Potentially Toxic Elements in Saltmarsh Sediments and Common Reed (Phragmites australis) of Burullus Coastal Lagoon at North Nile Delta, Egypt: A Survey and Risk Assessment

Sabry M. Shaheen¹,²,³*, Mohamed A. S. Abdelrazek³, Mahmoud Elthoth⁴,⁵, Farahat S. Moghanm¹, Radi Mohamed⁶, Ahmad Hamza⁷, Nagwan El-Habashi⁸, Jianxu Wang⁹,², Jörg Rinklebe²,⁰*

¹University of Kafrelsheikh, Faculty of Agriculture, Department of Soil and Water Sciences, 33 516 Kafr El-Sheikh, Egypt; emails: smshaheen@agr.kfs.edu.eg (S.M. Shaheen); fsaadr@yahoo.ca (F.S. Moghanm)
²University of Wuppertal, School of Architecture and Civil Engineering, Institute of Foundation Engineering, Water- and Waste-Management, Laboratory of Soil- and Groundwater-Management, Pauluskirchstraße 7, 42285 Wuppertal, Germany; email: rinklebe@uni-wuppertal.de
³University of Kafrelsheikh, Faculty of Agriculture, Department of Chemistry and Toxicity of Pesticides, 33 516 Kafrelsheikh, Egypt, email: masabdelrazek@yahoo.com
⁴University of Kafrelsheikh, Faculty of Veterinary Medicine, Department of Hygiene and Preventive Medicine, 33 516 Kafr El-Sheikh, Egypt; Email: m_eltholt@yahoo.com
⁵Institute of aquaculture, University of Stirling, Stirling, United Kingdom, FK9 4LA
⁶University of Kafrelsheikh, Faculty of Aquatic and Fisheries Sciences, Aquaculture department (Fish Welfare), 33 516 Kafr El-Sheikh, Egypt; Email: r.mohamed.vet@gmail.com
⁷Private aquaculture consultant, Aquavet for fish health and nutrition, Kafr El-Sheikh, Egypt; Email: ahmad_hamza1@yahoo.com
⁸University of Kafrelsheikh, Faculty of Veterinary Medicine, Department of Veterinary Pathology, 33 516 Kafr El-Sheikh, Egypt; Email: nagwan_hab@yahoo.com
⁹State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, P.R. China; Email: wangjianxu@vip.gyig.ac.cn
¹⁰Department of Environment, Energy and Geoinformatics, Sejong University, Seoul 05006, Korea

*Corresponding author: Jörg Rinklebe; Email: rinklebe@uni-wuppertal.de
**Co-corresponding author: Sabry Shaheen; E-mail: smshaheen@agr.kfs.edu.eg

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Abstract

Burullus Lagoon is the second largest lake in Egypt. However, there has never been a comprehensive survey which studied nineteen potentially toxic elements in sediments and plants and evaluated the associated potential risk. Thus, we aimed to study the total and potentially available content of As, Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Sb, Se, Sn, Tl, V, and Zn in the sediments and common reed (*Phragmites australis*) at thirty two sites along the entire lagoon and connected drains. Contamination Factor (CF), Pollution Load Index (PLI), Geo-accumulation Index (*I*$_{geo}$), and Enrichment Factor (EF) were calculated to assess the grade of contamination. Element accumulation factor (AF) and bio-concentration ratio (BCR) were also calculated. Aluminium showed the highest median (mg kg$^{-1}$) total content (41,200), followed by Fe (30,300), Mn (704.7), V (82.0), Zn (75.5), Cr (51.2), Cu (47.8), Ni (44.3), As (31.9), Tl (24.6), Co (21.4), Se (20.3), Sb (17.6), Sn (15.6), Mo (11.3), and Hg (16.6 µg kg$^{-1}$). Values of the EF, CF, and *I*$_{geo}$ showed that the sediments were heavily contaminated with As, Sb, Se, Tl, Mo, Sn, Co, Ni, and Cu. The drained sediment had significantly higher values of total and potentially available element content than the lagoon sediments. Sediments of the middle and western area showed significantly higher contents of total and available elements than the eastern section. The BCR and AF values indicate that the studied plant is efficient in taking up high amounts of Zn, Fe, As, Sn, Tl, Ni, Mo, Mn; then Co, Cu, and V. The results exhibit a dramatic contamination at certain sites of the lagoon, and the studied PTEs have a predominant role in contamination-related ecological risk. Further investigations concerning redox-induced mobilization of PTEs in sediments, the risk of fish contamination and the potential health hazards are highly recommended.

