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Organic contaminants in North Sea sediments -

Development of assessment criteria for the contaminant pollution status through multidimensional analyses

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Dedicated to Heike, Gisela Frida Anna and Rita Elisabeth.

Abstract

Since the beginning of the industrialization, the North Sea and its coastal areas are heavily affected by anthropogenic activities, which has resulted in significant chemical pollution with a variety of diverse contaminants. Pollution by contaminants leads to substantial pressure and profound effects on the ecosystem at different levels and has therefore resulted in various legislative instruments to protect the marine environment (e.g Marine Strategy Framework Directive (MSRL) or Oslo/Paris Convention (OSPAR)). However, the assessment of contaminants in marine sediments, mandated by policies such as Descriptor 8 of the MSFD, lacks targeted indicators and criteria. To address parts of this gap, three different approaches were applied within this thesis to investigate alternative assessment strategies for a wide range of organic contaminant groups in sediments from different scientific perspectives.

First, bulk sediment and its corresponding fine grain fraction (< 63 μm) from 25 stations in the German exclusive economic zone (EEZ) were evaluated for 41 hydrophobic organic contaminants (HOCs). The study provides a comprehensive overview of HOC concentrations in sediment fines (< 63 μm) for the study area and therefore in the bioavailable fraction of the sediment. Also, the study serves to compare the results obtained by the analysis of sediment fines, and thus by a total organic carbon (TOC) independent physical normalization through wet-sieving, with existing normalization methods (2.5 % TOC, OSPAR/ICES). The investigation offers a basis for discussion on the urgently needed further standardization of measurement results of organic contaminants in sediments. The results indicate that the applied wet-sieving method is capable of normalizing the concentrations of the investigated HOCs and is useful for the comparison of different sediment types such as present in the German EEZ. Sieving separates the coarse, mostly chemically inert fraction and thus indirectly concentrates the contaminants. This offers the possibility of lowering the detection limits (LOD) through the analytical sample preparation procedure used, thus generating a higher number of results $>$ LOD leading to more informative data sets. In contrast to the commonly used normalization to 2.5 % TOC, the statistical analyses performed indicate that physical normalization allows a better differentiation of sampling sites by contaminant sources and geographic location rather than their sediment characteristics.

Second, historical pollution trends were investigated in a set of sediment cores sampled in the Skagerrak, one of the North Seas' main sedimentation area. Next to the investigation of historical pollution trends, the study serves to verify the effectiveness of changing environmental legislation. Altogether, 90 contaminants covering inorganic and organic pollutant groups were analyzed. Additionally, samples were radiometrically dated and PAH and PCB levels in porewater were determined using equilibrium passive sampling. Thereby a chemical pollution fingerprint was developed recording the constant input of contaminants over time and illustrating their continued great relevance for the present. The results reveal that for all organic contaminant groups covered (PAHs, OCPs, PCBs, PBDEs and PFASs) as well as the elements lead (Pb) and titanium (Ti), determined concentrations decreased towards more recent deposited sediment. These decreasing trends could be linked to the time of introductions of restrictions and bans and therefore the results confirm, amongst possible other factors, the effectiveness of environmental legislation by revealing a successive change in contamination levels over the decades. Additionally, concentration trends for ΣPAH and ΣPCB measured in porewater correspond well with the ones found in sediment suggesting that this method can be a useful expansion to traditional bulk sediment analysis. Furthermore, Arsenic (As) concentrations were increasing towards younger sediment layers, potentially caused by emissions of corroded warfare material disposed in the study area after WW II.

And third, a toxicological screening-test for marine sediments applying effect based analyses and capturing mixed toxicities was developed. As mixed toxicities in marine sediments are up to now not adequately represented in assessment programs, the study serves as a basis for the risk assessment of marine sediment contamination that goes beyond the determination of target contaminant concentrations. Therefore, the application of high performance thin layer chromatography (HPTLC)-bioluminescence coupling as a cost- and time-efficient tool has been applied to marine sediments for the first time. Furthermore, an easy-to-use R-script for the semi-quantitative evaluation of resulting bioluminescence inhibition images has been programmed. The developed method was applied to sediment extracts of two different sample sets: 1. Fourteen marine sediment samples from the German Bight representing a wide range of contaminant loads and sediment properties and 2. sediment samples from a core representing temporal trends of contamination. The results show that the developed method is able to separate major HOC classes found in marine sediments. Therefore, it was possible to link the observed effects to results from target analysis. This is demonstrated by a very good correlation ($R^2 = 0.91$) of the determined inhibition Γ-values for the PAH inhibition zone to measured PAH concentrations with GS-MS/MS. In conclusion, the HPTLC-bioluminescence approach reveals to be a promising tool to be further developed and implemented as a toxicity test for marine sediments.

Zusammenfassung

Seit Beginn der Industrialisierung sind die Nordsee und ihre Küstengebiete stark von anthropogenen Aktivitäten betroffen. Dies hat zu einer erheblichen chemischen Verschmutzung mit einer Vielzahl unterschiedlicher Schadstoffe geführt. Die Verschmutzung durch Schadstoffe resultiert auf unterschiedlichen Ebenen zu erheblichem Druck und tiefgreifenden Auswirkungen auf das Ökosystem und hat daher zur Implementierung von verschiedenen Rechtsinstrumenten zum Schutz der Meeresumwelt geführt (z.B. Meeresstrategie-Rahmenrichtlinie (MSRL) oder Oslo/Paris-Übereinkommen (OSPAR)). Bei der Bewertung von Schadstoffen in Meeressedimenten, die durch politische Maßnahmen wie den Deskriptor 8 der MSRL vorgeschrieben sind, fehlt es jedoch an gezielten Indikatoren und Kriterien. Um einen Teil dieser Lücke zu schließen, wurden in dieser Arbeit drei verschiedene Ansätze angewendet, um alternative Bewertungsstrategien für ein breites Spektrum an organischen Schadstoffgruppen in Sedimenten aus unterschiedlichen wissenschaftlichen Perspektiven zu untersuchen.

Zunächst wurden Gesamtsedimentproben und die entsprechende Feinkornfraktion ($< 63\ \mu$m) von 25 Stationen in der deutschen ausschließlichen Wirtschaftszone (AWZ) auf 41 hydrophobe organische Schadstoffe (HOC) untersucht. Die Studie gibt einen umfassenden Überblick über die HOC-Konzentrationen in der Feinkornfraktion ($< 63\ \mu$m) im Untersuchungsgebiet und damit in der bioverfügbaren Fraktion des Sediments. Darüber hinaus dient die Studie dem Vergleich der Ergebnisse, welche durch die Analyse der Feinkornfraktion und damit durch eine vom organischen Gesamtkohlenstoff (TOC) Gehalt unabhängige physikalische Normalisierung durch Nasssiebung gewonnen wurden, mit Ergebnissen von bestehenden Normalisierungsmethoden (2.5 % TOC, OSPAR/ICES). Die Untersuchung bietet eine Diskussionsgrundlage für die dringend notwendige weitere Standardisierung der Messergebnisse von organischen Schadstoffen in Sedimenten. Die Ergebnisse zeigen, dass es mit der angewandten Nasssiebungsmethode möglich ist einen Vergleich verschiedener Sedimenttypen, wie sie in der deutschen AWZ vorkommen, in Bezug auf die untersuchten HOCs, vorzunehmen. Durch die Siebung wird die grobe, meist chemisch inerte, Fraktion abgetrennt und damit die Schadstoffe indirekt aufkonzentriert. Dies bietet die Möglichkeit, die Nachweisgrenzen (LOD) durch das verwendete analytische Probenvorbereitungsverfahren zu senken und so eine höhere Anzahl von Ergebnissen > LOD zu liefern. Dies führt zu aussagekräftigeren Datensätzen. Im Gegensatz zur üblicherweise angewandten Normierung auf 2.5 % TOC, weisen die durchgeführten statistischen Analysen darauf hin, dass die physikalischen Normierung eine bessere Abgrenzung der Probenahmestellen nach Schadstoffquellen und geografischer Lage anstelle ihrer Sedimenteigenschaften ermöglicht.

Zweitens wurden historische Schadstofftrends in einer Gruppe von Sedimentkernen untersucht, die an einer Messstation im Skagerrak, einem wichtigen Sedimentationsgebiet der Nordsee, entnommen wurden. Neben der Untersuchung historischer Schadstofftrends dient die Studie dazu, die Wirksamkeit der sich ändernden Umweltgesetzgebung zu überprüfen. Insgesamt wurden 90 Schadstoffe aus anorganischen und organischen Schadstoffgruppen analysiert. Zusätzlich wurden die Proben radiometrisch datiert und der PAK- und PCB-Gehalt im Porenwasser mittels Gleichgewichts-Passivsammlerprobenahme bestimmt. Auf diese Weise konnte ein Fingerabdruck der chemischen Verschmutzung erstellt werden, der den konstanten Eintrag von Schadstoffen im Laufe der Zeit zeigt und ihre anhaltend hohe Relevanz für die Gegenwart verdeutlicht. Die Ergebnisse zeigen, dass für alle erfassten organischen Schadstoffgruppen (PAHs, OCPs, PCBs, PBDEs und PFASs) sowie die Elemente Blei (Pb) und Titan (Ti) die ermittelten Konzentrationen hin zu jüngeren Sedimentablagerungen abnehmen. Diese rückläufigen Trends konnten mit den Einführungen von Beschränkungen und Verboten der entsprechenden Substanzen in Verbindung gebracht werden. Neben möglicher anderen Faktoren, wird durch die Ergebnisse deutlich, dass Umweltgesetzgebungen wirksam sind und zu einer sukzessiven Abnahme der Konzentrationen im Laufe der Jahrzehnte geführt haben. Darüber hinaus stimmen die Konzentrationstrends für ΣPAH und ΣPCB, die im Porenwasser gemessen wurden, gut mit denen im Gesamtsediment bestimmten Konzentrationen überein. Dies deutet darauf hin, dass diese Methode eine mögliche Ergänzung zur herkömmlichen Analyse von Gesamtsedimentproben darstellen kann. Zusätzlich konnten ansteigende Arsenkonzentrationen (As) in jüngeren Sedimentschichten festgestellt werden, was möglicherweise auf Emissionen von korrodiertem Kriegsmaterial zurückzuführen ist, welches nach dem Zweiten Weltkrieg im Untersuchungsgebiet entsorgt wurde.

Und drittens wurde ein toxikologischer Screening-Test für marine Sedimente entwickelt. Dieser wendet wirkungsbasierte Analysen an und dient der Erfassung von Mischtoxizitäten. Da Mischtoxizitäten in Bewertungsprogrammen für marine Sedimente bisher nicht angemessen berücksichtigt werden, dient die Studie dazu eine Grundlage für die Risikobewertung von Schadstoffgemischen in marinen Sedimenten zu schaffen und geht damit über die Bestimmung von Einzelstoffkonzentrationen hinaus. Die Hochleistungs-Dünnschichtchromatographie (HPTLC)-Biolumineszenz-Kopplung wurde als kosten- und zeiteffizientes Werkzeug erstmals für marine Sedimente angewendet. Zusätzlich wurde ein einfach zu bedienendes R-Skript zur semi-quantitativen Auswertung für die resultierenden Biolumineszenz-Inhibitionsbilder programmiert. Die entwickelte Methode wurde anschließend auf Sedimentextrakte aus zwei verschiedenen Probensätzen angewandt: 1. vierzehn marine Sedimentproben aus der Deutschen Bucht, die ein breites Spektrum an Schadstoffbelastungen und Sedimenteigenschaften repräsentieren, und 2. Sedimentproben aus einem Sedimentkern, die zeitliche Trends der Schadstoffbelastung darstellen. Die Ergebnisse zeigen, dass die entwickelte Methode in der Lage ist, die wichtigsten in marinen Sedimenten vorkommenden HOC-Gruppe zu trennen. Daher war es möglich, die beobachteten Effekte mit den Ergebnissen der massenspektrometrischen Bestimmung von Zielanalyten zu verknüpfen. Dies wird durch eine sehr gute Korrelation ($R^2 = 0.91$) der ermittelten Γ-Hemmungswerte für die Elutionszone der PAK zu den mit GS-MS/MS gemessenen PAK-Konzentrationen belegt. Zusammenfassend lässt sich sagen, dass die HPTLC-Biolumineszenz-Methodik ein vielversprechendes Instrument ist, welches als Toxizitätstest für Meeressedimente weiter entwickelt und eingesetzt werden kann.

List of Publications and Conference Contributions

Parts of this thesis have been published in peer-reviewed journals and were presented at national and international conferences. The relevant publications and conference contributions are listed below.

Publication I

"Distribution of hydrophobic organic contaminants in marine sediment fines – an alternative normalization strategy?"
A. Logemann, S. Röhrs, B. Brockmeyer
Contributions: Anna Logemann: Formal analysis; data curation; investigation; methodology; resource procurement; validation; visualization; writing—original draft. Steffen Röhrs: Formal analysis; data curation; investigation; methodology; writing—review and editing. Berit Brockmeyer: Conceptualization; supervision; project administration; funding acquisition; resources; writing—review and editing.
Manuscript accepted: January 18th 2023
Manuscript status: published
DOI: 10.1002/ieam.4744
Journal: Integrated Environmental Assessment and Management

Publication II

"Assessing the chemical Anthropocene – Development of the legacy pollution fingerprint in the North Sea during the last century"
A. Logemann, M. Reininghaus, M. Schmidt, A. Ebeling, T. Zimmermann, H. Wolschke, J. Friedrich, B. Brockmeyer, D. Pröfrock, G. Witt
Contributions: A. Logemann prepared and led the sediment sampling, conducted the analytical chemistry work for HOCs in sediments, and prepared the initial draft of the paper. M. Reininghaus conducted the laboratory work for HOCs in porewater and contributed to drafting the paper. M. Schmidt conducted all analytical chemistry work for metal isotopes and trace metals in the sediments. H. Wolschke and J. Friedrich carried out the radiometric dating, its interpretation and contributed to drafting the paper. A. Ebeling and T. Zimmermann contributed to drafting the paper. B. Brockmeyer, D. Pröfrock and G. Witt obtained funding, provided supervision and guidance on writing and final drafting the paper.
Manuscript accepted: February 18th 2022
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DOI: 10.1016/j.envpol.2022.119040
Journal: Environmental Pollution

Publication III

"Using the HPTLC-bioluminescence bacteria assay for the determination of acute toxicities in marine sediments and its eligibility as a monitoring assessment tool"

A. Logemann, M. Schafberg, B. Brockmeyer

Contributions: Anna Logemann: Conceptualization, Methodology, Data curation, Software, Visualization, Investigation, Writing - original draft. Michaela Schafberg: Conceptualization, Methodology, Resources, Writing - review & editing. Berit Brockmeyer: Supervision, Project administration, Funding acquisition, Writing - review & editing.

Manuscript accepted:	May 27th 2019
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Journal:	Chemosphere

Conference Contribution I

"Historischer Eintrag und Risikobewertung hydrophober organischer Schadstoffe ausgewählter Sedimentkerne"
A. Lau, M. Reininghaus, F.S. Krüger, T. Ranftl, B. Brockmeyer, G. Witt
Poster presentation
Conference: Küno Meeting 2017

Conference Contribution II

"Towards a cost-effective and rapid toxicological screening method for organic contaminants in marine matrices using HPTLC-bioluminescence detection with *Aliivibrio fischeri*"
M. Schafberg, **A. Lau**, U. Kraus, B. Brockmeyer
Oral presentation
Conference: DIOXIN 2018

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List of Abbreviations

BAC	background assessment concentration
BC	background concentration
BfR	Federal Institute for risk Assessment
BLANO	Bund/Länder-Arbeitsgemeinschaft Nord- und Ostsee
BLMP	German Bund/Länder Messprogramm
BSH	Federal Maritime and Hydrographic Agency
CEMP	coordinated environmental monitoring program
CHCs	chlorinated hydrocarbons
CIS	cold injection system
CRS	constant rate of supply
dw	dry weight
EAC	environmental assessment concentration
EC	European Commission
EC_{50}	median effective concentration
EDA	effect-directed analysis
EEZ	Exclusive Economic Zone
EPA	Environmental Protection Agency
EPSMs	equilibrium passive sampling methods
EQS	environmental quality standards
ERL	effect range low value
ESBTU	equilibrium partitioning sediment benchmark toxic units
EU	European Union
FFH Directive	Fauna-Flora-Habitats Directive
GC-MS	gas chromatography - mass spectrometry
GC-MS/MS	gas chromatography - tandem mass spectrometry
GES	good environmental status
GPC	gel permeation chromatography
HELCOM	Helsinki Commission
HOC	hydrophobic organic contaminant
HPTLC	high performance thin layer chromatography
ICP-MS	inductively coupled plasma mass spectrometer
ICP-MS/MS	inductively coupled plasma tandem mass spectrometer

IS	internal standard
LC-MS/MS	liquid chromatography with mass spectrometry detection
LDPE	low density polyethylen
LOD	limit of detection
LOQ	limit of quantification
MARPOL Convention	International Convention for the prevention of marine pollution from ships
MC	multi collector
MOAH	Mineral Oil Aromatic Hydrocarbons
MOSH	Mineral Oil Saturated Hydrocarbons
MRI	magnetic resonance imaging
MSFD	Marine Strategy Framework Directive
MUC	multi corer
NOAH	North Sea Observation and Assessment of Habitats
OC	organic carbon
OCPs	organochlorine pesticides
OSPAR	Oslo-Paris Convention
PAHs	polycyclic aromatic hydrocarbons
PBDEs	polybrominated diphenyl ether
PBT	persistent, bioaccumulative and toxic
PCBs	polychlorinated biphenyls
PDMS	polydimethylsiloxane
PFASs	per- and polyfluoroalkyl substances
POPs	persistent organic pollutants
QAQC	quality assurance qualitiy control
QC	quality control
RIV	reciprocal iso-inhibition volume
R_F	retention factor
SEC	size exclusion chromatography
SI	supporting information
SPE	solid phase extraction
SPME	solid phase micro extraction
SQGs	sediment quality guidelines
TCEs	technology-critical elements
TLC	thin layer chromatography
TOC	total organic carbon
TWSC	trilateral cooperation for the protection of the wadden sea
UK	United Kingdom
UN	United Nations
UN SDGs	United Nations sustainable development goals
UV	ultra violett
VFD	Birds Directive

WFD	Water Framework Directive
WW II	world war II

Chapter 1

Introduction, Thesis Objectives and Outline

1.1 Introduction

The North Sea faces increasing usage requirements (e.g. through offshore wind-energy) while simultaneously serving as an important wildlife habitat. This requires not only the sustainable use of the North Sea, but also the protection of its natural resources. Hence, the European Union's Marine Strategy Framework Directive (MSFD) as well as national- and regional-level marine conventions (e.g. Oslo-Paris Convention OSPAR, Helsinki Convention HELCOM) mandate that a good environmental status (GES) of marine habitats have to be maintained or reached. In order to initiate further political measures achieving GES, in addition to recording the current state of the environment through data collection within monitoring programs, suitable assessments criteria have to be developed on a scientific basis. Regarding the characteristic „Contaminants" (Descriptor 8 of the MSFD), the existing assessment is not sufficient to meet the requirements of the MSFD (BLANO, 2012). A recent review by da Costa Filho et al. (2022) summarizes that despite technological advances in analytical techniques, current assessment methods for contaminants are still unable to link concentrations to more meaningful data, such as bioavailability and whether concentrations are posing a risk to the marine environment. Also, mixed toxicities caused by the cocktail of contaminants present in the environment are not captured adequately by current assessment methods (Kienzler et al., 2017). Therefore, a comprehensive approach was applied within this thesis to investigate alternative assessment strategies for a wide range of organic contaminant groups in sediments. For this purpose, several concepts have been explored in detail to address the topic of assessment strategies for contaminants in sediments from different scientific perspectives:

- Investigating contaminant concentrations in the fine grain fraction of sediments to obtain a spatially extended inventory of contaminant concentrations in the bioavailable fraction of sediment. Simultaneously current standardization procedures will be reviewed and investigated to determine whether a better comparability of the results can be achieved (Chapter 2).
- Investigating the temporal evolution of contaminant concentrations and to reconstruct the effectiveness of political measures using sediment cores (Chapter 3)
- Investigating mixed toxicities in marine sediments by implementing and adapting a chemical-toxicological screening test using bioluminescence bacteria in combination with high performance thin layer chromatography (Chapter 4)

This thesis was carried out in the framework of the NOAH synthesis project (North Sea Observation and Assessment of Habitats). The NOAH synthesis project aimed to extend the geo-referenced inventory of sea floor properties in the German Exclusive Economic Zone of the North Sea, which were developed in the first phase of the project ("habitat atlas"). In combining different scientific disciplines and investigating sedimentological, physical, chemical and biological properties of the sea floor as well as anthropogenic pressures acting on it, the data derived from the project form the basis for the assessment of the sea floor state as demanded from MSFD requirements (Emeis et al., 2019).

1.1.1 Contaminants in marine sediments - sources and pathways

Chemical substances are part of humans everyday life and are essential for modern societies, leading to many desired benefits (Wang et al., 2020). They are either naturally occurring (e.g. trace metals), unintentionally produced as industrial by-products (e.g. dioxins and furans) or intentionally synthesized for a specific application (OSPAR, 2009b). This results in a large amount of chemicals produced annually, and numbers are increasing with for example over 1000 newly registered substances every year in Europe under REACH between 2008 and 2018 (ECHA, 2018). Wang et al. (2020) recently estimated that over 350.000 chemicals have been registered so far. However, these chemicals can be released during their lifecycle and distributed into the environment, potentially causing adverse effects in humans, wild life and the environment. Particularly problematic are contaminants that have persistent, bioaccumulative and toxic (PBT) properties. Among others, PBT substances include known problematic compound groups such as polychlorinated biphenyls (PCBs), polybrominated diphenyl ether (PBDEs), per- and polyfluoroalkyl substances (PFASs), specific polycyclic aromatic hydrocarbons (PAHs) or certain organochlorine pesticides (OCPs) (further information provided in section 1.1.2).

Contaminants can be released into the environment via various diffuse or direct sources.

These include land-based sources such as waste water treatment plants, industrial processes, urban and agriculture run-off, traffic or construction (see Figure 1.1) (OSPAR, 2009b). For example, the United Nations (UN) estimates that about 80 % of the global wastewater enters the environment without proper treatment, thereby releasing large amounts of nutrients and contaminants into the environment (United Nations, 2017). Once released, contaminants are entering the marine environment mainly through river discharge or atmospheric transport and subsequent deposition (Ernst et al., 1988). On the other hand, marine pollution can be caused directly at the seas, such as by aquaculture, shipping, deep-sea mining, or the oil and gas industry (see Figure 1.1) (Tornero and Hanke, 2016). As a result, the marine environment is burdened with a complex mixture of contaminants, which is consequently vulnerable to the accumulation of contaminants in its various environmental compartments (e.g, water column, suspended particulate matter, sediment, pore water, and biota) and can thus act both as a sink as well as contribute to global distribution depending on the PBT properties of the compounds in question (Scott et al., 2012; Vethaak et al., 2017).

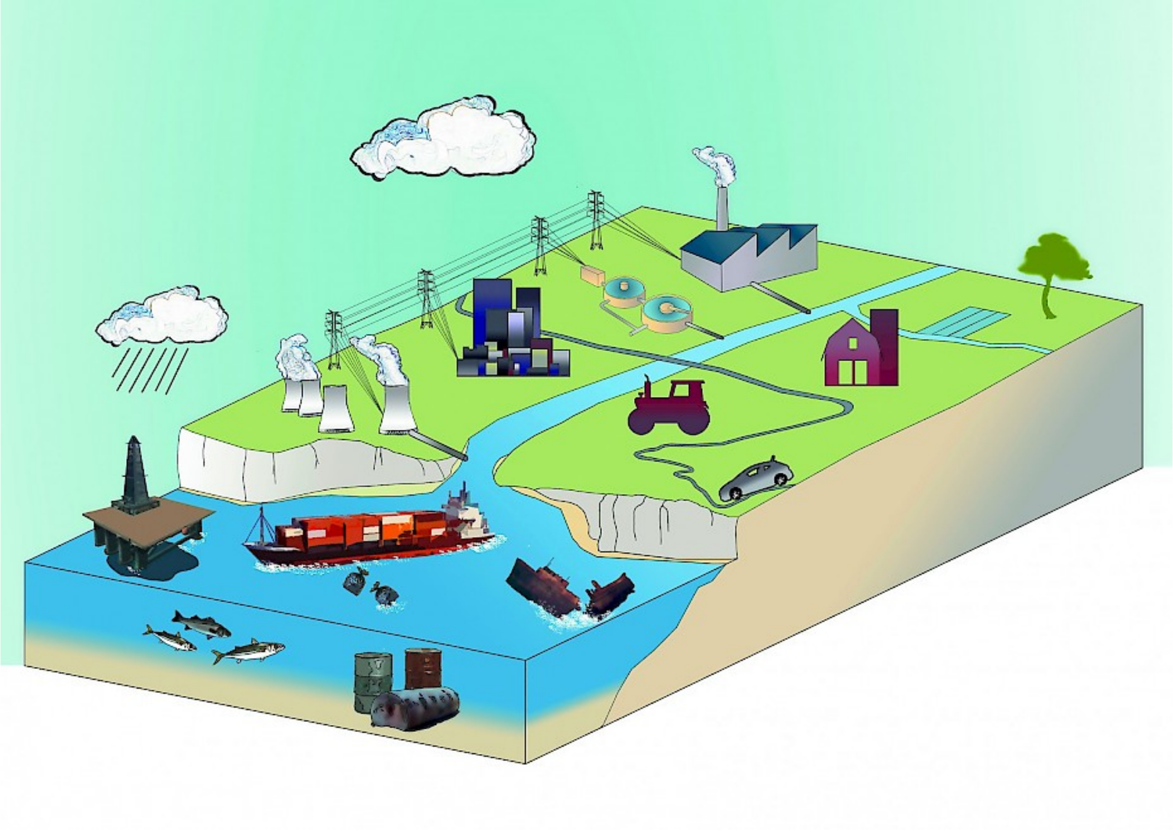

Figure 1.1: *Schematic display of sources of contaminants and their pathways into the marine environment (retrieved from OSPAR, 2010)*

The physico-chemical properties of individual contaminants including the partitioning coefficients $log\ K_{OW}$ or $log\ K_{OC}$ determine their distribution between the marine environmental compartments water, suspended particulate matter, sediments, its porewater and food web (biota) (Gschwend and Wu, 1985). Other relevant physico-chemical properties including pH-value and the total organic carbon (TOC) content in the sediment also play important roles in the distribution of contaminants in the marine environment

(Calmano, 2001). PBT substances are often characterized by *log* K_{OW} values > 3, meaning they preferentially partition to suspended particulate and organic matter and are subsequently prone to accumulation in marine sediments. Because sediments are not subject to the rapid temporal and spatial changes in contamination that can be observed for other environmental compartments such as water, they are frequently referred to as the "memory of the oceans" that builds up slowly over time. This is why sediment is particularly well suited for environmental assessment approaches, partly because they are easier to obtain, analyze and interpret than, for example, biological samples (Birch, 2003). In addition, marine sediments provide habitats for numerous organisms as well as bacterial, plant and animal microorganisms (Calmano, 2001) and are, for this reason, a large component of the marine food web forming the basis of aquatic ecosystems (Birch, 2003). Besides their major role within contaminant transport and storage, analysis of sediments offer the possibility to identify contaminant sources and dispersion pathways, which in turn underlines the great importance of sediments for contaminant analysis in the marine environment and its assessment on the path to reaching GES (see 1.1.3) (Birch, 2003).

Sediments consist of both an inorganic and an organic fraction and have different compositions of grain size distributions (coarse fraction < 2 mm - > 63 μm, fine fraction < 63 μm, Figge, 1981). The inorganic, mostly coarse fractions of the sediment consists mainly of carbonates and silicates (Herut and Sandler, 2006; Schmolke, 2016), while the organic fraction is composed of organic matter that consists e.g. of carbohydrates and other biological macromolecules (Pusceddu et al., 1999). The organic matter originates e.g. from detritus of living organisms (bacteria, plankton, plants or animals) and is transported from catchments or originates directly from the marine environment. In principle, the higher the content of fine grain material in the sediment, the higher the content of organic matter (for example quantified as TOC). Due to their binding affinities, organic contaminants preferentially accumulate in the organic fraction of the sediment. However, the origin and structure of the organic matter itself also has an influence on the sorption of contaminants (e.g. soot). In addition, the inorganic parts of the fine grain fraction, containing e.g. clay minerals, iron(III) oxide hydrates, manganese(IV) oxide hydrates and iron(II) sulphides, also have a high sorption capacity for contaminants due to their high surface/volume-ratio (Eisma and Irion, 1988; Schmolke, 2016). Hence, contaminant concentrations also correlate with the sediments' grain size distribution, meaning that the fine sediments' higher sorption capacities result in higher contaminant concentrations in comparison to sandy sediment (Loring, 1991). Even though sediments act as a sink for organic contaminants, a continuous partitioning process takes place between the sediment, its porewater, the biota, and the aqueous layer above it (Figure 1.2). However, mobilization between the sediment and the overlying water is generally caused by extensive physical disturbance, such as through turbulent mixing, resuspension and remobilization processes caused by e.g. increased storm events, tidal currents, bioturbation and -irrigation, or human interferences such as dredging (Kersten, 1988).

Therefore, contaminated sediments can also become a secondary source and contribute to contaminant releases (Hollert et al., 2002; OSPAR, 2009b), an effect that could be amplified through climate change.

In the future, climate change will likely result in regime shifts in the marine environment with regard to contaminants in sediments: For example, higher temperatures and changes in salinity result in altered physico-chemical parameters that govern contaminant distribution. As a result, increased remobilization of contaminants from sediment to water and the resulting distribution of these may be observed (UNEP/AMAP, 2011). Furthermore, the predicted increased frequency and magnitude of storm events will likely result in increased resuspension of contaminants in shallow seas such as the North Sea (BLANO, 2022a; Driscoll et al., 2014). Moreover, climate change could vary contaminant distribution and presence through input from other marine areas or the melting of polar ice, as well as by changes in the marine carbonate system that might lead to altered solubility of e.g. heavy metals that are currently bound in sediments (BLANO, 2022a). In addition, climate change may indirectly increase contaminant concentrations in marine sediments if atmospheric warming increases the transport of certain substances and more rainfall, flooding, and increased runoff in the hinterland result in higher contaminant inputs to the marine environment (OSPAR, 2009b).

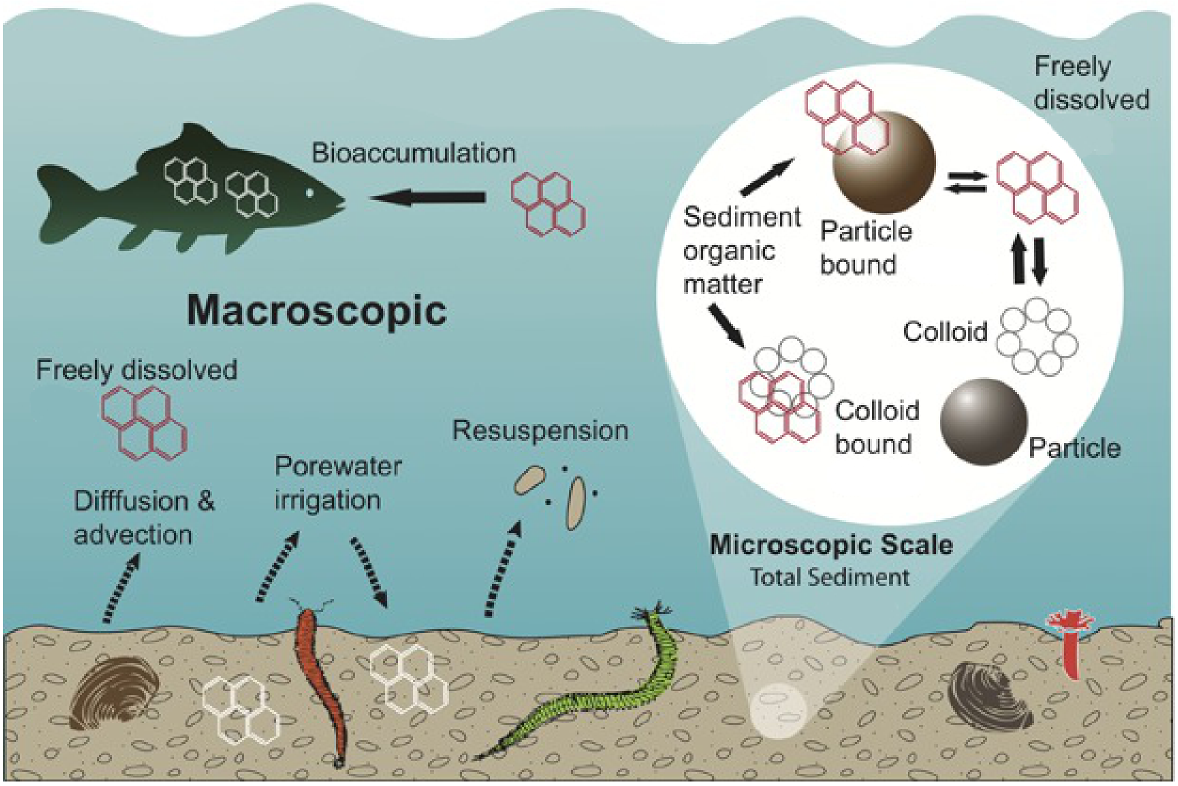

Figure 1.2: *Contaminant partitioning in the sediment-water system (retrieved and adapted from Mayer et al., 2014, CC BY-NC 4.0)*

1.1.2 Hydrophobic organic contaminants studied in this thesis

In this thesis, hydrophobic organic contaminants (HOCs), which are still of relevance to marine sediments due to their characteristic properties, have been studied. HOCs are lipophilic, persistent and therefore poorly biodegradable and have a low vapor pressure, which results in very long environmental half-lives and a preferential association with suspended solids and accumulation in the food chain. HOCs studied in this thesis include substances from the following contaminant groups: PAHs, PCBs, OCPs, and PBDEs. Some contaminants within the latter three groups are also known as persistent organic pollutants (POPs) and are listed by the Stockholm Convention (United Nations, 2001). However, due to their above described properties, HOCs are up until today detected in seawater or sediments, even though being banned more than 20 years ago (Avellan et al., 2022) and therefore preventing marine environments from reaching GES (BLANO, 2022a).

