

Article

# Critical Processes of Trace Metals Mobility in Transitional Waters: Implications from the Remote, Antinioti Lagoon, Corfu Island, Greece

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Received: 6 August 2019; Accepted: 2 September 2019; Published: 4 September 2019



MDP

**Abstract:** The Antinioti Lagoon is a karstified, rather pristine, and shallow coastal lagoon located in the northern part of Corfu Island in NW Greece. The present study examines the levels of metals (Al, Fe, Mn, Cd, Cu, Pb, and Zn) in the dissolved and particulate phase, as well as in surface and core sediments, and identifies the critical processes that define their behavior. The major transport pathway of dissolved Mn, Cd, and Pb, and particulate Mn, Cd, and Zn into the lagoon is through freshwater springs, whereas surface runoff dominates the transport of particulate Al, Fe, and Cu. Interestingly, large particles (>8  $\mu$ m) contain higher amounts of Al, Fe and Mn than the finer ones (<8  $\mu$ m), due to flocculation of oxyhydroxides that, eventually, scavenge other metals, as well. Cadmium and Zn bound to the large particles were found to be less prone to desorption than the smaller ones and were effectively captured within the lagoon. In the sediments, diagenetic processes are responsible for post-depositional changes in the forms of metals (particularly Fe, Mn and Cd). Enrichment factors (EFs) based on local background showed that sediments are enriched in restricted areas in Cd and Pb by maximum factors 4.8 and 10, respectively. These metals were predominantly found in potentially labile forms. Thus, any interventions introducing changes in the physico-chemical conditions may result in the release of metals, with negative implications on the lagoon's ecological quality.

**Keywords:** coastal lagoon; dissolved and particulate metals; sediments; labile forms; enrichment factor; early diagenetic process; groundwater discharges

# 1. Introduction

Trace metals enter coastal lagoons through several pathways, such as atmospheric depositions [1], industrial and urban discharges [2,3], agricultural run-off [4,5], riverine inputs [6], groundwater discharges [7], as well as benthic fluxes [8,9]. Upon reaching the lagoons, trace metals, under variable physicochemical gradients, participate in a series of complex physical, geochemical, and biological processes that greatly affect the distribution of trace metals over the particulate and dissolved phases, as well as the composition of the deposited sediment, and eventually, the fluxes of metals that reach the adjacent sea. These critical biogeochemical processes include complexation reactions of trace metals with dissolved organic and inorganic ligands, adsorption/desorption reactions onto inorganic and organic suspended particles, flocculation and coagulation of colloidal and particulate species, and remobilization from sediments. All these processes vary with pH, ionic strength, the amount and the composition of suspended particles, as well as with redox conditions [10,11].

The limited water exchange with the open sea and the dominant low energy regime from tides, waves and currents, favors the long residence time of water and suspended particulate matter at

the fresh – saline water interface, which in turn, kinetically enables the chemical reactions between the dissolved and particulate phase to take place [12]. Furthermore, the prevailing low energy hydrological regime, favors the accumulation of major and trace elements in sediments [2,13] as well as the accumulation of high amounts of organic matter of autochthonous and allochthonous origin [14,15]. Oxidation of organic matter directly influences the redox potential of the sediment pore water [15]. Once oxygen is consumed, the oxidation of organic matter proceeds via other oxidants following the theoretical sequence:  $O_2 > NO_3/MnO_2 > Fe(OH)_3 > SO_4^{2-}$  [16,17]. Diagenetic processes may have a profound, direct or indirect, effect on the mobility, thus the bioavailability of trace elements [1,18,19]. The remobilization of trace metals occurs principally when Fe and Mn oxyhydroxides are reduced, but such remobilization can be partially or totally prevented in the presence of sulfide, which reacts to form metal sulfide complexes whose solubility controls the fraction of metals dissolved in solution [17,20]. Furthermore, a number of other natural or anthropogenic disturbances, such as re-suspension of

when occurring in shallow settings [21] with potentially hazardous effects for the biota. The Antinioti Lagoon is a rather remote, non-industrialized, moderately urbanized, shallow coastal system located at the northern part of Corfu (Kerkyra) Island in northwestern Greece. The site is of great ecological significance, and as such, is included in the Natura 2000 network as special area of conservation for Europe and is declared as a Site of Community Importance and Special Protection Area [22]. It is also important for fisheries supplying the local market. Despite its importance, previous studies on the area are rare.

sediments due to storms and waves, eutrophication events, and dredging of sediments, could turn sediments from sinks to a long-term source of contaminants to the water column [4,11], particularly

The site is also of scientific interest from the geochemical perspective. In a previous publication it was shown that post-depositional formation of iron sulfide minerals, predominantly pyrite, and incorporation of trace elements into the pyrite phase takes place extensively in deposited sediments, limiting the mobility, and thus the bioavailability of trace metals [23]. In the present study, the distribution of trace metals in three phases, the dissolved, suspended particulate matter, and deposited sediments is examined. The interactions of trace metals between the three phases are investigated in relation to the physicochemical and geochemical parameters. Core sediments are used to estimate the local background levels and reveal temporal trends of accumulation of trace metals due to natural and anthropogenic sources. The main purpose of this study is to identify the critical processes that define trace metals' mobility and fate within the transitional fresh-saline water interface and beyond. In a broader context, the results of the study may contribute to the understanding of the overall behavior of trace metals in similar coastal lagoonal systems, which represent a typical set of transitional ecosystems in the Mediterranean Sea.

### 2. The Study Area

Antinioti Lagoon (39° 49′ N, 19° 52′ E) is part of the homonymous wetland consisting of the lagoon itself (40 ha), and marshes and wet meadows (60 ha) that extend to the southeastern part of the lagoon. The lagoon is shallow with depths ranging from 20 cm to 150 cm and communicates with the Ionian Sea through two channels, separated by the Agia Aikaterini Islet (Figure 1).

Besides surface runoff and precipitation, the freshwater inputs included a series of groundwater springs seeping at the bottom of the lake (close to sites A3, A5, A8; Figure 1) with various yields; another spring flows as a surface stream (site A13) discharging at the southeastern part of the lake (hereafter "stream"). These springs are related to the karstified carbonate formations outcropping in the study area [24]. Two major karstic formations are developed: the upper unit of medium permeability represented by Upper Jurassic – Upper Cretaceous Vigla limestones and the underlying highly permeable Jurassic limestones and dolomites of Pantokrator. An impermeable sequence of Jurassic Posidonia schist interposes between the carbonate rocks and influences the penetration of water from the upper carbonate strata to the lower one, as well as the surface water and groundwater flow paths [24,25]. The main solid phase characterization of sediments by powder XRD [23] revealed

the abundance of quartz followed by calcite, the presence of common phyllosilicates (clays and micas), traces of dolomite, as well as significant amounts of pyrite. This is in accordance with the previous study by Tserolas et al. [26], describing the geology of the wider area.

The wetland sustains a variety of habitats (marshes and water fringed vegetation) and is important for several species of flora, fauna, in particular avifauna, some of which are endangered. Antinioti Lagoon supports also the local economy, as it is exploited for semi-natural extensive fish farming of mullets, seabreams, and eels. Its catchment area is partly agricultural (mainly olive trees) and partly touristic, with intense seasonality in the tourism flow. The greatest threats to the site and its conservation derive from lack of effective management, combined with: (a) the unauthorized disposal of solid wastes and occasionally of domestic wastewater; (b) the excessive use of fertilizers and pesticides in adjacent cultivated areas (e.g., olive groves); (c) the increase of dwellings and tourist infrastructures; and (d) the lack of awareness of the local community about the importance of the wetland [22].