Keywords: Wetlands; Toxic metal(loid)s; Contamination indices; Accumulation factors.
1. Introduction

Burullus lagoon is a UNESCO-protected Area in the north of Nile Delta, Egypt. This lake supplies a considerable percentage of the annual Egyptian fish yield. Thus, there is a considerable health risk when these lagoon sediments have high levels of potentially toxic elements (PTEs). The lagoon receives drainage water through several drains (El-Badry and Khalifa, 2018). The water sources for the lake are mainly derived from agricultural drainage, municipal sewage, and industrial wastewater (Gu et al., 2012). Therefore, the lake environment is vulnerable to environmental changes particularly related to enhanced anthropogenic pressure (Eid and Shaltout, 2004; Nassar and Gharib, 2014) such as agricultural, industrial and sewage discharge and fishing activates (Okbah and Hussein, 2006; Abukila, 2015).

Wetland sediments are important sinks for PTEs and play a significant role in the remobilization of contaminants in aquatic ecosystems under certain conditions (Ali and Fishar, 2005; Ghosh et al., 2018). Information on PTEs, in particular some emerging contaminates such as Se, Sb, Sn, Th, and V in coastal lagoon sediments and plants, is still limited. Although some authors (e.g., Chen et al., 2010; Gu et al., 2012; El-Badry and Khalifa, 2018) studied partially a few elements at certain sites in the Burullus lagoon, there is no comprehensive study which would links nineteen PTEs in sediments and plants in this lake with the associated potential risk. Therefore, we aim 1) to study the total and potentially available content of As, Al, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Sb, Se, Sn, Tl, V, and Zn in the sediments and common reed in the Burullus lagoon, 2) to assess the grade of contamination and the associated eco-toxicological risk using different contamination indices such as Contamination Factor (CF), Pollution Load Index (PLI), Geo-accumulation Index ($I_{geo}$), and Enrichment Factor (EF), and 3) to investigate the suitability of common reed as a hyperaccumulator of the studied PTEs using the accumulation factor (AF) and bio-concentration ratio (BCR) indices.
2. Materials and methods

2.1 Study area and sampling

The Burullus Lake is located in the Kafr El-Sheikh governorate at the north of the Egyptian Nile Delta (31° 14' 60" N and 31° 14' 60" E) (Appleby et al., 2001). The lagoon extends between 31° 22' - 31° 26' N and 30° 33' - 31° 07' E (Fig. 1). The entire lake is 47 km long and about 5 km wide, and has a water surface area of about 440 km² (Chen et al., 2010). The lagoon is connected to the Mediterranean Sea with a small waterway called Al-Bughaz (Fig. 1). In the southern part of the lagoon, many drains are connected to the Burullus lagoon. Through these drains, untreated agricultural, domestic, and industrial drainage from the local towns and villages directly flow into the lagoon. We divided the studied area into six sections as follows: 1) all (include the lake and the drains), 2) drains (include the drains connected with the lake), 3) lake (include the lake without the drains), 4) eastern sector (include the lake and drains in the eastern part of the studied area), 5) middle sector lake (include the lake and drains in the middle part of the studied area), and 6) western sector (include the lake and drains in the western part of the studied area) (Fig. 1).

Thirty-two sampling sites were selected across the lagoon and its main drainage water supplies during the period from March 1 to June 1, 2014. Samples of sediments and common reed (Phragmites australis) plants were collected in triplicates of each site resulting in ninety-six samples in total. The sediment samples were collected from the surface layer (0-10 cm) using polyvinylchlorid (PVC) cores. The sediments were morphologically described; thereafter the samples were placed into plastic bags. Whole plants of common reed were collected, washed using the lake water, and placed into plastic bags.

[Insert Figure 1]

2.2 Preparation and characterization of studied samples

The sediment samples were homogenized, air-dried, crushed, and passed through a 2-mm sieve. Salinity, pH, and total organic carbon of the ninety-six sediment samples were analyzed. Sediment pH was measured in 1:1 (w/v) suspension using a calibrated pH-meter (JENWAY 3510). The salinity was measured using EC-meter (MI 170, Italy). Organic carbon was determined by loss on ignition using a muffle furnace at 500°C for 5 hours (Cambardella et al., 2001). The sediment texture was identified by...
finger test (Whiting et al., 2016). The plant biomass of the common red was thoroughly washed with 1 M HCl; thereafter deionized water, and dried to constant weight at 70 °C with a force-drought oven. The samples of the dry biomass were grounded to fine powder in a stainless steel grinder.

2.3 Extraction and analysis of PTEs in sediment and plant samples

Sediment samples were digested in an advanced microwave digestion system (Milestone; ETHOS EASY, Germany) to determine the pseudo-total element concentrations (US EPA 3051a, 2007). Total content of Hg in sediment samples were measured using a direct mercury analyzer (DMA-80, Milestone Inc., Sorisole, Italy). The potentially available form of the elements (except for Hg) was extracted using a solution of ammonium bicarbonate (1M NH₄HCO₃) - diethylene tri amine penta acetic acid (0.005 M DTPA) (AB-DTPA) according to Soltanpour and Schwab (1977).

