coasts

MDPI

Communication

Indications from C:N:P Ratios in Surface Sediments along Land-to-Sea Gradients to Support Coastal Nutrient Management

Svenja Karstens [1,2,*], Jenny Friedrich [1], Jana K. Geuer [3], Katharina Grosser [4] and Jens Schneider von Deimling [1]

1 Marine Geophysics and Hydroacoustics, Institute of Geosciences, Kiel University, Olshausenstr. 40, 24118 Kiel, Germany
2 Center for Ocean and Society, Kiel University, Neufeldtstr. 10, 24118 Kiel, Germany
3 Max Planck Institute for Marine Microbiology, Celsiusstr. 1, 28359 Bremen, Germany
4 Institute for Ecosystem Research and Institute for Natural Resource Conversation, Kiel University, Olshausenstrasse 75, 24118 Kiel, Germany
* Correspondence: svenja.karstens@ifg.uni-kiel.de; Tel.: +49-431-880-6702

Abstract: Shallow, semi-enclosed coastal systems are particularly prone to eutrophication. Depending on local site conditions and historical nutrient legacies, sea-based measures might be necessary in addition to land-based nutrient removal. In this study, C:N:P ratios were combined with open-source bathymetric information and linked with the prevailing geomorphological and sedimentological regimes to gain insights into nutrient hotspots and understand their sources and fate in coastal waters. Land-based sediment samples were taken behind outlets at three sites in Eckernförde Bay (Baltic Sea), and complemented with ship-based sampling at locations approximately 8 m and 12 m water depth. The total carbon, nitrogen and phosphorus concentrations in surface sediments increased at deeper sites. This suggests that an increased downslope particle transport and deposition regime, based on local geomorphology, might influence nutrient hotspots to a larger extent than proximity to sources (e.g., outlets). Overall, the recorded C:N ratios (mean = 28.12) were closer to the ratio of terrestrial plants than those of marine phytoplankton, indicating allochthonous sources of organic matter.

Keywords: C:N:P ratios; nutrients; sediment; Baltic Sea

check for updates

Citation: Karstens, S.; Friedrich, J.; Geuer, J.K.; Grosser, K.; Schneider von Deimling, J. Indications from C:N:P Ratios in Surface Sediments along Land-to-Sea Gradients to Support Coastal Nutrient Management. *Coasts* **2023**, *3*, 414–425. https://doi.org/10.3390/coasts3040025

Academic Editor: Donald C. Barber

Received: 4 September 2023
Revised: 6 November 2023
Accepted: 23 November 2023
Published: 12 December 2023

1. Introduction

Shallow, semi-enclosed coastal systems, including lagoons and transitional waters, provide a variety of ecosystem services while being subject to various kinds of anthropogenic pressures at the same time [1]. Eutrophication, defined as the increased rate of primary production and accumulation of organic matter, remains a lasting challenge in these ecologically and economically important ecosystems [1,2]. Eutrophication results from excess inputs of nitrogen and phosphorus. However, in semi-enclosed systems, the problem is aggravated by enhanced water residence time [3,4]. The resulting algal blooms limit light penetration and reduce water transparency, and adverse impacts of eutrophication can range from the die-off of submerged vegetation and the development of anoxic zones to mass fish mortality [5]. Oxygen depletion is intensified if calm and warm conditions prevail and mixing through waves, currents or turbulence is low [6–8].

In order to reduce nutrient loads and manage coastal water systems, it is necessary to identify the nutrients' origins, i.e., allochthonous or autochthonous [9,10], and adjust potential mitigation measures accordingly. In shallow, semi-enclosed coastal systems, the sediment surface area to water volume ratio is high. Major biogeochemical processes take place at the water–sediment interface, and sediments are sensitive components that can act as triggers for processes in the water column [1,11]. However, the monitoring focus remains often on the water column and less on the sediment. Yet, sediment data, in particular, could be helpful in gaining a better understanding of system dynamics. The ratios of carbon, nitrogen and phosphorus have been widely used as source indicators of organic matter in a variety of coastal waters with salinity gradients, e.g., [10,12–14]. Redfield et al. (1963) [15] showed that marine phytoplankton has a C:N ratio of 6.6:1 and a C:P ratio of 106:1. In contrast to this, C:N ratios for terrestrial plants with soft tissue range from 10:1 to 110:1 and C:P ratios range from 300:1 to 1300:1 [16]. Stable isotopic analyses are another important source of information beyond elemental ratios that could reduce uncertainties regarding nutrient sources. However, decision-makers must weigh cost-benefit analyses that include individual financial feasibility and the availability of laboratory equipment. Thus, simple information on nutrient concentrations in sediments and their ratio in combination with bathymetric data could be a first step in supporting coastal nutrient management. The geomorphology and hydrodynamic environments impact land–sea material transport processes. Fine-grained particles, often richer in phosphorus and organic matter, tend to be transported in suspension and settle in deeper, quieter areas [17].

The objectives of this study are (1) to determine total phosphorus (P), total nitrogen (N) and total carbon (C) concentrations in surface sediments of a shallow, semi-enclosed coastal system along the Baltic Sea (Eckernförde Bay), (2) to characterize C:N:P ratios along land-to-sea transects, and (3) to derive indications for potential nutrient hotspot areas from bathymetric data. The goal is to gain first insights into land-to-sea trends and approach the question of whether autochthonous or allochthonous sources are dominant in this transitional waterbody.

2. Materials and Methods

2.1. Study Site

Eutrophication and hypoxia remain major environmental challenges in the Baltic Sea region [18]. The Baltic Sea is a geologically young, non-tidal shallow sea with an average depth of 52 m [19–21]. It is a brackish sea with strong salinity gradients from west to east, lowering the biodiversity towards the east [22]. Residence time for the water in the Baltic is long (~35 years) and sporadic inflows of saline and oxygen-rich water from the North Sea are particularly important for bottom water conditions [23,24]. Morphological shaping during the last glaciation resulted in the formation of shallow bays, lagoons and estuaries along the German coast [25]. This study focuses on Eckernförde Bay in Schleswig-Holstein, Germany, and investigates carbon, nitrogen and phosphorus nutrient concentrations along land-to-sea gradients behind three outlets: Hemmelmarker See, Goossee and Aschauer Lagune (Figure 1). As a result of shore-parallel sediment transport, spit formation in Eckernförde Bay started and former lagoons, like the Hemmelmarker See and the Goossee, were cut off from Baltic influences [26]. The sizes of the catchment areas are 7.34 km^2 for the Hemmelmarker See, 11.61 km^2 for the Goossee and 44.7 km^2 for the Aschauer Lagune [27,28]. All sites suffer from eutrophication [26], and outlets are still a major pathway for phosphorus inputs [29]. Another important nutrient pathway in the region is groundwater inflow [29,30] and more than 22% of the seafloor of Eckernförde Bay is affected by freshwater and active fluid venting [31]. Major phytoplankton blooms in Eckernförde Bay generally occur in early spring and autumn, while minor blooms are observed during summer [32–34]. Eckernförde Bay also suffers from seasonal hypoxia and associated fish kills [35].