Figure 1. Location of the study area and sampling stations. Rectangles mark groundwater discharges.

#### 3. Materials and Methods

## 3.1. Sampling

Two sampling campaigns were carried out in May 2006 and May 2007, under calm weather conditions. Water samples were collected during both campaigns, surface sediments were collected during the first campaign, and core sediments were collected during the second one. Two stations at the seawater inlets represent the seaward boundary conditions (A1, A12), one station the freshwater stream (A13), while the rest of the stations represent the conditions in the inner part of the lagoon (A2–A11; Figure 1). *In situ* measurements of temperature, salinity, conductivity, pH, and dissolved oxygen were conducted by YSI 63 and YSI 57 portable instruments throughout the water column.

Water sampling bottles were soaked in 10% HNO<sub>3</sub> for at least 48 h, then thoroughly rinsed with deionized water (18 M $\Omega$ ·cm) and stored in double polyethylene bags in a laminar flow bench. In the field, the bottles were rinsed twice with ambient water, and then the samples were collected by hand by submersing pre-cleaned polyethylene bottles at up to 20 cm beneath the water surface. During sampling, all necessary precautions were taken to avoid contamination. The samples were transported in two polyethylene bags stored in a portable refrigerator.

Surface sediment samples were collected by an Ekman-Birge grab sampler. A short sediment core was collected from station A8 (Figure 1) with a Plexiglas tube 60 cm-long and 10 cm-wide, attached to a push-tube coring device. The core was sectioned immediately after the collection into 1–2 cm intervals. Sediment samples were stored in pre-cleaned polyethylene vessels and transported in a portable refrigerator.

#### 3.2. Samples Pretreatment

All labware used in the analytical procedures were soaked in 10% HNO<sub>3</sub> for at least 48 h, and then thoroughly rinsed with deionized water. Precautions were taken during all stages in order to avoid contamination.

The water samples were filtered under a clean laminar bench. The filtration was carried out in succession through 8  $\mu$ m and 0.45  $\mu$ m Millipore filters in order to separate the dissolved (<0.45  $\mu$ m) and the particulate phase (>0.45  $\mu$ m) and determine the suspended particulate matter (SPM) in two grain-size fractions (0.45  $\mu$ m < diameter (d) < 8  $\mu$ m and d > 8  $\mu$ m). The filtrates for the determination of dissolved metals were acidified to pH < 2 by HNO<sub>3</sub> prior to pre-concentration on Chelex-100 (100–200 mesh, BioRad Laboratories) and subsequent elution of trace metals [27].

The filters for particulate metals (0.45  $\mu$ m < d < 8  $\mu$ m and d > 8  $\mu$ m) were dried to constant weight and then digested with concentrated HNO<sub>3</sub> on a hot plate (85 °C approximately) overnight [27].

Sediment samples were freeze-dried in a Labconco apparatus. Then the silt and clay fraction (<63  $\mu$ m) was separated by means of sieving. This approach has been widely used to reduce the physical variability of metal content due to grain size effects [28–30], although recently its effectiveness has been questioned, particularly if coatings of metal scavengers exist in coarse-grained particles [31]. Total metals contents were determined after complete dissolution of sediments with an acid mixture of HNO<sub>3</sub>-HClO<sub>4</sub>-HF acids [32]. The 0.5 N HCl extractable metals were determined after the method of Agemian and Chau [33].

# 3.3. Analytical Procedures

Trace metals analysis was performed by means of Flame and Graphite Furnace AAS (Varian SpectrAA-200 and Varian SpectrAA-640 Zeeman) (Varian, Australia), depending on the concentration levels of each determined element. Procedural blanks were run in the same way as samples and were usually below Limits of Detections (LOD), reported in Table 1.

Variable	Al	Cd	Cu	Fe	Mn	Pb	Zn						
Dissolved phase													
LOD ( $\mu g \cdot L^{-1}$ )	-	0.0038	0.044	1	0.0085	0.040	0.50						
CASS-4:	-	-	-	-	-	-	-						
Assigned value	-	$0.026 \pm 0.003$	$0.592 \pm 0.055$	-	$2.78 \pm 0.19$	$0.0098 \pm 0.0035$	$0.381 \pm 0.057$						
Measured value	-	$0.024 \pm 0.002$	$0.570 \pm 0.030$	-	$2.79 \pm 0.12$	$0.0089 \pm 0.0023$	$0.409 \pm 0.030$						
Pacouom <sup>9</sup> (apileas)		106-102-102% at	99–96–93 at	73–80 at	98–98–101 at	99–93–92 at	105–101–100 at						
Recovery /8 (spikes)	-	0.05–0.1–0.2 μg·L <sup>−1</sup>	0.2–1.0–2.0 μg·L <sup>–1</sup>	5–7.9 μg·L <sup>-1</sup>	0.2–1.0–5.0 μg·L <sup>-1</sup>	0.2–1.0–2.0 μg·L <sup>–1</sup> L	1.0–2.0–5.0 μg·L <sup>−1</sup>						
Popostshility <sup>0</sup> (spilos)		$6.4\%$ at $0.05~\mu g \cdot L^{-1}$	5.4% at 0.2 $\mu$ g·L <sup>-1</sup>	2.3% at 5 $\mu$ g·L <sup>-1</sup>	$4.8\%$ at 0.2 $\mu$ g·L <sup>-1</sup>	6.9% at 0.2 μg·L <sup>-1</sup>	5.8% at 1.0 μg·L <sup>-1</sup>						
Repeatability /8 (spikes)	-	$3.5\%$ at $0.2 \ \mu g \cdot L^{-1}$	1.9% at 2.0 μg·L <sup>-1</sup>	4.0% at 7.9 μg·L <sup>−1</sup>	$2.7\%$ at $5.0 \ \mu g \cdot L^{-1}$	2.8% at 2.0 μg·L <sup>−1</sup>	5.2% at 5.0 μg·L <sup>-1</sup>						
			Particulate p	ohase									
LOD part. metals ( $\mu g \cdot L^{-1}$ )	0.62	0.0019	0.022	0.5	0.0042	0.020	0.25						
Repeatability%	20% at 50 $\mu$ g·L <sup>-1</sup>	12% at 0.0022 μg·L <sup>-1</sup>	$15\%$ at 0.05 $\mu g \cdot L^{-1}$	5.5% at 15 μg·L <sup>-1</sup>	9.6% at 0.13 μg·L <sup>-1</sup>	5.3% at 0.19 μg·L <sup>-1</sup>	$11\%$ at 0.93 $\mu g \cdot L^{-1}$						
			Sediments (total o	ligestions)									
LOD (mg⋅kg <sup>-1</sup> )	1.7	0.015	0.177	4	0.034	0.16	2						
PACS-2:	-	-	-	-	-	-	-						
Assigned value	$66200 \pm 3200$	$2.11 \pm 0.15$	$310 \pm 12$	$40900 \pm 600$	$440 \pm 19$	$183 \pm 8$	$364 \pm 23$						
Measured value	$63000 \pm 800$	$2.2 \pm 0.2$	$300 \pm 10$	$41700 \pm 600$	$440 \pm 10$	$187 \pm 8$	$380 \pm 15$						
Recovery% (PACS-2)	95	104	97	102	99	102	104						
Repeatability% (PACS-2)	1.3	6.8	3.3	1.4	2.3	4.3	3.9						

Table 1. Quality assurance data of the methods employed for the determination of metals in the dissolved and particulate phase and total contents in sediments.

