

Original Research Article

Spatial distribution and mobilization of heavy metals in different wetland soils and sediments in north of the Nile Delta as affected by wetting and drying conditions

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Abstract

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Heavy metal contamination of soils has been a long-standing environmental problem in many parts of the world, and poses enormous threats to ecosystem and human health. Spatial distribution and mobilization of heavy metals in wetlands is crucial to assessing environmental risks from contaminated soils and sediments. In this study, the spatial variability of total and mobile concentrations of copper (Cu), iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn) in soils and sediments of three different wetland soils and sediments in north of the Nile Delta, Egypt were assessed. Furthermore, the impact of wetting and drying conditions on the total and mobilization of the metals in the different wetlands were investigated. Soil and sediment samples were collected under dry and wet conditions from three different wetland ecosystems i.e., rice paddy soils (RS), fish farms sediments (FFS), and Burullus Lake sediments (BLS). Total (Aqua regia) and mobile (ammonium bicarbonate–diethylene triamine penta acetic acid) concentrations of the metals were extracted. Geo-statistical analytical technique (ArcGIS 10) was used to interpolate data for mapping spatial variability of the metals in the studied area. The soils were alkaline and poor in organic carbon content. The texture of the RS and FFS was dominated by silt and clay, while the BLS was characterized by a relatively high content of sand followed by silt, and clay respectively. The total metal concentrations (mg kg^{-1}) ranged from 4.0 to 76.5 for Cu, 3100.0 to 80350.0 for Fe, 86.8 to 1107.0 for Mn, 0.2 to 3.8 for Pb, and from 14.3 to 140.0 for Zn. The concentrations (mg kg^{-1}) of mobile Cu, Fe, Mn, Pb, and Zn varied from 0.2 to 16.0, 8.0 to 123.1, 0.3 to 4.8, 0.2 to 3.8, and from 0.04 to 4.5, respectively. Mobilization of Cu decreased significantly under wetting/reducing conditions in the three wetlands probably caused by sulfide precipitation and as a result of the reduction of Cu^{2+} to Cu^{1+} . Mobilization of Fe and Mn significantly increased under wetting conditions in the three wetlands, which might be explained by reduction of Fe-Mn (hydr)oxides to soluble Fe^{2+} and Mn^{2+} . Mobilization of Pb and Zn showed an inconsistent trend under drying and wetting conditions in the wetlands. Our findings suggest that the wetland types and flood-dry conditions affect metal mobilization in the soils and sediments. These results are an aid to provide information's aiming to develop a reliable risk assessment and the sustainable management of those wetland ecosystems.

Key words: Metal solubility, Redox potential, Risk assessment, Trace elements, Wetlands

INTRODUCTION

The Nile Delta is one of the world's largest river deltas. The Nile Delta covers the area between Cairo and the shoreline of the Mediterranean Sea and comprises the two branches of the Nile River; the Damietta branch in

the east and the Rosetta branch in the west. From north to south, the delta is approximately 160 kilometers (99 miles) in length. From west-to-east, it covers some 240 kilometers (150 miles) of coastline. The Nile Delta is

strongly populated, with a population density of up to 1,600 inhabitants per km². The Nile Delta represents only 2.3 % of the area of Egypt, but as much as 46% of the total cultivated area and it accommodates approximately 45% of Egypt's inhabitants (Bruggers, 2010). The Nile Delta is the largest area of vegetation in Egypt and represents an important agricultural sector for the Egyptian national economy. The Nile Delta is a rich agricultural region and includes fertile soils. However, since the delta no longer receives an annual supply of nutrients and sediments from upstream due to the construction of the Aswan High Dam, the soils of the floodplains have become poorer and large amounts of fertilizers and agrochemicals are now used. As a consequence, the various anthropogenic activities, as well as the use of fertilizer, pesticides, and agrochemicals in the farmlands are dispersing contaminants including potentially toxic elements (PTEs) into the soils, and waters (Elsokkary and Muller, 1990; Shaheen et al., 2013).

The Nile Delta includes different wetland ecosystems i.e., rice paddy soils, fish farms, and lakes. Rice cultivation is practiced in the Egyptian Nile delta, especially in northern areas. In the delta, rice is cultivated in rotation with "dry-food" crops. While the Egyptian Ministry of Agriculture and Land Reclamation has updated their estimate of the rice area cultivated in May 2011/12 to about 610,000 hectare (ha), the Ministry of Irrigation and Water Resources as well as traders estimate the rice area at about 730,000 ha accounting for about 24 % of the total area cultivated (3.2×10⁶ ha) in Egypt. The Kafr El-Sheikh governorate in the northern Nile Delta is the second governorate of Egypt concerning the rice production with more than 70 % of the cultivated land area in the summer under rice cultivation (USDA, GAIN Report, 2012).

Fish farms are one of the flooded systems in the Nile Delta. Many anaerobic processes taking place in the fish farm bottom lead to the production of reduced and potentially toxic compounds (Avnimelech and Ritvo, 2003). Fish ponds are occupied 60400 ha which equal to (40%) of the study area (Macfadyen et al., 2011). Burullus Lake of the Nile delta is a UNESCO-protected Area. Burullus Lake is the second largest lake in Egypt with an area of 113 thousand hectares at the central Nile delta coast with 47 km long and about 5 km wide, covering a water surface area of 460 km². The water sources for the lake are mainly from the agriculture drainage canals through which sewerage either treated and/or untreated directly reaches the lake. Fish farms and Burullus Lake produce the significant part from the fish production in the Nile Delta.

The delta coasts of the world are densely populated and highly industrialized during the past century. Environmental issues of the Nile delta coast have become more prominent recently due to increasing population and intensifying industry (Abdel-Moati, 1998;

El-Rayis, 2005). This has discharged a large quantity of wastewaters into the estuaries, leading to severe pollution of the wetlands and the associated social issues in relation to degraded environment (Abdel-Moati and El-Sammak, 1997; Soliman et al., 2006).

The PTEs are toxic pollutants, which are able to transfer hierarchically into human society through the food chain (Farmer, 1991), and some of which, under certain circumstances, can be further transformed into more toxic compounds (Chen et al., 2000). Wetland ecosystems have, both spatially and temporally, a unique aerobic and anaerobic soil environment. Wetlands can be net sinks for PTEs. However, during different wetting and drying conditions, these wetland soils and sediments may act as a source for pollutants resulting an adverse impact on the agricultural environment (Shaheen et al., 2014a,b,c; Rinklebe et al., 2016a,b; Frohne et al., 2011; Schulz-Zunkel et al., 2015; DeLaune and Seo, 2011). The intensity of soil reduction can be rapidly characterized by soil oxidation–reduction (redox) potential (E_H), which allows for the prediction of the mobilization of various nutrients and PTEs in soils and sediments (e.g., Yu et al., 2007; DeLaune and Seo, 2011; Shaheen et al., 2016). The mobilization of PTEs under different wetting and drying conditions is controlled by E_H and pH, dissolved organic carbon (DOC), iron (Fe)-manganese (Mn) oxides, and sulphate (SO_4^{2-}) (Rinklebe and Du Laing, 2011; Rupp et al., 2010; Shaheen et al., 2014b,c; Rinklebe et al., 2016a,b; Shaheen et al., 2016). Thus, according to the state-of-the-art of soil science in wetlands, we hypothesized that different wetting and drying conditions in wetland soils and sediments may affect the mobilization of the redox-dependent pollutants due to changes of E_H /pH-values, DOC, Fe, Mn and SO_4^{2-} .

Despite of the scientific progress, our knowledge regarding the mobilization of PTEs in different wetland ecosystems under different wetting and drying conditions are incomplete. Particularly, studies that specifically address redox-induced mobilization processes of these elements in alkaline wetlands from different ecosystems like rice soils (RS), fish farms sediments (FFS), and Burullus Lake sediments (BLS) are still rare. In addition, analyses of spatial distribution of PTEs in these wetland ecosystems are useful to recognize the degradation processes of wetlands for better environmental assessment and management.