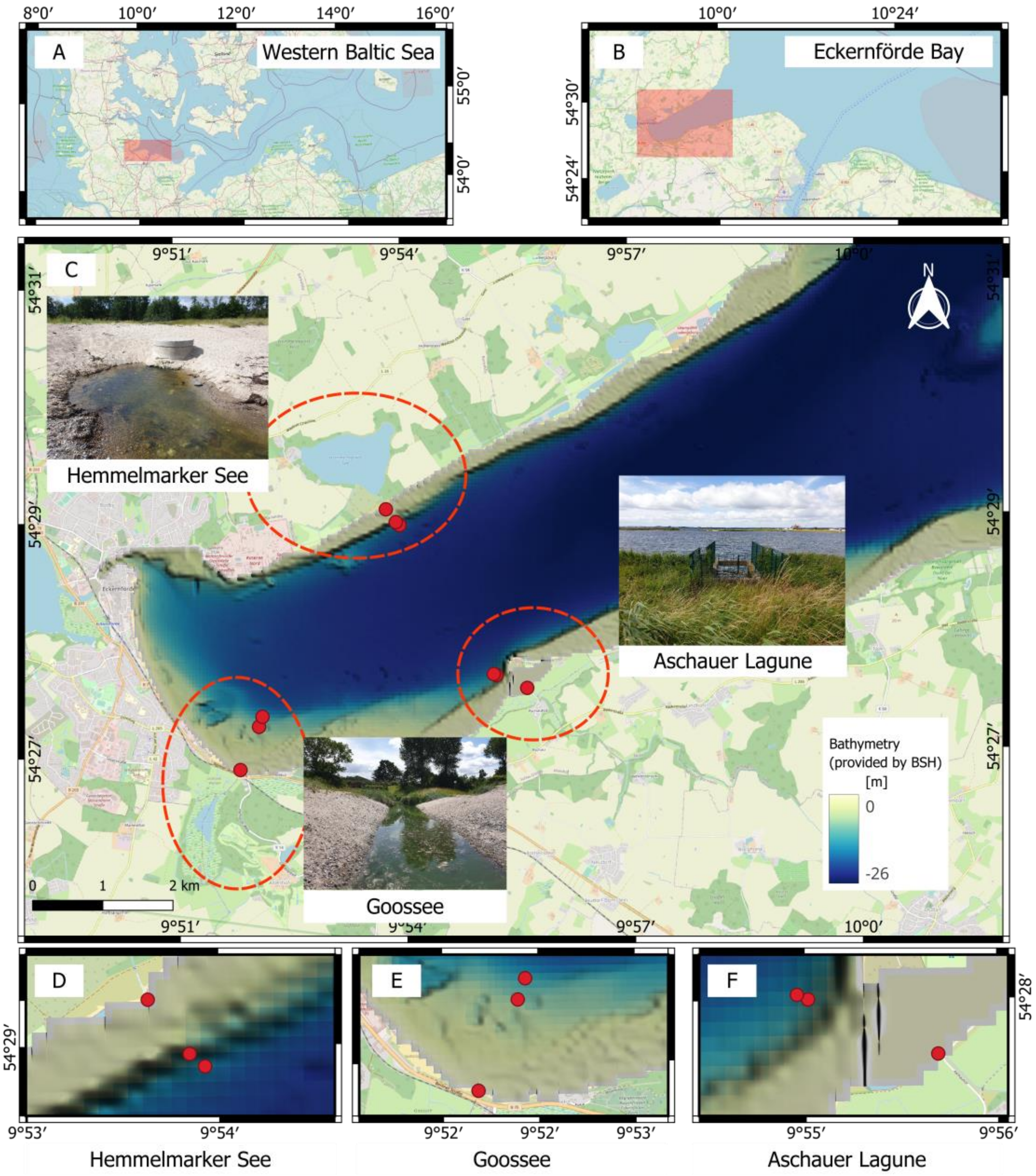

Figure 1. Overview of study sites. Sampling (red dots) took place along land-to-sea transects at Eckernförde Bay, a shallow, semi-enclosed coastal water system in the Baltic Sea (**A**,**B**). Surface sediments were taken directly behind the outlets of the Goossee, the Hemmelmarker See and Aschauer Lagune (3 replicates each) at shallow water depths (<8 m depth, 3 replicates each) and a little deeper (<12 m depth, 3 replicates each). Photos in (**C**) show outlets. Bathymetry with a 10 m resolution (**D**–**F**) was provided by the Federal Maritime and Hydrographic Agency of Germany (German: Bundesamt für Seeschifffahrt und Hydrographie, BSH). Background maps were provided by Open Street Map.

2.2. Sediment Sampling Taking into Consideration Local Bathymetry

Surface sediment samples were taken along land-to-sea gradients in Eckernförde Bay at three sites: (1) the outlet Hemmelmarker See, (2) the outlet Goossee and (3) the outlet Aschauer Lagune (Figure 1). At each site, samples were taken behind the outlet (3 replicates), in <8 m water depth (3 replicates) and in <12 m water depth (3 replicates), resulting in a total of 27 samples. Ship-based sediment samples during R/V Littorina cruise L1022a were taken with a Van Veen Grab on 6 July 2022. In addition, freely available bathymetry provided by the Federal Maritime and Hydrographic Agency of Germany was used to choose suitable sites at the transition from very shallow to deeper waters (Figure 1D–F). This approach is transferable to other coastal waters, and bathymetric data inter alia for European waters is available at https://emodnet.ec.europa.eu/en/bathymetry (accessed on 20 April 2023), and for U.S. waters at https://woodshole.er.usgs.gov/data/submergedlands/ (accessed on 20 April 2023). Furthermore, the National Oceanic and Atmospheric Administration is the primary source of bathymetric data for the world's oceans (https://www.ncei.noaa.gov/products/seafloor-mapping, accessed on 20 April 2023). Physical description of mean grain size and sorting (after Folk and Ward 1957) based on data from the Federal Maritime and Hydrographic Agency of Germany is for all sites fine silt, moderately sorted. Overall, for the Eckernförde Bay, a wave-dominated basin, the grain size distribution in surface sediments follows the bathymetry with medium to fine sands on slopes and marine mud below the wave base [36]. For land-based sampling on 10 July 2022, a Hydrobios stainless-steel corer was used. All sampling sites were not vegetated (neither by seagrass nor by emergent or submerged macrophytes behind the outlets). The samples were sieved (<2 mm), dried at 40 °C and ground. The total carbon and total nitrogen were quantified by combustion in a CN Analyzer (Euro EA 3000). Samples were not treated with acid; thus, carbonates could contribute to the total carbon concentrations and we measured total carbon (not organic carbon). The total phosphorus was analyzed by photometric determination (Specord 50 Plus, Analytik Jena GmbH+Co. KG, Jena, Germany) of phosphorus based on DIN EN ISO 6878 after acid (HNO_3) microwave digestion (MARS 6). Following Qu et al., 2014 [37], the total carbon, nitrogen and phosphorus concentrations (mg kg^{-1}) were transformed to a unit of mmol kg^{-1} and C:N, C:P and N:P ratios were calculated as molar ratios rather than mass ratios.

