Distribution of Geochemical Species of P, Fe and Mn in Surface Sediments in the Eutrophic Estuary, Northern Taiwan

Tien-Hsi Fang * and Cheng-Wen Wang

Abstract: The Danshuei River Estuary (DRE) in northern Taiwan is a seriously eutrophic estuary due to the domestic effluent discharge. Surface sediment samples were collected from the DRE to study the concentrations and spatial distributions of different fractions of phosphorus through the five-step sequential extraction method which chemically divides the sedimentary P into five fractions: \( P_{\text{SORB}} \), \( P_{\text{CDB}} \), \( P_{\text{CFA}} \), \( P_{\text{DET}} \), and \( P_{\text{ORG}} \). The Fe and Mn contents in the extracted solution were also determined. The total organic carbon (TOC) and grain size in sediment samples were analyzed as well. The sedimentary total P (TP) concentrations ranged within 537–1310 mg/kg and mostly exceeded 800 mg/kg, suggesting that the DRE sediments were moderately polluted by phosphorus. The \( P_{\text{CDB}} \) was the dominant fraction of P, averagely contributing 58% of TP, followed by \( P_{\text{DET}} \) 31%. The contributions of the \( P_{\text{SORB}} \) and \( P_{\text{CFA}} \) fractions to the TP were relatively minor. Two fractions, \( \text{Fe}_{\text{CDB}} \) and \( \text{Fe}_{\text{ORG}} \), of sedimentary Fe equally shared approximately 70% of total Fe, followed by \( \text{Fe}_{\text{DET}} \) with 22%. The contribution of different fractions of sedimentary Mn followed the sequence: \( \text{Mn}_{\text{CDB}} \) (36%) > \( \text{Mn}_{\text{CFA}} \) (29%) > \( \text{Mn}_{\text{ORG}} \) (14.7%) > \( \text{Mn}_{\text{DET}} \) (14.5%) > \( \text{Mn}_{\text{SORB}} \) (5.3%). The sedimentary \( P \), Fe, and Mn within the DRE are easily mobilized because they were mainly present in the reducible fraction. The concentrations of sedimentary TP positively correlated with the TOC contents and inversely negatively correlated with grain size, suggesting that the TOC and grain size play the crucial roles in influencing the distribution of sedimentary P within the DRE. Finally, the Fe(III) (hydro)oxides seems to play an important carriers to adsorb dissolved P because \( P_{\text{CDB}} \) positively correlated with \( \text{Fe}_{\text{CDB}} \).

Keywords: phosphorus; iron; manganese; TOC; sequential extraction method

1. Introduction

Phosphorus and nitrogen are the most important essential elements among the trace elements for marine organisms, especially for phytoplankton, and they control the primary productivity in the marine environment [1]. Both elements play a crucial role in influencing the marine carbon cycle and consequently affect the global biogeochemical cycles [1–3]. The dissolved nitrogen can be utilized by picophytoplankton, such as Prochlorococcus and Synechococcus, in oligotrophic waters through nitrogen fixation processes. Thus, phosphorus is generally considered as the bio-limiting element in the oligo oceanic environment due to the lack of a P source [2]. However, in the last three decades, estuarine and coastal environments have been frequently reported as being subject to eutrophic or hypereutrophic conditions because most rivers worldwide are more or less polluted by nutrients due to anthropogenic inputs, such as increased land drainage, agriculture fertilization, livestock, and urban/industrial wastewater input [4–8]. The eutrophication in the aquatic environment, especially in estuaries, is recognized as a globally pertinent environmental issue [3,9].

Unlike dissolved nitrogen, phosphorus is not a redox sensitive element, and orthophosphate is the dominant species of dissolved inorganic P (DIP) in estuarine and...
coastal water [3]. DIP is recognized as a high affinity ion with particles, especially iron (III) (hydro)oxides and hydrous aluminum oxides, which have positive surface charges at slightly acid to neutral pH, inducing high affinities for anions, the important adsorbents for DIP in the water column ([10], and references cited therein). Despite that, the desorption of particulate phosphorus (PP) during estuarine mixing is frequently observed in the estuary where the salinity increases and enhances the major anion (Cl\(^{-}\) & SO\(_4^{2-}\)) competition for adsorption sites, a process that promotes PP desorption [11,12]. The PP is not desorbed during the estuarine mixing and settles to the estuarine sediment, where it becomes an important reservoir of P within the sediments [13–15]. However, the settled PP in the sediment could be desorbed from the resuspension sediment [16,17] or re-dissolved, accompanying the dissolution of iron (Fe) (oxyhydr)oxides under the anoxic condition [18–20]. Sedimentary P cycling in the marine environment is quite complicated due to the speciation transformation. The classical diagram of P recycling after burial in marine sediment is that the non-refractory fraction of sedimentary phosphorus is released to interstitial waters due to the degradation of organic materials or desorption of the redox sensitive phosphorus associated with iron oxyhydroxides. The released P may be adsorbed by the grain surface or captured by iron oxyhydroxides, but P is ultimately taken up in situ in a mineralized form, most likely the authigenic minerals which may include the calcium (Ca)-P mineral carbonate fluorapatite [21–23] and vivianite, an Fe(II)-P mineral [24,25], within the sediments. The authigenic carbonate fluorapatite and detrital forms of P are considered as the refractory fraction of sedimentary phosphorus and are not regenerated during the diagenetic processes [26]. Thus, for better understanding the geochemical behavior of sedimentary P during the burial process, it is necessary to quantify the sedimentary P speciation. Many sequential extraction methods, chemically separating the sedimentary P according to different speciation, have been developed [20,26–30]. One of the most popular sequential extraction methods is the five-step sequential extraction method (SEDEX) developed by Ruttenberg [26], who indicates that the analytical method can successfully separate two of the main categories of authigenic phosphate phases. The method chemically divides the sedimentary P into five fractions: P\(_{\text{exchangeable}}\), P\(_{\text{CFAP}}\), P\(_{\text{Fe}}\), P\(_{\text{detrital}}\) and P\(_{\text{Organic}}\). A detailed description of the individual P speciation analyzed by the SEDEX method can be found in the work of Ruttenberg [26]. This method is widely used to differentiate the sedimentary P speciation, and to study the P distribution and geochemical cycle in the marine environment [31–36].

The Danshuei River Estuary (DRE) in Northern Taiwan (Figure 1) is characterized by relatively high DIP and DIN (dominated by ammonium) concentrations, exceeding 10 \(\mu\)M and 500 \(\mu\)M, respectively [8,37,38]. The dissolved oxygen in the water column of the estuary generally ranges within 2–5 mg/L, falling in moderately dysoxic to oxic conditions. The upper estuary, at salinity < 5 psu region, frequently approaches the conditions of a hypoxic environment due to the domestic sewage effluent discharge, and the dissolved oxygen gradually increases with salinity due to mixing with the tidal seawater [37,38]. Comprehensive studies focusing on the partitioning, distribution, and species of P and N in the estuarine water were addressed in previous works [8,37–39]. Some of the partitioning characteristics of P found in our previous studies are that the dissolved P was the dominant P (50–89% of total P pool) and inorganic species was the major fraction in both dissolved and particulate phases within the DRE. The higher dissolved organic P concentrations were generally relevant to the higher Chl.a concentrations [8]. The total and inorganic particulate P concentrations correlate well with those of the particulate Fe and Mn elements, suggesting that particulate Fe and Mn played important roles in regulating the particulate P within the DRE [8,39]. Meanwhile, the current understanding of the phosphorus pollution status in the DRE sediment is very limited, and it is well documented that the geochemical cycle of sedimentary P is rather complicated and can be strongly influenced by the speciation of sedimentary P, as mentioned above. In order to understand the geochemical fraction, spatial distribution, and pollution status of sedimentary P within the DRE, this study employed the SEDEX method to quantify sedimentary P speciation in the DRE and to
establish such a knowledge in the seriously eutrophic estuary. In addition, the sedimentary Fe and Mn concentrations in the SEDEX extracted solutions were also analyzed because both elements usually play the crucial roles in altering the sedimentary P geochemistry in the marine environment.

Figure 1. Sampling stations (1–13) along the Danshuei River Estuary in the northern Taiwan. (WWTP: wastewater treatment plant). R1-R3 represents the investigation stations of the water quality carried out by EPA, Taiwan. These three stations are located in the tributaries, namely the Keelung (R1), the Hsintien (R2) and the Tanhan (R3), of the Danshuei River system.

2. Sampling and Methods

2.1. Study Area

The DRE, located on the outskirts of northern Taipei, is the largest estuary in northern Taiwan with a drainage area of 2726 km$^2$. More than six million people, over a quarter of Taiwan’s entire population, reside in the catchment area. The main tributaries of the Danshuei River are the Tanhan, Hsintien, and Keelung Rivers. The Hsintien River merges with the Tanhan River in the Banqiao county of the New Taipei City to form the upper estuary of the DRE. The Keelung River joins the DRE at the lower estuary in the Shezidao region of the Taipei City. The monthly average river fluxes, ranging within 1.54–142.794 m$^3$/s, of the three major tributaries of the DRE during 2018–2019 are plotted in Figure 2. The monthly average precipitation, ranging within 13.8–439.3 mm, in the catchment area of the DRE during the periods 2018–2019 is shown in Figure 2 (http://www.cwa.gov.tw, accessed on 12 October 2021). Most precipitation occurred during the late May and June, which is influenced by the southwest monsoon. In addition, a heavy precipitation may occur during July to September depending on the tropical typhoon coming or not. The long-term average annual river flux in the Danshuei River system is $6600 \times 10^6$ m$^3$/y with freshwater contributions from the major tributaries, namely 27% from the Keelung River, 31% from the Dahan River, and 37% from the Hsintien River, respectively [37].
Figure 2. (a) The monthly average river fluxes of the three main tributaries of the DRE, and (b) the monthly average precipitation in the catchment area of the DRE during the periods 2018–2019.

