Characteristic regional differences in trace element pattern of 2014 German north sea surface wadden sediments – A judge and assessment

Marcus von der Au [a,c], Tristan Zimmermann[a], Ulrike Kleeberg[b], Wolf von Tümpling[d], Daniel Pröfrock [a,*]

[a] Helmholtz-Zentrum Hereon, Institute of Coastal Environmental Chemistry, Inorganic Environmental Chemistry, Max-Planck Str. 1, 21502 Geesthacht, Germany

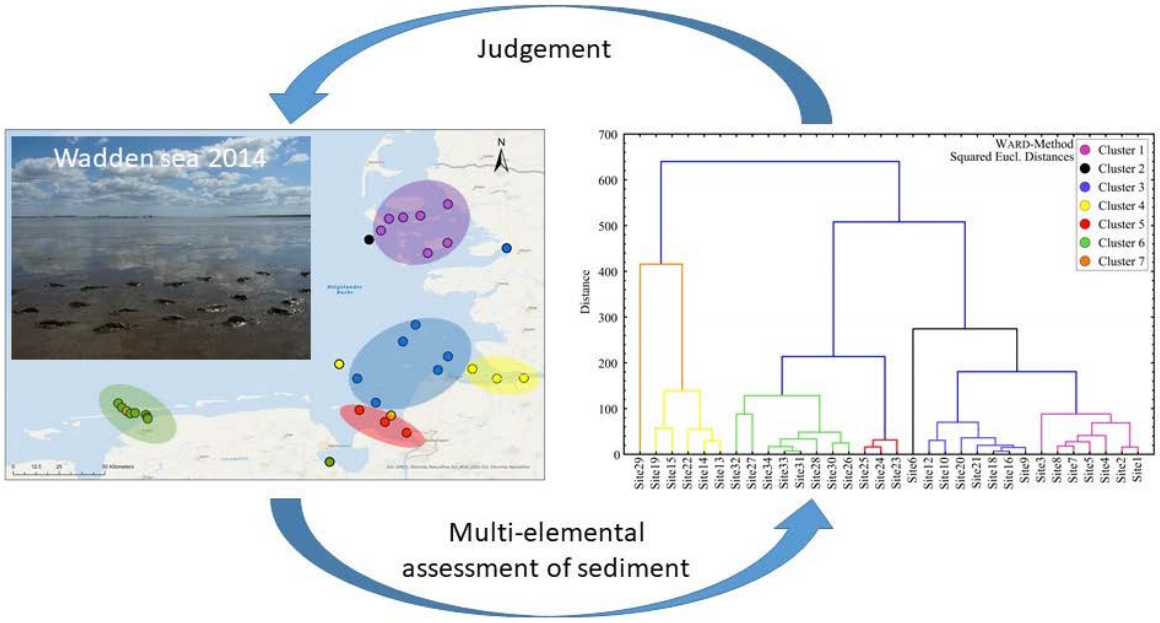
[b] Helmholtz-Zentrum Hereon, Institute of Carbon Cycles, Helmholtz Coastal Data Center, Max-Planck Str. 1, 21502 Geesthacht, Germany

[c] Bundesanstalt für Materialforschung und -prüfung, Fachbereich 1.1, Richard-Willstätter-Straße 11, 12489 Berlin, Germany

[d] Helmholtz Zentrum für Umweltforschung, Wateranalytics and Chemometrics, Brückstrasse 3a, 39144 Magdeburg, Germany

*Corresponding author: daniel.proefrock@hereon.de

Graphical Abstract:



Keywords: trace elements, enrichment factors, chemometrics, ICP-MS

Highlights:

- Comprehensive metal pollution fingerprint for the German Wadden Sea
- Analysis of 42 elemental mass fractions in <20 µm grain size fraction
- Chemometric assessment revealed distinct local pollution patters
- Results indicate an improvement of the pollution status of the investigated region

Abstract

The European Marine Strategy Framework Directive (MSFD) requires good ecological status of the marine environment. This also includes the Wadden Sea located in the southeastern part of the North Sea and its chemical status of sediments. Based on results from campaigns conducted in the 1980s, 32 surface sediment samples were taken in 2014 to check whether the sampling strategy required for characterizing the trace element content in sediments is representative and to determine the degree of pollution and potential changes over the last decades. For this purpose the elemental mass fractions of 42 elements were assessed in the ≤20 µm grain size fraction of the surface sediments.

Based on cluster analysis a clear correlation between the element distribution and the geographical location of the sampling locations of the German Wadden Sea could be found. As a result of the principal component analysis, three sub-catchments were significantly separated from each other by the characteristic element distributions in the sediments (Norderney and Weser, Elbe and offshore areas, and North Friesland). With the help of discriminant analysis, the classification was confirmed unambiguously. Small anomalies, such as potentially contaminated sites from WWII, could be identified. This proved that the sampling strategy for sediment characterization with reference to trace elements in the Wadden Sea of the German Bight is representative.

The impact of regulation and changes on the overall sediment quality is most evident when looking at the environmentally critical elements such as As, Cd, Hg, and Cr. For these elements the mean mass fractions show a significant reduction over the last three decades. Current sediments feature only slightly elevated mass fractions of Ag, Cd, Ce, Cs, Nd, Pb, Se at some sampling locations.

1. Introduction

The Wadden Sea of the North Sea extends from Den Helder peninsula in the Netherlands, through the estuaries of the different German rivers (Ems, Weser, Elbe), along the Frisian Islands, to its northeastern boundary at the island of Skallingen in Denmark. Within these boundaries, its length is about 500 km and its maximum width is approximately 40 km, covering an area of up to 10000 km^2 (Van den Brink and Kater, 2006) (Wolff, 1988). Hence, the coastal area of the Wadden Sea represents Europe's largest wetland biotope and the largest mudflats area in the world (Lotze, 2007). Consequently, three national parks and three biosphere reserves have been recognized as World Heritage Sites by the Organization of United Nations for Education, Science and Culture (UNESCO) since 2009, and are therefore under its protection (Gittenberger et al., 2016).

The North Sea in its entirety is subjected to an enormous anthropogenic influence because it is surrounded by one of the most industrialized areas in the world and is heavily used for shipping and off-shore constructions (Enemark, 2005). Thus, construction measures such as dike building, draining of areas or pre-washing of sand for coastal protection cause a continuous change of natural conditions, which, among other things, also affects the ecosystem of the (German) Wadden Sea (Kabat et al., 2012; Lotze et al., 2005). Furthermore, the North Sea is affected by inputs of waste from highly industrialized neighboring countries, which enter the water body via the atmosphere, sewage and especially via the rivers flowing into the German Bight (Freese et al., 2008).

A class of pollutants which are of high concern for the environment due to their toxicity are metal(loid)s like As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. Discharges of this class of pollutants have decreased in recent decades, but inputs are still noticeable (Logemann et al., 2022). Quantitatively, the highest input of metal(loid)s origins from major rivers discharging into the North Sea. For example, the input of cadmium from the Elbe River into the Wadden Sea has decreased from about 10 tons per year in 1986 to about 3 tons in 2000 (Essink et al., 2005b). However, regular extreme events such as flooding result in the transport of large amounts of dissolved and particulate bound pollutants originating from legacy pollutant deposits present in the different river catchments, like the Elbe River (Pepelnik et al., 2005).