One gram of the plant material was dry-ashed in a muffle furnace at 450°C for five hours, extracted with 20% hydrochloric acid (Jones et al., 1991) to analyse the plant tissue concentrations of the studied elements. The element concentrations in the sediment and plant samples were measured by ICP-OES (Ultima 2, Horiba Jobin Yvon, Unterhaching, Germany).

2.4 Quality control and statistical analyses

Quality control of the extraction efficiency of the pseudo-total element concentrations was performed using certified soil reference materials (CRM051 and CRM042) obtained from the Labmix24 GmbH, Germany. The average recovery of the studied elements ranged between 86 and 101%. To ensure that the results were reliable, blank and triplicate measurements were employed during the analyses. Standard solutions (Merck) of the elements were used to guarantee high-quality results. The maximum allowable relative standard deviation (RSD) among replicates and was set to 15 % for sediments and plant analyses. The detection limits were 28 µg L⁻¹ for Al, 10 µg L⁻¹ for As, 2.7 µg L⁻¹ for Cd, 7.0 µg L⁻¹ for Co, 7.1 µg L⁻¹ for Cr, 5.4 µg L⁻¹ for Cu, 12 µg L⁻¹ for Mo, 10 µg L⁻¹ for Ni, 1.5 µg L⁻¹ for Se, 6.25 µg L⁻¹ for Sn and Sb, 12.5 µg L⁻¹ for Ag and Tl, 7.5 µg L⁻¹ for V, and 1.8 µg L⁻¹ for Zn. Values below the detection limit
were as equal to 1/8 of the detection limit for statistical purposes. The statistical analyses were carried out using IBM SPSS Statistics 23 (NY, USA). The means for the variables were tested using a one-way ANOVA with Duncan's multiple range tests at a significance level of 0.05. OriginPro 9.1 b215 (OriginLab Corporation, Northampton, USA) was used to create the figures.

2.5 Sediment contamination and risk assessment indices
We calculated the following indices to assess the risk by the PTEs studied:

2.5.1 Contamination Factor (CF):
The CF is calculated according to the following equation as reported in Islam et al. (2015a,b) and Antoniadis et al. (2017a,b):

\[
CF = \frac{C_S}{C_{\text{RefS}}}
\]

where \(C_S\) is total element concentration in the sediments; \(C_{\text{RefS}}\) is the background reference element concentration in uncontaminated sediments. The background reference concentrations were obtained from Kabata-Pendias (2011, p. 41) as “crustal average“ (Table 1). We have used these background reference concentrations due to the lack of local element background information and also to have a uniform scale for all elements studied, because some emerging contaminants such as Se, Sb, Sn, and Tl have no reported background value in sediments (Birch, 2017). The contamination level according to the CF value may be classified as follows: low degree \((CF < 1)\), moderate degree \((1 \leq CF < 3)\), considerable degree \((3 \leq CF < 6)\), and very high degree \((CF \geq 6)\) (Luo et al., 2007; Shaheen et al. 2017a; Ghosh et al., 2018).

2.5.2 Pollution Load Index (PLI)
The PLI is defined as the \(n^{th}\) root of the multiplications of the contamination factor of elements (Bhuiyan et al., 2010; Islam et al., 2015a,b; Shaheen et al., 2018):

\[
PLI = (CF_{s,1} \times CF_{s,2} \times \ldots \times CF_{s,n})^{1/n}
\]

where \(CF_{s,1}, CF_{s,2}, CF_{s,n}\) are the element CF; 1, 2, \ldots, \(n\), and \(n\) is the number of measured elements.
2.5.3. Enrichment Factor (EF):

The enrichment factor (EF) is calculated by normalizing the given elements concentration in sediments to concentration of Al (Islam et al., 2015a; Antoniadis et al., 2017a,c):

\[ EF = \frac{C_S}{Al_S} / \frac{C_{RefS}}{Al_{RefS}} \]

where \( Al_S \) is total Al concentration in the sediments, and \( Al_{RefS} \) is the background reference value of Al (taken as equal to 20000 mg/kg). We have used 20,000 mg kg\(^{-1}\) as reference value of Al because Salminen et al. (2004) reported that the value 0.2% (20,000 mg kg\(^{-1}\)) is the lowest median total content of Al in the stream and floodplain sediments. In addition the lowest value of total Al in the studied lake sediments (except for three sandy texture samples) is 21,100 mg kg\(^{-1}\); thus we considered 20,000 mg kg\(^{-1}\) as background value of Al in the studied sediments. Generally, an EF value of 1.0 suggests that a given PTE may be entirely from crustal materials or natural processes of weathering (Rashed, 2010). The EF value ranges of 1.5–3, 3–5, 5–10 and > 10 is considered as evidence of minor, moderate, severe, and very severe contamination, respectively (Islam et al., 2015b).

