampler would obtain if it was equilibrated with sediments having concentrations at BAC, EAC, or ERL level. This data represent the range of the required detection limits.

Chapter 5 further discusses the required properties of passive sampler materials used for equilibrium passive sampling. Sampler construction materials should be sufficiently permeable and uptake of substances should be by absorption (dissolution). In addition, absorption isotherms should be linear and not affected by the matrix from the compartment the sampler is exposed to. Furthermore, degradation of substances should be prevented

Methodological issues like the assessment whether depletion of a chemical from the sediment by the sampler occurred, leading to underestimation of concentrations, are also discussed. An underestimation may also occur if equilibrium in the sediment-sampler system was not attained. Both depletion and equilibrium can be assessed from the release of Performance Reference Compounds (PRCs) dosed to the samplers prior to exposure.

1.6 Evaluation of passive sampling methods

In chapter 6 the passive sampling applications are evaluated in relation to the requirements listed in chapter 5. Silicone polymer, low density polyethylene (LDPE), and polyoxymethylene (POM) all show sufficient affinity and the absorption isotherms of most hydrophobic pollutants are linear. The fastest diffusion of substances was measured in silicone polymers followed by LDPE. Diffusion in POM was extremely slow, which principally implies insufficient permeability. Saturation with fish oil had no effect on sorption of silicone polymers. This may also be expected for other materials.

Equilibrium passive sampling can also be applied with micro samplers (e.g. SPME or SBSE) that can be directly desorbed by thermal desorption for instrumental analysis. Larger samplers, as sheets or coatings are solvent extracted allowing clean-up before instrumental analysis. For both methods, exposures are mostly applied in the laboratory but also field applications are reported.

Often researchers include a verification of equilibrium by exposing samplers for different time periods but do not consider depletion of chemicals concentrations in the sediment by the sampler uptake that leads to underestimation of the results. A laboratory method where different film thicknesses are applied allows checking for both depletion and equilibrium. The use of PRCs for this purpose is rarely reported. Although equilibrium passive sampling is commonly targeted to polluted situations they all suggest sufficient sensitivity or can be potentially modified to do so.

In several investigations passive samplers were applied by inserting them to sediment in-situ in the field. In situ samplers exchange with the immediate surroundings in reasonable time

but the exchange rate decreases rapidly with the increasing distance from the sampler. It is suggested to use PRCs to correct for this non-equilibrium but the modelling is not straightforward.

Non-exhaustive extraction with Tenax focuses on a full depletion of sediment and is basically operationally defined by the exposure time and the sediment capacity-Tenax mass ratio. With air in the pores of Tenax the uptake process is not understood well. Extraction with 2-Hydoxypropyl-β-cyclodextrin (HPDC) also aims for estimating the available fraction but the yield may depend on the sediment-HPDC capacity ratio. The HPDC method has been mainly applied for sampling PAHs in polluted situations and only rarely applied for other compounds and no applications in marine areas are known.

1.7 Discussion

The potential of different passive sampling methods for the application in diffusively polluted marine areas is discussed in chapter 7. Here the practical application is also considered.

Non-exhaustive extraction using HPCD or Tenax results in concentration on sediment basis and would need to be normalised using the organic carbon content, a practice that actually should be avoided because of the variable nature of organic carbon. For the same reason conversion to a freely dissolved concentration gives a high uncertainty.

In-situ static exposures need long equilibration and application in offshore conditions is not a practical option. Alternatively static exposure in the laboratory with repositioning the sampler at set time intervals would be an option but to achieve equilibrium in acceptable time still would require very thin samplers that can easily be damaged in samples containing high percentages of sand. Thinnest samplers can be achieved by coatings on an object inserted in the sediment but a more practical application is coating the inside wall of a jar or bottle. This cannot be repositioned and shaking has shown abrasion of the coating. However repositioning an inserted sampler is effectively equal to turning or rolling the bottle to replace the sediment in "contact" with the sampler. Slowly rolling jars with a coating of few micrometres had been successful for low contaminated sandy sediments. Thicker coatings or sheet samplers (LDPE, POM or silicone polymer) are more robust towards wearing but will increase equilibrium times proportionally.

1.8 Way forward with equilibrium passive sampling

To meet the sensitivity requirement on BAC level a sampler should have a mass of not less than 100 mg. In a 2.5 or 4 L bottle this would require a coating with a film thickness of around 1 µm. Several options are listed to prevent wearing or to improve the coating strength. Procedures for checking the mass or the uptake capacity of the sampler after exposure, the application of PRCs, addition of a biocide, should be set up as part of quality assurance. If the sample needs to be liquefied to improve rolling, water collected from the sampling site should be used. Methods that can be tested to reduce the equilibrium time include the addition of a small concentration of HPCD (with an uptake capacity less than that of the sampler) or methanol. Both approaches increase solubility of organic substances in the aqueous phase and consequently increase the permeability (solubility × diffusivity) of the aqueous phase, which in turn results in higher exchange rates chemicals between sediment and sampler. The application of PRCs will detect whether depletion occurs but it is advisable to apply multi-ratio passive sampling once at different locations to characterise the sediments in terms of their sorption isotherms for substances of interest. There is an advantage in using fluorinated silicone polymers as such polymers do not swell in hexane and allow a simpler extraction compared to using acetonitrile or methanol. Fluorinated silicone polymers show similar absorption behaviour and are also resistant to mineral oil.

Conversion of concentrations in passive samplers equilibrated with sediment to lipid basis is more appropriate than freely dissolved as corrections for temperature and salinity are not necessary.

1.9 Approaches for method development and cost aspects

Based on the evaluation in this report chapter 9 describes the technical way to further develop passive sampling using coated bottles. It is proposed to first investigate different coating and glass treatments in order to tackle the risk of abrasion. Then a trial can be started with real samples representative for the Dutch monitoring area. In parallel, using samples of the trial, several conditions like agitation, exposure time and effect of HPCD will be investigated. The method will include application of PRCs as quality assurance on the exchange process. Abrasion will be checked by measuring sampler sorption from a test solution. This proposal should deliver data for a first interpretation in comparison with the present method as well as methodological developments towards a standard procedure. It should be considered to include OSPAR countries already in this stage by either supplying coated bottles or finding a common basis for cooperation.

The latter section in chapter 9 compares the running cost and investments of a passive sampling method (once developed) with the present sediment sample processing including sieving. The time for sieving an average sample (5 kg) is considerably longer that preparation of a coated bottle and starting the equilibrations. The analytical part is roughly equal for both methods. Application of passive sampling in sediments will reduce the sieving costs but since the proposed approach is not (yet) applicable for metals limited sieving may need continuation.

1.10 International perspective – Implementation

With the development and validation of the passive sampling method for robust routine application as proposed in this document the Netherlands can take an advance on the application of passive sampling in sediment in OSPAR monitoring that will likely be adopted by the Marine Strategy Framework Directive (MSFD). An ICES workshop, the Marine Chemistry and Sediment Working Groups, as well as the EU guidance (doc nr25) for sediment and monitoring have given recommendations for inclusion of passive sampling in the monitoring. The ICES WGs actually have the preparation of guidelines for passive sampling in sediment in their terms of reference. In Chapter 10 a list is given for which substances the passive sampling would apply and discusses which procedural steps are usually needed within OSPAR to implement parameters in the Coordinated Environmental Monitoring Programme. The proposed trial and development (chapter 379) will help the ICES groups moving forward and help to convince Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME) to evaluate inclusion in the Pre-CEMP.

2 Introduction

For the North Sea area Rijkswaterstaat executes the spatial and temporal monitoring of the environmental quality as a requirement from OSPAR. This includes monitoring of the metals Hg, Cd, Pb, and organic compounds like PCBs, PAHs, organotin compounds, PBDEs, HCB and HCBD. This requirement will continue under the MSFD. In contrast to inland waters where for the Water Framework Directive (WFD) the water column is the selected test compartment, OSPAR programmes in the marine area assess the environmental quality by monitoring concentrations in sediment and, in a few regions, also in biota. Firstly this is because concentrations in samples of the water column are very low as a result of the low solubility of monitored substances. Secondly, even if concentrations are measurable, they are highly variable because of the strong dependence of concentrations on the amount and nature of the suspended matter in the water column. Sediment is a sink for substances that are poorly soluble in water and also acts as a buffer for the water phase meaning that concentrations are more stable in time in sediment than in the water phase. Sediment is therefore seen as a more suitable matrix for monitoring the spatial and temporal trends of contaminant concentrations.

Actually, like concentrations in the water column depend on the amount of suspended matter, to a certain extent this also applies to the sediment, where the amount of "settled suspended matter" largely determines the concentrations. In environmental perspective sand is largely inert and can be regarded as a diluter. Consequently, concentrations in sediments also depend strongly on the sediment composition. In ICES working groups it has been debated for several decades on how to correct for this i.e. normalise. A consensus has been reached in 2004 taking into account the different methods used in the various European countries[1]. The applied method is largely based on earlier work done in the Netherlands[2]. By error propagation also an error estimation was provided that takes into account the analytical and natural variability of the parameters used to recalculate to a normalised sediment composition.

Around 1990, the Netherlands has opted for analysing contaminants and co-factors in the fraction < 63µm isolated by sieving the sediments. This resulted in a significant reduction in the sampling variation[3]. The sieving of sediment samples was highly automated by RIKZ and several aspects of the procedure were validated. Yet it remains a laborious and therefore costly procedure, which is only limitedly applied in the other OSPAR contracting parties (UK, Belgium (63µm), Germany (20µm). Sieving is of course not needed if the sediment consists almost entirely of fine material, like for instance in Norway.

Although normalisation, and especially normalisation based on concentrations measured in sieved fractions, is strongly improving comparability of environmental chemical concentrations, uncertainty remains about what the results mean in relation to the risk caused by the contaminants to the aquatic biota (bioavailability). To convert concentrations to a normalised sediment composition the contents of aluminium/lithium and organic carbon (as C) are used as being representative for clay and organic matter, respectively. These parameters are considered to be the main constituents responsible for the binding capacity for most of the substances. Such conversion based on the quantity of clay and organic matter thus improves the comparability of the data, but it does not account for the differences in the material properties. The type of clay and the composition of organic matter may vary in time and space. More soot in the organic matter can result in much more binding without proportional increase of the organic carbon content

Therefore the current method of measuring concentrations in the sieve fraction is a good practice, especially for sandy samples but has its limitations as a representative for

environmental quality in terms of bioavailability. Along with the high cost of the sieving procedure it is meaningful to explore the possibilities to quantify sediment quality with better comparability and possibly lower costs.

This document reports on an investigation of alternative methods that may comply with the requirements for temporal land spatial trend monitoring of organic contaminants in sediment. This includes equilibrium passive sampling with polymeric materials, but also non-exhaustive extraction methods using Tenax or cyclodextrin (HPDC) are evaluated. Chapter 3 discusses the application of the equilibrium partitioning theory and the chemical activity concept and shows the relation to the potential role of passive sampling. This relation is further elaborated graphically and mathematically in chapter 4. In chapter 5 a conversion of present quality standards to freely dissolved and sampler based concentrations is performed indicating the concentration range alternative methods should apply to. Here also general criteria for passive sampling materials and methodological considerations are listed. On the basis of these requirements the different methods applied in literature are then individually evaluated in chapter 6 and discussed more conclusively in chapter 7. In chapter 8 the options are suggested for developing a method suitable for sandy sediment taking all process quality assurance on board. Also improvements are suggested and pitfalls mentioned. Based on suggestions made chapter 9 proposes how to proceed with method development in a practical way and also compares cost of passive sampling versus the classical approach. The report is concluded by placing the outcome in perspective of discussions on this subject in international forum (chapter 10).

3 Basis for sediment quality assessment

3.1 Environmental quality

The objective of this document is to explore the possibilities of monitoring contaminants in sediment in order to assess the environmental quality of sediment in space and time in a comparable way. Supported by proficiency testing schemes like QAUSIMEME[4], analytical methods can be used to accurately measure concentrations of contaminants in sediment but the obtained concentration is not necessarily a reflection of the quality or risk to organisms. E.g. sediments with high or strong sorption characteristics commonly show high concentrations whereas more sandy sediments a few meters away will show much lower concentration. Organisms do not sense that difference in concentrations and will experience only one environmental exposure level of a contaminant. The suitability of a sediment monitoring method to reflect environmental quality is largely determined by how closely it can represent that level of exposure for organisms. This could also be addressed as "potential" exposure since organisms can also metabolise or regulate uptake of chemicals which can lead to higher or lower internal concentrations than would be predicted using the equilibrium partitioning approach. So at best sediment monitoring can reflect that "potential external" exposure level

3.2 Chemical activity

The concentration to uptake capacity ratio is a simple way to express chemical activity. Reichenberg and Mayer[5] suggested chemical activity as expression of the potential exposure level. This concept is also the basis for the equilibrium partitioning theory as applied by Di Toro et al[6]. The chemical activity for the water phase was defined as the ratio of freely dissolved concentration and the (sub cooled) solubility, i.e. ratio of concentration and capacity. In a system where thermodynamic equilibrium exists the chemical activity of a substance is equal in all environmental compartments. The difference in chemical activity in situations of non-equilibrium between or within environmental compartments is the driving force for diffusive transport or uptake. Chemical activity would therefore be an ideal measure to assess the environmental quality. Basically, the above concept is also the underlying reason why contaminant concentrations in sediment are commonly expressed on organic carbon basis where organic carbon content is considered to be proportional to the chemical uptake capacity. Clearly, organic matter has a variable composition and uptake properties. It can comprise various fractions of soot and other carbonaceous materials with undefined and often non-linear sorption[7] resulting in an uptake capacity that is hard to define[8,9]. Attempts have been made to develop models to characterise sorption capacity for black carbon types but without consensus[10,11,12]. In spite of the above, organic carbon based concentrations have nevertheless a better proportionality to the chemical activity than whole sediment based concentrations, although a considerable variability (uncertainty) remains as is revealed by the large variability observed in published organic carbon-water partition coefficients (K_{OC})[9,13].

Within the environment there are hardly any compartments with a distinct uptake capacity. Also biota comprise of different phases and would also include unpredictable variability if sediment quality would be determined by measuring concentrations in reference organisms (e.g. worms) equilibrated with the sediment. Such method would also suffer from difficulties confirming equilibrium and biological variability.