Due to the treated and untreated municipal wastewaters discharged into the river system, there is a long record of nutrient pollution in the DRE [8,37–39]. Three wastewater treatment plants (WWTP) are located in the river estuary system (Figure 1). The largest one, namely the Bali WWTP, with daily sewage treatment of approximately $1.05 \times 10^6$ m$^3$/d, is located on the DRE mouth west bank, and the treated effluent is discharged into the seawater through an ocean outfall pipe. The other two WWTPs are located on the upper estuary and discharge the treated effluent into the river. Each of these two WWTPs has daily sewage treatment of approximately $4.0 \times 10^5$ m$^3$/d [40]. Figure 3 shows the historical data of dissolved inorganic nitrogen (DIN, ammonium + nitrite + nitrate) and dissolved total P (DTP) concentrations at the survey stations during the period of 2002–2016 according to the water quality survey data in the three major tributaries of the Danshuei River system investigated by EPA, Taiwan [41]. The DIN concentrations observed at these three stations ranged within 49–774 µM (0.68–10.84 mg/L), with an average value of 240 µM (3.56 mg/L), and ammonium generally dominated the DIN concentration. The DTP concentrations ranged within 1.30–222.1 µM (0.04–6.88 mg/L), with an average value of 12.1 µM (0.38 mg/L). Figure 3 also indicates that values of DIN and DTP found at the Tanhan (R3) River were relatively higher than those of the Hsintien (R2) River. The reason for this is probably attributed to the dilution effect of the river fluxes. It can be seen in Figure 2 that the river fluxes of the Hsintien River were significantly higher than that of the Tanhan River during 2018–2019. The municipal wastewaters discharged into the DRE are inducing the DRE to become a poorly eutrophic estuary according to the indicator threshold values of DIP > 0.1 mg/L and DIN > 1 mg/L [9].
The water depth of the whole estuary is generally about 2 m at low tide and the maximum depth may be over 10 m at high tide. Tidal seawater, which can intrude into the upper estuary approximately 25 km from the river mouth, can mix well with the river water during floods but is partially mixed during ebb [42]. The distinctive difference between the upper and the lower estuary of the DRE is that the dissolved oxygen concentration in the upper estuary is generally <3 mL/L and approaches saturation due to mixing with the tidal coastal water [8,37–39]. One of the characteristics of the Taiwanese rivers is that most rivers are small mountainous rivers which have great sediment yields and their values are generally 2–3 orders of magnitude greater than the global average [43,44]. The mean annual sediment deposition rates, sediment load, and sediment yield of the DRE during 1949–1990 were 0.28–2.2 cm/year, 1.45 Mt/year, and 4200 t/km$^2$/year, respectively [43,44]. Due to the presence of mountains and narrowness of the river, there is no significant wind-induced current, except for the occasional storm surges induced by the Western Pacific typhoon. The major forcing mechanisms of the barotropic flows are astronomical tide at the river mouth and river discharges at upriver ends. Semi-diurnal tides are the principal tidal constituents, with a mean tidal range of 2.22 m and a spring tidal range of 3.1 m, respectively [42].

2.2. Sampling

The DRE estuarine water and surface sediment samples were collected on 18 April, 26 September, 17 December 2018, and 4 April 2019 by employing a small fishing boat. The surficial sediment samples were collected using a grabber and placed in clean plastic bags. Samples were immediately placed in a cooler box on board. The sampling stations along the DRE are shown in Figure 1. After returning to the laboratory, one portion of the sediment sample at each station was gently rinsed with Milli-Q water to remove the interstitial water and was freeze-dried for 5 days using a freeze drier instrument. Rinsing sediment samples with Milli-Q water and the freeze-dried samples should have no influence on the analytical results. Berner and Rao [45] indicate that the sedimentary P measurements were not affected by oxidation during the drying process. The dried sediment samples were ground with a mortar and pestle and placed in glass vials for analysis. One portion of the untreated sediment sample at each station was directly analyzed for grain size.
2.3. Analytical Methods

One portion of the dried sediment collected at each station was analyzed for the different P species based on the five-step sequential extraction method (SEDEX) and the analytical procedure, the reaction mechanisms and operationally defined P forms of the SEDEX method can refer to Ruttenberg [26]. Briefly, the SEDEX method chemically divides the sedimentary P into five fractions: loosely sorbed P, hereafter referred to as $P_{\text{SORB}}$; ferric iron-bound P ($P_{\text{CDB}}$); authigenic carbonate fluorapatite + biogenic apatite + CaCO$_3$-bound P ($P_{\text{CFA}}$); detrital apatite P ($P_{\text{DET}}$); and organic P ($P_{\text{ORG}}$). A brief analytical procedure is described here. The bulk sediment sample (ca. 0.5 g) was extracted with 30 mL of the chemical reagent used in each fraction. The mixture was centrifuged at 4000 rpm for 5 min after the analytical procedure. Due to the phosphorus content differing from each extractant, a different proportion of the supernatant in each extractant was transferred into the 30 mL polypropylene vials and diluted to 25 mL with Milli-Q water. The measurement of P in the diluted solution was employed the molybdenum blue spectrophotometric method [46]. The dilution of each extractant can also eliminate the interference from the extracting chemicals and the matrix leached from the samples. Prior to the next step of the analysis, the sample was washed with 30 mL of Milli-Q water twice to remove the chemicals residual in the sample.

In addition, the iron and manganese concentrations in the extracted solution in each fraction were also determined using flame atomic absorption spectrophotometry (GFAAS) by a Perkin Elmer Analyst 900, and their analyzed species were also referred to as the same species as P. In order to examine the analytical accuracy of the five-step sequential extraction method, the MESS-3 and BCSS-1 reference materials (National Research Council of Canada) were used to trace the analytical quality. The analytical results are shown in Table 1 and the total concentrations of P, Fe, and Mn measured in the MESS-3 and BSCC-1 reference materials ($n = 6$, one standard deviation) are as follows: P, 1203 ± 100 mg/kg and 583.3 ± 69.4 mg/kg; Fe, 4.34 ± 0.11 % and 2.43 ± 0.09 %; Mn, 291.6 ± 17.1 mg/kg and 200.1 ± 5.85 mg/kg, respectively. The measured concentration ratios to the certified value and precision (one standard deviation) are as follow: P, 100.2 ± 8.4% and 86.8 ± 8.4%; Fe, 76.6 ± 6.2% and 73.9 ± 2.7%; Mn, 90.0 ± 5.3% and 87.4 ± 2.6 %. The analytical accuracy of P measurement obtained in MESS-3 material is better than that of BCSS-1 material and the analytical accuracy in the both reference materials ranges within 85–100%, suggesting that the analyzed data of the five-step sequential extraction method are reliable. The analyzed results for Fe and Mn obtained in both materials differ slightly. However, the analytical accuracy of Fe in both materials approaches 75% of their certified values, suggesting that the SEDEX method cannot destroy the element present in the residual fraction of the minerals. These results are in good agreement with the literature published by Kryc et al. [28] who use a modified sequential extraction procedure outlined in three published methods to evaluate the analytical accuracy of some reference materials, such as BCSS-1, MESS-1, MAG-1, and NIST-1. Their analytical results indicate that Fe and Mn ratios of the sum of sequential extraction concentrations to the total certified BCSS and MESS-1 values are approximately 0.8 and 0.75, and under-recovery is related to the lithology of sedimentary reference materials. Thus, the analyzed trace metal concentrations will be underestimated when the SEDEX method is used to analyze the sediment samples, as mentioned above (The data of this study can be found in the supplementary materials).
Table 1. The analytical accuracy and precision (1std) of P, Fe and Mn of the MESS-3 and BCSS-1 reference materials are analyzed using the SEDEX method. (Concentration unit, P and Mn in mg/kg; Fe in %).

| Species | Element | SORB | CDB | CFA | DET | ORG | Total Conc. | Certified Values | Accuracy (%) |
|---------|---------|------|-----|-----|-----|-----|-------------|-----------------|--------------|
| MESS-3  |         |      |     |     |     |     |             |                 |              |
| P       | 7.13 ± 2.07 | 562.7 ± 137.4 | 143.3 ± 57.9 | 353.2 ± 58.9 | 136.2 ± 42.8 | 1203 ± 100 | 1200 | 100.2 ± 8.4 |
| Fe      | ND      | 1.41 ± 0.23 | 0.24 ± 0.04 | 0.95 ± 0.11 | 0.72 ± 0.10 | 3.32 ± 0.27 | 4.34 ± 0.11 | 76.6 ± 6.2  |
| Mn      | 18.9 ± 8.7 | 92.2 ± 11.6 | 67.0 ± 21.9 | 64.7 ± 25.1 | 48.7 ± 9.2  | 291.6 ± 17.1 | 324 ± 12 | 90.0 ± 5.3  |
| BCSS-1  |         |      |     |     |     |     |             |                 |              |
| P       | 8.8 ± 3.2  | 169.2 ± 60.5 | 47.1 ± 18.6 | 301.4 ± 23.2 | 56.8 ± 16.2 | 583.3 ± 69.4 | 672 ± 67 | 86.8 ± 10.3 |
| Fe      | ND      | 0.59 ± 0.13 | 0.12 ± 0.05 | 0.56 ± 0.13 | 1.17 ± 0.14 | 2.43 ± 0.09 | 3.29 ± 0.1  | 73.9 ± 2.7  |
| Mn      | ND      | 18.95 ± 1.44 | 56.3 ± 2.94 | 34.8 ± 3.3  | 90.0 ± 1.3  | 200.1 ± 5.85 | 229 ± 15.1 | 87.4 ± 2.6  |

ND: Not detected.

The dried sediments were also analyzed for total organic carbon (TOC) using a Horiba carbon analyzer 8210 after the samples were smoked with concentrated HCl acid in a closed container for 48 h to remove the inorganic C content. The detailed TOC analytical procedure can be found in Fang and Hong [47]. The sediment grain size measurement was based on the analytical method published by Folk [48] and the grain size in each sample was divided into four fractions: medium sand (MS, >177 µm); fine sand (FS, 125–177 µm); very fine sand (VFS, 3–125 µm); mud (<63 µm).