2.5.4. Geo-accumulation Index (\( I_{geo} \)):

The \( I_{geo} \) is calculated according to the following equation:

\[ I_{geo} = \log_2 \left( \frac{C_S}{1.5C_{RefS}} \right) \]

The level of contamination as recorded by \( I_{geo} \) is indicated by Latin numbering, as follows:

Class I: \( I_{geo} < 0 \), class II: \( I_{geo} = 0-1 \), class III: \( I_{geo} = 1-2 \), class IV: \( I_{geo} = 2-3 \), class V: \( I_{geo} = 3-4 \), class VI: \( I_{geo} = 4-5 \), and class VII: \( I_{geo} > 5 \) (as per Kasa et al., 2014; Li et al., 2014; Yakun et al., 2016; Ghosh et al., 2018).

3. Results and discussion

3.1. Characterization of studied sediments

The studied sediments were alkaline with pH values ranging from 7.1 to 9.1, with a median value of 8.1. The median pH value of the sediments in the middle section of the studied lake and drains was lower than that of the other parts (Fig. 2). The sediment alkalinity might be explained by its high content of...
carbonates originating from the carbonaceous broken shells and the high salinity, in particular water soluble and exchangeable sodium content (Shaheen et al., 2013). The sediment salinity showed high and significant variety and ranged between 0.8 dS m\(^{-1}\) and 14.5 dS m\(^{-1}\). The highest values of sediment salinity were recorded in the middle section, while the lowest were in the western section (Fig. 2). The sites close to the Mediterranean Sea (e.g., sites No. 8 and 15) showed higher salinity than the other sites, which might be due to the seepage of the highly saline sea water. The lake receives high amounts of saline drainage water from the agricultural drains, which might be also another reason for the high salinity of lake sediments. The sediments were poor in their organic matter content (0.2-2.7%; Fig. 2). The sediments of the middle section showed the highest percentages of organic matter, while the lowest ones were in the eastern part. The higher value of OM in the middle section of the lake might be explained by the higher growing biomass in this section than the other margins sections. The high content of organic matter in the middle part may be probably assisted by the expected biological activity in the upper sediment part caused by the establishment of grown plants. Plant residues especially contribute considerably high organic matter levels. The sediments had a silty / clayey texture in all sites except for sites number 5, 25, and 29, which had a sandy texture (data not shown). Our findings corroborate with those of Chen et al. (2010) and El-Badry and Khalifa (2017), who conducted work in the same area.

[Insert Figure 2]

The sediments (except for the sandy texture sites number 5, 25, and 29) were rich in the total content of Al and Fe. Iron showed higher total content (2.2 g kg\(^{-1}\) to 61.2 g kg\(^{-1}\)) than Al (1.4-58.3 g kg\(^{-1}\)) (Fig. 2). The middle section sediments contained the highest median value of total Al and Fe content, while the eastern section sediments contained the lowest median concentrations of both elements (Fig. 2). This likely indicates differences in sediments concerning (hydr)oxides contents. Mean values of total Al differed significantly only between the middle and the eastern part, while Fe content was without significant differences between the sections. The high contents of total Fe and Al in the lake clayey sediments could be explained by the dominance of phyllosilicate minerals and the hydrous oxides of iron and aluminum. High values of total contents of Al and Fe in the lake sediments are in agreement with
those reported by Chen et al. (2010) and Gu et al. (2012) in works that have been conducted in the same area. Consequently, the large differences in the above mentioned properties are expected to affect the total and potentially available PTE concentrations among the lake sites.

3.2. Total content of PTEs in the sediments

Total content (mg kg\(^{-1}\)) of the studied PTEs (As (2.4-59.7), Co (1.4-37.3), Cr (1.4-37.3), Cu (2.2-103.5), Mn (100.3-1897.8), Mo (0.51-19.8), Ni (2.4-82.2), Sb (0.82-32.9), Se (1.2-39.3), Sn (≤0.07-30.7), Tl (1.1-50.1), V (8.4-154.5), and Zn (5.8-156.8)) ranged widely in the studied lake and drains sediments (Fig. 3). Mercury showed the lowest concentrations and varied from 1.6 µg kg\(^{-1}\) to 65.5 µg kg\(^{-1}\). The order of the elements based on their total median content (mg kg\(^{-1}\)) was as follows: Manganese showed the highest median content value (704.7), followed by V (82.0 mg kg\(^{-1}\)), Zn (75.5 mg kg\(^{-1}\)), Cr (51.2 mg kg\(^{-1}\)), Cu (47.8 mg kg\(^{-1}\)), Ni (44.3), As (31.9), Tl (24.6), Co (21.4), Se (20.3), Sb (17.6), Sn (15.6), Mo (11.3), and Hg (16.6 µg kg\(^{-1}\)) (Fig. 3). Total content of Cd was lower than the detection limits (2.7 µg L\(^{-1}\)) in all sites except for drain 9 (site no. 16).