In the pore-water or water column contaminants are distributed between multiple phases with variable compositions (and capacities), e.g. suspended particulate matter, dissolved organic matter and freely dissolved. Only the latter, the freely dissolved phase, has a distinct and even defined uptake capacity (solubility).

The freely dissolved concentration (mostly measured through passive sampling) was identified as the key parameter to predict body residues in sediment dwelling organisms that agree well with observed values[14]. Uptake by organisms may follow different parallel routes that are all driven by a gradient in the chemical activity between environment and organism. In sediment systems where equilibrium between sediment and pore water may be assumed, the freely dissolved concentration also represents the chemical activity of the sediment while the concentration in the whole sediment does not. Consequently uptake through the freely dissolved concentration route or directly from sediment will thermodynamically both aim for the same equilibrium concentration in the organism.

3.3 Passive sampling

The above makes clear that the freely dissolved concentration is a comparable measure for quality being a well-defined phase while most environmental compartments comprise multiple and non-homogeneous phases in variable ratios. A passive sampler, mostly an organic polymer permeable for organic contaminants, is usually seen as a measuring tool but is essentially a reference phase with defined or at least constant uptake properties[15]. Provided appropriate conditions are selected, concentrations measured in passive samplers equilibrated with different sediments will directly reflect the difference in chemical activity between these sediments and basically can be used for quality assessment if quality standards were expressed as the chemical concentration in the material from which the passive sampler was constructed[16]. With predetermined sampler–water partition coefficients the concentration in the passive sampler can be converted to freely dissolved concentrations, a more accepted parameter to express exposure levels or "bio-availability" and equally proportional to the chemical activity. Moreover, equilibrium concentrations in passive samplers can be converted to equivalents in any other matrix through predetermined sampler-matrix partition coefficient. Obviously, that only makes sense for matrices with constant or defined properties so a sampler-matrix partition coefficient can be considered constant. A very relevant matrix is lipid which on one side shows quite comparable properties even for variable compositions[17] and lipid based concentrations derived from passive sampling closely reflect those that can be expected in organisms in equilibrium with the sampled medium[14,18].

4 Equilibrium partitioning and passive sampling

4.1 Model of equilibrium passive sampling

Adopting the equilibrium partitioning theory means that all phases or compartments are interconnected and in such case the environmental quality can be determined in any of them[15]. The partition coefficient between phase X (e.g. sediment, suspended matter, DOC, biota but also a passive sampler) and water, $K_{X,W}$ (L/kg), represents the ratio between the concentration in a phase X (C_X) and that in water (C_W) at equilibrium. In the ideal case when sorption isotherms are linear, this also implies that K_{XW} is the ratio between the uptake capacity in phase X (U_X in kg/kg) and the solubility in water (S_W).

$$K_{X,W} = \frac{C_X}{C_W} = \frac{U_X}{S_W}$$ (3.1)

The U_X is a kind of "solubility" in phase X and the $K_{X,W}$ represents the factor that this solubility is higher than that in water. In other words $K_{X,W}$ represents the water volume needed to dissolve the same amount of chemical as is present at equilibrium in 1 kg of phase X. Consequently, the water volume capacity (V_X) in L for m_X kg of phase X would equal:

$$V_X = m_X \, K_{X,W}$$ (3.2)

Using this water volume capacity, in Figure 4.1 a schematic representation is given how amounts of a contaminant are distributed over compartments, which are considered to be at equilibrium with each other (for clarity not all compartments are included e.g. dissolved organic matter and particulate matter are omitted). The concentration in the water (C_W) is plotted in the y-direction The height of the boxes in the figure equals the solubility (S_w) of the contaminant of interest and the length of the box basis represents the water volume capacity (V_x) of the compartment X. For water that is obviously equal to the volume of water present and for sediment V_{sed} equals $K_{sed,w} \, m_{sed}$ (L) where $K_{sed,w}$ (L/kg) is the sediment-water partition coefficient and m_{sed} (kg) the mass of sediment. In a similar way the basis length of the boxes representing the passive sampler or the lipid, equal V_p and V_{lip}, respectively.
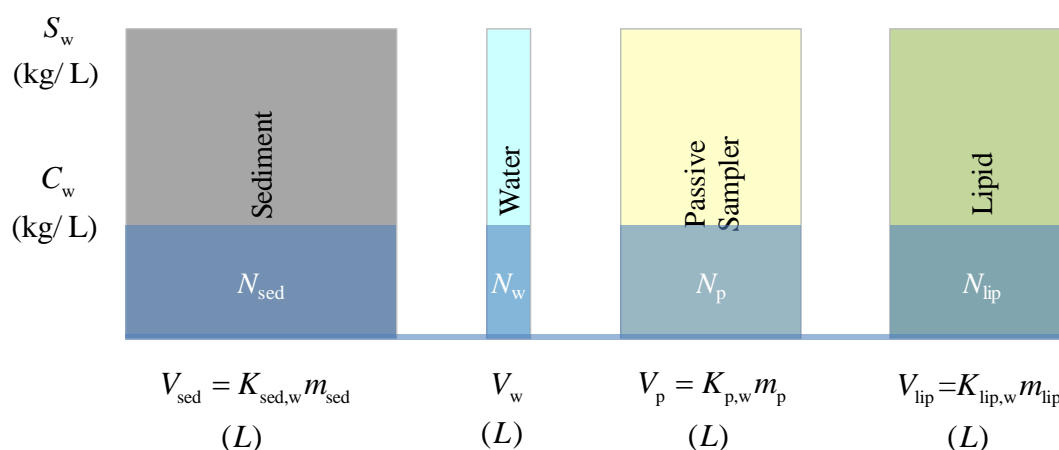
Figure 4.1   Schematic representation of the water volume capacities of some environmental phases and a passive sampler with masses m_x. The shaded blocs represent the amount (N_x) of the contaminant and C_w is the concentration in that water volume. See text for further explanation.

The modelling focuses at C_W but this can easily be converted to represent chemical activity in terms of ratio between the amount of chemical present in compartment X (N_x) and uptake

capacity ($^{max}N_x$) (For water this is C_w/S_w where S_w equals the subcooled liquid solubility of the chemical of interest). Note that the areas of the boxes in Figure 4.1 essentially represent the uptake capacities for each compartment x, and therefore N_x equals:

$$N_X = height * width = C_W * K_{X,W} m_X \tag{3.3}$$

Rewriting after substituting $K_{X,W}$ using eq 3.1 gives:

$$N_X = height * width = \frac{C_W}{S_W} * U_X m_X \tag{3.4}$$

This approach presents the y axis as a unitless parameter C_w/S_w, with a scale that ranges from 0 to 1. At low levels the C_w/S_w or $N_x/(U_x m_x)$ are equal to the chemical activity (α) and directly represent the level of contamination by the chemical of interest in the environment. Chemical activity α is, besides unit less, also independent of temperature. Of course S_w or U_x applied for the calculation should be valid at the temperature at which C_w or N_x were measured.

4.2 Evaluation

Contaminant fractions in the sediment that do not or extremely slowly interact with the water phase[19,20] present pools that are not available for mobilisation to water phase and thus are difficult to place into Figure 4.1. They cannot be translated to a water volume capacity since the unavailability implies an infinitely high $K_{sed,w}$ value. For PAHs these unavailable pools can often comprise over 80% of the concentration present in the sediment[20]. This fraction is likely contained inside material that originates from the process of incineration during which PAHs have been locked inside the particles. In such state they are virtually unavailable for release to the water phase. Equilibrium passive sampling gives a measure for environmental quality without requiring the knowledge of the size of available and unavailable pools or sediment composition.

Expressing environmental quality as α would greatly simplify assessments and specially integrated assessments since a direct comparison of levels between compartments is possible[21]. Also quality criteria could basically be set equal for all equilibrating compartments.

The modelling above is based on known scientifically sound equilibrium partitioning theory that is here presented in an alternative way to stress and explain that monitoring should, in addition to the measurement of concentrations, also consider the chemical uptake capacities of the compartment, matrix or phase measured.

The model clearly shows that sediment pore water concentration C_w can very well be estimated by equilibrating passive samplers with the sediment. For estimating C_w sampler water partition coefficients must be known when comparing to quality criteria. In the case of spatial or temporal monitoring it is only essential that the passive sampler matrix is constant to assure comparison. In practice recalculation to C_w (or alternatively to model lipid basis) is preferable to ensure comparability because different researchers/laboratories/countries may use different materials. Also it is expected that in future other or better passive sampler materials may be developed.

5 Objectives and requirements

5.1 Objectives

An alternative method for monitoring contaminants in sediment must perform equally sensitive (in terms of method detection limit) as presently applied methods and allow comparison with set quality criteria. For compounds measured in sediment often no quality standards exist for the free dissolved concentration in sediment pore water. However, application of methods to derive the standards expressed as concentration in sediment allows also extraction of quality standards expressed as C_w that will give an equal level of protection. These can often also be extracted from biota standards as well as both can be converted to lipid based concentrations. Relations between organic carbon and lipid based concentrations in sediment and biota, respectively, have also been used to convert environmental assessment criteria (EAC) from sediment to biota[22]. This approach can be used to set criteria for alternative sediment monitoring methods in terms of detection or quantification limits.

5.2 Required detection limits

Performance criteria for passive sampling methods to assess sediment quality can be derived from existing quality standards. Proposed quality standards for sediment and biota are listed in the MSFD Task Group 8 Report[22], equal to those applied by OSPAR. These are Background Concentrations (BC); Background Assessment Concentrations (BAC), Environmental Assessment Concentrations (EAC) and, only for sediment, an Environmental Range-Low (ERL), which is the USA EPA version of the EAC.

For six organic substances (representing all) quality standards for sediment and biota were extracted. These were converted to OC and lipid based concentrations for sediment and biota, respectively, and further recalculated to C_w using $K_{oc,w}$ and $K_{lip,w}$, both being approximated by K_{ow}. In the next step from the C_w the concentration in passive sampler material was calculated using the available $K_{p,w}$ values. Here $K_{p,w}$ values of the Altesil silicone polymer were used as representative for all PDMS type samplers acknowledging about a factor 2 variability of $K_{p,w}$ between various silicone polymer materials..

The data are collected in Appendix A. The table shows that the magnitude of BAC values for C_w derived from sediment criteria is in the low ng/L range for PAHs and in the low pg/L range for PCBs, respectively. Note that BACs are threshold concentrations for which it is, taking into account analytical and sampling variability, technically possible to prove that concentrations at the sampled station are below that threshold with 90% confidence. BACs were developed to assess whether the OSPAR goal "reduction of pollution to background levels" is achieved and does not relate to health risk. Consequently, BACs are not related to EACs, which intend to represent levels at which biological effects are unlikely. EAC values are both lower (benz[a]anthracene) than BAC as well as higher for some compounds (fluoranthene and benz[a]pyrene). For PCBs EACs are higher than BAC with PCB118 still as low as 4 pg/L. Because for most substances $K_{oc,w}$, K_{ow} and $K_{p,w}$ are of the same order of magnitude a recalculation to sampler based concentrations gives results of the same magnitude as OC and lipid based values. Because the sampler based concentrations are most relevant these are extracted Appendix A and also listed in Table 5.1.

Sampler based concentrations basically represent quality standards in µg/kg sampler material but of course are not intended as such. The levels are however useful to a priori assess applicability of considered passive sampling methods in terms of quantification limits. Table 5.1 shows that for checking compliance with BACs sampler based concentrations of less than 100 and 2 ng/g need to be quantifiable for PAHs and PCBs, respectively. For compliance with

EACs this level may be about a factor 10-20 higher, except for benz[a]anthracene and PCB118, for which the EACs are set very low; for benz[a]anthracene even considerably lower than the BAC. For OSPAR goals the BACs are relevant while for the MSFD the levels of the EACs will be leading. Since BAC levels partly include state of the art analytical performance it is rational to expect that new methodology has equal or better performance and the BAC requirements will be used as the primary criterion for sensitivity, i.e. LODs around100 and 2 ng/g for PAHs and PCBs, respectively.

Table 5.1 Sampler (Altesil) based concentrations (µg/kg) corresponding to quality standards set for sediment and biota.

Sampler based (n/g)	Derived from sediment			Derived from biota	
	BAC	EAC	ERL[a]	BAC	EAC
Fluoranthene	370	2500	7500	54	540
Benz[a]anthracene	166	15	3300	19	420
Benz[a]pyrene	540	11300	9800	20	5400
PCB 52	4	102 [b]		1.9	102[b]
PCB 118	3	10 [b]		5	10 [b]
PCB 153	5	990[b]		1-16	990[b]

a) The ER-Low (ERL) value is the USA version of the EAC

b) As EAC biota was estimated from EAC-sediment using OC-lipid BASF=1 sampler based results become equal.

5.3 Passive sampler properties

A number of properties are important for polymer materials to be effective partition passive samplers.

- Material must be attractive for target substances to obtain sufficiently higher concentrations in the sampler compared to the sampled medium.
- The uptake should be based on absorption, substances dissolve in the sampler material, and not only, or dominantly, adsorb to the material surface.
- Diffusion of the substances of interest in the sampler material should be sufficiently high so the permeability of the sampler material for compounds of interest is not limiting for the uptake process.
- The partitioning between sampler and sample medium should follow linear isotherms.
- The sampler or properties of material should not be affected by the sample.