PAHs are composed of carbon-hydrogen atoms and form molecules containing two or more aromatic rings with delocalized electrons. While PAHs are unintentionally produced as a result of anthropogenic or natural incomplete combustion processes (e.g. coal or fossil fuel combustion, shipping industry, oil exploitation, forest fires) (Bigus et al., 2014; Pérez-Fernández et al., 2016; Wenning and Martello, 2014; Witt, 1995; Wolska and Rogowska, 2012), PCBs are man-made substances originally manufactured due to their good dielectric properties and very low flammability for wide range of industrial purposes (ELSA, 2016; Gałuszka et al., 2020). PCBs consist of 209 congeners resulting from the varying degree of chlorination on their biphenyl main structure (Ballschmiter et al., 1987). PCBs were originally marketed as complex mixtures with different compositions (e.g. AroChlor 1016 or 1254), resulting in approx. 113 of the 209 congeners being detectable in the environment (Crisp et al., 1998). Depending on the position of the chlorine atoms (none in ortho-position), there are existing coplanar PCBs that have similar properties to dioxins and are therefore particularly problematic. Due to the non-trivial analysis of all individual PCB congeners, it has been agreed in environmental analysis to examine individual congeners, usually these include 28, 52, 101, 118, 138, 156 and 180. Likewise, PBDEs form a group of chemicals with 209 similar substances, but consisting of a diphenyl ether main structure substituted with an corresponding number of bromine atoms. PBDEs are grouped by their commercial mixtures decabromodiphenyl ether (deca-BDE), octabromodiphenyl ether (octa-BDE) and pentabromodiphenyl ether (penta-BDE). They have commonly been used as flame retardants in consumer products such as furniture, and have been in global use since the 1980s (Korosi et al., 2015).

OCPs are a group of chemicals comprised mainly of pesticides that have been applied in agriculture and households for several decades within the 20th century. Probably the best-known representative of this group is the insecticide dichloro-diphenyl-trichloroethane

(DDT), which transformation products led to eggshell thinning of birds of prey eggs as a result of its application (Vos et al., 2000). In particular, the publication of Silent Spring by Rachel Carson (1962) resulted in an increasing awareness of the consequences using these pesticides which ultimately marked the beginning of an environmental movement towards a more mindful use of chemicals.

1.1.3 Current status of contaminant assessment in sediments and sediment monitoring

Contamination of the marine environment by hazardous substances is a major environmental concern in European waters. Painting et al. (2020) state that contaminants are one of the top three most commonly identified pressures within European member states threating marine waters, along with shipping activity and marine litter. Consequently, there are several strategies and programs in place in the European Union (EU) to combat contaminants and the resulting pollution, which include important legal measures, policies and conventions for marine areas and surface waters that are outlined in this section (Vethaak et al., 2017). In Germany, for example, various EU directives as well as regional and international conventions on marine protection must be considered and implemented nationally (LAWA, 2014). This coexistence of several policy instruments affecting the marine environment and its monitoring is illustrated in Figure 1.3.

As marine conservation starts inland, directives aiming towards an improvement of upstream water quality are of central importance, directly influencing the status of marine waters through improvement of ground and surface waters. These include, among others, the Bathing Water Directive (EU 2006/7/EC, 2006), Waste Water Directive (EU 91/271/EEC, 1991), the Nitrate Directive (EU 91/676/EEC, 1991), the EQS Directive (EU 2008/105/EC, 2008; EU 2013/39/EU, 2013), the Flood Risk Management Directive (EU 2007/60/EC, 2007) and the Waste Directive (EU 2008/98/EC, 2008). Additionally, the Habitats Directive (EU 92/43/EEC, 1992)), Birds Directive (EU 2009/147/EC, 2010), Trilateral Cooperation for the Protection of the Wadden Sea (TWSC, 2010) and the MARPOL Convention (IMO, 1973) are of great and direct importance for the environmental protection of marine habitats (LAWA, 2014) (Figure 1.3). However, with regard to contaminants in the marine environment, and therein especially contaminants in sediments and their monitoring, the Water Framework Directive (EU 2000/60/EC, 2000), the regional marine conventions OSPAR (Convention for the Protection of the Marine Environment of the North- East Atlantic, OSPAR (1992)) and HELCOM (Baltic marine Environment Protection Commission, HELCOM (1974)) as well as the MSFD (EU 2008/56/EC, 2008) are the key policy drivers (Lyons et al., 2017; Painting et al., 2020).

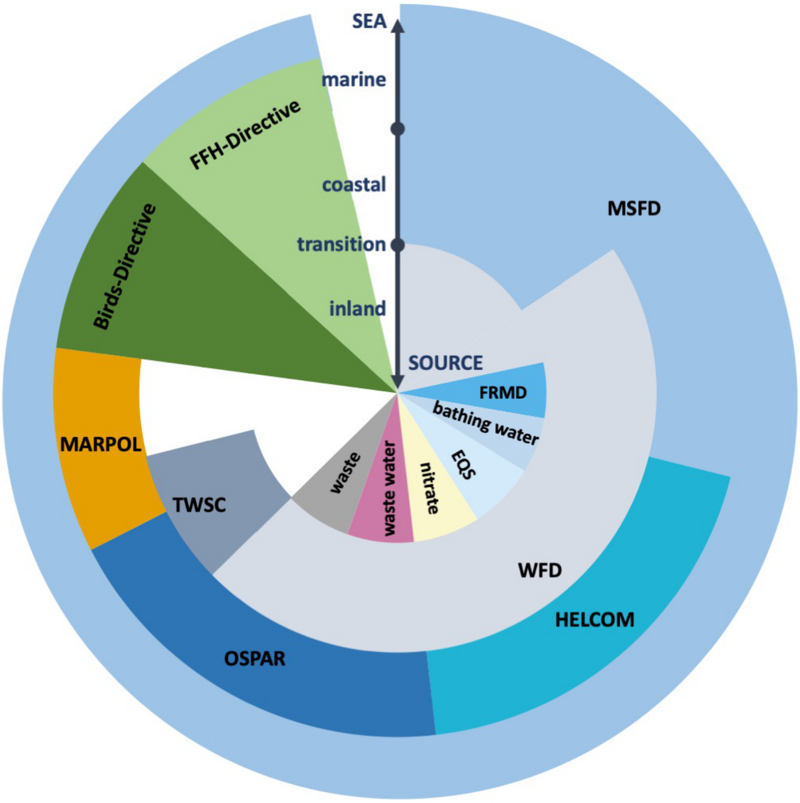

Figure 1.3: *Illustration of the co-existence and approximate scopes of different environmental legislations and conventions that affect and relate to the marine environment from source to sea. FFH-Directive: Habitats Directive (EU 92/43/EEC, 1992), Birds-Directive (EU 2009/147/EC, 2010), MARPOL: International Convention for the Prevention of Marine Pollution from Ships (IMO, 1973), TWSC: Trilateral Wadden Sea Cooperation (TWSC, 2010), OSPAR: Oslo/Paris Convention (OSPAR, 1992), HELCOM: Helsinki Convention (HELCOM, 1974), WFD: Water Framework Directive (EU 2000/60/EC, 2000), MSFD: Marine Strategy Framework Directive (EU 2008/56/EC, 2008), waste: Waste Directive (EU 2008/98/EC, 2008), waste water: Waste Water Directive (EU 91/271/EEC, 1991), nitrate: Nitrate Directive (EU 91/676/EEC, 1991), EQS: EQS Directive (EU 2008/105/EC, 2008), bathing water: Bathing Water Directive (EU 2006/7/EC, 2006), FRMD. Flood Risks Management Directive (EU 2007/60/EC, 2007) (created and adapted from illustrations published by HELCOM, 2021; LAWA, 2014; Rabe, 2012)*

The MSFD has set up a legal framework for a comprehensive assessment and monitoring of the state of the marine environment. The objective of the MSFD is to achieve a good environmental status (GES) for all European marine habitats by 2020 (EU 2008/56/EC, 2008). For reaching GES, a good chemical status is indispensable prerequisite (Laane et al., 2012). According to Laane et al. (2012), there are two strategies for achieving GES with regard to contaminants. First, the precautionary principle, which aims to achieve near-zero anthropogenic emissions, and second, an adaptive management that is evidence-based and takes scientific research into account by reducing uncertainties, considering possibilities, and calculating risks (Laane et al., 2012). Whereas the WFD applies the precautionary principle, which is reflected for example in the application of the "one-out-all-out" (OOAO) principle, the MSFD is designed to integrate the adaptive management approach for reaching GES.

The MSFD describes the GES using 11 descriptors, one of which is explicitly addressing pollution trough contaminants (GES Desciptor 8, “Concentrations of contaminants are at levels not giving rise to pollution effects”). In detail, Descriptor 8 describes four criteria for the assessment of contaminants (EU (EU) 2017/848, 2017):

- D8C1: “Within coastal and territorial waters, the concentrations of contaminants do not exceed ... threshold values”
- D8C2: “The health of species and the condition of habitats are ... not adversely affected due to contaminants including cumulative and synergetic effects.”
- D8C3: “The spatial extent and duration of significant acute pollution events are minimized”.
- D8C4: “The adverse effects of significant acute pollution events on the health of species and on the condition of habitats ... are minimized and, where possible, eliminated”

To ensure consistency and comparability in the assessment of GES within the EU, the development of common indicators and methodological standards had to be assured in the first phase of the MSFD implementation (Lyons et al., 2017). In terms of Descriptor 8, it was recommended that specific indicators and methodological standards should be based on the existing approaches developed and guided in the Regional Sea Conventions (e.g. OSPAR, HELCOM) (Lyons et al., 2017). Consequently, OSPAR and HELCOM, established in 1992 and 1974, respectively, are important not only for the implementation and coordination of marine strategies, but also due to their existing valuable data resources available for MSFD assessment (Lyons et al., 2017). The MSFD thus complements the requirements of the WFD on a spatial and technical level and sets requirements for future marine protection, which highlights the importance of setting and applying quality objectives for sediments or suspended sediments (Keller and Schwartz, 2015). However, in the WFD, sediment has so far been considered only to a very limited extent. Yet, this is in contrast to the fact that banned or heavily regulated, persistent contaminants, which are released mainly from sediments, are partly responsible for the failure achieving GES (BLANO, 2022a). Due to their slow degradation rates, these contaminants will continue to be released and thus continue to prevent the achievement of the GES in the near future (BLANO, 2022a).

In terms of sediment quality guidelines[1] (SQGs) for contaminant assessment in sediments, OSPAR/ICES has developed and established background concentrations (BC), background assessment concentrations (BAC), environmental assessment concentrations (EACs), and low concentrations (LC) in combination with published effect range low

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[1] The term SQG is used here as an umbrella term for the variety of terms used for “target values” of contaminants in sediment in the different institutions and countries.

values (ERL) by the US Environmental Protection Agency (EPA) as an interim solution where recommended EACs are not available (ICES, 2008; Long et al., 1995; OSPAR, 2009a). These sediment quality guidelines (SQGs) form a traffic light-like system for the assessment of contaminants in sediments. The criteria for GES are not met if concentrations are above the EAC, ERL or EC (Figure 1.4) (Lyons et al., 2017; OSPAR, 2010). However, unlike the environmental quality standards (EQSs) of the WFD, which include sediment-EQSs for arsenic, chromium, copper, 7 PCB congeners, triphenyltin cation and zinc in Germany, OSPAR SQGs are not legally binding (BRD, 2016). An additional problem is that OSPAR SQGs are only available for a limited number of known contaminants and have mostly only been defined for heavy metals and the "classic" or so called “ever-given” organic contaminants (e.g. PAHs, PCBs). While these classic organic contaminants are and will remain relevant, novel compounds and compounds that are not included in this category are not captured by the framework, thereby not reflecting the full compound “cocktail” present in sediments. Nevertheless, several countries have introduced individual SQGs for contaminants of emerging concern (CESs): For example, Norway, Canada and Switzerland have published SQGs or proposals for SQGs for additional organic contaminants (Casado et al., 2022; CCME, 2022; Environment and Climate Change Canada, 2021; Olsen et al., 2019; Tornero et al., 2021) indicating a first step towards SQGs that go beyond the classic organic contaminants. These include SQGs for perfluorooctanesulfonic acid (PFOS), perfluoroctanic acid (PFOA), hexabromocyclododecane (HBCDD), chloroalkanes, bisphenol A, tetrabromobisphenol A (TBBPA), and others.

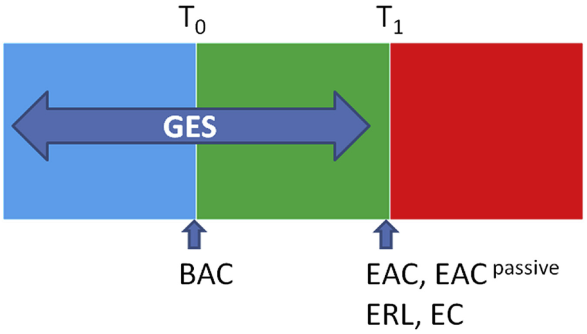

Figure 1.4: *Illustration of the proposed traffic light system for contaminants and biological effects, indicating proposed transition points depending on the different assessment criteria used (reprinted from Lyons et al., 2017, CC BY-NC-ND 4.0)*

Of course, SQGs for surface waters are of central importance for preventive marine protection, as are those developed at, for example, the river basin level (Schwartz, Bergemann, and Keller, 2015), for coastal areas (BRD, 2016; Olsen et al., 2019), or for contaminated sediment such as the targeted transfer of harbor sediments (BRD, 2009). However, the comparatively low number of available SQGs in contrast to the various amount of contaminants relevant for sediments, becomes even smaller when one considers that even less were derived directly for the marine environment. Often this can be directly attributed to the partially insufficient data situation in marine areas, as was the case for PBDEs until recently for the derivation of BACs (OSPAR, 2010). This is a circular problem. If there are no data, no SQGs can be derived for substances, but if there are no SQGs or a regulation, the corresponding substances are not included in monitoring due to a lack of cost justification, which in turn leads to the problem of insufficient data. Frequently, the reason for the lack of data is also that the TOC, required for assessment as a cofactor in marine sediments, cannot be quantified above the limit of quantification due to the very low TOC contents that are often present. This is complicated by the fact that SQGs are based on different reference systems and are therefore not directly comparable (e.g., 2.5 % TOC, 1 % TOC, dry weight). According to Batley and Warne (2017), there is an urgent need to harmonize the method to derive SQGs, not least because of the immense cost savings that can be achieved by data sharing of, for example, costly toxicity tests. This could possibly contribute to an accelerated implementation of SQGs. In addition to SQGs for surface and coastal waters, there is a lack of SQGs for marine areas (Tornero et al., 2021). Harmonized SQGs between member states for more contaminants in sediments would improve consistency and avoid conflicting assessments between MSFD, WFD and OSPAR/HELCOM (Tornero et al., 2021).

A summary of ecosystem components that should be included into monitoring and assessment has been compiled by Vethaak et al. (2017) and is displayed in Figure 1.5. Besides the assessment of sediment chemistry in the form of SQGs, further assessment tools and indicators such as sediment bioassays and benthic fauna are necessary to meet the requirements of the MSFD. With the implication of further SQGs alone, it will not be possible to detect and assess for example mixed toxicities. Hence, it is important that the assessment of contaminants in sediments evolves towards a comprehensive approach, for example analyzing many contaminant groups at the same time, and that potentiating effects are addressed. Additionally, the investigation of historical contaminant data is essential in understanding long term trends and aids to draw implications for future legislation. Therefore, more research with a comprehensive and broad scope is needed to improve the assessment of contaminants in sediments.

In addition to the above mentioned shortcomings, the policy paper published by JPI Oceans (2021) and Tornero et al. (2021) summarizes the following inconsistencies and deficiencies within the integrated assessment of chemical contaminants in the marine environment:

- Insufficient data availability for evaluating GES, only few member states monitor contaminants offshore, beyond their territorial waters.
- The geographical overlap between the MSFD and WFD in coastal zones could cause difficulties in harmonized interpretation and assessments (e.g. due to their different ecosystem approaches)
- Member States carry out the assessment at different temporal intervals, depending

on if it's based on WFD, OSPAR/HELCOM etc., which hampers the understanding of the actual marine environmental status.

- For the MSFD, there is no specific rule for assessing the state of the environment, which means that Member States can define different criteria for assessment (contrary to OOAO principle used in WFD)
- Adapt nomination of CECs for Watch-List (EU 2013/39/EU, 2013) according to risks involved for marine environment.
- Inconceivable number of contaminants entering the environment calls for novel approaches and methodologies, that foremost include CECs and provide an early warning system
- Even though standardized biological effects assessments approaches (D8C2) are available, there is a high variability in the number of biological effects methods reported by member states.
- Where primary assessment criteria are exceeded, tiered approaches combining biological effect assessments with non-target chemical screening should be applied (as developed for marine sediments by Vethaak et al. (2017)).
- Link of tiered approaches with the newly developed Smart Integrated Monitoring

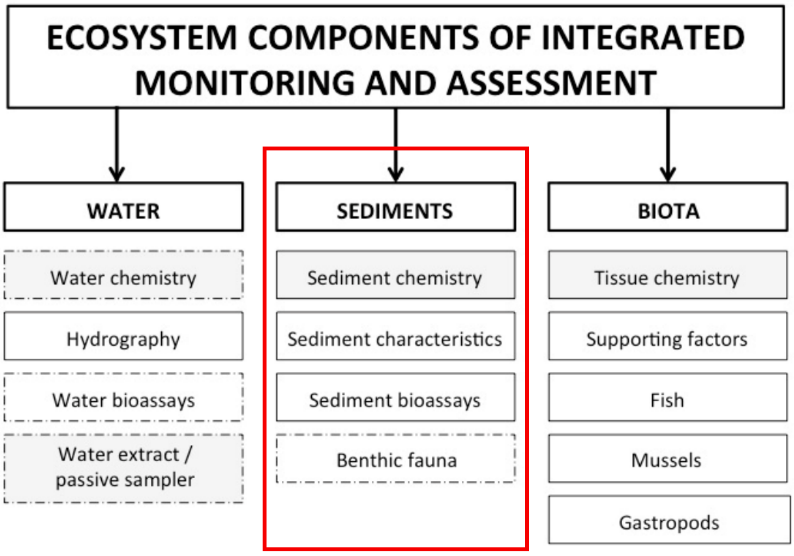

Figure 1.5: *"Overview of components in a framework for an integrated monitoring program for chemical contaminants and their biological effects developed by ICES and OSPAR. Solid lines, core methods; broken lines, additional methods." The red box marks the sediment assessment relevant for this thesis. Reprinted and adopted from Marine Environmental Research, 124, Vethaak et al., "Integrated indicator framework and methodology for monitoring and assessment of hazardous substances and their effects in the marine environment", 11-20, 2017, with permission from Elsevier, License No. 5359270036465.*

1.1.4 Study area

The North Sea is a shallow semi-open shelf sea of 750000 km^2, with an average depth of 90 m (Ducrotoy et al., 2000). It stretches from the Dover Strait in the south to the Norwegian Trough in the north with a large opening to the Atlantic Ocean. To the east, the North Sea is connected via the Skagerrak and the Kattegat to the brackish Baltic Sea, which is defined as a marginal sea of the North Sea feeding it with low salinity water. As a result of this and the constant supply of freshwater from rivers, the North Sea has a lower salinity of 33 psu in the southern coastal area compared to the Atlantic with approx. 35 psu (Ducrotoy et al., 2000; Emeis et al., 2015; Reid et al., 1988). The North Sea is surrounded by highly industrialized European countries, with its catchment inhabiting more than 140 million people, resulting in a high input of nutrients, leading to high biomass production and high input of contaminants (Emeis et al., 2015). Additionally, the North Sea is further threatened by direct anthropogenic impacts such as fisheries with overfishing and trawling, heavy ship traffic, wind energy production, oil and gas excavations, dredging and dumping (Ducrotoy et al., 2000; Emeis et al., 2015).

The area of the North Sea studied in this thesis is mainly limited to the German Exclusive Economic Zone (EEZ) located in the German Bight. Here, the Wadden Sea, which stretches from the Netherlands to Denmark, is of central ecological importance as a habitat and nursery ground for many marine species.

As the majority of the North Sea is shallow and coastal, extensive sedimentation areas, also located in the German Bight around Helgoland, with high mud contents can be distinguished (Bockelmann et al., 2018; Ducrotoy et al., 2000). A considerable part of the suspended matter is carried into the North Sea via rivers. Currents along the coast transport discharges from Rhine, Ems and Elbe into the German Bight, therefore affecting the input of contaminants via suspended particulate matter into this area of the North Sea.

1.2 Thesis objectives and outline

Through the shortcomings described in section 1.1.3, the adequate assessment of contaminants in sediments following Descriptor 8 of the MSFD is still not ideal and more research is needed to improve it. Therefore, this thesis aims to explore alternative assessment approaches for contaminants in marine sediments by applying three separate concepts that allow to shed light on contaminant assessment in sediments from different scientific perspectives. In addition, their possible applicability in context of the MSFD shall be examined and discussed.

First, the necessary normalization of contaminant concentrations in sediments is currently not carried out uniformly and further research on alternatives and possible standardization have to be investigated. In section 1.1.3 it was outlined that currently different normalization methods (e.g. 2.5 % TOC, 1% TOC, dry weight) are used, also in relation to SQGs, which make a comprehensive assessment difficult. In addition, the most commonly used co-factor for normaliaztion TOC is often below the determination limit in marine sediments, raising the question for TOC-independent normalization methods for contaminant concentrations in sediments.

Second, trend analyses of contaminants in sediments can contribute not only to necessary data for the derivation of SQGs, but also review the effect of existing environmental legislation and derived measures (e.g. the restrictions on perfluorooctane sulfonates (EU 2006/122/EC, 2006)). As outlined by Brockmeyer and Theobald (2016) and Minh et al. (2021), grab-sampling revealed disadvantages in terms of trend analyses e.g. due to the high variability within the data, changing sampling locations, and different analytical methods used. Therefore, the study of historical trends of contaminants in sediment cores provide an important contribution to the understanding long-term changes in the ecosystem and can highlight important arguments for further policy action.

Third, as outlined in section 1.1.3, there are several biological effect assessments available (Tornero et al., 2021), however – only two acute tests are designed for sediments within OSPAR (Lillicrap, 2021). The assessment of mixed toxicities is currently not adequately represented. Additionally, there is a need for the identification of non-target pollutants/CECs in combination with effect-directed bioassays (JPI Oceans, 2021). Hence, easy to apply and rapid toxicological screening tests that are applicable within monitoring, need to be developed offering the option for subsequent non-target screening.

The three different investigated approaches along with their particular research questions are shortly summarized below:

- **Determination of contaminant concentrations in sediment fines**
  Due to their large surface area, high mobility, and bioavailability, sediment fines (particles $< 63\ \mu$m) play an important role for the accumulation of organic

contaminants in sediments, as well as for the distribution processes of contaminants between the environmental compartments. The spatial survey conducted in the first project phase of NOAH was significantly expanded to answer the following research question:

  - How can the comparability of contaminant measurements in sediments be improved?
  - Does the measurement of HOCs in sediment fines represent an alternative to the measurement of HOCs in the total sediment?
  - Can the physical normalization by sieving be compared with a normalization to TOC and is this method suitable for routine use?

  The results will be presented in Chapter 2 (Cumulative Part I).

- **Investigation of pollution trends through the analysis of sediment profiles.**
  By sediment profile analysis, both actual pollution by organic contaminants in sediments and their temporal trends can be evaluated. Due to the increasing economic pressure, e.g. through offshore wind energy production, new pressures occur which are affecting the environmental status whose „chemical fingerprint“ might be detected in sediment profiles. Through analysis of deeper sediment layers, background concentrations can be determined which are of critical importance for the definition of threshold values for GES. The following research questions were raised:

  - How can sediment cores contribute to trend monitoring of contaminants, the determination of background concentrations, and to the verification and justification of the impact of environmental legislation for wide range of contaminant groups?

  The results will be presented in Chapters 3 (Cumulative Part II).

- **Mixed toxicity and effect based analyses**
  A large challenge for contaminant investigations in marine sediments is the existing knowledge gap of the overall toxicity of compound mixtures. Therefore, a biological screening test using high-performance-thin-layer chromatography (HPTLC) combined with the bioluminescence bacteria *Aliivibrio fischeri* (Beijerinck, 1889) was developed. This approach also offers a combination with target- and nontarget chemical contaminant analysis. The following research questions were asked:

  - Is the development of a toxicological screening test for HOCs in marine sediments based on HPTLC-bioluminescence coupling possible?
  - Is it an eligible assessment tool for the evaluation of marine sediment quality?

  The results will be presented in Chapter 4 (Cumulative part III)

Chapter 2

Cumulative Part I

Distribution of hydrophobic organic contaminants in marine sediment fines – an alternative normalization strategy?

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Highlights:

- Spatial distributions of organic contaminant concentrations in sediment fines ($< 63\ \mu$m) for the German EEZ are provided.
- Total organic carbon (TOC, 2.5 %) normalized bulk sediment concentrations (OSPAR/ICES) and concentrations in sediment fines (physical normalization) are comparable.
- Statistical analyses indicate that physical normalization allows a better differentiation of sampling sites by source and geographic location rather than their sediment characteristics

Abstract:

The necessary normalization of contaminant concentrations, in order to be able to compare contaminant content in sediments with different sediment properties, is currently not standardized within environmental monitoring and assessment programs. Therefore, this study investigates an alternative normalization strategy for hydrophobic organic contaminants (HOCs) by removing the coarse and chemically inert sediment fraction using an improved, half-automated wet-sieving method. We compare the results to commonly used TOC normalization (2.5 % total organic carbon [TOC], OSPAR). Simultaneously, the study provides a comprehensive overview of HOC concentrations in sediment fines ($< 63\ \mu$m) for the German Exclusive Economic Zone and therefore gathers information about the more bioavailable and mobile part of the sediment that particularly accumulates HOCs due to its high surface area. We analyzed bulk sediment samples and their corresponding fine grain fractions from 25 stations in the German Exclusive Economic Zone for 41 HOCs including polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and organochlorine pesticides. The results indicate that the wet-sieving procedure is capable of physically normalizing the concentrations of the investigated HOCs and is useful for the comparison of concentrations in different sediment types. The wet-sieving procedure is more time consuming than the normalization to the TOC content. However, it offers the possibility of lowering the detection limits (LODs) through the analytical sample preparation procedure used, as sieving concentrates the contaminants. Therefore, a higher number of results > LOD were detected in sediment fines, leading to more informative data sets. In contrast to the commonly used normalization to 2.5 % TOC, the statistical analyses carried out (principal component analysis with subsequent cluster analysis) additionally indicate that physical normalization allows better differentiation of sampling sites by contaminant sources and geographic location rather than their sediment characteristics.

Keywords: Polycyclic aromatic hydrocarbons, chlorinated biphenyls, sediment sieving, North Sea, normalization

2.1 Introduction

Hydrophobic organic contaminant (HOC) analyses in sediments are a key component of state-run monitoring programs to assess the pollution status of habitats. Due to the contaminants' affinity to organic carbon and consequently also to smaller grain size fractions of the sediment, challenges arise when investigating sediments with different properties such as the total organic carbon (TOC) content and grain size distribution. This variability in the TOC content and grain size distribution between sediment samples means that measured concentrations cannot be compared directly. As a result, there is an increased overall variance in reported contaminant concentration data and this can even be the primary source of variation (ICES, 2009). One approach to counter this variation arising from differences in bulk sediment properties is to normalize HOC concentrations (Ackermann et al., 1983; ICES, 2009). Usually, HOC concentrations measured in sediments are normalized to their TOC content in order to achieve comparability of the results (ICES, 2021). However, use of TOC as a co-factor for normalization leads to some disadvantages when investigating sandy sediments such as those present in the German Exclusive Economic Zone (EEZ) of the North Sea (Bockelmann et al., 2018; Emeis, 2012; M. Magnusson et al., 2022). First, contaminant and TOC concentrations are often below the detection limits, which leads to a higher uncertainty of the results when applying this approach (M. Magnusson et al., 2022). Second, the correlation between contaminant and TOC may be weak or even absent, and third, the reference values (e.g. OSPAR 2.5 % TOC) may not be applicable for all areas (ICES, 2009). Furthermore, the composition of TOC can differ between samples temporally (seasonality) and spatially, as TOC can arise from various sources (e.g., algal blooms, suspended matter transported by rivers, or soot) and, therefore, its affinity for contaminants can also vary (ICES, 2009; Lazăr et al., 2012; Lu et al., 2020; Pusceddu et al., 1999).

One of the goals of the Maritime Strategy Framework Directive (MSFD) is to achieve good environmental status of all European seas; however, the applicability of assessment criteria such as environmental quality standards for such a wide range of regions requires that contaminant concentrations can be compared between a wide variation of different sediment types. Consequently, there is a need for alternative normalization strategies for HOCs in sediments that can be implicated for different sediment types. Therefore, we investigated the applicability of sediment wet-sieving and subsequent analysis of sediment fines ($< 63\ \mu$m) for HOCs as an alternative physical normalization strategy (Kersten and Smedes, 2002; Klamer et al., 1990). Due to the correlation of HOC concentrations with the share of the $< 63\ \mu$m fraction, the fine grain fraction is also applicable as a co-factor for concentration normalization (OSPAR, 2018). Normalization to sediment fines has already been implemented for the analysis of trace metals in sediments for several decades (BRD, 2016; OSPAR, 2018), because concentrations of trace metals in the bulk sediment are usually very low (Ackermann et al., 1983). Besides potentially improved normalization of HOC concentrations for different sediment types, the analysis of sediment fines is further advantageous due to (i) its particular importance for the accumulation of contaminants because of its high surface area, (ii) its high mobility resulting in temporal and seafloor near transport, and (iii) its role as an indicator for distribution processes of organic contaminants between compartments (sediment, water, biota) (Opel et al., 2011). However, several problems arise when samples are sieved to determine the organic contaminant content: In order to achieve reliable results, complete sieving of the samples has to be assured. In our experience, dry-sieving is not as suitable for the complete recovery of the smaller grain size fractions (< 20 and < 63 μm) and is also not recommended by ICES/OSPAR for the sieving of smaller grain size fractions (< 63 and < 20 μm) (OSPAR, 2018). This was also confirmed by findings of Nham (2017), whose systematic investigation of sieving techniques showed better applicability of wet-sieving compared to dry-sieving for sandy sediments. Therefore, wet-sieving was applied here, which, however, may cause problems when contaminants leach into sieving water during the sieving process. Additionally, the risk of contaminating the sample during sieving is high. To overcome these problems, we implemented an improved, half-automated wet-sieving method that required no manual sieving and used a minimum amount of water to minimize leaching and contamination. In comparison to Klamer et al. (1990), we used additional agate balls on the sieves that were chaotically moved by a rocking table installed beneath a vibratory shaker to ensure complete sieving.

The aim of this study was to evaluate the suitability of an alternative normalization strategy for determining HOC contents in sediments based on wet sediment sieving of sediment fines. Forty-one HOCs including 27 polycyclic aromatic hydrocarbons (PAHs), seven polychlorinated biphenyls (PCBs), and seven organochlorine pesticides (OCPs) were analyzed in both the sediment fine fraction (< 63 μm) and the bulk sediment at 25 sampling locations in the German EEZ in the North Sea. Henceforth, PCBs and OCPs will be referred to as a combined group of chlorinated hydrocarbons (CHCs). Additionally, the TOC content in sediment fines versus bulk sediment was determined, as well as the grain size distribution of the bulk sediment samples. The specific objectives for this study were (i) to obtain extended spatial concentrations of HOCs in sediment fines in the German EEZ, (ii) to gain a better understanding of HOC concentrations in sediments, and (iii) to evaluate implications for future monitoring programs and international data reporting using concentrations of HOCs in sediment fines (Kersten and Smedes, 2002; Klamer et al., 1990; OSPAR, 2008; Szava-Kovats, 2008). This study shall serve as a baseline for further discussions on normalization methods used to compare HOC concentrations in sediments between different monitoring programs and in international databases (e.g., ICES, 2.5 % TOC, OSPAR).

2.2 Material and methods

2.2.1 Chemicals

The organic solvents used for the analyses included acetone, *n*-hexane, dichloromethane, and 2,2,4-trimethylpentane; these were all gradient grade and purchased from J.T. Baker (Avantor Performance Materials). Tetrahydrofuran (for liquid chromatography), hydrochloricacid ($\geq$ 25 % and 32 %, p.a.), silica gel 60 (for column chromatography), copper powder ($<$ 63 μm), and sodium sulfate (anhydrous, p.a.) were purchased from Merck. Nitrogen 5.0 (LINDE) was used for solvent evaporation. A detailed list of the 41 HOC target analytes and internal standards including their suppliers is provided in the Supporting Information: Tables S1 and S2 (Appendix A).

2.2.2 Sampling

Marine sediment samples were taken during monitoring ship cruises carried out by the Helmholz Centre Geesthacht (now HEREON) together with Hamburg University and the German Federal Maritime and Hydrographic Agency (BSH), respectively, in the German EEZ with the research vessels FS Heincke (HE422; May 2014) and VWFS Atair (AT239; June 2016). The coordinates of the sampling sites are listed in Table 2.1 (BSH, 2016; Lüdmann, 2014). At 16 sampling sites (indicated with a * in Table 2.1), three box corer samples were taken (A, B, and C). The upper two centimeters of each box corer were cut off and were stored at -18 °C in pre-rinsed aluminum trays until sample preparation. Sample A was used for the bulk sediment analyses, while samples B and C were combined and homogenized in the laboratory for the sieving experiments to obtain enough sample material. An aliquot of each sample A was stored at 4 °C for grain size analyses. At the remaining sites, only one box corer sample was taken for the analyses of fine grain and bulk sediment fraction, but sample preparation and storage were carried out in a similar manner. The sampling sites were categorized according to their location, anthropogenic influence, and proportion of the $<$ 63 μm fraction (Figge, 1981; see Figure 2.1).