2.3. Statistical Analysis

All statistical analyses were conducted in R version 4.1.3 (www.r-project.org, accessed on 20 April 2023). For the correlation matrix, Spearman's rank correlation coefficient was used as the data was not normally distributed and thus the preconditions for Pearson's correlation coefficient were not given (R package 'corrplot' [38]). The Kruskal–Wallis test was used to compare C, N and P concentrations and ratios within and across groups. This test is used when the requirements for an analysis of variance are not met. Pairwise group comparisons were conducted using the Wilcoxon test in a post-hoc analysis (p value adjustment method: Bonferroni).

3. Results

Overall, the total carbon, nitrogen and phosphorus concentrations are higher at deeper sites compared to land-based samples, with the highest values at the deep Aschau site and the lowest behind the outlet at the Aschauer Lagune (Table 1, Figure 2). Carbon, nitrogen and phosphorus concentrations are strongly correlated (Figure 3). Comparisons across groups showed that there were no significant differences between sites considering only the labels 'Aschau, Goossee, Hemmelmark' (Kruskal–Wallis test, p-values all >0.05). However, there were significant differences for C, N, P concentrations concerning the distance from land (p-values all <0.05). Pairwise post-hoc comparisons using the Wilcoxon rank sum test showed that, for C, N, P concentrations, the sites at <12 m water depths always differed significantly from the sites behind the outlets, whereas, for N, the site at <8 m water depth differed significantly from the land-based samples.

C:N:P ratios are shown in Table 2 (for comparison data, see Table 3). The Spearman's correlation matrix (Figure 3) shows a significant positive correlation between the C:P and N:P ratios, whereas the C:N ratio is negatively correlated with the N:P ratio. Regarding the ratios, there were no significant differences between sites nor between distances to land (Kruskal–Wallis test, p-values all >0.05). A sole exception was the N:P ratio where the sites at <12 m water depths differed significantly from the sites behind the outlets (Wilcoxon rank sum test, $p < 0.05$).

Table 1. Mean carbon, nitrogen and phosphorus concentrations with standard deviations for all sites sampled.

Site	Bathymetry	C [%]	N [%]	P [%]
Aschau	(behind outlet)	0.092 ± 0.018	0.009 ± 0.002	0.007 ± 0.001
Aschau	<8 m	2.970 ± 0.333	0.176 ± 0.016	0.046 ± 0.001
Aschau	<12 m	2.656 ± 0.119	0.119 ± 0.015	0.043 ± 0.002
Goossee	(behind outlet)	0.589 ± 0.034	0.013 ± 0.002	0.019 ± 0.001
Goossee	<8 m	0.093 ± 0.014	0.011 ± 0.002	0.016 ± 0.001
Goossee	<12 m	0.948 ± 0.073	0.038 ± 0.006	0.025 ± 0.004
Hemmelmark	(behind outlet)	0.405 ± 0.017	0.008 ± 0.001	0.022 ± 0.005
Hemmelmark	<8 m	1.271 ± 0.694	0.072 ± 0.026	0.029 ± 0.005
Hemmelmark	<12 m	1.865 ± 0.372	0.102 ± 0.015	0.041 ± 0.002

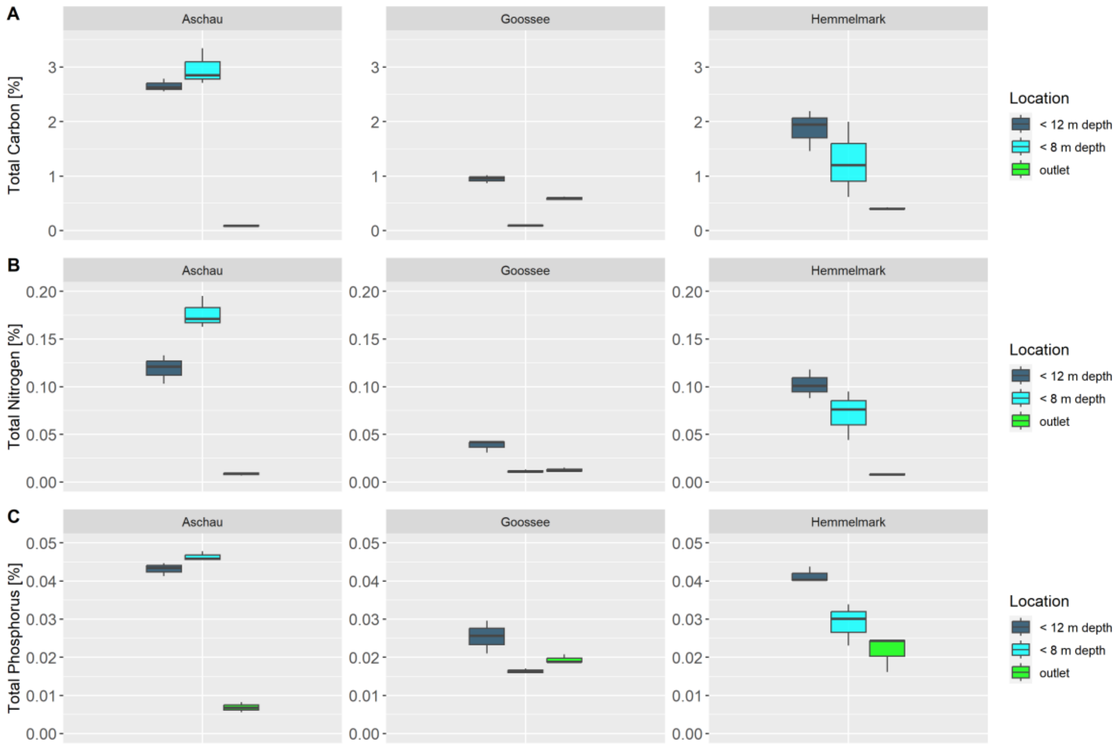

Figure 2. Total carbon (**A**), total nitrogen (**B**) and total phosphorus (**C**) concentrations [%] in surface sediments at three different sites (from left to right: Aschau, Goossee, Hemmelmark) and three different distances from the outlets at Eckernförder Bay, Baltic Sea. In each plot, the left box shows the most distanced location with <12 m water depth (dark blue), the middle box shows the site with water depths <8 m (turquoise) and the right box shows the sediment samples directly behind the outlets (green).

Table 2. Summary of sediment C, N and P stoichiometry in Eckernförder Bay, Baltic Sea. R_{CN} = Carbon: Nitrogen ratios, R_{CP} = Carbon: Phosphorus ratios, R_{NP} = Nitrogen: Phosphorus ratios, R_{CNP} = Carbon: Nitrogen: Phosphorus ratios. All ratios were calculated as molar ratios (atomic ratios) rather than mass ratios (cf. Qu et al., 2014).