5.4 Methodological requirements

5.4.1 Depletion

For the concentration in the passive sampler to be representative for levels in the sampled medium it is important that the concentration in the sampled medium does not largely change because of uptake by the sampler. When the sampler depletes the sample the result underestimates the contaminant levels in the sample. An a priori estimation of the required maximum sampler mass can be made by comparing the water volume capacity of the sampler in comparison to that expected in the investigated sample[23]. Both the appropriate sampler and the sample size can be selected to assure that the water volume capacity of the sample is more than10 times higher than that of the sampler:

$$\frac{V_{sed}}{V_P} = \frac{K_{OC}\, f_{OC}\, m_{sed}}{K_{P,W}\, m_P} > 10 \qquad\qquad 4.1$$

See section 4 for explanation of the symbols. The criterion V_{sed}/V_P >10 limits the depletion to 10% and is therefore a minimum requirement, but where possible a larger ratio (e.g. 50) is preferable[23]. This pre-estimation of the depletion requires an estimate of the organic carbon content and the K_{OC} value. The accurate value of the latter will likely not be available and mostly the K_{OW} value needs to be used as a surrogate of K_{OC}. Although for available portions bound by partitioning mechanism in the sediment the assumption $K_{oc} \approx K_{ow}$ is generally acceptable, large deviations in specific situations cannot be excluded and any passive sampling procedure needs additional measures to confirm that sediment depletion did not occur. One way is performing multiple equilibrations of sampler with sediment with different ratios of V_{sed}/V_p that should result in equal concentrations in the sampler[24]. Alternatively, similarly to procedures applied for sampling in water performance reference compounds (PRCs) can be added to the samplers. A complete release of a PRC from the sampler after equilibration with sediment will confirm that V_p is insignificant compared to V_{sed}. The most critical substances are those for which the $K_{p,w}$ value is much larger than K_{oc} or K_{ow}.
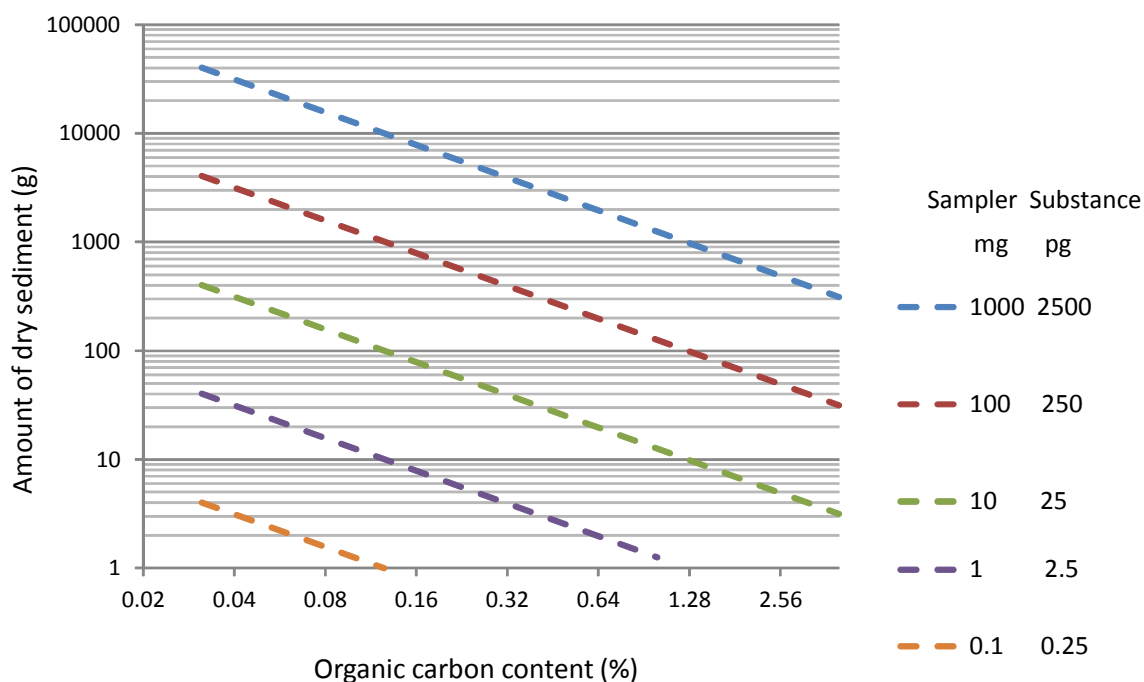
Figure 5.1   Indication of the amount of sediment (g dw) required in relation to the organic carbon content for different sampler sizes (mg) in order to avoid depletion (V_{sed}/V_p =20) of the system for PCB153. The legend shows the sampler size corresponding to the line (left-hand number) and the amount of pg PCB153 that can be expected to be accumulated in the sampler for sediment concentrations at the level of the BAC (right-hand number).

5.4.2   Equilibrium
The uptake of a substance by a passive sampler from a sample is driven by the chemical activity gradient between the both phases[15]. The transport is controlled by the diffusion of substances through a water boundary layer between the aqueous sample medium and the sampler. This process is similar to passive sampling of water and the uptake rate can also be expressed in a virtual extracted water volume per time unit; i.e. sampling rate in L/d. Consequently, the time to attain equilibrium increases with increasing hydrophobicity as the

water volume capacity ($m_p \times K_{p,w}$) of the sampler is much higher for hydrophobic substances and more "water" needs to be extracted, which in turn requires a longer time. Because the sampling rate is proportional to the surface area and the water volume capacity is proportional to the mass of the sampler, equilibrium is attained faster for samplers with high surface to mass ratios, i.e. thin films. Sampling rates are also higher when the thickness of the water boundary layer is reduced by agitation. Also, high suspension densities increase mass transfer because the particle content in the water boundary layer is higher, which effectively reduces the diffusion distance for uptake[20]. In exposure setups where samplers are fixed in a medium under agitation exchange is more efficient than in those where the sampler is freely suspended. This is because the relative velocity of the sampler against suspended particles is slower when the sampler moves with the suspension. .

Note that release rates of sediment are not considered to be relevant for the equilibration time. Firstly, considering the ideal non-depletive situation only a very small portion of the amount of substance in the sediment is extracted by the sampler. Secondly, assuming the water boundary also controls release from sediment the total surface area of the sediment particles will surmount that of the sampler. This is confirmed by non-exhaustive extraction methods like Tenax which extract in about 6 hours a much larger fraction than is absorbed by an equilibrium passive sampler.

Equilibrium can be confirmed by recording the uptake kinetics to the sampler until equal concentrations are observed with substantially increasing incubation time. It has been reported that equilibration times are reduced under depletive conditions[20]. With V_{sed}/V_p as low as unity equilibration can be about ten times faster than at non depletive conditions because the large decrease of the concentration in the sample assists the equilibrium attainment. In other words, under depletive conditions the sampler requires lower water volume to be extracted to equilibrate with sediment[20]. Therefore, reported equilibrium times that are not accompanied by confirmation of negligible depletion should be considered with caution. The application of the so called 5% rule, i.e. the amount of substance in the sampler is < 5% of that in the sediment, is not entirely adequate since only a small portion of the substance in the sediment may be available for exchange. If such available portion is e.g. 10%, 5% on the sampler still causes a substantial (factor 2) depletion.

A better approach is the method using different film thicknesses confirming non-depletive sampling[24] that can also confirms whether equilibrium has been attained because a thicker film requires longer equilibration time. Equal concentrations in samplers with various film thicknesses confirm equilibrium while in the case of slightly lower results for the thicker film modelling can also can confirm equilibrium for the thinner film, provided the deviation is not caused by depletion, i.e criteria in eq 4.1 are widely met.

Also when PRCs were applied in the sampler a complete PRC dissipation confirms not only absence of depletion but also confirms equilibrium. Again, it is the group of most hydrophobic substances that are most critical. When using several PRCs distributed over a wide hydrophobicity range a plot of the retained fraction versus $K_{p,w}$ will reveal up to which hydrophobicity equilibrium may be assumed. Residual fractions of PRCs in the sampler after exposure which are significantly different from zero but do not increase with the increasing PRC hydrophobicity indicate that the sampler capacity was too large and depletion has occurred. Correction for depletion using the PRC release is difficult as that would require the ratio between K_{oc} and $K_{p,w}$ to be substance independent, which is in general not the case. However, approximations can be made.

5.4.3 Degradation

To assure equilibrium is attained for all target substances extended incubation times (>14 days) under agitation are needed. Partial degradation of sensitive target substances may occur and addition of biocides (sodium azide or mercury chloride) to prevent this seems prerequisite. Presently no simple systems are known that allow monitoring whether degradation took place. PRCs cannot be used because they are supposed to be entirely released from the sampler and there is no way to assess whether degradation played a role in that.

5.4.4 Wearing

It is relevant to confirm sampler mass after incubation as abrasion may occur during agitation with the sediment suspension. Especially for thin film coated bottles with sandy samples weighing is not always accurate as the wearing of the sampler or the usually heavy bottle is not distinguishable. Alternatively, the mass can be confirmed or estimated from the uptake of a test substance from a solution as is mentioned later (6.7.1).

6 Passive sampling methods for organic compounds

6.1 Type of polymers used

The larger passive samplers are exposed to larger amounts of sediment in the laboratory but also can be applied directly in the field. After exposure/equilibration the samplers are extracted using organic solvents, which is followed by clean-up, substance group separations and various analyses in the fractionated extracts. Provided the sampler had sufficient capacity the extract can also be applied in toxicity experiments, directly or through passive (re-)dosing. A recent review showed that the polymeric materials commonly applied for passive sampling in water are also used for investigations with sediment[25]. These are semipermeable membrane devices (SPMD), low density polyethylene (LDPE), polydimethylsiloxane, (PDMS) or different forms of silicone rubber (SR), polyoxymethylene (POM) and ethylene vinyl acetate copolymer (EVA). The SPMD and EVA occur less often in literature. The SPMDs are difficult to use in agitated systems because they are rather vulnerable by abrasion and due to the high capacity also have long equilibration times. Moreover, SPMDs have no benefits compared to using only LDPE[26]. EVA is applied as a very thin film (<1µm) in small vials[27]. Although application with larger capacities would be possible they were not found in literature.

Samplers made from LDPE are the most frequently used and available in thicknesses down to 25 µm while 70-80 µm is most commonly applied. POM was introduced in 2001 for investigating sorption to soot like materials that would not stick to this material[28] but POM was also widely used with sediments. Besides the application of silicone in the form of thin film coatings (e.g. in SPME or SBSE) PDMS or silicone rubber can also be used as sheet material and in that form it is very robust and can be applied under strong agitation conditions. The minimum sheet thickness that can be commercially obtained is 100µm. Thinner sheets would be difficult to handle. Next to outside surface coating (SPME and SBSE) silicone based polymers can also be coated on the inside wall of glass jars with thicknesses of 10 µm[29] and down to 2 µm**[24]**.

6.2 Polymer properties.

The polymers above were all selected on the basis of meeting the criteria listed in section 5.3. All materials have *affinities* for hydrophobic substances not largely different from OC or lipid and uptake is based on *absorption* or dissolution, what is the case with almost any organic polymer, but clearly demonstrated for silicone polymer[30]. Absorption also implies that a substance will be released from sampler when it is absent or below the corresponding equilibrium concentration in the exposure medium. Thus the exchange process is isotropic[31], i.e. chemical uptake and release rate constants are equal. Absorption properties of a polymer may not come to an effect if diffusion into the polymer is extremely slow (see below). Measurements to confirm *linearity* of absorption were reported for POM[28] and silicone polymer[32,33] but evidence has not been found in the literature for LDPE. There is however little reason to doubt on linearity for LDPE and this was no point of evaluation in a recent review[34].

6.3 Diffusion

Diffusion of hydrophobic substances like PCBs and PAHs was studied for all three above mentioned materials. Diffusion coefficients of these hydrophobic substances in silicone polymers were by far the highest, followed by those in LDPE being about two to three orders of magnitude lower[35]. Data for diffusion coefficients for POM are only available for phenanthrene and pyrene with a log D_{POM} averaging -14 m^2/s[36]. In comparison log D values

measured in LDPE and silicone polymer were -12.6 and -10.4, respectively[35]. The low diffusion coefficients found in POM are in agreement the maximum log D values reported by Rusina et al[37]. It is not clear whether the slow diffusion is the cause of the reported film thickness-dependent POM-water partition coefficients [32]. For sampling of hydrophobic substance as PCBs and PAHs in water uptake rates will likely never be impeded using silicone polymer[31,37] and only for less hydrophobic substances using LDPE[34,37]. For POM, however, the diffusion in the polymer should be seriously considered as a factor limiting the chemical uptake[38].

6.4 Sample matrix influence

The possible influence of sample matrix was investigated for silicone polymer by simultaneous headspace dosing of coated fibres that were equilibrated with the respective matrices prior to the headspace dosing[39]. Matrices investigated were sediment, soil, humic and fulvic acids different types of fat containing foodstuff and aqueous biota including fish oil. Uptakes of test substances did not differ more than 10% from the non-exposed control with the samplers exposed to lipid containing matrices all showing deviations on the high end, possibly caused by residual lipid remaining at the surface after exposure. Such investigations were not found for LDPE or POM but it's likely that for these polymers a matrix effect will also be absent, what will certainly be the case for POM because of its more closed structure. Olive oil (mainly triolein) diffuses rather rapidly in SR and LDPE arriving to saturated concentrations of 5 and 20 mg/g, respectively. Such concentration, however, did not significantly affect the absorption properties of the polymers for the hydrophobic target substances[40]. One relevant matrix not investigated in the research above is mineral oil for which it is known that it can cause severe swelling of silicone polymers (except fluorinated ones) and will likely also affect properties of LDPE. This is certainly an issue important for measurements in oil spill areas with nonaqueous phase liquid present in the sediment. Author`s personal experience with sediments heavily contaminated with mineral oil (~10%) showed up to 20% weight increase of the silicone polymer samplers..

6.5 Influence of applied methodology

Laboratory applications of passive sampling in sediment are basically all following similar methodology. A sampler is exposed to sediment under some form of agitation for a period of time followed by analysis for the content of substances sorbed by the sampler. Variations include sampler type, size, thickness, sampler-sediment ratios and different degrees of agitation. Provided $K_{p,w}$ values are accurate, and when conditions of equilibrium and negligible depletion are fulfilled, theoretically all obtained results should be comparable.