2.2.3 Grain size and TOC

The grain size distribution of the bulk sediment samples was determined using a particle-laser sizer (Analysette 22; Fritsch) and the TOC content of sediment fines and bulk sediment samples was determined with a *VarioEL* (Elementar) in CN mode at 950 °C. Bulk sediment samples were dried (72 h at room temperature under a clean bench) and ground with a ball mill (PM400; Retsch) before TOC analyses. Sediment fines were not

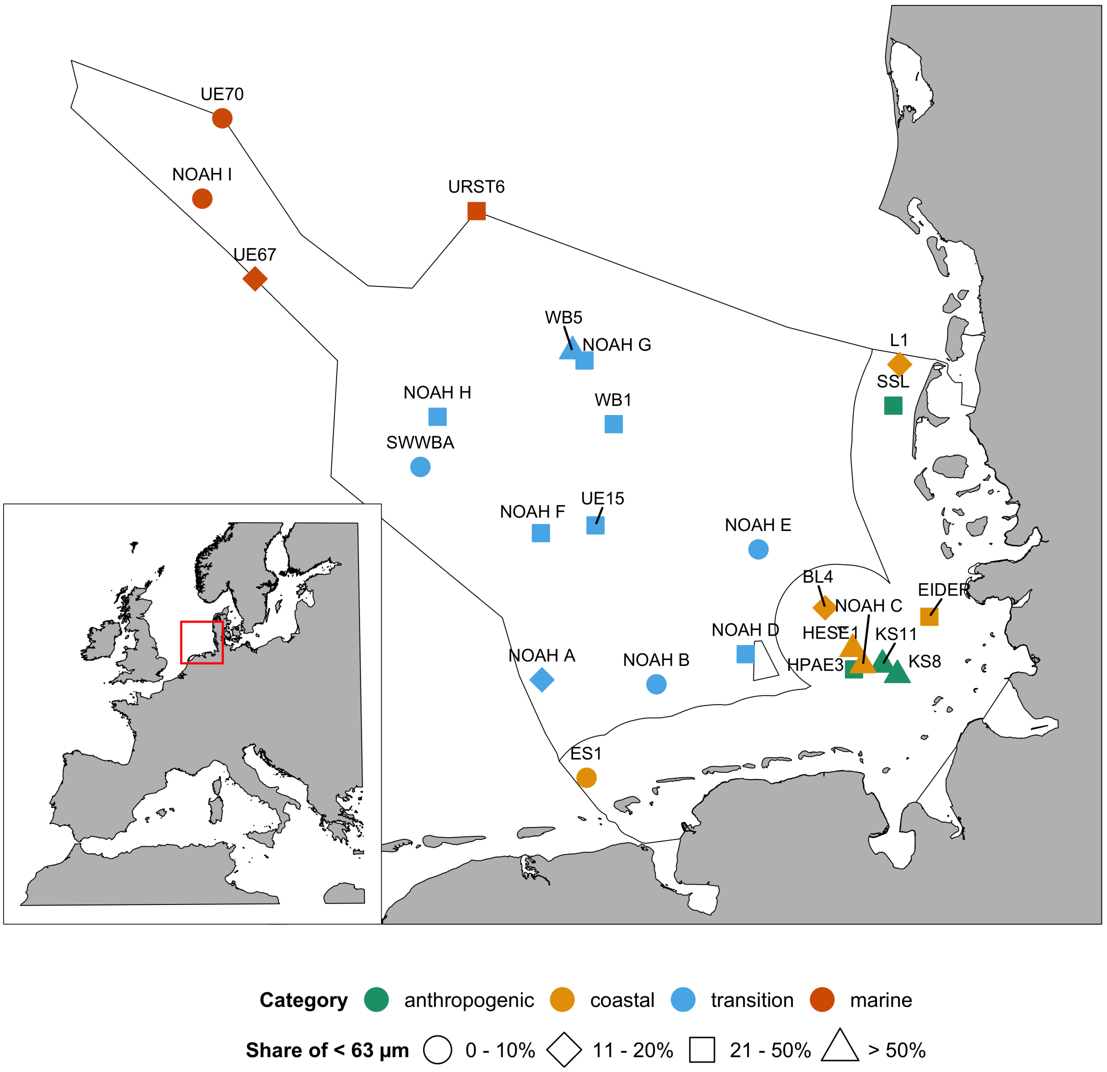

Figure 2.1: *Location of investigated sampling sites in the German Exclusive Economic Zone, defined categories for geographical location or anthropogenic influence, and sediment characteristics (share of < 63 μm fraction) (after Figge, 1981)*

ground due to the small amount of material available. The samples were weighted in silver capsules, acidified with 2 M hydrochloric acid (32 %), and placed in an oven for 3 h at 110 °C to remove the inorganic carbon. The silver capsules were folded and pressed into tin capsules. For quality control of the TOC measurements, an acetanilide standard (C_8H_9NO) was used and all sediment samples were analyzed in duplicate. Bulk sediment samples for which TOC values below the limit of quantification (LOQ) but above the limit of determination (LOD) were determined (see Table 2.1) were nonetheless further considered for TOC normalization as the duplicate TOC analyses showed no significant variation. However, these results may be subject to higher uncertainty. Bulk sediment samples with TOC values below LOD were not considered for TOC normalization and were therefore not included in the evaluation (see Table 2.1).

Table 2.1: *Coordinates (WGS 84), water depths, results of the total organic carbon (TOC) analysis (in bulk sediment and sediment fines), and the sediment grain size distribution analyses (share < 63 μm) for the 25 investigated sampling sites in the German Exclusive Economic Zone*

Station	Latitude [dec]	Longitude [dec]	Depth [m]	total sediment TOC [%]	sediment fines TOC [%]	share of < 63 μm [%]
BL4*	54.25	7.80	27	0.142	1.67	17.4
EIDER*	54.23	8.38	13	0.344	0.969	36.0
ES1*	53.67	6.50	21	(0.128)	3.77	5.80
HESE1*	54.12	7.96	37	0.752	1.06	89.6
HPAE3*	54.05	7.97	33	0.489	1.17	32.8
KS11*	54.07	8.13	22	0.642	0.939	72.4
KS8*	54.03	8.21	19	0.456	1.50	51.3
L1*	55.05	8.20	15	(0.128)	2.86	11.8
SSL*	54.92	8.17	20	0.498	2.96	42.6
SWWBA*	54.67	5.50	44	(0.103)	0.921	9.90
UE15*	54.50	6.50	39	0.239	0.953	29.7
UE67*	55.25	4.50	46	0.158	2.35	15.8
UE70*	55.77	4.25	37	(0.102)	2.64	4.20
URST6*	55.51	5.75	50	0.359	1.62	43.6
WB1*	54.83	6.58	41	0.388	0.843	49.1
WB5*	55.07	6.33	45	0.524	1.00	87.4
NOAH A	53.99	6.23	28	< LOD	1.17	10.5
NOAH B	53.99	6.87	26	(0.0640)	2.44	9.76
NOAH C	54.06	8.02	24	0.670	1.10	79.8
NOAH D	54.09	7.36	35	0.201	0.627	22.5
NOAH E	54.45	7.42	25	(0.0510)	3.70	8.14
NOAH F	54.47	6.20	37	0.167	1.07	29.6
NOAH G	55.04	6.40	42	0.208	1.14	43.8
NOAH H	54.83	5.58	40	(0.109)	1.44	22.4
NOAH I	55.50	4.17	25	< LOD	1.90	3.31

Note: At sampling sites marked with *, three box corer samples A, B, and C were taken (A for bulk sediment analyses, B and C for analyses in sediment fines). Otherwise, one box corer was taken. TOC results stated within parentheses were detected below the limit of quantification, < LOD: below limit of detection.

2.2.4 Sediment sieving

To obtain sediment fines, bulk sediment samples were wet-sieved on a device consisting of stainless-steel sieves (125 and 63 μm; Retsch) with agate balls on a vibratory sieve shaker (Fritsch) that was placed on a rocking table powered by an electric motor (Klamer et al., 1990). The setup ensured constant agitation of the sediment and thus prevented mesh clogging (a figure showing the schematic installation can be found in the Supporting Information: Figure S1, Appendix A). Therefore, the experimental setup enabled a half-automated sieving process, as agate balls were moved chaotically over the sieves by the three-dimensional movement of the rocking table in combination with the vibratory sieve shaker. Depending on the sample, 75 - 700 g of bulk sediment material was used for sieving. The collection tray under the sieves was coupled to a flow-through centrifuge equipped with a rotor containing a collection insert (Contifuge 17RS Heraeus; Thermo Fisher Scientific). The system was constantly wetted with approx. 3 L of ultrapure water (Integral 5; Millipore) circulated by a pump (Gather). Sediment fines ($< 63\ \mu$m) were recovered from the rotor insert and the sieving water was recovered by centrifugation (Contifuge; Thermo Fisher Scientific, 3000 rpm, 20 min). After that, the sample was dried under a clean bench (Holten "Lamin Air") at room temperature for 72 h. The dried sample was homogenized in a mortar and stored in amber glass jars at room temperature until analysis. All parts of the sieving apparatus were thoroughly cleaned and scrubbed under water as well as rinsed with acetone and *n*-hexane, except for the o-rings of the centrifuge rotor, after every sieving process. Additionally, sieves were cleaned in an ultrasonic bath to remove any blockages that may have occurred during sieving.

2.2.5 Sample extraction and instrumental analysis

Bulk sediment (dried and ground) and sediment fine (dried and homogenized) samples were spiked with internal standards (IS), mixed with 0.2 - 0.5 g of activated copper powder for sulfur reduction, and extracted with acetone/*n*-hexane (1:1, v/v) in a microwave (μPrep, MLS). After volume reduction with a parallel evaporator (Büchi), extracts were purified by solid-phase extraction (SPE) using silica gel 60 (1 % activated) and eluted with dichloromethane/*n*-hexane (1:3, v/v). Gel permeation chromatography (high-performance liquid chromatography-size exclusion chromatography [HPLC-SEC]) was performed as a second cleanup step, where tetrahydrofuran was used as the mobile phase on a phenogel^{TM} column (5 μm, 50 Å, 300 x 7.8 mm; Phenomenex) with a phenogel^{TM} guard column (5 μm, linear/mixed, 50 x 7.8 mm; Phenomenex). After volume reduction to 100 μL by parallel evaporation using nitrogen, the solvent was exchanged to 2,2,4-trimethylpentane. Samples were stored at 4 °C until analysis.

Analyses of HOC content were performed using gas chromatography-mass spectrometry (GC-MS/MS) detection as described in Brockmeyer et al. (2015). Briefly, PAH compounds were quantified using a GC-MS/MS system (GC CP-3800 coupled to Varian 1200, both Varian), and CHCs were quantified using a GC-MS ion trap system (GC CP3800 coupled to a Saturn 2200, both Varian). A full list of the analyzed and quantified substances and used internal standards is available in the Supporting Information: Tables S1 and S2 (Appendix A).

2.2.6 Quality assurance/quality control

The repeatability caused by sieving was investigated by performing multiple sieving of different sediment types and subsequent analyses of the replicate samples (see 2.3.2).

Additionally, heated sea sand served as blank samples for the sieving procedure. The blank samples (individually processed for rotor/centrifuge and sieves) were processed to check for possible cross contamination through the sieving apparatus. Also, certified reference material was sieved and analyzed to quantify possible leaching of certain compounds into the sieving water and to assess the quality of the overall sample preparation procedure including the wet-sieving. For the sample preparation procedure (extraction, SPE, HPLC-SEC, and GC-MS/MS measurements), blanks, LOD, LOQ, recoveries, and repeatability were examined. The validity of the sample preparation procedure was also checked with certified reference material (IAEA-408, International Atomic Energy Agency) and using round-robin tests (Quasimeme Project Office). The LODs and LOQs of HOCs were determined by DIN 32645 (2008) and results were corrected for the concentrations detected in the corresponding blank samples. Detailed information on quality assurance parameters is shown in Supporting Information: Tables S1 and S2 (Appendix A). Average recoveries of the internal standards for sediment fines were 83 ± 36 % for PAHs (across 6 IS) and 103 ± 36 % for CHCs (across 4 ISs). For the bulk sediment, average recoveries for the internal standards were 70 ± 46 % for PAHs and 86 ± 39 % for CHCs.

2.2.7 Statistical methods

Statistical analyses were performed using R and RStudio for MacOS (version 4.2.0 and Prairie Trillium, respectively) utilizing, among others, the packages factoextra, FactoMineR, and ggplot2 (Kassambara and Mundt, 2020; Lê et al., 2008; RStudio Team, 2022; The R Core Team, 2022; Wickham, 2016). A full list of the used R packages is presented in the Supporting Information (Appendix A). The statistical analyses were conducted independently on the two resulting data sets from chemical analyses: (1) measured HOC concentrations in sediment fines, and (2) measured HOC concentrations in bulk sediment normalized to 2.5 % TOC. Due to several measuring values below LOD in the bulk sediment data set, for the statistical analyses, both data sets were first reduced to a representative number of substances to minimize missing values. Afterwards, all monitoring stations still containing measuring values below LOD were dropped in both data sets to ensure comparability. Data sets were then log-transformed and standardized due to highly skewed concentrations caused by anthropogenic enrichments. The principal component analyses, followed by hierarchical cluster analyses (Ward's method, Euclidian distance) of the first two principal components were then performed on the two data sets containing 22 variables (substances) and 15 individuals (sampling sites). The number of clusters for the data set of sediment fines was determined using the Silhouette method (n = 3). This was transferred to the bulk sediment data set to obtain comparable results.

2.3 Results and discussion

2.3.1 TOC and grain size analyses

The distribution of sediments in the German EEZ (SE North Sea, Figure 2.1) has been described by Figge (1981) and has been considered to be stable since then (Emeis, 2012). The sediment inventory of the German EEZ shows high heterogeneity and is dominated by well-sorted sands, coarse-grained and poorly sorted sands, gravels, and low-energy areas where fine grain sediments accumulate (Emeis, 2012; Miller et al., 2012; Schmolke, 2016). The composition of particle sizes within the sediment is a main driver for the distribution of contaminants in sediments for several reasons: First, smaller sediment particles have a higher surface/volume ratio than larger ones, which increases their ability to adsorb HOCs (Szava-Kovats, 2008). Second, sediments with a high proportion of fine-grained particles usually show higher TOC contents, which again increase their ability to adsorb contaminants (Brockmeyer and Theobald, 2016). Because the TOC content and the proportion of sediment fines, besides the physicochemical properties of the contaminants themselves, are known to be essential drivers for the distribution of HOCs in sediment, normalization of contaminant concentrations to either a co-factor (e.g., TOC) or to physical parameters (e.g., grain size distribution) is the requirement for comparability of results (Ackermann et al., 1983; ICES, 2009). This normalization can be difficult under very low TOC conditions, suggesting that viable alternatives are needed in such cases (further discussed in 2.3.2). One such alternative can be the physical normalization to sediment fines using sieving.

An analysis of the extended data set with BSH data from 2011 to 2018, including data from this study, demonstrates a very good correlation of $R^2 = 0.89$ between TOC and the share of sediment fines < 63 μm (Figure 2.2, ordinary least square regression). This correlation between TOC content and < 63 μm fraction also reveals the problem that the prescribed normalization values (2.5 % TOC) often do not adequately reflect the sediment conditions in the study area. Here, for example, a normalization value of 1.1 % would be more appropriate (intersection at 100 % share of < 63 μm fraction, Figure 2.2). Additionally, the correlation of 39 HOCs to TOC and the share of sediment fines in the extended data set ($n = 112$ - 139) were investigated and it was found that correlation coefficients were significantly higher in terms of sediment fines for 18 HOCs, predominantly PAHs, whereas correlation coefficients were significantly higher in terms of TOC for 12 HOCs, predominantly CHCs (Fisher's z-transformation, $\alpha = 0.05$, Revelle, 2022). This underlines the potential to physically normalize contaminant concentration to sediment fines by sieving rather than to TOC (see 2.3.2). Such normalization to sediment fines has been practiced for heavy metals in the German state-run monitoring programs for several years (BRD, 2016). Results from this study confirmed the presence of heterogenic sediment conditions in the study area, as reported previously (Figure 2.2, orange data points) (Bockelmann et al., 2018; Emeis et al., 2013; Schmolke, 2016). The measured TOC values in the samples investigated ranged from 0.05 % to 0.75 % and determined shares of sediment fines $< 63\ \mu$m ranged from 1.7 % to 89.6 % (Table 2.1).

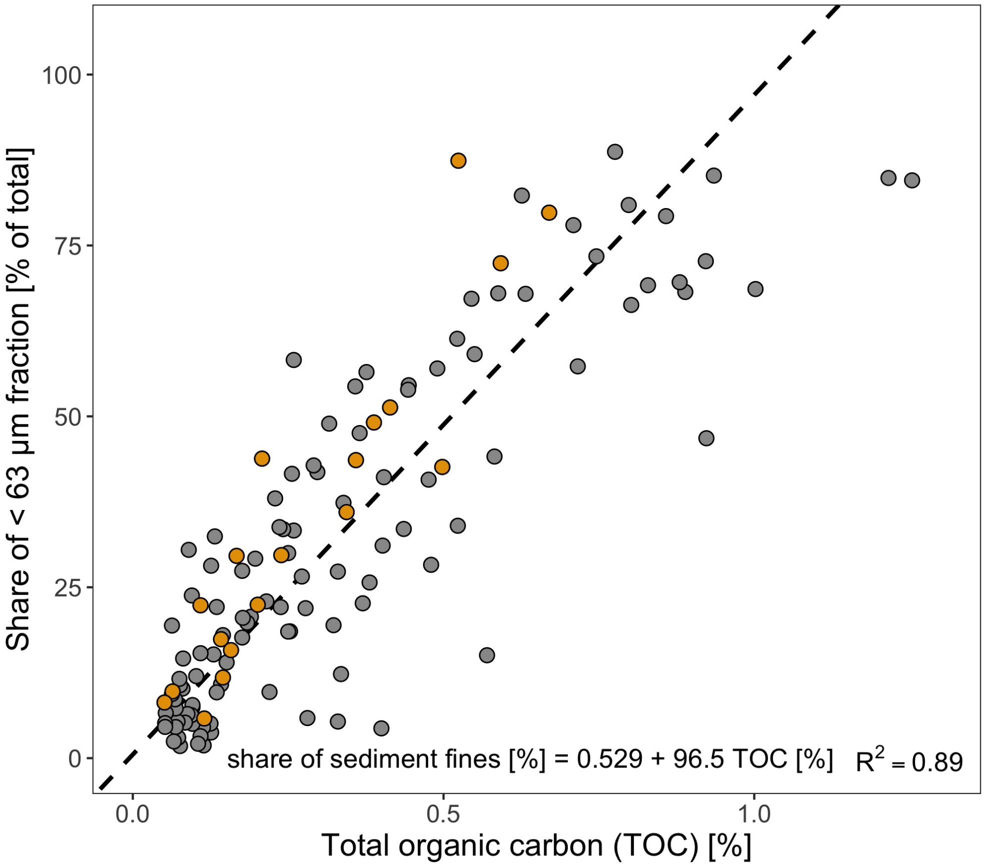

Figure 2.2: *Comparison of the total organic carbon content (%) and share of sediment fines ($< 63\ \mu$m fraction % of total) of various samples taken in the German Exclusive Economic Zone by the BSH from 2011 to 2018 applying reduced major axis regression (black dashed line), coefficient of determination (R^2) of ordinary least square regression through origin. Outliers $> 3 \cdot \sigma$ were excluded. Orange points show samples investigated in this study.*

2.3.2 Applicability of the wet sieving method

To enable contaminant quantification in sediment fines $< 63\ \mu$m, sediment samples analyzed were wet-sieved using a through-flow centrifuge (see 2.2.4). While wet-sieving can potentially lead to cross contamination, complete sample sieving is also very important for the reliability of results. As wet-sieving has been shown to be advantageous for sandy sediment samples (Nham, 2017), it was preferred over dry-sieving for our study, as a large proportion of the samples in the sample set are characterized by a high proportion of coarser grain size fractions (Table 2.1). Additionally, the sieving process can result in increased variability and can thus cause greater uncertainty of the analytical procedure. However, a study by Smedes et al. (2000) came to the conclusion that the variability of the sieving yield is smaller than the variability of the analytical and sampling procedure. Additionally, wet-sieving is a standard practice in heavy metal and metal analyses and is therefore subject to standardized lab procedures controlled by, for example, round-robin tests. Another potential error within the wet-sieving process can be the leaching of target analytes into the used water. Here, leaching was reduced by applying a closed system in which as little water as possible was recirculated while sieving and centrifuged after the sieving process. Thereby, the ratio of water to sediment was kept small and leaching effects and contamination were minimized (Kersten and Smedes, 2002; Röhrs, 2017). The use of ultrapure water for wet-sieving can also have an influence on the structure of the sediment sample, as it has different physiochemical characteristics compared to seawater from the sampling site and could hence desorb during sieving (Birch and Taylor, 2000). However, Birch and Taylor (2000) considered ultrapure water to be sufficient for use for sieving, although ambient seawater should be preferred (ICES, 2009).

The applicability of the wet-sieving method was tested by multiple sieving experiments of samples from three different sampling sites with heterogeneous sediment properties (see Table 2.2). The calculated standard deviations for the analyzed substance groups are comparable with previously reported values (Klamer et al., 1990). The standard deviations for the overall sample preparation of < 30 % for all contamination groups were considered sufficient. Additionally, leaching of target analytes was investigated by the analysis of the sieving water after the sieving and centrifugation process and was considered as negligible, due to the high $log\ K_{OW}$ values of target analytes (all > 3, please refer to the Supporting Information: Table S2, Appendix A), resulting in a low transfer rate to water. The sieving procedure is obviously more elaborate and time consuming than the measurement of TOC. Especially, the higher sample amounts needed for HOC in comparison to heavy metal analyses lead to longer sieving times (Smedes, 2014). However, physical normalization by sieving has four main advantages:

1. Since HOCs are associated with sediment fines, the sieving process concentrates contaminants and hence increases the likelihood of compounds to be measurable above the detection limits (Smedes and Nummerdor, 2003). This can considerably increase the informative value of data sets and thus strengthen monitoring programs in marine areas. In the two methods investigated here (normalization to TOC vs normalization to sediment fines), approx. 21 % of the measured values were below LOD in bulk sediment samples, whereas only approx. 8 % were below the LOD in the sediment fines.
2. The advantage of TOC determination over sieving as the normalization technique becomes a disadvantage when sandy sediments with a very low TOC content, such as present in the German EEZ, are analyzed. Here, the relative analytical error of contaminant concentrations in bulk sediment as well as the TOC determination becomes high, because of the relatively small measured values, often below or close to the detection limit even when sample weights are maximized (Smedes and Nummerdor, 2003). As a result, data sets with very low significance are produced.

3. The TOC content in sediments can differ temporally (seasonally) and spatially (e.g., algae blooms, suspended matter transported by rivers, or soot) (Lazăr et al., 2012; Lu et al., 2020; Pusceddu et al., 1999). This might have an influence on the comparability of contaminant concentrations in sediments when TOC normalization is applied, raising questions for TOC-independent normalization methods. As the organic matter content increases with higher shares of sediment fines (Figure 2.2), this would also apply to physical normalization by sieving. However, we suppose that the effect could be much smaller, when HOC concentrations are measured in sediment fines. This is because the inorganic part of the sediment, which also has high sorption capacities for contaminants due to the high surface/volume ratio (Eisma and Irion, 1988; Schmolke, 2016), mostly makes up a greater proportion of sediment fines thus being able to reduce this effect.

4. Sediment fines are highly relevant for contaminant transport in surface sediments due to the higher mobility of the small particles. Furthermore, sediment fines have a higher bioavailability for organisms living in the benthic area. To maximize their organic carbon uptake, organisms therefore also maximize particle-bound contaminant uptake through the uptake of fine particles (Ahlf et al., 2001; Talley et al., 2002). Thus, measurements in sediment fines are worth considering not only for normalization purposes but also to provide data that allow qualitative statements about the condition of the seabed as a habitat.

Table 2.2: *Standard deviations for the overall sample preparation procedure including the wet-sieving method*

Station	of sievings	TOC [mg g^{-1}]	$<$ 63 μm [%]	PAHs [%]	PCBs [%]	OCPs [%]
SSL	3	4.98	42.6	21	24	15
UE67	4	1.58	15.8	9	22	27
URST6	3	3.59	43.6	11	16	13

Note: The standard deviations of the means of all analyzed unmethylated PAHs, PCBs, and OCPs are listed.

Abbreviations: OCP, organochlorine pesticide; PAH, polycyclic aromatic hydrocarbon; PCB, polychlorinated biphenyl; TOC, total organic carbon.

2.3.3 Spatial distribution of HOCs in sediment fines

The concentrations of contaminants in sediment fines determined in this study expand the spatial inventory of the sediment pollution status of the German EEZ and could therefore be of importance for the estimation of contaminant bioavailability and remobilization through sediment transport processes. Contaminant concentrations in sediment fines were analyzed at 25 sampling sites, representing a comprehensive data set first recorded for the German EEZ. The measured concentrations in sediment fines varied significantly between samples and ranged from 0.32 to 204 μg kg^{-1} dw for PAHs, from 0.02 to 2.2 μg kg^{-1} dw for PCBs, and from 0.03 to 1.55 μg kg^{-1} dw for OCPs. Thereby highest concentrations in each contaminant group were recorded for benzo(*b*)fluoranthene (204 μg kg^{-1} dw), PCB153 (1.6 μg kg^{-1} dw) and *pp*-DDD (2.2 μg kg^{-1} dw), respectively.

For PAHs, the highest concentrations (ΣPAH $>$ 1000 μg kg^{-1} dw) were determined at sampling sites HPAE3 and KS11 (Figure 2.3 A). These sampling sites, including KS8, are affected by anthropogenic activities. At HPAE3 dumping of harbor sludge from Hamburg port was permitted until the end of 2021 (HPA, 2017), whereas at KS8 and KS11 sewage sludge was dumped between 1961 and 1980 (Dethlefsen, 1991). Additionally, these sampling sites are located in a sedimentation area and are strongly influenced by Elbe and Weser effluents (Dethlefsen, 1991). The second highest concentrations can be found at sampling sites located in the area of the “Weiße Bank” in the middle of the German EEZ, WB5, NOAH H, and NOAH F (see Figure 2.3 A). Theobald (2016) suggests that these comparatively high PAH concentrations along the “Weiße Bank” might be a result of local point sources such as oil spills originating from the westerly located shipping route (GeoSeaPortal, 2022). Generally, lower PAH concentrations were recorded south east (ES1, NOAH A) and north east of the study area (UE 70, NOAH I). However, the relatively uniform distribution pattern as compared to the CHCs (Figure 2.3 B) can be understood by examining the main source of PAH entry into the German North Sea: atmospheric deposition (Mai, 2012; OSPAR, 2009a).

For CHCs, the highest concentrations for ΣPCBs and ΣOCPs were also recorded at sampling sites HPAE3 and KS11, known to be a result of direct anthropogenic activity (see above). Also, at the closely located sampling site NOAH C, high PCB concentrations were determined. In contrast to the spatial distribution of PAHs, CHCs show a clear decreasing gradient from coastal to marine sampling sites (see Figure 2.3 B). A possible explanation is that CHC distribution along the coast is dominated by riverine input (Laane et al., 2013; Lohse, 1991; Niehus et al., 2019) and amounts of particulate matter in the water column decrease towards areas located further away from the coast (Theobald, 2016). In addition, the relatively uniform distribution around the ”Weiße Bank” and the “Entenschnabel” suggest that atmospheric deposition is the main input pathway for CHCs into the marine surface water in these areas, thereby explaining the relatively lower quantities observed, as compared to coastal sampling stations (Mai, 2012).

In conclusion, the distribution of contaminant concentrations in the German EEZ in sediment fines showed a differential picture. In comparison to the non-normalized concentrations measured in bulk sediment, distribution patterns can be better highlighted and compared between sampling stations, especially between neighboring ones (further discussed in 2.3.4). In comparison to non-normalized bulk sediment concentrations, maximum to minimum ratios of HOCs are reduced from $>$ 100 to $<$ 15 in sediment fines (mean values across the 41 analyzed substances).

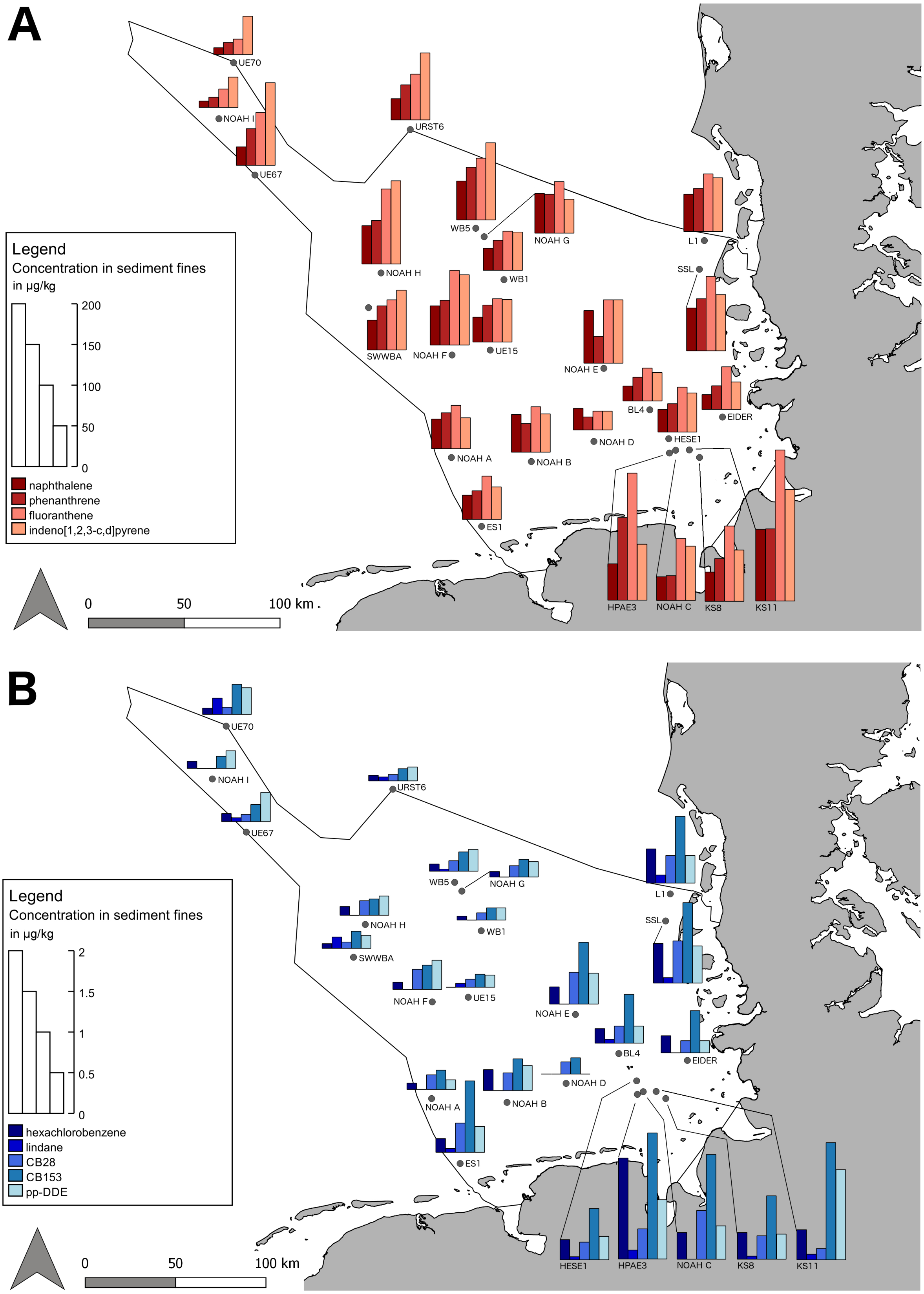

Figure 2.3: *Spatial distribution of selected lead contaminants naphthalene, phenanthrene, fluoranthene, indeno[1,2,3-c,d]pyrene, hexachlorobenzene, lindane, PCB 28 (CB28), PCB 153 (CB153), and dichlorodiphenyldichlorethene (pp-DDE) (after Brockmeyer and Theobald, 2016) for polycyclic aromatic hydrocarbon (A) and chlorinated hydrocarbon (B) concentrations in sediment fines (< 63 µm) in* $\mu g\ kg^{-1}$ *dw in the German Exclusive Economic Zone*

2.3.4 Comparison of normalization strategies

The results of the parallel analyses of HOC concentrations in bulk sediment and corresponding sediment fines (< 63 μm) conducted in this study were primarily intended to gain insights into the comparison of the normalization strategies of bulk sediment concentrations normalized to 2.5 % TOC versus the physical normalization of sieving. For the comparison of these two methods, several analyses are presented in this section.

Direct comparisons of the determined concentrations with both normalization methods are shown in Figure 2.4. Due to the wide range of measured concentrations due to anthropogenic enrichments, axes are displayed on a logarithmic scale. The comparison of both normalization strategies shows good agreement ($R^2 = 0.87$), considering the relatively large number of target analytes ($n = 41$) covering a wide amplitude of concentrations in the samples. On closer examination, for sandy sediments with a fine grain fraction of ≤ 20 %, the comparison is slightly better than that for muddier samples with a share of sediment fines > 20 %, where the regression line runs parallel below the bisectrix, and therefore indicates that concentrations in sediment fines are generally overestimated (see Supporting Information: Figures S2 and S3, Appendix A). However, for samples with a share ≤ 20 % of sediment fines, the number of data points available was much lower than that for samples with sediment fines > 20 % due to the high number of detections below the LOD in the bulk sediment data set for sandy sediments. However, this might indicate that samples with higher shares of sediment fines (> 50 %) do not necessarily need to be sieved.