3. Results
3.1. Grain Size and TOC

The grain sizes and TOC concentrations in the DRE surface sediments range within 20–470 µm and 0.11–2.00 % during the four surveys and their distributions at the studied stations are plotted in Figure 4, which shows the values were inconsistent and rather scatter during different surveys. However, Figure 4 shows that the grain sizes at the middle estuary stations (station 4–9) were relatively smaller than those found at the upper and the lower estuary stations which were mostly fine sand (125–177 µm), very fine sand (63–125 µm) and mud (<63 µm). The percentages of the four fractions of sediment grain sizes at each station obtained in the four surveys are plotted in Figure 5, and the percentage ranges of each fraction were as follows: MS, 0.5–94.5%; FS, 1.2–91.9%; VFS, 0.1–45.2%; and mud, <0.1–85.8%, respectively. The salinity, data taken from the previous study [8], in surface water at each station was also shown in Figure 5. The salinity ranged within <0.1–32.2 psu and varied in different surveys. A relatively lower salinity, 10–22 psu, was observed at the lower estuary during 17 December, 2018 survey, which is attributed to the falling tide during the sampling period. Figure 5 indicates that the sediment grain sizes at each station during the different surveys were not consistent and varied significantly. The sediment grain sizes at stations of the middle estuary were primarily dominated by fine sand and very fine sand, with exception of 18 April 2018 survey which was dominated by the MS, especially at stations of the upper and lower estuary. The reason for such phenomenon is not clear. However, it can be seen in Figure 2 that the river water fluxes during the period of March–May 2018 were the least among the times of 2018–2019, implying that the flow mechanism could not flush the medium sand out to the lower estuary and medium sand resided in the lower estuary is probably from the Keelung River transportation. This assumption needs further investigation. In contrast to the sediment grain size result, the TOC concentrations found at the middle estuary stations were relatively higher than those found at the upper and the lower estuary stations. Such a contrasting result will be addressed in the discussion section.
Figure 4. Seasonal distribution of (a) grain size and (b) TOC in the DRE surface sediments.

Figure 5. Percentage distributions of four sediment grain size fractions in the DRE during the different surveys. (a) 18 April 2018, (b) 26 September 2018, (c) 17 December 2018, and (d) 4 April 2019. (MS: medium sand (>177 µm), FS: fine sand (125–177 µm), VFS: very fine sand (63–125 µm) and mud (<63 µm)).
3.2. Phosphorus

The concentration and percentage ranges of the five fractions and total concentration of phosphorus in DRE surface sediments obtained in the four surveys are tabulated in Table 2. The total P concentrations in DRE surface sediments range within 537–1310 mg/kg (17.33–42.30 µmol/g) and the concentrations found at each station are plotted in Figure 6, which indicates that the concentration variations are significant during the different surveys. The distributions of total P concentrations within the DRE are also scattered and no specific trend can be described. Figure 7 clearly shows that the total P concentrations within the DRE surface sediments are completely dominated by P\textsubscript{CDB}, accounting for 38–75% (average 58%) of total P pool, followed by P\textsubscript{DET}, accounting for 15–52% (average 31%) of total P pool. The contributions of P\textsubscript{CFA} and P\textsubscript{ORG} to the total P pool are generally <5% and 10%, respectively. The importance of P\textsubscript{SORB} is relatively minor and is generally <2% of the total P pool.

Table 2. The concentration and percentage ranges of sedimentary P in the five fractions of the sediments collected from the DRE.

| Sampled Time   | Concentration (mg/kg) | Percentage (%) |
|----------------|-----------------------|----------------|
|                | \(P_{\text{SORB}}\) | \(P_{\text{CDB}}\) | \(P_{\text{CFA}}\) | \(P_{\text{DET}}\) | \(P_{\text{ORG}}\) | Total P | \(P_{\text{SORB}}\) | \(P_{\text{CDB}}\) | \(P_{\text{CFA}}\) | \(P_{\text{DET}}\) | \(P_{\text{ORG}}\) |
| 18 April 2018  | Min 4.05              | 225.1          | 7.95           | 195.8          | 4.23           | 546.1          | 0.74   | 40.53              | 1.18           | 23.48           | 4.38           |
|               | Max 18.39             | 757.5          | 46.66          | 288.3          | 83.2           | 1151.5         | 2.17   | 65.78              | 5.50           | 51.92           | 10.50          |
| 26 September 2018 | Min 2.50             | 307.1          | 18.98          | 169.9          | 14.5           | 541.9          | 0.39   | 49.93              | 2.76           | 17.06           | 2.68           |
|               | Max 26.96             | 907.5          | 76.45          | 259.2          | 122.5          | 1310.3         | 2.10   | 70.39              | 6.56           | 39.74           | 11.74          |
| 17 December 2018 | Min 1.11             | 217.8          | 15.07          | 120.5          | 28.2           | 548.3          | 0.09   | 38.42              | 2.68           | 20.38           | 4.56           |
|               | Max 10.89             | 773.6          | 72.17          | 279.5          | 103.3          | 1193.8         | 1.84   | 67.75              | 6.05           | 49.30           | 9.82           |
| 4 April 2019   | Min 3.07              | 235.0          | 18.09          | 125.5          | 17.3           | 536.7          | 0.29   | 43.78              | 2.03           | 15.03           | 1.94           |
|               | Max 14.70             | 884.9          | 79.83          | 276.6          | 73.6           | 1233.9         | 1.69   | 74.70              | 9.56           | 42.71           | 6.86           |

Figure 6. Seasonal distributions of the five P concentration fractions in the DRE surface sediments during the different surveys (a) 18 April 2018, (b) 26 September 2018, (c) 17 December 2018, and (d) 4 April 2019.
3.3. Iron and Mn

The analyzed results for iron and Mn in DRE sediments obtained in the four surveys are shown in Tables 3 and 4, respectively. The concentrations found at each station are plotted in Figures 8 and 9. The total Fe concentrations in DRE surface sediments ranged within 1.48–4.10%. The distributions also varied with the different stations and no trend could be specified. Figure 8 shows that the total Fe concentrations within the DRE surface sediments are generally dominated by Fe$_{CDB}$ and Fe$_{ORG}$, each accounting for 23–48% of the total Fe pool. The importance of Fe$_{DET}$ and Fe$_{CFA}$ ranked third and fourth and accounted for 16–31% and 4–17% of the total Fe pool, respectively. The concentrations of Fe$_{SORB}$ in all extractants were generally less than 0.1 mg/L and were not detected by the flame AAS (Perkin Elmer Analyst 900).

The total Mn concentrations in the DRE surface sediments ranged within 109–502 mg/kg and were generally dominated by Mn$_{CDB}$ and Mn$_{CFA}$, accounting for 19–65% (average 36%) and 14–48% (average 29%) of the total Mn pool, respectively. The Mn$_{DET}$ and Mn$_{ORG}$ contributions to the total concentrations nearly equalized and accounted for 5.7–30.3% (average 14.5%) and 5.0–24.7% (average 15%) of the total Mn pool, respectively. The Mn$_{SORB}$ contribution to the total concentrations was minor and generally <5% of the total Mn pool.
Figure 8. Seasonal distributions of the five Fe concentration fractions in the DRE surface sediments during the different surveys (a) 18 April 2018, (b) 26 September 2018, (c) 17 December 2018, and (d) 4 April 2019.

Figure 9. Seasonal distributions of the five Mn concentration fractions in the DRE surface sediments during the different surveys (a) 18 April 2018, (b) 26 September 2018, (c) 17 December 2018, and (d) 4 April 2019.
Table 3. The concentration and percentage ranges of sedimentary Fe in the five fractions of the sediments collected from the DRE.

| Sampled Time | Concentration (%) | Percentage (%) |
|--------------|-------------------|----------------|
|              | Fe\textsubscript{SORB} | Fe\textsubscript{CDB} | Fe\textsubscript{CFA} | Fe\textsubscript{DET} | Total | Fe\textsubscript{SORB} | Fe\textsubscript{CDB} | Fe\textsubscript{CFA} | Fe\textsubscript{DET} | Fe\textsubscript{ORG} |
| 18 April 2018 | Min 0.50 | 0.10 | 0.32 | 0.60 | 1.87 | <0.1 | 24.27 | 3.86 | 17.11 | 29.06 |
|              | Max ND | 1.26 | 0.19 | 0.81 | 1.15 | 3.16 | 42.78 | 8.02 | 31.27 | 43.07 |
| 26 September 2018 | Min 0.62 | 0.17 | 0.34 | 0.54 | 1.71 | <0.1 | 29.32 | 4.97 | 16.34 | 26.18 |
|              | Max ND | 1.96 | 0.31 | 0.75 | 1.50 | 4.10 | 47.79 | 11.85 | 23.29 | 45.86 |
| 17 December 2018 | Min 0.57 | 0.13 | 0.35 | 0.40 | 1.48 | <0.1 | 26.46 | 4.15 | 15.86 | 27.03 |
|              | Max ND | 1.33 | 0.25 | 0.77 | 1.30 | 3.37 | 40.56 | 10.10 | 25.52 | 45.56 |
| 4 April 2019 | Min 0.56 | 0.19 | 0.39 | 0.66 | 2.28 | <0.1 | 23.03 | 5.86 | 17.11 | 23.24 |
|              | Max ND | 1.52 | 0.54 | 0.78 | 1.56 | 3.97 | 47.89 | 16.67 | 23.04 | 48.15 |

ND: Not detected.