The accuracy and repeatability of dissolved metals determinations by the Chelex-100 resin has been tested in the laboratory using spiked seawater samples at three concentration levels, as well as by analyzing the certified reference material (CRM) CASS-4 (from National Research Council of Canada, NRCC) (Table 1). In the case of the sediment samples, the accuracy and repeatability of total sediment digestions was evaluated by analyzing the certified reference materials PACS-2 (NRCC) with satisfactory results (Table 1).

## 3.4. Statistical Analyses

Statistically significant differences of metal concentrations (dissolved and particulate) among the three sectors of the system, i.e., the inlets, the inner part of the lagoon and the freshwater spring, were explored by independent *t*-test on log transformed values to correct for departure from normality. The relationships among the considered variables were tested by using non-parametric Spearman coefficient. A probability level below  $\rho < 0.05$  was set as statistically significant. Statistical analyses were carried out using the IBM SPSS software v. 21.0 (IBM corp, Armonk, NY, USA).

# 4. Results

#### 4.1. Physicochemical Parameters and SPM

Summary statistics of the physicochemical parameters and SPM in the three sectors of the system, the stream, the inner part, and the inlets, is presented in Table 2; the detailed results per each sampling are given in Table A1. Salinity values exhibited significant spatial variation (Table 2) due to mixing of seawater and freshwater. Higher values were found at the inlets (A1 and A12) due to seawater intrusion. During both sampling periods, the western inlet exhibited higher values of salinity than the eastern, signifying that this part of the lagoon is more exposed to sea currents (Table A1). In fact, in the past, considerable amounts of sediments were transferred after strong and persistent northerly winds and sealed the inlet (a feature known as sediment plug), which was artificially re-opened in order to facilitate water circulation and fishing activities. Concerning the inner stations, surface salinity ranged from 8.6 to 17.6. Bottom salinity was higher than in surface layers (data not shown).

At the inlets, pH obtained typical values of seawater (7.9–8.3), whereas the values found at the inner part of lagoon and the stream were 7.5–8.3 and  $\leq$  7.5, respectively (Table 2).

Parameter	Stream	Inner Sector	Inlets
salinity	4.70-4.80 (4.75)	8.60-19.4 (13.6)	22.0-37.7 (33.8)
pH	7.26-7.51 (7.38)	7.45-8.30 (7.94)	8.01-8.24 (8.17)
SPM $(mg \cdot L^{-1})$	1.53-1.95 (1.74)	7.04-14.2 (10.4)	13.4-20.9 (14.6)
d. Fe ( $\mu g \cdot L^{-1}$ )	2.61-5.23 (3.92)	0.42-6.32 (1.99)	0.43-6.36 (2.12)
d. Mn ( $\mu g \cdot L^{-1}$ )	2.91-15.4 (9.14)	1.32-7.67 (4.31)	1.12-4.36 (1.47)
d. Cd ( $\mu g \cdot L^{-1}$ )	0.069–0.164 (0.116)	0.016-0.079 (0.038)	0.018-0.025 (0.019)
d. Cu( $\mu g \cdot L^{-1}$ )	0.16-0.47 (0.32)	0.09-1.53 (0.35)	0.18-0.66 (0.30)
d. Pb ( $\mu g \cdot L^{-1}$ )	0.20-0.27 (0.24)	0.02-0.34 (0.08)	0.03-0.06 (0.06)
d. Zn ( $\mu g \cdot L^{-1}$ )	3.17-9.94 (6.56)	1.00-15.0 (4.18)	1.20-3.37 (2.35)
p. Al (mg·kg <sup>−1</sup> )	3406-4204 (3805)	4905–90457 (8334)	2432-15629 (7152)
p. Fe (mg·kg <sup>−1</sup> )	6731-12793 (9762)	3496-58612 (6024)	2379-11996 (6279)
p. Mn (mg·kg <sup><math>-1</math></sup> )	1667-1945 (1806)	173–1213 (385)	36-258 (109)
p. Cd (mg·kg <sup>−1</sup> )	3.76-5.23 (4.50)	0.63-4.20 (1.84)	0.09-0.78 (0.40)
p. Cu (mg·kg <sup>−1</sup> )	51-101 (76)	10-177 (25.6)	7-22 (19)
p. Pb (mg·kg <sup><math>-1</math></sup> )	22.8-36.9 (29.9)	5.91-81.7 (16.2)	7.0-16.5 (10.4)
p. Zn (mg·kg <sup>−1</sup> )	198–1790 (994)	22-423 (193)	12-107 (62)

**Table 2.** Ranges (min–max) and median values (in parenthesis) of salinity, pH, SPM and dissolved (d.) and particulate (p. in w/w) metals in the three sectors of the Antinioti Lagoon system, during both sampling periods.

Suspended Particulate Matter (SPM) concentrations were higher at the inlets than in the inner part of the lagoon (Table 2), due to the turbulent mixing of seawater and fresh/brackish water and the re-suspension of sediments. The lowest concentrations were found at the stream, station A13 (1.5 mg·L<sup>-1</sup> and 2 mg·L<sup>-1</sup> in the first and second sampling, respectively). Particles with diameter  $d > 8 \mu m$  accounted for  $68 \pm 14\%$  (mean  $\pm$  sd) of total SPM at the inlets,  $64 \pm 8\%$  of SPM at the inner part of the lagoon, and  $38 \pm 23\%$  at the stream.

# 4.2. Trace Metals in Water

#### 4.2.1. Levels and Spatial Variation

The Water Framework Directive 2000/60/EC [34] identified Cd and Pb as priority substances, posing a threat to, or via, the aquatic environment at the EU level. Environmental quality standards (EQS) have been set by its Daughter Directive 2013/39/EU [35] with annual average values for Cd:  $0.2 \ \mu g \cdot L^{-1}$  and  $1.3 \ \mu g \cdot L^{-1}$  for Pb. The concentrations of dissolved metals in the inner sector and the inlets were well below the EQS (Table 2). However, dissolved Cd in the stream (0.116  $\mu g \cdot L^{-1}$ ) was marginally below the EQS, suggesting that this element is of environmental concern and should be regularly monitored.

The stream, of groundwater origin, was the major source of Cd into the lagoon. This is evidenced by the fact that dissolved, total, i.e., the sum of dissolved and particulate (w/v) shown in Figure 2, as well as particulate (w/w; Table 2) Cd concentrations were significantly higher in the stream than the inner sector. Furthermore, the stream constituted the primary source of dissolved Pb, dissolved and particulate (both in w/w and w/v) Mn, and particulate (w/w) Zn. In contrast, the concentrations of Fe and Pb in the particulate phase (w/v) were significantly higher in the inner sector than the stream, suggesting that other sources (e.g., runoff) rather than the emanating groundwater are responsible for the transport of these elements into the lagoon.



**Figure 2.** Spatial variation of dissolved and particulate (w/v) concentrations for (**a**) Fe, (**b**) Mn, (**c**) Cd, (**d**) Cu, (**e**) Pb, and (**f**) Zn.

Figure 3 illustrates the detailed distribution of particulate elements between the two fractions of suspended particles (d < 8  $\mu$ m and >8  $\mu$ m). The concentrations of particulate metals are expressed in

w/w in order to compensate for differences of the SPM concentrations among the stations. Particles with  $d > 8 \mu m$  contained larger amounts of Al and Fe than the finer ones, of  $d < 8 \mu m$ . This distribution pattern is in contrast to the general and well established trend that as the grain size of particles decreases, the surface area increases, as does the particulate metal concentrations [36,37].