After the release of (heavy) metals and metalloids into a water body, only a small amount of the metal(loid)s ions is present in the water phase due to hydrolysis, adsorption as well as co-precipitation. By far the biggest part of the metal(loid)s ions is retained in the sediment due to particulate properties and chemical composition (Bastami et al., 2014). The accumulation of metal(loid)s ions in the sediment, or the ability to re-dissolve and thus be dispersed by the water stream, depends on a variety of factors, such as redox potential, pH, salinity or the presence of organic ligands. Therefore, sediments can also serve as source, apart from sink, for a wide range of pollutants including metal(loid)s (Bastami et al., 2014; He et al., 2012; Wang et al., 2014). Due to the fact that they usually serve as sinks, sediments can be used to monitor and assess the status of water bodies regarding metal(loid)s (Chabukdhara and Nema, 2012; Ioannides et al., 2015). Due to the toxic and non-biodegradable nature of many metal(loid)s, the determination of their mass fraction in various environmental matrices like sediment, suspended matter or biota is of great interest. In a large area like the Wadden Sea, the elemental composition and quality of sediments is influenced by different parameters like the adjacent North Sea or river discharges (Postma, 1981). Hence, sediments are defined by natural characteristics, which are based on their geographical location, *e.g.*, protection by a barrier island, its geological origin or anthropogenic impacts. A wide variety of parameters are required to fully characterize a sediment sample in terms of its nature and geographic location, which makes both the analytical process, and the following data processing, much more demanding.

Developments in the field of analytical chemistry enabled the rapid digestion of sediment samples and the determination of their elemental composition *e.g.*, by ICP-MS. The automatization in terms of sample preparation, as well as sample introduction allows for the generation of large datasets, which can be subjected to cross examination for multivariate statistics. Methods, like cluster analysis or principal component analysis, allow for the interpretation of large amounts of data. Consequently, they can be put into context in terms of geographic location and anthropogenic influence. The benefits of this combined approach have already been exhibited by Reese *et al*. (Reese et al., 2019). In this study statistical approaches, based on elemental mass fractions and isotopic signatures of selected elements, were used to unravel tracers for dynamic processes like sediment transport and mixing. A similar approach was used by Deng *et al.* (Deng et al., 2021) for the Weser river.

In this study, we investigated the elemental composition of surface sediments (grainsize ≤20 µm) taken from the Wadden Sea and incorporated different statistical approaches (cluster analysis, principal component analysis and discriminant analysis), to evaluate suspected geological and anthropogenic influences. Furthermore, the obtained data is compared with older Wadden Sea sampling campaign data, which took place in the years 1984 to 1991.

2. Experimental

2.1. Materials, Reagents and Standards

For sample digestion hydrochloric acid (30 % *w*/*w*, Suprapur; Merck KGaA, Darmstadt, Germany), nitric acid (65 % *w*/*w*, Suprapur; Merck KGaA, Darmstadt, Germany), hydrogen peroxide (30 % *w*/*w*, Ultrapure; Merck KGaA, Darmstadt, Germany) and tetrafluoroboric acid (48 % *w*/*w*; Sigma Aldrich Corp., Missouri, USA) were used. Hydrochloric acid and nitric acid were double sub-boiled in quartz stills (AHF Analysentechnik, Tübingen, Germany) under clean room conditions. After digestion, samples were transferred to precleaned DigiTUBEs (SCP Science, Quebec, Canada). For dilution, type I reagent grade water obtained from a Milli-Q-System was used (>18.2 MΩ·cm; Merck Millipore, Darmstadt, Germany). For quality control, four different reference materials were used: SRM2702 and NBS 1646 (National Institute of Standards and Technology, Gaithersburg, USA), GBW 07313 (National Research Center for Certified Reference Materials, Beijing, China) and PACS-2 (National Research Council of Canada, Ottawa, Canada).

Four custom-made, multi elemental standards (all traceable to NIST standards; Inorganic Ventures, Christiansburg, USA) and four single element standards (In, Rh, Sc (Certipur; each 1000 mg L^{-1}), Hg (Certipur; 100 mg L^{-1}) (Merck KGaA, Darmstadt, Germany)) were used as internal standards and for calibration purposes.

All preparatory laboratory work, as well as measurements, were performed in a class 10000/1000 clean room. Measurements were conducted on an Agilent 8800 ICP-MS/MS system (Agilent Technologies, Inc., Tokyo, Japan) coupled to an ESI SC-4 DX FAST autosampler (Elemental Scientific, Omaha, Nebraska, USA) equiped with a discrete sampling system.

The data were processed using the MassHunter Software version 4.2 (Agilent Technologies, Tokyo, Japan) and the multivariate statistics were carried out with Statistica Version 12.7 (StatSoft, Inc., Oklahoma, USA).

2.2. Sampling Sites and Sampling

In total 32 surface sediment (top 2-3 cm) samples were taken in the German part of the Wadden Sea, during June and July of 2014. Depending on the field station, samples were either collected from the Ludwig Prandtl research vessel, using a jaw or boxcorer or, if the sampling site was accessible on foot, using a sampling cylinder. The surface sediment samples were collected in pre-cleaned 2 L LDPE bottles and stored at -20 °C until further processing. A map of all sampling locations can be found in SI Fig. 1.

2.3. Sample Preparation and Measurement

The sediments were freeze-dried (Christ Gefriertrocknungsanlagen, Osterode, Germany) and the ≤ 20 µm fraction was separated using a sieve tower, equipped with PTFE sieves and a continuous flow centrifuge equipped with a titanium rotor (Contifuge Stratos, Thermo Scientific, Waltham, USA). Subsequently, two optimized microwave digestions methods were applied to cover the analysis of 54 elements. The samples were digested and measured as triplicates. For sample digestions, two different CEM microwave systems (CEM Corp., Kamp Lintfort, Germany) were used: i) MARS Xpress5 with 55mL TFM vessels and ii) Discover SP-D with 35 mL Pyrex vessels. For the Elements As, Cd, Fe, Ga, Hg, Se, Tl, a method based on the Mars Discover SP-D was used (50 mg Sample, 3 mL HNO_3, 1 mL HCl, 1 mL H_2O_2: i) 120 °C, 3 min ramp, 3 min hold, ii) 160 °C, 3 min ramp, 4 min hold, iii) 200 °C, 3 min ramp, 4 min hold)). For the other 47 elements (Ag, Al, Ba, Be, Bi, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Gd, Ho, La, Lu, Mg, Mn, Mo, Nd, Ni, Pb, Pd, Pr, Pt, Rb, Re, Ru, Sb, Sc, Sm, Sn, Sr, Tb, Te, Th, Ti, Tm, U, V, W, Y, Yb, Zn, Zr), a method based on the Mars Xpress 5 was used (5 mL HNO_3, 2 mL HCl, 1 mL HBF_4; i) 180 °C, 60 min ramp, 300 min hold). Further details regarding the digestion protocol can be found elsewhere (Zimmermann et al., 2020a). Both methods were optimized with reference materials NBS 1646, GBW 07313, PACS-2 and NIST 2702. The success and repeatability of the digestions was checked based on the reference material NIST 2702 for each digestion batch. For drift correction 10 µL of a 10 mg L^{-1} Rh solution were added before the digestion and 10 µL of a 10 mg L^{-1} In solution was added after transferring the sample to 50 mL DigiTUBEs and diluting to 50 mL with ultra-pure water. The samples were analyzed using an 8800 Agilent ICP-MS/MS System. For each element, the available cell conditions were tested (cell gas: He, NH_3, H_2, No Gas; mass shift or not) and the optimal setup, in terms of recovery, was used. A list of measured elements, their corresponding isotopes and measuring modes can be found in SI

Tab. 1. The MS-System was tuned on a daily basis using a 10 µg L^{-1} tune solution containing Li, Co, Y, Ce and Tl

2.4. Data analysis

2.4.1 Calculation of I_{geo}

To assess the current state of the investigated sediment, the *Geoaccumulation Index* (I_{Geo}) as developed by Müller (Müller, 1979) was applied. The index is defined as follows:

$$I_{Geo} = \log_2 (C_n/1.5\ B_n) \quad \text{Eq. 1}$$

With C_n being the measured mass fraction of the element in the sediment, B_n the geochemical reference value. The constant 1.5 allows taking natural variance into account and to neglect minimal anthropogenic influences. Müller 1979 defined seven classes ranging from Class 0 (I_{Geo}=0, unpolluted) to Class 6 (I_{Geo}>5, extremely polluted).