Table 4. The concentration and percentage ranges of sedimentary Mn in the five fractions of the sediments collected from the DRE.

| Sampled Time | Concentration (mg/kg) | Percentage (%) |
|--------------|-----------------------|----------------|
|              | Mn\textsubscript{SORB} | Mn\textsubscript{CDB} | Mn\textsubscript{CFA} | Mn\textsubscript{DET} | Mn\textsubscript{ORG} | Total | Mn\textsubscript{SORB} | Mn\textsubscript{CDB} | Mn\textsubscript{CFA} | Mn\textsubscript{DET} | Mn\textsubscript{ORG} |
| 18 April 2018 | Min 12.1 | 68.1 | 62.4 | 28.0 | 50.5 | 242.7 | 3.7 | 19.6 | 20.8 | 8.3 | 15.9 |
|              | Max 18.1 | 166.2 | 129.9 | 103.5 | 69.1 | 353.4 | 6.0 | 49.9 | 37.8 | 31.0 | 21.8 |
| 26 September 2018 | Min 8.6 | 48.0 | 102.2 | 32.2 | 34.3 | 250.7 | 2.5 | 19.1 | 24.3 | 9.6 | 13.1 |
|              | Max 25.8 | 250.0 | 147.9 | 58.5 | 66.8 | 502.2 | 6.9 | 49.8 | 43.0 | 19.6 | 17.6 |
| 17 December 2018 | Min 8.5 | 66.6 | 29.5 | 21.1 | 30.9 | 199.3 | 4.3 | 27.0 | 14.8 | 9.8 | 14.1 |
|              | Max 27.0 | 222.4 | 88.4 | 55.5 | 60.1 | 421.7 | 8.7 | 52.7 | 35.8 | 21.2 | 21.6 |
| 4 April 2019 | Min 8.0 | 60.6 | 47.9 | 13.5 | 16.0 | 195.1 | 2.8 | 27.5 | 16.6 | 5.7 | 5.0 |
|              | Max 17.2 | 209.3 | 135.8 | 60.5 | 29.2 | 321.3 | 7.7 | 65.2 | 48.1 | 19.7 | 13.3 |

4. Discussion

4.1. Grain size and TOC

The concentration of chemical constituents in marine sediment is generally positively correlated well with organic carbon (OC) contents and is inversely proportion to the sediment grain size (GS) because the OC has the higher adsorption capacity and the finer the GS, the larger the surface area [49]. The plots of TOC against grain size in DRE sediments obtained in the present study are depicted in Figure 10, which shows that TOC concentrations exhibited an inversely exponential decrease with increasing grain size, with a correlation coefficient approaching $-0.83$ ($p < 0.05$). A similar result is also seen for the plot of total P concentrations against the grain size, with a good correlation coefficient ($r = -0.71$, $p < 0.05$). In addition, total P and P\textsubscript{ORG} concentrations significantly positively correlated well with the TOC ($r = 0.89$, $p < 0.05$ and $r = 0.81$, $p < 0.05$, respectively), as shown in Figure 10. These results suggest that the sediment grain size and TOC contents are the important factors controlling the sedimentary total P concentrations within the DRE, in agreement with many studies focused on estuarine and inshore environments [31,32,36,50,51].
4.2. Phosphorus

The total P concentrations in DRE sediments ranged within 537–1310 mg/kg (17.33–42.30 µmol/g), with an average value 769 ± 236 mg/kg. Figure 7 shows that the total P concentrations in the DRE surface sediments observed on 18 April 2018 survey were relatively lower than those of the other surveys, probably because the grain size effect. It has been indicated that the chemical compositions in inshore sediment may differ significantly from the grain size, bulk minerals, and heavy mineral fractionation [52]. However, many studies have tried to establish the P value in sediment to classify the sediment quality. The total P values in sediment exceed 700 mg/kg (22.6 µmol/g) representing that the environment is significantly influenced by the anthropogenic impact [53,54]. Another criterion established by Berbel et al. [35] suggests that sedimentary total P values ranging within 495–1300 mg/kg (16–42 µmol/g) are moderately polluted and the values exceeding 1300 mg/kg (>42 µmol/g) are highly polluted with P. The latter guideline seems to be more reasonable because the P contents in the upper continental crust generally range within 665–709 mg/kg [52,55,56]. The sediment P polluted status of the DRE can be classified as the moderately polluted, based on the classification by Berbel et al. [35].

Table 5 compares the total P concentrations and the P species in DRE sediments with eutrophic estuaries worldwide recently reported in the literature. The total P concentrations in the different estuarine sediments may vary 2–4 folds and the P species also significantly differ in the different estuaries.
Table 5. Comparison the total concentrations range and percentage range of five sedimentary P species analyzed by the SEDEX method [26] obtained in the Danshuei River Estuary with the other eutrophic estuaries worldwide.

| Study Area                    | Total Conc. (mg/kg) | P_{SORB} (%) | P_{CDB} (%) | P_{CFA} (%) | P_{DET} (%) | P_{ORG} (%) | Reference                  |
|-------------------------------|---------------------|--------------|-------------|-------------|-------------|-------------|----------------------------|
| Danshuei RE, Taiwan           | 537–1310            | 0.1–2.2      | 38.4–74.7   | 1.2–9.6     | 15.0–52.0   | 1.9–11.7    | This study                 |
| Changjaing RE, China          | 465–663             | 1.4–5.3      | 0.3–3.7     | 2.9–9.6     | 62.4–85.7   | 5.5–26.2    | [31]                       |
| Laizhou Bay                   | 316–582             | 0.4–3.4      | 0.2–1.6     | 5.2–19.2    | 13.4–55.0   | 4.8–17.3    | [32]                       |
| Qinzhou Bay                   | 136–867             | 1.5–5.9      | 15.5–37.9   | 7.6–26.9    | 3.9–23.5    | 25.1–55.6   | [32]                       |
| Seine RE, France              | 133–1375            | 0.9–15.6     | 2.0–21.7    | 14.8–87.3   | ND          | 4.8–54.9    | [33]                       |
| Mondego RE, Portugal          | 465–836             | 1.1–2.5      | 13.1–32.3   | 16.3–43.2   | 10.7–20.5   | 24.5–46.1   | [34]                       |
| Santos-Sao Vicente RE, Brazil | 118–2296            | 4.9–27.1     | 20.9–53.2   | 5.1–34.2    | 9.2–46.8    | [35]         |                            |
| Yamuna R, Delhi, India        | 1510–4340           | 2.6–29.6     | 0.9–12.5    | 31–53       | 18.5–61.9   | 1.7–16.6    | [57]                       |
| Patuxent RE, Chesapeake Bay   | 829–2255            | 0.04–4.7     | 52.3–85.1   | 7.7–22.0    | 2.2–8.5     | 3.0–12.4    | [58]                       |
| Penze RE, France              | 370–1672            | 8–20         | 20–57       | 14–23       | 12–60       | 19–43       | [59]                       |

ND: no data. [31] Meng et al., 2014 [32] Zhuang et al., 2014 [33] Andrieux-Loyer and Aminot 2001, [34] Coelho et al., 2004 [35] Berbel et al., 2015 [57] Moturi et al., 2005 [58] Hartzell, et al., 2010 [59] Andrieux-Loyer et al., 2008.

The estuarine sediments are derived mainly from the riverine SPM, and partly from the other sources, such as the atmospheric input, generalized within the estuary and the tidal water intrusion [60]. The phosphorus contents in the riverine SPM in the world’s rivers range within 560–2000 mg/kg (18.1–64.6 µmol/g), with a mean value of 1146 mg/kg (37.0 µmol/g) [61]. As a result, the total P concentrations in the estuarine sediment worldwide differ by as much as 2–4 folds regardless of whether the estuary is contaminated or not because the riverine suspended particulate matter (SPM) source varied. However, the riverine SPM influences controlling the sedimentary total P concentrations decrease with increasing seaward. Fang et al. [62] indicate that the total P concentrations in some coastal sediments worldwide, such as the Yellow Seas, the Iberian Sea, the Gulf of Mexico, the Amazon Shelf, and the North Sea, generally remain within a narrow range from 465 mg/kg to 774 mg/kg (15–25 µmol/g) due to the dilution effect.

It can be seen in Table 5 that the ranking of P species in DRE sediments followed the sequence: P_{CDB} > P_{DET} > P_{ORG} > P_{CFA} > P_{SORB}. Such a sequence is generally inconsistent with the results reported in the literature. The comparable result with the present study is probably the study reported by Hartzell et al. [58] who indicate that the P_{CDB} species entirely governed the total sedimentary P, 53–85% of total P pool, in the Patuxent RE, Chesapeake Bay sediments. Meanwhile, the contribution of the second important species, P_{CFA}, was relatively minor and occupied 8–22% of total P pool. In fact, it seems that P species in the estuarine sediment generally differs from the different estuaries, as shown in Table 5. For example, the P_{DET} fraction, dominating the sedimentary total P, was reported in the Changjiang RE [31] and the Laizhou Bay [32]. Moreover, the sedimentary total P mainly governed in the P_{ORG} species was seen in the Pearl RE [63], the Qinzhou Bay [32], and the Mondego RE [34]. In contrast, the P_{CFA} species was the most important species in the Seine RE [33]. One of the most common characteristics of P species in the sediment is probably that the contribution of P_{SORB} is relatively minor and generally <5% of the total P pool. However, such a characteristic was not obeyed in the Seine RE [33], the Penze RE [59], the Yamuna River [57], and the Santos-Sao Vicente RE, Brazil [35].

P_{SORB} is the essential species of sedimentary P which can be easily released through the degradation of sediment organic matter and of decaying cells of bacterial biomass [33,64]. However, it is well documented that P_{SORB} is easily desorbed from SPM or suspended sediment as salinity increased due to sulphate competition for adsorption sites, a process which also promotes desorption at higher salinities [11]. Thus, P_{SORB} is generally the least important fraction among the P fractions in the marine sediment. However, the relatively higher percentage of P_{SORB} in marine sediment has been observed in some studies, attributing to the highly adsorbed by Fe oxides [33] and the sewage effluent discharge [35], as shown in Table 5. The latter effect is not seen in the DRE which is also strongly interfered with by the domestic sewage effluent discharge, enhancing the higher DIP concentration (>10 µM) in its upper estuary [8].
PCDB was the most abundant sedimentary P fraction in the DRE and its contribution to the total P pool was significantly higher than the recent literature reports. The mechanism inducing such a result in the present study is not clear. However, it could be relevant to the WWTP effluent discharge, implying that a higher concentration of dissolved total P (>10 µM) commonly exists in the water column of the upper estuary of the DRE [8,38]. It is known that Fe is generally used in the modern wastewater treatment plant to prevent hydrogen sulfide emissions during anaerobic digestion and acts as a coagulant to improve sludge dewatering [10]. Our previous study indicates that the DRE water column enriched in particulate Fe and the concentrations of particulate total inorganic P, extracted by 1 N HCl acid, positively correlated well with particulate Fe within the DRE. This result suggests that particulate Fe plays an important role in influencing the P content in the DRE water column [8].