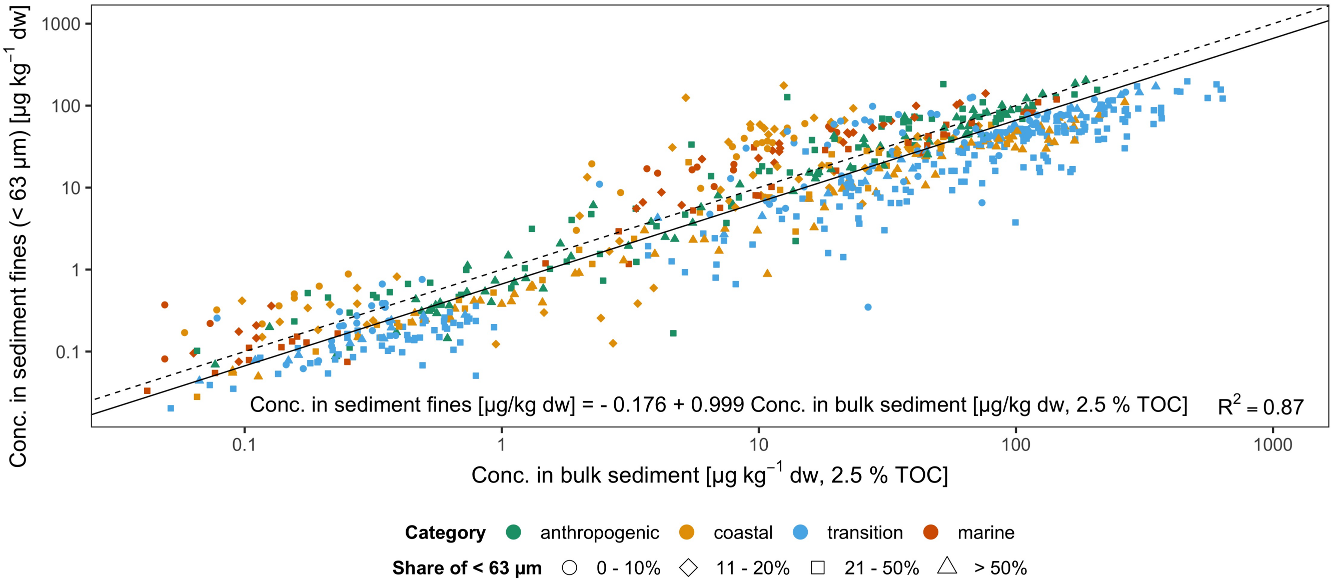

Figure 2.4: *Comparison between hydrophobic organic contaminant concentrations measured in bulk sediment samples in µg kg⁻¹ dry weight (dw) normalized to 2.5 % total organic carbon (TOC) (OSPAR, 2008) and corresponding sediment fines (< 63 µm) in µg kg⁻¹ dw. Dashed black line: bisectrix, solid black line: reduced major axis regression of logarithmic values. Coefficient of determination (R^2) of ordinary least square regression. Data points are colored and shaped according to the geographical location or anthropogenic influence (dumping and sand excavation sites and the determined proportion of sediment fines (share of < 63 µm) of the corresponding sampling sites)*

For the comparison between the two evaluated normalization strategies, the contaminant distribution patterns as well as HOC concentrations from sampling sites that are located in close proximity, yet show very different sediment characteristics, are of great importance. Here, normalizing to account for different sediment properties is of particular concern to be able to highlight sources and sinks of HOCs (Ackermann et al., 1983). As an example, we present the results for both normalization approaches for sampling sites SSL and L1 (see Figure 2.5). Because both sampling stations are located relatively close to each other, they should show similar concentration levels after normalization. Both sampling sites show differential sediment properties with a TOC of 0.13 % (SSL) and 0.50 % (L1) as well as 12 % and 43 % shares of the < 63 μm fraction, respectively. The observed differences in sediment properties are due to anthropogenic sand excavations at SSL, resulting in the accumulation of sediment fines in this area. When comparing the HOC distribution patterns between both stations, it can be recognized that they do not only significantly differ for PAHs and CHCs between stations but also between both normalization methods (Figure 2.5). However, the HOC concentrations in sediment fines are less different at L1 and SSL, while for 2.5 % TOC normalized concentrations in bulk sediment, a discrepancy between the two stations is visible. When calculating a factor between concentrations for each substance for the two stations, bulk sediment concentrations normalized to 2.5 % TOC differ by a factor of 2.7 ± 1.2, while this factor is only 1.2 ± 0.2 for the concentrations in sediment fines. Comparable findings can be observed for sampling sites NOAH H

(TOC: 0.11 %, share of < 63 μm: 22 %) and SWWBA (TOC: 0.10, share of < 63 μm: 10 %), where factors between measured concentrations were 1.8 ± 0.8 and 1.4 ± 0.4, respectively. This underlines that the measurement of HOC concentrations in sediment fines can be a powerful normalization tool for sampling sites with different sediment characteristics.

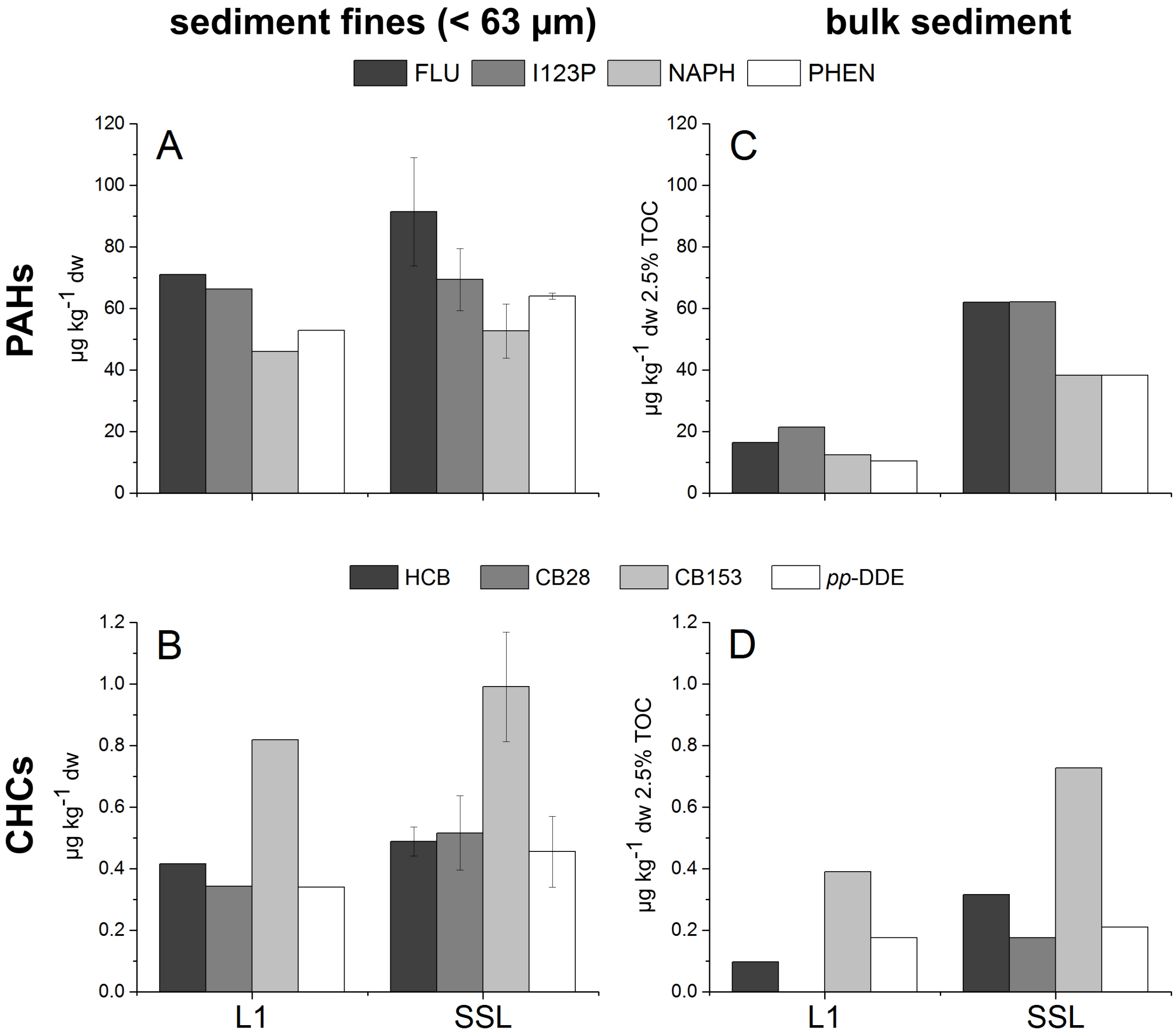

Figure 2.5: *Comparison of concentrations of fluoranthene (FLU), indeno[1,2,3-c,d]pyrene (I123P), naphthalene (NAPH), phenanthrene (PHEN) (A and C), and hexachlorobenzene (HCB), PCB 28, PCB 153, and dichlorodiphenyldichlorethene (pp-DDE) (B and D) at sampling locations L1 and SSL in sediment fines (< 63 μm) separated from the coarse fraction by wet-sieving in μg kg^{-1} dw (A and B) and in bulk sediment in μg kg^{-1} dw normalized to 2.5 % total organic carbon (TOC) (OSPAR, 2008) (C and D). The error bars in A and B indicate the standard deviation of replicate sieved and analyzed samples (n = 3)*

Furthermore, we conducted principal component analyses (PCA) with subsequent hierarchical clustering on the first two principal components for both data sets to determine potential statistical differences between the two normalization methods. Due to the large number of measuring values below LOD in the bulk sediment data set, both data sets were reduced to exclude compounds not present at both locations (see 2.2.7). The results for the PCAs are shown in Figure 2.6 A, B. In our analysis, the first two principal components for each data set explain $>$ 85 % of the variation, which we deemed acceptable. In both PCAs, the quality of representation of variables on the first and second principal components was comparable. Whereas for the first principal component, the highest values for the quality of representation were found for PAHs, for the second PC, CHCs had the highest values (see the Supporting Information: Figures S6 and S7 for details, Appendix A). Additionally, loadings in both PCAs for the variables were consistent, showing PAHs and methylated PAHs on the right/in quadrant IV and CHCs on the top or top right/quadrant I (see the Supporting Information: Figures S8 and S9, Appendix A).

However, when comparing the plot of individuals (sampling sites) for sediment fines (Figure 2.6 A) and bulk sediment normalized to 2.5 % TOC (Figure 2.6 B), the results of the PCAs and subsequent hierarchical cluster analyses show a few differences. For sediment fines, a good distribution of sampling sites by the geographical location and therefore by contaminant sources (river effluent) can be seen. All sampling sites located inside of the 12 nm zone are located in the upper half (except for NOAH B), whereas marine and transitional sampling stations are located in the lower half of the plot. Additionally, the sampling sites KS11 and HPAE3, where dumping of sewage and harbor sludge took place (see 2.3.3), are isolated in the upper right part of the plot (Figure 2.6 A). The results of the hierarchical clustering (marked with gray dashed lines) support this, as clusters confirm the groups described above. For sediment fines, the first cluster includes strongly anthropogenically influenced sampling sites (KS11, HPAE3, and SSL), the second cluster summarizes coastal sites, and the third aggregates marine and transitional sampling sites. The assignment of KS8 to the cluster of coastal stations is explained by the fact that generally lower concentrations have been detected there in the past than at KS11, despite sewage sludge dumping (Brockmeyer and Theobald, 2016; Theobald, 2016). The allocation of NOAH B to the cluster of coastal stations is reasonable, as this sampling site is located close to the 12 nm zone. Instead, the allocation of SSL together with HPAE3 and KS11 does not fit entirely, as elevated contaminant concentrations at SSL are not caused by the active introduction of contaminated sediment material. However, a potential explanation can be that the sedimentation regime at SSL is considerably modified by sand excavations, causing an energy minimum zone leading to enrichment effects.

In comparison, for bulk sediment concentrations normalized to 2.5 % TOC, the distribution by geographical location and anthropogenic influence is not as clear as that for sediment fines (Figure 2.6 B). In particular, the observed cluster of anthropogenically influenced locations (HPAE3, KS11, SSL) is not as obvious when normalizing to 2.5 % TOC than to sediment fines. Also, coastal stations BL4, EIDER, and SSL form a cluster with marine sampling sites UE67 and URST6. These results indicate that normalization to sediment fines may be more effective than normalization to 2.5 % TOC when differentiating sources and sinks of contaminants in the German EEZ, although further studies with increased sample sizes are recommended to verify this. One reason for this may be the different possible sources of TOC (e.g., algal blooms, suspended matter transported by rivers, or soot) that may also differ with seasons and locations, whereas physical normalization by wet-sieving is less susceptible to such variations. This is in line with the conclusions of Opel et al. (2011), who consider TOC not ideal for normalization due to its influence by abiotic and biotic degradation processes, even though TOC is of crucial importance for the partitioning of contaminants.

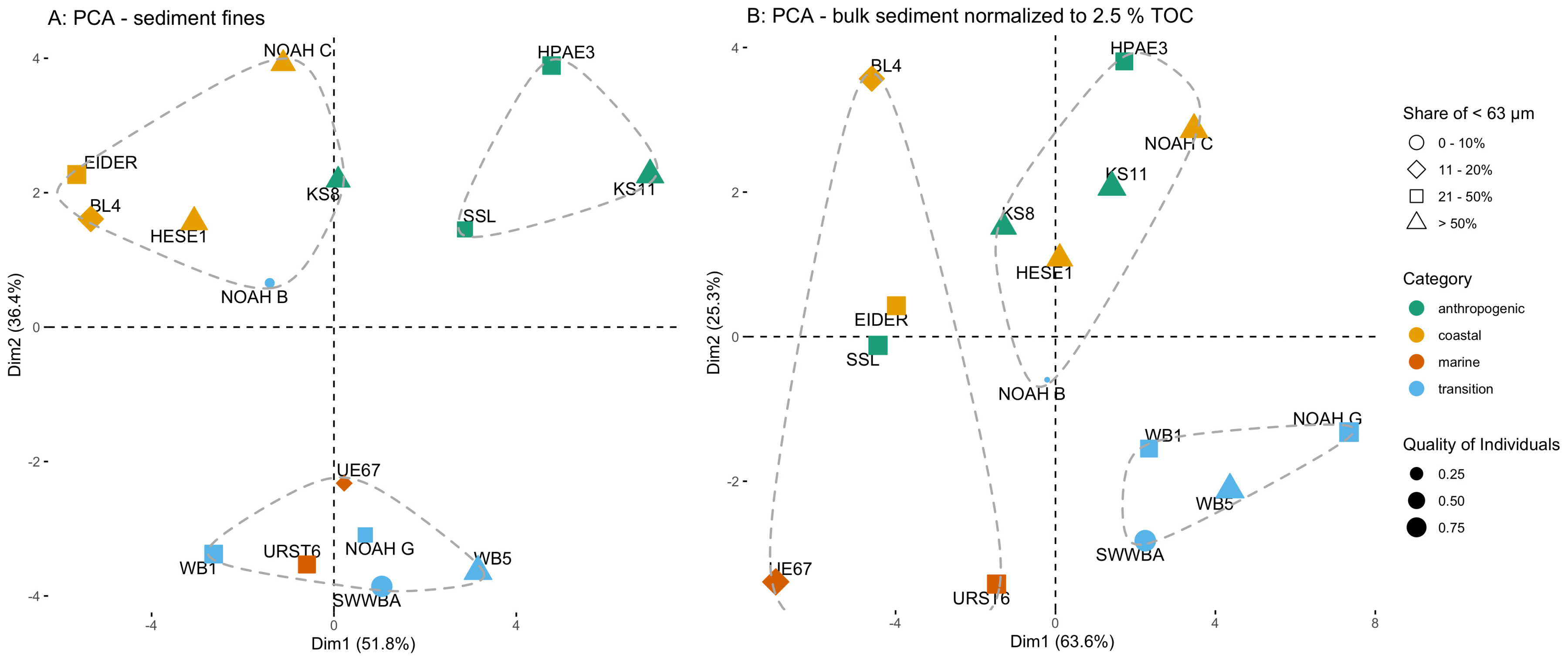

Figure 2.6: *Results of the principal component analysis (PCA) conducted for concentrations in sediment fines (< 63 µm) (A) and corresponding bulk sediment normalized to 2.5 % total organic carbon (TOC) (OSPAR, 2008) (B) at the studied sampling sites. The PCA was conducted on a reduced data set of 31 compounds (out of 41) and 15 stations (out of 25) to exclude results below the limit of detection. Dashed gray lines mark the identified clusters from the hierarchical cluster analyses performed on the first two principal components (HCPC). Sampling sites are colored and shaped according to their geographical location or anthropogenic influence (dumping and sand excavation) and the determined proportion of sediment fines (< 63 µm)*

2.4 Conclusion

The quantification of HOCs in marine bulk sediment is often hampered in sandy sediment, such as that present in the German EEZ, due to the low concentrations of both HOCs and TOC content, which in turn leads to high uncertainty when the common normalization of HOC concentrations to 2.5 % TOC (OSPAR) is applied. Here, we describe an alternative normalization method for HOCs, namely, physical normalization to sediment fines (particles $< 63\ \mu$m) achieved by wet-sieving, and compare the results to normalization to 2.5 % TOC. The results demonstrate that sediment sieving appears to be a good alternative and/or supplement to the commonly practiced normalization to 2.5 % TOC, especially when sampling sites with a wide range of sediment properties are to be monitored (from very sandy to muddy, as well as high and low TOC contents). Additionally, the data presented here represent a first spatial inventory of HOCs in sediment fines of the German EEZ and therefore provide valuable information about the entry and distribution of these problematic 41 HOCs into the German EEZ and, ultimately, the whole North Sea and beyond. Of particular concern is that HOCs preferentially adsorb to sediment fines due to their high surface/volume, and yet, sediment fines are also most prone to further distribution due to their small size and mass. However, we recommend additional studies with larger sample sizes to verify the presented results before considering the inclusion of wet-sieving in routine monitoring schemes for HOCs.

Chapter 3

Cumulative Part II

Assessing the chemical Anthropocene – Development of the legacy pollution fingerprint in the North Sea during the last century

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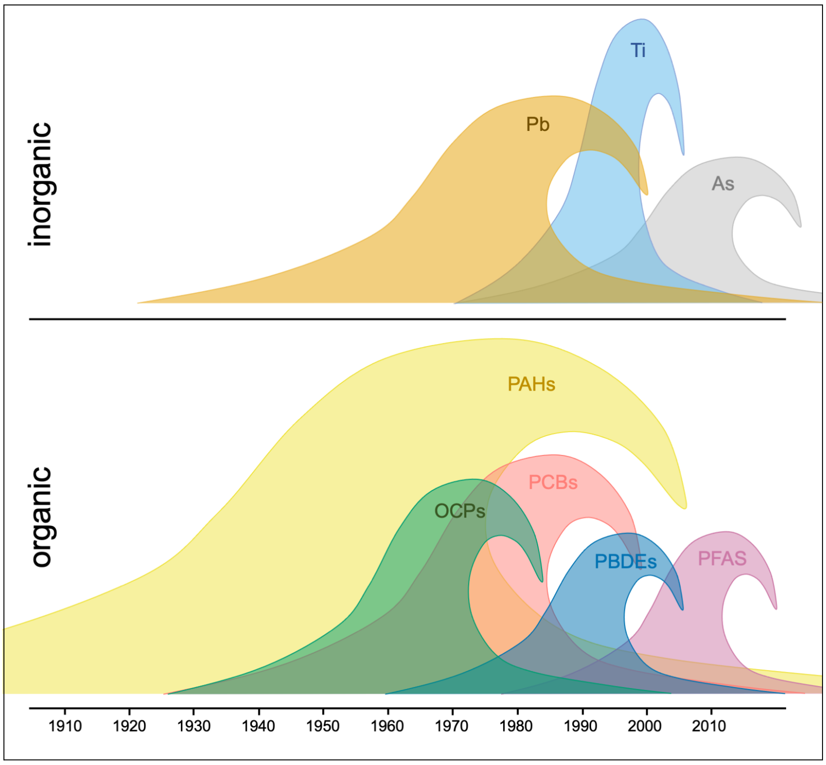

Figure 3.1: *Graphical Abstract*

Highlights:

- Comprehensive pollution fingerprint for the North Sea covering the last 100 years.
- Quantification of 90 contaminants in sediment cores covering 6 contaminant groups.
- Concentration declines of pollutants could be linked to restrictions and bans.
- As levels observed in recent years were linked to discarded ammunition from WW II.
- Concentration trends in sediment and porewater were comparable for PAHs and PCBs.

Abstract:
The North Sea and its coastal zones are heavily impacted by anthropogenic activities, which has resulted in significant chemical pollution ever since the beginning of the industrialization in Europe during the 19^{th} century. In order to assess the chemical Anthropocene, natural archives, such as sediment cores, can serve as a valuable data source to reconstruct historical emission trends and to verify the effectiveness of changing environmental legislation. In this study, we investigated 90 contaminants covering inorganic and organic pollutant groups analyzed in a set of sediment cores taken in the North Seas' main sedimentation area (Skagerrak). We thereby develop a chemical pollution fingerprint that records the constant input of pollutants over time and illustrates their continued great relevance for the present. Additionally, samples were radiometrically dated and PAH and PCB levels in porewater were determined using equilibrium passive sampling. Furthermore, we elucidated the origin of lead (Pb) contamination utilizing non-traditional stable isotopic analysis. Our results reveal three main findings: 1. for all organic contaminant groups covered (PAHs, OCPs, PCBs, PBDEs and PFASs) as well as the elements lead (Pb) and titanium (Ti), determined concentrations decreased towards more recent deposited sediment. These decreasing trends could be linked to the time of introductions of restrictions and bans and therefore our results confirm, amongst possible other factors, the effectiveness of environmental legislation by revealing a successive change in contamination levels over the decades. 2. concentration trends for ΣPAH and ΣPCB measured in porewater correspond well with the ones found in sediment which suggests that this method can be a useful expansion to traditional bulk sediment analysis to determine the biologically available pollutant fraction. 3. Arsenic (As) concentrations were higher in younger sediment layers, potentially caused by emissions of corroded warfare material disposed in the study area after WW II.

Keywords: pollution fingerprint, hydrophobic organic contaminants, trace metal, PFAS, sediment core, North Sea

3.1 Introduction

During the last three centuries mankind became an incessant driving force affecting the natural environment and its related biogeochemical cycles. Therefore, Paul J. Crutzen and Eugene F. Stoermer proposed the term “Anthropocene” for the current geological epoch (Crutzen, 2002; Crutzen and Stoermer, 2000). Since the start of the industrial revolution in the 19^{th} century across Europe, the resulting measurable pollution fingerprint has become one of the Anthropocene’s main characteristic features (Dellasala et al., 2018; Emeis et al., 2015; Mineau, 2018). Pollution fingerprints can be categorized into classical, emerging, and yet unknown inorganic and organic contaminants such as polychlorinated biphenyls (PCBs), heavy metals or per- and polyfluoroalkyl substances (PFASs) (Aliff et al., 2020; Chiaia-Hernándes et al., 2017; Dong et al., 2020; EEA, 2015; Gałuszka et al., 2020; Irabien et al., 2020).

As marine environments are prone to contaminant entry from a variety of sources (e.g. atmosphere, rivers, shipping, point sources, etc.), pollution fingerprinting is particularly visible in coastal and marine regions and distinctively insightful to study in sediment cores (Bigus et al., 2014; Korosi et al., 2015; Laane et al., 2013).

Concerns about the various environmental contaminants that have been released into the marine environment over several decades and the resulting, often complex impacts have led countries to regulate and control European coastal and marine regions through regional marine sea conventions (OSPAR, HELCOM), on national level (e.g. German Bund/Länder Messprogramm (BLMP)), and international agreements (Marine Strategy Framework Directive (MSFD) or United Nations Sustainable Development Goals (UN SDGs)). Thereby marine sea conventions and legislation ensure that riparian countries are involved into reaching the good environmental status (GES) and thus overcoming the transboundary problem of pollution, environmental impacts and the use of marine regions and their resources as common goods (tragedy of the commons (Hardin, 1968)). Organic contaminants, metals and trace metals in the aquatic environment play a key role for the GES of habitats, which is reflected by the implementation of limit values for selected organic contaminants and metals by different directives (EU 2000/60/EC, 2000; EU 2008/56/EC, 2008; OSPAR, 2010). Additionally, the defined sustainability goal number 14 for marine regions by the United Nations underlines the importance of regional marine conventions and their resulting environmental protection efforts (United Nations, 2015). A review of enacted legislations for restrictions and bans covering specific compounds and compound groups in several European countries and the UK and their inclusion into the Stockholm Convention has been assembled in Table 3.1; these include lead, polychlorinated biphenyls (PCB), polybrominated diphenyl ethers (PDBE), hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDT) and related metabolites (DDX), dieldrin (DIELD), hexachlorocyclohexanes (HCHs), and several polyfluorinated compounds (PFASs, e.g. PFOS, PFOA, PFHxS).

However, environmental protection efforts by marine conventions and legislation struggle with contaminant evaluation and assessment as well as justification of restriction and bans (BLANO, 2018a, 2018b; HELCOM, 2018; OSPAR, 2017). One reason for this is that implemented monitoring schemes miss additional indicators for a comprehensive environmental pollution assessment or for example missing environmental assessment criteria (OSPAR, 2017). Although effective monitoring in the marine environment is being conducted by the Federal Maritime and Hydrographic Agency (BSH) for the German part of the North Sea, and related agencies in other North Sea adjacent countries, monitoring efforts focus mostly on legacy metal pollutants (e.g. Ni, Cu, Zn, Cd, Hg and Pb) or classical hydrophobic contaminants (e.g. PCBs, polycyclic aromatic hydrocarbon (PAHs) and organochlorine pesticides (OCPs)). However, growing concerns about new, emerging metal and organic contaminants reveal the need for extended monitoring schemes and new powerful screening methods. Examples for the release of emerging metals are metal containing pharmaceuticals (e.g. Gd based MRI contrast agents or Pt containing anti-cancer drugs) or the usage of so called technology-critical elements (TCEs) for various high tech applications (IT sector, electro mobility or renewable energy production) (Nuss and Blengini, 2018; Petersen et al., 2016; Wojcieszek et al., 2018). One example for a group of emerging organic contaminants yet out of monitoring focus, except PFOA and PFOS, are PFASs which are meanwhile regularly detected in marine regions (Ahrens et al., 2010, 2009; Joerss et al., 2019, 2020). Also, it is still difficult to cover the threats and effects caused by the multitude of different known and unknown contaminants in the marine environment by the implemented monitoring schemes, as they cannot entirely be covered by chemical analysis using mass spectrometric methods, for example (Simon et al., 2015). In addition, the determination of absolute contaminant concentrations in environmental matrices alone cannot be used to adequately assess associated impacts and risks. For example, the lack and uncertainty of threshold values for many contaminants hamper their adequate assessment and evaluation to reach a GES (BLANO, 2018a, 2018b; HELCOM, 2018; OSPAR, 2017) or to support the UN SDGs. Hence, additional indicators for a comprehensive environmental pollution assessment, including emerging and future contaminants or bioavailable concentrations, need to be implemented into current monitoring schemes (Altenburger et al., 2019; Muz et al., 2020).

As mentioned above, one promising approach for pollution assessment is based on the analysis of sediment cores (Bigus et al., 2014; Korosi et al., 2015). Due to variable accumulation of contaminants over time, depending on entry into the aqueous layer above and the contaminants' physical chemical properties, sediments serve as time records of aquatic systems' pollution and can thus serve as a powerful indicator for contaminant presence and allow the assessment of a time-integrated pollution status (Bigus et al., 2014; Förstner, 1985; Johannessen and MacDonald, 2012; Korosi et al., 2015). Several powerful examples exist for the application of sediment cores to reconstruct pollution over time, for example monitoring the beginning of industrialization or contamination phase-outs (Arp et al., 2011; Combi et al., 2019; Götz et al., 2007; MacInnis et al., 2019; Pérez-Fernández et al., 2016; Peters et al., 2020; Shahabi-Ghahfarokhi et al., 2020; Sobek et al., 2015); however, the technique requires that sediment layers are not disturbed by bioturbation, sediment transport processes, or other processes that disturb regular sediment deposition (Johannessen and MacDonald, 2012; Noji et al., 2002). As a result, the analysis of sediment cores can be used to verify the effects of contaminant regulations and bans and thus sediment cores can serve as crucial evidence for the justification of regulatory measures. Thus, sediment cores can provide insights and guidance for new and emerging contaminants that may appear in the marine environment. Also, bioavailable concentration via measurements in sediment porewater can be investigated in parallel. In addition, sediment core data can be used to suggest and establish background concentrations of specific contaminants which are needed for the future broader evaluation of factors defining the good environmental status (GES) (Bigus et al., 2014; Boitsov et al., 2020; Pérez-Fernández et al., 2016).

Because of its heavily impacted coastal regions currently inhabited by more than 140 million people (Emeis et al., 2015), the North Sea Region is particularly relevant for the determination of pollution fingerprinting by sediment cores. Since the water circulation within the North Sea Basin results in a continuous transport of the water into the Skagerrak region, followed by regular sediment deposition (Anckar et al., 1998; Rosenberg et al., 1996), the Skagerrak is suitable to study the fingerprint of pollutants present in the North Sea over longer periods of time. A further advantage of the Skagerrak region is the comparably high sedimentation rate with up 3 mm per year, which ensures that changes in the pollution fingerprint can be possibly clearly distinguished (Boitsov et al., 2013).

Our study therefore focused on (1) on the analysis of routinely measured contaminants (PAHs, PCBs, OCPs, Cd, Cr, Cu, Ni, Pb, Ti and Zn) as well as emerging organic and inorganic contaminants (As and PFASs) plus the determination of Pb stable isotope ratios in dated sediment cores; (2) creating a time-resolved chemical fingerprint in the Skagerrak as a measure of man-made pollution of the “Anthropocene”; (3) determining PAH and PCB concentrations in porewater to evaluate their bioavailability; (4) the value of sediment core data for the environmental assessment of contaminants in the marine environment within environmental legislation (OSPAR, HELCOM, MSFD) including the possible determination of background values or providing insights into environmental regulation effects on contaminant levels.

Table 3.1: *Years of introduced restrictions/bans for contaminants and contaminant groups in European countries, the UK and their inclusion into the Stockholm Convention. The references are coded with numbers within the table, which are then itemized further on below the table.*

	Germany		**Sweden**		**Denmark**		**Norway**		**EU**		**United Kingdom**		**Stockholm Conv.**	
Phase-out of lead containing fuel	1972^{d}, 1988^{d}, 2000	62, 63, 72	1994	70, 71	1995	69, 70	1996	72	1978^{d}, 1985^{d}, 2000	66, 67, 68	2000	72		73
PCBs	1978^{a}, 1989	1, 2	1972^{a}, 1978	3, 4	1977^{a}, 1986	5, 6	1980	7, 8	1976^{a} 1985^{b}	11, 12	1972a, 1986	9, 10	2004	
PBDE	2005^{d}	16	2003^{d}	17	2004^{d}	5, 18, 51	2002^{b}, 2004	8, 19	2006^{d}	27	2004	21, 22	2009	
-penta, -octa	2004^{d}	39	2003^{d}, 2004	4	2004^{d}	51, 5	2004	8, 19	2003^{d}, 2009^{d}	26, 29	2003, 2004	21, 22	2009	
-deca	2004^{c}, 2005^{d}, 2019^{d}	40, 16, 28	2003, 2007^{h}, 2008	17, 4	2006^{d}, 2019^{d}	52, 53	2006, 2008^{d},	8, 19, 20	2006^{d}, 2019^{d}	27, 28	2004^{c}, 2008^{d}, 2019^{d}	23, 24, 25	2017	
HCB	1977	44, 45	1980	4	1992^{d}, 2003	53, 54	n.a., 2002	56	1978 1981	30	1981	9	2004	
DDX	1972^{d}, 1977	42, 44, 45	1970, 1975	4, 48, 49	1970^{d}, 1984^{d}, 2003	53, 54	1970, 1989	56	1978 1981	30	1986	9	2004	
DIELD	1974	43, 44	1970	4, 49	1992^{d}, 2003	53, 54	n.a., 2002	56	1978 1981	30	1981	9	2004	
HCHs	1977^{d}	41, 44, 45	1970^{d} (γ), 1989	4, 49, 50	1992, 1994 (γ), 2010	52, 53, 55	1992^{j} (γ), 1995	57	1978 1981	30	1982 (α, β), 2002^{d} (γ)	21	2009	
PFAS	joint activity for a broad restriction in EU under REACH (with NED)f 64													
-PFOS	2007^{d,i}, 2020^{g}	46, 47	2007^{d,i}, 2020^{g}	31, 47	2006^{d,i}, 2020^{g}	31, 47	2005b, 2007^{d}, 2020^{g}	19, 31, 47, 57	2006^{d}, 2019	31, 32, 36	2007^{d}	59, 60, 61	2009	
-PFOA	2020^{d}	34, 37	2020^{d}	17, 34	2020	34, 37	2014^{d}, 2020^{d}	19, 37, 58	2013^{e}, 2020^{d}	33, 34, 37	2020^{d}	36, 37	2019	
-PFHxS									2017^{e}, 2022^{f}	35, 38			2021^{f}	

The content of the POP-Ordinance is applicable law in all EU-member states.
n.a. never authorized
1 BRD (1978); 2 BRD (1989); 3 Koppe and Keys (2000); 4 Swedish EPA (2012); 5 Danish EPA (2006); 6 Larsen et al. (2014); 7 Miljøstatus (2021); 8 Norwegian Ministry of Climate and Environment (2017); 9 Department for Environment Food and Rural Affairs UK (2007); 10 United Kingdom (1986); 11 EU 76/769/EEC (1976); 12 EU 85/467/EEC (1985); 16 BRD (2005); 17 Swedish EPA (2020); 18 Danish EPA (2021); 19 Produktforskriften (2004) and its amendments; 20 Norwegian Pollution Control Authority (2008); 21 Department for Environment Food and Rural Affairs UK (2013); 22 United Kingdom (2004); 23 Environment Agency UK (2019); 24 United Kingdom (2008a) and its amendments; 25 United Kingdom (2008b); 26 EU 2003/11/EC (2003); 27 EU 2002/95/EC (2003) RoHS 1; 28 EU (EU) 2017/227 (2017); 29 EU (EC) No 552/2009 (2009); 30 EU 79/117/EEC (1978); 31 EU 2006/122/EC (2006); 32 EU (EU) No 757/2010 (2010); 33 ECHA (2013); 34 EU (EU) 2017/1000 (2017); 35 ECHA (2017); 36 EU (EU) 2019/1021 (2019); 37 EU (EU) 2020/784 (2020); 38 BMU (2021); 39 BRD (2003); 40 VECAP (2006); 41 UBA (2006); 42 BRD (1972); 43 BRD (1974); 44 BVL (2009); 45 BRD (1977); 46 BRD (2007); 47 EU (EU) 2020/1203 (2020); 48 KEMI (2020); 49 Sveriges Giftnämnden (1969); 50 KEMI (2020); 51 Denmark (2004); 52 Danish EPA (2018); 53 Danish EPA (2006); 54 Denmark (2003); 55 Denmark (1994); 56 Miljøverndepartment (2006); 57 Miljøverndepartment (2013); 58 Norwegian Ministry of Climate and Environment (2021); 59 United Kingdom (2007b) and its amendments; 60 Department for Environment Food and Rural Affairs UK (2013); 61 United Kingdom (2007a); 62 BRD (1971); 63 BRD (1987); 64 German EPA (2020); 66 EU 78/611/EEC (1978); 67 EU 85/210/EEC (1985); 68 EU 98/70/EC (1998); 69 United Nations (1999); 70 Löfgren and Hammar (2000); 71 Lovei (1998); 72 Ministry of Environment of Denmark (2003); 73 United Nations (2019)

[a] Open uses.
[b] Action plan.
[c] Voluntary.
[d] Partial ban/restriction.
[e] Classified as SVHC under REACH.
[f] Restriction/ban expected.
[g] Exceptions deleted or partially deleted.
[h] Attempted.
[i] EU wide restrictions.
[j] Phase out.