The release of many PTEs is a concern for wetland ecosystems and for surface- and groundwater quality since these toxic elements might be released from soil solid phase to soil solution particularly under different wetting and drying cycles, and thus, they can be transferred to the ecosystem and food chain, thereby posing a hazard to environment and human health. Therefore, to elucidate the mobilization of PTEs in different wetland soils and sediments is highly relevant and challenging at the same time. Study the mobilization of PTEs in the wetlands in Nile Delta is very important

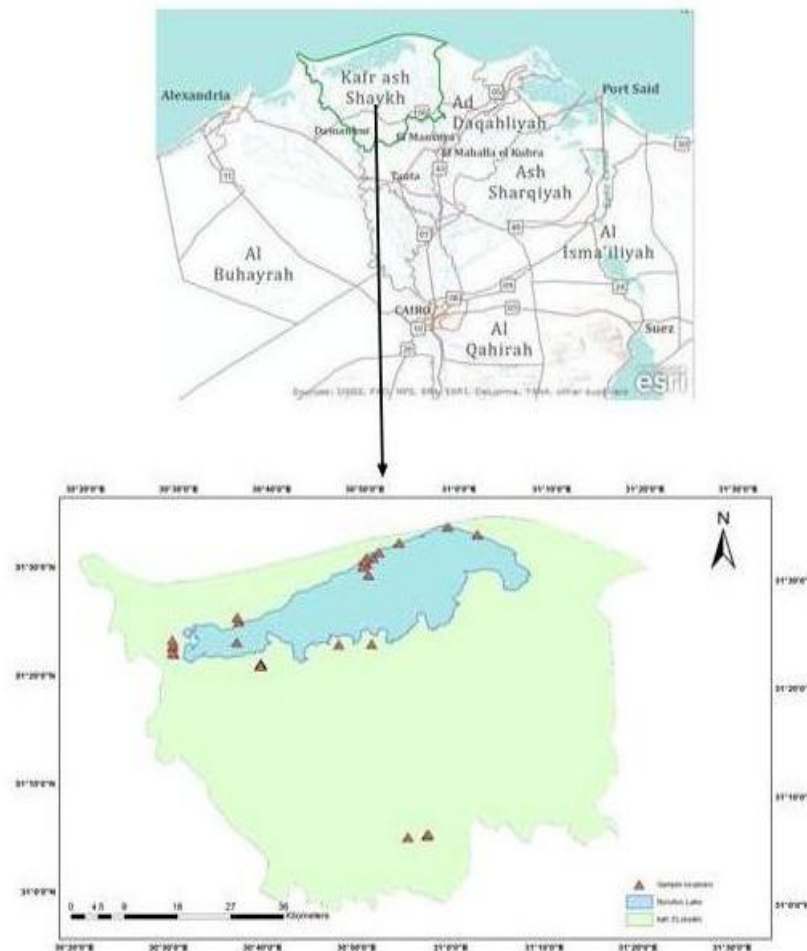


Figure 1. Location of the study area.

since the rice soils, fish farms, and Burullus Lake ecosystems cover several hundreds of square kilometers. Therefore, the respective authorities are coerced by law to conduct an appropriate risk assessment and to implement practical actions to eliminate (or reduce) these environmental problems in wetland ecosystems. Moreover, the results are required to answer both scientific and practical questions regarding protection of groundwater, fishes and rice plants, sustainable management of wetland s or explain the pathways of environmental harmful substances (Shaheen et al., 2014a and Du Laing et al., 2009a).

Therefore, the objectives of our study were to i) study the impact of wetting and drying conditions on the mobilization of copper (Cu), iron (Fe), manganese (Mn), lead (Pb), and zinc (Zn) in soils and sediments of three different wetland ecosystems i.e., rice paddy soils, fish farms, and Burullus Lake in north of the Nile Delta, Egypt, 2), investigate the spatial variability of total and mobile concentrations of the studied metals in the previous mentioned systems through interpolating the studied

points, and iii) to provide information's aiming to develop a reliable risk assessment and the sustainable management of those wetland ecosystems.

MATERIAL AND METHODS

Study sites and sampling of soils and sediments

The study sites are located in the Kafr El-Sheikh governorate at the north of the Egyptian Nile Delta (Figure 1). The Nile delta is located along the southern coast of the Mediterranean Sea ($30^{\circ} 00' - 31^{\circ} 40' N$ and $30^{\circ} 00' - 32^{\circ} 30' E$; Fadlelmawla and Dawoud, 2006). The Nile Delta has a Mediterranean climate, with dry mild summers and fairly cool and wet winters with an annual precipitation of <100 mm (Bruggers, 2010). Soil and sediment samples were collected under dry and wet conditions from three different wetland ecosystems i.e., rice paddy soils, fish farms, and Burullus Lake. (Figure 1)

The soil samples were collected from fluvial deposits

which are under rice production each summer, as they are periodically flooded for five months every year. Eight composite surface (0-20 cm deep) soil samples were collected from different rice fields existing in the area (flooded soils). Eight composite surface samples (0–25 cm deep) were collected from the adjacent dry corn fields and served as dried soils/drying conditions. Ten flooded sediment samples were collected from different fish farms in the studied area. In addition, ten sediments samples were collected from the adjacent dry part in the same fish farm to represent relatively similar sediments under drying conditions. Nine flooded sediment samples were collected from different parts in the Burullus Lake. In addition, twelve sediments samples were collected from the adjacent dry island in the same location in the lake to represent relatively similar lake sediments under drying conditions. Three samples were collected from each site, pooled, and well-mixed to prepare a composite sample considered being representative. The soil and sediments samples were sealed in polyethylene bags and transported to the laboratory for analysis. Therefore, in total twenty seven wet composite samples and thirty dry composite samples were collected from the three wetlands.

Preparation and characterization of the studied soils and sediments

The wet soil and sediment samples were divided for two parts. The first part was used in wet form for determination of moisture content, soil pH, and extraction the metal mobile fraction using ammonium bicarbonate-diethylene triamine penta acetic acid (AB-DTPA). The second part was homogenized, air-dried, and crushed handily and passed through a 2-mm sieve. Soil properties were determined in the dried and sieved samples according to Sparks et al. (1996) as follow: Soil pH was measured in 1: 1 (soil: deionized water suspension) using a calibrated pH- meter (JENWAY 3510, Ser. NO. 1171; sensitivity 0.01pH unit). Soil salinity (Electric-conductivity; EC) was measured in 1: 5 (soil: deionized water) using EC- Meter (MI 170, Italy). Organic carbon (OC) was determined by loss on ignition method using the muffle furnace at 550 °C for 5 hours (Cambardella et al., 2001; Tan, 2005). Available soil phosphorus (P) was extracted using AB-DTPA according to Soltanpour and Schwab (1977), and determined calorimetrically by the ascorbic acid method (Murphy and Riley, 1962) using +80 UV-Visible spectrophotometer.

Extraction and analysis of metal mobile fraction

The mobile fraction of the studied metals was extracted in the wet and dry soil and sediment samples using ammonium bicarbonate–diethylenetriaminepentaacetic

acid (AB-DTPA) with 1M NH_4HCO_3 + 0.005M DTPA solution according to Soltanpour and Schwab (1977). The metal concentrations were measured using atomic absorption spectrometry (GBC Avanta E, Victoria, Australia; Ser. No. A5616).

Spatial variability and geo-statistical analysis of TMs in the studied locations

To interpolate data for mapping spatial variability of TMs in wet and dry locations, geostatistical analytical technique was used. The data was processed in ArcGIS 10 software using topographic map for the studied area.

Quality control and statistical analysis

All the used equipments were calibrated and uncertainties were calculated. Internal and external quality assurance systems were applied in the laboratory according to ISO/IEC 17025 requirements for laboratory accreditation. In all measurements, blanks, triplicate measurements of metals in extracts, and analysis of certified reference materials for each metal (Merck) were routinely included for quality control. Depending on the studied element, the recovery was between 92 and 103 %. Additionally, a test of recovery were carried out at five different concentration levels (1000, 100, 50, 25, and $12.5 \mu\text{g L}^{-1}$) as an internal quality control. The average relative standard deviation (RSD) was less than 5 %. The relative standard deviation of replicate analysis was below 5%. In a very few cases the standard deviation of the measurements was above 5%. These values were not included in the statistical analyses. The limits of detection (LOD) obtained for Cu, Fe, Mn, Pb, and Zn were 5.4, 6.2, 1.4, 42.0, and $1.8 \mu\text{L}^{-1}$, respectively. Quality control of the analyses efficiency was performed using certified reference materials obtained from the Webby Environmental (WS1011; Nov., 2011) and Phenova certified reference material (WS0113; Feb., 2013). The data collected were analyzed statistically with SPSS 18 software. Statistical analysis was performed with analysis of variance (ANOVA). Duncan's multiple range tests were used to compare the means of the treatments, variability in the data was expressed as the standard deviation, and $P < 0.05$ was considered to be statistically significant.

RESULT AND DISCUSSIONS

Characterization of the studied soils and sediments

Variations of soil pH, salinity, soil organic carbon, and mobile P in the studied soils and sediments under drying and wetting conditions in the three wetlands are

Table 1. Variations of particle size distributions, soil pH, salinity, soil organic carbon, and available P in the studied soils and sediments under drying and wetting conditions in the three wetland ecosystems.