6.5.1 Equilibrium and depletion

Time to attain equilibrium is often initially tested but a comparison between different conditions applied needs considering the depletion level next to sampler dimensions and properties. The depletion level can generally not be estimated in advance as the water volume capacity of the sediment ($V_{sed}=m_{sed}K_D$) is unknown. Why equilibrium is attained faster in depletive situation can be explained using the presentation form used in Figure 6.1 (similar to Figure 4.1). Here a situation of negligible depletion (A) and one with severe depletion (B) are displayed. Both sediment and sampler are expressed in their water volume capacity (V_{sed} and V_p in L) and the connection represents the exchange rate that is governed by a diffusion process and therefore can be expressed as a sampling rate of volume per time unit. Assuming no limitations by polymer diffusion and sediment release rate this sampling rate is only related to the surface area of the sampler and the dynamics in the system, which are usually constant. When V_{sed} is infinitely large the water volume of V_p need to be extracted by the sampler to attain equilibrium. On the other hand when V_p is twice as large as V_{sed} only a

water volume equal to one third of V_p needs to be extracted for equilibration. This requires much shorter time than in the infinite situation since the sampling rate is the same in both cases. Extending this further with a V_{sed} ten times smaller than V_p a volume about equal to 90% of the that capacity and only a volume of 10% of the sampler's water volume capacity need to be extracted, which results in a ten times shorter equilibrium time compared to negligible depletion conditions. Due to the limited surface area of the passive samplers compared to sediment it is always the sampler that controls the exchange rate, except maybe when the amount of sediment becomes unrealistically small. Note that only the bio-accessible or releasable portion takes part in the passive sampling process and full depletion would mean that this portion is extracted while still a non-accessible portion may remain in the sediment.
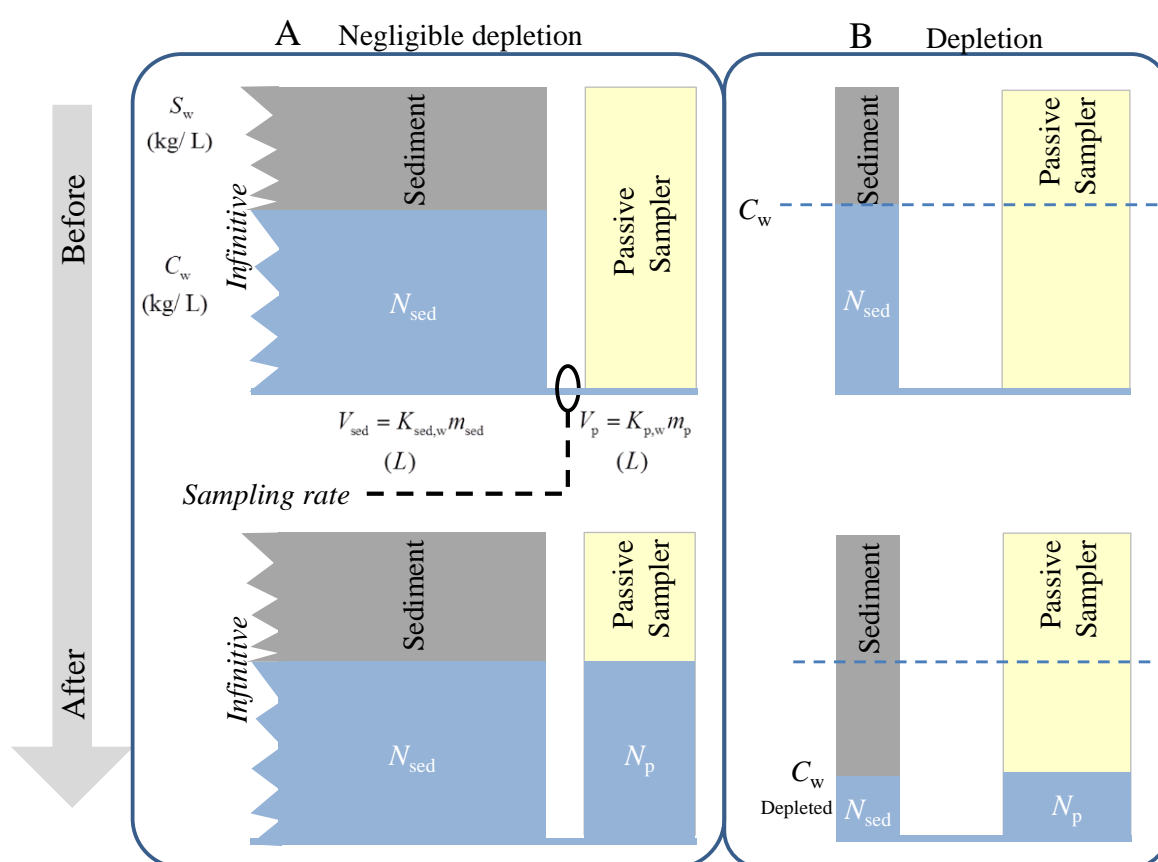
Figure 6.1   Distribution of a compound after equilibration for (A) a situation of negligible depletion and (B) severe depletion when the sampler-sediment capacity ratio is large. The upper graphs show the situation at time is zero and the bottom graphs after equilibration..

6.5.2   Multi-ratio equilibrium passive sampling.

To evaluate the different applications of passive sampling it is illustrative to firstly discuss the recently published multiple phase-ratio passive sampling (MR-PS)**Error! Bookmark not defined.**. This ethod is based on the construction of a release isotherm of compounds from sediment by plotting the equilibrium concentration of a chemical in pore water C_w versus the residual concentration in the sediment from exposures using largely varying sediment-sampler ratios. The different ratios cause different levels of compound depletion from sediment and consequently different final C_w's and different portions extracted from the sediment. An example for benzo(a)pyrene in sediment from the Wadden Sea area is given in Figure 6.2 panel A. At the x-axis the right hand arrow indicates the total concentration in the sediment as

determined by soxhlet extraction. The y-axis represents the equilibrium C_w and data clearly show that the estimated C_w's decrease with sediment-sampler ratio that ranges from 30 for the highest and 1 for the lowest observed Cw. The capacity ratio following equation 4.1 ranged from 12 to 0.4.

Multi ratio passive sampling also supplies a few more informative parameters. Extrapolating the regression line in Figure 6.2 panel A to the x-axis gives an estimate of the accessible concentration in the sediment, defined by the authors as the concentration that needs to be extracted/released from the sediment for the C_w to approach zero. Consequently, also the inaccessible portion of a substance in the sediment can be estimated. The slope of the line equals the reciprocal value of the sediment-water partition coefficient (K_D) for only the accessible portion of the substance in sediment.

Understanding the relation between C_w, C_{sed} and the effect of depletion allows placing the different approaches applying a single sediment-sampler ratio in comparative perspective as is depicted in panel A of Figure 6.2. The upper end represents the ideal situation of negligible depletion where estimated C_w is not affected by uptake of the passive sampler. Lower down the line the C_w is affected by severe depletion giving a biased result if a single exposure was performed. Unless the K_D of the accessible portion (and consequently V_p) is known, no correction is feasible. A bias remains if extrapolation using a regression line through the origin is used to correct for the amount depleted from the sediment. Sediment-sampler ratios lower than 1 or capacity ratios <0.2 will in most case be more similar to a non-exhaustive extraction (Tenax of HPDC see 6.8).
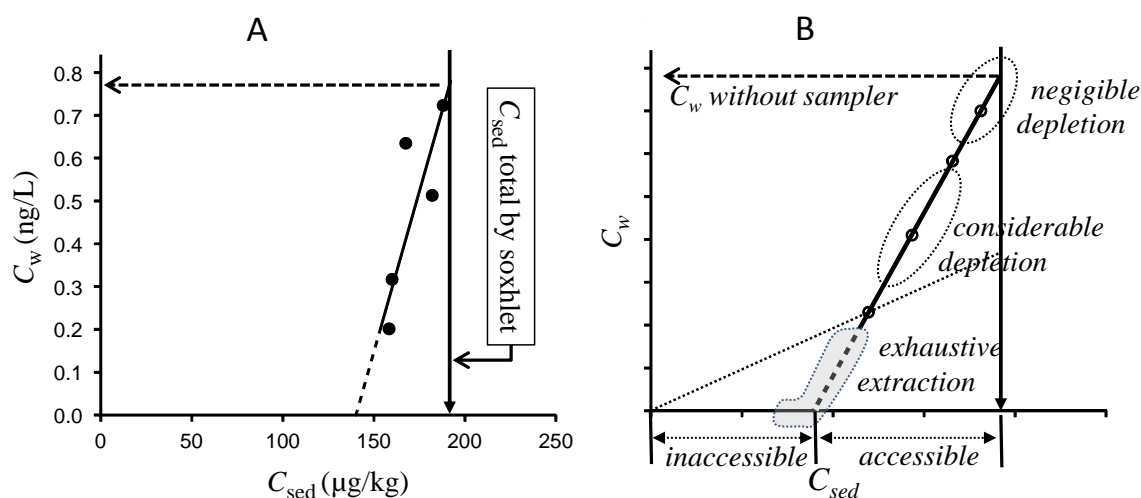
Figure 6.2   Results of multi ratio passive sampling equilibrating sediment and sampler at different ratios. The x-axis represents the residual concentration in the sediment and the y-axis is the Cw, both after exposure. Panel A show measurements in sediment from the Wadden Sea area. Panel B indicates the where different methodologies should be placed.

6.6   Micro sorptive equilibrium passive sampling.

For micro equilibrium passive sampling methods the samplers are very small and the whole amount of sorbed substances is transferred to the actual instrumental analysis. The advantages include high sensitivity and little use of solvents. Often thermal desorption is applied for the transfer of analytes from the sampler to the gas chromatographic separation. Micro samplers are rather small, sometimes fragile, and therefore commonly applied in the laboratory and rarely in the field. Another aspect is that no clean-up or pre-separation in target groups is possible. Analysis cannot be repeated unless multiple samplers are exposed

in parallel. For analysis of a wide range of substances multiple parallel exposures are inevitable because different analysis or instruments will be involved.

6.6.1 Solid phase micro extraction

Solid phase micro extraction (SPME)[41] technique is based on the use of a thin glass fibre (~0.5 mm diameter) coated with an organic polymer with thicknesses ranging from 7 to 100 µm. Most common polymers used are PDMS and polyacrylate. After exposure to the sample the SPME fibre is placed in the injection port of a GC system where the analytes are thermally desorbed and re-concentrated on the analytical column, with or without cooling the trapping area, depending on the volatility of the analytes. After that analyte separation and analysis is performed the same way as is used when liquid sample extract is injected. Extensive literature is available on the application of this method[42] while the scientific basis for use in quality assessment is also discussed[15].

SPME is frequently used to measure concentration in water samples or their headspace. The commercially available syringe-type of SPMEs have a coated fibre of 1 cm length with a phase volume of 0.05-0.5 µL with 7-100 µm coating thickness. For exposure in sediment PDMS coated optic fibres (15µm film and 10µL/m) custom cut in appropriate sizes were successfully applied for estimating free dissolved concentrations in pore water of Ketelmeer sediments[23]. With the help of agitation the equilibration time was found around 20 days for e.g. PCB153. Also equilibrium times as short as two days from Benzo(ghi)perylene were reported[32]. Sampler based LODs were around 10 ng/g. Later application of this method using an injection system based on an automated liner exchange system (ALEX) where the fibre was placed in that liner reported LODs to be less than 2 ng/g and LOQs ranging from 3-9 ng/g[43]. Another interesting issue in this paper is the application of in-situ exposure of coated fibres by inserting them in a messing protective housing in the sediment. The authors reported that a static exposure resulted in equilibrium for PAH and PCBs in about 20 and 70 days, respectively. This conclusion cannot likely be generalised as for a 30µm coating to obtain equilibrium about half a cm sediment around the sampler is involved (assuming 2% OC). Earlier work where the same authors demonstrated existence of strong gradients in pore water over cm's distance in cores of deposited sediment indicating a much slower transport[44]. Application of PRCs in the procedure will rapidly confirm either one or the other.

6.6.2 Stir bar sorptive extraction

Stir bar sorptive extraction[a] (SBSE or Twister) works in many aspects the same way as SPME does. A SBSE is a small 1 or 2 cm glass enclosed magnetic stir bar coated with a PDMS layer on the outside. Automatic thermal desorption units (TDU) coupled to a programmable temperature vaporiser inlet (cryo trap) are available for transferring the compounds to GC instrumental analysis. The thickness of the PDMS layer is either 0.5 or 1 mm resulting in phase volumes ranging from 50-200 µL[45], considerably higher than applied in SPME. This results in higher sensitivity of analysis in the many cases where capacity matters. An SBSE is dominantly used to perform an exhaustive extraction of a selected sample volume assisted by stirring. When thermal desorption of analytes is not possible because of their low volatility the SBSE can also be extracted with solvents and because of the large capacity concentrations of substances in the extract may still be sufficiently high for analysis and also allow repeated analyses. Few applications of SBSE as *in*-situ passive sampler in water[46,47] were found in literature but none was found where the SBSE was applied as equilibrium passive sampler in sediment suspensions. Severe wearing during the high speed stirring may prevent the use with sediments while also the rather thick films would require long exposures. Nevertheless the "medium" micro passive sampling of sediments

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[a] *The SBSE is applied as a micro sampler but has phase volume similar to the macro samplers below*

followed by thermal desorption would be an interesting approach if it was adapted to circumvent the above mentioned drawbacks.

6.7 Macro sorptive equilibrium passive sampling

6.7.1 Silicone polymers

Except for the multi ratio method above that was actually already performed in 2001, silicone polymers in sheet form were not often applied. Instead silicone polymers were applied as coatings on the walls of bottles[29,48] or vials[24], which resulted in faster equilibrium, i.e. 5 days for PAHs. The first wide use of coated bottles was reported in a survey and intercalibration exercise where 13 laboratories participated and together performed sampling at about 30 marine coastal stations[48]. For the survey aspect of the exercise all samplers were analysed in one laboratory. For the exposure amber bottles (1 L) were coated with 300mg silicone polymer resulting in a film thickness of around 8 μm. A range of PRCs was spiked to the sampler before it was sent to the participants. At basically all stations the target compounds (PCBs and PAHs) were absorbed by the samplers in quantifiable amounts (2-200ng). Incomplete release of PRCs indicated whether depletion had occurred or when equilibrium was not attained for the most hydrophobic substances. The use of coated jars resulted in very easy and practical procedures that could be applied by participating laboratories. The procedure involved just addition of about half a litre wet sediment into the coated bottle, which was then liquefied with a small volume of water collected at the sampling site and shaken for four weeks. After exposure the sediment was removed and the bottle was quickly rinsed, the water was swung out as much as possible and the analytes were extracted with acetonitrile. The extract was then processed and analysed following procedures available for sediment or biota analysis. Exposure was performed in two parallel samples. One sample was analysed by the participant laboratory, the other was sent for analysis to a central laboratory that processed samples from all sampling sites. The results participating laboratories obtained in a parallel exposed coated bottle agreed with the central laboratory analysing the replicate sampler for survey purposes within a factor 1.5 and often better for higher concentrations[49]. Pure sandy samples showed often depletion and would require lower sampler mass. Due to the intensive shaking selected in this exercise abrasion of the film was observed for samples that contained very sandy sediments. So after the extraction the residual amount of polymer was measured from the uptake of phenanthrene and fluoranthene from a methanolic standard solution. Weighing was not a good measure as it sometimes indicated a negative mass. Out of 25 in two cases ~25% and two cases ~50% of the sampler material was lost.