Site	Bathymetry	R_{CN}	R_{CP}	R_{NP}	R_{CNP}
Aschau	(behind outlet)	12.50 ± 1.77	13.44 ± 0.54	2.85 ± 0.54	13.4:2.9:1
Aschau	<8 m	19.64 ± 0.79	63.96 ± 4.49	8.40 ± 0.45	63.9:8.4:1
Aschau	<12 m	26.16 ± 1.97	61.61 ± 2.15	6.11 ± 0.52	61.6:6.1:1
Goossee	(behind outlet)	55.34 ± 8.47	30.37 ± 2.14	1.45 ± 0.25	30.4:1.5:1
Goossee	<8 m	9.49 ± 0.31	5.66 ± 0.61	1.54 ± 0.13	5.7:1.5:1
Goossee	<12 m	29.13 ± 2.63	37.83 ± 3.99	3.35 ± 0.20	37.8:3.4:1

Table 2. *Cont.*

Site	Bathymetry	R_{CN}	R_{CP}	R_{NP}	R_{CNP}
Hemmelmark	(behind outlet)	59.74 ± 7.92	19.37 ± 3.52	0.87 ± 0.26	19.4:0.9:1
Hemmelmark	<8 m	19.67 ± 3.45	41.88 ± 13.28	5.36 ± 0.84	41.9:5.4:1
Hemmelmark	<12 m	21.39 ± 3.55	44.89 ± 6.05	5.46 ± 0.47	44.9:5.5:1

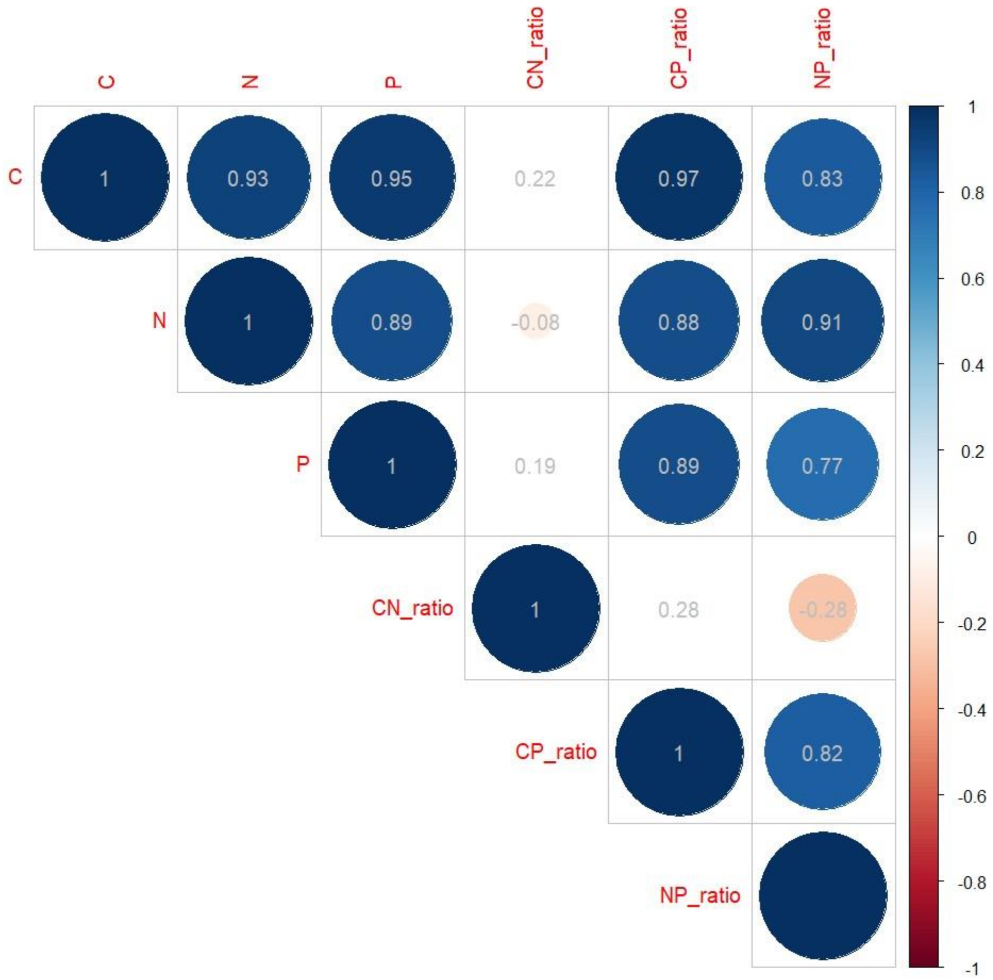

Figure 3. Correlation matrix (using Spearman's rank correlation coefficient). Numbers and size of circles represent correlation coefficients. Spaces with non-significant coefficients were left blank (confidence level of 0.95). R package corrplot was used (Wei and Simko 2021).

4. Discussion

4.1. Source and Fate of Nutrients

Total carbon, nitrogen and phosphorus concentrations in surface sediments at Eckernförde Bay increased at deeper sites compared to land-based samples behind outlets (Table 1). This suggests that oceanographic regimes and geomorphological structures might drive nutrient deposition instead of solely proximity to nutrient sources (e.g., outlets). The modelled residence time of water parcels at the sampled sites in Eckernförde Bay varies between 21 and 42 days depending on the season [35]. Bathymetry (Figure 1) helps to analyze the current geomorphology and to identify preferred mass transport pathways and deposition opportunities. Surface sediment distribution and mean grain size follow the bathymetry [36], and the deepest area of Bay (26–28 m), where we did not sample, is covered by mud [31]. Thus, nutrient and organic matter concentrations might even increase with increasing depth and decreasing sediment grain size. In the area under consideration, there are neither sufficiently accurate wave data nor sediment transport measurements available to make any statements about the annual mean sediment transport [26]. However, dominant, local sediment transport behind the three outlets is parallel to the shoreline with minor transport from land-to-sea at the Aschauer Lagune and the Hemmelmarker See but not at the Goossee [39]. This might explain why nutrient concentrations in surface sediments were always higher at the deeper sites of Aschau and Hemmelmark and why this signal was not as pronounced for Goossee. Nutrient loads in the watershed are still high and outlets represent a major nutrient source [29]. However, directly behind the outlets at all three sites, the high nutrient input is not reflected in the sediment. Possibly, nutrients are translocated away from sources and deposited under calmer conditions at deeper sites. A similar land-to-sea pattern was observed by Emeis et al., 2000 [40], where maximum phosphorus concentrations were recorded in the deeper waters of the Gulf of Gdańsk (Baltic Sea), whereas, close to the coast, phosphorus concentrations were much lower. The outlets of Aschau and Goossee are regulated by sluice gates, whereas water from the Hemmelmarker See is channelized below ground via a concrete culvert (see photos in Figure 1C). Flow velocity is enhanced in these strongly altered outlets compared to naturally developed river mouth estuaries with wetlands. Due to longer water residence times, wetlands are generally more efficient in nutrient retention than streams [41], and restoration measures should regard the hydrological connectivity of streams and wetlands in terms of nutrient retention [42].

Table 3. Comparison data for C:N:P ratios from studies conducted with surface sediments in coastal waters. Comparison data is listed in descending order based on C:N values. * Values averaged over all sites.