Unit	Wet					Dry					
	Min.	Max.	Mean	SD	n	Min.	Max.	Mean	SD	n	
Rice Soils											
Clay	43.0	50.0	45.4	2.1	8	42.0	50.0	44.9	2.4	8	
Silt	40.0	50.0	46.8	3.2	8	41.0	50.0	46.5	3.3	8	
Sand	6.0	11.0	7.9	2.0	8	6.0	11.0	8.6	1.7	8	
pH	-	7.69	8.26	7.98	0.19	8	7.56	8.08	7.73	0.18	8
EC	dSm ⁻¹	0.26	2.73	1.45	0.78	8	0.26	1.74	0.92	0.58	8
OC	%	0.86	1.39	1.11	0.17	8	0.76	1.91	1.32	0.40	8
P	mg kg ⁻¹	0.61	2.51	0.97	0.83	8	0.99	10.60	3.93	3.14	8
Fish Farms											
Clay	33.4	41.0	37.0	2.5	10	34.4	41.0	37.7	2.3	10	
Silt	54.4	63.4	57.0	3.2	10	52.4	62.4	56.4	2.8	10	
Sand	3.2	11.9	6.0	2.8	10	3.0	10.9	5.8	2.6	10	
pH	-	7.59	8.46	8.09	0.31	10	7.53	8.01	7.83	0.13	10
EC	dSm ⁻¹	0.39	0.97	0.55	0.19	10	1.12	2.45	1.74	0.45	10
OC	%	0.54	1.21	0.68	0.21	10	0.48	0.79	0.66	0.09	10
P	mg kg ⁻¹	0.34	10.91	4.32	3.61	10	3.07	17.39	11.30	4.75	10
Burullus Lake											
Clay	5.0	45.0	31.3	14.6	12	5.0	40.0	21.8	15.1	9	
Silt	5.0	45.0	31.9	12.8	12	6.0	40.0	23.2	15.3	9	
Sand	10.0	90.0	36.8	27.0	12	20.0	88.0	55.0	30.4	9	
pH	-	7.45	8.18	7.74	0.24	12	7.33	8.23	7.71	0.25	9
EC	dSm ⁻¹	0.70	2.89	1.32	0.61	12	1.18	11.56	5.96	3.23	9
OC	%	0.07	1.60	0.73	0.52	12	0.62	1.15	0.62	0.41	9
P	mg kg ⁻¹	0.50	11.84	3.73	3.55	12	9.94	16.34	9.94	4.73	9

EC: Electric conductivity; OC: Organic carbon; P: Available phosphorus

presented in Table (1).

The studied soils and sediments showed a different particle size distribution. The texture of the RS and FFS was dominated by silt and clay, while the BLS was characterized by a relatively high content of sand followed by silt, and clay, respectively (Table 1). Soil acidity differed between the studied soils and sediments and was alkaline. The values of pH ranged from 7.33 (BLS) to 8.46 (FFS). The variation between the wetting and drying conditions were non-significant. However, the mean pH values were relatively high under wet conditions as compared to the dry conditions in the three wetlands (Table 1). An increase of pH with a decline in E_H in the flooded wet systems might be due to the consumption of protons required for the reduction of NO_3^- , Mn^{4+} , and Fe^{3+} (Yu et al., 2007; Reddy and DeLaune, 2008; Frohne et al., 2011; Rinklebe et al., 2016a). The soils and sediments were poor in the organic carbon (OC) content. The values of OC ranged between 0.62 % in BLS under dry conditions to 1.32 % in RS under dry conditions (Table 1). The relatively increase of OC in the RS might be explained by the application of the organic fertilizers and the accumulated plant roots and residuals at the surface layer. Consequently, the differences in the soil and sediments properties and the wide variation between the moisture content, redox chemistry and governing factors such as soil pH, dissolved organic carbon,

sulfates, and iron oxides were expected to affect the spatial distribution and mobilization of the studied metals in the different wetlands.

Spatial variability and mobilization of the metals

The variations of total and mobile (AB-DTPA-extractable)- Cu, Fe, Mn, Pb, and Zn in the studied soils and sediments under drying and wetting conditions in the three wetlands are presented in Table (2). The geo-spatial distribution of total and mobile metals in the studied wetlands is shown in Figures 2-6. The variability of total and mobile metals is demonstrated in the geospatial maps for the entire region. The concentrations of total and mobile metals exhibited clear differences among the three wetlands and represent clear evidence of the influence of wetting and drying conditions on metal accumulation and mobilization in soils and sediments.

Copper

Spatial variability of total and mobile Cu

Table 2 provides the total and mobile concentrations of Cu in the different wetlands under wetting and drying

Table 2. Variations of total and AB-DTPA-extractable Cu, Fe, Mn, Pb, and Zn (mg kg^{-1}) in the studied soils and sediments under drying and wetting conditions in the three wetland ecosystems.

Metal	Wet					Dry				
	Min.	Max.	Mean	SD	n	Min.	Max.	Mean	SD	n
Rice Soils										
Total metal concentrations										
Cu	42.5	74.5	58.0 ^a	10.9	8	43.5	76.5	57.3 ^a	12.1	8
Fe	46700	62950	53872 ^a	6039	8	45350	59950	52875 ^a	5732	8
Mn	740.3	1025	853.7 ^a	100.4	8	716.5	1064	895.8 ^a	129.6	8
Pb	2.0	11.0	5.9 ^a	3.2	8	0.5	11.0	5.8 ^a	3.7	8
Zn	72.5	140	86.6 ^a	22.3	8	70.0	92.5	80.4 ^a	8.3	8
AB-DTPA-extractable metal concentrations										
Cu	1.38	12.51	5.31 ^b	3.36	8	5.23	10.95	8.44 ^a	1.84	8
Fe	8.02	123.1	36.89 ^a	37.40	8	10.32	21.35	13.05 ^a	3.75	7
Mn	0.27	4.71	1.55 ^a	1.40	8	0.36	3.80	1.33 ^a	1.22	8
Pb	0.48	1.94	1.23 ^a	0.55	8	0.60	2.44	1.24 ^a	0.67	8
Zn	0.26	2.37	0.88 ^a	0.66	8	0.47	2.98	1.10 ^a	0.81	8
Fish Farms										
Total metal concentrations										
Cu	47.5	62.0	54.9 ^a	4.7	10	51.0	63.0	56.3 ^a	3.8	10
Fe	47800	58725	52860 ^a	4134	10	44875	58575	51975 ^a	4122	10
Mn	676.8	939.3	821.3 ^a	73.1	10	735	1107	838.2 ^a	114.5	10
Pb	0.5	3.5	1.4 ^a	1.2	10	0.4	8.0	2.7 ^a	2.4	10
Zn	72.5	92.5	80.2 ^a	6.8	10	67.5	85.0	76.3 ^a	5.6	10
AB-DTPA-extractable metal concentrations										
Cu	<0.20	7.39	1.59 ^b	2.50	9	2.18	11.36	8.75 ^a	2.85	10
Fe	19.88	87.61	37.54 ^a	20.09	10	10.63	54.41	27.74 ^a	15.34	10
Mn	0.78	4.79	2.65 ^a	1.08	10	0.65	2.08	1.24 ^b	0.56	10
Pb	0.72	2.19	1.50 ^a	0.53	10	<0.20	2.13	0.71 ^b	0.58	10
Zn	0.26	3.92	2.22 ^a	1.21	10	<0.05	4.51	0.94 ^b	1.46	10
Burullus Lake										
Total metal concentrations										
Cu	4.0	50.0	27.0 ^a	15.7	12	10.1	58.5	28.5 ^a	20.2	9
Fe	3100	80350	27312 ^a	21708	12	8025	55300	23533 ^a	19792	9
Mn	86.8	882.5	433.5 ^a	292.9	12	140.5	682.3	323 ^a	222.6	9
Pb	1.0	19.5	10.1 ^a	6.0	12	0.1	26.3	8.5 ^a	10.8	9
Zn	15.0	122.5	54.4 ^a	31.8	12	14.3	82.5	48.6 ^a	23.8	9
AB-DTPA-extractable metal concentrations										
Cu	<0.20	2.90	0.30 ^b	0.84	12	1.98	16.01	6.56 ^a	4.46	9
Fe	10.13	113.20	54.60 ^a	39.77	12	8.97	49.59	23.49 ^b	14.00	8
Mn	0.36	3.28	1.45 ^a	0.94	12	0.35	2.14	1.08 ^a	0.67	8
Pb	0.20	2.27	1.05 ^a	0.49	12	0.59	3.83	1.39 ^a	1.19	8
Zn	0.04	3.18	0.66 ^a	0.85	12	0.28	2.12	0.86 ^a	0.68	8

conditions. The values of total Cu varied from 4.0 mg kg^{-1} in the BLS to 76.5 mg kg^{-1} in the RS. The values of AB-DTPA extractable Cu varied from 0.2 mg kg^{-1} to 16.01 mg kg^{-1} in the BLS. According to the critical concentrations in soils as indicated by Kabata-Pendias (2011), the total concentrations of Cu in the RS and FFS were found to be higher than the lower limit of the maximum allowable soil concentrations (MAC: $60\text{-}150 \text{ mg kg}^{-1}$), implying a relatively harmful soil alterations.