Other examples of the application of silicone polymer coatings include the use to estimate chemical activity in contaminated soil[24]. Here equilibrations with different film thicknesses were applied to confirm conditions of negligible depletion and equilibrium (see also 5.4).

The coated jar method with film thickness ranging from 2-8 μm and 14 days incubation is now frequently used in different areas[50,51] and demonstrated excellent sensitivity at femtogram/L level as freely dissolved concentration[52]. A paper on the application equilibrium sampling for measuring freely dissolved concentration of PCBs in sediments from the river Elbe is in preparation[53]. Furthermore the German Federal Institute of Hydrology has monitored sediments from major German rivers as well as around a dumpsite for dredged material in the North Sea (German Bight) using the coated jar method and more work is on-going. Their experience learned that depending on the sediment characteristics depletion and non-equilibrium for the more hydrophobic analytes in particular PCBs was observed showing the need for further improvement (Personal communication Sabine Schäfer, Federal Institute of Hydrology).

An application of silicone polymer sheets to 13 open sea sediments collected between Iceland and the Mediterranean sea was performed within the ICES-ICON project. Silicone

samplers of three gram spiked with PRCs were exposed to about two kg of sediment and shaken for 6 months. Because of the sandy nature of the sediments some PRC residues were found in the samplers indicating depletion had occurred. In the samplers PCBs, PAHs, alkyl-phosphates, musk's, PBDEs, dioxins, and miscellaneous pesticides like lindane ,p,p'-DDE, chlordanes were detected at mostly quantifiable levels[54] while virtually only PAHs were measurable in parallel analyses of total sediment samples. Data for PCB180, tri-n-butylphosphate and cis-chlordane are displayed in Appendix B. Comparing the spatial patterns shows that the continent is still the source for PCB180 and tri-n-butylphosphate but for cis-chlordane, which was never used in Europe, concentration gradient from mainland to open sea was entirely absent.

The success of the application of silicone polymers in SPME is further enhanced by coated bottles that have demonstrated detection limits[52] that comply well with the requirements listed in 5.2. The advantage over SPMEs is a larger volume of extract that allows clean-up and various and repeated instrumental analyses as well as regular routine QA/QC. The silicone polymer further meets all the criteria listed in chapter 5. It is not clear what the behaviour would be if nonaqueous phase layers (NAPL) were present in the sediment. In the marine area this is however only an issue in the case of oil spills but not for regular trend and spatial sediment quality monitoring.

In situ exposure of silicone polymers in sheet form were not noted in literature but applications of SPME type samplers were applied in situ as indicated above but no research was noted where PRCs were applied with in-situ exposures of SPME (6.6.1).

6.7.2 Laboratory application of LDPE

SPMDs are rather vulnerable for application with sediment and the high capacity prevented rapid equilibrium. The LDPE material itself however has sufficient capacity to act as passive sampler and is more robust. LDPE is applied in the laboratory with agitation but also applied in-situ in the field (see below). Exposing LDPE (70µm thickness) to sediment while tumbling in a sediment slurry equilibrium times were e.g. 50 d for chrysene and estimated to be about 100 d for higher PCBs[55]. Using similar conditions also slightly faster equilibration times were reported too, but it is not clear if that is because of different sediment properties, slurry density or shaking speed[56,57]. In the work referenced above uptake rate coefficients compare well with the corresponding dissipation rate coefficients of PRCs. Consequently, confirmation of depletion and equilibrium can be obtained from PRC dissipation. Research indicates that for 70 µm LDPE equilibration times of around 50 days or more[58] are required to approach equilibrium up to e.g. PCB180. This could probably be reduced using a commercially available LDPE of only 25 µm thickness but except for a limited experiment supporting in-situ exposures[59] no application was noted of use of these very thin films in agitated incubations. A thickness of 25 µm is very thin and may easily damage during agitation with sandy samples.

6.7.3 Field exposure of LDPE

In situ exposures of 70 µm LDPE in the lab and field for 28 days showed an overall average degree of equilibrium of about 2-20% when compared to equilibrium achieved by agitation[55,58]. Uptake in stagnant conditions will get slower with time as after the sediment in the vicinity (touching the sampler) is extracted (depleted) the substances have to travel a longer distance; effectively the water boundary layer increases with time[55]. A higher degree of equilibrium is obtained if the capacity of the sediment is higher (high organic carbon content) and the sampler needs to extract sediment over a smaller distance to attain equilibrium. Also if the sampler has lower capacity (thinner or lower $K_{p,w}$) a smaller distance around the sampler needs to be extracted also decreasing the diffusion distance getting closer to equilibrium. Modelling confirmed that the exchange with sediment in the vicinity of the sampler is a rather fast process but after that section is exhausted the exchange rate heavily

reduces and uptake levels off what may be mistakenly be considered as equilibrium. For example 36 days for 90% equilibrium for benzo[ghi]perylene using 80 μm LDPE sheet in static conditions[60] is unlikely. The use of PRCs seems therefore prerequisite for static in-situ sampling however the modelling[61] is complicated[62] and needs more assumptions than passive sampling in only the water phase. Sampler capacity needs to be carefully adjusted to the sediment properties as a low capacity in the sediment compared to the sampler may result in insufficient exchange to quantify the dissipation of the PRCs accurately. This is definitely an issue for sandy sediments.

6.7.4   Laboratory application of Polyoxymethylene (POM)
Jonker and Koelmans introduced POM as a passive sampler in 2001[28]. It was successfully used in studying relations with organisms although the requirements in terms of the level of diffusion inside the polymer is likely not met and the dependency of the POM-water partition coefficients with the thickness is a peculiar property. With the first introduction of POM-SPE to sediment 0.6 g sediment (dw, f_{oc}=0.065) was equilibrated with 1 g of POM (thickness 0.5 mm). This results for e.g. PCB101 in a sediment-sampler capacity ratio of 1.2 (eq 4.1) where 10 to 20 would have been appropriate to avoid depletion. The method was applied in many sediment studies using the same ratios. In one particular study[63] more, 5 g sediment (dw, f_{oc} =0.049), was equilibrated with 700 mg POM resulting in a capacity ratio of ~9 for benz(a)pyrene. Comparing the amount taken up by the POM with the amount in the applied sediment indeed suggested a depletion of <2%, which can be considered negligible. However, in fact the effective depletion could be calculated as 80% when compared to the accessible portion in the sediment which the authors estimated in parallel by a 30 h Tenax extraction. In Figure 6.2 panel B the results would be situated in area between severe depletion approaching exhaustive extraction. Consequently, the equilibration lowered the C_w and the unaffected value is likely about five times higher than reported and would seriously affect the reported sorption parameters for BC. Work with lower capacity ratios has been reported that very likely are more like exhaustive extraction but not interpreted like that[64]. Equilibrium times for POM are as low as 28 days for PAHs[65] and PCBs[66] but with the capacity ratios in the range of 1-2 following equation 4.1 the "equilibrium" could as well be the exhaustive endpoint of the extraction. Depletive incubations obtain equilibrium faster than non-depletive (see 6.5). No uptake curves were noted in literature where an obvious excess sediment capacity was applied that could confirm that equilibrium times are realistic, nor any research where PRCs were applied to do so. A single unpublished experiment where excess sediment was applied showed, after an initial faster uptake, a slow but significant continuation of uptake still continuing towards the end of the incubation (70 days)[67].
POM is very practical in use and sufficiently low detection limits were obtained with POM for PCBs[66] and PAHs[65]. Therefore, it is an interesting material, in spite of gaps in knowledge on behaviour in non-depletive situations, diffusion issues and the uncertainty whether PRCs can be applied.

6.7.5   Field exposure of POM
In field exposures POM behaves rather similar to LDPE. Investigating the influence of activated carbon amendment to sediment on the freely dissolved concentrations in pore water 17 μm POM and 51 μm LDPE were applied in parallel at 8 different depths[68]. Although POM generally released more of the added PRCs than the LDPE, none of the PRCs were fully released. For the most hydrophobic PRCs about 40% was released by POM and less than 20% by LDPE. The higher release of POM can partly be explained by the higher surface to volume ratio, i.e. the capacity per unit of surface area is higher for the LDPE sampler and more is left after providing the sediment at the sampler surface with PRCs. This is also reflected by the uptake, presented in ng/g sampler, which is twice higher for the POM caused

by its twice as high surface per mass unit. This more or less shows that, provided the sampler is far from equilibrium, the amount in the contact layer is responsible for the uptake. The release profiles also confirm that after an initial relatively fast exchange with the contact layer release almost ceases for PRCs and so is uptake for the target substances. Concerning application in marine areas with sandier samples the same conclusions can be drawn as for LDPE and application of POM is not (yet) recommended.

6.8 (Non)-exhaustive extraction methods

For estimating the accessible concentrations exhaustive, or better depletive, extraction methods exist that intends to estimate the amount of a substance in a sediment sample that is releasable to the water phase and consequently is also available for uptake by organisms or degradation. Compared to equilibrium passive sampling it is considered an exhaustive method but compared to a chemical analyses using soxhlet or accelerated solvent extraction it is non-exhaustive. In literature non-exhaustive is frequently used while full depletive extraction would be a less confusing term. Two methods, namely Tenax and HPDC extraction, will be discussed below.

Concentrations obtained by non-exhaustive extraction methods have little meaning for sediment quality if not related to sediment properties, i.e. converted to OC basis or C_w. Conversion to a sediment composition of 2.5% would allow comparison with BAC and EAC in case when these criteria represent fully accessible concentrations. This is likely not the case for BACs that are based on measurements of real sediments in pristine areas, cores or variation in measurements. But EACs, on the other hand, should be accessible concentrations if were derived in laboratory tests where substances are added and concentrations controlled. Recalculation the result of no-exhaustive extraction to 2.5% OC assumes OC to be adequately representing the exchangeable uptake capacity of the sediment or basically that the K_{oc} of a substance is equal for all OC, what is clearly not the case[9,13]. Nevertheless, expressing non-exhaustive concentrations on OC basis is better reflecting environmental quality than the present situation where total concentrations are expressed on OC.

6.8.1 Tenax extraction

The principle of Tenax extraction differs from passive sampling methods. Portions of substances are defined by the rate of desorption and results are consequently operationally defined. Procedures include an agitated exposure of about 1-5 g sediment to 0.5-1.5 g of Tenax in about 100 mL water for a defined period of time[69,70]. Tenax is considered to be an infinite sink for the substances that release from the sediment under conditions of zero concentration in the aqueous phase. Loosely bound, readily partitioning, substances release fast and when this portion is exhausted the more strongly bound portion will cause a minimal C_w in the next stage. Consequently the uptake by the Tenax decreases or even diminishes[71]. The method is an operationally defined extraction and literature suggests various exposure time periods like, 6, 24 and 30 days. The extracted amounts can be related to biota uptake either directly or expressed on organic carbon basis but are also converted to C_w using generic K_{oc} values. For the comparisons with biota uptake that are usually performed on a log scale this may be sufficiently accurate.

Applications generally focus on chlorobenzenes, PCBs and PAHs for which the time to extract the rapidly desorbable fraction increases with hydrophobicity. Assuming that uptake of Tenax is also somehow controlled by the water boundary around the particles, a much larger water volume needs to be extracted when the K_{ow} increases because V_{sed} increases proportionally with compound hydrophobicity. For extracting a larger volume more time is required. For BDEs the V_{sed} is extremely high and Tenax was not able to deplete the

sediment in the regular exposure times[72] because of the obviously extremely low concentration in the water phase. This outcome was however interpreted as the slow fraction being large while no evidence was provided that uptake was not limited by Tenax. These limits come apparent from a study on uptake of Tenax[73] from which sampling rates of 40-100 L per day per gram Tenax could be derived while V_{sed} of higher BDEs can be over 1000 L/g when assuming $K_{ow} \approx K_{oc}$.

It is remarkable that the minimum process QA, i.e. demonstration that full recovery can be achieved of compounds added to the sediment just before Tenax application, has never been mentioned in literature.

In addition it should be noticed that the pores of the Tenax are filled with air. Tenax polymer has a density of 1.2 g/cm^3 and would settle if pores were filled with water. This means that after contaminant ad- or ab-sorption on the outside of the particle further uptake depends on transport through the air phase or diffusion inside the polymeric phase. Both routes will be slow for BDEs with high molecular mass.

Summarising, the operational character of the Tenax extraction and the peculiar uptake route, $C_w \rightarrow air \rightarrow Tenax$, does not give confidence that the method can be easily developed to a well understood and robust method to monitor sediment quality.

6.8.2 HPCD extraction

2-Hydoxypropyl-β-cyclodextrin (HPCD) is a cyclic oligosaccharide with about 6 OH groups substituted with hydroxyl-propyl groups These functional groups give the molecule a cup shape with a nonpolar interior, whereas the outside of the molecule is hydrophilic. Small molecules of non-polar compounds can interact with the hydrophobic part in the "cavity" of the HPDC molecule and in this way the solubility of nonpolar compounds in the aqueous phase can be artificially increased so it can become an extract for the target substances. A typical procedure of HPDC is mixing soil or sediment (1-2 g) with a 20 mL solution of HPCD (75 g/L) for a 24hr and extract the isolated aqueous phase, separated by centrifugation, with an organic solvent e.g. hexane. This implies the amount of applied HPCD is selected about equal to the amount of sediment.

Most applications are based on depletive extraction of available substances in order to predict the bioavailability for biota[74] or the portion that can be degraded in a remediation process for PAHs[75]. The HPDC extraction method was also investigated for assessing availability of pesticides like cypermethrin and chlorfenvinphos[76] and mineral oil. HPCD can also capture PCBs, but no full extraction was obtained[77,78]. No work was noted with regard to PBDEs or dioxins.

The method is basically operationally defined and actually the HPCD acts as a passive sampler and can partly be interpreted in a similar way (Figure 4.1). The high HPCD amount should create such an chemical uptake capacity that the sediment and the water get fully depleted (i.e. $C_w \rightarrow 0$), (Figure 6.2 panel B, shaded part of the desorption isotherm). A full depletion is not always the case as a second extraction can still yield another 20%[79]. It appears that the selected 1:1 ratio of HPCD to soil/sediment and the 24 hr. exposure is not sufficient as a rule. For extraction of cypermethrin and chlorfenvinphos 3.5 g HPCD per g soil was recommended with 48hr shaking[76] while extraction of hydrocarbons was almost instantaneous[77]. A way of achieving rapid and full depletion is to include a silicone polymer phase as absorption sink for a significant increase of the uptake capacity[80]. In this case the HPCD is actually only the carrier for fast transport[81] from soil or sediment to the silicone polymer.