**Figure 3.** Spatial variation of particulate metal contents (w/w) of the >8  $\mu$ m and the <8  $\mu$ m fraction of SPM: (a) Al, (b) Fe, (c) Mn, (d) Cd, (e) Cu, (f) Pb, and (g) Zn.

The most probable explanation of the rather unusual, relative enrichment of larger particles is that these are agglomerated grains, consisting of aggregates of smaller particles [38] that are produced *in situ* through flocculation processes at the fresh-saline water interface [27,39,40]. The elevated Al, Fe, and Mn contents of the larger particles indicate that these phases are either: (a) linked to the original, smaller individual particulates, as a result of coagulation and precipitation of colloids and/or as surface coatings on clays [41]; or (b) that the newly formed agglomerates are cemented together by Fe/Mn coatings [37,38]. Some of the cement coatings could be organic in nature as well [37,42], since bacterially mediated processes may promote flocculation of smaller particles [43].

The presence of Al and Fe/Mn onto the larger particles increases their ability to sorb other metals. This is supported by the significant correlations between the elements in the > 8  $\mu$ m fraction, shown in Table A2. Significant correlations of Cd, Cu, Pb, and Zn with Al, Fe, and Mn in the >8  $\mu$ m fraction of SPM (r = 0.505–0.853;  $\varrho$  < 0.05) are consistent with the scavenging of metals by Al-Fe-Mn oxyhydroxides, and explains the enrichment with metals of the suspended particles >8  $\mu$ m in relation

to the finer particles (<8  $\mu$ m) (Figure 3). The strong correlation of suspended Pb with Al, Fe and Mn (r = 0.619–0.779) explains its predominant partitioning in all samplings and stations in the > 8  $\mu$ m fractions of particles. Furthermore, the higher correlation coefficient of Pb and Fe over Al and Mn is compatible with its strong affinity (stability constant) for freshly precipitated Fe oxyhydroxides [32]. Cadmium and Zn correlated strongly with Mn (r = 0.949, and 0.710, respectively), suggesting the preferential association of these elements with Mn oxyhydroxides. According to Turner et al., [44] Cd binding onto Mn oxides is much stronger than on Fe oxyhydroxides or other phases.

The concentrations of particulate Mn, Cd, and Zn (in w/w) were significantly lower in the inlets than the inner part of the lagoon. This pattern suggests that these elements are entrapped within the lagoon. No statistical differences were determined for the other metals (Fe, Cu, Pb) between the inner sector and the inlets.

During the first sampling period, at the eastern inlet an inflow of relatively dense saline water (S: 37.2) near the bottom and an outflow of brackish water (S: 22.0) at the surface was evident from salinity measurements. An additional sample for trace metals and SPM determinations was collected from the near-bottom, saline layer at this site, to get insights into the processes occurring at this interface. Figure 4 shows the detailed distribution of particulate SPM, Al, Fe, and Mn between the two fractions of suspended particles (<8  $\mu$ m and >8  $\mu$ m) in the two water layers. SPM concentrations in the bottom, saline layer were higher (sum of both fractions: 41.9 mg·L<sup>-1</sup>) than in the surface (13.4 mg·L<sup>-1</sup>), suggesting the re-suspension of bottom sediments. The coarser fraction of SPM was the predominant one. Despite the re-suspension, the metal contents of the larger particles of the bottom water layer were slightly higher than those of the surface layer. Aluminum, Fe and Mn contents of the smaller particles were higher at the surface water layer than the bottom layer. Apparently, the flocculation and the enrichment mechanisms described above continued under the high salinity regime.



**Figure 4.** Concentrations of (**a**) SPM, and (**b**) Al, (**c**) Fe, and (**d**) Mn (w/w) contents of particulate solids with diameter  $d < 8 \mu m$  and  $d > 8 \mu m$  in the brackish surface and the saline bottom water layer of station A1.

#### 4.2.2. Partitioning and Interactions between the Dissolved and Particulate Phases

According to Figure 2, in the inner part of the lagoon, Fe and Pb were primarily particle-bound (on average 94% and 70% of the total concentrations, respectively), Cd and Zn were found to be predominantly in the dissolved phase (67% and 70% of the total concentrations, respectively), whereas Cu and Mn were equally associated with the solid and solution phases. In the stream water, all elements were predominantly found in the dissolved phase, except Fe. The predominance of the dissolved phase for Mn and the particulate phase for Fe in stream water sample is compatible with the fact that oxidation kinetics of Mn(II), emanating from groundwater, is slower than that of Fe(II) [8,45].

Solid-solution partitioning of metals in estuarine systems has been widely described by the partition coefficient  $K_D$ , defined as [46]:

$$KD = \frac{Particulate concentration\left(\frac{w}{w}\right)}{Dissolved concentration\left(\frac{w}{v}\right)}$$
(1)

The partition coefficient should be constant for a given composition of suspended particles and of solution; however, any change of the particle surface reactivity and/or solution properties may result in K<sub>D</sub> changes [47]. The partition coefficient is calculated in this study for all particles (K<sub>D-T</sub>), for the large particles with diameter > 8  $\mu$ m (K<sub>D-L</sub>), and for the small particles with diameter d < 8  $\mu$ m (K<sub>D-S</sub>); (Table 3). This distinction allows the investigation of the role of each fraction of particles on the solid-solution partitioning in detail.

**Table 3.** Partition coefficient (log<sub>10</sub>)  $K_{D-T}$  for all the particles,  $K_{D-L}$  for particles with diameter d > 8  $\mu$ m, and  $K_{D-S}$  for particles with 0.45  $\mu$ m < d < 8  $\mu$ m.

Partition Coefficient K <sub>D</sub>	Statistics	Fe	Mn	Cd	Cu	Pb	Zn
	mean	6.53	5.01	4.50	4.90	5.27	4.59
	min	5.74	4.51	3.59	3.86	4.86	3.76
K	max	7.45	5.82	5.19	5.80	5.88	5.75
ND-1	mean inlets	6.51	4.89	4.11	4.63	5.23	4.30
	mean inner	6.57	4.99	4.68	4.94	5.33	4.65
	mean stream	6.40	5.43	4.62	5.42	5.11	5.03
	mean	6.71	5.12	4.48	4.86	5.38	4.45
K <sub>D-L</sub>	min	5.95	4.58	3.60	3.88	4.93	3.67
	max	7.57	6.48	5.11	5.48	5.95	5.47
	mean	5.77	4.16	4.52	4.89	4.91	4.55
K <sub>D-S</sub>	min	4.56	3.08	3.33	3.70	3.63	2.50
	max	7.10	5.87	5.45	5.86	5.67	5.81

The average  $K_{D-T}$  follows the order Fe < Pb < Mn < Cu < Zn, Cd (Table 3), and their values are similar to the ones reported for other transitional waters [48,49]. The elevated  $K_{D-T}$  values for Fe and Pb indicate these metals are associated with and transported in the particulate phase, whereas the low  $K_{D-T}$  values for Zn and Cd confirm their affinity to the dissolved phase.