The RS showed higher concentrations of total and mobile Cu than the BLS and FFS (Table 2). The increment of Cu in RS might be attributed to the increase of clay percentage in the RS as compared to the FFS and

BLS (Table 1). In addition, excessive Cu concentration in RS might be due to long-term anthropogenic activities and the agricultural management practices (Shaheen et al., 2015a,b). Also, Surdyk et al. (2010) mentioned that the ions of Cu were reported to be found in pesticides and/or in fertilizers.

The geo-spatial distribution of total and mobile Cu in the studied wetlands is shown in Figure 2. In general, the high concentrations of total and mobile Cu both under wet and dry conditions were distributed in the western part of the studied area (Figure 2). The results indicated that soils contaminated with Cu in the soil surface are predominantly in the west section with total and mobile

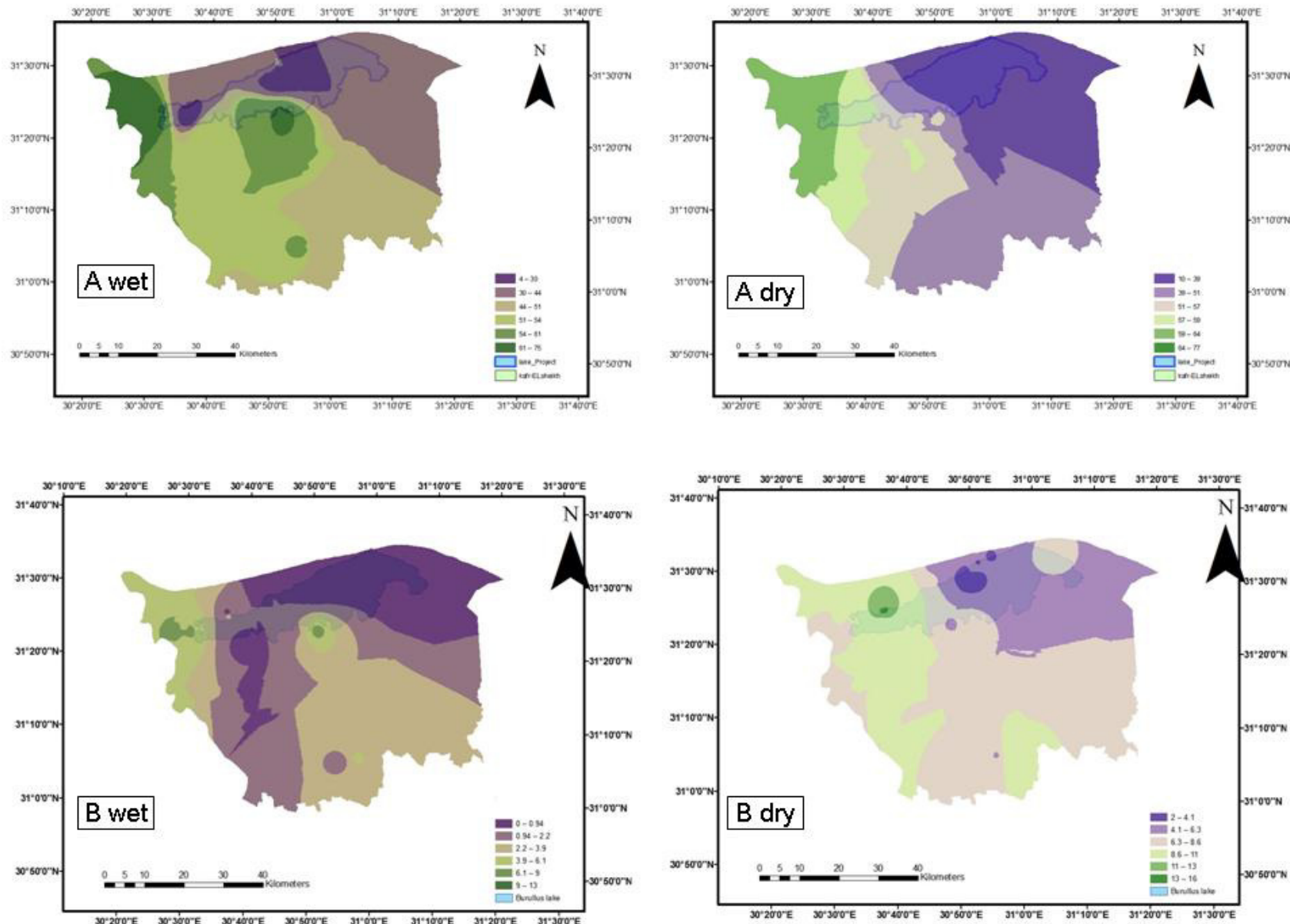


Figure 2. Spatial distribution of Cu in the studied wetlands A) Total and B) AB-DTPA under wet and dry conditions.

Table 3. ANOVA statistical analysis of Cu, Fe, Mn, Pb, and Zn concentrations at the different wetlands as affected by wetting and drying conditions.

Metal	Source	Wet	Dry
Total metals			
Cu	DF	2	2
	F ratio	11.768	1.202
	Sig	0.000**	0.318
Fe	DF	2	2
	F ratio	0.950	2.782
	Sig	0.399	0.084
Mn	DF	2	2
	F ratio	3.598	2.782
	Sig	0.041*	0.842
Pb	DF	2	2
	F ratio	2.067	1.660
	Sig	0.146	0.212
Zn	DF	2	2
	F ratio	8.186	0.094
	Sig	0.002**	0.910
AB-DTPA extractable metals			
Cu	DF	2	2
	F ratio	22.365	12.94
	Sig	0.000**	0.000**
Fe	DF	2	2
	F ratio	11.757	17.043
	Sig	0.000**	0.000**
Mn	DF	2	2
	F ratio	14.819	33.597
	Sig	0.000**	0.000**
Pb	DF	2	2
	F ratio	11.974	1.75
	Sig	0.000**	0.195
Zn	DF	2	2
	F ratio	5.481	12.03
	Sig	0.01**	0.000**

Cu concentration more than 61 and 13 mg k g⁻¹, respectively. In contrast, the North West area exhibited the lowest values of total and mobile Cu. (Figure 2)

Impact of wetting and drying conditions on total and mobilization of Cu

The mean values of total Cu were 58.0, 54.9, and 27.0 mg kg⁻¹ in the RS, FFS, and BLS, respectively under wetting conditions, while these values under drying conditions were 57.3, 56.3, and 28.5 mg kg⁻¹ in the RS, FFS, and BLS, respectively. The variations between total Cu under wetting and drying conditions in the studied wetlands were non-significant.

The mean values of AB-DTPA extractable Cu were 5.31, 1.59, and 0.3 mg kg⁻¹ in the RS, FFS, and BLS, respectively under wetting conditions, while these values under drying conditions were 8.44, 8.75, and 6.56 mg kg⁻¹ in the RS, FFS, and BLS, respectively. Therefore, mobilization of Cu differed significantly under wetting and drying conditions. As indicated from one-way ANOVA

(Table 3), there was a significantly difference in total and mobile Cu concentrations as affected by the studied systems, there were significantly differences in total Cu concentrations under wetting conditions between the studied systems, while there were significantly differences in concentrations of mobile Cu under both of wetting and drying conditions. (Table 3)

Mobilization of Cu increased under drying/oxidizing conditions compared to wetting/reducing conditions in the three wetlands (Table 2). The behavior of Cu might be explained by different mechanisms: Firstly, the relatively low mobilization of Cu under reducing conditions can be attributed to the reducing of Cu²⁺ to Cu¹⁺ with the help of electron donors such as Fe²⁺ and bacteria. Our results extended beyond the findings of Frohne et al. (2011), Schulz-Zunkel et al. (2013), and Shaheen et al. (2014b) whose reported an increase in soluble Cu during periods with high redox potentials. They reported that Cu which occurs as Cu²⁺ in oxidizing conditions may be reduced as Cu¹⁺ or even as Cu⁰ in reducing environments.