2.4.2 Cluster Analysis

The robustness of the groups and subgroups of the cluster analysis was tested by randomly choosing 5% of the dataset and vary these values by ± 15% or ± 25%, respectively. This procedure was repeated ten times for both percentages. Furthermore, to test the robustness of the groups against other clustering methods, three different clustering methods (*Single Linkage*, *Complete Linkage* and *Unweighted Pair-Group Linkage*), besides the Ward-Method, were used. A detailed description of the statistical analysis can be found elsewhere (Reese et al., 2019) (Deng et al., 2021).

3. Results and Discussion

The sampling sites were chosen based on their geomorphological and hydrodynamic characteristics, representing the different characteristic mud flat areas within the German Wadden Sea. Therefore, four different zones were defined: i) high and constant salinity, sheltered back tidal flats in west/east direction (East Frisia), with offshore barrier islands, narrow intertidal, and high turbidity (nine samples; Number 1-9 (Fig. 1a); ii) estuarine tidal flats with variable salinity, high exposure and pronounced morphological dynamics with high turbidity in the area of the Weser and the Elbe Rivers (16 samples; Number 10-25 Fig. 1a); iii) high salinity, bay mudflats with predominant sedimentation of fine-grained material and low turbidity (one sample; number 26 Fig. 1a) and iv) high salinity, protected and exposed tidal

flats in south/north direction (North Friesland) without barrier islands, with broad intertidal and low turbidity (eight Samples; number 27-34 Fig.1a).

3.1. Assessment of the presence and intensity of anthropogenic contaminants

To assess the current environmental state of the investigated sediments, the *Geoaccumulation Index* (I_{Geo}) as developed by Müller (Müller, 1979) was applied.

Different reference values were used: i) world wide data by Turekian and Wedepohl (Turekian and Wedepohl, 1961) for all analyzed elements; ii) reference values (≤20 µm grain size fraction) obtained for unpolluted Elbe river sediment at Tangermünde by Prange *et al.* (Prange, 1997) for all analyzed elements excluding Hg, Pd, Pt, Re, Ru, Se, Te (elements are arranged alphabetically); iii) the smallest measured mass fraction of each element of the sampling campaign 2014 under the assumption that this value is close to the geogenic value in the study area, as described by Tümpling *et al.* (Tümpling et al., 2013) and iv) the reference values of Lake Victoria sediment obtained by Ribbe *et al.* (Ribbe et al., 2021) for Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Pb, Rb, Se, Sn, Sr, Ti, V and Zn. Within this context reference values published by Turekian and Wedepohl are used as classical reference values for the I_{Geo}. In addition, since the Elbe is one of the main sources of metal(loid)s pollution discharging into the Wadden Sea, the mass fractions determined by Prange *et al.* for this river near the Wadden Sea (Tangermünde) were used. Finally, the mass fractions of sediments from Lake Victoria were used as additional reference values because these sediments are not as affected by industrialization as the Wadden Sea sediments studied. Indeed, bedrock geology of the Lake Victoria will be different compared to the Wadden Sea (Okungu et al., 2005).

Using the standard established by Turekian and Wedepohl, most elemental mass fractions for the stations are in the range of Class 0 to Class 1 and are therefore classified as unpolluted or only slightly affected by anthropogenic influences. For sampling site 13-24 (located at Elbe and Weser Rivers), the index for Pb reaches class 2, showing the influence that these rivers still have on the sediments of the Wadden Sea. The I_{geo} class for Ag it is *Class 2* for most stations and *Class 3* for the stations 13, 14, 15 and 22. The data are shown in SI Fig. 2.

The mass fractions determined by Prange *et al.* refer to the ≤20 µm grain size fraction of the sediment(Prange, 1997). Tangermünde is located close to the Wadden Sea, therefore these data are well suited as reference value. Using the mass fractions as reference values, some

changes in the classification of some elements become apparent. For Ag the I_{Geo}-Class is reduced to *Class 0* and *Class 1* instead of being between *Class 2* and *Class 3*. Amendments also appear for Sr and Sn. For Sr, the classification increases for most sampling sites to Class 1 and for sampling site 6 to 2. For Sn the I_{Geo}-Class for stations 12-15, 19, 20, 22-26, 28-34 increased from Class 0 to Class 1. The greatest change is observable for Mo. Here the I_{geo}-class is increased up to class 5. The data are shown in SI Fig. 3.

Another possibility is to use the smallest measured value of a parameter of the measurement campaigns as a reference value under the assumption that this value is close to the geogenic background of the study area. The indices calculated under this assumption are mostly in Class 0, which indicates how close the stations are towards each other for most of the elements.

For Comparison, values determined by Ribbe *et al*. were also taken as reference values. An great increase is evident for the elements As (Class 3 to 4), Cd (Class 3 to 4), Mg (Class 2 to 3), Mn (Class 2 to 4), Mo (Class 1 to 5), Pb (Class 2 to 3), Se (Class 2 to 3), Sr (Class 2 to 3) and Ti (Class 2 to 3). The deterioration of the sediment classification using these mass fractions was expected, since, as mentioned above, Lake Victoria sediments were not subject to strong industrialization effects. The data are shown in SI Fig. 4.

These results indicate that reliable and local reference mass fractions are needed to evaluate the presence and intensity of anthropogenic pollutant depositions of sediments. Since the area under study is geographically close to the data collected in Tangermünde in 1993–1997, this is the best reference data available. Based on these mass fractions, the sediments sampled from the tidal flats are in good condition and, according to I_{Geo}, are predominantly uncontaminated to moderately contaminated (Class 0-2).

3.2. Changes in the sediment quality during the last 30 years (1984-2014)

In the years 1984 to 1991 a similar region as presented in this study was investigated by the *Helmholtz-Zentrum Hereon*. This period falls in a time when the Rhine River, as well as the Elbe River were strongly used, and high amounts of various pollutants were released into these river systems (Ciszewski and Grygar, 2016; Müller and Förstner, 1975; Stigliani *et al.*, 1993; Vink et al., 1999). In addition, different North Sea regions were used for the dumping of contaminated harbor sediments or acidic chemicals from the TiO_2 production (Pickaver, 1982). In the last 30 years, the use and release of metal(loid)s has been greatly reduced, especially

through stricter regulations, rules and laws. In addition, some flood events took place during this time period, increasing the runoff and the effects of altered metal(loid) loading in the major rivers that flow into the North Sea.(Engel, 1997; Pfister et al., 2004; Van der Ploeg and Schweigert, 2001) Therefore, a change should be observed over the years. The sampling locations for both sampling campaigns are shown in Fig. 1.