The PCDB is generally attributed to Fe-oxides which are the important adsorbents for DIP in the aquatic environment [16,19,26,65]. The PCDB is considered as the redox-sensitive sedimentary P fraction because P is generally accompanied with the FeCDB reduction and is released from surface sediments into the overlying waters under hypoxic or anoxic conditions [63,66,67]. Figure 11 shows that the PCDB with FeCDB plot concentrations in DRE surface sediments also have a good correlation (r = 0.62), consistent with the particulate Fe and P results in our previous study [8]. The FeCDB/PCDB mole ratios observed in the DRE surface sediments range within 5.42–20.83 (average 12.3), which is lower than the literature reports indicating that the FeCDB/PCDB ratio for newly buried iron oxides ranged within 20–26 in the marine environment [20,27,68]. The mole ratio of FeCDB/PCDB can be used to estimate the spare sorption capacity of Fe oxyhydroxides, and the ratio value, approximately 6.7, is suggested to correspond to surface binding sites supersaturation of nanoscale ferrihydrite, the phase with the highest P sorption capacity [20,69]. The FeCDB/PCDB ratio in the marine sediments reported in the literature varies widely, ranging within <2–45 ([70], and references cited therein), suggesting that many factors, such as the sediment texture and grain size, the anthropogenic source, the redox condition of the environment, and the transformation of sedimentary P during the burial processes, may alter the ratio. The relatively lower mole ratio of FeCDB/PCDB found within the DRE sediments is probably due to the effect of domestic sewage effluents, which elevates the dissolved P concentrations and is adsorbed by SPM, raising the particulate P concentration and reducing the ratio. In spite of that, future work needs to examine whether the PCDB transformation occurs or not during the sediment burial within the estuary.

The PCFA contributions to the total P pool within the DRE sediment are relatively low, ranging within 1.2–9.6% with an average 3.8%. PCFA in sediments is generally derived from detritus of biogenic apatite, such as skeletal materials from fish, authigenic carbonate fluorapatite (CFA) precipitation, and the chemical combination of P with CaCO3 [26]. In addition, PCFA formation in sediments can be favored at the expense of PORG and PCDB during the diagenetic process, enhancing a higher proportion of PCFA observed in the marginal and open sea sediments [21,71,72]. The PCFA concentration dominating the sedimentary total P pool is rarely reported in estuarine studies but can be found in the Bay of Seine and in the Mondego RE, and the source of PCFA is derived mainly from marine origin [31] and the adsorption of DIP by calcite [32].

PDET ranked the second most abundant sedimentary P fraction within the DRE and averagely accounted 31% of total P pool. Its contribution to the total P pool was slightly higher than the recent literature reports, as shown in Table 5. However, the relatively higher proportions of PDET, accounting for 62–86 % of sedimentary total P, were observed in the surface sediments of the Changjiang RE and the inner shelf of the adjacent East China Sea where the surface sediments were completely dominated by PDET species and governed by illilite, chlorite, quartz, and feldspar minerals [31]. PDET is mostly derived from igneous and metamorphic rocks and magma and is abundant in surface sediments that are under the substantial influence of riverine input [26]. Many studies suggest that the coarse sandy and sandy marine sediments contain relatively higher proportions of PDET than that of
the silt and mud marine sediments, suggesting that the primary minerals may contain a relatively higher concentration of $P_{\text{DET}}$ than that of the secondary minerals [31,70]. The present result also finds that the $P_{\text{DET}}$ concentration is slightly positively correlated with medium sand ($r = 0.43, p < 0.05$), but obviously negatively correlated with mud ($r = -0.64, p < 0.05$). This result is consistent with the literature report. In addition, $Fe_{\text{DET}}$ correlates well with the $P_{\text{DET}}$ ($r = 0.50, p < 0.05$) in the present study and the mole ratio of $Fe_{\text{DET}}/P_{\text{DET}}$ is about 8.7. The molar ratio of $Fe_{\text{DET}}/P_{\text{DET}}$ in marine sediment is rarely discussed in the literature. The reason for this is probably due to the fact that the monoculture of $Fe_{\text{DET}}$ is not as clear as the $P_{\text{DET}}$, due to 1 M HCl dissolving some fractions of the clay minerals but not the most crystalline Fe oxides [19], and that the $P_{\text{DET}}$ species, considered as the inert fraction of sedimentary $P$, is not involved in the redox reaction of iron or during the diagenetic processes [26].

**Figure 11.** Scatter plots of the four fractions $P$ and $Fe$ concentrations in the DRE surface sediments (a) $P_{\text{CDB}}$ against $Fe_{\text{CDB}}$, (b) $P_{\text{CFA}}$ against $Fe_{\text{CFA}}$, (c) $P_{\text{DET}}$ against $Fe_{\text{DET}}$, and (d) $P_{\text{ORG}}$ against $Fe_{\text{ORG}}$.

Although $P_{\text{ORG}}$ ranked the third most abundant sedimentary $P$ fraction within the DRE, the percentage only accounted for 1.9–11.7% (average 6.3%) of sedimentary total $P$ pool. These percentages are much lower than those reported in many estuarine studies, such as the Mondego RE [34], the Santos-Vicente RE [35], and the Peel-Harvey RE [73], indicating that the $P_{\text{ORG}}$ was generally > 30% of the sedimentary total $P$ pool. Relatively higher percentages (>50%) of $P_{\text{ORG}}$ have been reported in some estuaries, such as the Qinzhou RE [32], the Seine Bay [33], and the Pearl RE [63], generally attributed to anthropogenic inputs, such as the wastewater, domestic sewage effluent, and agricultural activities. In contrast, our previous studies also indicated that the DRE is seriously impacted by the domestic sewage effluents, inducing its upper estuary to contain relatively higher concentrations of dissolved inorganic $P$ (>10 $\mu$M) and dissolved inorganic $N$ (>500 $\mu$M). The total dissolved and particulate concentrations of both elements are completely dominated by inorganic species [8,38]. These findings may explain why the $P_{\text{ORG}}$ contribution occupied a small amount of sedimentary total $P$ pool within the DRE.

$P_{\text{ORG}}$ storage in the estuarine sediment is chiefly facilitated by the autochthonous and allochthonous organic matter. The source of autochthonous is calculated according to the Redfield ratio, which is commonly employed to identify the source, provenance, decomposition, and preservation of sedimentary organic matters [70,74,75] and the trans-
formation of P in sediments [76,77]. It can be seen in Figure 10 that the P$_{\text{ORG}}$ concentration is also positively correlated very well with the TOC ($r = 0.81$) in the DRE and the whole OC/OP$_{\text{ORG}}$ mole ratio during the four surveys is about 443. This ratio value is much higher than the Redfield ratio (106) of marine plankton and falls in the 300–1300 range for terrestrial higher plants with soft tissues [74,78,79]. The OC/OP$_{\text{ORG}}$ ratio value obtained in the present study may suggest that the allochthonous source may play an important role in dominating the sedimentary organic matters within the DRE. However, it is worth noticing that the discharge of the domestic sewage effluent within the DRE may interfere with the TOC/P$_{\text{ORG}}$ ratio in the sediment, which needs further investigation.

4.3. Iron and Mn

It can be seen in Table 3 that the sedimentary total Fe concentration extracted by the SEDEX method within the DRE surface sediments is mainly present in the Fe$_{\text{CDB}}$ and Fe$_{\text{ORG}}$ species, each fraction accounting for an average of approximately 35% of total Fe pool, and Fe$_{\text{DET}}$ occupies on average nearly 22% of the total Fe pool. Ruttenberg [26] indicated that ferrihydrite, lepidocrocite, and goethite, the most common sedimentary Fe oxyhydroxide phases, and hematite, which is considerably less reactive than oxyhydroxides, are completely dissolved by neutral pH CDB reagent. Such a result is also confirmed by Slomp et al. [18] who studied the percentage of Fe extracted from the common Fe-containing standard minerals using different kinds of chemical reagents and indicated that the CDB reagent is a stronger chemical that totally dissolves the Ferrihydrite (Fe$_5$O$_8$·4H$_2$O), Amorphous (FeS), Goethite ($\alpha$-FeOOH), Hematite ($\alpha$-Fe$_2$O$_3$), and Magneite (Fe$_3$O$_4$). In general, Fe$_{\text{CDB}}$ is often used as a measure of total Fe-oxides in the sediment [24]. Understanding the Fe$_{\text{CDB}}$ fraction present in sediment is important because such a fraction is easily remobilized under anoxic conditions, whether the hypoxic condition takes place seasonally in bottom sediments or the diagenetic process occurs during the sedimentary burial processes. The release of Fe$_{\text{CDB}}$ and P$_{\text{CDB}}$ into the water column will elevate the dissolved concentration of both elements and could strongly alter the Fe$_{\text{CDB}}$ and P$_{\text{CDB}}$ fractions and their mole ratio within the sediment profile [24,66,68,80]. The present results provide useful information concerning how many Fe$_{\text{CDB}}$ and P$_{\text{CDB}}$ fractions exist in the DRE surface sediment when studying the diagenetic processes of the sedimentary P and Fe in the DRE sediment.