3.2 Materials and methods

3.2.1 Sample material

The analyzed sediment cores were taken on a monitoring ship cruise carried out by the German Federal Maritime and Hydrographic Agency (BSH) in August 2017 on the RV CelticExplorer (Cruise CE17013a). The sediment cores were taken with a multi corer (MUC, Oktopus, Kiel, Germany) equipped with eight 10 cm i.d. pre-cleaned plexiglas tubes at 57°49.8 N and 7°59.9 E in the Skagerrak at 520 m water depth (Figure 3.2). As known from previous studies (Brockmeyer and Theobald, 2016; Theobald et al., 2012), this area has been shown to be explicitly eligible to sample sediment cores due to high sedimentation rates and possible undisturbed stratification (Anckar et al., 1998; Rosenberg et al., 1996).

In order to confirm the results from radiometric dating, an additional longer core was taken with a Frahm Lot (MacArtney A/S, Esbjerg V, Denmark) at the same position. After retrieval, the sediment cores were immediately frozen at -18 °C, except for the ones used for radiometric dating purposes (see 3.2.3 Dating). To cut the frozen sediment cores, a self-developed device was used. The device enabled the precise cutting of the sediment cores into slices of 1 cm without defrosting them (an image is provided in SI 1.1, Appendix B). Core slices for trace metal and isotopic analysis were filled into pre-cleaned LDPE sample containers. Core slices for HOC and PFAS analyses in bulk sediment and sediment porewater were filled into solvent pre-rinsed aluminum trays. After cutting, all samples were kept frozen at -18 °C until analysis.

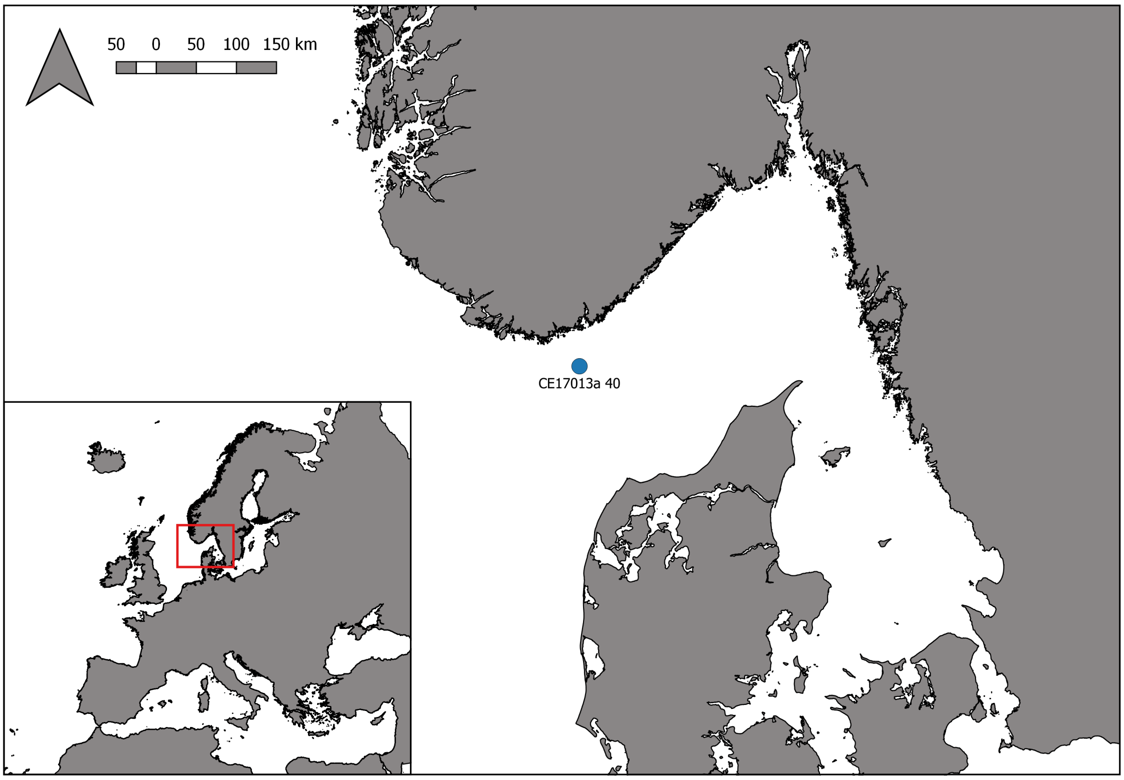

Figure 3.2: *Sampling location (blue) of the sediment cores analyzed taken on monitoring cruise CE17013a*

3.2.2 Chemicals

Chemicals used for sample preparation as well as analysis and quantification of HOCs, PFASs, trace metals and radiometric dating in bulk sediment and sediment porewater are stated in SI 1.2 to SI 1.6 (Appendix B).

3.2.3 Experimental

Dating

For the radiometric dating, one core taken with the MUC (42 cm length) and a second core (73 cm length) for confirmation from the same position taken with the Frahm Lot were analyzed. Sample preparation for radiometric dating was carried out as described previously (Bunzel et al., 2020). Briefly, the cores were sectioned into slices of 1 cm thickness directly after sampling, filled into plastic containers, sealed with isolating tape, and kept at -20 °C for transportation and storage. Each section was dried and homogenized by ball mill. Finally, an aliquot was sealed in a gas-tight Petri dish and stored for a minimum of 28 days to ensure ^{226}Ra had reached equilibrium conditions with its product isotopes ^{222}Rn, ^{214}Pb, and ^{214}Bi. The quantification of ^{210}Pb, ^{137}Cs, ^{214}Pb, ^{214}Bi was performed using a high-purity low-level germanium detector (BE 3830P-7500SL-ULB Mirion Technologies (Canberra), Ruesselsheim, Germany). Further details on the sample analysis are provided in SI 1.2 (Appendix B).

Measurements were performed by the accredited Laboratory for Environmental Radiochemistry at the Helmholtz-Zentrum Hereon. For calibration, an artificial reference material was prepared by mixing silica gel with reference solutions of ^{137}Cs and ^{226}Ra. (Eckert & Ziegler Nuclitec GmbH, Braunschweig, Germany). Measurement times varied between 90 000 s - 600 000 s depending on the sample activity.

Multi-element and isotopic measurements

Sample preparation for trace element- and isotope ratio analysis in sediment was carried out as described in Zimmermann et al. (2020). Briefly, digestion of sediment samples was performed with a microwave system (MARS 5 Xpress or MARS 6, CEM Corp., Kamp Lintfort, Germany) using HNO_3, HCl and HBF_4 and subsequent dilution of the digests to 50 mL with Milli-Q water. Elemental quantification in the sediment digests was performed using an inductively coupled plasma tandem mass spectrometer (ICP-MS/MS) (Agilent 8800, Agilent Technologies, Tokyo, Japan). For analysis of Pb isotope amount ratios, a multi collector inductively coupled plasma mass spectrometer (MC ICP-MS) (Nu Plasma II, Nu Instruments Ltd, Wrexham, UK) was used. Further details on sample preparation and measurement for trace element- and isotope ratio analysis can be found in SI 1.3 (Appendix B).

For method validation the reference marine sediment GBW-07311 (National Research Centre for Certified Reference Materials, Beijing, China) was processed in duplicates for each digestions batch and used for method validation of the elemental quantification. All samples were processed as triplicates. Combined uncertainties ($U(k{=}1)$) were estimated using a Kragten spreadsheet approach (Kragten, 1994) considering the standard deviation of the sample triplicate and the precision of the measurements. The Limits of Quantification (LOQ) were calculated according to German DIN 32645 (2008) and DIN ISO 11843-2 (2006). Therefore, the LOQ is defined as 3 x *SD* of the blank. The significant number of digits of mass fractions are given according to GUM and EURACHEM guidelines, whereby the uncertainty determines the significant number of digits to be presented with the value (Ellison and Williams, 2012; B. Magnusson et al., 2015).

For isotope analysis total combined uncertainty budgets ($U(k{=}2)$) were determined considering precision of the isotope ratio measurement for samples and within-run-repeatability of the measured isotope ratio in the bracketing standards, as well as the uncertainty of the reference material SRM 981. Details can be found in SI 1.3

(Appendix B). The obtained instrumental precision was typically better than 20 ppm for $n(^{208}\text{Pb})/n(^{206}\text{Pb})$.

HOC analysis

Sample preparation for 61 HOCs in sediment was carried out as described in Logemann et al. (2019) using accelerated solvent extraction followed by a SPE and GPC clean-up step. The chromatographic analysis was performed using a GC–MS/MS system (GC 7890B/ MS 7000C, Agilent Technologies, Santa Clara, CA, USA). Further details regarding the sample preparation and chromatographic separation are stated in SI 1.4 (Appendix B). The quantification of target analytes was achieved by using a multipoint calibration. A number of internal standards where used (see SI 1.4, Table 4, Appendix B). Parallel to the sediment core samples, certified reference material (IAEA-408, International Atomic Energy Agency) was processed in duplicate. All listed analytes were within the stated confidence intervals for the recommended values, except for γ-HCH where concentrations were slightly above the stated recommended value. Additionally, one internal reference sediment sample (produced by the BSH lab) was processed in triplicate for which the overall standard deviation of the results was 11 %. The standard deviation of a 10x injection of the lowest calibration standard injected into the GC-MS/MS instrument was below 5 % for all analytes, except for dieldrin, BDE66 and the higher brominated congeners analyzed, which were below 10 %. Overall recovery rates for the internal standards in processed samples were 74 ± 15 %. Furthermore, in each sample batch, two blank samples were processed to correct and check for contamination through sample preparation process and measurement. The sample analysis was conducted in a lab that is accredited under DIN EN ISO 17025 and regularly participates in round robin tests (IAEA/QUASIMEME). Individual LOQ and LOD values as well as the internal standard composition are stated in the SI (SI 1.4, Table 8 an 9, Appendix B).

PFAS analysis

Sample preparation for 21 PFAS was carried out following DIN 38414-14 (2011), which includes extraction with methanol, shaking and ultrasonic treatment. For clean-up, an automated SPE system (Dionex AutoTrace 280, Thermo Fisher Scientific) equipped with Strata XAW cartridges (Phenomenex) was used. The subsequent quantification of target analytes in sample extracts was conducted using an LC-MS/MS system (LC: Agilent 1260 pump, Agilent 1200 oven, MS: Sciex QTrap 5500, Agilent Technologies, Waldbronn, Germany and Sciex, Framingham, USA). Further details regarding the sample preparation and chromatographic separation are stated in SI 1.5 (Appendix B). The quantification of target analytes was achieved by using a multipoint calibration. A number of isotopically labeled internal standards were used (see SI 1.5, Table 10,

Appendix B). To check for contaminations during sample preparation and measurement in each sample batch, at least one procedural blank was prepared using sea sand, which was treated as a real sample. Additionally, blank samples containing table water were injected before, within and after each sample batch to monitor possible carry over effects and blank values. The calibration was checked with an AQS-standard within each batch, which was prepared from a different stock solution as the calibration and spike standards. Furthermore, the Signal-to-Noise ratio at the LOQ was monitored and had to be below 10. The sample preparation was checked by duplicate preparation of every forth sample - one as the original sample and one with standard addition spiking 0.05 μg mL^{-1} to the sample methanol extract. The recovery rate of these spiked QC samples was 96 ± 16 %. Overall recovery rates of internal standards for PFASs in sediment samples were 73 ± 14 %. Furthermore, the overall performance of the method is regularly evaluated by the participation in round robin proficiency tests. The determination of the LOQ was carried out by using the blank value method DIN 32645 (2008). Based on that the LOD was calculated as one third of the LOQ. The LOQ and LOD values as well as the internal standard composition are stated in the SI 1.5, Table 11 (Appendix B). The sample analysis was conducted in a lab that is accredited for DIN EN ISO 17025.

HOC analysis in porewater

Equilibrium passive sampling methods (EPSMs) were used to determine freely dissolved concentrations (C_{free}) of HOCs in the sediment cores porewater. Experiments were conducted using commercially available PDMS fibers (see SI 1.6 for details, Appendix B). Fibers were equilibrated in the sediment for 21 days and subsequently analyzed in triplicates for each sample for 12 PAHs and 7 indicator PCBs using thermo desorption with a cold injection system (CIS) coupled to a GC-MS system (GC 7890B/MS 5977A, Agilent Technologies, Santa Clara, Ca, USA). Further details regarding the sample preparation and chromatographic separation settings are stated in SI 1.6 (Appendix B) and Witt et al. (2009).

The determination of HOC in porewater sediment samples was accompanied by several QAQC measures: All sediment core samples were tested using at least three fibers per testing vial. New and pre-cleaned SPME fibers were used for all procedures described and GC liners were checked for chemical purity during the course of the experiments. Fibers were stored cooled at 4 °C in ultra-pure water before the experiment to limit contamination uptake. The calibration for GC-MS measurements was achieved with an external 5-point calibration (2.0 – 500 μg L^{-1}) with a correlation coefficient > 0.99. Plain fibers served as analytical blanks for method detection and quantification limits (LOD and LOQ). LOQ and LOD were calculated using the average PAH and PCB concentration in the blanks plus 10 times (LOQ) or 3 times (LOD) the standard deviation.

Data were then converted to C_{PDMS} (pg μL^{-1}). The LOD_{PDMS} and LOQ_{PDMS} were at all times below the lowest measured concentration for any substance. LOQ_{PDMS} ranged between 3.6 and 8.9 pg μL^{-1} and 3.2 - 7.2 pg μL^{-1} for PAHs and PCBs, respectively.

Method quantification limits on a C_{free} basis (LOQ_{free}) were orders of magnitude lower and decreased with increasing PDMS to water partition coefficients (K_{PDMS}):

$$LOQ_{free} = \frac{LOQ_{PDMS}}{K_{PDMS}} \tag{3.1}$$

The time for reaching chemical equilibrium between GF10 PDMS and sediment porewater for the analyzed compounds was set at 21 days, as several studies showed that this time period is sufficient for reaching a 90 % equilibrium (Reininghaus et al., 2020; Witt et al., 2010, 2013). To establish non-depletion criteria, it was assured that the fiber uptake did not reduce the concentration of any substance within the system by more than 5 % (Bartolomé et al., 2018; Witt et al., 2013). Considering the different compartments and the corresponding partitioning coefficients, the following equation can be applied:

$$K_{PDMS}V_{PDMS} < \frac{K_{OC} \cdot m_{OC}}{100} \tag{3.2}$$

where m_{OC} is the mass of organic carbon (OC) in the sediment. Using equation (3.3), the K_{OC} was calculated from the organic carbon normalized sediment concentration of the target components (C_{OC}) and the freely dissolved concentration:

$$K_{OC} = \frac{C_{OC}}{C_{free}} \tag{3.3}$$

Total organic carbon analysis

The TOC analysis was carried out with a VarioEL (Elementar, Germany) in CN mode at 950 °C. The dried and homogenized samples were weighted in silver capsules, acidified with 200 μL of 2 M HCl (32 %) and placed in an oven for 3 h at 110 °C to remove the inorganic carbon. Afterwards, the silver capsules were folded and pressed into tin capsules. For quality control of the TOC measurements, an acetanilide standard (C_8H_9NO) was used.

3.3 Results and discussion

The following section will present the development of concentrations for the targeted pollutant classes over time within the analyzed sediment cores. The results represent a time frame of approximately 100 years as derived from the ^{210}Pb and ^{137}Cs dating, respectively, with margins of error of 5 – 20 years depending on sediment depths (see corresponding data publication for details). We refer to sediment depth throughout the results and discussion naming the respective year in parentheses. Detailed results for all compounds covered in our study are also available in the corresponding data publication. Substance abbreviations used throughout the manuscript can be found in the SI 1 (Appendix B).

3.3.1 Dating

The age of the sediment core layers was determined using ^{210}Pb and ^{137}Cs radionuclides; a method commonly used for dating of marine and lacustrine sediments (Sanchez-Cabeza and Ruiz-Fernández, 2012). The age of the individual sections and sedimentation rates was determined from the supported ^{210}Pb activity using the constant rate of supply (CRS) model described by Appleby and Oldfield (1978) and correlated with the measurable fallout (^{137}Cs) of the nuclear bomb tests in 1963 and the Chernobyl disaster in 1986. Details on the application of the model have been reported elsewhere (Arias-Ortiz et al., 2018; Bunzel et al., 2020; Sanchez-Cabeza and Ruiz-Fernández, 2012). Supported ^{210}Pb was determined based on the measured activities of its product isotopes ^{226}Ra (^{214}Pb and ^{214}Bi). The unsupported ^{210}Pb, which represents the atmospheric fallout, was calculated by subtracting the supported ^{210}Pb from the total ^{210}Pb activity.

Overall, the cores had a maximum unsupported ^{210}Pb activity of 232 ± 4 Bq kg^{-1} with a decreasing trend from the top towards the bottom sections of the core. In comparison the activity of the supported ^{210}Pb (^{226}Ra) varied between 20 ± 0.6 Bq kg^{-1} to 44 ± 1.2 Bq kg^{-1}. The activity of ^{137}Cs ranged from 24 ± 1.5 Bq kg^{-1} at 20 cm to zero at the bottom of the cores.

The application of the CRS model to the core showed a sedimentation rate between 0.3 cm a^{-1} and 1.3 cm a^{-1} over a time span of approximately 100 years. The ^{137}Cs-marker fitted very well with a difference of 3 years to the CRS model. The ^{137}Cs signal of the nuclear bomb test were observed in both analyzed cores. The uncertainty of the age dating was estimated with 5 years for the upper section and 10 years for the lower section of the short core. The longer core taken with the Frahm Lot confirmed the results of the shorter core taken with the MUC.

3.3.2 Trace metals

The elements arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), lead (Pb), titanium (Ti) and zinc (Zn) were detected in all sections of the investigated core which covers most environmentally/toxicologically relevant trace metals. All measured concentrations of the individual elements present in the analyzed sediments were above the LOQ of the applied ICP-MS/MS methodology (Zimmermann et al., 2020).

Monitoring elements (As, Cd, Cr, Cu, Ni, Pb, Ti, Zn)

For the North Sea, only a small number of elements are assigned with assessment criteria from national authorities (e.g. German Federal Maritime and Hydrographic Agency (BSH)) or EU conventions (Oslo and Paris Convention (OSPAR)). Table 3.2 summarizes the BSH BC criteria (Schmolke, 2016) as well as BC and BAC values from the OSPAR CEMP data assessment (OSPAR, 2014) which have been used for the assessment of the measured concentration profiles.

Table 3.2: *Assessment criteria for the measured element mass fractions in the sediment samples to estimate the natural geogenic background based on the BSH BC criteria (Schmolke, 2016), as well as BC and BAC values from the OSPAR CEMP data assessment (OSPAR, 2014)*

	As	Cd	Cr	Cu	Ni	Pb
BSH BC (mg kg^{-1})		0.08 - 0.26		16 - 29		12 - 38
OSPAR BC (mg kg^{-1})	15	0.2	60	20	30	25
OSPAR BAC (mg kg^{-1})	25	0.31	81	27	36	38

The concentration profiles of elements analyzed (As, Cd, Cr, Cu, Ni, Pb, Ti and Zn) in the investigated sediment core are shown in Figure 3.3. Most striking were the measured concentrations for As, which varied between 13.5 ± 0.4 mg kg^{-1} and 46 ± 11 mg kg^{-1} dw. As concentrations are fluctuating within background levels from the bottom to -15 cm (approx. 1996), but a significant concentration increase can be observed from -15 cm upwards, which are up to 3-fold larger than the OSPAR BC of 15 mg kg^{-1} (Table 3.2 and Figure 3.3). We assume that this increase of As concentrations may be related to the discard of As-containing chemical warfare agents after WWII. It is estimated that approx. 50 000 t to 190 000 t of chemical ammunition were discarded in the Skagerrak and the Baltic Sea, respectively (Bełdowski, Brenner, and Lehtonen, 2020). In addition, a recent study estimated that 13 ships were scuttled in the Skagerrak with chemical warfare agents on board (Tørnes et al., 2006). As a result, after decades of ongoing corrosion, organo-arsenic compounds originating from warfare agents are detectable in sediment samples (Tørnes et al., 2006).

All analyzed samples contained also significantly higher Pb concentrations than the BSH BC and OSPAR BAC, suggesting that Pb levels are significantly influenced by human activity. Pb was found in increasing concentrations starting at -30 cm (approx. 1958) until -23 cm (approx. 1978). After peaking at -22 cm (approx. 1981), Pb concentrations continually decreased up until the most recent years and are now comparable to levels found in the beginning of the 20th century (Figure 3.3). This trend is in a very good agreement with findings from Shahabi-Ghahfarokhi et al. (2020), who investigated sediment cores from the Baltic Sea and attributed the observed decrease to the restrictions of Pb-based fuel additives, implemented throughout Europe in the

1970s and 1980s (see 3.3.2 Pb isotopes ratios and Table 3.1). Additionally, measured Pb concentrations (53.9 ± 0.3 mg kg^{-1} to 85 ± 6 mg kg^{-1}) were within the same magnitude of other studies reporting loads of Pb in sediment cores of neighboring regions (Boxberg et al., 2020; Shahabi-Ghahfarokhi et al., 2020; Vallius, 2014).

Measured concentrations of Cd and Cr varied between 0.20 ± 0.04 mg kg^{-1} to 0.29 ± 0.07 mg kg^{-1} and 81.7 ± 0.6 mg kg^{-1} and 99 ± 13 mg kg^{-1}, respectively. Concentrations were within the range of BSH and OSPAR BC for Cd and only slightly higher than the OSPAR BAC of 81 mg kg^{-1} for Cr. Both elements showed no significant trend within the analyzed sediment core.

Measured Cu concentrations varied between 18.5 ± 0.7 mg kg^{-1} and 22.5 ± 0.4 mg kg^{-1} and were within the range of BSH BC. However, younger sediment material features significantly higher Cu concentrations than older material, which could be a result of an increasing anthropogenic Cu production in the 20th century (Henckens and Worrell, 2020). Several studies report the existence of very toxic Cu compounds in bottom sediments of harbors, shipping routes and regions with high ship traffic (Byrnes and Dunn, 2020; Claisse and Alzieu, 1993; OSPAR, 2016). In contrast, the upper 5 cm layer suggest a decrease of anthropogenic Cu inputs in recent years.

For Ni and Zn measured concentrations varied between 36.5 ± 1.2 mg kg^{-1} to 43.6 ± 0.9 mg kg^{-1} and 109.7 ± 1.6 mg kg^{-1} to 134 ± 7 mg kg^{-1}, respectively and are slightly higher than the OSPAR BAC of 36 mg kg^{-1} for Ni and within BSH BC and OSPAR BAC for Zn in most parts of the core. The concentration profiles of the elements Ni and Zn show an opposing picture. Similar to Cu, for Ni younger sediment material features significantly higher concentrations than older material. In contrast, for Zn recent values are slightly lower than values of the beginning of the 20th century, were a significant increase until around -20 cm (approx. 1985) can be seen. However, next to riverine inputs, new sources of Zn resulting from offshore activities (as second most abundant element in Al-anodes), could lead to local increases of concentrations in marine regions (Kirchgeorg et al., 2018).

The concentration profile of Ti shows a maximum at -12 cm (approx. 2005) with 4580 ± 120 mg kg^{-1}. Concentrations are decreasing towards the upper layers of the core to 3680 ± 120 mg kg^{-1}. In deeper sediment layers (-40 cm to -25 cm) concentrations vary around 3900 ± 100 mg kg^{-1}. The commercial use of Ti from 1945 onwards within the metal, plastics and electrical industry correlates well with the concentration increase determined in the analyzed sediment core. This increase could be also attributed to the discarding of diluted acid, a waste product of titanium dioxide processing, into the North Sea starting in the 1960s. During the 1980s up to 2.5 mio t per year were discarded into the German North Sea (Pickaver, 1982). In 1989, such disposal of diluted acid was banned and therefore could be an explanation for the decreasing concentrations of Ti towards the upper sediment layers (Skjaerseth, 1992).

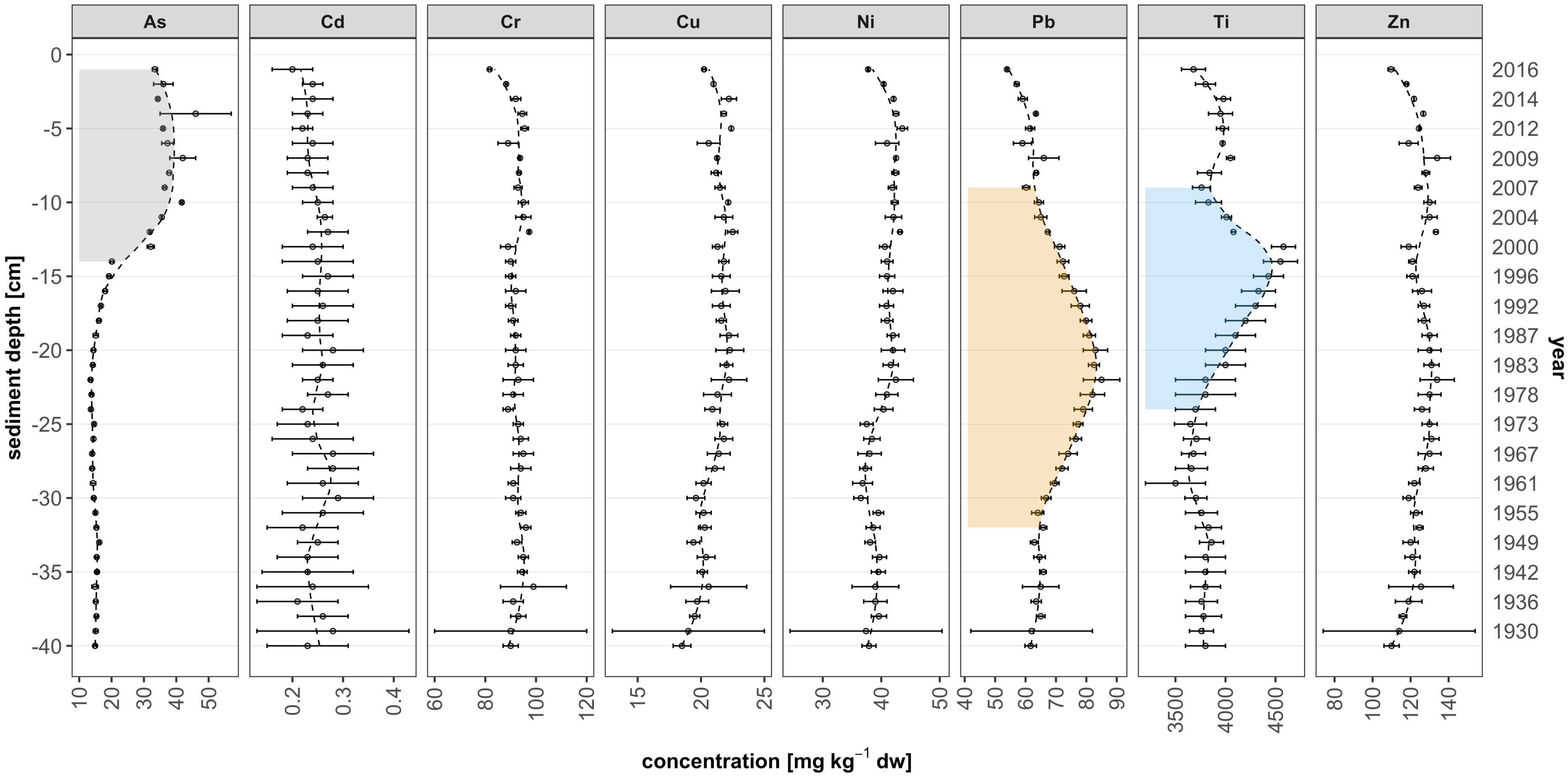

Figure 3.3: *Profiles of arsenic (As), cadmium (Cd), chrome (Cr), copper (Cu), nickel (Ni), lead (Pb), titanium (Ti) and zinc (Zn). Error bars correspond to combined uncertainties U(k=1). Colored areas highlight the discussed concentration peaks*

Pb isotopes ratios

Pb is among the most frequently studied isotope systems in geochemistry (Faure and Mensing, 2004). The continuous production of radiogenic Pb isotopes (^{206}Pb, ^{207}Pb, and ^{208}Pb) results in natural isotope-abundance variations of Pb ores. Therefore, Pb containing products reflect the Pb isotope ratio of the ores used for their production and are not subjected to changes by other natural processes. Thus enabling a source tracing of anthropogenic Pb contamination e.g. by ore mining/smelting, coal burning or emissions by leaded gasoline (Komárek et al., 2008).

Pb isotope ratios of $n(^{208}\mathrm{Pb})/n(^{204}\mathrm{Pb})$[1], $n(^{207}\mathrm{Pb})/n(^{204}\mathrm{Pb})$, $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$, $n(^{207}\mathrm{Pb})$ $/n(^{206}\mathrm{Pb})$ and $n(^{206}\mathrm{Pb})/n(^{204}\mathrm{Pb})$ were analyzed in every centimeter of the sediment core. All isotope data is provided in the corresponding data publication. The measured isotope ratio $n(^{208}\mathrm{Pb})/n(_{204}\mathrm{Pb})$ within the analyzed sediment core (A) and the three isotope plot ($n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ versus $n(^{206}\mathrm{Pb})/n(^{207}\mathrm{Pb})$) (B) is shown in Figure 3.4. The Pb isotope ratio $n(^{208}\mathrm{Pb})/n(^{204}\mathrm{Pb})$ underlies significant variability ranging between 38.606 ± 0.017 and 38.346 ± 0.016. The lowest isotope ratios can be found at around at around -20 cm (approx. 1985) and corresponds very well to the time frame where highest Pb concentrations were detected (Figure 3.3) indicating a significant input of anthropogenic Pb during the 1970s and 1980s.

The three isotope plot (Figure 3.4, B) indicates a mixing of at least two different endmembers: presumably natural Pb (-40 cm core depth; $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$: $\sim$2.07; $n(^{206}\mathrm{Pb})/n(^{207}\mathrm{Pb})$: $\sim$1.19) and an anthropogenic endmember (-20 cm core depth; $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$: $\sim$2.08; $n(^{206}\mathrm{Pb})/n(^{207}\mathrm{Pb})$: $\sim$1.18).

Studies by Hinrichs et al. (2002) determined the natural isotopic composition $n(^{206}\mathrm{Pb})/$ $n(^{207}\mathrm{Pb})$ of the German Bight to be 1.207 ± 0.008, which is close to the highest observed $n(^{206}\mathrm{Pb})/n(^{207}\mathrm{Pb})$ of 1.1903 ± 0.0002 in our study. Therefore, the lowest part of the analyzed sediment core is close to the natural geogenic background and in fact already influenced by anthropogenic Pb inputs. Main anthropogenic Pb sources during the 20th century were leaded gasoline, coal combustion and metallurgical activities, each of them having a distinct, but variable isotopic composition. Western European gasoline featured the world-wide lowest ratio of $n(^{206}\mathrm{Pb})/n(^{207}\mathrm{Pb})$ (around 1.03 - 1.04) because of the commonly used Pb ore originating from the Broken Hill deposit in Australia (Komárek et al., 2008). After the worldwide ban of leaded gasoline, coal combustion is the predominant source of anthropogenic Pb emissions. The isotopic signature $n(^{206}\mathrm{Pb})/n(^{207}\mathrm{Pb})$ of coal combustion in Central Europe is significantly higher than the one of leaded gasoline and relatively close to natural Pb sources ($\sim$1.19) (Komárek

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[1] IUPAC-recommended notation for SI-traceable isotope-amount ratios $r{=}n(^{i}\mathrm{E})/n(^{j}\mathrm{E})$, with the amount of substance n, and the isotopes ^{i}E and ^{j}E of the element E. **The notation $^{i}\mathbf{E}/^{j}\mathbf{E}$ (e.g. $^{208}\mathbf{Pb}/^{204}\mathbf{Pb}$) is commonly used interchangeably**, even though lacking information on the type of quantity (microscopic vs. macroscopic) (see also Coplen (2011))

et al., 2008). The significant decrease of $n(^{206}\text{Pb})/n(^{207}\text{Pb})$ reaching its maximum at around -20 cm is clearly associated to the input of anthropogenic Pb by leaded gasoline. This is in good agreement to Grousset et al. (1994) who observed the lowest $n(^{206}\text{Pb})/n(^{207}\text{Pb})$ isotopic signature of European aerosols to be between 1970s to early 1980s. The analyzed sediment core therefore clearly reflects the decreased anthropogenic Pb inputs in Central Europe during the last decades, which is due to various bans of leaded gasoline (Table 3.1). Despite decreased Pb inputs the isotopic composition of today's sediments are still significantly different from the beginning of the 20th century, which illustrates the changing input sources of Pb to the marine environment. Furthermore, our results illustrate how international bans may significantly decrease the emissions of toxic heavy metals.