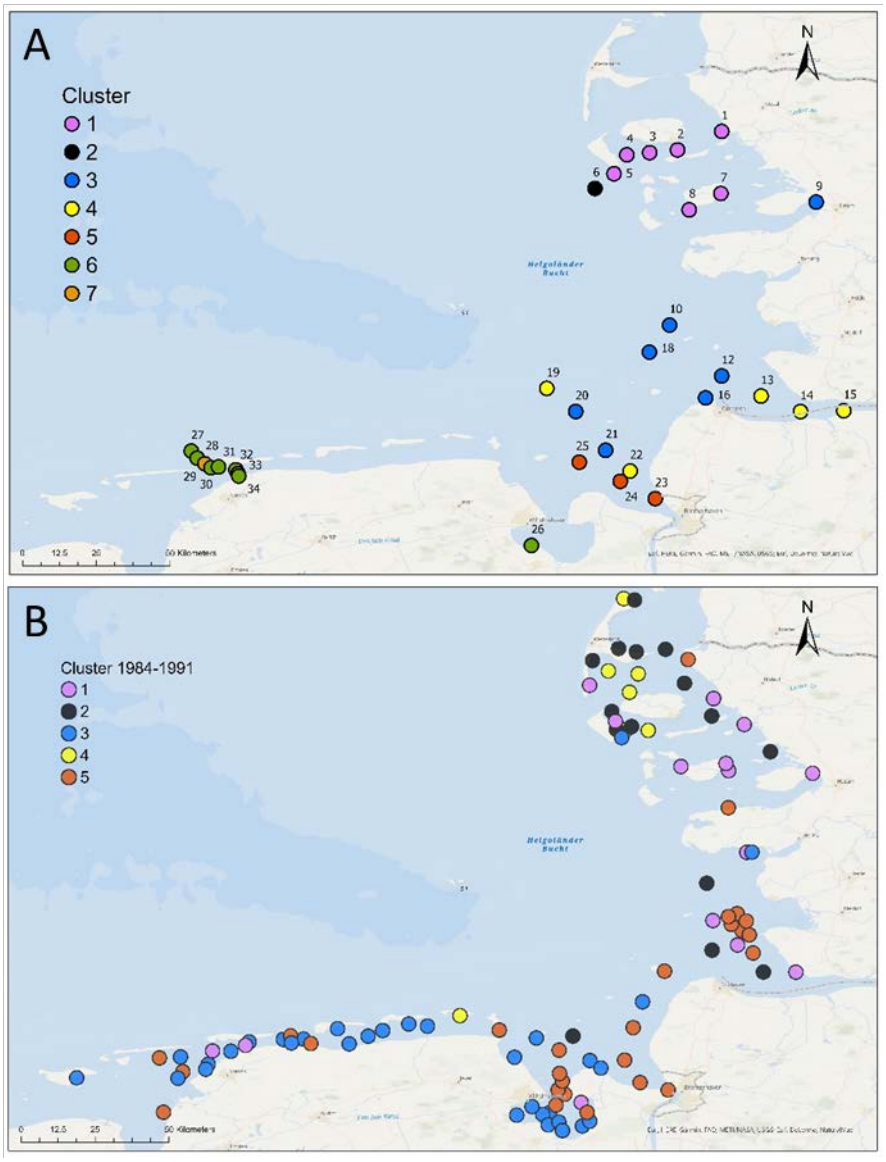


Figure 1: A) Locations of the 34 sampling sites where sediment samples were collected during the 2014 sampling campaign B) Locations of the sampling sites where sediment samples were collected during campaigns from 1984 to 1991. The numbers and symbols indicate the groups identified in the respective cluster analysis. All data relate to ≤20 µm grain size fraction.

This comparison is possible for 15 (As, Cd, Cr, Cu, Fe, Ga, Hg, Mn, Ni, Pb, Rb, Sr, V, Y, Zn) of the 17 elements studied in the sampling campaign from 1984-1991, since they are measured in both studies for the ≤20 µm grain size fraction. The key values for these two studies are summarized in Tab. 1.

Table 1: Mass fractions (as min, max, mean, median) and average/median ratios obtained in the two different studies from 2014 and from 1984-1991 (1980s). All elemental mass fractions relate to ≤20 µm grain size fraction.

	As		Cd		Cr		Cu		Fe		Ga		Hg		Mn	
	1980s	**2014**	**1980s**	**2014**	**1980s**	**2014**	**1980s**	**2014**	**1980s**	**2014**	**1980s**	**2014**	**1980s**	**2014**	**1980s**	**2014**
Min[µg/kg]	7	15	0.06	0.31	40	63	4.0	17	17000	26000	5.0	22	0.06	0.14	230	480
Max[µg/kg]	130	45	2.6	1.2	190	130	48	41	63000	69000	21	57	1.0	0.75	390	1900
Avg.[µg/kg] (2*SD*)	35 (40)	23 (13)	1.0 (1.1)	0.52 (0.35)	110 (55)	88 (34)	21 (15)	25 (11)	38000 (20000)	40000 (22000)	14 (7)	33 (15)	0.39 (0.29)	0.34 (0.30)	680 (920)	780 (610)
Median [µg/kg]	30	21	0.92	0.48	110	83	22	24	38000	36000	15	32	0.37	0.30	560	700
Avg./Median	0.98	1.1	1.1	1.1	0.99	1.1	0.97	1.1	1.1	1.10	0.95	1.04	1.0	1.1	1.2	1.1
	Ni		**Pb**		**Rb**		**Sr**		**V**		**Y**		**Zn**			
	1980s	**2014**	**1980s**	**2014**	**1980s**	**2014**	**1980s**	**2014**	**1980s**	**2014**	**1980s**	**2014**	**1980s**	**2014**		
Min[µg/kg]	21	29	11	41	44	71	87	180	49	75	13	17	47	120		
Max[µg/kg]	68	51	140	120	150	140	330	750	220	130	42	31	480	240		
Avg.[µg/kg] (2*SD*)	45 (18)	40 (11)	65 (51)	60 (30)	110 (52)	110 (28)	210 (120)	280 (210)	130 (66)	110 (33)	25 (12)	21(6)	220 (150)	160 (60)		
Median [µg/kg]	47	40	64	56	110	110	210	250	130	100	25	20	210	150		
Avg./Median	0.96	1.0	1.0	1.1	0.97	1.0	0.96	1.12	1.0	1.0	1.0	1.1	1.1	1.1		