The drains sediments contained higher median concentrations of all studied elements (except for Hg) than the lake sediments (Fig. 3). Among the studied drains, sediments of drain 9 (site 16) and drain 8 (site 19) contained the highest total concentrations of all studied elements (except for Hg). High concentrations of these elements in the drains, in particular drains 9 and 8, are closely related to domestic and industrial wastewater discharges in these drains, particularly in densely populated catchments (Chen et al., 2010; Ali, 2011; Abukila, 2015; El-Badry and Khalifa, 2017). Among the lake sections, the middle and western sections showed higher median concentrations of As, Cu, Mo, Sb, Se, Sn, Tl, V, and Zn than the eastern section (Fig. 3). Thus, the significant increases in PTEs pollution recorded in the western part of the lake can be attributed to the increase of the pollutant load to the lake from these drains (Abukila, 2015; Shaheen and Tsadilas, 2009).

The sandy sites (sites No. 5, 25, and 29) contained lower concentrations of all elements than the clayey sites, which may indicate the significant contribution of geogenic sources in element enrichment in the
clayey sediments. The close elemental and clay mineralogical association in different sediments is well reported (e.g., Hooda, 2010; Kabata-Pendias, 2011; Vuba et al., 2015). Positive relations between clay content and total element concentrations in sediments and soils were reported in many studies (e.g., Shaheen et al., 2017b; Shaheen and Rinklebe, 2017).

The total content of all elements (except for Hg) correlated positively with total Fe (with r values ranged between 0.79** and 0.96**) and all elements with total Al (r = 0.79**- 0.94**). Chromium, Co, Ni, V, and Zn were more closely correlated with total Fe than Al, while As, Cu, Sb, Se, Sn, Tl, and Hg had better correlation with total Al. The substantial impact of total Fe and Al and their oxides on the studied elements indicates that these elements are strongly associated (bounded and/or occluded) with Fe-Al oxides and tends to replace Fe and Al in crystal structures. For example, elements such as V, Cr, and Fe are reported to be closely associated and usually co-exist in sediments/soils (Edwards et al. 1995; Aide 2005; Rinklebe et al., 2016; Shaheen and Rinklebe 2017).

Also, the positive correlations between the elements (except for Hg) and sediment organic matter (r = 0.64 – 0.82; P ≤ 0.05) point to the association of those elements with sediment organic carbon and their possible distribution in the organic fraction as suggested by Shaheen and Rinklebe (2014) for Cu and Zn, and by Shaheen et al. (2017b) for As. Also, Shaheen et al. (2017a) found that the total concentrations of Al, Cd, Cr, Cu, Fe, Mn, Ni, and Zn were higher in a soil rich in organic carbon than in an adjacent soil poor in organic carbon. Moreover, Zhou et al. (2018) supported the crucial role of OM in the distribution of Cd and Zn. The maximum total content of all PTEs (except for Hg) in the studied sediments was higher than the average crustal content (Table 1). Maximum values of total As, Cu, Hg, Ni, V, and Zn were higher than the upper continental crust composition. Also, maximum values of total Cu, Mn, Ni, V, and Zn in the studied sediments were higher than their content in the shales (Table 1).

The level of PTEs in sediments at the studied sites was evaluated by the ERL (effects range low) and ERM (effects range medium) analysis (Table 1) as described by Long et al. (1995) and reported in Coynel.
et al. (2016) and DeLaune et al. (2016). Long et al. (1995) identified nine PTEs (Ag, As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) that were observed to have ecological or biological effects on organisms (in sediments). The ERL values are defined as the lowest concentration of an element that produced adverse effects in 10% of the data reviewed whereas the ERM data designates the level at which half of the studies reported harmful effects. Element concentrations below the ERL value are not expected to elicit adverse effects, while levels above the ERM value are like to be very toxic. Based on the ERL and ERM values, total Hg and Cr contents were lower than the ERL values resulting in no eco-toxicological effects. Arsenic, Cu, and Zn was below the ERM values, but greater than the ERL values, which would perhaps suggest that there could be some toxicity under certain conditions. Nickel total content was higher than the ERM, which indicates high toxicity of Ni under certain conditions (US EPA, 2002). Evaluation of the level of PTEs based on the ERL and ERM indicates that the studied sediments are more contaminated by Ni, As, Cu, and Zn than other march sediments in the Wax Lake Delta (DeLaune et al., 2016) and the Loire Estuary, France (Coynel et al., 2016).

A large area of the studied lake was drained and used as a cultivated soil. Therefore, to assess the contamination of the studied sediments as a soil, we compared the total content of the studied PTEs with the world-soil average as reported in Kabata-Pendias (2011), and found that the total content of all PTEs (except for Cr and Hg) in the studied sediments was clearly higher than the world-soil average content. Also, the total content of all PTEs (except for Hg) in the studied sediments was clearly higher than the maximum allowable concentrations of these elements in soils as reported in Kabata-Pendias (2011). This is an indication of enrichment of these PTEs in the studied sediments.