The values of  $K_{D-L}$  for the large particles were, in general, higher than the  $K_{D-S}$  values for the smaller ones. This is consistent with the removal from solution through flocculation of Fe and Mn and co-precipitation processes for trace metals, resulting in elevated metal contents of the large particles (Figures 3 and 4). Figure 5 illustrates the variation of  $K_D$  values for Cd, Zn, and Cu with salinity in the inner part of the lagoon (n = 10). These plots are advantageous to the widely used metals concentrations/salinity relationships because they allow for the exchange processes between the dissolved and particulate phases to be considered [49]. The  $K_{D-S}$  values for Cd and Zn decreased with increasing salinity (r = -0.869;  $\varrho = 0.001$  and r = -0.740;  $\varrho = 0.013$ , respectively), but not the  $K_{D-L}$ . These results show that the exchange processes take place predominantly between the smaller fraction of

SPM (<8  $\mu$ m) and the dissolved phase, rather the coarser fraction of SPM (>8  $\mu$ m). The lack of a clear relationship of the K<sub>D-L</sub> values for Cd and Zn with salinity could be attributed to their strong binding to Mn oxyhydroxides of the large particles (Table A2). Turner et.al. [44] showed that, when Cd is bound to Mn oxides, it is less prone to desorption across the salinity gradient. In contrast, the decrease of the K<sub>D-S</sub> values with increasing salinity could be attributed to desorption. In the case of Cd, this behavior is often attributed in the formation of highly stable and soluble chloro-complexes [1,50,51]. As far as Cu is concerned, both K<sub>D-S</sub> and the K<sub>D-L</sub> values decreased with increasing salinity, suggesting the removal of both SPM fractions to the solution. The non-conservative behavior of Cu has been ascribed in more detailed studies to the strong Cu-complexing ligands such as organic colloids and dissolved organic matter [52,53]. Dissolved Cu concentrations did not vary between the inner part and

the inlets of the lagoon. Thus, it can be suggested that desorption from the solid phase enhances the

dispersion of dissolved Cu beyond the boundaries of the lagoon.



**Figure 5.** Variation of partition coefficient ( $K_D$ ) with salinity the inner part of the lagoon: (**a**)  $K_{D-S}$  for Cd of the small particles (<8  $\mu$ m) (**b**)  $K_{D-L}$  for Cd of the large particles (d < 8  $\mu$ m), (**c**)  $K_{D-S}$  for Zn, and (**d**)  $K_{D-L}$  for Cu, and (**f**)  $K_{D-L}$  for Cu.

# 4.3. Surface Sediments

Organic carbon content in the silt and clay fraction (<63  $\mu$ m) of the surficial sediments of two inlets was low and ranged from 0.26% to 0.59%, whereas at the inner part and the outlet of the stream it ranged between 3.97%–8.20%, and 10.40%, respectively (Table 4). Organic-rich sediments are common in coastal lagoons [14], mainly due to the high productivity of these systems in relation to other coastal marine and estuarine systems.

Sampling Stations/ Statistics	OC	Al-T	Fe-T	Fe-Ext	Mn-T	Mn-Ext	Cd-T	Cd-Ext	Cu-T	Cu-Ext	Pb-T	Pb-Ext	Zn-T	Zn-Ext
						Surf	ace Sedim	ents						
A1	0.26	11000	3130	1260	350	330	0.14	0.08	12	2.04	4.05	2.04	9.23	5.36
A2	4.32	25000	10700	4980	190	150	0.69	0.45	25	13.9	31.8	23.9	50.4	27.4
A3	5.92	30100	12100	4370	140	73	1.89	1.09	32	18.7	29.3	23.7	75.1	36.4
A4	8.52	31100	18200	3630	170	68	2.04	1.79	41	37.6	33.1	31.9	89.2	56.9
A5	10.6	39300	20800	5140	200	66	3.42	3.12	50	22.4	66.1	49.6	106	49.7
A7	4.78	62600	30800	4930	310	153	1.66	1.02	56	23.8	23.1	18.9	121	47.4
A8	7.79	48000	24000	8910	180	75	1.71	1.02	57	28.6	36.5	25.8	122	46.4
A9	3.97	28800	17500	10760	170	150	0.22	0.17	32	17.9	22.9	18.5	72.5	31.1
A10	11.2	41900	31700	14200	330	210	0.43	0.41	75	42.4	25.3	23.1	98.4	55.2
A12	0.59	9790	3800	1980	150	140	0.17	0.05	13	3.10	8.29	2.33	17.2	8.80
A13	10.4	33900	20100	10100	210	190	0.59	0.48	37	20.6	25.3	19.4	70.8	32.2
Mean	6.2	32800	17500	6390	220	150	1.18	0.88	39	21.0	27.8	21.7	75.6	37.2
Median	5.9	31100	18200	4980	200	150	0.69	0.48	37	20.6	25.3	23.1	75.1	36.4
Min	0.3	9790	3130	1260	140	66	0.14	0.05	12	2.04	4.05	2.04	9.23	9.23
Max	11.2	62500	31700	14200	350	330	3.42	3.12	75	42.4	66.1	49.6	121.7	56.9
Sd	3.8	15300	9520	4050	73	80	1.05	0.91	20	12.4	16.1	13.0	37.8	15.5
						Со	re Sedime	nts						
Mean	7.3	56900	24000	7406	129	33.4	1.47	1.24	57	28.0	74.4	48.2	143	39.6
Median	6.9	49800	21600	5713	123	21.1	0.81	0.64	58	28.9	40.4	28.8	141	41.6
Min	2.4	33500	19300	1762	105	11.7	0.23	0.19	36	18.6	19.9	8.13	91.1	27.3
Max	11.9	90200	40300	21276	178	88.4	3.51	2.97	69	32.9	566	300	202	53.2
Sd	3.3	17400	5800	5631	19.0	25.2	1.17	1.08	9.4	4.15	113	62.9	28.6	8.38

**Table 4.** Organic carbon (OC in%), total (T in  $mg \cdot kg^{-1}$ ) and 0.5 N HCl extractable (Ext in  $mg \cdot kg^{-1}$ ) metal contents in the surficial and core sediments.

Total metals contents in the surface sediments followed the order (median values): Al  $(33100 \text{ mg} \cdot \text{kg}^{-1}) > \text{Fe} (18200 \text{ mg} \cdot \text{kg}^{-1}) > \text{Mn} (200 \text{ mg} \cdot \text{kg}^{-1}) > \text{Zn} (75 \text{ mg} \cdot \text{kg}^{-1}) > \text{Cu} (37.0 \text{ mg} \cdot \text{kg}^{-1}) > \text{Pb} (25.3 \text{ mg} \cdot \text{kg}^{-1}) \text{Cd} > 0.69 \text{ mg} \cdot \text{kg}^{-1})$ , and varied widely on the spatial scale (Table 4). Aluminum, the structural component of clay minerals, ranged from 6790 to 62,500 mg} \cdot \text{kg}^{-1}. The lower Al values were determined at the two inlets, due to the high abundance of carbonates and quartz at these sediments. The higher ones were determined at the central part of the lagoon (stations A7, A8), as well as the outlet of the stream (station A10), indicating the preferable accumulation of terrigenous aluminosilicates at these sites.

The large variation of Al contents suggests that granulometric and mineralogical differences exist among the sediment samples. This is despite the fact that sieving out the sand fraction provides theoretically a more homogeneous fraction of the sediment for metal levels estimation and distribution patterns analysis. Thus, normalization to Al was employed in order to further minimize grain-size effects [15,28].

Figure 6 shows the spatial variation of metal to Al (Me/Al) ratios. The highest Fe/Al values were observed at the outlet of the stream, whereas the lowest ones at the two inlets. A similar distribution pattern is observed for Cu. Copper correlated with Al (r = 0.936;  $\rho < 0.0005$ ) and Fe (r = 0.982;  $\rho < 0.0005$ ), suggesting their common transport pathway through land run-off and a similar deposition pattern in the surface sediments. Cadmium to Al, as well as Pb/Al ratio values were higher at the eastern part of the lagoon and exhibited maxima at the sediments of station A4. Values of Zn/Al were rather homogeneous throughout the lagoon, however, a local maximum was observed at station A4. Zinc correlated with Al (r = 0.918;  $\rho < 0.0005$ ) and Fe (r = 0.918;  $\rho < 0.0005$ ), which is indicative of their common origin from terrestrial sources.