Study Site	R_{CN}	R_{CP}	R_{NP}	Source
Eckernförde Bay, Baltic Sea, Germany (coastal waters close to outlets)	28.1	35.5	3.9	This study *
Yellow River Delta, Yellow Sea, China (at farmland converted into wetland)	40.5	71.2	2.0	Qu et al., 2014 [37]
Yellow River Delta, Yellow Sea, China (at newly formed wetland)	26.5	42.6	1.6	Qu et al., 2014 [37]
Gulf of Trieste, Northern Adriatic Sea, Italy	13.3	563.0		Faganeli et al., 1988 [43]
Darss-Zingst-Bodden Chain, Baltic Sea, Germany (at reed fringe zone, Dabitz)	11.4	112.6	25.4	Karstens et al., 2016 [44]
Bothnian Sea, Baltic Sea, Sweden	11.4	78.0	6.8	Carman and Cederwall 2001 [45]
Bothnian Bay, Baltic Sea, Sweden	11.2	90.6	8.1	Carman and Cederwall 2001 [45]
Nakaumi, coastal lagoon, Sea of Japan, Japan	10.2	143.0	14.2	Yamamuro 2000 [46]
Shinji, coastal lagoon, Sea of Japan, Japan	9.6	89.0	9.3	Yamamuro 2000 [46]
Gulf of Finland, Baltic Sea, Finland	9.6	68.7	7.2	Carman and Cederwall 2001 [45]
Pojo Bay, Baltic Sea, Finland	9.6	51.0		Heiskanen et al., 1999 [47]
Shallow part of the Gulf of Gdansk, Baltic Sea, Poland	9.3	82.2		Łukawska-Matuszewska and Bolałek 2008 [48]
Baltic proper, Baltic Sea, Sweden	9.2	118.8	12.9	Carman and Cederwall 2001 [45]
Pomeranian Bight, Baltic Sea	8.7	93.0	10.7	Emeis et al., 2000 [40]
Darss-Zingst-Bodden Chain, Baltic Sea, Germany (at reed fringe zone, Michaelsdorf)	8.6	145.7	43.9	Karstens et al., 2016 [44]
Deeper part of the Gulf of Gdansk, Baltic Sea, Poland	8.2	560.7		Łukawska-Matuszewska and Bolałek 2008 [48]
Daya Bay, South China Sea, China	7.7	49.7	6.5	Chen et al., 2021 [49]

Nutrients in coastal waters are derived from a variety of sources, including allochthonous input from the watershed via outlets or autochthonous sources from planktonic and benthic primary production [46]. Organic matter degradation enhances oxygen depletion and can amplify eutrophication problems; thus, identification of potential sources is important for managing coastal water systems [47]. C:N ratios at our study sites were highest close to the outlets of the Goossee and Hemmelmarker See, which may be attributed to a higher proportion of land-derived organic matter (cf. [40]). Overall, the recorded C:N ratios were closer to the ratio of terrestrial plants (10–100, [16]) than those of marine phytoplankton (6.6:1, [15]) for both sea-based and land-based samples. Comparison data from surface sediments in other shallow, semi-enclosed coastal systems (Table 3) show a wide range of C:N ratios from 8.2 up to 40.5. Our C:N:P ratios were closest to those of newly formed wetland sites in the Yellow River Delta, underlining the terrestrial influence. However, this signal could not be observed for C:P or N:P ratios (Table 2). Thus, the interpretation of C:N:P ratios as a proxy to explain the source of organic matter (autochthonous vs. allochthonous) is more complex. Phosphorus is a redox-sensitive element: Under anoxic conditions, bacterial sulphate reduction stimulates iron reduction and leads to phosphorus release from the sediment to the water column [50–53]. The transition from oxic to anoxic conditions at deeper, calmer sites, and fine-grained sediments and the associated redox-sensitive phosphate release could result in increasing N:P and C:P rations, as observed at our study sites in the deeper areas. Anoxia and bacterial sulphate reduction prevail in most of the sediments in Eckernförde Bay [54]. A similar pattern was detected in the Gdansk and the Gotland Basin of the Baltic Sea, where increases in C:P sediment ratios indicated phosphate losses from the sediment ([40,48]; Table 3). The release of phosphorus from anoxic sediments in the deeper Baltic Sea like the Gotland Basin was identified as a major source of phosphorus [40]. Our ability to control this driver of re-eutrophication is limited as anoxia in the deeper Baltic Sea is primarily influenced by salt water inflows from the North Sea [55]. The results of this study show that the problem of phosphorus reflux might not be limited to very deep areas but could also occur in coastal waters, which require different management options.

4.2. Management Implications

A remarkable long-term time series station in Eckernförde Bay (Boknis Eck) provides a record of oxygen, nutrient and chlorophyll-a concentrations in the water column since 1957. Bottom water oxygen concentration continues to decline, although measured nutrient and chlorophyll-a concentrations decreased [56]. It is argued that hypoxic conditions in Eckernförde Bay are correlated with the high variability in wind-driven ventilation rather than with a high variability in local respiration [35]. However, measurements at Boknis Eck are conducted monthly and only in the water column: event-based phosphorus pulses from anoxic sediments could be missed and thus eutrophication dynamics would be misinterpreted. In the case that phosphorus release from anoxic sediments is a significant source and driver of re-eutrophication, sea-based nutrient reduction measures would be needed in addition to land-based measures.

For coastal waters, sea-based mitigation measures (also known as an 'end-of-pipe solution') have been actively debated in recent years, e.g., [57–59]. Sea-based mitigation measures are usually differentiated into hydrological engineering (e.g., manipulating water residence time), geoengineering (e.g., aluminum injections in sediments) and ecological engineering (e.g., mussel, algae or macrophyte culture) [60]. Ecological interventions that generate habitats, such as the restoration of *Zostera marina* meadows or creating reefs as habitats for *Fucus* spp., target not only nutrient reduction but offer other co-benefits like carbon storage or wave attenuation [61]. The land–sea interface should be at the center of restoration strategies. The connectivity of streams and their wetlands plays an important part in the nutrient retention capacity [62]. Technological structures that restrict the ecological connectivity between streams and wetlands, such as pipes or culverts, need to be removed. Near-natural watercourse development and estuary formation with open coastal wetlands should be initiated in order to partially restore biogeochemical functioning [63]. Both seagrass meadows (*Zostera marina*) as well as coastal reed beds (*Phragmites australis*) are typical Baltic ecotones, also found along the Eckernförde Bay, that link terrestrial and aquatic ecosystems [64,65]. Land- and sea-based restoration actions are always connected due to reciprocal matter exchange and management of vegetative systems should be a centerpiece not only with regard to biodiversity and blue carbon debates but also with respect to eutrophication mitigation. Nutrient concentrations in surface sediments and C:N:P ratios together with bathymetric data are first steps to approaching the question of source and fate of organic matter and to identifying restoration hotspots. However, resolution in this study was limited to 10 m and a higher resolution would be more suitable to precisely identify local depositional regimes and sedimentation sinks. If possible, studies using multiple tracers, such as elemental ratios in combination with stable isotopic signatures, should be added to reduce uncertainties [16].