In comparison with the Fe$_{\text{CDB}}$, the discussion of Fe$_{\text{DET}}$ and Fe$_{\text{ORG}}$ in the literature is very limited, probably because the Fe$_{\text{DET}}$ fraction is considered an unreactive iron and is not dissolved during the reduction reaction under an anoxic environment [26]. The Fe$_{\text{DET}}$ fraction is analyzed by 1 N HCl acid extraction, whereby metal speciation in sediment is regarded as the weakly bound or non-detrital trace metals which correlate well with the biological availability [81]. Although the experimental results suggest that the bioavailability of mineral-bound Fe(III) in intertidal sediment of the microbial utilization is weaker than that of the chemical extraction [82], it should be taken into consideration for Fe$_{\text{DET}}$ fraction utilization by benthic organisms during the sediment burial processes. The strong complexation of iron hydroxides with organic compounds (OC) due to the negative surface charge of OC leads to the flocculation/aggregation of dissolved Fe occurs in the estuarine mixing zone and induces the removal behavior of dissolved Fe in the estuary [83,84]. Thus, the Fe concentration generally correlates well the OC concentration, and the fate of iron always accompanies the OC and vice versa in the marine environment ([85], and references cited therein). Such a phenomenon is also attributed to the grain size effect. The finer the grain size, the greater the surface area for adsorption [49]. The Fe$_{\text{ORG}}$ fraction in the DRE sediment ranged within 22–48%, with an average 36%, of total Fe pool. Such a percentage seems to be relatively higher than the literature reports which employed the Tessier sequential extraction method to study the iron fraction in the marine sediments and indicated that the percentage of iron bound to organic matter was generally less than 5% of the total Fe pool [86,87]. However, the total Fe concentrations in the marine sediments differ according to analytical methods and the total concentrations could vary by 20–30%
between with and without the total decomposition methods [28]. Thus, the contributions of Fe\textsubscript{ORG} fraction to the total Fe pool in the marine sediment may vary substantially with the different analytical methods.

![Figure 12](image_url)

**Figure 12.** Scatter plots of the five fractions P and Mn concentrations in the DRE surface sediments (a) P\textsubscript{SORB} against Mn\textsubscript{SORB}, (b) P\textsubscript{CDB} against Mn\textsubscript{CDB}, (c) P\textsubscript{CFA} against Mn\textsubscript{CFA}, (d) P\textsubscript{DET} against Mn\textsubscript{DET}, and (e) P\textsubscript{ORG} against Mn\textsubscript{ORG}.

The percentage variations of Mn species in sediments of the DRE during the four surveys are significant. However, the Mn\textsubscript{CDB} and Mn\textsubscript{CFA} species dominated the total Mn concentrations and each fraction accounted for an average of 36% and 29% of the total Mn pool, respectively. The corresponding values for Mn\textsubscript{DET} and Mn\textsubscript{ORG} accounted for an average of 15% of the total Mn pool, respectively. These results agree well with the literature regarding the marine sediments, e.g., in the East China Sea [86], the Daya Bay, China [88], the North Sea [89], and the southwest coast of Spain [90], indicating that sedimentary Mn is mainly present in the non-residual fraction which includes the exchangeable, carbonate, (Fe, Mn)-oxhydroxide and sulphides/organic species. The Mn geochemistry characteristics include the fact that Mn is also the redox sensitive element and easily moves from dissolved phase into particulate phase under an oxic environment, and vice versa under an anoxic environment [91]. In addition, the dissolved and particulate Mn in the water column can be adsorbed onto the CaCO\textsubscript{3} surface [92,93]. As a result, these characteristics imply that the sedimentary Mn is mainly present in the non-residual fraction, especially in the (Fe, Mn)-oxhydroxide and carbonate phases, rather than the residual fraction, as observed in the present study and in the literature. It is noticeable that the SEDEX method can extract nearly 90% of total Mn concentrations of the reference materials (MESS-3 and BCSS-1). Thus, the residual fraction of Mn concentration in the marine sediment will be underestimated when the SEDEX method is employed. Figure 12 shows that the five fractions of sedimentary Mn do not have any correlation with the corresponding fraction of sedimentary P in the DRE sediment, suggesting that Mn may play a minor role in influencing the distribution of sedimentary P in the DRE. This result is contradictory to our previous study which indicated that particulate Mn significantly correlated well with particulate P within the DRE [8]. Basically, particulate P and Mn within the DRE exhibited a similar distribution. The higher concentration generally occurred in the upper estuary, at salinity < 5 psu. Afterwards, the concentrations decreased with increasing salinity and remained fairly constant in the lower estuary, at salinity > 20 psu [8]. In contrast, P and Mn within the DRE exhibited different distributions. The reason for this phenomenon is
probably that the $P_{\text{CFA}}$ was a minor fraction, <5% of total P pool, and $Mn_{\text{CFA}}$ was a major fraction, on average approximately 30% of the total Mn pool, respectively, in the sediment samples. The dominant fraction of sedimentary P differs markedly from the sedimentary Mn, indicating that both elements in the sediment deviated from each other.

5. Conclusions

The present work is a pioneering study on the geochemical speciation of sedimentary P in the DRE sediment. The analyzed results show that the sedimentary total P concentrations ranged within 537–1310 mg/kg (with mean value 769 mg/kg), suggesting that the DRE surface sediments are mildly contaminated by P. The signal of P pollution status in the surface sediment is not as significant as in the water column, which contains relatively higher concentrations of total dissolved P (>10 $\mu$M) and DIN (>500 $\mu$M), and is recognized as a seriously eutrophic estuary. The most striking finding of the present study is that the sedimentary total P concentrations are completely dominated by $P_{\text{CDB}}$, accounting for an average of 58% of TP. Such a high percentage of $P_{\text{CDB}}$ speciation is rarely reported in the marine sediment, which may be attributed to the influence of the wastewater treatment plant effluent discharge. This assumption needs further investigations. It is worth noting that $P_{\text{CDB}}$ species is more easily dissolved under the anoxic condition and elevates the dissolved P concentration in the water column. The diffusion flux of dissolved P under the diagenetic processes needs further study. Finally, the sediment grain size and TOC content seem to play crucial roles in determining the sedimentary total P content in the DRE sediment. The river water fluxes may strongly influence the distribution of the sediment grain size within the DRE.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/w13213075/s1.

Author Contributions: The analytical works of the present study were completed by C.-W.W. during she studied her master degree with her supervisor, T.-H.F., at the National Taiwan Ocean University, Taiwan. T.-H.F. arranged this research study and wrote the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the Ministry of Science and Technology, Taiwan, under grants MOST 108-2611-M-019-011 and 107-2611-M-019-003.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: The data of this study can be found in the supplementary file.

Acknowledgments: This research was financially supported by the Ministry of Science and Technology, Taiwan, under grants MOST 108-2611-M-019-011 and 107-2611-M-019-003. The authors are also grateful to the anonymous referees for their constructive comments and suggestions, which led to significant improvements to the manuscript.

Conflicts of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationship that could be constructed as a potential conflict of interest.

References

1. Benitez-Nelson, C.R. The biogeochemical cycling of phosphorus in marine systems. *Ear. Sci. Rev.* 2000, 51, 109–135. [CrossRef]
2. Paytan, A.; McLaughlin, K. The oceanic phosphorus cycle. *Chem. Rev.* 2007, 107, 563–576. [CrossRef] [PubMed]
3. Statham, P.J. Nutrients in estuaries—An overview and the potential impacts of climate change. *Sci. Total Environ.* 2012, 434, 213–227. [CrossRef] [PubMed]
4. Eliani-Russak, E.; Herut, B.; Sivan, O. The role of highly stratified nutrient-rich small estuaries as a source of dissolved inorganic nitrogen to coastal seawater, the Qishon (SE Mediterranean) case. *Mar. Pollut. Bull.* 2013, 71, 250–258. [CrossRef] [PubMed]
5. Wang, B.; Xin, M.; Wei, Q.; Xie, L. A historical overview of coastal eutrophication in the China Seas. *Mar. Pollut. Bull.* 2018, 136, 394–400. [CrossRef]
6. Cozzi, S.; Ibáñez, C.; Lazar, L.; Raimbault, P.; Giani, M. Flow Regime and Nutrient-Loading Trends from the Largest South European Watersheds: Implications for the Productivity of Mediterranean and Black Sea’s Coastal Areas. *Water* 2019, **11**, 1. [CrossRef]

7. Yu, D.; Chen, N.; Krom, M.D.; Lin, J.; Cheng, P.; Yu, F.; Guo, W.; Hong, H.; Gao, X. Understanding how estuarine hydrology controls ammonium and other inorganic nitrogen concentrations and fluxes through the subtropical River Estuary, S.E. China under base flow and flood-affected conditions. *Biogeochemistry* 2019, **142**, 443–466. [CrossRef]

8. Fang, T.H.; Wang, C.W. Dissolved and particulate phosphorus species partitioning and distribution in the Danshuei River Estuary, Northern Taiwan. *Mar. Pollut. Bull.* 2020, **151**, 110839. [CrossRef]

9. Lemley, D.A.; Adams, J.B.; Taljaard, S.; Strydom, N.A. Towards the classification of eutrophic condition in estuaries. *Est. Coast. Shelf Sci.* 2015, **164**, 221–232. [CrossRef]

10. Wilfert, P.; Kumar, P.S.; Korving, L.; Witkamp, G.J.; van Loosdrecht, M.C.M. The relevance of phosphorus and iron chemistry to the recovery of phosphorus from wastewater: A review. *Environ. Sci. Technol.* 2015, **49**, 9400–9414. [CrossRef]

11. Caraco, N.; Cole, J.; Likens, G.E. A comparison of phosphorus immobilization in sediments of freshwater and coastal marine systems. *Biogeochemistry* 1990, **9**, 277–290. [CrossRef]

12. Fox, L.E.; Sager, S.L.; Wofsy, S.C. The chemical control of soluble phosphorus in the Amazon estuary. *Geochim. Cosmochim. Acta* 1986, **50**, 783–794. [CrossRef]

13. Lehtoranta, J.; Heiskanen, A.S.; Pitkanene, H. Particulate N and P characterizing the fate of nutrients along the estuarine gradient of the River Neva (Baltic Sea). *Est. Coast. Shelf Sci.* 2004, **61**, 275–287. [CrossRef]

14. Van der Zee, C.; Roevros, N.; Chou, L. Phosphorus speciation, transformation and retention in the Scheldt estuary (Belgium/The Netherlands) from the freshwater tidal limits to the North Sea. *Mar. Chem.* 2007, **106**, 76–91. [CrossRef]

15. Yu, Y.; Song, J.M.; Li, X.G.; Yuan, H.M.; Li, N. Distribution, sources and budgets of particulate phosphorus and nitrogen in the East China Sea. *Cont. Shelf Res.* 2012, **43**, 142–155. [CrossRef]

16. Froelich, P.N. Kinetic control of dissolved phosphate in natural rivers and estuaries: A primer on the phosphate buffer mechanism. *Limnol. Oceanogr.* 1988, **33**, 649–668. [CrossRef]