**Figure 6.** Spatial distribution of (**a**) Fe/Al, (**b**) Mn/Al, (**c**) Cd/Al, (**d**) Cu/Al, (**e**) Pb/Al, and (**f**) Zn/Al values in the surface sediments of the Antinioti Lagoon.

The potential mobility of metals under changing environmental conditions, thus their (bio)availability, can be estimated by extracting the sediment samples with dilute HCl (0.5 N) [54]. The procedure extracts the fraction of metals retained in sediments by adsorption, complexation and precipitation processes [55].

The extractability of metals (i.e., the percentage of 0.5 HCl extracted contents in relation to total contents) in the surface sediments followed the order (median value): Fe (40%) < Zn (48%) < Cu (56%) < Mn, Cd (65%) < Pb (77%), suggesting that Fe and Zn were the most inert metals, whereas Pb, Cd and Mn the potentially more mobile metals under changing environmental conditions. The extractability of Mn at the sediments of the two inlets and the stream accounted for more than 90%. This substantial increase of the extractability in the inlets and the stream compared to the inner part of the lagoon (median value: 51%) suggests that in the former areas Mn is found in more labile phases, which are related to the flocculation processes discussed previously.

Dilute HCl extractable Cd, Cu, Pb and Zn contents were significantly correlated with OC content (r = 0.629–0.827;  $\rho < 0.05$ ), which is consistent with the findings of Yuan et al. [42]. The association of this fraction of metals with OC may result in the mobilization of metals along with the oxidation of OC. [8,18]. More insights into diagenetic processes are gained through the examination of core sediments.

#### 4.4. Core Sediments

Organic carbon content varied widely with depth and ranged from 2.4% to 11.9% (Figure 7). The lower values found in the sediments below 25 cm depth, indicate the decomposition of organic matter with time, while the higher values found within the 4–20 cm sediment interval imply buried organic matter not yet degraded [56]. High OC contents result in high oxygen consumption and, subsequently, in the establishment of sub-oxic, anoxic, and/or sulfidic conditions in the sub-surface sediments. Black-gray bands and dots were observed within the 6–24 cm sediment interval, which indicate the presence of sulfides. Deeper in the sediment column, in the 24–31 cm interval, sediments had a reddish-brown color that indicates the presence of iron oxyhydroxides [45,57].



**Figure 7.** Vertical distributions of total, 0.5N HCl extractable, and normalized to Al metal contents in the core sediments.

The levels of Al, Fe, Cd, Cu and Zn in the core sediments were similar to those found in the surficial ones, whereas the levels of Mn were slightly lower (Table 4). The extractability of metals by 0.5 N HCl in the core sediments followed the order (median): Mn (17%) < Fe (25%) < Zn (28%) < Cu (49%) < Pb (71%) < Cd (83%). The lower percentages of extracted metals, particularly for Mn and Fe, compared to the surface sediments, signify their presence in different forms. This could be attributed to: (a) the processes occurring in the water column that involve the complexation of metals with organic and inorganic ligands and the formation of metal precipitates; and (b) the processes occurring in the sediment column that involve the redistribution of metals on the geochemical substrates, or even a partial release from the sediments to the water column, triggered by diagenetic redox processes.

The extractability of Mn by the dilute HCl decreased from 44% of the total content at the surface layer to less than 20% within the 9–30 cm sediment interval. The profile of 0.5N HCl extracted Mn (Figure 7) shows an increasing trend from the depth of 30 cm towards the surface, which is typical of the progressive dissolution of Mn oxyhydroxides, upward diffusion of at least part of Mn(II) dissolved ions, and re-oxidation/precipitation at the surface layer where higher redox potentials are met [58]. With this process, the least labile fraction of Mn is left behind, thus the extractability of Mn is lower in the subsurface sediments than in the surficial ones.

The amount of Fe extracted by the dilute HCl varied widely with depth from 9% to 71% of the total Fe content. The highest percentages coincide with the observed orange- bands, which are attributed to accumulations of Fe oxyhydroxides that are fully recovered by the extractant [59]; the lower percentages coincide with the black-grey bands, which could signify the presence of pyrite, the end-product of metastable Fe-monosulfides with hydrogen sulfide [60], which are not extracted by HCl [59]. Previous research at the site [23] confirmed the presence of pyrite in the subsurface sediments of the Antinioti Lagoon by means of X-ray Diffraction and Scanning Electron Microscope analysis. However, within the pyritized sediments, micro-environments of authigenic Fe/Mn oxides (Mn containing goethite) were identified through synchrotron radiation micro X-ray fluorescence (SR  $\mu$ -XRF).

Total and 0.5 N HCl extracted Cd contents were significantly correlated with OC content (r = 0.695 and 0.783, respectively;  $\varrho < 0.0005$ ). The profiles were similar to each other and showed lower contents near the water-sediment interface, a substantial increase in the 4–20 cm sediments layers, followed by a further decrease after this depth. This distribution pattern has been described in previous studies [19,58], and is consistent with Cd dissolution after the oxic degradation near the surface of fresh organic carbon with which Cd was originally bound, and downward diffusion and fixation, in the thick zone of sub-oxic to anoxic grey-black colored, underlying sediments, which are depleted in Mn. This pattern is typical in sub-oxic sediments where authigenic accumulations, as CdS precipitates, take place [19,58,61,62]. Cadmium sulfide minerals are fully recovered by HCl [63], and this explains the high amounts of Cd extracted by the procedure (median value: 85%) in relation to the total metal.

The vertical distribution of total and 0.5 N HCl-extracted Pb is dominated by two extreme values at 23 cm (203 and 161 mg·kg<sup>-1</sup>, respectively) and 30 cm (566 and 300 mg·kg<sup>-1</sup>, respectively). These peaks are most probably attributed to distinct and occasional events of pollution, which are unknown to us.

#### 4.5. Enrichment Factors

The magnitude and spatial extent of human-induced change was determined by expressing current normalized to Al metal contents as enrichment over pre-anthropogenic or background levels through the widely used Enrichment Factor (EF) [53,64]. The EF is estimated according to the formula:

$$EF = \frac{(\text{element/Al})\text{sample}}{(\text{element/Al})\text{background}}$$
(2)

For the calculation of the local background levels, the median elements values of the deeper part (30–37.5 cm) of the core were used. The sedimentation rate in the lagoon, estimated in another core obtained from station A4 by <sup>210</sup>Pb analysis, is  $0.3 \text{ cm} \cdot \text{y}^{-1}$  [23]. Thus, the 30–37.5 cm sediments interval corresponds to accumulations more than 100-years old, i.e., well before the urbanization of the study area. Additionally, those sediments had a light brown color, are thus considered as being oxic, and no apparent authigenic accumulations were observed. The metal contents used as the local background were:  $38 \text{ mg} \cdot \text{kg}^{-1}$  for Cu,  $104 \text{ mg} \cdot \text{kg}^{-1}$  for Zn,  $25 \text{ mg} \cdot \text{kg}^{-1}$  for Pb and  $0.69 \text{ mg} \cdot \text{kg}^{-1}$  for Cd. These values are similar to the upper boundaries of the 2N HCl extractable metal contents reported by Voutsinou-Taliadouri [65] at the unpolluted, Kerkyra strait, i.e., the marine area between the island and NW Greece:  $3-30 \text{ mg} \cdot \text{kg}^{-1}$  for Cu,  $7-24 \text{ mg} \cdot \text{kg}^{-1}$  for Pb and  $21-94 \text{ mg} \cdot \text{kg}^{-1}$  for Zn. Therefore, the levels proposed here are considered as the best approximation of the local background levels.