5. Conclusions

Our study results showed that total carbon, nitrogen and phosphorus concentrations in surface sediments at Eckernförde Bay increase at deeper sites compared to land-based samples behind stream outlets. High nutrient loads in the watershed and nutrient export via outlets are not reflected in the sediment directly behind the outlets of the Goossee, Hemmelmarker See and Aschauer Lagune. Nutrients might be translocated away from sources and deposited under calmer conditions at sink sites. Overall, the recorded C:N ratios were closer to the ratio of terrestrial plants than those of marine phytoplankton, indicating allochthonous sources of organic matter. The interpretation of C:P or N:P ratios is more complex: Phosphorus is a redox-sensitive element and is released again from sediments under anoxic conditions. The transition from oxic to anoxic conditions at deeper, calmer, finer-grained sites and the associated redox-sensitive phosphate release could result in increasing N:P and C:P ratios. Thus, the problem of legacy phosphorus in the Baltic is not limited to very deep areas like the Gotland Basin. This could be regarded as a chance to test sea-based nutrient removal measures, which might be more realistic and more feasible in shallow waters than deep waters. Merging interdisciplinary datasets supports the identification of suitable sites for different restoration strategies, such as the creation of *Phragmites* wetlands at restored estuaries and *Zostera marina* meadows in shallow waters or reefs in deeper areas as habitats for *Fucus* spp. Linking regional, high-resolution land-to-sea bathymetry with hydrodynamic data in the next phase could provide a deeper understanding of geomorphological structures, sediment transport pathways and local sedimentation sinks.

Author Contributions: S.K. developed the article concept, took care of the data collection and did most of the article writing. J.F., J.K.G. and K.G. supported the data collection, data analyses and commented on the paper. J.S.v.D. acquired project funding and supported the article concept development and writing. All authors have read and agreed to the published version of the manuscript.

Funding: This research is part of the following projects: (1) sea4soCiety—Searching for solutions for Carbon-sequestration in coastal ecosystems (Federal Ministry of Education and Research of Germany (BMBF), CDRmare, project number 03V01653) and (2) Multi-dimensional Ocean Hazard Risk Assessment (allocation of funds from the state of Schleswig-Holstein for the measure ensuring top-level interdisciplinary and transdisciplinary research in the marine sciences in Kiel, project number FON-2020-04). We acknowledge financial support by Land Schleswig-Holstein within the funding programme Open Access Publikationsfonds.

Data Availability Statement: All C:N:P data are directly presented in the results section of this study. Publicly available bathymetric datasets were analyzed in this study. This data can be requested from the Federal Maritime and Hydrographic Agency of Germany.

Acknowledgments: We would like to thank the R/V Littorina captain and his crew as well as Kiel Marine Science (KMS), which performs a central coordinating role for all researchers at Kiel University in natural sciences, the humanities and social sciences whose works concern oceans, coasts and their interaction with humanity.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Newton, A.; Icely, J.; Cristina, S.; Brito, A.; Cardoso, A.C.; Colijn, F.; Riva, S.D.; Gertz, F.; Hansen, J.W.; Holmer, M.; et al. An overview of ecological status, vulnerability and future perspectives of European large shallow, semi-enclosed coastal systems, lagoons and transitional waters. *Estuar. Coast. Shelf Sci.* **2014**, *140*, 95–122. [CrossRef]
2. Rabalais, N.N.; Turner, R.E.; Díaz, R.J.; Justić, D. Global change and eutrophication of coastal waters. *ICES J. Mar. Sci.* **2009**, *66*, 1528–1537. [CrossRef]
3. Cloern, J.E. Our evolving conceptual model of the coastal eutrophication problem. *Mar. Ecol. Prog. Ser.* **2001**, *210*, 223–253. [CrossRef]
4. Lloret, J.; Marín, A.; Marín-Guirao, L. Is coastal lagoon eutrophication likely to be aggravated by global climate change? *Estuar. Coast. Shelf Sci.* **2008**, *78*, 403–412. [CrossRef]
5. Chislock, M.F.; Doster, E.; Zitomer, R.A.; Wilson, A.E. Eutrophication: Causes, consequences, and controls in aquatic ecosystems. *Nat. Educ. Knowl.* **2013**, *4*, 10.
6. Kemp, W.M.; Testa, J.M.; Conley, D.J.; Gilbert, D.; Hagy, J.D. Temporal responses of coastal hypoxia to nutrient loading and physical controls. *Biogeosciences* **2009**, *6*, 2985–3008. [CrossRef]
7. Berg, P.; Røy, H.; Janssen, F.; Meyer, V.; Jørgensen, B.B.; Huettel, M.; de Beer, D. Oxygen uptake by aquatic sediments measured with a novel non-invasive eddy-correlation technique. *Mar. Ecol. Prog. Ser.* **2003**, *261*, 75–83. [CrossRef]
8. Karstens, S.; Buczko, U.; Glatzel, S. Phosphorus storage and mobilization in coastal *Phragmites* wetlands: Influence of local-scale hydrodynamics. *Estuar. Coast. Shelf Sci.* **2015**, *164*, 124–133. [CrossRef]
9. Krull, E.; Haynes, D.; Lamontagne, S.; Gell, P.; McKirdy, D.; Hancock, G.; McGowan, J.; Smernik, R. Changes in the chemistry of sedimentary organic matter within the Coorong over space and time. *Biogeochemistry* **2009**, *92*, 9–25. [CrossRef]
10. Yamamuro, M.; Kamiya, H. Elemental (C, N, P) and isotopic ($^{\delta 13}$C, $^{\delta 15}$N) signature of primary producers and their contribution to the organic matter in coastal lagoon sediment. *Landsc. Ecol. Eng.* **2014**, *10*, 65–75. [CrossRef]
11. Kjerfve, B. Chapter 1 Coastal Lagoons. *Elsevier Oceanogr. Ser.* **1994**, *60*, 1–8.
12. de la Lanza-Espino, G.; Flores-Verdugo, F.J.; Hernandez-Pulido, S.; Penié-Rodríguez, I. Concentration of nutrients and C:N:P rations in surface sediments of a tropical coastal lagoon complex affected by agricultural runoff. *Univ. Cienc.* **2011**, *27*, 145–155.
13. Nasir, A.; Lukman, M.; Tuwo, A.; Hatta, M.; Tambaru, R. The use of C/N ratio in assessing the influence of land-based material in Coastal Water of South Sulawesi and Spermonde Archipelago, Indonesia. *Front. Mar. Sci.* **2016**, *3*, 266. [CrossRef]
14. Meng, L.; Qu, F.; Bi, X.; Xia, J.; Li, Y.; Wang, X.; Yu, J. Elemental stoichiometry (C, N, P) of soil in the Yellow River Delta nature reserve: Understanding N and P status of soil in the coastal estuary. *Sci. Total Environ.* **2021**, *751*, 141737. [CrossRef]
15. Redfield, A.C.; Ketchum, B.H.; Richards, F.A. The influence of organisms on the composition of seawater. In *The Sea*; Hill, M.N., Ed.; Wiley: Chichester, UK, 1963; Volume 2, pp. 26–77.
16. Ruttenberg, K.C.; Goñi, M.A. Phosphorus distribution, C:N:P ratios, and $\delta^{13}C_{oc}$ in arctic, temperate, and tropical coastal sediments: Tools for characterizing bulk sedimentary organic matter. *Mar. Geol.* **1997**, *139*, 123–145. [CrossRef]
17. Davidson-Arnott, R.; Bauer, B.; Houser, C. *Introduction to Coastal Processes and Geomorphology*; Cambridge University Press: Cambridge, UK, 2019.
18. Reusch, T.B.H.; Dierking, J.; Andersson, H.C.; Bonsdorff, E.; Carstensen, J.; Casini, M.; Czajkowski, M.; Hasler, B.; Hinsby, K.; Hyytiäinen, K.; et al. The Baltic Sea as a time machine for the future coastal ocean. *Sci. Adv.* **2018**, *4*, eaar8195. [CrossRef]
19. Hupfer, P. *Die Ostsee—Kleines Meer mit Großen Problemen*; Borntraeger: Stuttgart, Germany, 2010.
20. HELCOM. Ecosystem Health of the Baltic Sea 2003–2007: HELCOM Initial Holistic Assessment. In *Baltic Sea Environment Proceedings*; Baltic Marine Environment Protection Commission: Helsinki, Finnland, 2010; Volume 122, p. 2010.
21. Snoeijs-Leijonmalm, P.; Andrén, E. Why is the Baltic Sea so special to live in? In *Biological Oceanography of the Baltic Sea*; Springer: Dordrecht, The Netherlands, 2017; pp. 23–84.
22. Elmgren, R.; Hill, C. Ecosystem function at low biodiversity—The Baltic example. In *Marine Biodiversity: Patterns and Processes*; Cambridge University Press: Cambridge, UK, 1997; pp. 319–336.
23. Seibold, E.; Exon, N.; Hartmann, M.; Kögler, F.C.; Krumm, H.; Lutze, G.F.; Newton, R.S.; Werner, F. *Marine Geology of Kiel Bay*; Kramer, Geologisch-Paläontologisches Institut Kiel: Kiel, Germany, 1971.
24. Kullenberg, G.; Jacobsen, T.S. The Baltic Sea: An outline of its physical oceanography. *Mar. Pollut. Bull.* **1981**, *12*, 183–186. [CrossRef]
25. Sterr, H. Assessment of vulnerability and adaptation to sea-level rise for the coastal zone of Germany. *J. Coast. Res.* **2008**, *24*, 380–393. [CrossRef]
26. Ahrendt, K. *Untersuchungen Möglicher Standorte für Ein Künstliches Hartsubstrat als Tauchrevier in der Eckernförder Bucht*; Contract work for the city of Eckernförde; Büro für Umwelt und Küste: Kiel, Germany, 2006.
27. MELUR. Managementplan für das Fauna-Flora-Habitat-Gebiet "DE-1526-391 Südküste der Eckernförder Bucht und vorgelagerte Flachgründe" Teilbereich "Ostseeflächen" sowie Managementplan für das Europäische Vogelschutzgebiet "DE 1525-491 Eckernförder Bucht mit Flachgründen". 2016. Available online: https://www.schleswig-holstein.de/DE/fachinhalte/S/schutzgebiete/ffh/FFHSchutzgebiete.html?nn=b438bc76-d74c-40b3-944d-b550def6a663 (accessed on 2 July 2023).
28. MEKUN. Seen Schleswig-Holstein. 2023. Available online: https://umweltanwendungen.schleswig-holstein.de/nuis/wafis/seen/seenanzeige.php?see=hemmelmarker&alle=ja (accessed on 2 July 2023).