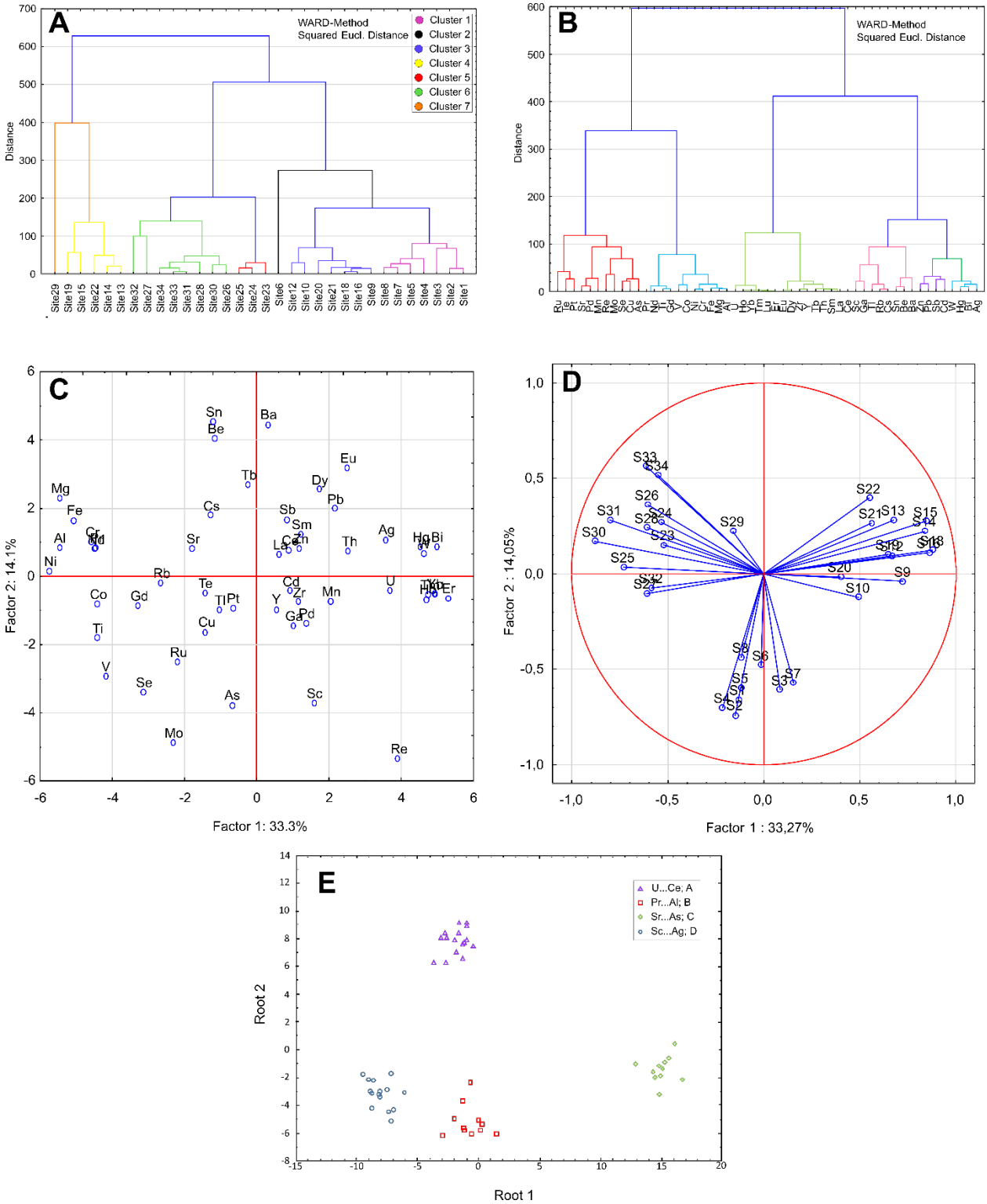
The impact of regulation and changes in use is most evident when looking at the average mass fractions of environmentally critical elements such As (23 µg/kg in 2014 vs. 35 µg/kg in 1980s), Cd (0.52 µg/kg in 2014 vs. 1.0 µg/kg in 2014), Cr (88 µg/kg in 2014 vs. 110 µg/kg in 1980s) or Zn (160 µg/kg in 2014 vs. 220 µg/kg in 1980s). For these elements, the mean value shows a significant decrease over the last three decades.

An anomaly which appeared in the data set are increased Ga mass fractions in the investigated sediment samples (33 µg/kg in 2014 vs. 14 µg/kg in 2014). This could be due to the increased use of Ga and the production of Ga components, which can lead to an increased release of Ga into the environment. Since Ga production industry is present along the Elbe River, this assumption is supported by observations made Prange *et al.* in 2001. Increased Ga mass fractions were measured locally within the Elbe estuary (Prange, 2001). In addition, increased construction of offshore structures protected by galvanic anodes may also lead to increased Ga mass fractions in sediments during recent years. The aluminum alloys predominantly used here contain a significant proportion of gallium (Reese et al., 2020).

The cluster analysis performed for the 1984–1991 data set did not result in a geographic separation of the stations. Resulting in a separation into five groups along their specific pollution fingerprint. There may be two reasons for this: i) the number of elements studied is not high enough to expose typical geologic structures or ii) the anthropogenic influence is too extensive and masks the original geogenic fingerprint.

3.3. Revealing possible metal(loid)s pollutant fingerprints using cluster analysis and principal component analysis

To determine possible characteristic fingerprints within the sediment samples for the different sampling sites (2014), multivariate statistics were incorporated. As a first approach and to categorize the sediments, a cluster analysis (*Ward* Method) was used (Fig. 2 A). Three different clustering methods (*Single Linkage*, *Complete Linkage* und *Unweighted Pair-Group Linkage*), besides the Wade-Method, were used. All tested procedures and dataset changes led to the same grouping and subgrouping of the dataset. Hence, the grouping is appropriate, and the clusters, and therefore the element mass fractions are characterizing stable sediment regimes.



311

312 **Figure 2: A: results of the cluster analysis for 32 sampling stations (2014), regarding their**
313 **elemental mass fractions; B results of the cluster analysis for the 42 analyzed elements,**
314 **regarding their mass fraction within the sampling sites; C: score plot of the PCA for the 32**
315 **sampling sites and the 42 elements; D: loading plot for the performed PCA for the 32 sampling**
316 **sites and the analyzed 42 elements; E: discriminant analysis performed for the 4 groups**
317 **obtained from the cluster analysis. All data relate to ≤20 µm grain size fraction.**

318 The dendrogram splits the sampling sites into seven clusters (Fig. 2 A), based on their
319 elemental composition. While most of the clusters contain at least three sampling sites, two
320 sampling sites form their own cluster. Sampling site 29, which is located at the western end
321 point of the island of Norderney, has the furthest distance from any adjacent group and forms
322 its own cluster, even though it is located close to the other sampling sites around the island
323 of Norderney. This sampling site is characterized by an increased elemental mass fraction of
324 technical critical elements (TCE) especially the rare earth elements (REE). The mass fractions
325 of La and Gd are up to 2.5 times higher than for all other sampling stations of this campaign.
326 Most of the sampling sites along the East Frisian Island of Norderney (sampling site 27-34) are
327 located on a tidal inlet (Norderney Seegat). Thus, are in a corridor that has high currents
328 during tides, resulting in erosion. However, sampling site 29 appears to have a different flow
329 path that results in a sink of anthropogenically released elements that accumulate in the
330 sediment of this sampling site. This sink can be a result of the coastal protection system, *e.g.*,
331 groynes, which may affect the stream and lead to a more diffuse flow at this sampling point
332 (Kunz). This would favor the accumulation of sediments in the region of sampling site 29. A
333 similar situation can be found in the Jade Bay (sampling site 26). This area exhibits a turbulent
334 flow with a lower water velocity, which leads to the deposition of sediment from the North
335 Sea (Jin and Liebezeit, 2012). So this area is mainly influenced directly by the North Sea. This
336 explains why the elemental pattern of this region has a higher similarity towards the East
337 Frisian islands than towards the adjacent Weser estuary sediment, since its mostly influenced
338 by the North Sea. This observation can also be explained by the main current of the North Sea
339 which is going from west to north (van Beusekom et al., 1999).