Interestingly, the local background for Cd is twice higher than the average shale ( $0.3 \text{ mg} \cdot \text{kg}^{-1}$ ) reported by Turekian and Wedepohl, [66], and almost 8 times higher than the value of upper continental crust ( $0.09 \text{ mg} \cdot \text{kg}^{-1}$ ) [67]. A possible reason for this discrepancy is that phosphate bearing limestones, which outcrop in Kerkyra Island, have been found to contain significant amounts of Cd as impurities [68].

Enrichment factors of 1.5–3, 3–5, 5–10 and >10 times are classified as minor, moderate, severe and very severe modification, respectively [69]. The median values of EFs for the anthropogenic metals were low, falling within the range of minor contamination (Cu: 1.1; Zn: 0.9; Pb: 0.9; Cd: 1.4). However, the maximum values of EF for Cd (5.7 at station A5; 3.5 at station A4; and 3.4 at station A3; see elevated Cd/Al values in Figure 6), indicate moderate anthropogenic modification, confined in localized areas of the lagoon. There are no industries located at the wider area of the lagoon that could explain this enrichment. Considering the land uses of the Antinioti drainage basin, Cd may partly derive from phosphate fertilizers that are applied in the adjacent cultivated areas. Another possible source of these metals could be the leaching of solid wastes improperly disposed at the riparian area. Nevertheless, the incidence of high levels in sediments, the suspended matter and the dissolved phase close to the freshwater seepage sites (e.g., A5, A8, A13), complicates further the source apportionment. So far, our results suggest that the freshwater inputs contribute significantly to Cd contamination. Yet, it is unclear whether the percolating water through the karstic formations becomes enriched by anthropogenic activities throughout its flow path prior to its discharge into the lagoon, or it becomes enriched by leaching of bedrock, or other complex geochemical processes.

In the core sediments, EFs ranges were 0.7–1.4 for Cu, 0.7–1.2 for Zn, 0.1–4.1 for Cd and 0.6–10 for Pb. The vertical distributions of EFs, i.e., the evolution of contamination, are similar to the profiles of elemental ratios to Al shown in Figure 7. The highest EF values for Pb were recorded at distinct sediment layers, consistent with the distinct contamination events discussed previously. The highest EF values for Cd correspond to the thick sediment layer at the top 20 cm of the core that is influenced by diagenetic alterations; thus this should not be attributed entirely to contamination. The values of EF for Cu and Zn, remained low and rather constant in time.

# 5. Discussion

Antinioti Lagoon is a remote, shallow, non-industrialized and not particularly urbanized system that has a high biodiversity and is of major geochemical interest. The present assessment of heavy metals in the various compartments of this lagoonal system provides a series of conclusions and raises some critical issues to be addressed in forthcoming research projects that will be discussed hereafter.

The freshwater spring of groundwater origin that flows as a stream into the lagoon, is the major source of dissolved Mn, Cd, and Pb, as well as particulate (w/w) Mn, Cd, and Zn (Table 2). The importance of groundwater discharges as a transport pathway of nutrients, carbon, and trace metals has been acknowledged in other coastal lagoon settings [7,70] and they are considered as a rival contributor to riverine inputs of land-derived material into the ocean [45,71,72]. Groundwater seepage in the Antinioti Lagoon is a field for future research, in order to elucidate whether the enrichment

ascribes to natural geochemical processes, i.e., diagenesis, or to anthropogenic activities (e.g., the use of Cd- bearing phosphate fertilizers) throughout its catchment area.

Trace metals participate in a series of critical, physical and geochemical processes that define their mobility and fate within the transitional fresh-saline water interface and beyond. Precipitation of Al, Fe, Mn oxyhydroxides, and flocculation are probably the most important ones. These processes are considered to be responsible for the rather unusual enrichment of large (> 8  $\mu$ m) particles, both at the stream and within the lagoon (Figure 3). Precipitates of clays and Fe/Mn oxyhydroxides on large suspended solids (>8  $\mu$ m), probably as composite coatings with organic matter, strongly affect the ability of this fraction of SPM to bind trace metals. Scavenging of Pb predominantly by Fe oxyhydroxides, Cd and Zn by Mn oxyhydroxides and Cu by Al and Fe/Mn phases explains the enrichment of the coarser particles (>8  $\mu$ m) with metals in relation to the finer ones (<8  $\mu$ m). Furthermore, the large particles were found to be less prone to desorption processes than the smaller ones. With increasing salinity, the partition coefficient of the small particles for Cd, and Zn decreased, as a result of desorption. In contrast, the variability of K<sub>D-L</sub> values was much smaller (Figure 5).

Scavenging of trace metals by large particles, with higher settling velocities than the finer ones, has serious implications on their transport and dispersion patterns across the system. Although the density of flocs is unknown and particle settling rates cannot be accurately estimated, in the grain-size range of 1–100  $\mu$ m, the settling velocity of grains of ~100  $\mu$ m is in the order of 10<sup>4</sup> larger than the settling velocity of particles of 1  $\mu$ m [73]. Thus, the enrichment mechanism of large particles with metals, combined with the irreversible adsorption of Cd and Zn onto Mn oxyhydroxides may explain the efficient entrapment of Mn, Cd, and Zn within the boundaries of the lagoon, evidenced by their significantly lower particulate concentrations (w/w) in the inlets than in the inner part. The behavior of Cu was differentiated from Cd, and Zn in the way that desorption occurred from both fractions of SPM, causing the dispersal of Cu in the dissolved phase beyond the system. According to Roussiez et al., [53] the removal of Cu into solution was not restricted in the fresh-saline water interface but instead, continued well after the deposition of fluvial material through the degradation of organic matter with which Cu was originally bound.

Resuspension of bottom sediments is expected to cause a decrease of particulate trace metal contents due to the mixing of enriched brackish water particles with high trace metal contents with coarse particles with low metal contents of marine origin [74]; this was not the case in our study. Aluminum, Fe, and Mn contents of the coarser fraction of the SPM in the bottom saline water were higher than in the surface layer, despite the resuspension of sediments (Figure 4). Such an enrichment is attributed to flocculation processes occurring at high salinity regimes. Sholkovitz [75], with a series of laboratory experiments, showed that although the amount of flocculated Al is maximized at salinity 12, at higher salinities the removal of Al from solution reaches a constant value. In the case of Mn, its removal from the solution increases and levels off at salinities 15–25, whereas an additional removal occurs at salinities 27–30. At the same time, the finer fraction of SPM increased at the surface layer. The presence of fine-grained particles in suspension has been described by Eisma [73] as re-flocculation observed in several estuarine systems. According to the latter author, at the saline part of the estuary, flocs of fluvial origin are broken up by organisms that consume the organic matter gluing the particles together. Re-suspension of organic matter will then result in newly formed flocs with organic matter of estuarine origin. Although the exact mechanism is not known, flocculation at the seaward boundary of transitional water systems may have serious implications on the transport and dispersion of pollutants across a system, as suggested by previous studies [53,76–78].

In the sediments, the occasionally elevated values of EF for Cd and Pb, falling within the range of moderate modification in the surface sediments to severe modification in the core sediments, prioritize these elements in terms of environmental concern and pollution abatement measures. The labile fractions of Cu, Cd, Pb and Zn in the surface sediments were found to be associated with organic matter. Future studies should consider the analysis of planktonic samples to further elucidate the role of organic matter in the transport and accumulation of trace elements in the sediments. Nevertheless,

the high organic carbon content in the core sediments (up to 12%) has been shown to influence the post-depositional distribution of total and labile fractions of metals. Accumulations of Cd coinciding with Mn depletions in gray-black sub-surface sediments, suggest that the profiles of these elements are greatly influenced by diagenetic processes.