29. Tetzlaff, B.; Keller, L.; Kuhr, P.; Kreins, P.; Kunkel, R.; Wendland, F. Räumlich differenzierte Quantifizierung der Nährstoffeinträge ins Grundwasser und in die Oberflächengewässer Schleswig-Holsteins unter Anwendung der Modellkombination RAUMIS-GROWA-WEKU-MEPhos. Endbericht zum Forschungsprojekt, Forschungszentrum Jülich. 2017. Available online: https://www.schleswig-holstein.de/mm/downloads/Fachinhalte/Wasserrahmenrichtlinie/endberichtNaehrstoffmodellierung.pdf (accessed on 2 July 2023).
30. Kreuzburg, M.; Scholten, J.; Hsu, F.H.; Liebetrau, V.; Sültenfuß, J.; Rapaglia, J.; Schlüter, M. Submarine Groundwater Discharge-Derived Nutrient Fluxes in Eckernförde Bay (Western Baltic Sea). *Estuar. Coasts* **2023**, *46*, 1190–1207. [CrossRef]
31. Schlüter, M.; Sauter, E.J.; Andersen, C.E.; Dahlgaard, H.; Dando, P.R. Spatial distribution and budget for submarine groundwater discharge in Eckernförde Bay (Western Baltic Sea). *Limnol. Oceanogr.* **2004**, *49*, 157–167. [CrossRef]
32. Smetacek, V. The annual cycle of Kiel Bight plankton: A long-term analysis. *Estuaries* **1985**, *8*, 145–157. [CrossRef]
33. Bange, H.W.; Bergmann, K.; Hansen, H.P.; Kock, A.; Koppe, R.; Malien, F.; Ostrau, C. Dissolved methane during hypoxic events at the Boknis Eck time series station (Eckernförde Bay, SW Baltic Sea). *Biogeosciences* **2010**, *7*, 1279–1284. [CrossRef]
34. Steinle, L.; Maltby, J.; Treude, T.; Kock, A.; Bange, H.W.; Engbersen, N.; Zopfi, J.; Lehmann, M.F.; Niemann, H. Effects of low oxygen concentrations on aerobic methane oxidation in seasonally hypoxic coastal waters. *Biogeosciences* **2017**, *14*, 1631–1645. [CrossRef]
35. Dietze, H.; Löptien, U. Retracing Hypoxia in Eckernförde Bight (Baltic Sea). *Biogeosciences* **2021**, *18*, 4243–4264. [CrossRef]
36. Jensen, J.B.; Kuijpers, A.; Bennike, O.; Laier, T.; Werner, F. New geological aspects for freshwater seepage and formation in Eckernförde Bay, Western Baltic. *Cont. Shelf Res.* **2002**, *22*, 2159–2173. [CrossRef]
37. Qu, F.; Yu, J.; Du, S.; Li, Y.; Lv, X.; Ning, K.; Wu, H.; Meng, L. Influences of anthropogenic cultivation on C, N and P stoichiometry of reed-dominated coastal wetlands in the Yellow River Delta. *Geoderma* **2014**, *235*, 227–232. [CrossRef]
38. Wei, T.; Simko, V.; R Package 'Corrplot': Visualization of a Correlation Matrix. (Version 0.92). 2021. Available online: https://github.com/taiyun/corrplot (accessed on 2 July 2023).
39. Sterr, H. *Das Ostseelitoral von Flensburg bis Fehmarnsund: Formungs- und Entwicklungsdynamik einer Küstenlandschaft*; Habilitation treatise; University of Kiel: Kiel, Germany, 1988; 465p.
40. Emeis, K.C.; Struck, U.; Leipe, T.; Pollehne, F.; Kunzendorf, H.; Christiansen, C. Changes in the C, N, P burial rates in some Baltic Sea sediments over the last 150 years—Relevance to P regeneration rates and the phosphorus cycle. *Mar. Geol.* **2000**, *167*, 43–59. [CrossRef]
41. Saunders, D.L.; Kalff, J. Nitrogen retention in wetlands, lakes and rivers. *Hydrobiologia* **2001**, *443*, 205–212. [CrossRef]
42. Rücker, K.; Schrautzer, J. Nutrient retention function of a stream wetland complex—A high-frequency monitoring approach. *Ecol. Eng.* **2010**, *36*, 612–622. [CrossRef]
43. Faganeli, J.; Malej, A.; Pezdic, J.; Malacic, V. C:N:P ratios and stable c-isotopic ratios as indicators of sources of organic-matter in the Gulf of Trieste (Northern Adriatic). *Oceanol. Acta* **1988**, *11*, 377–382.
44. Karstens, S.; Buczko, U.; Jurasinski, G.; Peticzka, R.; Glatzel, S. Impact of adjacent land use on coastal wetland sediments. *Sci. Total Environ.* **2016**, *550*, 337–348. [CrossRef]
45. Carman, R.; Cederwall, H. Sediments and macrofauna in the Baltic Sea—Characteristics, nutrient contents and distribution. In *A Systems Analysis of the Baltic Sea*; Springer: Berlin/Heidelberg, Germany, 2001; pp. 289–327.
46. Yamamuro, M. Chemical tracers of sediment organic matter origins in two coastal lagoons. *J. Mar. Syst.* **2000**, *26*, 127–134. [CrossRef]
47. Heiskanen, A.S.; Tallberg, P. Sedimentation and particulate nutrient dynamics along a coastal gradient from a fjord-like bay to the open sea. In *Biological, Physical and Geochemical Features of Enclosed and Semi-enclosed Marine Systems, Proceedings of the Joint BMB 15 and ECSA 27 Symposium, Åland Islands, Finland, 9–13 June 1997*; Springer: Dordrecht, The Netherlands, 1999; pp. 127–140.
48. Łukawska-Matuszewska, K.; Bolałek, J. Spatial distribution of phosphorus forms in sediments in the Gulf of Gdańsk (southern Baltic Sea). *Cont. Shelf Res.* **2008**, *28*, 977–990. [CrossRef]
49. Chen, D.; Ke, Z.; Tan, Y. Distribution of C/N/P stoichiometry in suspended particulate matter and surface sediment in a bay under serious anthropogenic influence: Daya Bay, China. *Environ. Sci. Pollut. Res.* **2021**, *28*, 29177–29187. [CrossRef] [PubMed]
50. Giordani, G.; Bartoli, M.; Cattadori, M.; Viaroli, P. Sulphide release from anoxic sediments in relation to iron availability and organic matter recalcitrance and its effects on inorganic phosphorus recycling. *Hydrobiologia* **1996**, *329*, 211–222. [CrossRef]
51. Correll, D.L. The role of phosphorus in the eutrophication of receiving waters: A review. *J. Environ. Qual.* **1998**, *27*, 261–266. [CrossRef]
52. Heijs, S.K.; Azzoni, R.; Giordani, G.; Jonkers, H.M.; Nizzoli, D.; Viaroli, V.; van Gemerden, H. Sulphide-induced release of phosphate from sediments of coastal lagoons and the possible relation to the disappearance of *Ruppia* sp. *Aquat. Microb. Ecol.* **2000**, *23*, 85–95. [CrossRef]
53. Zhang, Y.; Song, C.; Ji, L.; Liu, Y.; Xiao, J.; Cao, X.; Zhou, Y. Cause and effect of N/P ratio decline with eutrophication aggravation in shallow lakes. *Sci. Total Environ.* **2018**, *627*, 1294–1302. [CrossRef]
54. Whiticar, M.J. Diagenetic relationships of methanogenesis, nutrients, acoustic turbidity, pockmarks and freshwater seepages in Eckernförde Bay. *Mar. Geol.* **2002**, *182*, 29–53. [CrossRef]
55. Matthäus, W.; Ulrich Lass, H. The recent salt inflow into the Baltic Sea. *J. Phys. Oceanogr.* **1995**, *25*, 280–286. [CrossRef]