17. Prastka, K.; Sanders, R.; Jackels, T. Has the role of estuaries as sources or sink of dissolved inorganic phosphorus changed over time? Results of a Kd study. *Mar. Pollut. Bull.* 1998, **36**, 718–728. [CrossRef]

18. Sundby, B.; Gobeil, C.; Silverberg, N.; Mucci, A. The phosphorus cycle in coastal marine sediments. *Limnol. Oceanogr.* 1992, **37**, 1129–1145. [CrossRef]

19. Slomp, C.P.; Van der Gaast, S.J.; Van Raaphorst, W. Phosphorus binding by poorly iron oxides in North Sea sediments. *Mar. Chem.* 1996, **52**, 55–73. [CrossRef]

20. Anschutz, P.; Zhong, S.; Sundby, B.; Gobeil, C. Burial efficiency of phosphorus and the geochemistry if iron in continental margin sediments. *Limnol. Oceanogr.* 1998, **43**, 53–64. [CrossRef]

21. Ruttenberg, K.C.; Berner, R.A. Authigenic apatite formation and burial in sediments from non-upwelling, continental margin environments. *Geochim. Cosmochim. Acta* 1993, **57**, 991–1007. [CrossRef]

22. Filippelli, G.M.; Delaney, M.L. Phosphorus geochemistry of equatorial Pacific sediments. *Geochim. Cosmochim. Acta* 1996, **60**, 1479–1495. [CrossRef]

23. Slomp, C.P.; Epping, E.H.G.; Helder, W.; van Raaphorst, W. A key role for iron-bound phosphorus in authigenic apatite formation in North Atlantic continental platform sediments. *J. Mar. Res.* 1996, **54**, 1179–1205. [CrossRef]

24. Jilbert, T.; Slomp, C.P. Iron and manganese shuttles control the formation of authigenic phosphorus minerals in the euxinic basins of the Baltic Sea. *Geochim. Cosmochim. Acta* 2013, **107**, 155–169. [CrossRef]

25. Eggar, M.; Jilbert, T.; Behrends, T.; Rivard, C.; Slomp, C. Vivianite is major sink for phosphorus in methanogenic coastal surface sediments. *Geochim. Cosmochim. Acta* 2015, **169**, 217–235. [CrossRef]

26. Ruttenberg, K.C. Development of a sequential extraction method for different forms of phosphorus in marine sediments. *Limnol. Oceanogr.* 1992, **37**, 1460–1482. [CrossRef]

27. Schenau, S.J.; De Lange, G.J. Phosphorus regeneration vs. burial in sediments of the Arabian Sea. *Mar. Chem.* 2001, **75**, 201–217. [CrossRef]

28. Kryc, K.A.; Murry, R.W.; Murry, D.W. Elemental fractionation of Si, Al, Ti, Fe, Ca, Mn, P, and Ba in five marine sedimentary reference materials: Results from sequential extractions. *Anal. Chim. Acta* 2003, **487**, 117–128. [CrossRef]

29. Pardo, P.; Rauet, G.; Lopez-Sanchez, J.F. Shortened screening method for phosphorus fractionation in sediments a complementary approach to the standards, measurements and testing harmonized protocol. *Anal. Chim. Acta* 2004, **508**, 201–206. [CrossRef]

30. Babu, C.P.; Nath, B.N. Process controlling forms of phosphate in surficial sediments from eastern Arabian Sea impinged by varying bottom water oxygenation conditions. *Deep Sea Res. Part II Top. Stud. Oceanogr.* 2005, **52**, 1965–1980. [CrossRef]

31. Meng, J.; Yao, P.; Yu, Z.G.; Bianchi, T.S.; Zhao, B.; Pan, H.H.; Li, D. Speciation, Bioavailability and preservation of phosphorus in surface sediments of the Changjiang Estuary and adjacent East China Sea inner shelf. *Est. Coast. Shelf Sci.* 2014, **144**, 27–38. [CrossRef]

32. Zhuang, W.; Gao, X.; Zhang, Y.; Xing, Q.; Tosi, L.; Qin, S. Geochemical characteristics of phosphorus in surface sediments of two major Chinese mariculture areas: The Laizhou Bay and the coastal waters of the Zhangzi Island. *Mar. Pollut. Bull.* 2014, **83**, 343–351. [CrossRef]
33. Andrieux-Loyer, F.; Aminot, A. Phosphorus forms related to sediment grain size and geochemical characteristics in French coastal areas. *Est. Coast. Shelf Sci.* 2001, 52, 617–629. [CrossRef]

34. Coelho, J.P.; Flindt, M.R.; Jensen, H.S.; Lillevang, A.L.; Pardal, M.A. Phosphorus speciation and availability in intertidal sediments of a temperate estuary: Relation to eutrophication and annual P-fluxes. *Est. Coast. Shelf Sci.* 2004, 61, 583–590. [CrossRef]

35. Berbel, G.B.B.; Favaro, D.T.; Braga, E.S. Impact of harbour, industry and sewage on the phosphorus geochemistry of a subtropical estuary in Brazil. *Mar. Pollut. Bull.* 2015, 93, 44–52. [CrossRef]

36. Yang, B.; Zhou, J.B.; Lu, D.L.; Dan, S.F.; Zhang, D.; Lan, W.L.; Kang, Z.J.; Nings, Z.M.; Cui, D.Y. Phosphorus chemical speciation and seasonal variations in surface sediments of the Maowei Sea, northern Beibu Gulf. *Mar. Pollut. Bull.* 2019, 141, 61–69. [CrossRef] [PubMed]

37. Wen, L.S.; Jian, K.T.; Liu, K.K. Seasonal variation and flux of dissolved nutrients in the Danshuei Estuary, Taiwan: A hypoxic subtropical mountain river. *Est. Coast. Shelf Sci.* 2008, 78, 694–704. [CrossRef]

38. Fang, T.H.; Chen, W.H. Dissolved and particulate nitrogen species partitioning and distribution in the Danshuei River Estuary, Northern Taiwan. *Mar. Pollut. Bull.* 2021, 164, 111981. [CrossRef] [PubMed]

39. Fang, T.H. Partitioning and behavior of different forms of phosphorus in the Tanshui Estuary and one of its tributaries, Northern Taiwan. *Est. Coast. Shelf Sci.* 2000, 50, 689–701. [CrossRef]

40. Available online: https://www.sso.gov.taipei/Content_List.aspx?n=CDB035368AB25997 (accessed on 10 February 2021).

41. Available online: https://www.wq.epa.gov.tw/EWQP/zh/Default.aspx (accessed on 10 February 2021).

42. Liu, W.C.; Chen, W.B.; Kuo, J.T.; Wu, C. Numerical determination of residence time and age in a partially mixed estuary using three-dimensional hydrodynamic model. *Cont. Shelf Res.* 2008, 28, 1068–1088. [CrossRef]

43. Kao, S.J.; Milliman, J.D. Water and sediment discharge from small mountainous rivers, Taiwan: The role of lithology, episodic events, and human activities. *J. Geol.* 2008, 116, 431–448. [CrossRef]

44. Huh, C.A.; Chen, W.; Hsu, F.S.; Su, C.C.; Lin, S.; Liu, C.S.; Huang, B.J. Modern (<100 years) sedimentation in the Taiwan Strait: Results and source-to-sink pathways elucidated from radionuclides and parti-cle size distribution. *Cont. Shelf Res.* 2011, 31, 47–63. [CrossRef]

45. Berner, R.A.; Rao, J.L. Phosphorus in sediments of the Amazon River and estuary: Implications for the global flux of phosphorus to the sea. *Geochim. Cosmochim. Acta* 1994, 58, 2333–2339. [CrossRef]

46. Grasshoff, K.; Kremling, K.; Ehrhardt, M. *Methods of Seawater Analysis*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2009.

47. Fang, T.H.; Hong, E. Mechanism influencing the spatial distribution of trace metals in surficial sediments of the South-Western Taiwan. *Mar. Pollut. Bull.* 1999, 38, 1026–1037. [CrossRef]

48. Folk, R. *Petrology of Sedimentary Rocks*; Hamphill’s: Austin, TX, USA, 1974.

49. Stumm, W.; Morgan, J.J. *Aquatic Chemistry*, 3rd ed.; John Wiley & Sons: New York, NY, USA, 1996.

50. Kang, X.; Song, J.; Yuan, H.; Shi, X.; Yang, W.; Li, X.; Li, N.; Duan, L. Phosphorus speciation and its bioavailability in sediments of the Jiaozhou Bay. *Est. Coast. Shelf Sci.* 2017, 188, 127–136. [CrossRef]

51. Sudheesh, V.; Movitha, M.; Hatha, A.A.M.; Renjith, K.R.; Resmi, P.; Rahiman, M.; Nair, S.M. Effects of seasonal anoxia on the distribution of phosphorus fractions in the surface sediments of southeastern Arabian Sea shelf. *Cont. Shelf Res.* 2017, 150, 57–64. [CrossRef] [PubMed]

52. Rudnick, R.L.; Gao, S. *Composition of the Continental Crust*; Holland, H.D., Turekian, K.K., Eds.; Treatise On Geochemistry; Elsevier: Amsterdam, The Netherlands, 3rd, 2003, pp. 1–64.