3.3 Contamination indices

Sediment contamination indices may help in identifying the level of enrichment of a sediment/soil with PTEs (Birch, 2017). We calculated the Contamination Factor (CF), Pollution Load Index (PLI), Enrichment Factor (EF), and geo-accumulation index ($I_{geo}$). The sediments were enriched and contaminated by the studied PTEs as indicated by the values of EF (Appendix A in Table S1), CF
293 (Appendix A in Table S2), $I_{geo}$ (Appendix A in Table S3), and $PLI$ (Fig. 4). A conclusion of the sediments
294 contamination degree based on the EF, CF, and the $I_{geo}$ is included in Table 2.
295
296 An EF value of 1.0 suggests that a given PTE may be entirely to sediments/soils from geogenic sources
297 (Rashed, 2010), while samples having EF > 1.5 are considered under human influence (Islam et al.,
298 2015a; Antoniadis et al., 2017a,c). The studied PTEs (except for Cr, Cu, Hg, and V) showed EF values
299 higher than 1.5. Values of the EF, CF, and $I_{geo}$ (Table 2) showed that the sediments were severe/heavily
300 contaminated by As, Sb, Se, Tl, Mo, Sn; then these were followed by Co and Ni. Such results of high EF,
301 CF, and $I_{geo}$ values exhibit a clear indication of dramatic contamination at certain sites as also agreed by
302 others (e.g., El-Badry and Khalifa, 2017; Ghosh et al., 2018).
303 To assess the pollution load in the sediments by all studied PTEs, the $PLI$ was calculated and presented in
304 Figure 4. The high $PLI$ is generated as a result of a multi-contamination by the studied elements
305 (Antoniadis et al., 2017a,b; Birch, 2017). The $PLI$ values ranged between 0.27 and 8.4 with a median
306 value of 4.85 in the studied sediments. The PLI indicated that the studied sediments especially the drain
307 sediments were contaminated by the studied elements as shown by its values which were higher than
308 unity. However, As, Sb, Se, Tl, Mo, Sn contributed the highest CF values, followed by Co and Ni, and
309 Zn. Therefore, the contribution of As, Sb, Se, Tl, Mo, Sn to the sediment pollution was higher than that of
310 the other studied elements. This shows that sediment contamination of the studied areas constituted a
311 multi-element contamination case. Higher $PLI$ values were observed in the drain sediments than the lake
312 sediments, in particular in the eastern area. Comparing the lake sections, the $PLI$ values in the western and
313 middle parts were higher than in the eastern part (Fig. 4). The lower pollution load in the eastern section
314 might be due to the dilution of the contaminated water in the lake by the sea water, where the eastern part
315 of the lagoon is connected to the Mediterranean Sea with a small waterway called Al-Bughaz (Fig. 1).
316 The higher pollution load in the middle and western sections of the lake might be linked to down-stream
317 industrial activity discharged and deposited when the drains water/sediments (in particular drains No. 8
and 9) enter into the western and middle parts of the lake. The wastewater sources is encompassing all
discharge in the entire catchment area and it covers also industrial and domestic activities, agricultural
sources, discharge of wastes, and discharge of communal wastes. The connected drains with the lake
collect different types of agricultural, sewage, and industrial wastewaters through the industrial cities
north of Nile delta and also from the rural domestic activities along these drains.

The high EF, CF, $I_{\text{geo}}$, and $PLI$ values indicate the significant contribution of the anthropogenic sources in
increasing these elements, in particular As, Sb, Se, Tl, Mo, Sn, Co, Ni, Cu, and Zn (Table 2), in the lake
and drain sediments. On other hand, the low EF, CF, and $I_{\text{geo}}$ values of Cr, Hg, and V indicate that the
geogenic source might be the main source of these elements in the studied sediments (Rashed, 2010). As
for anthropogenic inputs, the industrial, municipal, and farm wastewater are the main sources of PTEs-
contaminated waters/sediments (Sorme and Lagerkvist, 2002; Houhou et al., 2009; Barakat, 2011). For
instance, widespread use of PTEs in electroplating, metal finishing, pigments, textile and dyeing, and leather
tanning industries, wood treatment using mixture of copper-chromium-arsenate, and electrical and electronic
equipment may increase the level of these elements in the industrial wastewaters. In this respect, Shaheen et
al. (2013) also found that the textile and dyeing factories wastewater contains high Cu and Zn contents.