56. Lennartz, S.T.; Lehmann, A.; Herrford, J.; Malien, F.; Hansen, H.P.; Biester, H.; Bange, H.W. Long-term trends at the Boknis Eck time series station (Baltic Sea), 1957–2013: Does climate change counteract the decline in eutrophication? *Biogeosciences* **2014**, *11*, 6323–6339. [CrossRef]
57. Ringbom, H.; Bohman, B.; Ilvessalo, S. Combatting eutrophication in the Baltic Sea: Legal aspects of sea-based engineering measures. *Brill Res. Perspect. Law Sea* **2018**, *2*, 1–96. [CrossRef]
58. Boesch, D.F. Barriers and bridges in abating coastal eutrophication. *Front. Mar. Sci.* **2019**, *6*, 123. [CrossRef]
59. Ritzenhofen, L.; Schumacher, J.; Karstens, S.; Schernewski, G. Ecosystem service assessments within the EU water framework directive: Marine mussel cultivation as a controversial measure. *Appl. Sci.* **2022**, *12*, 1871. [CrossRef]
60. Duarte, C.M.; Krause-Jensen, D. Intervention options to accelerate ecosystem recovery from coastal eutrophication. *Front. Mar. Sci.* **2018**, *5*, 470. [CrossRef]
61. Duarte, C.M.; Losada, I.J.; Hendriks, I.E.; Mazarrasa, I.; Marbà, N. The role of coastal plant communities for climate change mitigation and adaptation. *Nat. Clim. Chang.* **2013**, *3*, 961–968. [CrossRef]
62. Trepel, M.; Kluge, W. WETTRANS: A flow-path-oriented decision-support system for the assessment of water and nitrogen exchange in riparian peatlands. *Hydrol. Process.* **2004**, *18*, 357–371. [CrossRef]
63. Jickells, T.D.; Andrews, J.E.; Parkes, D.J.; Suratman, S.; Aziz, A.A.; Hee, Y.Y. Nutrient transport through estuaries: The importance of the estuarine geography. *Estuar. Coast. Shelf Sci.* **2014**, *150*, 215–229. [CrossRef]
64. Andreu, V.; Gimeno-García, E.; Pascual, J.A.; Vazquez-Roig, P.; Picó, Y. Presence of pharmaceuticals and heavy metals in the waters of a Mediterranean coastal wetland: Potential interactions and the influence of the environment. *Sci. Total Environ.* **2016**, *540*, 278–286. [CrossRef]
65. Vazquez-Roig, P.; Andreu, V.; Onghena, M.; Blasco, C.; Picó, Y. Assessment of the occurrence and distribution of pharmaceuticals in a Mediterranean wetland (L'Albufera, Valencia, Spain) by LC-MS/MS. *Anal. Bioanal. Chem.* **2011**, *400*, 1287–1301. [CrossRef]