Secondly, the low mobilization of Cu at flooded conditions compared to drying toxic conditions could be

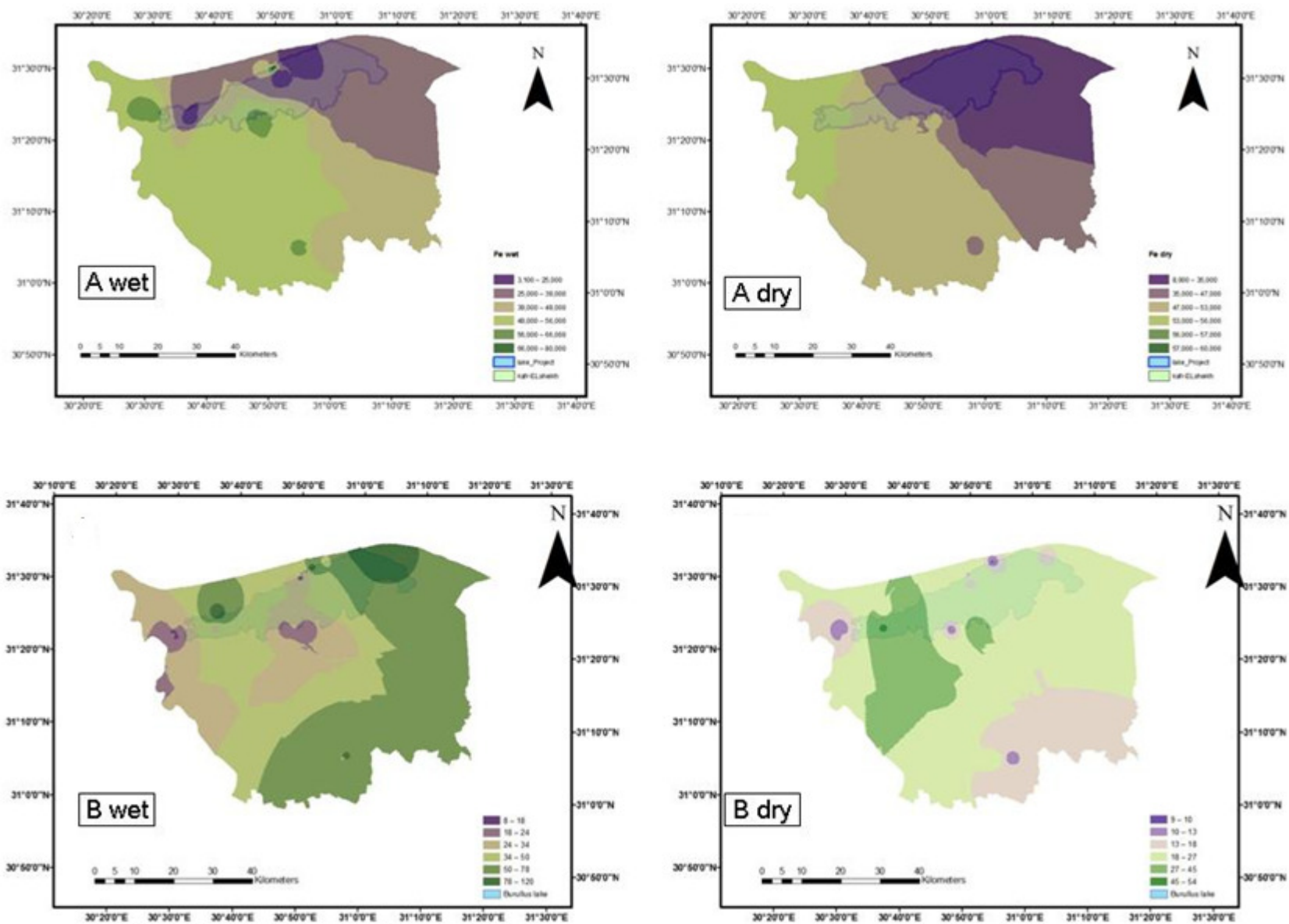


Figure 3. Spatial distribution of Fe in the studied wetlands A) Total and B) AB-DTPA under wet and dry conditions.

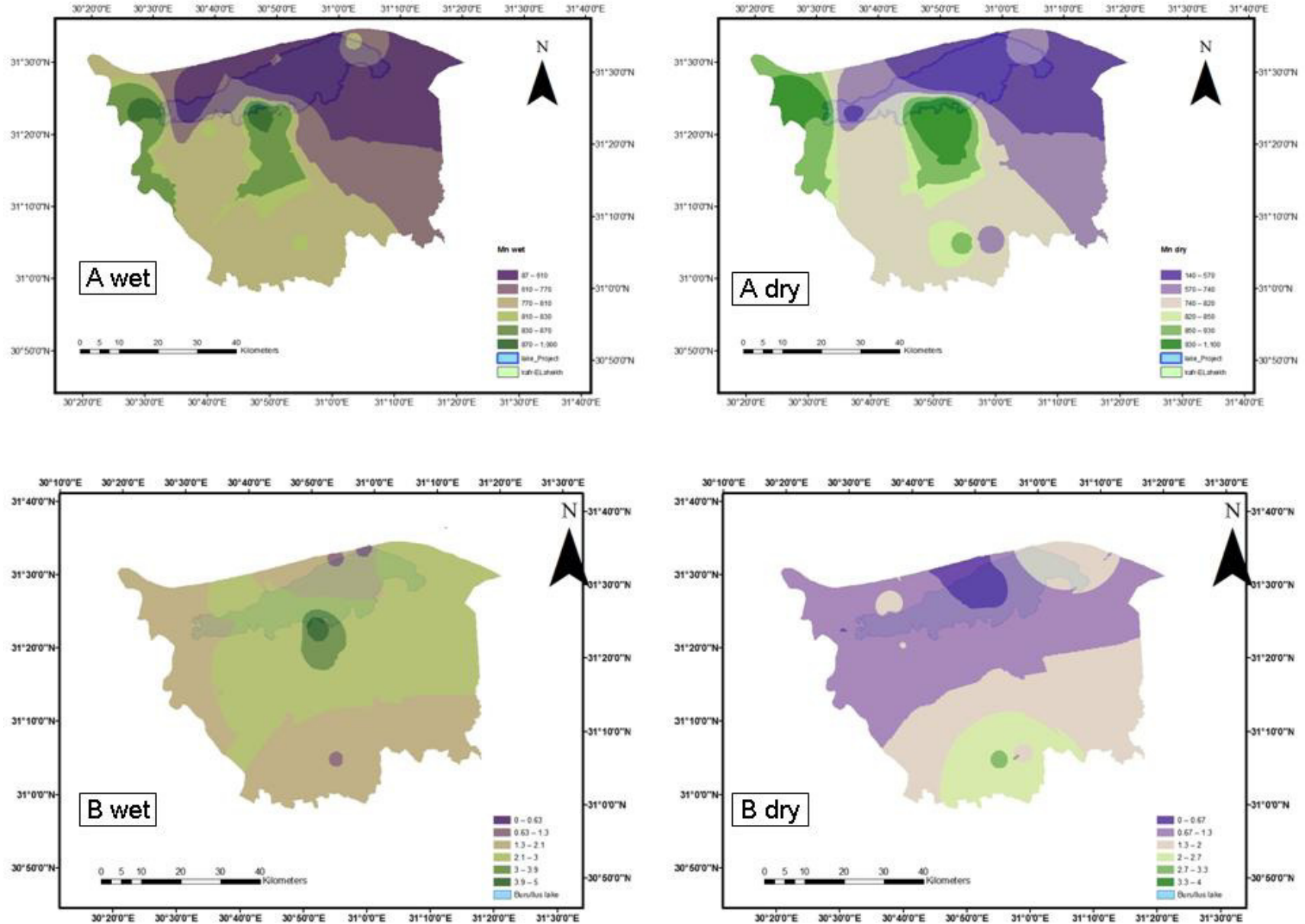


Figure 4. Spatial distribution of Mn in the studied wetlands A) Total and B) AB-DTPA under wet and dry conditions

caused by sulfide precipitation (Frohne et al., 2011; Shaheen et al., 2014b; Rinklebe et al., 2016a,b). The possible decreasing of E_H under wetting conditions suggests that sulfides might be formed in the soils and sediments. Moreover, only a very small amount of sulfides is needed to precipitate Cu (Luther et al., 2002). In this respect, Frohne et al. (2011) and Shaheen and Rinklebe (2014) found that mobile Cu concentrations increased with increasing redox potentials in floodplain soils and attributed that to dissolution of sulfides and the resulted release of Cu in a mobile form. Luther et al. (2002) showed that reaction of Cu (II) with equimolar amounts of sulfide led to Cu reduction and formation of aqueous Cu-(poly)sulfide complexes and polynuclear clusters as intermediates during Cu sulfide precipitation. These aqueous clusters and freshly formed primitive Cu sulfide phases are thought to have a Cu/S ratio close to unity (Patrick et al., 1997; Rozan et al., 2000). The amount of biogenic sulfide formed during soil reduction might be a key factor for the Cu dynamics in wetland soils with respect to changes in the solid phase speciation and solubility of Cu during soil reduction and subsequent reoxidation. The results of Fulda et al. (2013) emphasized the key role of the amount of mobile sulfate which constrains the maximum amount of sulfide formed by microbial sulfate reduction during soil flooding, since mineralization of organic S under anoxic conditions is typically too slow to provide a significant alternative source of biogenic sulfide over a single flooding event. However, also in the case of relatively high sulfate availability, biogenic sulfide formation during soil reduction may be limited if the flooding period is not long enough to reach major sulfate reduction. Therefore, Fulda et al. (2013) concluded that precipitation of Cu(0) and complexation of Cu(I) by reduced organic S groups are important processes in periodically flooded soils if sulfide formation is limited by the amount of mobile sulfate or the duration of soil flooding.