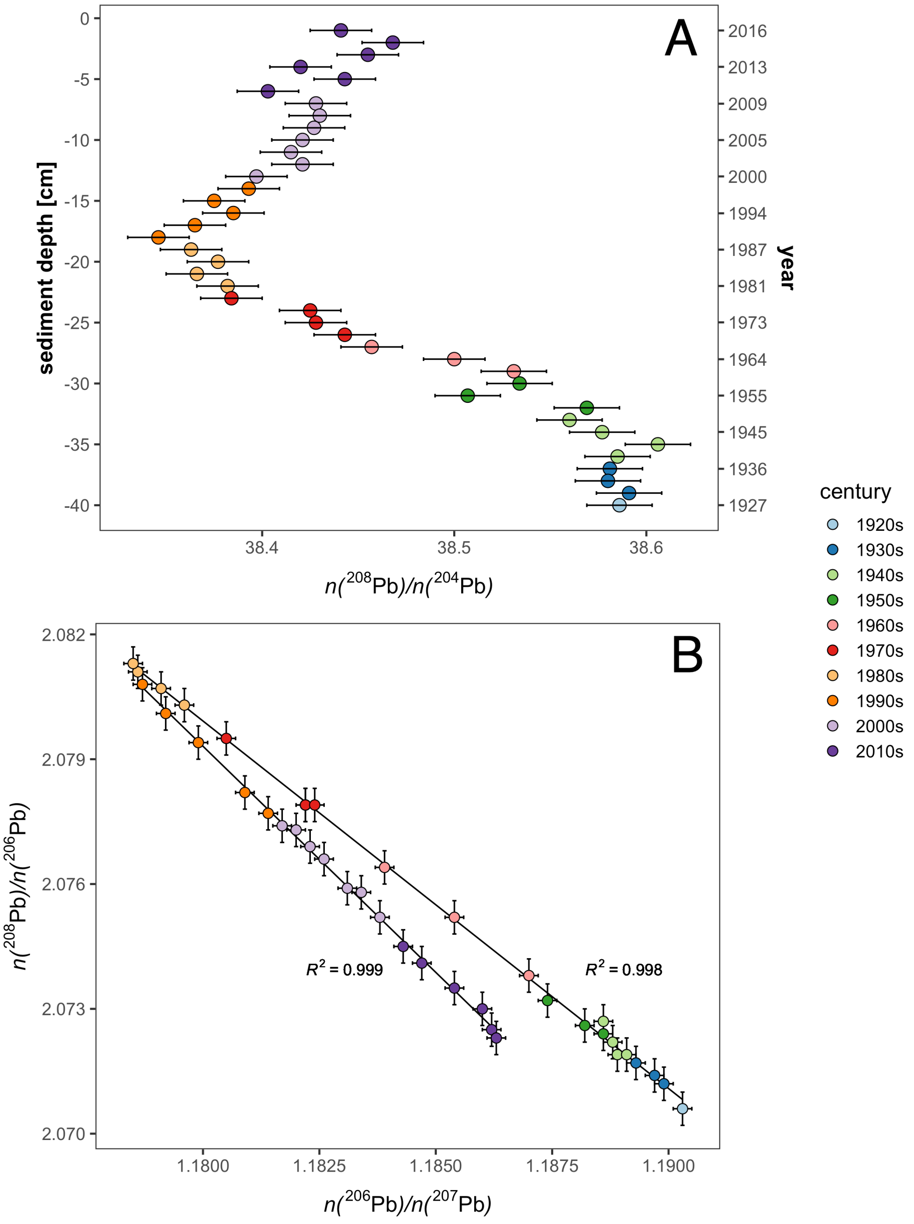

Figure 3.4: *Isotope ratio $n(^{208}Pb)/n(^{204}Pb)$ in the analyzed sediment core (A). Three isotope plot of $n(^{208}Pb)/n(^{206}Pb)$ versus $n(^{206}Pb)/n(^{207}Pb)$ of the analyzed sediment core (B). Error bars correspond to expanded uncertainties U(k=2)*

3.3.3 HOCs in sediments

Altogether, 61 HOCs were analyzed in sediment in 23 layers of the sediment core (core depth = 49 cm), including 39 PAHs (including methylated PAHs), 8 OCPs, 7 PCBs and 7 PBDEs (see SI 1.4, Table 8 and 9, Appendix B). Except for γ-HCH, dieldrin and PBDE 28 all HOCs were detected above the LOD in the majority of analyzed sediment layers, allowing the identification of continuous concentrations profiles throughout the sediment core. These profiles show only minimal variation, indicating no significant disturbance of the natural sedimentation, for example by bioturbation, as also confirmed by the radiometric dating results. Most of the analyzed HOCs showed profiles with a pronounced maximum and decreasing concentrations towards the upper sediment layers. Thereby, the maximum concentration of the individual analyzed HOC groups were observed in different sediment depths. The individual concentration profiles of analyzed HOCs are displayed in SI 1.4, Figure 2 a – c, all data can be found in the corresponding data publication (Appendix B). In the following sections, the results of the different analyzed contaminant groups will be discussed in detail. Measured HOC concentrations in sediment layers displayed in Figure 3.5 were not normalized to the organic carbon content (TOC), since TOC concentrations were stable throughout the sediment core (detailed results for TOC are displayed in the corresponding data publication).

PAHs

PAHs are ubiquitously distributed and are mainly entering the marine environment via the atmosphere, riverine input, oil spills and offshore activities (OSPAR, 2010). PAHs are a result of incomplete combustion processes, with the main source being of anthropogenic origin, such as from coal or fossil fuel combustion, the shipping industry and oil exploitation; a small fraction is also naturally emitted, for example during forest fires (Bigus et al., 2014; Pérez-Fernández et al., 2016; Wenning and Martello, 2014; Witt, 1995; Wolska and Rogowska, 2012). Some PAHs are known to be toxic, bioaccumulative, carcinogenic and causing long-term effects on the environment (Boitsov et al., 2013; Neff et al., 2005). Even though PAHs are not subject to the Stockholm Convention, selected PAHs are listed as priority pollutants in several governmental regulations or international agreements (EU POP-Ordinance, EU WFD, US EPA).

Within the OSPARs' Coordinated Environmental Monitoring Program (CEMP), the International Council for the Exploration of the Sea (ICES) and the US EPA several threshold values for PAHs and other contaminants in sediments were developed (Long et al., 1995, 1998; OSPAR, 2009a, 2012; U.S. EPA, 2002). These include background concentrations (BC), background assessment concentrations (BAC), environmental assessment criteria (EAC) and effect range low values (ERL) for 10 parent PAH compounds and several groups of alkylated PAHs as well as dibenzothiophene. The comparison of measured concentrations for PAHs with ERL, EAC, BAC and BC values revealed that for most PAHs concentrations were below ERL but higher than BC values. For NAPH, FLU, BAA, and CHRTRI, concentrations were higher than EAC values but lower than ERL values in the entire or parts of the analyzed sediment core. I123P, BGHIP and dimethyl-naphtalenes exceed the ERL values in the majority of the analyzed sediment layers. However, for I123P a positive trend was detectable in the upper sediment layers were concentrations fall below the ERL.

All PAHs investigated in our study were detected above the LOD in the analyzed sediment layers. For the resulting profiles of PAHs in the sediment core (see Figure 3.5), three groups can be distinguished. Lower aromatic PAHs (e.g. ACY, FL, PHEN) show a concentration maximum at -21 cm (approx. 1983), while higher aromatic PAHs peaked at -28 cm (approx. 1964). In contrast, concentration profiles of methylated naphthalenes and phenanthrenes showed no pronounced concentration maximum. For example, concentrations of methyl-naphthalenes and dimethyl-naphthalenes increased up to -9 cm (approx. 2007). The highest concentrations among the PAHs were recorded for BBF with 434 ng g^{-1} dw, followed by BEP, I123P and BGHIP (up to 334, 307, and 304 ng g^{-1} dw, respectively). PAH levels in our study were comparable to findings from Biselli et al. (2005) and Boitsov et al. (2013) who conducted studies in the same area.

The maximum for ΣPAH[2] concentrations in sediment was found at a depth of -28 cm with 1790 ng g^{-1} dw (see Figure 3.5), which is approx. analogous to the year 1964. This corresponds well with findings from a study by Arp et al. (2011), showing maximum ΣPAH levels around the end of the 1950s in a dated sediment core from the Oslo harbor. In another study, Rose and Rippey (2002) found the highest levels of the 16 EPA PAHs for the time period of 1905 - 1935 in a remote northwestern Scottish study area. In contrast, Duan et al. (2018) found the highest levels of sixteen EPA priority PAHs in layers of sediment cores equivalent to a period between 1975 and 1980, sampled at Oujiang River estuary, Yangtze River estuary and at the west coast of the Yellow Sea, possibly indicating the later start of industrialization in this region. However, it can be expected that PAH levels will differ by geographic location based on differences in local PAH entry, which has been considered the most important route of entry (Kukučka et al., 2010).

Since the results of radiometric dating with ^{210}Pb revealed a time frame of approx. 100 years for the analyzed sediment cores, no statement about the pre-industrial status of PAH sediment concentrations can be made with our data. However, most PAHs reach lower or equal concentrations in the upper compared to the lowest analyzed sediment layers. For example, higher aromatic PAHs (DBAHA, I123P, BGHIP) concentrations were significantly lower in the upper five than in the lowest five analyzed sediment layers. Whereas Boitsov et al. (2013), who sampled the area in 1992 - 1995, could not

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[2] CEMP PAHs: anthracene, benz[a]anthracene, benzo[g,h,i]perylene, benzo [a]pyrene, chrysene, fluoranthene, indeno[1,2,3-*c,d*]pyrene, pyrene, phenan- threne, naphthalene, dibenzothiophene.

detect a decreasing trend for PAHs in most analyzed sediment cores, our study results show a clear decreasing trend for PAHs towards younger sedimented material, which indicates lower recent PAH emissions from anthropogenic sources.

Calculated diagnostic ratios between pyrogenic and petrogenic PAHs for source identification (Bigus et al., 2014; Kanwischer et al., 2020; Neff et al., 2005; Pérez-Fernández et al., 2016; Wang et al., 2020) were all stable throughout the sediment core and revealed that PAH most likely originate from sources of mixed pyrogenic origin such as coal, biomass and petroleum combustion. In contrast, concentrations of most methylated PAHs, which originate mainly from petrogenic sources, increase towards the top layers of the sediment core. This increase of methylated PAHs could be attributed to an increased ship traffic in the North Sea (Clean North Sea Shipping, 2014) as well as oil pollution from oil field activities in the North Sea (Christiansen et al., 2009). Here we hypothesis, that our data suggests that the diagnostic ratios of PAHs to each other are not as meaningful for petroleum sources as the ratio of methyl- to non-methyl PAHs. This underlines the importance of determining methyl-PAHs in sediments, showing that they should have greater significance within monitoring programs.

PCBs

PCBs are a group of contaminants formed by 209 congeners, which were widely used industrially mainly due to their good dielectric properties and very low flammability (ELSA, 2016; Gałuszka et al., 2020). PCBs are ubiquitously distributed in the environment, persistent, bioaccumulative, and toxic (PBT substances) and their input pathways are considered to be mainly point sources (effluents, leakage), combustion and atmospheric deposition (Christiansen et al., 2009; OSPAR, 2010; Wolska and Rogowska, 2012). Therefore, PCBs have been restricted and banned by several countries starting in the 1970s and 1980s (see Table 3.1) and were internationally banned by the Stockholm Convention in 2004.

Seven indicator PCB congeners were quantified in the sediment core (28/31, 52, 101, 118, 138, 153, 180). All measured concentrations for PCBs were below their EAC value (see 3.3.3 PAHs). At the bottom of the core, concentrations were even below BC values (if not below the LOD). However, in contrast to PAHs, in younger sediment material PCBs are not reaching concentration levels lower or as low as concentrations detected in layers below -40 cm. Instead, they are still approx. six times higher at the upper five analyzed sediment layers indicating the very long phase out time still needed for PCBs compared to the time of their wide range application (approx. 40 years). When assuming a further constant linear decrease of ΣPCB_7 deposition, BC values (0.05 ng g^{-1} 2.5 % TOC) would be reached in approx. the 2040s. This matches predictions by Breivik et al. (2007) for ΣPCB_{22} phase out from primary emissions probably being reached around 2050. However, secondary emissions of PCBs must be taken into account, which are likely to play a role until at least 2100 (Breivik et al., 2007).

All measured PCBs congeners show a very similar trend: At the bottom of the core, very low levels below or just above the LOD were detected. From -35 cm (approx. 1942) onwards, concentrations are rapidly increasing to a maximum at -23 to -21 cm (approx. 1978 – 1983). Beyond this point, PCB concentrations are constantly decreasing to the top of the sediment core (see Figure 3.5). The highest concentrations were recorded for CB138 with up to 1.03 ng g^{-1} dw and maximum concentrations for ΣPCB_7 reached up to 3.56 ng g^{-1} dw. With an average of 30 %, PCB138 is the major contributor to ΣPCB_7 concentrations in all analyzed sediment layers. These results are in very good agreement with other studies conducted in the area (Blanz et al., 1999; Christiansen et al., 2009; Ricking et al., 2005; Theobald et al., 2012). The percentages shares of congener profiles were relatively stable throughout the sediment core, showing highest shares for hexa-PCBs, which has also been shown by Christiansen et al. (2009); ELSA (2016) and Ricking et al. (2005). Possible reasons for this are the greater affinity of higher chlorinated PCBs to absorb to particles/organic matter as well as their lower mobility. Taking the results of the sediment dating into account, the observed concentration increase at -35 cm (approx. 1942) matches with the start of PCBs' widespread application starting in the 1940s and 1950s (Gałuszka et al., 2020). The observed constant decrease in PCB concentrations from -21 cm (approx. 1983) upwards matches the growing concerns about PCBs arising at this time and the subsequent restrictions and bans thereafter introduced successively throughout Europe (see Table 3.1) (Koppe and Keys, 2000). Hence, the decrease of PCB concentrations in the analyzed sediment layers is reasonable and illustrates the impact of these restrictions. Furthermore, the observed ΣPCB_7 concentrations are in good agreement with Rose and Rippey (2002), who found highest ΣPCB_7 concentrations in a sediment core layer covering a period between 1965 and 1979. Furthermore, the results show PCB pollution trends that were summarized before by e.g. Bigus et al. (2014) (and references therein). Due to the comparably consistent temporal trends for PCBs which are demonstrated globally uniformly, Dong et al. (2020) and Gałuszka et al. (2020) suggest PCBs as chemical markers for the Anthropocene.

OCPs

OCPs are a group of chemicals comprised mainly of pesticides that have been applied in agriculture and households for several decades until restrictions and bans and the Stockholm Convention banned these compounds internationally (see Table 3.1). Amongst others, these implemented bans and restriction could be attributed to the raising concerns for these contaminants, for example by the publication of Silent Spring (Carson, 1962), as a result of their ubiquitous detection in various environmental compartments as well as their toxicity and persistence. Here, we analyzed HCB, HCHs, DDT, DDX, and DIELD as representative of this contaminant group.

All analyzed OCPs showed comparable concentration trends within the sediment core (see Figure 3.5). However, γ-HCH and DIELD were found above LOD only in a few layers, rendering their interpretation unreliable. The maximum of ΣOCP concentrations in the sediment core were detected at a sediment depths of -28 cm (approx. 1964, Figure 3.5). Concentrations for *p,p'*-DDT and its metabolites *p,p'*-DDD and *p,p'*-DDE rapidly decreased after peaking at -28 cm (approx. 1964) with 0.51, 1.06 and 0.65 ng g^{-1} dw, respectively, reflecting the bans and restrictions for DDT beginning in Europe in the 1970s (see Table 3.1). Combi et al. (2019) and Theobald et al. (2012) could also demonstrate a peak of DDX concentrations followed by a steep decline of concentrations in the same time period in Amazonas and Skagerrak region, respectively. The measured concentrations for α- and β–HCH peaked at -28 cm (approx. 1964) as well but do not decrease until cm -21 cm (approx. 1983, SI 1.4 Figure 2c, Appendix B). However, the constant decline of concentrations towards the upper sediment layers is an indication that restrictions and bans effectively resulted in declining OCP use in the area (see Table 3.1). In general, our results for OCPs correspond well with findings summarized by Bigus et al. (2014) and references therein, who also demonstrated that OCP concentrations in sediment cores increased in correlation with their application and production.

PBDEs

PBDEs are a group of brominated contaminants formed by 209 congeners which are most commonly used as flame retardants in consumer products such as furniture, and have been in global use since the 1980s (Korosi et al., 2015). They are grouped by their commercial mixtures decabromodiphenyl ether (deca-BDE, not analyzed here), octabromodiphenyl ether (octa-BDE) and pentabromodiphenyl ether (penta-BDE) (Korosi et al., 2015). Similar to most HOCs analyzed here, PBDEs are lipophilic and thus preferably bind to particles when present in the marine environment, resulting in their preferential accumulation in sediments (Wenning and Martello, 2014). PBDEs are mainly transported via atmospheric deposition and via currents suspended to particles into the marine environment (Wenning and Martello, 2014; Zegers et al., 2003).

Here, we analyzed seven PBDE congeners (28, 47, 66, 99, 100, 153, 154). In 2020, OSPAR published BAC values of 0.05 ng g^{-1} 2.5 % TOC for the assessment of PBDEs in sediments (OSPAR, 2020). Measured concentrations for BDE47 and 99 are exceeding this BAC value from -23 and -21 cm upwards, respectively. The measured PBDE concentrations in sediment layers were detected in the range of 0.0035 – 0.228 ng g^{-1} dw. Most detections above LOD and highest concentrations were determined for BDE47, which was detected above LOD in every sediment layer except for the lowest (-46 to -49 cm). Second highest concentrations were recorded for BDE99 with up to 0.156 ng g^{-1} dw. This corresponds well with penta-BDE being the dominant congeners found (Wenning and Martello, 2014; Zegers et al., 2003). Compared to other studies investigating PBDE in sediment cores conducted in Lake Than and Western Scheldt river, the concentrations detected in our study were very low (Bogdal et al., 2008; Covaci et al., 2005). However, concentrations are expected to be much lower in marine regions and lower concentrations have been also reported by Nylund et al. (1992) and Zegers et al. (2003).

The analyzed PBDEs all showed comparable concentration profiles. From the bottom of the core to approx. -25 cm (approx. 1973), PBDE concentrations were predominantly below the LOD. From -23 cm (approx. 1978) onwards, ΣPBDE concentrations rapidly increased to a maximum of 0.526 ng g^{-1} dw at -17 cm (approx. 1992). After -13 cm (approx. 2000), ΣPBDE levels constantly decreased (Figure 3.5). Taking this observed concentration decrease into account and assuming a further constant linear decrease of PBDE depositions, BAC values for BDE47 and 99 would approx. be reached in the 2020s.

Our results are in very good agreement with consumption and emission data of penta-BDE in Europe, peaking in the 1990s (Prevedouros et al., 2004), as well as with introduced restrictions and bans for penta- and octa-BDE in the early 2000s (see Table 3.1). The course of the PBDEs profiles (see Figure 3.5) are also in good agreement with data presented by Nylund et al. (1992) and Zegers et al. (2003). However, in these two studies a substantial decrease of PBDE concentrations has not yet been documented.

PFASs in sediment

PFASs are a group of compounds that have been used globally for industrial and commercial applications since the 1950s, in particular for surfactant and polymer applications (Joerss et al., 2019; Wenning and Martello, 2014). Especially "long chain" PFASs (e.g. PFOA, PFOS, PFHxS) raised concerns due to their BPT properties, which led to several restrictions and bans in the recent past (see Table 3.1) as well as voluntary phase-outs by industry, for example in 2000 by 3M (Joerss et al., 2019; Wenning and Martello, 2014). Ahrens et al. (2010) and Joerss et al. (2019) identified riverine input and input from local sources as the main pathways for PFASs into the North Sea.

Altogether, we analyzed 21 PFASs in 25 sediment layers of the sediment core. The analyzed PFASs can be sorted into three different groups. 1. PFAS compounds detected only below LOD (PFBS, PFBA, PFHpS, 4:2 FTS, 6:2 FTS, 8:2 FTS, HFPO-DA, PFPeS and PFTeDA), 2. PFAS compounds with sporadic detection above the LOD (PFHxS, PFHpA, PFDS, PFDoA, and PFTrDa), and 3. PFAS compounds with more than ten positive detections above the LOD (PFOS, PFOA, PFNoA, PFDA and PFUdA) as well as PFPeA, which was reliably detected above the LOD in the five upper most sediment layers. The predominant detection of long-chain PFASs (C_8 – C_{14}) in sediment is excepted since they are associated with the particulate phase (and correlate with TOC) due their physicochemical properties (Ahrens et al., 2009; Joerss et al., 2019).

The highest detected concentrations were recorded for PFOS and ranged from 0.0084 to 0.254 ng g^{-1} dw. The concentration profile for ΣPFAS (group 3 mentioned above) shows a pronounced maximum at -4 cm (approx. 2014) and decreasing concentrations thereafter (see Figure 3.5). The observed concentration decrease suggests the legislative measures taken for PFOS and other PFASs beginning at late 2000s were successful in reducing PFAS entry into the marine environment (see Table 3.1). The concentrations measured and the spectrum of PFASs detected above the LOD match with other studies conducted in the area (Joerss et al., 2019; Theobald et al., 2012). However, Ahrens et al. (2009); Codling et al. (2018); MacInnis et al. (2019) and Theobald et al. (2012), could not detect a decreasing trend of PFAS concentrations within sediment cores. Nevertheless, it is likely that our data shows the beginning of decreasing input of the investigated PFASs into the North Sea as the sediment core was cut into slices of only 1 cm allowing a high-resolution of recently deposited sediment material. Even though a decreasing trend for ΣPFAS can be seen here, attention should be drawn to the emerging PFASs (such as HFPO-DA, PFPiAs[3]) and the vast number of other PFASs that have not been analyzed in our study and are not subject to environmental legislation yet.

3.3.4 HOCs in porewater

In addition to the measurements of HOCs in bulk sediment, PAHs and PCBs were also determined in the sediment cores porewater (C_{free}) using a passive sampling approach (see 3.2.3 and SI 1.5, Appendix B). Freely dissolved PAH and PCB concentrations were determined in every second sediment layer, resulting in 21 measurements per core (core depth = 41 cm). Measured PDMS concentrations were converted into freely dissolved porewater concentrations (C_{free}) using Eq. 3.4

$$C_{free} = \frac{C_{PDMS}}{K_{PDMS-water}} \tag{3.4}$$

Detected C_{free} concentrations ranged between 735 and 8340 pg L^{-1} for ΣPAHs[4] and 6.49 and 18.7 pg L^{-1} for ΣPCBs. The highest concentrations for the considered single PAH

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[3] perfluoroalkyl phosphinic acids.

[4] For ΣPAH benz[a]anthracene, benzo[a]pyrene, benzo[g,h,i]perylene, benzo [k]fluoranthene, chrysene dibenz[a,h]anthracene, fluoranthene, indeno[1,2,3-c,d]pyrene, and pyrene were considered.

and PCB compounds were determined for FLU (-23 cm, 7450 pg L^{-1}) and PCB28/31 (-1 cm, 7.08 pg L^{-1}), respectively.

HOC contents in porewater were compared with the contents measured in bulk sediment (see Figure 3.5), and the trends in ΣPAH and ΣPCB concentrations obtained were generally consistent with the two different methods, confirming the reliability of the achieved data. Additionally, with porewater analysis information about the bioavailable fraction and therefore toxicity to organisms is gathered. A good agreement between porewater and bulk sediment concentrations in sediment cores for PAHs and PCBs was also determined by Arp et al. (2011) and for other HOCs by Lin et al. (2017). For ΣPAH, the small difference in content around -30 cm (local minimum in porewater data; Figure 3.5) can be explained by the grouping of all data. One hypothesis for the differences might also be a different soot content within the sediment layers leading to different sorption of PAHs to the sediment and therefore to different bioavailabilities and hence different concentration trends between porewater and bulk sediment (Lang et al., 2015).

When comparing single compound profiles for PAHs, concentration trends matched especially well between bulk sediment and porewater for PAHs with low volatility, specifically for higher aromatic PAHs (e.g. BAP, BKFBJF, CHRTRI, DBAHA, BGHIP, BAA and I123P). Indeed, more volatile PAHs do not follow the same trends as closely: compared to higher aromatic PAHs, concentrations are fluctuating. This can potentially be explained by the used experimental technique: some of the more volatile HOCs are likely to be lost to evaporation during the thermal desorption process during the porewater measurements, especially when using thin PDMS fibers.

The collected PCB concentration profiles for C_{free} and bulk sediment were similarly comparable for both ΣPCB concentrations and the 7 single PCB depth profiles (PCB28/31, 52, 101, 118, 138, 153, 180; Figure 3.5; SI 1.6 Figure 4, Appendix B). ΣPCBs show highest concentrations at -23 cm for both measurement methods, which approx. marks the year 1978 (see 3.3.3 PCBs). The slightly higher variability of ΣPCBs in the porewater results largely from individual data points in PCB28/31 and PCB52, therefore at -1 cm and -39 cm outliers were excluded for calculation of ΣPCB. One explanation for the better agreement of porewater and bulk sediment concentration trends for PCBs could be that they, other than PAHs, are less prone to soot adsorption, and therefore PCBs' bioavailability is less dependent on the composition of the sediment matrix.

In any case, the measurement of C_{free} offers a conclusive and informative data set, which results in a comparable contamination pattern to that of measurements in bulk sediment. Porewater concentrations complement traditional bulk sediment analysis by revealing knowledge about bioavailable concentrations. Therefore, the significance of porewater concentrations to monitoring programs is shown here.

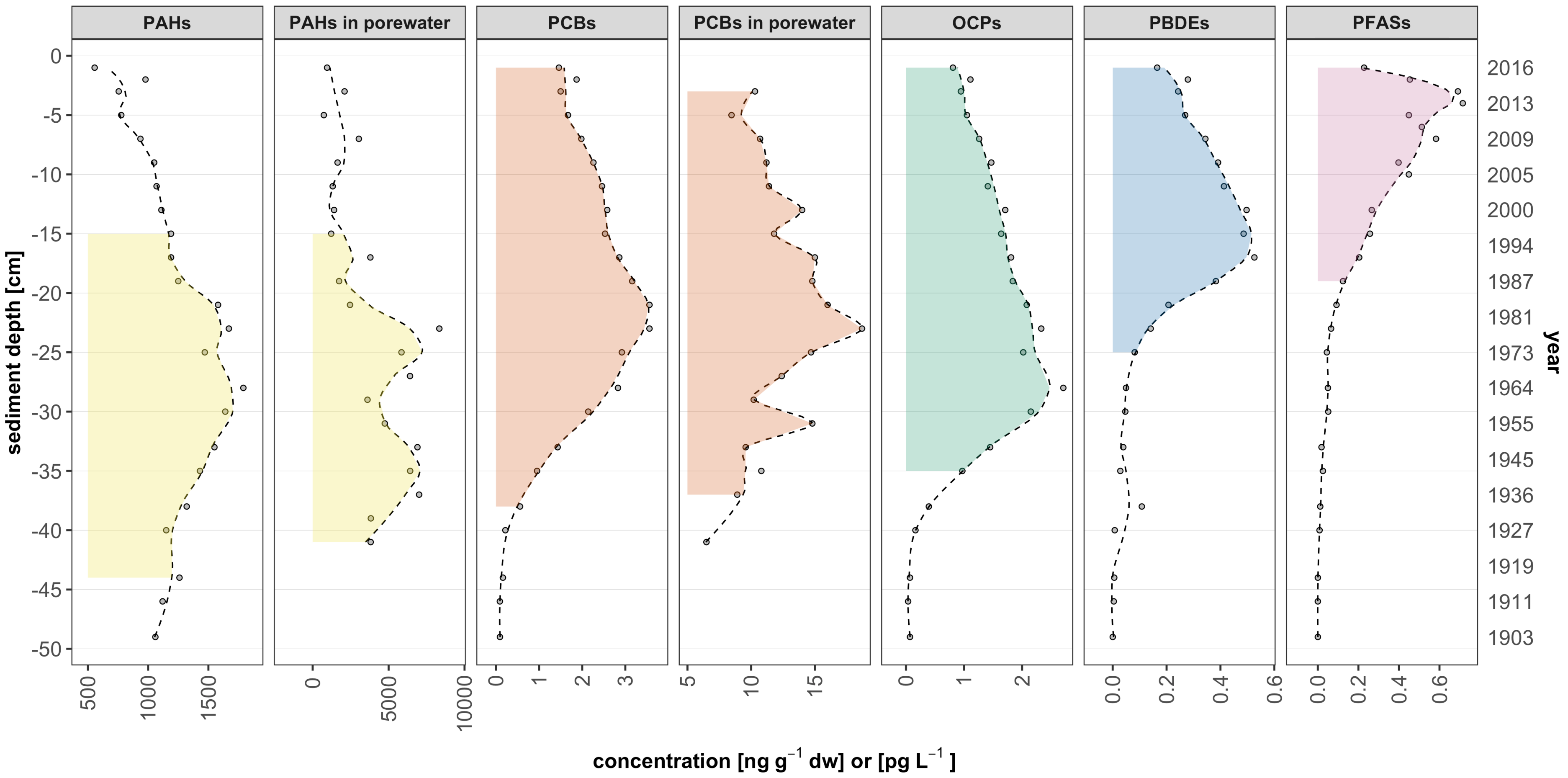

Figure 3.5: *Profiles in bulk sediment and porewater for ΣPAHs, ΣPCBs, ΣOCPs, ΣPBDEs and ΣPFASs. Colored areas highlight the discussed concentration peaks. Porewater ΣPCB concentrations at -1 and -39 cm were excluded due to outlier values*

3.3.5 Joint discussion

This study is another example how to use the technique of sediment core sampling to determine emission trends and analyze the most recent concentration trends. In order to have enough sample material for the multitude of analyses conducted (radiometric dating, porewater, elemental and isotopic as well as HOC and PFAS) sediment cores were analyzed from the set of cores taken with the MUC. Despite this drawback, results were in very good agreement between the different analyzed sediment cores. Especially, the agreement between porewater and bulk sediment analyses of PAHs and PCBs shows that results are reliable and comparable between neighboring cores taken with the MUC.

In addition, valuable data was collected for future complementary assessment purposes in the OSPAR region by documenting the current status quo. For example, according to OSPARs' latest Intermediate Assessment Report 2017, the temporal trends for PBDEs have not been assessed comprehensively in the OSPAR region (OSPAR, 2017). Thus, the presented data can be useful for future assessments. As outlined before, this is of importance since a lack of data is often hampering effective implementation of restrictions and legislations. Since a direct response of contaminant concentrations to bans and restrictions is evident in our data, the importance of environmental legislation becomes even more apparent. However, the comparatively languid legal process is not appropriate answering the fast-moving industrial processes constantly introducing new chemicals of emerging and future concern. Taking the European Water Framework Directive (WFD) as an example, it took about 30 years from the first regulations for POPs (see Table 3.1) to legally binding environmental quality status (EQS) values in 2008 (EU 2008/105/EC, 2008). However, these EQS values are often still missing for marine regions and most chemicals! Furthermore, potential inputs of new chemicals through industry and human consumption into the marine environment will further enhance the chemical pollution of the North Sea and other marine regions showing the importance of the data presented here. This is also pointing out the need for expanded legislation and a comprehensive database based on such monitoring approaches.

It is to be expected, that with the coming decades, climate change and remobilization of legacy contaminants, for example by sediment dumping, will contribute to the permanent chemical background observed in environmental media. As shown here, pollutants that have long been phased out can still be detected at significant levels and thus are relevant for pollution fingerprinting. Lower molecular HOCs can to some extend be subject to degradation, however their persistence and emissions from new secondary (point) sources will further contribute to emissions. For PCBs unintentional productions have been recognized and also PCBs already bound in permafrost soils might leak to the atmosphere again (Cabrerizo et al., 2013; Cui et al., 2013; Ren et al., 2019; Zhao et al., 2020). For PBDEs, improper disposal at the end of product life, such as incineration, may represent a possible second emission source (Xie et al., 2011). Recent studies have also identified melting arctic ice and glaciers as a likely relevant point source of PFAS contamination (Chen et al., 2019; Joerss et al., 2020; Pućko et al., 2015). Inputs of trace metals and metals into the environment by extensive mining for industrial purposes or improper waste disposal will be a point-of-no-return as they are not subject to decay. As shown for our sample site we could demonstrate a fingerprint of waste disposal through increased As and Ti concentrations, caused by corroding ammunition and diluted acid dumping.

3.4 Conclusion

In this paper we presented a comprehensive overview of the North Seas pollution fingerprint characterizing the Anthropocene by the analysis of a set of sediment cores taken in the Skagerrak, one of the North Seas' main sedimentation area. Detailed concentration profiles of 90 contaminants (8 elements and 82 organic compounds) as well as stable Pb isotope ratios were presented covering a time frame of approximately 100 years. The results show that for all analyzed organic contaminant groups as well as for elements Pb and Ti, concentrations are decreasing towards younger deposited materials indicating fewer anthropogenic pollution of investigated substances in recent years. Thereby, for PCBs, OCPs, PFASs, Pb and Ti, concentration maximums could be linked to the time of political measure implementation. The findings for Pb concentrations were supported and refined by Pb isotope ratios. This underlines the importance, effectiveness and justification of legislative measures and their positive impact towards reaching GES. However, our results show that even when regulatory measures are taken, long time periods are required for contaminants to return to natural background levels (OCPs, PCBs, PBDEs). Moreover, only a few years of the use of certain chemical compound use can lead to long-term deposition of such compounds in marine sediment, resulting in an only slow phase out of pollution impact in marine environments. This unbalanced ratio between application and deposition stresses the need for strongly enhanced and flexible governmental monitoring schemes, covering both known and emerging, and ideally also novel contaminants. Such monitoring schemes need to be adaptive to a changing landscape of pollutants, must be able to collect relevant data in relatively short times frames, and the collected data should be used for setting sediment quality guidelines in appropriate time frames. In addition, more than the determination of concentrations and individual substance classes alone to adequately assess risks. As shown here, the presence of a comprehensive mixture of substances, consisting of both old and new substances, which interact with each other and can increase toxicity to organisms and has to be addressed via monitoring. Ideally, concepts such as green chemistry and benign-by-design are adapted by the chemical and other relevant industries, that avoid the generation and use of hazardous chemical compounds altogether, while also ensuring their rapid degradation once present in the environment. In such a scenario, the need for extensive and rapid environmental monitoring is less important in the short term, yet remains important for understanding legacy pollution.