340 The cluster closest to sampling site 29 is mostly dominated by spots in or close to the Elbe
341 River estuary – but with a large squared Euclidian distance between these two clusters. Since
342 most of the sampling sites in this cluster also show a high REEs mass fractions, these two
343 clusters are mostly dominated by anthropogenic contamination (like increased Hg
344 concentration for the Elbe River), but still feature a different elemental signature. This fact
345 explains their grouping, since there are similarities within an elemental group (REE) but they
346 are mostly different in terms of elemental composition. Since the Elbe River is one of the most
347 frequently used rivers, as well as one of the highest anthropogenically influenced rivers in the
348 European Union it has been thoroughly studied, and the present findings are in good

agreement with the literature (Kulaksız and Bau, 2007; Zimmermann et al., 2020b). Also, the average flow of the river Elbe into the North Sea is about 700 m^3s^{-1} (van Beusekom et al., 1999), which is about 2 times higher than the inflow of other rivers such as the Weser River (300 m^3s^{-1}) (van Beusekom et al., 1999), into the North Sea. That leads to the influence of its elemental composition towards sediments, which are further away (Sampling Site 19). The group of this cluster that consists of the sampling sites within the Elbe estuary and sampling site 29, which is located around the island of Norderney, is mainly defined by an elevated REE concentration and therefore shows a strong anthropogenic influence.

The second branch of the dendrogram is mostly defined by a sorting along the geogenic fingerprint. The Weser River sampling sites and the Norderney sampling sites are closely grouped together into two clusters. The sampling sites located between the Elbe River and the North Sea and the sampling sites around the North Frisian Islands are grouped into two clusters as well. Sampling site 6 is an exception to that – this station features a similar signature as stations around the North Frisian Islands, but some elements show exceedingly high mass fractions of As, Cu, Mn, Sr and Se which may be caused by the existence of a former dumping site for ordonnance and other war related equipment since mass fractions of these elements (As (chemical weapon), Cu (shell), Mn (shell), Sr (tracer ammunition) and Se (ammunition)) greatly differ to the other stations (Ahvo et al., 2020; Beldowski et al., 2019; Liebezeit et al., 2003; Pirrone et al., 2013). In contrast to other studies the Hg concentration, which has been used as specific marker for military dumping sites, was not elevated (Gębka et al., 2016). Since the geogenic fingerprint is similar, sampling site 6 is separated by the algorithm from the other North Frisian Islands sampling sites, but it is still grouped close to them. The small distance between these two groups may be also explained by the fact that, dumping sites for dredged material from the river Elbe are located around them (Essink et al., 2005a). This is evidenced by the presence of Sc, Ga, Tl, Rb, Cs, Sn, Be and Ba along the North Frisian Islands (Sampling Site 1-5), with decreasing elemental mass fractions along the transect into the open sea. This trend was proven significant by a trend analysis according to Neumann (p = 0.95, for the sampling site series 1-5). The area around the North Frisian Islands is mostly influenced by the North Sea, while the area further offshore the Elbe River estuary is mostly influenced by the open sea, as well as by the elemental signature of the Elbe River runoff. That can be seen by the fact that some of these stations (19 and 22) are also connected

to the yellow branch and hence towards the Elbe River. Therefore, the clustering of these stations is explained by the influence of the different effects taking place, and the currents around the areas. It seems like there are significant similarities between the western part of the Weser estuary and the North Friesian Islands. So, the area seems to be also mostly characterized by the North Sea sediment, and only slightly by the Weser River itself. So, the Elbe River has a higher impact towards the sediment characteristics of the upstream regions – which can be explained by the river runoff volumes.

The same clustering procedure was also performed, in order to sort the elements into clusters, in order to find element groups describing the sampling sites, in order to obtain groups for the following discriminant analysis. For the 32 sampling sites, the 47 elements are divided into four groups based on their mass fractions. The result of the cluster analysis for the elements is shown in detail in Fig. 2 B. For each branch of the dendrogram, one element and the corresponding mass fraction are shown on the sampling campaign map (SI Fig. 5 to SI Fig. 10) to illustrate the difference between branches.

In order to interlink the element mass fractions and the sampling sites, and reveal fingerprints, which are indicate by the cluster analysis, a principal component analysis was performed with the given dataset as well. To reduce the data dimension and extract the main characteristics of the data set regarding correlations between the sampling sites, a principal component analysis was performed. The factors of the first and second principal components represent 33 % and 14% of the variance. Therefore, nearly 50% of the total variance is represented by these two components. The score plot of the PCA analysis is shown in Fig. 2 C. A table stating the factor loadings of all analyzed elements can be found in SI Tab. 2. The elements Ag, U, W, Hg, Bi, Ho, Yb, Er, Tm, and Lu show a high positive correlation for factor 1, while the elements Pr, Nd, Ti, Gd, V, Co, Ni, Cr, Fe, Mg and Al are highly negative correlated to factor 1. For the elements Pr-Al (negative correlation to factor 1), elemental mass fractions of the sampling sites 1-22 are nearly two times higher than for the sampling sites 23-34.This difference was statistically proven by an *F*-test (α=0.95) as well as *t*-test (α=0.95). Therefore, the elemental mass fractions are divided along the estuaries of the two main rivers Weser and Elbe. This finding implies, that the Elbe River has a great influence on these areas, since the median stream of the North Sea is counterclockwise and the sites located north of the

river Elbe are influenced, while the western sampling sites are mainly affected by Atlantic Sea water.

This splitting also reflects the subdividing done by van Beusekum et al**.**, who divided the German Wadden Sea into an East Frisian Wadden Sea and a North Frisian Wadden Sea, setting the border between the estuaries of the Elbe and Weser Rivers (van Beusekom et al., 1999). While the splitting for most of the elements can be mainly explained by a geogenic influence, the elevated gadolinium mass fraction in comparison to the Elbe's influenced area is unexpected. Indeed, elevated mass fractions of REEs at similar geographic locations within the Elbe estuary have been described by Reese et al. (Reese et al., 2019).

The elements Ag – Lu (positive correlation to factor 1) are significantly elevated within the Elbe estuary, contrary to the element set Pr-Al. So, these two sets of elements, which are greatly separated by factor 1, are describing the separation of the North Frisian Wadden Sea as well as the East Frisian Wadden Sea. For elements which show a high positive correlation towards factor 2 seem to have a lower mass fraction around the North Frisian Islands and vice versa.

Regarding the loading plot, which is shown in Fig. 2 D, anthropogenically influenced sediment samples featuring elevated REE mass fractions, are separated by positive factor 1 values. Meanwhile, the lowest REE mass fractions around the Island of Norderney are grouped around negative values along the factor 1. The geogenic fingerprint, *e.g.* Fe and Mg, is mainly considered within this factor. The sampling sites around the North Frisian Islands are mostly separated from the other sampling sites along factor 2, while factor 1 has a low effect on these sampling sites. Also, while the other sampling sites are mostly scattered around positive factor 2 values or just slightly negative, the sampling sites around the North Frisian Islands (sampling site 1-8) are all located at high negative factor 2 values. So, the sampling sites are mainly characterized by the mass fractions of elements like As, Cu, Mo, Sc, Re, Pt. Therefore, the positive values along this factor describe more geogenic features while the negative values represent anthropogenic effects. From a geomorphological point of view, the sediments along the East Frisian Islands and the estuaries of the Elbe and Weser are similar to each other, while the anthropogenic influence and footprint is quite different. Regarding the North Frisian Islands, while there are some similarities to the Elbe estuary, especially

regarding the element set Pr-Al, their elemental fingerprint is significantly different to the other two sampling areas.

By reducing the dataset to two factors with the highest variance, and therefore to the values with the highest information density, the sampling sites can be divided into three groups. These groups are geographically close to each other and define a separate region. One group is located around the Island of Norderney, the Jade Bay and parts of the Weser estuary. This is in good agreement to the dendrogram (Fig. 2 A) – only station 29 was not grouped within this region. Therefore, the PCA takes this effect into account (lower negative value along factor 1) but the main characteristic within this sediment allows for the grouping of the adjacent locations. The second group, sampling site 10-22, is mainly dominated by the sampling sites around the Elbe estuary and upstream regions. This region is dominated by the influence of the Elbe River and the specific offshore characteristics. The third group (sampling site 23-34) is located around the North Frisian Islands. This region is mainly influenced by the open sea.