53. Baturin, G.N. Phosphorus cycle in the ocean. *Lithol. Miner. Resour.* 2003, 38, 101–119. [CrossRef]

54. Teodoro, A.C.; Duleba, W.; Gubitoso, S.; Prada, S.M.; Lamparelli, J.E.; Bevilacqua, J.E. Analysis of foraminifera assemblages and sediment geochemical properties to characterize the environment near Araçá and Saco da Capela domestic sewage submarine outfalls of São Sebastião Channel, São Paulo State, Brazil. *Mar. Pollut. Bull.* 2010, 60, 536–553. [CrossRef] [PubMed]

55. Wedepohl, K.H. The composition of the continental crust. *Geochim. Cosmochim. Acta* 1995, 59, 1217–1232. [CrossRef]

56. Gao, S.; Luo, T.C.; Zhang, B.R.; Zhang, H.F.; Han, Y.W.; Hu, Y.K.; Zhao, Z.D. Chemical composition of the continental crust as revealed by studies in east China. *Geochim. Cosmochim. Acta* 1998, 62, 1959–1975. [CrossRef]

57. Moturi, M.C.Z.; Rawat, M.; Subramanian, V. Distribution and partitioning of phosphorus in solid waste and sediments from drainage canals in the industrial belt of Delhi, India. *Chemosphere* 2005, 60, 237–244. [CrossRef]

58. Hartzell, J.L.; Jordan, T.E.; Cornwell, I.C. Phosphorus Burial in Sediments Along the Salinity Gradient of the Patuxent River, a subestuary of the Chesapeake Bay (USA). *Est. Coast.* 2010, 33, 92–106. [CrossRef]

59. Andrieux-Loyer, F.; Philippon, X.; Bally, G.; Kerouel, R.; Youenou, A.; Le Grand, J. Phosphorus dynamics and bioavailability in sediments of the Penze Estuary (NW France): In relation to annual P-fluxes and occurrences of *Alexandrium Minutum*. *Biogeochimica* 2008, 88, 213–231. [CrossRef]

60. Chester, R.; Jickells, T. *Marine Geochemistry*, 3rd ed.; John Wiley and Sons, Ltd.: Chichester, UK, 2012.

61. Martin, J.M.; Meybeck, M. Elemental mass-balance of material carried by major world rivers. *Mar. Chem.* 1979, 7, 173–206. [CrossRef]

62. Fang, T.H.; Chen, J.L.; Huh, C.A. Sedimentary phosphorus species and sedimentation flux in the East China Sea. *Cont. Shelf Res.* 2007, 27, 1465–1476. [CrossRef]
63. Gao, L.; Li, R.; Liang, Z.; Yan, C.; Zhu, A.; Li, S.; Yang, Z.; He, H.; Gan, H.; Chen, J. Remobilization mechanism and release characteristics of phosphorus in saline sediments from the Pearl River Estuary (PRE), South China, based on high-resolution measurements. *Sci. Total Environ.* **2020**, *703*, 134411. [CrossRef]

64. Petterson, K. Phosphorus characteristics of settling and suspended particles in Lake Erken. *Sci. Total Environ.* **2001**, *266*, 79–83. [CrossRef]

65. Slomp, C.P.; Thomson, J.; de Lange, G.J. Controls on phosphorus regeneration and burial during formation of eastern Mediterranean sapropels. *Mar. Geol.* **2004**, *203*, 141–159. [CrossRef]

66. Kraal, P.; Slomp, C.P.; Reed, D.C.; Reichart, G.J.; Poulton, S.W. Sedimentary phosphorus and iron cycling in and below the oxygen minimum zone of the northern Arabian Sea. *Biogeosciences* **2012**, *9*, 2603–2624. [CrossRef]

67. Ghaisas, N.A.; Maiti, K.; White, J.R. Coupled iron and phosphorus release from seasonally hypoxic Louisiana shelf sediment. *Est. Coast. Shelf Sci.* **2019**, *219*, 81–89. [CrossRef]

68. Lucotte, M.; Mucci, A.; Hillaire-Marcel, C.; Tran, S. Early diagenetic processes in deep Labrador Sea sediments: Reactive and nonreactive iron and phosphorus. *Can. J. Earth Sci.* **1994**, *31*, 14–27. [CrossRef]

69. Markovic, S.; Liang, A.; Watson, S.B.; Depew, D.; Zastepa, A.; Surana, P.; Byllaardt, J.V.; Arhonditsis, G.; Dittrich, M. Reduction of industrial iron pollution promotes phosphorus internal loading in eutrophic Hamilton Harbour, Lake Ontario, Canada. *Environ. Pollut.* **2019**, *252*, 697–705. [CrossRef]

70. Dan, S.F.; Liu, S.M.; Yang, B. Geochemical fractionation, potential bioavailability and ecological risk of phosphorus in surface sediments of the Cross River estuary system and adjacent shelf, South East Nigeria (West Africa). *J. Mar. Sys.* **2020**, *201*, 103244. [CrossRef]

71. Delaney, M.L. Phosphorus accumulation in marine sediments and oceanic phosphorus cycle. *Glob. Biogeochem. Cycles* **1998**, *12*, 563–572. [CrossRef]

72. Kim, D.; Schuifert, J.D.; Kastner, M. Francolite authigenesis in California continental slope sediments and its implications for marine P cycle. *Geochim. Cosmochim. Acta* **1999**, *63*, 3477–3485. [CrossRef]

73. McComb, A.J.; Qiu, S.; Lukatelian, R.J.; McAuli, T.F. Spatial and temporal heterogeneity of sediment phosphorus in the Peel-Harvey estuarine system. *Est. Coast. Shelf Sci.* **1998**, *47*, 561–577. [CrossRef]

74. Van der Zee, C.; Slomp, C.P.; Van Raaphorst, W. Authigenic P formation and reactive P burial in sediments of the Nazaré canyon on the Iberian margin (NEAtlantic). *Mar. Geo. 2002*, *185*, 379–392. [CrossRef]

75. Sardans, J.; Rivas-Ubach, A.; Penuelas, J. The elemental stoichiometry of aquatic and terrestrial ecosystems and its relationship with organismic lifestyle and ecosystem structure and function: A review and perspective. *Biogeosciences* **2012**, *9*, 1–39. [CrossRef]

76. Ruttenberg, K.C. *The Global Phosphorus Cycle*; Holland, H.D., Turekian, K.K., Eds.; Treatise on Geochemistry; Elsevier: Amsterdam, The Netherlands, 2003; Volume 8, pp. 585–643.

77. Kraal, P.; Slomp, C.P.; Reed, D.C.; Reichart, G.J.; Poulton, S.W. Sedimentary phosphorus and iron cycling in and below the oxygen minimum zone of the northern Arabian Sea. *Biogeosciences* **2012**, *9*, 2603–2624. [CrossRef]

78. Ruttenberg, K.C.; Goni, M.A. Phosphorus distribution, C:N:P ratios, and δ13COC in arctic, temperate, and trophical coastal sediments: Tools for characterizing bulk organic matter. *Mar. Geo. 1997*, *139*, 123–145. [CrossRef]

79. Bastami, K.D.; Neystati, M.R.; Raeesi, H.; Shafeiain, E.; Baniamad, M.; Shirzadi, A.; Esmailzade, M.; Mozaffari, S.; Shahrokhi, B. Bioavailability and geochemical speciation of phosphorus in surface sediments of the Southern Caspian Sea. *Mar. Pollut. Bull.* **2018**, *126*, 51–57. [CrossRef]

80. Jilbert, T.; Slomp, C.P.; Gustafsson, B.G.; Boer, W. Beyond the Fe-P-redox connection: Preferential regeneration of phosphorus from organic matter as a key control on Baltic Sea nutrient cycles. *Biogeosciences* **2011**, *8*, 1699–1720. [CrossRef]

81. Luoma, S.N. *Processes Affecting Metal Concentrations in Estuarine and Coastal Marine Sediments*; Furness, R.W., Rainbow, P.S., Eds.; Heavy Metals in the Marine Environment; CRC Press: Boca Raton, FL, USA, 2018; pp. 51–66.

82. Hyacinthe, C.; Bonneville, S.; Van Cappellen, P. Reactive iron (III) in sediments: Chemical versus microbial extractions. *Geochem. Cosmochim. Acta* **2006**, *70*, 4166–4180. [CrossRef]

83. Figures, G.; Martin, J.M.; Meybeck, M. Iron behavior in the Zaire Estuary. *Nether. J. Sea Res.* **1978**, *12*, 329–337. [CrossRef]

84. Fox, L.E. The relationship between dissolved humic acids and soluble iron in estuaries. *Geochem. Cosmochim. Acta* **1984**, *48*, 879–884. [CrossRef]

85. Wang, D.; Zhu, M.X.; Yang, G.P.; Ma, W.W. Reactive iron and iron-bound organic carbon in surface sediments of the river-dominated Bohai Sea (China) versus the southern Yellow Sea. *JGR Biogeosci.* **2018**, *124*, 79–98. [CrossRef]

86. Yuan, C.G.; Shi, J.B.; He, B.; Liu, J.F.; Liang, L.N.; Jiang, G.B. Speciation of heavy metals in marine sediments from the East China Sea by ICP-MS with sequential extraction. *Environ. Inter. 2004*, *30*, 769–783. [CrossRef] [PubMed]

87. Dezileau, L.; Pizarro, C.; Rubio, M.A. Sequential extraction of iron in marine sediments from the Chilean continental margin. *Mar. Geo. 2007*, *241*, 111–116. [CrossRef]

88. Gao, X.; Chen, C.T.A.; Wang, G.; Xue, Q.; Tang, C.; Chen, S. Environmental status of Daya Bay surface sediments inferred from a sequential extraction technique. *Est. Coast. Shelf Sci.* **2010**, *86*, 369–378. [CrossRef]

89. Rajendran, A.; Kumar, M.D.; Bakker, J.F. Control of manganese and iron in Skagerrak sediments (northeastern North Sea). *Chem. Geo. 1992*, *98*, 111–129. [CrossRef]
90. Morillo, J.; Usero, J.; Gracia, I. Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere* **2004**, *55*, 431–442. [CrossRef]

91. Lewis, B.L.; Landing, W.M. The biogeochemistry of manganese and iron in the Black Sea. *Deep Sea Res.* **1991**, *38*, s773–s803. [CrossRef]

92. Wartel, M.; Skiker, M.; Auger, Y.; Boughriet, A.; Puskaric, E.; Guegueniat, P. Seasonal variation of Mn$^{2+}$ adsorption on to calcareous surfaces in the English Channel, and its implication on the manganese distribution coefficient. *Mar. Chem.* **1991**, *36*, 85–105. [CrossRef]

93. Bougheriet, A.; Ouddane, B.; Fischer, J.C.; Wartel, M.; Leman, G. Variability of dissolved Mn and Zn in the Seine estuary and chemical speciation of these metals in suspended matter. *Wat. Res.* **1992**, *26*, 1359–1378. [CrossRef]