Thirdly, the mobilization of Cu seems to be largely governed by the chemistry of Fe and Mn. Concentrations of dissolved Fe and Mn showed a different behavior as compared to Cu in the three systems (Table 2; Figure 2).

This might indicate that Cu may not directly co-precipitate with Fe-Mn(hydr)oxides under our experimental conditions. The role of organic material should be considered as a possible explanation for this behavior between Cu and Fe oxides. It is possible that the formation of mobile Cu-dissolved organic carbon complexes under oxidizing conditions prevented Cu from co-precipitating with or adsorbing to Fe (hydr)oxides (Schulz-Zunkel and Krüger, 2009; Frohne et al., 2011).

Fe and Mn

Spatial variability of total and mobile Fe and Mn

Figures 3 and 4 provide the spatial variability of total and

mobile Fe and Mn in the soils and sediments of the studied wetlands under wetting and drying conditions. The values of total Fe varied from 3100 mg kg^{-1} to 80350 mg kg^{-1} . Both the minimum and maximum values were recorded in the BLS. The values of AB-DTPA extractable Fe varied from 8.02 mg kg^{-1} to 123.1 mg kg^{-1} in the RS. The values of total Mn varied from 86.8 mg kg^{-1} in the BLS to 1107 mg kg^{-1} in the FFS. The values of AB-DTPA extractable Mn varied from 0.27 mg kg^{-1} in the RS to 4.79 mg kg^{-1} in the FFS. (Figure 3 and 4)

The Geo-spatial distribution of Fe in the studied soils and sediments is shown in Figure 3. This figure indicated high spatial variability of Fe when compared to other elements. It is indicated from the results that the highest Fe total concentrations are observed in the Northwest sections, while the lowest concentrations were observed in the North and Northeast sections in the studied area. On the other hand; the results indicated that the highest mobile Fe concentrations were observed in the East and North sections in the study area under wetting conditions, while the lowest concentrations were observed in small parts in the central or in the West sections in the study area. In contrast; under drying conditions; the highest concentration of Fe were observed toward the West section in the study area.

Moreover; the geo-spatial distribution of total Mn in the studied locations is shown in Figure 4. The results indicated that the highest total Mn concentrations were observed in the central and west sections in the study area; while the lowest concentrations were observed in the East and the North sections of the study area. The geo-distribution map in Figure 4 also indicated high concentrations of AB-DTPA extractable Mn were predominantly in central section under wetting conditions and toward the south in dry conditions; while the lowest concentrations were predominantly toward the north especially under drying conditions. Hamed et al. (2013) reported high level of Mn in fish farms is probably due to agricultural drainage water filled with fertilizers spilled into the drain. Additionally; they stated that fish farms adjacent to the drain use some chicken farms residuals rich with Mn for feeding fish.

Impact of wetting and drying conditions on total and mobilization of Fe and Mn

The mean values of total Fe were 53872, 52860, and 21708 mg kg^{-1} in the RS, FFS, and BLS, respectively under wetting conditions, while these values under drying conditions were 52875, 51975, and 23533 mg kg^{-1} in the RS, FFS, and BLS, respectively. The variations between total Fe under wetting and drying conditions in the studied wetlands were non-significant. The mean values of AB-DTPA extractable Fe were 36.89, 37.54, and 54.60 mg kg^{-1} in the RS, FFS, and BLS, respectively under wetting conditions, while these values under drying

conditions were 13.05, 27.74, and 23.49 mg kg⁻¹ in the RS, FFS, and BLS, respectively. Therefore, mobilization of Fe differed significantly under wetting and drying conditions only in Burullus Lake.

The mean values of total Mn were 853.7, 821.3, and 433.5 mg kg⁻¹ in RS, FFS, and BLS, respectively under wetting conditions, while these values under drying conditions were 895.8, 838.2, and 682.3 mg kg⁻¹ in RS, FFS, and BLS, respectively. The variations between total Mn under wetting and drying conditions in the studied wetlands were non-significant. The mean values of AB-DTPA extractable Mn were 1.55, 2.65, and 1.54 mg kg⁻¹ in the RS, FFS, and BLS, respectively under wetting conditions, while these values under drying conditions were 1.33, 2.08, and 2.14 mg kg⁻¹ in the RS, FFS, and BLS, respectively. Therefore, mobilization of Mn differed significantly under wetting and drying conditions only in fish farming.

Considering the difference between the studied systems as indicated from Table (3); there were insignificant differences in total Fe concentrations under wetting or drying conditions between the studied systems, while there were significant differences in mobile Fe concentrations under both of wetting and drying conditions. On the other hand; total Mn concentrations exhibited significant differences between the studied systems under wetting conditions, while AB-DTPA Mn followed similar trend such as AB-DTPA- Fe and differed significantly under both of wetting and drying conditions between the studied systems.

The above-mentioned results indicated that concentrations of mobile Fe and Mn showed wide ranges between wetting and drying conditions in the three wetlands (Table 2). The mobilization of Fe and Mn were significantly higher under wetting than drying conditions in the three wetlands. However, mobile Fe exhibited the largest range between wetting and drying conditions as compared to Mn and the other elements (Table 2). The increasing of Fe and Mn mobilization under wetting/reducing conditions than the drying/oxidizing conditions has been frequently described and can be attributed to the formation of Fe-Mn (hydr)oxides at high E_h under drying conditions (e.g. Yu et al., 2007; Frohne et al., 2011; Shaheen et al., 2014a,b,c), while Fe-Mn (hydr)oxides are reduced to soluble Fe²⁺ and Mn²⁺ at low E_h under flooded conditions (Shaheen et al., 2016). When soils reached reducing conditions under wetting cycles, soil redox-active species were transformed into their reduced forms, Fe³⁺ and Mn⁴⁺ to Fe²⁺ and Mn²⁺, respectively, resulting in higher soluble Fe and Mn concentrations. During oxidation, Fe and Mn can be immobilized via precipitation as Fe and Mn oxyhydroxides (Rinklebe and Du Laing, 2011).

The narrow variations between mobile Mn in both wetting and drying conditions in the three ecosystems might be due to that the reduction of Mn occurs at higher reduction potentials than Fe reduction (Reddy and

DeLaune, 2008). The precipitation–dissolution of Mn in soils is closely related to the oxidation–reduction processes. In this respect He et al. (2010) reported that the reduction of MnO₂ occurs after the depletion of O₂ at a pH of about 6.9. They also observed that at this stage Mn²⁺ concentration in soil solution may not increase as fast as expected, because the released Mn²⁺ will be partially captured by Fe oxides and hydroxides through sorption processes. With further development of reducing conditions, Fe oxides and hydroxides start to dissolve and Fe²⁺ release into soil solution. At this point Mn²⁺ concentration in soil solution will increase rapidly due to the dissolution of Fe oxides. The Fe-Mn (hydr)oxide reduction process also depends on the total content of Fe in the bulk soil which is high in our case (Table 1). The total Fe and Mn is high in the studied soil and sediments. This indicates that amorphous, oxalate-extractable Fe-Mn oxides such as ferrihydrite are abundant in the soil and sediments. Amorphous Fe oxides usually dominate hydromorphic soils (e.g., Fiedler and Kalbitz, 2003; Schulz-Zunkel and Krüger, 2009); however, crystalline compounds such as goethite may also exist in parallel.

Soil pH is also important to these reactions. Increasing of Fe and Mn mobilization under wetting conditions might be due to the relatively decrease of soil pH under the wet conditions than the dry condition in the three studied wetlands (Table 1). Low pH favours the production of Mn²⁺ and Fe²⁺ and vice versa as reported by others (e.g., DeLaune and Seo, 2011; Reddy and DeLaune, 2008; Shaheen et al., 2014a). Thus, the mobilization of Mn correlated negatively with pH in the Burullus lake (r = -0.61*).