3.5. Significance of sampling sites

In order to evaluate if sample sites are characterized by redundant elemental mass fraction data a discriminant analysis was performed. To carry out the discriminant analysis, the groups obtained from the cluster analysis were used. The results for the canonical variables are shown in Fig 2 E.

Fig 2 E shows that two functions are sufficient to sort the data into the expected groups. This separation is also apparent by the resulted Wilks' Lambda value of $5 \cdot 10^{-5}$. The separation also indicates a high representativeness of the obtained samples for the given locations. The high representativeness leads to the fact that the sampling sites 4, 5, 12, 14, 18, 23, 31 are carrying redundant information. As a result, 7 of the 32 investigated can be removed from the overall data set without changing the outcome of the statistical data analysis. This indicates that the pollution went so far down, that the geological fingerprint is significant and allows to separate the groups by their location.

Furthermore, the geographical and geomorphological areas (i) Sheltered back tidal flats in west/east direction; ii) Estuarine tidal flats with variable salinity and iv) protected and

exposed tidal flats in south/north) are represented within the multivariate analysis regarding their elemental fingerprint. Only Bay mudflats with far predominant sedimentation of fine-grained material did not show a unique elemental fraction pattern and were grouped into the adjacent group. This highlights the significance of the presence or absence of rivers and barrier islands on the elemental distribution and therefore the individual pollutant fingerprints of the investigated Wadden Sea areas.

4. Conclusion

The study conducted was able to demonstrate the value of multivariate statistics when applied to environmental datasets. The methods used were able to distinguish different geographical locations based on their elemental fingerprint and proved that these fingerprints are significant for the studied areas and the analyzed ≤20 µm grain size fraction. Considering a second data set obtained in 1984-1991, it was shown that the fingerprint changed over time and that sediment quality significantly improved during the last decades. Depending on reference values taken for the comparison it could be shown, that some trace element mass fractions like Cd, Pb, Sn or Zn of today's surface Wadden Sea sediments are still elevated. Future sediment core investigations could be helpful to further verify these observations. In addition to the report on the quality of the Wadden Sea, this study has shown that only a few samples need to be taken in selected areas to assess the environmental condition of sediments. Therefore, for future investigations, only a few samples need to be taken into account based on the identified, representative areas to evaluate their condition. Thus, making environmental monitoring less time consuming and more efficient.

5. Acknowledgements

The authors would like to thank the crew of the RV Ludwig Prandtl for their help during the campaign in 2014, as well as the Wadden Sea authorities to allow the sampling in the different Wadden Sea Areas. Carlo van Bernem, Ina Frings, Stephan Lassen, Burkhard Erbslöh, Anika Retzmann and Rainer Jablonski are acknowledged for fruitful discussions and assistance during sampling and sample preparation.

6. References

Ahvo, A., Lehtonen, K.K., Lastumaki, A., Straumer, K., Kraugerud, M., Feist, S.W., Lang, T., Tornes, J.A., 2020. The use of Atlantic hagfish (Myxine glutinosa) as a bioindicator species for studies on effects of dumped chemical warfare agents in the Skagerrak. 2. Biochemical biomarkers. Mar Environ Res 162, 105097.

Bastami, K.D., Bagheri, H., Kheirabadi, V., Zaferani, G.G., Teymori, M.B., Hamzehpoor, A., Soltani, F., Haghparast, S., Harami, S.R., Ghorghani, N.F., Ganji, S., 2014. Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian Sea. Mar Pollut Bull 81, 262-267.

Beldowski, J., Szubska, M., Siedlewicz, G., Korejwo, E., Grabowski, M., Beldowska, M., Kwasigroch, U., Fabisiak, J., Lonska, E., Szala, M., Pempkowiak, J., 2019. Sea-dumped ammunition as a possible source of mercury to the Baltic Sea sediments. Sci Total Environ 674, 363-373.

Chabukdhara, M., Nema, A.K., 2012. Assessment of heavy metal contamination in Hindon River sediments: a chemometric and geochemical approach. Chemosphere 87, 945-953.

Ciszewski, D., Grygar, T.M., 2016. A review of flood-related storage and remobilization of heavy metal pollutants in river systems. Water, Air, & Soil Pollution 227, 1-19.

Deng, F., Hellmann, S., Zimmermann, T., Pröfrock, D., 2021. Using Sr-Nd-Pb isotope systems to trace sources of sediment and trace metals to the Weser River system (Germany) and assessment of input to the North Sea. Science of The Total Environment 791, 148127.

Enemark, J., 2005. The Wadden Sea protection and management scheme—towards an integrated coastal management approach? Ocean & Coastal Management 48, 996-1015.

Engel, H., 1997. The flood events of 1993/1994 and 1995 in the Rhine River basin. IAHS Publications-Series of Proceedings and Reports-Intern Assoc Hydrological Sciences 239, 21-32.

Essink, K., Dettmann, C., Frake, H., Laursen, K., Lüerßen, G., Wiersinga, W., 2005a. Wadden Sea quality status report 2004. Common Wadden Sea Secretariat.

Essink, K., Dettmann, C., Frake, H., Laursen, K., Lüerssen, G., Wiersinga, W.A., 2005b. Wadden Sea Quality Status report 2004. Common Wadden Sea Secretariat, Wilhelmshaven, Germany.

Freese, E., Köster, J., Rullkötter, J., 2008. Origin and composition of organic matter in tidal flat sediments from the German Wadden Sea. Organic Geochemistry 39, 820-829.

527 Gębka, K., Bełdowski, J., Bełdowska, M., 2016. The impact of military activities on the
528 concentration of mercury in soils of military training grounds and marine sediments.
529 Environmental Science and Pollution Research 23, 23103-23113.
530 Gittenberger, A., Voorbergen-Laarman, M.A., Engelsma, M.Y., 2016. Ostreid herpesvirus
531 OsHV-1 muVar in Pacific oysters Crassostrea gigas (Thunberg 1793) of the Wadden Sea, a
532 UNESCO world heritage site. J Fish Dis 39, 105-109.
533 He, C., Bartholdy, J., Christiansen, C., 2012. Clay mineralogy, grain size distribution and their
534 correlations with trace metals in the salt marsh sediments of the Skallingen barrier spit,
535 Danish Wadden Sea. Environmental Earth Sciences 67, 759-769.
536 Ioannides, K., Stamoulis, K., Papachristodoulou, C., Tziamou, E., Markantonaki, C., Tsodoulos,
537 I., 2015. Distribution of heavy metals in sediment cores of Lake Pamvotis (Greece): a pollution
538 and potential risk assessment. Environ Monit Assess 187, 4209.
539 Jin, H., Liebezeit, G., 2012. Distribution of total mercury in coastal sediments from Jade Bay
540 and its catchment, Lower Saxony, Germany. Journal of Soils and Sediments 13, 441-449.
541 Kabat, P., Bazelmans, J., van Dijk, J., Herman, P.M.J., van Oijen, T., Pejrup, M., Reise, K.,
542 Speelman, H., Wolff, W.J., 2012. The Wadden Sea Region: Towards a science for sustainable
543 development. Ocean & Coastal Management 68, 4-17.
544 Kulaksız, S., Bau, M., 2007. Contrasting behaviour of anthropogenic gadolinium and natural
545 rare earth elements in estuaries and the gadolinium input into the North Sea. Earth and
546 Planetary Science Letters 260, 361-371.
547 Kunz, H., Groynes on the East Frisian Islands: History and Experiences. Coastal Engineering
548 1996, 2128-2141.
549 Liebezeit, G., Wehrmann, A., Hamacher, S., 2003. Modern concretions in intertidal flats of the
550 Lower Saxonian Wadden Sea, Southern North Sea. Senckenbergiana maritima 32, 147-154.
551 Logemann, A., Reininghaus, M., Schmidt, M., Ebeling, A., Zimmermann, T., Wolschke, H.,
552 Friedrich, J., Brockmeyer, B., Pröfrock, D., Witt, G., 2022. Assessing the chemical
553 anthropocene – Development of the legacy pollution fingerprint in the North Sea during the
554 last century. Environmental Pollution 302, 119040.
555 Lotze, H.K., 2007. Rise and fall of fishing and marine resource use in the Wadden Sea, southern
556 North Sea. Fisheries Research 87, 208-218.
557 Lotze, H.K., Reise, K., Worm, B., van Beusekom, J., Busch, M., Ehlers, A., Heinrich, D.,
558 Hoffmann, R.C., Holm, P., Jensen, C., Knottnerus, O.S., Langhanki, N., Prummel, W., Vollmer,