It was possible to deduct from reference 80, that the level of sorption of HPCD was at about the same as the silicone polymer. This raises the question whether HPCD can be applied as a passive sampler? There are several issues why this is not likely possible or practical. To be non-depletive only very low concentrations of HPCD would be allowed and overestimation of

the substance's concentration will easily occur because of inclusion of small amounts of particulates in the aqueous phase. Further a large amount of sediment may be easily saturating a small amount of HPCD with small molecules of natural substances which do not normally enter polymeric samplers. Compounds may use/require two HPCD molecules for dissolution causing exponential isotherms**[76]** and back calculation to an aqueous phase concentration may not be straightforward. There may, however, be an application for HPCD to increase the mass transfer rate of compounds[81] from sediment to passive sampler possibly reducing equilibration times.

7 Discussion

7.1 What is discussed?
In chapter 6 most common approaches for passive sampling and non-exhaustive extractions are evaluated. Most applications focus on really polluted situations in freshwater and estuarine areas but off shore marine applications at open sea are rare. The ICES Passive Sampling Trial Survey and even more the ICES ICON exercise showed that application to offshore sediment is very well possible. In both exercises PRCs spiked silicone polymers were applied aiming to attain equilibrium and non-depletive by using relatively large amount of sediment. Both surveys above show the great potential of passive sampling for large scale spatial monitoring. This discussion evaluates the potential of described methods for application to diffusively contaminated estuarine and offshore sediments, not only in terms of detectability but also practical issues connected to the procedure. Also possible modifications that would perhaps allow improvements are discussed.

7.2 Non-exhaustive or depletive methods
The operationally defined properties of the Tenax method prevent a straightforward approach of which the processes are understood PRCs could somehow help to improve understanding but it remains that measured amounts are small for sandy sediments and larger for fine grained sludge. To correct for the sediment properties, similar to results from conventional total extractions, concentrations actually need to be normalised to become comparable. Normalisation would also apply to the concentration obtained from an HPCD extraction. However normalisation should be avoided because of the disadvantages discussed in chapters 3 and 4 and therefore both HPDC and Tenax extractions are not the ideal way forward. Still, HPCD may in small concentrations be applied in combinations with polymeric samplers to enhance transport rate of compounds from sediment to sampler.

7.3 In-situ static exposure
Static application of PS in-situ in sediments will rely entirely on PRCs and the modelling is less straightforward than for water sampling. A relatively fast "contact" uptake is followed by a considerably slower and decreasing continuation of the uptake. The magnitude of the "contact uptake is depending on the capacity of the sediment around the sampler[61], larger for OC-rich sediments and small for low OC contents. This adds to the impracticalities related to in-situ exposure in offshore conditions and thus does not make in-situ exposure a realistic option for large scale routine monitoring.

7.4 Static exposure in the laboratory
Bringing a large sample to the laboratory would allow application of static exposures in the laboratory. The static exposure system could be supported by vibrating the sampler holder shortly at selected time intervals using systems like found in cell phones. In the laboratory the sampler can be repositioned from time to time in order to stepwise approach equilibrium. Of course equilibration times will be longer in comparison to shaking or tumbling where the sediment is refreshed nearly every second, but the advantage is that the requirements in terms of sampler robustness are much lower and shaking the amounts likely necessary for offshore sediments will require a large shaking capacity.

Basically all micro and macro equilibrium passive samplers can be applied but the thinner the film the better. Actually it is the capacity per unit of surface area, i.e. product of thickness and K_{pw} that matters, but each factor the sampler is thinner needs to be compensated by a higher surface area to maintain sensitivity. Parallel exposed PRC loaded SPME fibres (≤10 μm)

seem practical as progress of equilibration can be monitored by analysing a single fibre for its PRC release. These would require the use of thermal desorption systems for sample introduction (see 6.6) and do not allow for sample clean-up.

All methods using macro samplers also require using the thinnest options for achieving equilibrium but at the same time should have a mass of about 100 mg to comply with the LOD requirements. For LDPE foil the thinnest foil is 25 µm but it is not clear if sharp edged particles of sand may tear the foil. A mass of 100 mg would require a sheet of about 45 cm^2. The 17 µm POM could be used but this is not commercially available and very curly material that cannot be easily stuck in the sediment. Commercially available POM has a thickness of 76 µm what is likely too thick for achieving equilibrium in acceptable time. Thin silicone polymer can only be applied in form of a coating. For static exposure the silicone polymer could be coated on "knife-like" sampler (a giant SPME) that would be inserted in the sediment. With a 12 µm film coated on both sides the same surface area as for the LDPE option (45 cm^2) would be needed. Samplers can be coated with a thinner film, e.g. down to 2 µm but that would require a coating on a sheet of 17×17 cm to meet the LOD requirements. This is hard to handle if the core material that holds the coating is a stainless steel or glass plate, which is even more difficult to extract. Obviously a procedure with a coating on the wall of the exposure container and refresh the "contact" sediment on set time intervals by hand shaking is a much more realistic option that also does not require to open the exposure vessel and allows contact of sample and sampler to laboratory air. At the same time the extraction of a coated bottle is fairly simple.

7.5 Laboratory agitated exposure

Agitated exposures applying micro and macro samplers are most frequently applied in literature. Obviously the requirements on minimum sampler mass apply similarly as described in the previous section (7.4). Using the thinnest possible sampler is still advantageous but agitation can partly compensate for slower equilibrations applying thicker but more robust samplers. Application of passive sampling in sediments usually involves polluted situations and monitoring sandy sediments by passive sampling in marine offshore areas is not noted in literature. Sandy sediments pose a specific challenge to passive sampling. Because uptake capacity of sandy sediments is low, small samplers need to be exposed to large amounts of sand. Sand does not very well suspend in water and impedes shaking unless strong forces are used. Strong forces on the other hand may grind the softer particles in the sample and increase mobility of substances trapped inside[82], or wear the polymeric sampler. For polymers submersed in the shaking sediment wearing will be noted and can be corrected for by tracking the weight of the sampler. For coatings that are worn this is more difficult as the detection of a weight difference in mg of an over one kilo weighting bottle is not very accurate. Quality control is possible by measuring the uptake capacity through partitioning of a substance from a methanol-water mixture. This is a simple procedure but of course an extra analysis is necessary.

For sediment around a disposal site for dredged sediment in the North Sea (German Bight) the German Federal Institute of Hydrology applied rolling coated jars (silicone polymer 2, 4, and 8 µm thickness) at about 15 rpm and did not observe deterioration of the coating. Equilibrium was obtained in about 14 days for compounds with the hydrophobicity up to that equivalent of PCB153. The work also showed that sampler size and sediment quantity need to be carefully considered as on several occasions depletion occurred due to the low OC content and limited amount of sediment, while for sediments with sufficient capacity non-equilibrium was apparent for 4 and 8 µm coatings.

It is obvious that thicker coatings or sheets may require more time for equilibration if not compensated by lower $K_{p,w}$ values. The $K_{p,w}$ of LDPE is in the same range as silicon polymers for PCBs and for PAH increased with hydrophobicity to around an order of magnitude higher

for e.g. benzo[a]pyrene[83]. The firstly reported values for POM[28] (500µm) were around an order of magnitude lower than LDPE and silicone polymers but later values for thinner (76 µm) materials were about equal[65,66]. Consequently, thicker polymers will always extend equilibration times leading to the conclusion that, provided the agitation/rolling does not damage the coating, thin coatings have the largest potential for attaining equilibrium in a short time and for the most hydrophobic substances.

Furthermore, the use of multiple SPME samplers (as discussed in 7.4) may be an option although no application to offshore sediments is known and it is not clear if the fibre would survive in rolling sand.

7.6 Metals

The evaluated passive sampling methods and discussion above does not include metals. Methods for metals were also explored. The most frequently applied passive sampler for metals is the DGT (Diffusive Gradients in Thin films)[84], allowing detection limits of 10 ng L-1 and lower. DGTs are applied in the kinetic mode and from the uptake aqueous concentrations are calculated based on the calibrated diffusion rate through a film (hydrogel). However the next to freely dissolved metals also the metal ions labile bound to small complexes are taken up by the sampler. Consequently the result is depending on the presence of complexing material flawing the interpretation of DGT derived metal concentrations[85]. The ideal system, an equilibrium passive sampler for metals does probably not exist. All applied materials are based on ion exchange where competition is severe and sites will dominantly be occupied by the metals with the highest affinity displacing others. A recent review on passive sampling methods for metals in sediment [86] noted one paper on equilibrium sampling focussing on copper[87]. Although this paper promised future improvements no follow up was found in literature.

A method that would help to rank sediments in order of metal pollution would be to let two sediments separated by a membrane equilibrate with each other. Ultimately sediment samples could be compared with a defined reference sediment. Practically this could be done by incorporating a clay from pristine origin in an hydrogel that could be used as a "natural passive sampler" also giving natural equilibrium with equally natural competition between ions. Also pH may have limited effect. However until the potential is proven by a "proof of principle" this cannot yet be suggested as a way forward..

8 Equilibrium passive sampling: the way forward

As concluded in chapter 7 equilibrations using thin films coated on the inside of a bottle have a great potential for achieving the requirements set out in chapter 5. In this chapter, practical issues on dimensions, pitfalls and how to circumvent those, possible improvements and the alternatives that may become possible because of improvements are listed and discussed. The procedural steps are discussed for application of coated bottles but are often also valid if exchanged by a sheet type sampler

1   Sandy sediments often contain OC contents below 0.1% and sediment quantities of e.g. 2 kg would be needed when using the minimum sampler mass (100 mg) (Figure 5.1). This would require an exposure vessel with a minimum volume of 2.5 L but larger, 4 L would be more convenient. Assuming the bottles are coated laying while rolling the relevant wall surface area is 800 cm^2 to obtain ~ 1 µm thick coating for a sampler mass of 100mg.

2   The largest pitfall is the possible abrasion of the coating. It should be noted that abrasion was only observed for thicknesses <10 µm under strong shaking conditions. Coatings >10 µm are much more robust and still can compete with passive samplers in form of sheet or fibres. To prevent wearing several options exist:

2.1   Rolling instead of shaking showed no wearing for sandy sediment from the German Bight. Rolling is provides slightly less intensive motion but the sampler-particle contact remains and is refreshed continuously.

2.2   In addition, the adhesion of the film to the surface of exposure vessel may be improved by sandblasting the inside of the bottle or creating an opaque surface by exposure to hydrogen fluoride.

2.3   Investigate if different coatings, e.g. polyurethane, polyacrylate, are more robust.

2.4   Last and least, sand could be removed from the sample by sieving. Still, the most practical way forward is to avoid manipulations with the sample.

Of course quality control on the capacity of the sampler should be in place, certainly in the initial experience building phase of application.

3   Spiking samplers with PRCs covering a log K_{ow} range of 4-7 is a quality assurance measure that should always be part of the procedure. It primarily verifies absence of sample depletion if PRCs are fully dissipated. If not the presence of only PRCs with hydrophobicity above a certain value in exposed samplers indicates that equilibrium may not have been attained for more hydrophobic compounds.

4   Water collected at the sediment sampling site should be used if water needs to be added to liquefy the sediment. Note that excess water may decrease the exchange rate[20].

5   Addition of biocides to diminish biodegradation should be part of the procedure. Sodium azide is the most frequently used at about 10-50 mg/L water in the system. However, it may be logical to add sodium azide amounts based on sediment amounts or even more likely OC amounts.

6   Methods, other than agitation, that can influence the exchange process)

6.1   The presence of HPCD increases the concentration in the aqueous phase and promotes chemical exchange between sediment and sampler[81] and is more

effective when needed, i.e. for sampling strongly hydrophobic contaminants. HPCD is frequently applied to enhance solubility of PAHs but little is known about other compounds. Size may matter and for PCBs it was shown that randomly methylated β-cyclodextrin (RAMEB) was more effective than HPCD[77]. Wildly guessing this could be because RAMEB has a larger inner space as methyl groups take less space than propyl groups.

6.2   Addition of a cosolvent, e.g. 20% methanol, also enhances the concentration in the aqueous phase and if the methanol does not influence the sediment or sampler properties the equilibrium is not affected and concentrations in the sampler still represent the chemical activity. In that case also results of conversion to freely dissolved and lipid based concentrations are not affected.

HPCD, RAMEB or methanol can be added only to a certain limit since the addition increases the capacity of the aqueous phase that should remain small compared to that of the sampler to avoid significant contribution to depletion. Assuming approximately equal partitioning for HPDC and silicone polymer the solubility enhancement of 20 mg/L would be about a factor 20 for a substance with log K_{ow}=6 increasing proportional to log K_{ow} (factor 200 when the log K_{ow}=7, etc). The factor will decrease when also with log K_{ow} increasing molecular size of the substance cannot anymore be hosted by the HPCD, RAMEB molecules. The effective factor the exchange rate would increase is also reduced because of the lower diffusion coefficient of the substance HPDC/RAMEB complex

Addition of 20% methanol will show a similar increase, factor 20, in aqueous phase concentration, only limitedly increasing with log K_{ow}[83].

Solubility enhancing methods to shorten equilibrium times are worth investigating. The most relevant approach is to explore the applicability of HPCD or RAMEB for very hydrophobic substances as attaining equilibrium for those compounds is most troublesome.

7   Depletion is detected by applying PRCs but the use of PRCs to correct for depletion once it has occurred is limited and actually only can be applied when compounds are isotopically labelled isomers. Equilibrating the sample at different sampler sediment ratios that also include severe and when possible nearly full depletion does allow correction for depletion by plotting the C_w's measured versus the concentration extracted from the sediment by the sampler. Because these both parameters are calculated from the same measured amount on the sampler the actual calculation requires non-linear regression[20]. It is advisable to include this multi-ratio passive sampling once at different locations to characterise the sediments or the OC it contains in terms of their sorption isotherms.