Chapter 4

Cumulative Part III

Using the HPTLC-bioluminescence bacteria assay for the determination of acute toxicities in marine sediments and its eligibility as a monitoring assessment tool

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Highlights:

- First study with the HPTLC-bioluminescence bacteria assay for marine sediments.
- HPTLC development was optimized for separating hydrophobic organic contaminants.
- An evaluation script for bioluminescence images programmed with R is presented.
- Correlation of $R^2 = 0.91$ between inhibition and PAH concentrations was found.

Abstract:

For an integrated ecological risk assessment of marine sediment contamination, the determination of target-compound concentrations by e.g. mass spectrometric methods is not sufficient to explain sediment toxicity. Due to the presence of a multitude of environmental contaminants in this complex matrix causing a mixed toxicity, the identification and assessment of main toxicants is a challenge. One approach in identifying main toxicants is the application of effect-directed analysis (EDA). In this study, an EDA approach was developed using high performance thin layer chromatography (HPTLC) coupled to bioluminescence bacteria detection with *Aliivibrio fischeri* for the determination of marine sediments acute toxicity. In a first attempt, the HPTLC separation was optimized with a fast, two-step gradient to separate main hydrophobic organic contaminant (HOC) classes found in marine sediments. An easy-to-use evaluation script for the resulting bioluminescence inhibition images was programed using R. The developed method was applied to sediment extracts of two different sample sets: (i) Fourteen marine sediment samples from the German Bight representing a wide range of contaminant loads and sediment properties and (ii) sediment samples from a core representing temporal trends of contamination. Results from the HPTLC-bioluminescence bacteria assay were compared to HOC concentrations determined by GC-MS/MS. A correlation of the determined inhibition Γ-values for the PAH inhibition zone to PAH concentrations showed a very good agreement ($R^2 = 0.91$). The results of this study were used to evaluate the suitability of the EDA approach to be used as an assessment tool for marine sediments.

4.1 Introduction

Due to their countless ecosystem functions, marine sediments play an essential role for marine habitats (Snelgrove, 1997). However, they are also threatened by various man-made pressures such as bottom-trawling fishery, excavation measures, offshore wind energy and oil production or by contaminants entering the marine environment through rivers, atmosphere or points source releases. Marine sediments serve as a sink for a multitude of contaminants and in turn, they could also become a source of pollution due to a cleaner water column (Burgess et al., 2013), sediment transport processes (Hollert et al., 2000) or bioturbation (Granberg et al., 2008; Josefsson et al., 2010). Therefore, the control of contaminants in marine sediments has been implemented into several marine conventions (e.g. OSPAR, HELCOM) and governmental directives such as the European Marine Strategy Framework Directive (MSFD). For this purpose, member states are running monitoring programs to assess and evaluate the contamination status of marine sediments by chemical analysis. However, the determination of target contaminant concentrations alone by mass spectrometric methods is often not sufficient for a full risk assessment due the large number of contaminants present in the environment (Simon et al., 2015) and the lack and uncertainty of threshold values existing for many contaminants in sediments (BLANO, 2018a, 2018b; HELCOM, 2018; OSPAR, 2017).

Hence, additional tools for sediment risk assessment such as toxicity tests and toxicity profiling using a battery of endpoints are needed for an integrated evaluation (Hamers et al., 2013, 2010; Houtman et al., 2004; Jahnke et al., 2018; Vethaak et al., 2017). Next to the problems of in vivo bioassays which are often costly, time-intensive and require large sample volumes (Hong et al., 2016; Parvez et al., 2006), with high-throughput in vitro bioassays the observed effects cannot be fully explained by the accompanied chemical target analysis (Hong et al., 2016; Vethaak et al., 2017). Often this is a result of the complex mixture of contaminants present in sediments which could result in combined effects (Altenburger et al., 2015). For this reason, effect-directed analysis (EDA), where complexity is reduced by sample fractionation in combination with toxicity testing, is a promising tool to support monitoring and identify key contaminants majorly driving toxicity (Altenburger et al., 2019; Brack, 2003; Hong et al., 2016; Li et al., 2018).

One example of EDA is the application of high-performance thin layer chromatography (HPTLC) in combination with bioluminescence detection using *Aliivibrio fischeri* bacteria (Beijerinck, 1889). Derived from the standardized cuvette test (DIN EN ISO 11348-2, 2009), this approach utilizes the effect that *A. fischeris* bioluminescence is directly linked to the bacterium's metabolism. This means that metabolic disorders, caused for example by contaminants, can be detected by changes in the intensity of the bioluminescence (Weiss et al., 2017). The HPTLC-bioluminescence bacteria assay has been successfully applied to estimate the acute toxicity of contaminant mixtures in different environmental matrices such as surface water (Schulz et al., 2008) and wastewater (Reemtsma et al., 1999) as well as for bioactive compounds in marine sponges (Klöppel et al., 2008). The bioluminescence inhibition on the HPTLC plate is imaged by a light sensitive CCD camera. Thus, for a successful application of the HPTLC-bioluminescence bacteria assay for toxicity testing it must be possible to quantitatively evaluate the resulting images. This has been implemented by Baumgartner and Schwack (2010); Schulz et al. (2008, 2017) and Weiss et al. (2017). However, the software used for evaluation was either not commercially available or included many steps and different software and was thus not eligible.

Using HPTLC for EDA has three major advantages. Since HPTLC is an open separation system, after development the solvent from sample extracts and mobile phases evaporate completely and the subsequently applied bioassay is not influenced (Weiss et al., 2017). Furthermore, it favors cost-effectiveness and high through-put since several samples can be applied and separated simultaneously on the HPTLC plate. The most important advantage is that HPTLC can be directly coupled to other toxicological endpoints since the solvent is evaporated from the HPTLC plate prior to their application (see Weins (2008) and Weiss et al. (2017) for details). Additionally, the subsequent application of the bioluminescence bioassay with *A. fischeri* has several advantages. The bacteria are very easy to cultivate with minimal costs for supply and cultivation and show a very fast reaction so that the result is available within a few minutes (Baumgartner, 2013; Parvez et al., 2006). Also, the energy production of *A. fischeri* can be influenced in many ways so that it reacts sensitively to a wide range of contaminants (Baumgartner, 2013; Schulz et al., 2008). Finally, lots of data and studies are available because the bacteria have been used for a long time in the standardized cuvette test (DIN EN ISO 11348-2 (2009), e.g. Microtox®).

Several studies have been published, where other EDA approaches (e.g. with HPLC) in combination with different toxicological endpoints have been applied for sediments (Biselli et al., 2005; Giltrap et al., 2009; Grote et al., 2005; Ho and Quinn, 1993; Li et al., 2019; Qi et al., 2017; Regueiro et al., 2013; Reilly et al., 1986). But to our knowledge, HPTLC-bioluminescence coupling has not been applied to sediments or marine sediments yet. Since sediment assessment gains importance within conventions and directives (OSPAR, HELCOM, MSFD), our goal was to test the applicability of this simple, easy to implement and cost-effective approach to hydrophobic organic contaminants (HOCs) in marine sediments.

The aim of this HPTLC method was (1) to develop a fast HPTLC development able to separate main HOC groups such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) found in marine sediments, (2) to implement a simple evaluation script for the semi-quantitative evaluation of bioluminescence images using only one and also free available software, (3) to apply the developed HPTLC method in combination with bioluminescence coupling using the bacterium *A. fischeri* to two sets of sediment extracts (spatial and temporal) previously analyzed for HOCs with

GC-MS/MS to link concentrations to inhibition zones of acute toxicity, and (4) to evaluate the HPTLC-bioluminescence bacteria assay as an eligible assessment tool for the evaluation of marine sediment quality.

4.2 Material and methods

4.2.1 Chemicals

Organic solvents used were *n*-hexane, dichloromethane, *iso*-octane, methanol, acetone and were all ultra resi-analyzed and purchased from J.T. Baker (Avantor, Deventer, Netherlands). $(NH_4)_2HPO_4$, K_2HPO_4 x $3H_2O$, Glycerol 85 %, $MgSO_4$ x $7H_2O$, NaH_2PO_4 x H_2O, copper powder, and toluene were purchased from Merck (Darmstadt, Germany) as well as the Milli-Q® System (Integral 5) for the 18.2 MΩ ultrapure water. Peptone from Casein (pancreatic digest) was obtained from AppliChem (Darmstadt, Germany). NaCl was purchased at TH. Geyer (Renningen, Germany). Yeast extract was obtained from Fluka, Sigma-Aldrich (Steinheim, Germany). The HPTLC glass plates silica gel 60 Å F254 with a size of 20 x 10 cm were obtained from Merck (Darmstadt, Germany). Freeze-dried *A. fischeri* cultures were purchased from Hach Lange (Düsseldorf, Germany). The diatometheous earth was purchased from Thermo Fisher Scientific (Schwerte, Germany). The silica gel was purchased from Macherey-Nagel (Düren, Germany). The suppliers and the composition of single compound standards and the PAH-, PCB- and organochlorine pesticide-mix (OCP) used for standard applications on HPTLC plates, internal standards used for chemical analysis as well as purities of the used chemicals are provided in the SI (SI 1.1, SI 1.2 and SI 1.3, Appendix C).

4.2.2 Sample material

In this study, fourteen sediment samples collected at the monitoring stations of the Federal Maritime and Hydrographic Agency in the German Bight were analyzed, representing muddy to sandy sediments of different contamination loads. Samples were taken with a box corer on research cruise AT248 (RV Atair) in 2017 (Figure 4.1, blue points). The first 2 cm of each box corer sample were filled into pre-rinsed sample containers and kept frozen at -18 °C until analysis. Additionally, we analyzed a sediment core that was taken on research cruise HE468 (RV Heincke) in 2016 in the German Bight at 54°3.2 N and 8°1.1 E with a multi corer (Figure 4.1, red point). The core was cut into 2 cm slices, filled into pre-rinsed sample containers, and the samples were stored at -18 °C until analysis.

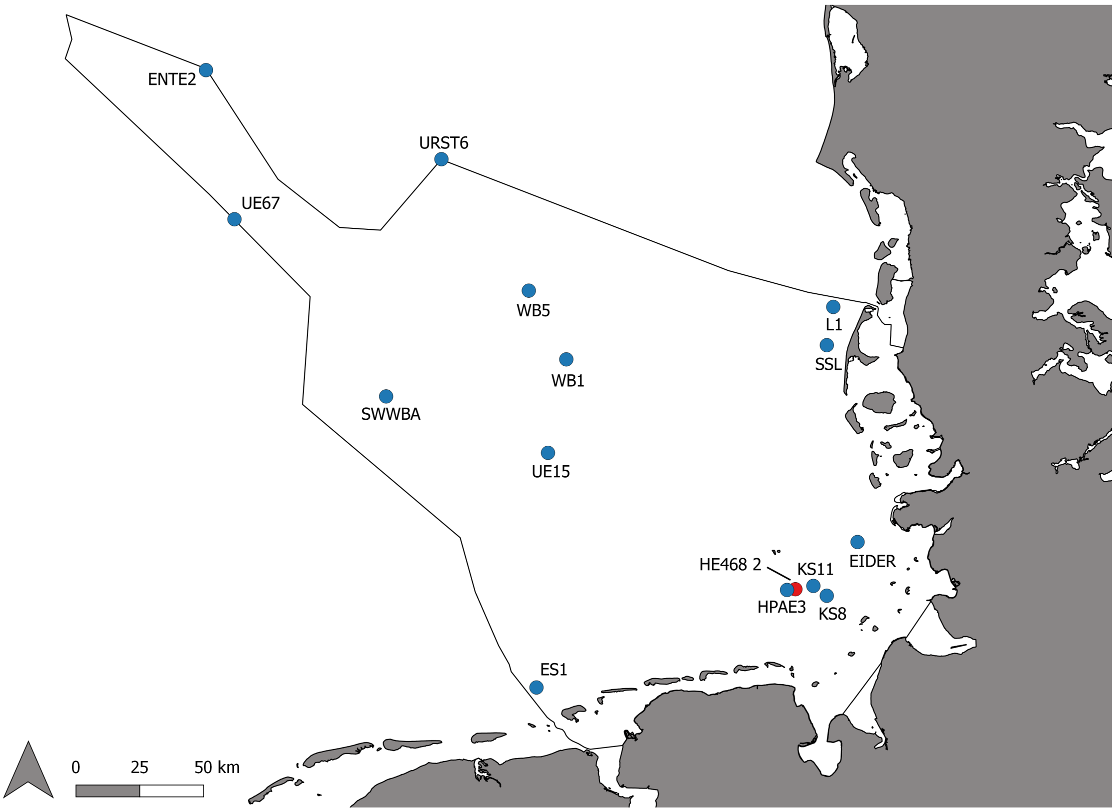

Figure 4.1: *Location of sampling stations from BSH monitoring cruise AT248 (blue) and the sediment core taken during research cruise HE468 (red). German Exclusive Economic Zone is marked with the black line*

4.2.3 Sample preparation

Before extraction, sediment samples were air dried for 72 h under a clean bench (LaminAir, Allerød, Demark now LaboGene, Allerød, Denmark) and homogenized with a ball mill (Retsch, Haan, Germany). The fourteen sediment samples from the German Bight were extracted using the procedure described by Niehus et al. (2019). The extraction procedure of samples from the sediment core is briefly summarized: 10 g of sediment was mixed with diatometheous earth (Thermo Fisher Scientific), spiked with internal standard solution and extracted with an Accelerated Solvent Extraction System (ASE 350, 2 cycles at 100 °C with 60 % purge volume and a static time of 10 min, Thermo Fisher Scientific) using acetone:*n*-hexane (1:1, v/v). Sulfur was removed from extracts by adding activated copper powder into the extraction cell. Extracts were volume reduced by parallel evaporation (Büchi, Flawil, Switzerland) and cleaned up over 0.5 g of silica gel (pore diameter 55 - 70 Å, particle size 20 - 50 μm, Macherey und Nagel). Silica columns were pre-cleaned with dichloromethane followed by *n*-hexane. Elution was performed using 8 mL of *n*-hexane:dichloromethane (7:3, v/v). Sample extracts were volume reduced under nitrogen and further cleaned using gel permeation chromatography on a phenogel 50 Å guard column and a phenogel 50 Å column (both Phenomenex, Torrance, USA) with dichloromethane as mobile phase and a flow rate of 1 mL min^{-1}. The collected fraction (8:30 until 16:30 min) was evaporated under nitrogen to 200 mL and solvent exchanged to *iso*-octane before GC-MS/MS analysis.

4.2.4 High-performance thin-layer chromatography

Extracted sediment samples, standard solutions and procedural blanks were analyzed by high-performance thin-layer chromatography (HPTLC). The chromatographic analyses were performed on 20 x 10 cm silica gel 60 F254 plates (Merck, Darmstadt, Germany) preconditioned once with *n*-hexane followed by methanol and dried for 20 min at 150 °C, respectively. The samples were applied by a HPTLC autosampler (ATS 4; CAMAG, Muttenz, Switzerland) and separated with an automated multiple development chamber (AMD 2; CAMAG). According to an official method for the determination of MOSH and MOAH by SPE of the Federal Institute for Risk Assessment (BfR) the development was adapted with the following modifications: using *n*-hexane for the first step as a clean-up with a migration distance of 75 mm followed by a separation step with *n*-hexane/dichloromethane/toluene (70/25/5; v/v/v) migrating 60 mm (BfR, 2012). Afterwards photo documentations were carried out with the TLC Visualizer (CAMAG) at 245 nm, 366 nm and white light using the software winCats (Version 1.4.5.2027; CAMAG) for evaluation. Furthermore, the detection of the PAH-, PCB- and OCP-mixes and single standards was carried out with the TLC Scanner (CAMAG) using the wavelengths 190 - 310 nm.

4.2.5 Post-chromatographic analysis with *Aliivibrio fischeri*

The toxicological potential of the sediment samples was determined by the intrinsic fluorescence of *Aliivibrio fischeri* (Beijerinck, 1889). *A. fischeri* (Hach Lange, Düsseldorf, Germany) was cultivated in a growth medium prepared as described in DIN EN ISO 11348-2 (DIN EN ISO 11348-2, 2009). The HPTLC plates were immersed into the bacteria solution with an immersion speed of 4 for 1 s using Immersion Device III (CAMAG). Excess liquid was wiped off gently and the plate was photographed 15 times with a BioLuminizer® (CAMAG) using the software BioLuminizer® (Version 1.0.3.2310; CAMAG) with an exposure time of 55 s and a trigger time of 1.2 min. Evaluation was carried out after approx. 5 min of incubation using the 4th image of series (271s exposure and trigger intervals plus approx. 30 s for transfer of immersed plate to BioLuminizer®). Bacterial growth was verified and considered as sufficient when the gain factor from the used Bioluminizer®‘s CCD camera was below 10. The gain factor was taken from the BioLuminizer® software (automatically set by the software).

4.2.6 Calculations

The quantification of *A. fischeris*' bioluminescence inhibition using images from HPTLC-bioluminescence coupling was previously described by Baumgartner and Schwack (2010), Schulz et al. (2008, 2017), and Weiss et al. (2017) and was deviated from the cuvette test (DIN EN ISO 11348-2, 2009). The inhibition is quantified using the pixel values of the greyscale image of the sample band $\mathrm{I_{S,RF}}$ and compared to the averaged reference/background bands $\mathrm{I_{R,RF}}$ left and right of the sample band at each $\mathrm{R_F}$-value.

$$Inh_{RF} = \frac{I_{R,RF} - I_{S,RF}}{I_{R,RF}} \tag{4.1}$$

This results in an inhibition chromatogram of the sample band, which shows broadened peaks compared to UV chromatograms due to the non-linear dose-response relationship and the diffusion effect (Schulz et al., 2008, 2017). Therefore, a Γ-value is calculated at each $\mathrm{R_F}$-value with equation 4.2 resulting in a chromatogram with sharper peaks.

$$\Gamma_{RF} = \frac{Inh_{RF}}{1 - Inh_{RF}} \tag{4.2}$$

In this study, the semi-quantitative evaluation of the images was performed by a self-programmed R-script (R Studio 1.0.153 (RStudio Team, 2016), R 3.4.1 (R Core Team, 2017), and amongst others the packages imager (Barthelme, 2017) and magick (Ooms, 2018)). This R evaluation script is based on the work of Baumgartner and Schwack (2010), Schulz et al. (2008, 2017), and Weiss et al. (2017). With the evaluation script it is possible to obtain the height of the inhibition Γ-value at specific R_F values as well as peak areas in the inhibition Γ-value chromatogram. For this study the inhibition Γ-value height was used for evaluation. The full code of the R evaluation script is available in the SI (SI 2, Appendix C).

Furthermore, equilibrium partitioning sediment benchmarks toxic units (ΣESBTU) were calculated from 23 PAH concentrations (refer to SI 1.4 for details, Appendix C) with equation 4.3 (Burgess, 2009; U.S. EPA, 2003, 2012). The concentration of the PAH measured in sediment $\mathrm{C_{OC,PAHi}}$ in μg $\mathrm{g^{-1}}$ OC is divided by the concentration that represents one toxic unit $\mathrm{C_{OC,PAHi,FCVi}}$ in μg $\mathrm{g^{-1}}$ OC. To compensate for the 34 PAHs that are used to calculate the toxic units, the $\mathrm{\Sigma ESBTU_{FCV}}$ for the 23 PAH were multiplied times 4.14 (95 % confidence interval) as stated by U.S. EPA (2003).

$$\Sigma ESTBU_{FCU} = \sum_{i} \frac{C_{OC,PAH_i}}{C_{OC,PAH_i,FCU_i}} \tag{4.3}$$

4.2.7 Gaschromatographic analysis

All sediment samples in this study were analyzed as described in Niehus et al. (2019). Target analytes and their mass transitions as well as detection limits are provided in the SI (SI 1.4, Appendix C).

4.3 Results and discussion

4.3.1 Quality assurance, method performance and evaluation

The developed HPTLC 2-step development followed by the application of the bioluminescence bacteria assay as well as the used evaluation R script were characterized and tested for their performances. The first three bands applied on each HPTLC plate in this study represented a pure solvent and two different standards for quality assurance purposes. The application of solvent (*iso*-octane) served as blank control for the solvent used for the samples and to check any possible contamination of the used plates. The first standard applied was caffeine (4 mg on plate) which served as a positive control for bioluminescence. The second standard, a PAH-mix containing 16 EPA PAHs plus 1- and 2-methylnaphtaline (16 ng on plate per compound), was used for the monitoring of the HPTLC development and bioluminescence.

Within the band of the solvent blank we detected no significant inhibition Γ-value on all evaluated plates within this study. The average retention factor (R_F) for the PAH standard mix was 0.53 and had a relative standard deviation (RSD) of 4 % (n = 32). Therefore, the reproducibility of the TLC 2-step HPTLC development of the method was considered reliable. The RSD of the inhibition Γ-value for the PAH standard mix at R_F 0.53 was 21 % and 28 % for the applied caffeine standard (R_F 0.00).

The developed evaluation script for the bioluminescence images using R was also tested for its reproducibility. We evaluated two different plates with 13 bands 10 times each and calculated an overall RSD of 4 % for the height of the inhibition Γ-value for all evaluated inhibition zones. For a semi-quantitative evaluation, we are considering the reproducibility of the evaluation script as adequate. Also, the applicability of the developed evaluation script was good since the evaluation of a plate takes less than 15 min and results in exported files for further data processing. The correctness of the evaluation script was further checked with a constructed test picture using different backgrounds and inhibition zones with known pixel values. The average deviation of the evaluation with the script to manually calculated Γ-values was 0.02 % with a maximum of 0.55 %. The reason for the slight deviation is the applied smoothing function for the creation of a Γ-value chromatogram. In contrast to the evaluation method for

HPTLC- biolumnescence images published by Baumgartner and Schwack (2010), for the evaluation with the presented R script only one single software is needed. The R script is executable and requires no manual modifications, transfer and importing of files. Further advantages are the possibility of potential users to modify the script to their needs and the exported Γ-value chromatograms (xy-files) that can be further processed with commercially available chromatographic software. The freely accessible existence of a quantitative evaluation script as well as the possibility to adapt this script to other HPTLC bioassays resulting in images makes HPTLC bioassay coupling more attractive to a wider range of users.

The main objective of the developed HPTLC gradient method using the AMD (CAMAG), was to generate a fast method with a sufficient separation of the main hydrophobic contaminant groups found in marine sediments. In this study, we focused on PAHs, PCBs and OCPs, as known from other studies to be among the main contaminants of marine sediments in the North Sea (Brockmeyer and Theobald, 2016; Laane et al., 2013; OSPAR, 2010). As shown in Figure 4.2, PAHs are eluting between R_F 0.35 and 0.60. The exemplarily display of fluoranthenes' and indeno[1,2,3-*c,d*]pyrenes' UV chromatograms show that lower aromatic PAHs (4 rings) have higher R_F-values than higher aromatic PAHs (6 rings). The Γ-value chromatogram for the PAH-mix illustrates that the inhibition of the bioluminescence has its maximum at R_F 0.53, which suggest a higher toxicity to *A. fischeri* for lower aromatic PAHs. A higher toxicity of 4-ring PAHs compared to higher aromatic PAHs to *A. fischeri* was also reported by Loibner et al. (2004) and El-Alawi et al. (2004). The PCB-mix eluted approx. between R_F 0.63 and 0.77 (Figure 4.2). Whereas the Γ-value chromatogram for the PCB-mix results in a sharp inhibition zone at approx. R_F 0.68. The exemplarily display of single PCB congeners 118 and 153 shows the distribution of congeners within the PCB elution zone. These results demonstrate that the HPTLC development using only a two-stage development (4.2.4) is able to separate the inhibition zones caused by PAHs and PCBs well, showing inhibition maxima at R_F 0.53 and 0.73, respectively. OCPs do not show a distinct elution zone like PAHs and PCBs, but are distributed over the whole migration distance, with maxima between R_F 0.00 and 0.45 due to their diverse chemical properties. These analytes are only sporadically coeluting with PAHs and PCBs. With the application of single standards, we were able to further characterize the elution profile of the development method (Figure 4.2). The detection of OCPs with the photo documentation system was not possible with the two available wavelengths (254 and 366 nm).

Due to the limited number of contaminants tested and comparably low separation performance of HPTLC compared to HPLC, a co-elution with other compounds in environmental samples cannot be excluded.

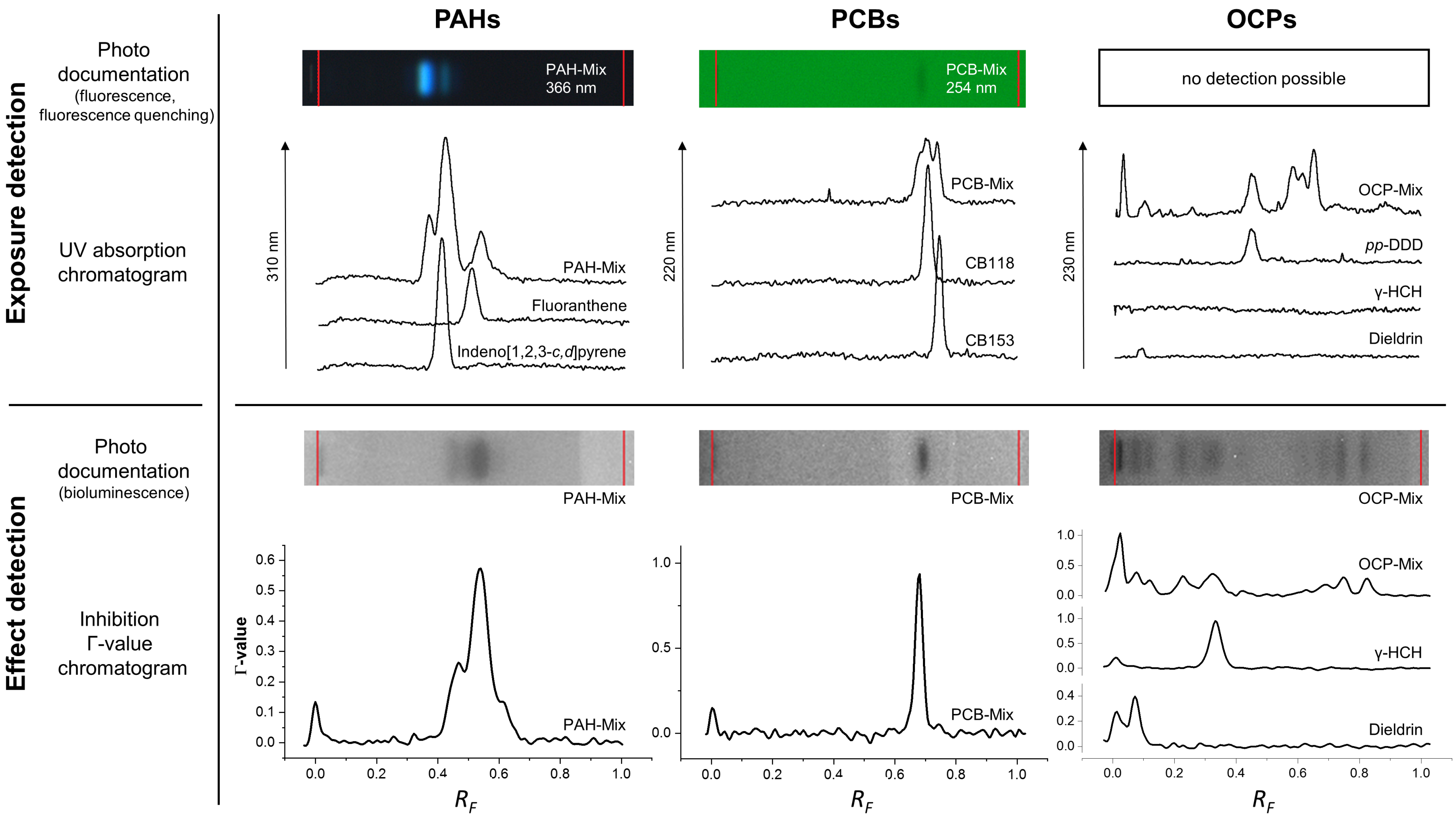

Figure 4.2: *Separation performance of the developed HPTLC gradient for three major compound classes of hydrophobic organic contaminants found in marine sediments: The first row shows pictures of bands on which standard mixtures were applied taken with the Visualizer (CAMAG), 366 nm fluorescence, 254 nm fluorescence quenching (F254 indicator). The second row shows the corresponding UV absorption chromatograms of the mix and additional single standards, the third row displays the band treated with Aliivibrio fischeri photographed with the BioLuminizer® (CAMAG), and the last row displays the inhibition Γ-value chromatograms generated with the developed R script for evaluation. The red lines in images of the developed area indicate $R_F = 0$ (left) and $R_F = 1$ (right). Polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs). Composition and concentrations of applied standards are available in the SI (SI 1.1, Appendix C)*

4.3.2 Spatial analysis of marine sediment samples

Fourteen sediment sample extracts from the German EEZ (Figure 4.1, blue points) previously analyzed for HOC concentrations with GC- MS/MS within the BSH monitoring program were tested for their acute toxicity using the HPTLC bioluminescence bacteria assay with *A. fischeri* (data available in MUDAB database - BfG, 2017). The samples covered a wide range of different sediment types with total organic carbon (TOC) concentrations ranging from 0.22 to 3.1 % and a share of the < 63 μm fraction ranging from 4.4 to 99.7 %. Accumulated HOC concentrations ranged from 0.90 to 790, 0.02 to 3.7, and 0.01 to 6.1 ng g^{-1} dw for 16-PAHs (acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[a]pyrene, benzo[k]fluorene, benzo[g,h,i]perylene, chrysene, triphylene, dibenzo[a,h]anthracene, fluorene, fluoranthene, indeno[1,2,3-*c,d*]perylene, naphthalene, phenanthrene, pyrene), eight PCBs (28, 31, 52, 101, 118, 138, 153, 180) and five detected OCPs (*pp*-DDT, -DDD, -DDE, hexachlorobenzene, and β-hexachlorohexane), respectively. Concentrations of PCBs and OCPs were in average a factor of approx. 500 and 1000 lower than the accumulated 16-PAHs concentrations and therefore probably too low to be detected via bioluminescence with this method. Additionally, Salizzato et al. (1998) stated that the sensitivity of *A. fischeri* to PCBs is lower than to PAHs. It can be assumed, that the detection limit of OCPs is also lower since they did not elute in a distinct zone like PAHs and PCBs. However, due to the separation performance of the studied method it can be expected that the inhibition of bioluminescence from higher concentrations of PCBs and most OCPs, e.g. from harbor sediments, would be detected reliably.

Since the sample extracts contained an internal standard mixture with several isotope-labeled components (see SI 1.2 for details, Appendix C), five procedural blanks (each applied in a three-fold determination) from the sample preparation process also containing internal standards were analyzed to quantify the inhibition caused by sample preparation process and the internal standards. The blank samples showed inhibition zones at R_F 0.01 and 0.53. The inhibition Γ-values were averaged for each of these two zones. Only inhibition Γ-values found in samples that were higher than the average blank inhibition at R_F 0.01 and 0.53 plus its standard deviation were considered for further data evaluation. As different sample amounts were used for extraction of each sample to compensate the differences in contaminant concentrations, the Γ-values for inhibition zones detected in the samples were normalized to the initial sample weight. Due to the non-linear dose-response relationship this approach is not ideal. However, low responses were excluded before due to blank corrections and for the remaining data this approach resulted in plausible results. Therefore, we assume the general statement of our results is not affected by this adjustment.

The fourteen sediment sample extracts were analyzed in a three-fold determination. The samples showed several inhibition zones over the development distance of the HPTLC plate at R_F 0.01, 0.08, 0.31, 0.52, 0.61, 0.72, and 0.82 (Figure 4.3 A). The number of detections at the different inhibition zones varied from 1 at R_F 0.08 and 0.72 (both sample ES1) to 10 at R_F 0.53. The highest inhibition Γ-value was identified for R_F 0.01 with 3.03 ± 0.19 for the sample EIDER. The inhibition zone at R_F 0.01 shows that also substances which are not chromatographable with the developed method are still detected via the subsequent bioluminescence bacteria assay.

From the seven identified inhibition zones only the one at R_F 0.53 could be assigned to a specific HOC class. As known from standard applications (4.3.1), the inhibition zone at R_F 0.53 is associated with PAHs. Ten out of the 14 analyzed samples showed an inhibition for PAHs (Figure 4.3 B). The highest inhibition Γ-value at R_F 0.53 with 1.90 ± 0.15 was detected for the station SSL, where sand excavations took place which results in fine grained material accumulation and therefore higher TOC concentrations (Brockmeyer and Theobald, 2016). This higher TOC content causes station SSL to be a pollution hotspot of HOCs, which could be identified with the HPTLC-bioluminescence bacteria assay. For stations KS8 and KS11, were sewage sludge was dumped (Brockmeyer and Theobald, 2016), the second and third highest inhibition Γ-values at R_F 0.53 were found with 1.16 ± 0.08 and 1.13 ± 0.08, respectively. Stations that were within the average inhibition Γ-value of procedural blanks (ENTE, ES1, L1, UE67) at R_F 0.53 were all within the five lowest accumulated 16-PAH concentrations.

The identified sample weight normalized inhibition Γ-values for R_F 0.53 correlated well ($R^2 = 0.91$) with the accumulated 16-PAH concentrations determined with GC-MS/MS (Figure 4.3 C). This reinforces the previously described association of PAHs with the inhibition zone at R_F 0.53. Although, a co-elution of other substances present in the samples cannot be fully excluded. A correlation between PAH concentrations and the inhibition of bioluminescence for sediment samples was also found in other studies where the 30-s kinetic bioassays and Microtox® assay were used for sediment toxicity determination (Jarque et al., 2016; Tay et al., 1992). However, Vethaak et al. (2017) could not find any significant correlation between PAH concentrations in marine sediments and the in vitro response of *A. fischeri* using 96-well plates.