559 M., Wolff, W.J., 2005. Human transformations of the Wadden Sea ecosystem through time: a
560 synthesis. Helgoland Marine Research 59, 84-95.
561 Müller, G., 1979. Schwermetalle in den Sedimenten des Rheins : Veränderungen seit 1971.
562 Umschau in Wissenschaft und Technik 79, 778-783.
563 Müller, G., Förstner, U., 1975. Heavy metals in sediments of the Rhine and Elbe estuaries:
564 mobilization or mixing effect? Environmental Geology 1, 33-39.
565 Okungu, J.O., Njoka, S., Abuodha, J.O.Z., Hecky, R.E., 2005. An introduction to Lake Victoria
566 catchment, water quality, physical limnology and ecosystem status (Kenyan sector). Lake
567 Victoria Environment Management Project (LVEMP).Pepelnik, R., Karrasch, B., Niedergesäß,
568 R., Erbslöh, B., Mehrens, M., Link, U., Herzog, M., Prange, A., 2005. Influence of the Flooding
569 in 2002 on the Plankton and the Quality of Water and Sediment of the River Elbe over Its
570 Longitudinal Profile. Acta hydrochimica et hydrobiologica 33, 430-448.
571 Pfister, L., Kwadijk, J., Musy, A., Bronstert, A., Hoffmann, L., 2004. Climate change, land use
572 change and runoff prediction in the Rhine–Meuse basins. River research and applications 20,
573 229-241.
574 Pickaver, A.H., 1982. Titanium dioxide waste dumping at sea time to call a halt. Marine
575 pollution bulletin 13, 375-379.
576 Pirrone, N., Bełdowski, J., Szubska, M., Emelyanov, E., 2013. Spatial variability of Arsenic
577 Concentrations in Baltic Sea surface sediments in relation to Sea Dumped Chemical
578 Munitions. E3S Web of Conferences 1.
579 Postma, H., 1981. Exchange of materials between the North Sea and the Wadden Sea. Marine
580 Geology 40, 199-213.
581 Prange, A., Bössow, E., Erbslöh, B., Jablonski, R., Jantzen, E., & Kause, P, 2001. Grafische
582 Darstellung der Längsprofile - Filtrate, Schwebstoffe, Sedimente. Erfassung und Beurteilung
583 der Belastung der Elbe mit Schadstoffen.
584 Prange, A., Bössow, E., Erbslöh, B., Jablonski, R., Jantzen, E., Krause, P., Krüger, F., Leonhard,
585 P., Niedergesäß, R., & Pepelnik, R, 1997. Geogene Hintergrundwerte und zeitliche
586 Belastungsentwicklung.
587 Reese, A., Voigt, N., Zimmermann, T., Irrgeher, J., Pröfrock, D., 2020. Characterization of
588 alloying components in galvanic anodes as potential environmental tracers for heavy metal
589 emissions from offshore wind structures. Chemosphere 257, 127182.

590 Reese, A., Zimmermann, T., Pröfrock, D., Irrgeher, J., 2019. Extreme spatial variation of Sr, Nd
591 and Pb isotopic signatures and 48 element mass fractions in surface sediment of the Elbe River
592 Estuary - Suitable tracers for processes in dynamic environments? Science of The Total
593 Environment 668, 512-523.
594 Ribbe, N., Arinaitwe, K., Dadi, T., Friese, K., Tümpling, W., 2021. Trace-element behaviour in
595 sediments of Ugandan part of Lake Victoria: results from sequential extraction and
596 chemometrical evaluation. Environmental Earth Sciences 80.
597 Stigliani, W.M., Jaffé, P.R., Anderberg, S., 1993. Heavy metal pollution in the Rhine basin.
598 Environmental science & technology 27, 786-793.
599 Tümpling, W., Einax, J., Scheibe, N., 2013. Extended Sediment Quality Rating for Trace
600 Elements in Urban Waters – Case Study Klinke, Germany. CLEAN - Soil Air Water 41, 565-573.
601 Turekian, K.K., Wedepohl, K.H., 1961. Distribution of the Elements in Some Major Units of the
602 Earth's Crust. GSA Bulletin 72, 175-192.
603 van Beusekom, J.E.E., Brockmann, U.H., Hesse, K.J., Hickel, W., Poremba, K., Tillmann, U.,
604 1999. The importance of sediments in the transformation and turnover of nutrients and
605 organic matter in the Wadden Sea and German Bight. Deutsche Hydrografische Zeitschrift 51,
606 245-266.
607 Van den Brink, P.J., Kater, B.J., 2006. Chemical and biological evaluation of sediments from
608 the Wadden Sea, The Netherlands. Ecotoxicology 15, 451-460.
609 Van der Ploeg, R., Schweigert, P., 2001. Elbe river flood peaks and postwar agricultural land
610 use in East Germany. Naturwissenschaften 88, 522-525.
611 Vink, R., Behrendt, H., Salomons, W., 1999. Development of the heavy metal pollution trends
612 in several European rivers: an analysis of point and diffuse sources. Water Science and
613 Technology 39, 215-223.
614 Wang, J., Liu, R., Zhang, P., Yu, W., Shen, Z., Feng, C., 2014. Spatial variation, environmental
615 assessment and source identification of heavy metals in sediments of the Yangtze River
616 Estuary. Mar Pollut Bull 87, 364-373.
617 Wolff, W.J., 1988. Impact of Pollution on the Wadden Sea, in: Salomons, W., Bayne, B.L.,
618 Duursma, E.K., Förstner, U. (Eds.), Pollution of the North Sea: An Assessment. Springer Berlin
619 Heidelberg, Berlin, Heidelberg, pp. 441-454.

Zimmermann, T., Au, M., Ebeling, A., Klein, O., Hildebrandt, L., Pröfrock, D., 2020a. Substituting HF by HBF 4 – an optimized digestion method for multi-elemental sediment analysis via ICP-MS/MS. Analytical Methods 12.

Zimmermann, T., Mohamed, A.F., Reese, A., Wieser, M.E., Kleeberg, U., Pröfrock, D., Irrgeher, J., 2020b. Zinc isotopic variation of water and surface sediments from the German Elbe River. Science of The Total Environment 707, 135219.