Contamination of the wastewater and sediments by trace elements such as Sn might be due to using this
element in many industrial activities such as alloys and steels, coating layer for major industrial materials
made of iron and steel, polymer stabilizer, various medical uses, and in soap or food additive (Clifford et
al., 2010; Jennings 2013). The main sources of PTEs in municipality wastewater are institutions,
households and commercial buildings which could discharge large amounts of PTEs (Bolan et al., 2009;
Abe et al., 2012). The farm wastewater or effluents (for example, those coming from poultry, piggeries
and dairy farms) is contaminated with PTEs and used as irrigation water and discharged from the drainage
to the lake as mentioned above, which increase the levels of PTEs (Fig. 3) and organic matter (Fig. 2) in
the lake sediments (Bolan et al., 2009; Abe et al., 2012).
3.4 Potential availability of the studied elements

The potential availability of the studied elements was assessed using AB-DTPA according to Soltanpour and Schwab (1977). The elements potential availability differed significantly among the elements and studied sites (Table 3). The AB-DTPA-extractable concentrations of Cd, Cr, Sb, and Se were lower than the detection limits in all sites. (Table 3). Iron showed the highest median potential availability, followed by Mn, Cu, V, Ni, Co, and Mo (Table 3). The potential availability of all elements (except for As, Mo, Sn, and Tl) was obviously higher in the drains than the lake sediments, and was also higher in the western part than in the eastern part of the studied area.

[Insert Table 3]

The main reason for the high potential availability of Fe and Mn in the sediments might be due to their high total content (Fig. 2). In addition, the continually flooded conditions in the lake and thus low redox potential of the lake sediments (-1.2 to -52.5 mV) may case reductive dissolution of Fe-Mn oxides and consequently release of Fe and Mn in dissolved form, which increase their mobilization and potential availability (Shaheen et al., 2014a). Also, increasing the mobilization of some other elements such as V, Co, Ni, and Mo might be due to their high total content and their association to Fe and Mn oxides; therefore, their release after the assumed reductive dissolution of the oxides (Rinklebe and Shaheen, 2017a,b). The AB-DTPA-extractable amounts of Mo, Ni, and V were positively correlated with the total amounts of Fe (r = 0.28* for Ni; r= 0.23* for Mo; r = 0.35** for V) and Mn (r = 0.29* for Ni; r= 0.57** for Mo; r = 0.49** for V). Also, the AB-DTPA-extractable amounts of Co, Mo, Ni, and V were positively correlated with the AB-DTPA-extractable amounts of Fe (r = 0.30* for Co; r = 0.41** for Ni) and Mn (r = 0.65** for Co; r = 0.68** for Ni; r = 0.41** for V). In this respect, Shaheen et al. (2014a) found that release and mobilization of Fe, Mn, Co, Ni, and V were increased in lacustrine soil originated from similar sediments around the studied lake. Also, Shaheen et al. (2014b) indicated the close association between dissolved Fe, Mn, and Mo in fluvial sediments. During flooding of wetland sediments, formation of iron oxyhydroxides is important in retaining PTEs in surface sediments/soils. When sediments become
reducing, the PTEs bound to Fe and Mn oxides are transformed into readily available forms due to dissolution of Fe and Mn oxides (Rinklebe, 2017a,b).

The lower portion of available form of the studied PTEs in comparison to the total content may indicate that the AB-DTPA was not able to extract a significant part from the mobile fraction of some elements such as Cr and Se, which in agreement with what was reported before in similar sediments of the Nile Delta by Shaheen et al. (2017b). Also, the lower portion of available form of the studied PTEs in comparison to the total content may be explained by the high alkalinity (Fig. 2) of the studied sediments. Negative relations between solubility of PTEs (except for Mo and V) are well-documented (Hooda, 2010; Kabata-Pendias, 2011). On the other hand, increasing the potential availability of some elements such as Mo and V might be explained by the higher pH, where these two elements have positive relations with sediment pH as reported in other studies (e.g., Evans and Barabash, 2010; Shaheen et al., 2017b; Shaheen and Rinklebe, 2017). For example Shaheen et al. (2017b) explained the higher relative mobilization of Mo in sediments of the Nile River by the alkaline pH of these sediments. Sediment pH affects solubility of PTEs, since H⁺ is a reactant in redox reactions. In addition, pH affects surface charge characteristics and speciation of metal ions; thus, it influenced adsorption-desorption process of the involved ions of those elements. Also, sediment pH may regulate other processes such as sulfide formation, which indirectly influence the solubility of PTEs (Rinklebe, 2017a,b).

3.5 Concentrations of the studied PTEs in common reed

Plant tissue concentrations of the studied elements differed significantly based on each element and between the studied sites (Fig. 5). The median plant tissue concentrations (mg kg⁻¹) of the elements were 1242.2 for Fe, 194.2 for Mn, 9.24 for Zn, 6.8 for Ni, 5.5 for Cu, 5.3 for V, 3.5 for As, 3.1 for Cr, 1.1 for Sb, 0.85 for Mo, 0.67 for Co, and 0.61 for Tl (Fig. 5). The plant tissue concentrations of Al, As, Co, Cu, Mn, Mo, S, Se, Tl, V, and Zn did not show significant variation among plants grown in the studied sections. However, the concentrations of Cr, Fe, Ni, and Sb differed significantly among the plants grown in the different lake sections (Fig. 5). The plants grown in the middle lake sections showed significantly
higher concentrations of Fe, and Sb than those in the other lake sections. The plants grown in the eastern lake sections showed significant higher concentrations of Cr than the other lake sections. The plant concentrations of all elements did not show significant correlations with the total element content.