Looking to the future, decision making should balance the sustainability of values and functions of the lagoon and the risks associated to the remobilization potential of toxic trace elements from the sediments. Dredging of sediments for the maintenance of the fish overwintering trench could result in the oxidation of sub-surface sediments, with high potential of releasing significant amounts of metals that would pose consequent environmental risks for the biota as well as economic and health risks for the end consumers.

**Author Contributions:** Conceptualization, F.B. and M.S.; methodology, F.B.; software, F.B. and A.K.; validation, F.B. and V.P.; formal analysis, F.B.; investigation, F.B., V.P.; resources, M.D. and M.S.; writing—original draft preparation, F.B.; writing—review and editing, F.B., A.K., M.S.; visualization, F.B. and A.K.; supervision, M.S.; project administration, F.B.; funding acquisition, M.S. and M.D.

Funding: This research received no external funding.

**Acknowledgments:** We wish to thank Eleftheria Aperi, Olga Chalkiadaki and Paraskevi Skourti for their valuable help in the laboratory. We also thank people in the Kerkyra Island for providing assistance in the field and useful information about the study area.

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

# Appendix A

**Table A1.** Detailed results of salinity, pH, Suspended Particulate Matter (SPM in  $mg \cdot L^{-1}$ ) and dissolved (d. in  $\mu g \cdot L^{-1}$ ), total (dissolved and particulate, t., in  $\mu g \cdot L^{-1}$ ) and particulate (p. in  $mg \cdot kg^{-1}$ ) metal concentrations of the 1<sup>st</sup> and 2<sup>nd</sup> sampling campaigns.

Sampling Stations	Salinity	pН	SPM	p. Al	t. Fe	d. Fe	p. Fe	t. Mn	d. Mn	p. Mn	t. Cd	d. Cd	p. Cd	t. Cu	d. Cu	p. Cu	t. Pb	d. Pb	p. Pb	t. Zn	d. Zn	p. Zn
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A1 surf.	22.0	8.0	13.4	7517	94.1	6.36	6571	7.80	4.36	258	0.030	0.019	0.78	0.54	0.31	16.9	0.18	0.06	9.6	2.63	1.2	107
A1 bott.	37.2	7.9	41.9	12195	633	7.19	14949	10.2	0.81	224	0.028	0.018	0.23	0.69	0.30	9.10	0.62	0.15	11.3	6.60	3.13	82.8
A2	15.0	8.2	14.2	6452	56.1	6.32	3496	14.5	6.98	531	0.099	0.073	1.83	0.37	0.20	12.3	0.21	0.07	10.0	7.72	5.03	189
A3	12.3	7.7	7.5	6219	37.2	5.91	4162	9.54	2.86	889	0.051	0.028	3.06	0.18	0.11	9.88	012	0.05	9.2	4.87	3.33	205
A5	12.2	7.9	8.1	6335	32.8	1.23	3899	6.85	4.42	301	0.061	0.027	4.20	0.35	0.16	24.1	0.11	0.02	10.4	3.19	1.23	243
A7	12.8	8.3	12.4	7818	62.7	2.93	4833	7.12	4.29	229	0.067	0.039	2.30	0.41	0.09	25.4	0.13	0.03	8.3	3.43	1.00	197
A9	9.8	7.8	9.8	15103	95.3	2.40	10032	10.1	7.13	316	0.057	0.036	2.23	0.34	0.15	20.6	0.21	0.03	19.5	3.02	2.01	108
A12	37.7	8.1	14.9	6787	92.5	3.58	5981	3.01	1.71	87	0.030	0.019	0.70	0.49	0.18	20.7	0.20	0.03	11.2	5.18	3.67	102
A13	4.7	7.3	1.5	4204	12.9	2.61	6731	5.89	2.91	1945	0.077	0.069	5.23	0.31	0.16	101	0.25	0.20	36.9	5.91	3.17	1790
									2nd sa	npling	campaig	gn										
A1	30.0	8.2	20.9	2432	50.4	0.66	2379	3.09	1.12	35.9	0.027	0.025	0.09	0.87	0.66	6.67	0.21	0.06	7.04	3.09	2.64	21.4
A2	17.6	8.0	13.8	4905	56.0	2.09	3923	10.0	4.20	301	0.081	0.071	0.69	1.68	1.53	11.1	0.34	0.17	12.4	10.0	8.99	80.7
A3	19.4	7.9	7.0	6776	42.9	1.03	5948	3.32	nm	407	0.041	0.037	0.63	0.63	0.47	22.9	0.15	nm	21.5	3.32	2.89	70.3
A5	17.1	7.5	13.2	32855	314	1.87	23572	9.82	2.15	419	0.059	0.035	1.81	2.37	0.83	105	0.81	0.34	35.2	9.82	7.62	212
A7	15.2	8.3	10.3	9091	63.3	0.42	6102	3.58	6.84	350	0.036	0.017	1.84	1.13	0.59	46.8	0.21	0.08	13.0	3.58	3.15	49.6
A9	14.3	8.0	10.5	90457	566	2.08	58612	9.42	4.31	1213	0.105	0.079	3.17	2.44	0.90	177	0.84	0.21	68.2	9.42	6.06	424
A12	37.5	8.2	14.3	15629	173	0.43	11996	2.24	1.23	131	0.019	0.018	0.09	0.62	0.30	22.1	0.30	0.06	16.5	2.24	2.06	11.9
A13	4.8	7.5	2.0	3406	30.1	5.23	12793	10.5	15.4	1667	0.171	0.164	3.76	0.64	0.47	51.3	0.31	0.27	22.9	10.5	9.94	198

Variable	Correlation Coefficient	Al	Fe	Mn	Cu	Cd	Zn	Pb
. 1	r	-	0.844 **	0.153	0.744 **	0.042	0.086	0.619 **
AI	$\varrho$	-	0.000	0.533	0.000	0.864	0.726	0.005
E.	r	0.844 **	-	0.364	0.853 **	0.209	0.179	0.779 **
Fe	$\varrho$	0.000	-	0.115	0.000	0.376	0.450	0.000
Mn	r	0.153	0.364	-	0.505 *	0.649 **	0.710 **	0.633 **
	$\varrho$	0.533	0.115	-	0.023	0.002	0.000	0.003
6	r	0.744 **	0.853 **	0.505 *	-	0.372	0.197	0.732 **
Cu	$\varrho$	0.000	0.000	0.023	-	0.107	0.405	0.000
	r	0.042	0.209	0.649 **	0.372	-	0.601 **	0.256
Ca	$\varrho$	0.864	0.376	0.002	0.107	-	0.005	0.276
Zn	r	0.086	0.179	0.710 **	0.197	0.601 **	-	0.395
	$\varrho$	0.726	0.450	0.000	0.405	0.005	-	0.084
D1.	r	0.619 **	0.779 **	0.633 **	0.732 **	0.256	0.395	-
Рb	$\varrho$	0.005	0.000	0.003	0.000	0.276	0.084	-

**Table A2.** Spearman correlation coefficient (r) of particulate elements (w/w) in the > 8  $\mu$ m fraction of particulates and significance level ( $\rho$ )

\*\* Correlation is significant at the 0.01 level (2-tailed); \* Correlation is significant at the 0.05 level (2-tailed).

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