Just as the measured accumulated 16-PAH concentrations ($R^2 = 0.87$), also the determined inhibition Γ-values for R_F 0.53 correlated ($R^2 = 0.84$) to the TOC content of the sediment samples (Figure 4.4 A). A correlation of sediment toxicity data and organic carbon was also found by Jarque et al. (2016), who investigated spatial patterns in river sediment toxicity with the 30-s kinetic bioassays based on *A. fischeri*. For the other identified inhibition zones with 5 or more detections, no correlation to TOC could be determined, except for R_F 0.61 ($R^2 = 0.53$). This suggests that the inhibition zones at R_F 0.01 and 0.82 might not be caused by HOCs but rather matrix or other compounds present in the samples. The reason for this could be the sensitivity of *A. fischeri* to a broad substance spectrum (Baumgartner, 2013; Schulz et al., 2008). Due to the correlation to organic carbon, as a first approach for the determination of assessment

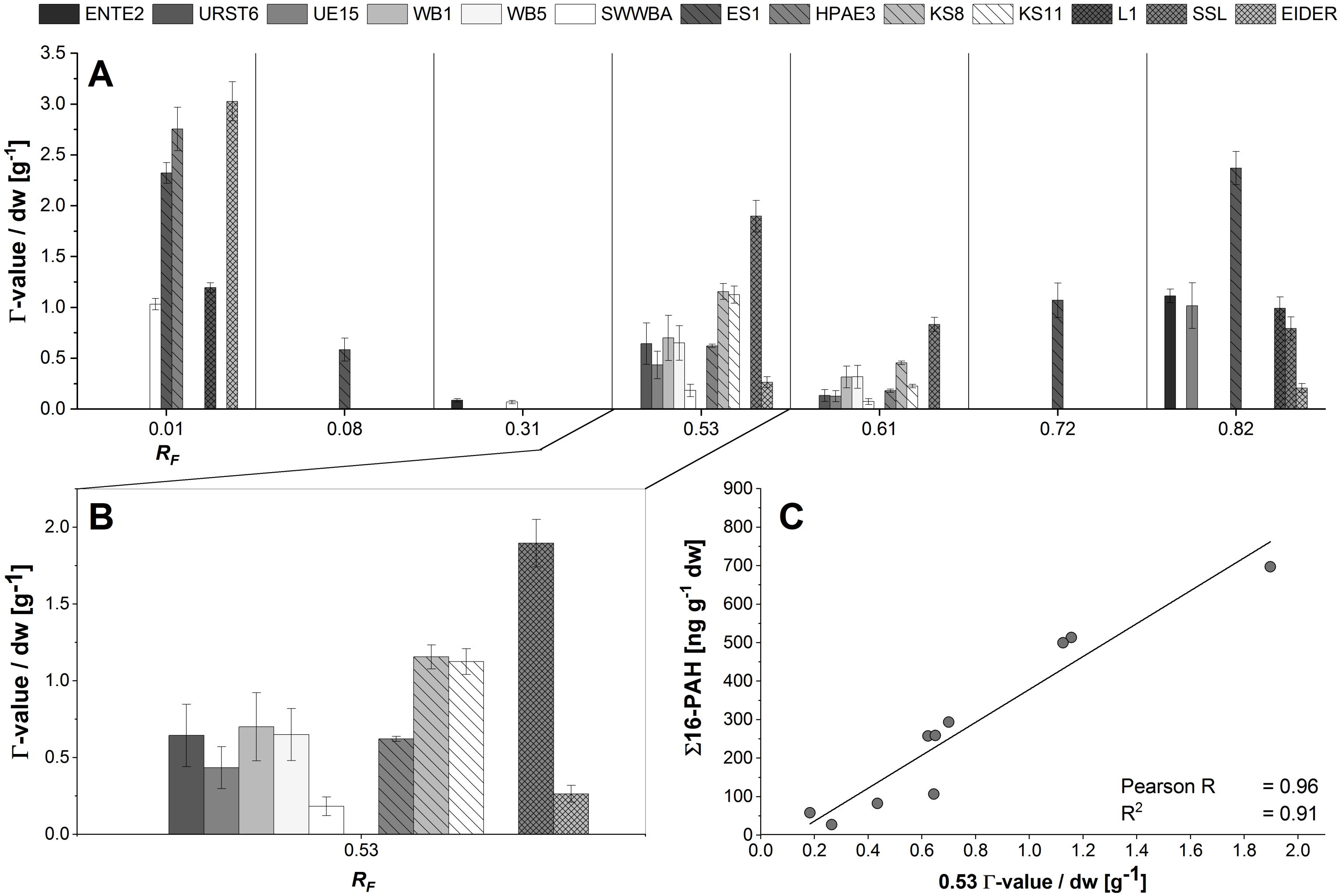

Figure 4.3: *Inhibition Γ-values normalized to sample weight for 14 spatial sediment samples at identified inhibition zones. B: Enlargement of inhibition Γ-values normalized to sample weight associated with PAH concentrations for R_F 0.53. C: Correlation of inhibition Γ-values normalized to sample weight at R_F 0.53 to accumulated 16-PAH concentrations. Error bars indicate the standard deviation from a threefold determination*

criteria for the HPTLC-bioluminescence bacteria assay for sediment toxicity analysis, toxic units (ΣESBTU) from 23 PAHs concentrations for each sample were calculated (4.2.6) and compared to the inhibition Γ-values for R_F 0.53 (TOC normalized). The correlation ($R^2 = 0.71$) suggests that the determined inhibition Γ-values could be used to assess PAH sediment toxicity for this study (Figure 4.4 B). However, sediment samples with, for example, much higher differences in contaminant concentrations or sediment characteristics, will probably not be comparable using the approach applied in this study. To overcome the problem of sample comparison in HPTLC-bioluminescence coupling due to the non-linear dose-response relationship, the reciprocal iso-inhibition volume (RIV) concept introduced by Schulz et al. (2017) can be applied. Due to limited amounts of sample extracts, we were not able to determine RIV values for the samples analyzed in this study, but focused on parallel determinations for method validation purposes.

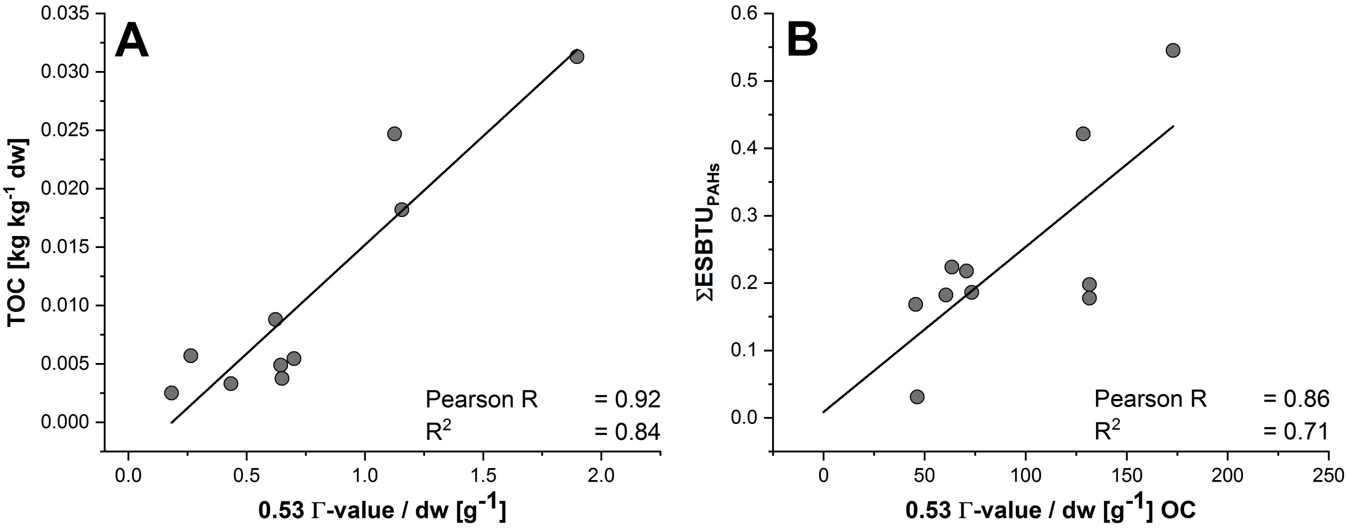

Figure 4.4: *A: Correlation of total organic carbon (TOC) to inhibition Γ-values at R_F 0.53 B: Correlation of ΣESBTU (toxic units) calculated with sediment concentrations from 23 PAHs to inhibition Γ-values at R_F 0.53*

4.3.3 Temporal analysis of marine sediment samples

Sample extracts from a 28 cm deep sediment core taken in the German EEZ that was sliced into 2 cm layers (Figure 4.1, red point) were previously analyzed for HOC concentrations with GC-MS/MS (Ranftl, 2017). In this study, the sample extracts were evaluated for temporal trends in acute toxicity using the described method. Detected accumulated HOC concentrations of the analyzed samples ranged from 78 to 530, 0.01 to 3.3, and 0.21 to 2.0 ng g^{-1} dw for 16-PAHs, seven PCBs (28, 52, 101, 118, 138, 153, 180), and five detected OCPs, respectively. TOC concentrations ranged from 0.90 to 1.4 %. All analyzed HOCs in this core showed a trend from lower concentrations at the bottom to higher concentrations to the upper sediment layers of the core. As one would expect, the HOC concentrations do not show a course of an undisturbed sediment core with a maximum and a decreasing trend of concentrations towards the upper layers, which would reflect the regulations and bans of many HOCs through national and international guidelines and laws (Brockmeyer and Theobald, 2016; Ranftl, 2017). This can be attributed to the area of the sampling location, which was used as dumping ground for low contaminated dredged sediments from the port of Hamburg (HPA, 2018). The trend for the accumulated 16-PAH concentrations from 0 to 28 cm depth is displayed in Figure 4.5 A.

Inhibition zones from 4 procedural blanks were identified at R_F 0.00, 0.18, 0.37, 0.82. All inhibition Γ-values from samples were higher than the ones detected in blanks plus their standard deviation (SI 1.6, Appendix C). For the layer 8 - 10 cm, a threefold application was performed which resulted in a RSD of 1.7 % for the inhibition zone at R_F 0.51 (Figure 4.5 B). The sample extracts of the sediment core showed several inhibition zones over the development distance of the HPTLC plate at R_F 0.00, 0.14, 0.18, 0.51, and 0.82. The inhibition zones at R_F 0.00, 0.51 and 0.82 were detected in all samples, whereas the one at R_F 0.14 was only identified in the layers 0 - 2, 2 - 4, 4 - 6, 6 - 8, and 10 - 12 cm. The inhibition Γ-values from R_F 0.51 were attributed to PAHs (4.3.1) and compared to the accumulated 16-PAHs concentrations measured by GC-MS/MS (Figure 4.5 B). The inhibition Γ-values at R_F 0.51 ranged from 0.73 to 1.36 and match the trend of the accumulated 16-PAH concentrations well (Figure 4.5 B). This reassures the attribution of PAH to the specific inhibition zone and enables the determination of their acute toxicity. Ingersoll et al. (2009) could also attribute the trend of PAHs and other HOC concentrations in sediment cores to toxicity data determined with the amphipod *Hyalella azteca.*

To test the comparability of the data of determined spatial (4.3.2) and temporal acute toxicities at R_F 0.53, inhibition Γ-values were correlated to the accumulated 16-PAHs concentrations, which resulted in a correlation coefficient (R^2) of 0.70 and a Pearson coefficient of 0.83. This indicates that inhibition Γ-values are comparable between the two sample sets and that besides the methodical drawback of normalizing Γ-values to the sample amount, the approach still provides reasonable results (results displayed in SI 1.6, Fig. 2, Appendix C).

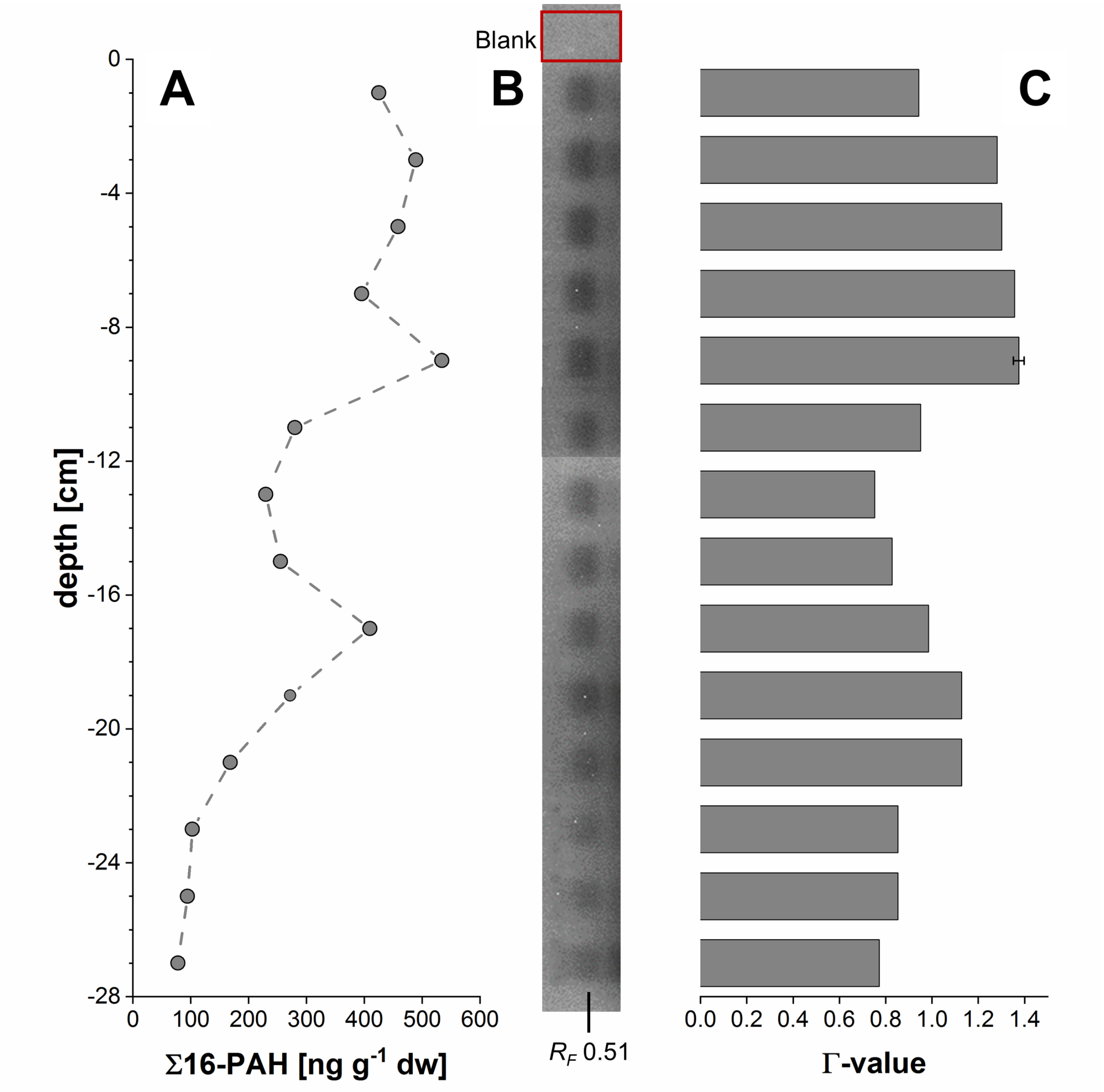

Figure 4.5: *A: Accumulated 16-PAH concentrations determined with GC-MS/MS of a sediment core sliced in 2 cm layers. B: Bioluminescence picture of corresponding samples, only inhibition zone at R_F 0.51 is shown. C: Inhibition Γ-value at R_F 0.51 for sediment core samples. Layer 8 - 10 cm was applied in triplicate; the error bar indicates the standard deviation*

4.3.4 Considerations for the suitability of the HTPLC-bioluminescence bacteria assay as an assessment tool for sediments

The results of this study show that the HPTLC-bioluminescence bacteria assay is a promising tool for the toxicity assessment of marine sediments. Differences between the acute toxicity of spatial sediment samples could be detected and the acute toxicity of an inhibition zone could be linked to PAH concentrations. Furthermore, the inhibition Γ-values determined for PAHs were comparable between two sets of sediment samples (spatial and temporal). Other advantages of EDA with the HPTLC-bioluminescence bacteria assay that support the suitability of this approach as a toxicological assessment tool for marine sediments are: EDA with HPTLC-bioluminescence coupling simultaneously offers the possibility to detect other potentially toxic substances without solvent interferences. With the help of elution head-based extraction, inhibition zones of unknown cause could be resolved from the plate for non-target screening purposes (Klingelhöfer and Morlock, 2014). The developed RIV concept for the HPTLC-bioluminescence bacteria assay by Schulz et al. (2017) further offers the possibility of determining EC_{50} values and direct comparison of samples. A further strength of using HPTLC in EDA is that the separation method can be applied in combination with other toxicological endpoints for, e.g., estrogenic effects (pYES, Schönborn and Grimmer (2013); Spira et al. (2013)), neurotoxic effects (AChE, Stütz et al. (2017); Weins and Jork (1996)), or genotoxic effects (Egetenmeyer and Weiss, 2017).

Hamers et al. (2010) state that EDA is not suitable for the sediment quality assessment within routine monitoring programs. However, we believe that due to its advantages, including cost-effectiveness and time-sufficiency, EDA with HPTLC could be interesting to be used within routine monitoring programs. But, thereby it can only serve as one tool next to others for environmental risk assessment in marine sediments. More research is needed for the further development of this approach. For example, standardized sample preparation protocols and verification of the comparability of results by, e.g., round robin tests are needed for the use within monitoring programs. Additionally, the hydrophobic substance spectrum covered in this study would be not sufficient for an appropriate assessment, as one extraction alone cannot account for the different contaminant groups found in the environment (Hamers et al., 2010). Therefore, the approach must be extended to more polar contaminants as well. But this could be hampered by limited amount of compounds which are separable by HPTLC (Schulz et al., 2017; Stütz et al., 2017). With the testing of organic extracts within this study, the bioavailability of contaminants has not been considered. However, bioavailability plays and important role in classifying and assessing the cause of sediment toxicity and should be considered in further studies (Brack et al., 2009; Burgess et al., 2013; Li et al., 2018). We assume that for example passive sampler extracts could be additionally tested for toxicity with EDA using HPTLC, although we found no studies where this has been investigated. The calculation of ΣESBTU for PAHs and their good correlation ($R^2 = 0.71$) to the inhibition Γ-values determined in this study shows that a link of toxicity data gathered with the HPTLC-bioluminescence bacteria assay to concentration derived toxicity data is possible. However, environmental quality criteria and baselines need to be developed and available to assess and classify the results.

4.4 Conclusion

The developed EDA approach is able to separate major contaminant compound classes found in sediments by a two-step HPTLC gradient. The EDA with HPTLC-bioluminescence detection enables the determination of the sediments' acute toxicity. In this study, spatial samples as well as temporal sediment samples from a core were investigated for their acute toxicity to *A. fischeri* and one inhibition zone could be linked to PAHs. A correlation of the determined inhibition Γ-values of this inhibition zone to PAH concentrations determined by GC-MS/MS showed a very good agreement ($R^2 = 0.91$). This means that the HPTLC-bioluminescence bacteria assay reveals to be a promising tool to be further developed as a toxicity screening tool for sediment analysis. This is also supported by its simplicity, rapidity and cost-effectiveness. However, HPTLC-bioluminescence coupling alone cannot serve as risk assessment tool for sediments and more research is needed until the use as such would be possible. For example, the testing of the bioavailable fraction needs to be included. Additionally, by implementing other toxicity endpoints, the approach could be further enhanced. Standardized sample preparation protocols and verification of the comparability of results are a further prerequisite for the use within monitoring programs. To cover a broad substance spectrum the approach must be extended to more polar contaminants. Finally, environmental quality criteria and baselines need to be available to assess and classify the results.

Chapter 5

Conclusions and Outlook

5.1 Conclusions drawn from research results

In this thesis, different approaches to improve sediment monitoring through alternative contaminant assessment methods were investigated. In particular, the distribution of HOC concentrations in sediment fines and their normalization by wet-sieving, trends in contaminant concentrations in sediment cores, as well as a toxicological screening test for sediments were evaluated with regard to their suitability in marine sediment monitoring.

In Chapter 2 sediment fines from the German EEZ were analyzed, which spatially expanded the contaminant inventory in sediment fines and thus provided valuable information on the more bioavailable fraction of the sediment. The investigations also served to compare the usually applied normalization to 2.5 % TOC with the physical normalization by sieving and subsequent contaminants analysis of sediment fines. It could be shown that the normalization of HOCs to TOC in sandy marine bulk sediments, such as those found in the German EEZ, is often hampered. This is mainly due to the low concentrations of both, HOCs and TOC, which caused a large uncertainty when the usual normalization to 2.5 % TOC (OSPAR/ICES) was applied. In contrast, physical normalization showed advantages in aligning HOC concentrations from neighboring sampling sites with different sediment characteristics. The statistical analyses revealed that HOC sources became more apparent in the PCA and HCPC due to a clear separation of anthropogenically influenced sampling sites when analyzing sediment fines. I concluded that physical normalization by wet-sieving, which has been practiced for trace metal analysis for several decades, can also be an alternative for monitoring HOCs in sediment, especially when sandy sediments are present. However, further validation of the method is required, both in spatial extent and in relation to further contaminant groups (e.g. PBDEs). In addition, the development of an fully automated method for wet-sieving would help to raise the attractiveness of this technique for routine application.

In Chapter 3, HOC concentrations in a sediment core from the Skagerrak were investigated. The study showed that contamination trend analyses using sediment cores were highly effective. Moreover, it could be shown that HOC concentrations were generally decreasing towards younger deposited sediment, indicating fewer anthropogenic pollution of investigated substances in recent years. The investigation of pollution trends was accompanied by radiometric dating, therefore a precise chemical fingerprint could be demonstrated. This was mainly possible due to the advantageous small-scale cutting of the sediment core into layers of only 1 cm thickness. Thereby, for PCBs, PBDEs, OCPs, and PFASs, lead, and titanium, concentration maximums could be linked to time-frames of implementation of political measures. As a result, the importance, effectiveness and justification of legislative measures targeting these contaminants and the resulting positive impact towards reaching good ecological status (GES) could be shown. However, the analyzed sediment core was not suitable for the determination or verification of background concentrations for HOCs, as preindustrial sediment layers where not retrieved. Unfortunately, it was not possible to take longer sediment cores during sampling. Nevertheless, the analyses of sediment cores for contamination trend analyses showed to be highly efficient and included emerging contaminants such as PFASs. I concluded that this technique should be given more attention within monitoring guidelines and programs.

In Chapter 4, the developed toxicological screening test based on EDA using HPTLC bioluminescence coupling was presented and applied to sediment sample extracts. The developed EDA approach was able to separate major HOC classes found in marine sediments and enabled the determination of the sediments' acute toxicity towards the studied bioluminescence bacteria (*Aliivibrio fisheri*). Thereby, one detected inhibition zone could be linked to PAHs. Concentrations of PAHs determined by GC-MS/MS correlated directly with inhibition Γ-values for this inhibition zone ($R^2 = 0.91$). The results also revealed that more research, such as the application on a broader scale and its extension to more polar contaminants is needed until the method can be applied in monitoring. I concluded that the testing of the bioavailable fraction and other toxicity endpoints should be considered in future studies. Also, standardized sample preparation procedures and evaluation scales in relation to environmental impacts need to be developed to ensure comparability of the results between different laboratories. However, the simplicity, rapidity and cost-effectiveness of the applied approach is promising and therefore recommends further development and research. Also, the approach offers the coupling to non-target screening approaches through the re-elution of inhibition zones from HPTLC plates using a TLC–MS Interface.

In summary, the approaches and results presented are valuable to enhance and extend research findings necessary to refine the assessment of contaminants in marine sediments in relation to MSFD Descriptor 8. The methods investigated were examined and evaluated for their applicability within routine monitoring programs. Although, the investigated approaches require more effort in sample preparation, sample processing, as well as the analysis of additional samples (especially true for approaches of Chapters 2 and 3), their application can compensate for the higher effort by providing improved and more relevant data.

5.2 General conclusion, implications and outlook

Due to the surface water pollution caused by anthropogenic activity that has occurred for centuries, such as sewage treatment plants, industrial processes, traffic, and construction, there are various problems visible in the marine environment. This is mainly expressed by the problem of accumulation in biomagnification of contaminants in sediments and marine fauna respectively (Bigus et al., 2014; Desforges et al., 2018; Korosi et al., 2015). Monitoring, reporting, addressing as well as assessing these problems are the main tasks to be fulfilled by governmental monitoring programs. Due to the complex nature and the vast number of chemical contaminants in addition to other stressors and the various parties involved, monitoring lacks quality and quantity of data in order to promote political legislation quickly and in a targeted manner. Although large amounts of data are collected through monitoring, it is difficult to turn this information into a value towards achieving GES - but it is precisely this qualitative and quantitative information that is needed to take appropriate action (Laane et al., 2012). This includes, for example, the strengthened integration of the contaminants bioavailability into assessment approaches. The data collected in monitoring must not only generate significance but above all relevance - it should serve less of an end in itself and more for environmental protection, contributing as value to a kind of "neighborhood protection" (Carls and Schwartz, 2021). The cross-border problem of pollution trough contaminants cannot be solved by individual member states, but must be taken up and dealt with in an international context (Keller and Schwartz, 2015). However, since marine protection already begins inland, it becomes clear that the WFD consistently disregards one of the most important matrices for the marine environment - sediment. Towards GES of the marine environment, sediments are of crucial importance, especially in the German Bight, due to the large and unique Wadden Sea, and as such should have a higher priority in monitoring. Sediments form both a reservoir and source of contaminants and can thus influence the marine environment over decades (Lehoux et al., 2020). However, to assess the entirety of stress caused for the ecosystem by contaminants, the respective environmentally relevant matrix should be monitored, showing that quality criteria for water, sediment, and biota from the limnic as well as marine habitats should be harmonized and interconnected (Keller and Schwartz, 2015). This clearly addresses the importance of a harmonized, coordinated monitoring across federal states and institutions with subsequent reporting to a central database. In this context, this thesis investigated and presented alternative approaches to extend and improve sediment monitoring.

Nevertheless, environmental legislation has shown itself to be quite capable of action, as for example the end of thin acid dumping and other examples demonstrate (Chapter 3, Skjaerseth, 1992). Still, too much time elapses between the identification of problematic substances and the establishment of legally binding environmental quality standards. Particularly, it took over 30 years from the first legislation on problematic substance groups to the enactment of legally binding target values in the environment (BRD, 1972, 1977; EU 2008/105/EC, 2008). For this reason, the continued inclusion of new substances in the Stockholm Convention is also of crucial importance for advancing marine protection from a higher-level institution.

A prerequisite for an appropriate sediment monitoring within the context of the MSFD and OSPAR/HELCOM is the comparability of the results over an extended marine area. Results from Chapter 2 can therefore contribute to a discussion about the application of currently applied TOC normalization. An essential point for comparability, besides the investigated normalization, are uniform sample allocations in a defined temporal resolution. Therefore, the use of sediment traps, as an additional option to the analysis of sediment fines (Chapter 2), might be advantageous compared to the often conducted grab-sampling (Schubert et al., 2012). As grab-sampling also revealed to be disadvantageous in terms of trend analyses (Brockmeyer and Theobald, 2016; Minh et al., 2021) e.g. due to the high variability within the data, changing sampling locations, and different analytical methods used, the periodic analyses of sediment cores at selected sampling sites should be included into monitoring programs (Chapter 3). Going beyond classical HOC analyses conducted in this study, including CECs, sediment cores could contribute to the generation of significant data for “new” contaminants. For this purpose, it is necessary that substances are evaluated for their specific risk to the marine environment and announced in centrally compiled lists (e.g. national or WFD watch lists) (Tornero et al., 2015). However, the relevance of long term measurements and continuity in monitoring programs remains undisputed (Minh et al., 2021). Investigating temporal trends of contaminant concentrations will also be important in the future to investigate the evolution of newly identified problematic compounds that can provide important data for policy analysis.

For effective monitoring, the location and selection of monitoring stations to ensure representation of all habitat types present in the study area, is equally significant. One good example is the NOAH habitat atlas, where characteristic habitat types were determined utilizing statistical methods to define representative sampling sites (Emeis et al., 2013). However, the extrapolation from point measurements of contaminant concentrations into a larger geographic area still remains challenging due to a high degree of uncertainty (Emeis et al., 2015). But the information on how contaminant concentrations are distributed over a large area remains one of the most important questions for future marine environmental assessments and international sea conventions in conjunction with the MSFD. The development of e.g. North and Baltic Sea Pressure Indices for estimating the spatial stress situation is a promising approach, however, a lack of data as well as different starting situations hamper their appropriate application (BLANO AG SbE, 2018).

A basis for harmonized, coordinated monitoring also involves a program of measures clearly addressing environmental pressures and threats. One example is the proposed measures for reducing micro plastics Nr. 418 (BLANO, 2016). Unfortunately, the measures proposed for descriptor 8 still leave room for improvement and extensions, since not much more than awareness campaigns are proposed (BLANO, 2022b). Nevertheless, the measures and assessment strategies for the MSFD need to be better embedded in the existing context of WFD, OSPAR, and HELCOM, and should help to resolve the problem of their coexistence and mutual influence on the environmental assessment. This is particularly important at the limnic marine transfer point, where a spatial, temporal, but also substantive overlap must be ensured. For the North Sea, regulations have been adopted in OSPAR and transferred to the MSFD to date. This shows that progress needs to be made, achieving that the MSFD can act independently and as a stand-alone instrument in this context, rather than disclosing an assessment cascade from the WFD to coastal areas to OSPAR (Carls and Schwartz, 2021).

In particular, effects-based monitoring and the use of sediment bioassays need to be expanded. Even though standardized biological effects assessments approaches (D8C2) are available, there is a high variability in the number of biological effects methods reported by member states, thus indicating research needs for standardized and easy to apply test protocols JPI Oceans (2021). This thesis has presented a simple approach for the determination of mixed toxicities for marine sediments using bioluminescence bacteria in Chapter 4. While more research is needed before a more sophisticated method can be developed, it has proven to be an extensible and adaptable approach. For example, the method can be extended to other toxicological endpoints and additionally to effect-based non-target screening. However, the developed toxicological screening test cannot cover for long-term effects. But there is a particular need for long-term sediment biotesting because they are not represented by currently existing sediment biotests (Babitsch, 2022).

Important for marine protection are also research questions addressing the investigation of other new relevant substances, which apply suspect or non-target screening approaches. Promising are for example projects within the Norman Network, naming CONnECT (CONtaminants of Emerging Concern and Threat in the marine environment) initiated by OSPAR and Pre-EMPT (Pre-empting pollution by screening for possible risks) by HELCOM. Here, ideas are being developed for an assessment indicator that could capture the increases and decreases of emerging substances, going beyond the single substance monitoring practiced to date.

In conclusion, however, it remains to be said that preventive marine protection should be given the highest priority. This means that harmful substances must be prevented from entering the environment in the first place. A contribution to this could be made, for example, by the nationwide introduction of a fourth treatment stage in municipal wastewater treatment plants. Additionally, concepts like “Green Chemistry“ and „Benign-by-Design" have to be adapted by the chemical and other relevant industries avoiding the release of harmful substances altogether.

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Other used Resources and Data

- DeepL translator www.deepl.com
- Meeresumweltdatenbank (BfG) MUDAB database BfG

Appendix

Appendix A

Supplementary Material to Chapter 2

As additional information to Chapter 2, Supporting Information can be found on the publisher's website. Moreover, two corresponding data publications have been published with PANGAEA. Additional data from BSH stations can be accessed in the MUDAB database.

- PANGAEA data publication for concentrations in bulk sediment and sediment fines ($< 63\ \mu$m) determined at NOAH stations.

  PANGAEA Data publication I (DOI: 10.1594/PANGAEA.875181)

- PANGAEA data publication for concentrations in bulk sediment and sediment fines ($< 63\ \mu$m) determined at BSH stations.

  PANGAEA Data publication II (DOI: 10.1594/PANGAEA.950287)

- Concentrations measured in bulk sediment at BSH stations can be queried in the MUDAB database.

  MUDAB database BfG (https://geoportal.bafg.de/MUDABAnwendung/)

- The Supporting Information contains additional and supporting data, for example, on QAQC, tables describing analytes and internal standards, and figures on the statistical analyses carried out.

  Supporting Information (https://setac.onlinelibrary.wiley.com/action/downloadSupplement?doi=10.1002%2Fieam.4744&file=ieam4744-sup-0001-20230119_Supporting_Information_Contaminantsinsedimentfines_final.docx)

Appendix B

Supplementary Material to Chapter 3

As additional information to Chapter 3, Supporting Information can be found on the publisher's website and a corresponding data publication has been published with PANGAEA.

- PANGAEA data publication for concentrations of all measured parameters in the sediment cores.

  PANGAEA Data publication (DOI: 10.1594/PANGAEA.944390)

- SI 1 consists of additional tables and figures showing additional data analyzed within the study and giving details on analytical methods, standards and QAQC parameters.

  SI 1 Multimedia component 1 (https://ars.els-cdn.com/content/image/1-s2.0-S0269749122002548-mmc1.docx)

Appendix C

Supplementary Material to Chapter 4

As additional information to Chapter 4, two documents can be found on the publisher's website:

- SI 1 consists of additional tables and figures showing additional data analyzed within the study and giving details on analytical standards and QAQC parameters.

  SI 1 Multimedia component 2 (https://ars.els-cdn.com/content/image/1-s2.0-S0045653519311683-mmc2.docx)

- SI 2 contains the executable code of the developed R script for the semi-quantitative evaluation of HPTLC plates in combination with bioluminescence bacteria as well as related explanations and definition of prerequisites.

  SI 2 Multimedia component 1 (https://ars.els-cdn.com/content/image/1-s2.0-S0045653519311683-mmc1.pdf)

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