8   Silicone polymers swell in hexane and are therefore are extracted with solvents like methanol or acetonitrile. Because there is always some residual water in the extract acetonitrile is preferred as it forms an azeotrope with water (15%) and water will be largely removed during Kuderna Danish concentration of the extract. Subsequently transfer to hexane is also performed azeotropically after addition of hexane to the concentrated acetonitrile extract. Here LDPE and POM have the advantage that a direct extraction with more apolar organic solvents like acetone or hexane is possible. In case fluorinated silicone polymers are used hexane extraction is applicable. Sorption properties of fluorinated silicone polymers are of the same magnitude as dimethylsiloxane based polymers[37].

9   For the interpretation of the data it is tempting to consider a temperature or salinity correction as a necessary step in calculation of C_w. However, when accepting the

"chemical activity" as basis of the quality this might not be necessary. Equilibrium passive sampling copies the "chemical activity" of compounds in the sediment. Organisms that dwell in sediment may be considered to be at equilibrium with the sediment, too. Conversion of passive sampling results to lipid basis is a shortcut directly reflecting the exposure level for organisms while it adds very little to the variability. Sampler-lipid partition coefficients can be accurately determined, do not differ for lipid types[17] and are temperature independent[40]. The route through freely dissolved concentrations relies on sampler-water partition coefficients ($K_{p,w}$) and bio-concentrations factors (BCF), which suffer from larger uncertainty. These parameters are also temperature and salinity dependent but that will likely level out if both steps are used. Conversion of equilibrium passive sampling results to indicate exposure levels on lipid basis is scientifically sound, technically accurate, but presents currently a large mind step for regulators.

10   The above may contain some pitfalls

   10.1   Wearing occurs in spite of precautions suggested above. Application of thicker coatings or sheets is inevitable.

   10.2   Some sediment may be very sandy and depletion may occur even when 2 kg sediment is applied. Besides increasing the amount of sediment or the sampler size several solutions are possible (1) apply multi-ratio passive sampling and extrapolate, (2) perform long term exposure of passive samplers in water at the sampling station instead of sampling sediment,(3) build a system to on board isolate fine material by washing and sedimentation from large amounts of sediment (4) avoid those stations.

   10.3   Very hydrophobic compounds like high molecular mass chlorinated dioxins may require an equilibration time that is not anymore feasible in laboratory practice. In that case isotopically labelled isomers of target compounds may need to be applied as PRCs.

9 Approaches for method development and cost aspects

The discussion in chapter 7 concludes that sediment quality for organic compounds is best monitored by equilibrium passive sampling. Taking into account the special circumstances for passive sampling in sandy sediments, and the general issues connected to equilibrium passive sampling, chapter 8 discusses the possible ways forward.

9.1 Further development

To advance the passive sampling in sediment by method development there are two slightly different approaches.

A. Scientific
   Here all individual steps and pitfalls are individually investigated. E.g. different coatings are tested for resistance to abrasion and sorption capacity (sampler-water partition coefficients, internal diffusion). One or two model sediments will be used for experiments to determine equilibrium times for different conditions, rolling, shaking, influence of HPCD addition after confirming HPDC has no affinity to the sampler material and sediment. The gained results are used to define an optimum method to be applied to sediments from real monitoring in a next step.

B. Practical
   Start with perform a trial survey based on the best available knowledge and experience. This should also include the most adequate quality assurance (PRCs) to encounter or detect possible pitfalls mentioned in the previous chapter. In parallel test solutions for pitfalls (different coatings, bottle wall treatments and thicknesses,) using a few selected samples from the trial serie. Additionally perform experiments investigating the process (roll or shake, vary equilibration time, use of HPCD, multi-phase ratios). Ideally the trial is based on the same sediment samples as are used for the regular sieving procedure so the resulting data can directly be interpreted in relation to each other and (provisional) assessment criteria.

The scientific option is a proven approach for method development and quantifying the impact of the individual aspects is a solid basis for defining a passive sampling procedure. This is especially relevant if passive sampling in sediments was in the idea stage. However for passive sampling of sediments a lot of knowledge is available and the methods proposed here were already successfully applied for regular sediments[13,20,29,88]. So the main challenge in the marine area is the sandy nature of the sediment, the associated low sorption capacity (OC content) and the risk for abrasion of the coated samplers. Abrasion was mostly observed while vigorously shaking but much less when rolling. Low capacity and abrasion risks may differ for different areas, i.e. the actual magnitude of both issues is unknown and it is unclear which one will be dominating if present.

Consequently Approach B is likely more efficient as it, before solving it, identifies the magnitude of a problem that perhaps may not exist when rolling. Furthermore, results are already available for interpretation in an early stage of the project. The mass of the coating should also be verified by measuring the sorption capacity of the sampler by the uptake of a test substance from a solution with defined capacity. The more scientific approach does not give a better guarantee that problems of abrasion will be avoided. It is however recommended to limitedly investigate the resistance to abrasion for a number of coatings and bottle wall pre-treatments prior to the start of the trial. This should include fluorinated ones

because of the time efficiency of the extraction. Then in parallel with the trial samples other issues listed in Approach B can be explored. When in the first phase a new coating will be selected this would also require estimating partition coefficients what in first instance can be performed by cross calibration with a sampler material with known (published) partition coefficients, i.e. Altesil or Silastic A. After the methodology has proven to be robust in the trial and routinely applicable in a later stage a direct determination of partition coefficients can be performed what preferably should include different laboratories.

9.2 Cost aspects trial and development

The elements of the trial suggested in approach B and associated experimental work are listed in Table 9.1. The labour of execution of the program, including analyses and reporting, is estimates at about 100 days and 15-20 k€ consumables/investment. This does not include ship costs for collecting the samples.

The mix of trial survey and research/validation will supply valuable data for a first interpretation, while the research component will indicate the reliability as well as giving direction to further understanding and improvements in terms of quality or robustness. It may also reveal issues or options for further investigations.

Table 9.1   Overview of activities based on approach B

	Subject
1	Select options for rigid coatings; purchase + bottles
2	Test preparation and abrasion of the different coatings; effect pre-treatments
3	Test sorption by cross calibration
4	Prepare coated bottles for all experiments, extract spike with PRCs
5	Select and agree on about 15 trial stations with wide spatial coverage
6	Passive sampling; equilibrating 6 weeks on roller with these 15 sediments samples
7[a]	Parallel 4 extra periods to construct a time curve for 2[b] samples (8 equilibrations)
8	Investigate sorption properties of HPCD
9[c]	Parallel 5 points time curve for 1 sample adding HPCD (5 equilibrations)
10	Parallel 2[d] samples on shaker
11[a]	Parallel 4 extra sampler sediment ratios for 2[d] samples (8 equilibrations) to assess sorption capacity
12	38 extractions and analyses target substances + 5 blanks/ references for PRCs
13	Verification of sampler masses
14	Data processing
15	Reporting

[a] a fifth point of the curve is part of 6
[b] a low capacity and a high capacity sample should be selected from the list made under 5
[c] a same sample as under line 7 should be used
[d] same as used for time curves

The proposal above is considering a trial in Dutch waters but in the trial part other countries could already be involved simply by supplying OSPAR contracting parties with coated bottles and methodological information. This would allow them to compare it with their present monitoring approaches. It could also be investigated if the proposal above could be a mutual development with different countries.

9.3 Routine application

In respectively the tables 9.2 and 9.3 the steps in the present routine monitoring and passive sampling are listed. The list is not complete but ends where the process is equal, i.e. analysis.

In the present routine sediment monitoring the sieving process is the most time consuming step. In average five kg (DW) sediment is sieved for each sample. Sieving is performed in portions of 500 g wet sediment that takes 20 minutes to sieve ending in about 4-5 hours. For the North Sea, Delta and Wadden Sea this average amount is 8, 4 and 2 kg respectively. The final costs when applying passive sampling is quite lower. However it should be kept in mind that sieving will still be required for monitoring metal concentrations until an alternative is found in passive sampling, another method or the metal contamination is phased out. Nevertheless sieving time can be largely reduced as only very small amounts of sample are required for metal analyses and in many cases one sieving cycle may be sufficient. The benefit of applying passive sampling is not only time but it is also aiming for results that are more environmental relevant with better temporal and spatial comparability.

Table 9.2   Elements of the present methodology and estimated cost or time(per sample)

	Present method.	**Costs €**	**Time hr.**
1	Sediment needed 2-10 kg		
2	Sieving equipment (investment)	70 k€[1]	
3	Sieving per sample (5 kg)		4-5 hr.
4	Freeze drying, homogenisation		½ hr.
5	Solvent extraction, ASE,		½ hr.
6	Solvent consumption, clean-up and analysis about equal for both methods		

[1] Investment with yearly depreciation

Table 9.3   As table 9.2 but for application of passive sampling

	Passive sampling	**Costs €**	**Time hr.**
1	Sediment needed 2-3 kg		
2	Rolling system ~20 bottles, taylor made (investment)	10-20 k€[1]	
3	Coated bottle, preparation, extraction, spiking	10 €	½ hr
4	Filling with sediment, in lab (or on board), add biocide		½ hr
5	Solvent extraction		
6	Solvent consumption, clean-up and analysis about equal for both methods		

[1] Investment with yearly depreciation

10 International perspective – Implementation

With the development and validation of the passive sampling method for robust routine application as proposed in the previous chapter the Netherlands can take an advance on the application of passive sampling in sediment in OSPAR monitoring and the Marine Strategy Framework Directive (MSFD) which will likely adopt the OSPAR scheme. Implementation of passive sampling methods has been suggested or recommended in several relevant documents, ICES working groups or workshops as described below. From section10.5 the implementation is discussed. For the substances monitored for OSPAR it is indicated whether contamination levels can be determined by passive sampling. This is followed by the requirements and procedural route for implementation within OSPAR.

10.1 EU-WFD

Within the EU-WFD guidelines on chemical monitoring of sediment and biota[89] were completed in 2010. In the annexes passive sampling in sediment was also mentioned as a technique that gives comparable data and the advantages of avoiding application of normalising techniques were addressed. Presently, for the monitoring of contaminants in biota more extensive guidance is under preparation.

10.2 SETAC Technical Workshop

In November 2012 a SETAC Technical Workshop "*Guidance on Passive Sampling Methods to Improve Management of Contaminated Sediments,*" was held in Costa Mesa, California, USA. This workshop discussed passive sampling in contaminated sediments and most of the issues discussed in the present document were also addressed in a series of papers just recently published[16,25,62,90,91,86]. This workshop also identified the free dissolved concentration obtained through equilibrium passive sampling the most accurate parameter for assessing the environmental quality and decided not to consider kinetic methods like Tenax. In polluted sediments the range of applicable methods is larger than for marine sandy sediments because of the capacity of the sediment is generally higher and so are the free dissolved concentrations.

10.3 ICES

The ICES trial survey in 2006/2007 was the first collaborative application of passive sampling in the ICES community[29,48,49]. On the basis of the results the Working Group on Marine Sediments in relation to pollution (ICES-WGMS) in 2007 recommended to start steps implementation of passive sampling in sediments and compiled the first draft guidelines. The reports of their meetings show extensive activities by several countries. Also the ICES Advisory Committee in 2012 recommends implementation by passive sampling for monitoring programmes for contaminants in sediments[92]. In 2013 ICES organised a '*Workshop on the Application of Passive Sampling and Passive Dosing to Contaminants in Marine Media*' (WKPSPD)[85]. This workshop considered passive sampling of polar compounds and metals insufficiently developed to use in marine monitoring, but concluded that passive sampling for hydrophobic contaminants in sediment and water was scientifically and practically sufficiently mature to justify application in OSPAR monitoring. For sediment monitoring the workshop recommended finalise/update the draft guidelines and further developing proficiency testing for this method. ICES will welcome the present document as a basis for their guidelines

10.4 Activities in various countries

On the basis of reports of the Working Group on Marine Sediments in relation to pollution and literature several countries include passive sampling in their research work or investigations on polluted areas. Only from Spain, Portugal and Ireland no activities were observed other than contribution to the ICES trial survey in 2006/2007. As mentioned earlier Germany has recently performed a trial for spatial monitoring of sediment in rivers with coated jars following the procedure adopted from Reichenberg et al[24]. Groups in Norway, Denmark, UK, France and Belgium are active and likely will be able to implement monitoring sediments by passive sampling on rather short term if OSPAR requires so.

Table 10.1   Parameters in the OSPAR CEMP lists. The right column indicates if passive sampling is possible

Substance group	Substances	Matrix	PS in Sediment?
Mandatory substances in CEMP			
Heavy metals	Cd, Hg and Pb	Biota Sediment	NO, Not yet
Polychlorinated biphenyls (PCBs)	CB28, CB52, CB101, CB118, CB138, CB153, and CB180	Biota Sediment	<u>YES</u>[1]
Polycyclic aromatic hydrocarbons (PAHs)	anthracene, benz[a]anthracene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, fluoranthene, indeno[1,2,3-cd]pyrene, pyrene and phenanthrene	Biota Sediment	<u>YES</u>
Tri-Butyltin	TBT (parallel with biological effects measurements)	Biota Sediment	yes[2], was tested once
Polybrominated diphenyl ethers	PBDEs 28, 47, 66, 85, 99, 100, 153, 154 and 183	Biota Sediment	yes, yet limitedly applied
Substances in Pre-CEMP			
Planar PCBs	CBs 77, 81, 105, 114, 118, 123, 126, 156, 157, 167, 169, 189	Biota Sediment	YES[3], Not tested
Alkylated PAHs	C1-, C2- and C3-naphthalenes, C1-, C2- and C3-phenanthrenes, and C1-, C2- and C3-dibenzothiophenes and the parent compound dibenzothiophene	Biota Sediment	YES, limitedly applied
PFOS	Polyfluourinated octyl sulphonic acid	Water, Biota Sediment	NO Probably other sampler type required
Polychlorinated dibenzodioxins and furans	Compound list given in the technical annex of 10 of the biota section in the JAMP guidelines1.	Biota and Sediment	yes, Not yet tested

1) <u>YES</u> : widely applied

2) yes : not widely applied

3) YES :limitedly applied and/or part of a compound group that <u>was</u> widely applied

10.5 CEMP substances monitored in Sediment.

In OSPAR the monitoring within maritime area is described and agreed in the Coordinated Environmental Monitoring Programme (CEMP)[93] and the national contributions are co-ordinated. The aim of the CEMP is to deliver comparable monitoring data from across the OSPAR. Substances of concern are identified within OSPAR and included in the CEMP based on criteria given in reference 93, Annex 1, part B. New candidate parameters are

usually first placed on a so called "Pre-CEMP" list and monitoring is essentially voluntary. Once guidelines for the monitoring, quality assurance tools, and assessment tools or criteria are established for "pre-CEMP" parameters they are transferred to the mandatory CEMP list. Table 10.1 shows the substances presently listed for monitoring in sediment. Note that also several confounding parameters like organic carbon, aluminium (and lithium) content and grain size fractions or distribution, need to be analysed in sediment samples as supportive information for data interpretation and corrections for grain size (normalisation). Except for PFOS and heavy metals all CEMP parameters in sediment can principally be determined by passive sampling. For PAHs and PCBs passive sampling in sediments has been widely applied and consequently application for alkylated PAHs and planar PCBs will also be possible. Based on substance properties there are no reasons passive sampling in sediment is not applicable for PBDEs; For water passive sampling of PBDEs is frequently applied. Also for TBT sampling in water was applied[94] and can likely be applied for sediments too, although it is not clear if this can be done form using the same sampler extraction as performed for the neutral hydrophobic organic substances.