Plants showed higher As and Cu concentrations than the critical levels (1-10 for As and 15-20 for Cu) as reported by Kabata-Pendias (2011). These results may indicate that common reed can grow on sediments contaminated with As and Cu; therefore this plant seem to tolerate these elements to the given levels. However, the common reed revealed element concentrations less than 1,000 mg kg\(^{-1}\) of all studied elements; thus, it is not considered as a hyperaccumulator of these elements (Baker and Brooks 1989).

The sediment-to-plant transfer factors, termed accumulation factor (AF) or bio-concentration ratio (BCR), are indices for evaluating the transfer PTEs from sediment to plants (Cui et al. 2004; Twining et al., 2004; Kabata-Pendias, 2004). Sediments-to-plant transfer factor can be used to estimate a plant's potential for phytoremediation purpose (Yoon et al. 2006; Tomovic et al. 2013; Shaheen and Rinklebe, 2015). The bio-concentration ratio was calculated according to Wang et al. (2006) as follows: \( \text{BCR} = \frac{\text{mg element kg}^{-1}\text{plant}}{\text{mg AB-DTPA-element kg}^{-1}\text{sediment}} \). Plants exhibiting BCR values less than 1 are considered to be unsuitable for phytoextraction (Baker and Brooks 1989). The studied plant BCR values were higher than 1 with all detected elements and the median values were 1.15 for Cu, 1.03 for V, 1.85 for Co, 5.03 for Mn, 5.31 for Mo, 9.31 for Ni, 1936 for Fe, 20.2 for Tl, 33.2 for Sn, 1092.5 for As, and 2283.6 for Zn, which means a high ability of these elements to be accumulated by the common reed.

We also calculated the accumulation factor (AF) as follows: \( \text{AF} = \frac{\text{mg element kg}^{-1}\text{plant}}{\text{mg Total-element kg}^{-1}\text{sediment}} \) (Wang et al., 2006; Shaheen and Tsadilas, 2009). The AF values ranged between 0.03-18.7 for Mn, 0.1-17.2 for S, 0.04-2.33 for Ni, 0.0-2.2 for Cu, 0.02-1.59 for Zn, 0.0-1.22 for Tl, 0.010.99 for Mo, 0.01-0.84 for As, 0.0-0.71 for Sb, 0.01-0.51 for V, 0.0-0.51 for Co, 0.01-0.44 for Al, and 0.01-0.27 for Fe, which means a high ability of the common reed to accumulate these elements. Thus, based on the BCR and AF values, the studied plant was efficient in taking up many of the studied elements as mentioned by Eid and Shaltout (2004).
4. Conclusions

We conclude that the sediments were severely contaminated by As, Sb, Se, Tl, Mo, and Sn, followed by Co and Ni. The PLI indicated that the studied sediments, especially the drain sediments, were contaminated by the studied elements, as exhibited by its values which were higher than unity. Evaluation of the eco-toxicological effects of the studied PTEs based on the ERL (effects range low) and ERM (effects range medium) indicated potential eco-toxicological effects of As, Cu, and Zn; also high toxicity of Ni and no eco-toxicological effects of Cr and Hg under certain conditions in theses sediments. The portion of the potential availability of the elements of the total content was low, which might be due to the alkalinity of the studied sediments. Based on the high values of BCR and AF, the common reed is considered efficient in taking up many of the studied elements. Future studies elucidating the temporal kinetics and release of PTEs from the sediments to solution under flooding conditions will offer a range of scientific opportunities for a comprehensive understanding of the processes determining the dynamics of these pollutants in wetland ecosystems. Also, further investigations concerning the risk of fish contamination of this lake and the potential health hazards are highly recommended. Additionally, mitigation strategies and routine monitoring programs should be developed so that necessary remediation approaches may be employed to ameliorate these PTE-contaminated sediments.

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References


Figure captions

Figure 1. Map of the studied area.

Figure 2. Sediments pH, redox potential, salinity, organic matter content and total content of Fe and Al in the studied lake and drains. Significance between values of the sediment properties and element concentrations in the studied sections is indicated with the Duncan letters.

Figure 3. Total concentrations of the studied PTEs in the studied lake and drain sediments. Significance between element concentrations in the studied sections is indicated with the Duncan letters.

Figure 4. Pollution load index (PLI) of the sediments of 32 sites of the studied lake and drain sediments. Significance between PLI values in the studied sections is indicated with the Duncan letters.

Figure 5. Concentrations of the studied PTEs in the common reed grown in the studied lake and drain sediments. Significance between element concentrations in the studied sections is indicated with the Duncan letters.