Lead and zinc

Spatial variability of total and mobile Pb and Zn

Geo-spatial distribution for total and mobile Pb and Zn in the soils and sediments of the studied wetlands under wetting and drying conditions are presented in Figures 5 and 6. The values of total Pb in the studied wetlands varied from 0.1 mg kg⁻¹ in the BLS to 26.3 mg kg⁻¹ in the BLS. The values of AB-DTPA extractable Pb varied from < 0.20 mg kg⁻¹ in the FFS to 3.83 mg kg⁻¹ in the BLS (Table 2). The values of total Zn varied from 14.3 mg kg⁻¹ in the BLS to 140 mg kg⁻¹ in the RS. The values of AB-DTPA extractable Zn varied from 0.04 to 4.51 mg kg⁻¹ in the FFS (Table 2). According to the critical concentrations in soils as indicated by Kabata-Pendias (2011), the total concentrations of Pb in the studied wetlands were found to be lower than the lower limit of the maximum allowable soil concentrations (MAC: 20-300 mg kg⁻¹). Also the total concentrations of Zn in agricultural soils were found to be less than the lower limit of the maximum allowable soil concentrations (MAC: 100-300 mg kg⁻¹). (Figure 5 and 6)

The geo-spatial distributions of Pb were shown in

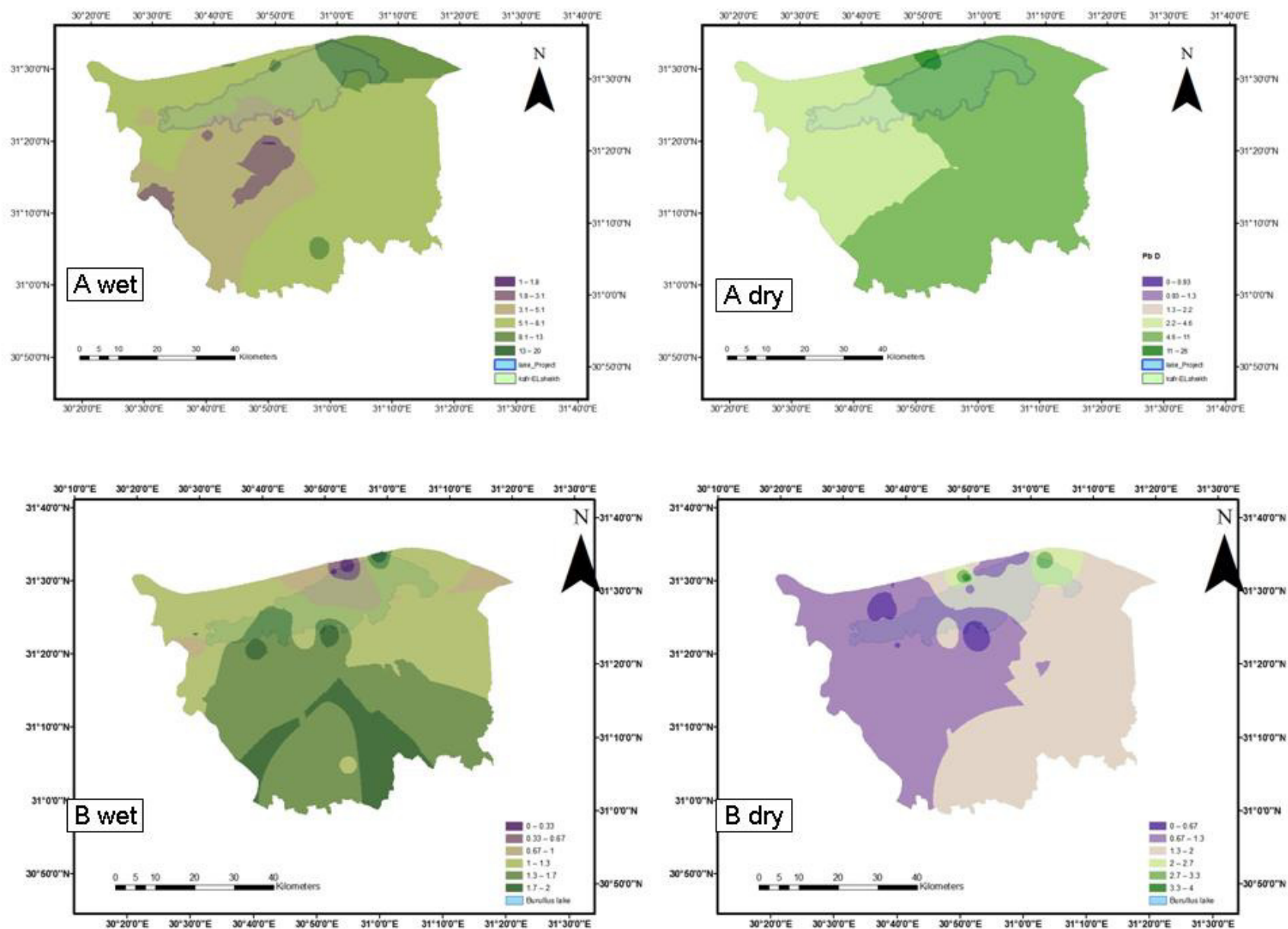


Figure 5. Spatial distribution of Pb in the studied wetlands A) Total and B) AB-DTPA under wet and dry conditions

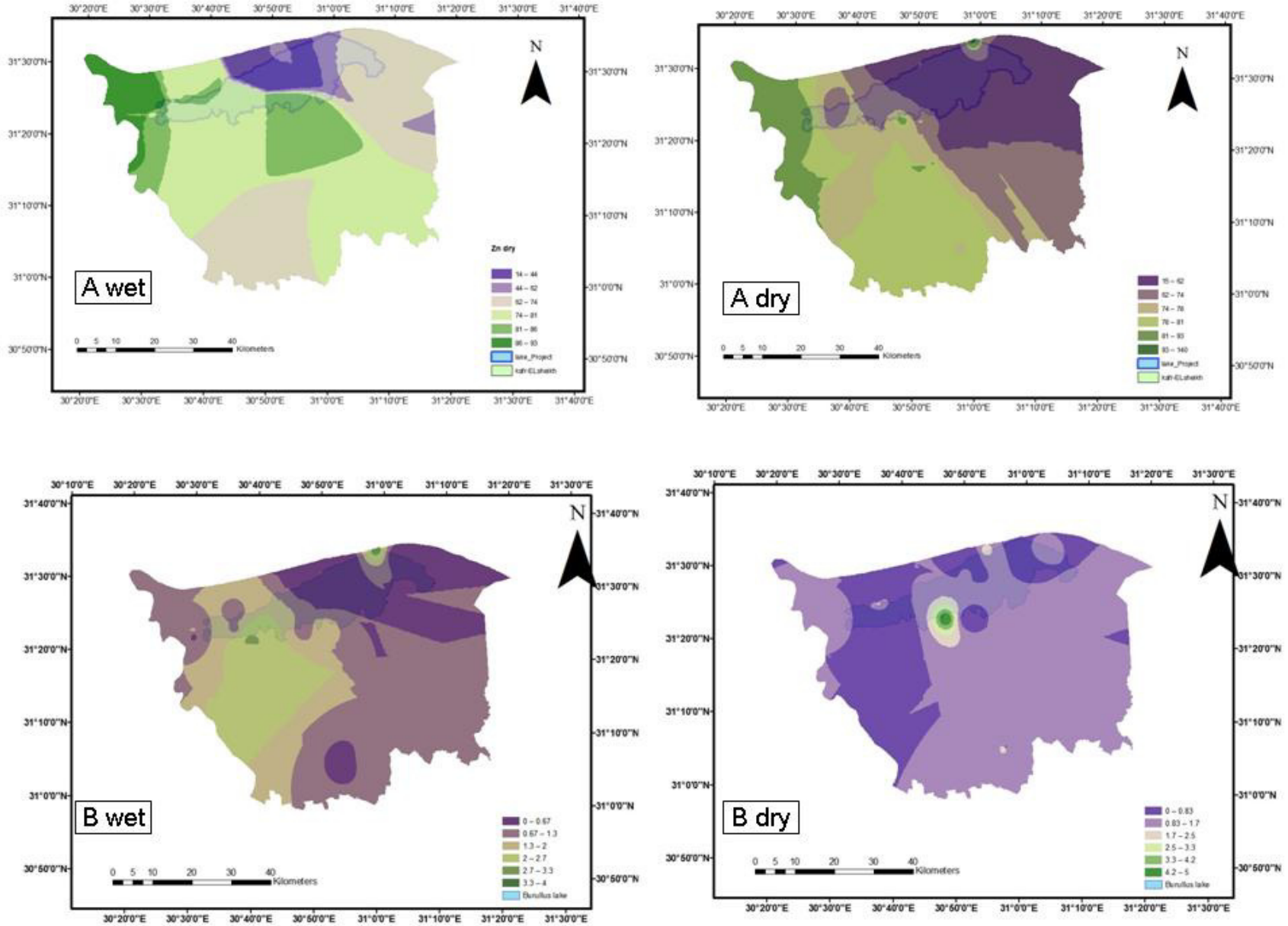


Figure 6. Spatial distribution of Zn in the studied wetlands A) Total and B) AB-DTPA under wet and dry conditions

Figure 5. As indicated in this figure, total Pb concentrations exhibited clear differences among the three studied locations. In contrast with other elements, the highest concentrations of total Pb were found toward the East and South sections in the study area; while the lowest concentrations were observed in the West. The highest level of Pb may be attributed to mixing irrigation water with industrial and agricultural discharge, mixture. As well as the dust which holds a huge amount of lead from the combustion of petrol in automobile cars might be another source of Pb (Saeed and Shaker, 2008).