10.6 Towards implementation

Application of passive sampling does not lead to including new parameters in CEMP but merely a new "matrix" to obtain better temporal and spatial comparability. Like classic matrices guidelines for the monitoring using passive sampling, quality assurance tools, and assessment criteria need to be established. To meet these requirements OSPAR requests advice from ICES working groups where members backed up by their home institutes provide guidelines and assessment criteria for adoption by OSPAR.

Guidelines
The Working Group on Marine Sediments in relation to pollution (WGMS) and the Marine Chemistry Working Group (MCWG) made a first draft guideline already in 2008 that also contained guidance on the determination of sampler-water partition coefficients. For several reasons progress was delayed but the item was picked up again in 2013 on the basis of clear recommendations of the ICES WKPSPD[85]. MCWG and WGMS decided to prepare separate guidelines for passive sampling in sediments and the determination sampler-water partition coefficients as the latter is also relevant for passive sampling in water. The underlying report will give relevant background to further develop the guidelines as well as the follow up work defined in chapter 9.

Quality assurance
Proficiency testing for passive sampling should be included in the QUASIMEME scheme. This is commonly included after preparation of the guidelines and some first experience is built by the countries participating in the OSPAR CEMP. Such scheme can be executed following the outline of the ICES PSTS[29]. Sampler-water partition coefficients should be validated by parallel determination by different laboratories following the prepared guidelines. In case passive sampler data are converted to lipid basis that also is needed for sampler-lipid partition coefficients.

Assessment criteria
Development of background and environmental assessment criteria (BAC and EAC) is usually a difficult task but those for passive sampling can be derived from criteria existing for biota and sediment. Existing assessment criteria for biota on lipid basis can probably even directly be applied after conversion of equilibrium concentration in samplers to lipid basis. Similarly lipid based concentrations in biota can be converted to sampler based and subsequently further converted to freely dissolved aqueous concentration using sampler-lipid

and sampler-water partition coefficients respectively. Also bio-concentration factors (BCF), measured or QSAR predicted can be used to calculate (free dissolved) aqueous phase assessment criteria from the corresponding biota assessment criteria. Likewise organic carbon organic carbon -water partition coefficients can be used to calculate aqueous phase assessment criteria from organic carbon based assessment criteria. It is foreseen that ICES can advise on the procedure for conversion of assessment criteria parallel to the finalisation of guidelines and establishment of sampler-lipid and sampler-water partition coefficients.

Implementation route
The basis and route for implementation of monitoring in sediments by passive sampling is known and ICES working groups are making good progress. The ICES WKPSPD proposed inclusion of passive sampling of water and sediment in the (Pre-)CEMP. The next step would be OSPAR to request the OSPAR Working Group on Monitoring and on Trends and Effects of Substances in the Marine Environment (MIME) to evaluate possible inclusion in the Pre-CEMP. MIME proposals/advice are forwarded to OSPAR's Hazardous Substances and Eutrophication Committee (HASEC) for final approval by member states. Clearly, the presence of a well-developed and documented methodology as proposed in chapter 9 will support a successful implementation. Before including passive sampling in sediments in CEMP will also effect in termination of classical sampling they will need to be performed in parallel.

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A   Matrix conversions of assessment criteria

Whole sediment criteria in µg/kg					Shellfish	Fish	Shellfish	Biota a)
	BAC	EAC	ERL b)		BAC	BAC	EAC	EAC passive
f_{OC}	0.025	0.025	0.02 c)	f_{lipid}	0.05	0.11	0.05	1
FLU	39	250	600		11.2		110	
BaA	16	1.5	261		3.6		80	
BAP	30	625	430		2.1		600	
PCB052	0.12	2.7				0.2		108
PCB118	0.17	0.6				1.3		24
PCB153	0.19	40			1.1	0.2		1600

OC based in µg/kg				Lipid based in µg/kg			
	BAC	EAC	ERL	BAC	BAC	EAC	EAC passive
FLU	1560	10000	30000	224		2200	
BaA	640	60	13050	72		1600	
BAP	1200	25000	21500	42		12000	
PCB052	4.8	108			1.8		108
PCB118	6.8	24			11.7		24
PCB153	7.6	1600		22	1.8		1600

Freely dissolved in ng/L					Freely dissolved in ng/L			
	LogKow	BAC	EAC	ERL	BAC	BAC	EAC	EAC passive
FLU	5.22	9	60	181	1.3		13	
BaA	5.91	0.8	0.07	16	0.09		2	
BAP	6.04	1.1	23	20	0.04		11	
PCB052	5.84	0.007	0.16			0.003		0.16
PCB118	6.74	0.0012	0.004			0.002		0.004
PCB153	6.92	0.0009	0.19		0.003	0.0002		0.19

Sampler d) based in µg/kg					Sampler based in µg/kg			
	logKpw e)	BAC	EAC	ERL	BAC	BAC	EAC	EAC passive
FLU	4.62	370	2500	7500	54		540	
BaA	5.32	166	15	3300	19		420	
BAP	5.69	540	11300	9800	20		5400	
PCB052	5.80	4	102			1.9		102
PCB118	6.42	3	10			5		10
PCB153	6.72	5	990		16	1		990

a) EAC passive is lipid based and estimated from EAC-sediment assuming OC-lipid BASF equals unity. "passive" refers to that only partitioning is considered but no bio-magnification is included.

b) The USA EPA version of the EAC is the ER-Low (ERL) value that is defined as the lower tenth percentile of a data set of concentrations in sediments which were associated with biological effects.

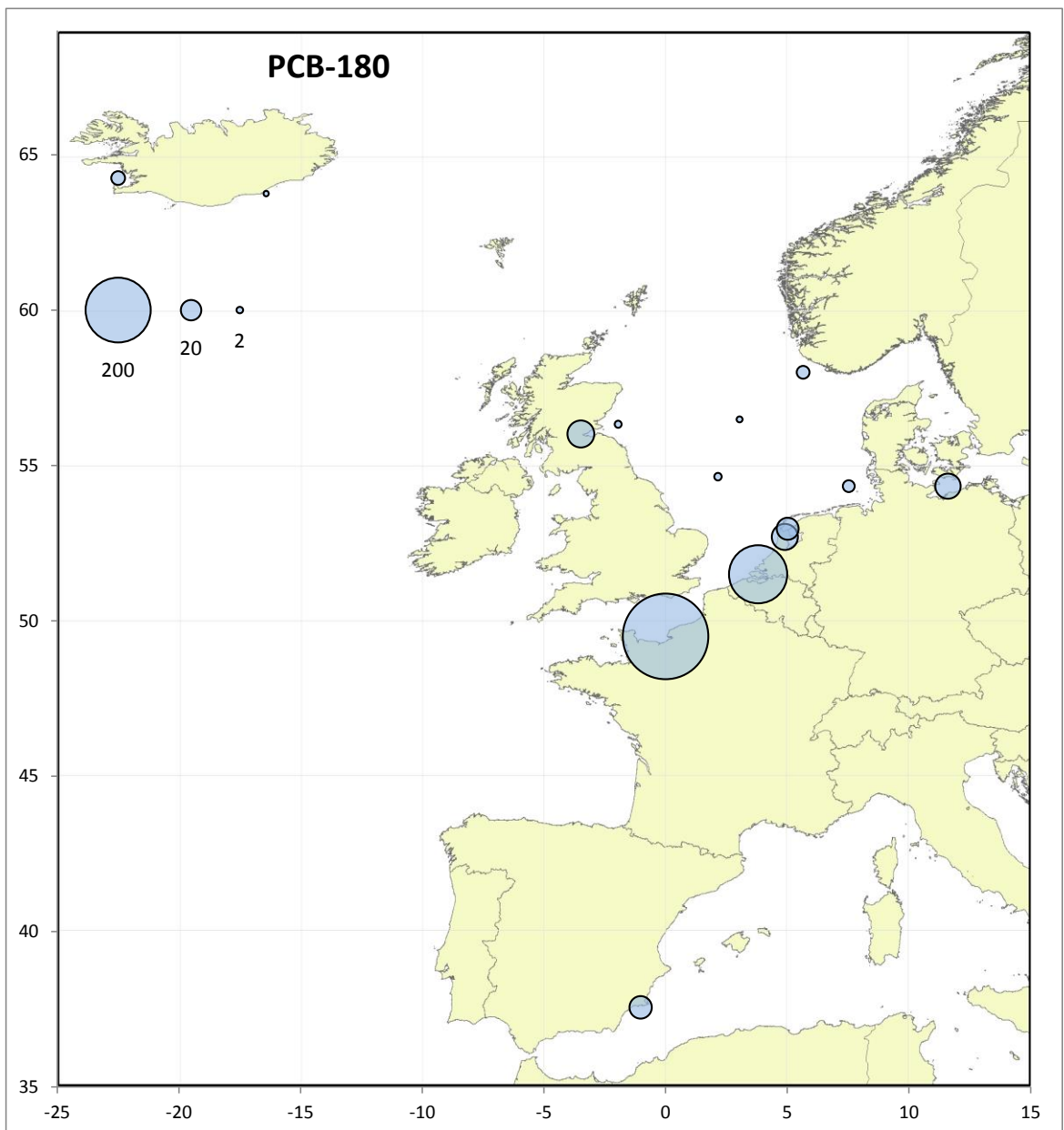c) ERL were set without specified OC content. In the table f_{OC}=0.02 is applied.

d) Sampler based means expressed on Altesil silicon polymer.

e) Sampler-water partition coefficients for Altesil
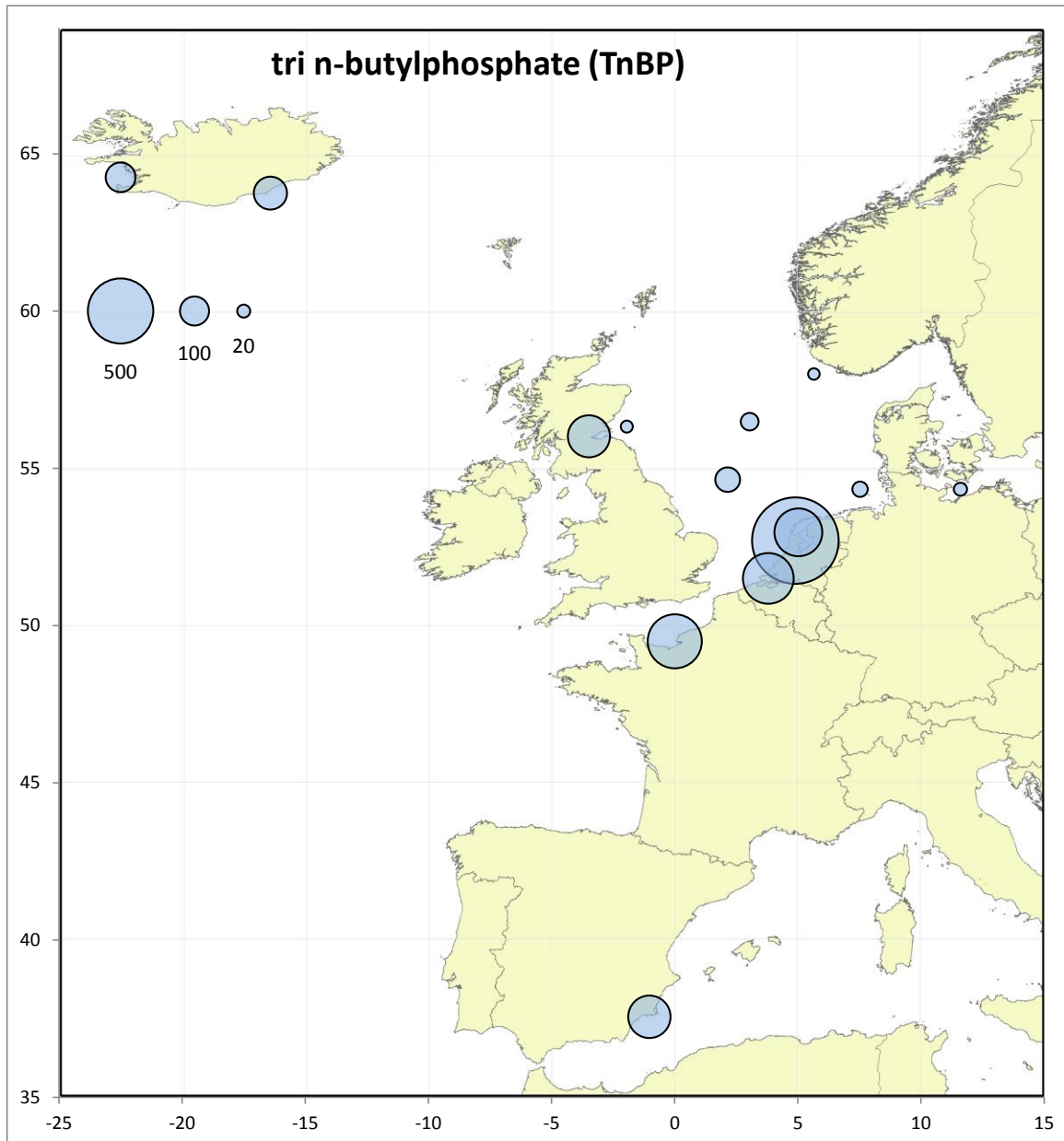
B Examples of ICES-ICON results

B.1

Amounts PCB180 (ng) collected on a 3 g silicone polymer sampler exposed to ~2 kg of sediment for 6 months.

B.2

See B1

B.3

See B1