The geo-distribution map in Figure 5 also indicated high concentrations of AB-DTPA extractable Pb were predominantly in the North under drying condition and in the West under wetting conditions. The geo-spatial distribution of total Zn in the three studied locations is shown in Figure 6. The results indicated that the highest concentrations of Zn was more concentrated in West section; while the lowest concentrations were observed in the East and Southeast sections under wetting conditions and in the North under drying conditions. Saeed and Shaker (2008) in their study on Northern Lake in Egypt attributed the high concentration of Zn likely to considerable amounts of zinc leached from protection plates of boats containing the active zinc. The geo-distribution map in Figure 5; also indicated high concentrations of AB-DTPA extractable Zn were predominantly in the East section under wetting conditions and in the central section under drying conditions; while the lowest concentrations were observed in the East sections.

Impact of wetting and drying conditions on mobilization of Pb and Zn

The mean values of total Pb were 5.9, 1.4 and 10.1 mg kg⁻¹ in the RS, FFS, and BLS, respectively under wetting conditions, while these values under drying conditions were 5.8, 2.7 and 8.5 mg kg⁻¹ in the RS, FFS, and BLS, respectively. The variations between total Pb under wetting and drying conditions in the studied wetlands were non-significant.

The mean values of AB-DTPA extractable Pb were 1.23, 1.50 and 1.05 mg kg⁻¹ in the RS, FFS, and BLS, respectively under wetting conditions, while these values under drying conditions were 1.24, 0.71, and 1.39 mg kg⁻¹ in the RS, FFS, and BLS, respectively. Therefore, mobilization of Pb differed significantly under wetting and drying conditions. The mean values of total Zn were 86.6, 80.2 and 54.4 mg kg⁻¹ in the RS, FFS, and BLS, respectively under wetting conditions, while these values under drying conditions were 80.4, 76.3, and 48.6 mg kg⁻¹ in the RS, FFS, and BLS, respectively. The variations between total Zn under wetting and drying conditions in the studied wetlands were non-significant. The mean values of AB-DTPA extractable Zn were 0.88, 2.22, and

0.66 mg kg⁻¹ in the RS, FFS, and BLS, respectively under wetting conditions, while these values under drying conditions were 1.10, 0.94 and 0.86 mg kg⁻¹ in the RS, FFS, and BLS, respectively. Therefore, mobilization of Zn differed significantly under wetting and drying conditions.

Considering the difference between the studied systems as indicated from Table (3); there were insignificant differences in total Pb concentrations under wetting and drying conditions between the studied systems, while there were significant differences in AB-DTPA Pb concentrations under wetting conditions. On the other hand, the differences between the studied systems were significant in total Zn concentrations under wetting conditions, while there were significant differences in AB-DTPA Cu concentrations under both of wetting and drying conditions.

The above-mentioned results indicated that mobilization of Pb and Zn showed an inconsistent trend under drying and wetting conditions in the studied wetland soils and sediments. Mobilization of Pb and Zn increased significantly under wetting conditions compared to drying conditions in the FFS. The opposite behavior was recorded in the BLS and RS, but the differences between the dry and wet conditions were non-significant (Table 2).

Un similar to other ions like As, Cr, Cu, Fe, Mn ions; Pb and Zn ions are rarely reduced or oxidized; thus, changes of the valence state of Pb and Zn as a consequence of E_H changes have not been observed in natural sediments and soils (Du Laing et al., 2009c; Frohne et al., 2011; Frohne et al., 2014; Kabata-Pendias 2011; Menzie et al. 2008; Rinklebe and Shaheen, 2014). Under our experimental conditions, we expect Pb²⁺ and Zn²⁺ ions to occur in the Burullus Lake sediments and rice soils under a wide range wetting and drying conditions as shown in Table 2 and in the E_H-pH diagrams (Takeno, 2005). In addition, the relatively decrease of Pb and Zn mobilization under wetting conditions as compared to drying conditions in the in the Burullus Lake sediments and rice soils in our experiment might be caused to a certain extent by sulfide precipitation, as also found by other authors (Du Laing et al., 2009a,b; Frohne et al., 2011; 2014). Increasing the mobilization of Pb and Zn under wetting conditions compared to drying conditions in the fish farm sediments might be due to the absorption of Pb to Fe(hydr) oxides in these sediments. Therefore, when the oxides are reductively dissolved, associated Pb and Zn will be released. Under oxidized conditions Fe- and Mn-oxides precipitate, and Pb and Zn is sequestered. The Fe/Mn oxide-bound Pb and Zn would be released during reductive dissolution of Fe/Mn oxides in reducing conditions (Guo et al., 2014). Therefore, reductive dissolution of Fe/Mn oxides might be the major cause for Pb and Zn mobilization in the moderately reducing conditions in the fish farm sediments, which is the most accepted mechanism for high Pb and Zn mobilization under wetting conditions in these sediments

(Frohne et al., 2011; Rupp et al., 2010; Shaheen et al., 2014b). Those findings suggest that the chemistry of both Fe and Mn might be important for the mobilization of soluble Zn in the fish farms sediments. De Jonge et al. (2012) reported that Zn-(Fe-Mn) complexes have high stability constants. Therefore, we suggest that Pb-Zn-(Fe-Mn) complexes have higher stability constants in the fish farms sediments compared to the rice soils and lake sediments.

Although Pb and Zn was released during reductive dissolution of Fe/Mn oxides, correlations between dissolved Pb, Zn on one hand and Fe and Mn on the other hand was weak and non-significant (Table 4). Three plausible reasons would be used to explain the weak correlations. One is that both reduced Mn and Fe would be reabsorbed onto residual Fe oxides (Guo et al., 2013, 2014; Stüben et al., 2003), due to strong adsorption of Fe(II) on the surface of Fe oxyhydroxide/oxides (Handler et al., 2009). The second one is that Fe(II) was co-precipitated together with S^{2-} in soil solution being oversaturated with respect to the relatively high S in our soils (Guo et al., 2014).

The changes in E_H/pH were found to be important factors controlling the mobilization of Pb and Zn in the fish farms sediments compared to the rice soils and lake sediments. The combined effects of pH and E_H on the mobilization of Pb and Zn are complex and highly metal-specific. The solubility of metal that can occur as free hydrated cations generally increases with decreasing pH. In this respect, DeLaune and Seo (2011) reported that low pH and E_H in sediment-water systems tend to favor the formation of soluble species of Zn; whereas in oxidized, nonacidic systems, slightly soluble or insoluble forms tend to be predominant.

CONCLUSION

The impact of wetting and drying conditions on the spatial variability of total and mobilization of Cu, Fe, Mn, Pb, and Zn in three different wetland ecosystems i.e., rice paddy soils, fish farms sediments, and Burullus Lake sediments were investigated. The motivation of our study was that the achieved results might contribute for a better understanding of the geo-spatial distribution of the metal concentrations in the different wetlands. Additionally, they might be an aid to answer both scientific and practical questions regarding the transfer of toxic metals into groundwater, rice plants, aqua plants, and fish. The toxic conditions in the dry soils and sediments increased the mobilization of Cu, while the reducing conditions in the wet soils and sediments increased the mobilization of Fe, Mn, Pb, and Zn. Total metal concentrations in the rice soils were higher than the fish farm and lake sediments. These findings suggest that a release of Fe, Mn, Pb, and Zn in temporally flooded rice soils should be considered due to increased mobility and the potential environmental

risks including food security in using metal-enriched soils for flooded agricultural systems. Thus, soils with a high frequency of flooding, high total metal content, and Fe-Mn oxides were assumed to be a hot spot of transformation due to frequent reducing conditions where the highest dissolved metal concentrations can be expected. In conclusion, the development of adequate remediation approaches of those contaminated sites leading to reduce the release of metals under reducing conditions in floodplain ecosystems should be a challenge for the near future aiming to minimize the potential risk to humans and to the environment. Additionally, in future, detailed research related to the metal speciation should improve our knowledge concerning the geochemical behavior of these elements in wetland soils and sediments.

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