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Environmental chemical study on the marsh of Fatimid cemetery at Aswan City, Egypt

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Abstract: Environmental chemical study were carried out on the Fatimid cemetery marsh at Aswan City (24°1'N and 32°9'E), Egypt. Marsh contents (water, soil, sediment, metal and nonmetal-bearing salts, and emergent weed) were analysed to know the source of marsh water, speciation of the different elements between the marsh contents, and the toleration of emergent weed (*Phragmites australis*) for different metals and their bioaccumulation coefficients. Thus, metals (Ca, Mg, Na, K, Ni, Fe, Mn, Cu, Zn, Cd and Pb) and nonmetals (CO_3^{2-} , HCO_3^- , Cl^- , SO_4^{2-} , PO_4^{3-} , NO_3^- , SiO_2 , organic matter and pH value) were determined in the samples. According to the chemical analysis, and applying the base exchange equation (water type) and calculate the hydrochemical parameters for marsh water samples, we can indicate that the marsh water is ground water with Na- SO_4 type and deep meteoric genesis. Topsoil of marsh dry land characterized by CaCl as dominant salt, while NaCl is a dominant salt in subsoil. The elevated pH values of marsh contents minimized the metal solubilities in different samples. *Phragmites australis* showed a strong ability to accumulate Mn and Fe in the aerial part in opposite to Co, Ni and Cd.

Keywords: marsh; water; soil; sediment; emergent; weed; Egypt

Introduction

Aswan governorate, Egypt, is famous for by monuments (Ancient, Coptic and Islamic). The foundation are of the first importance and care should be taken to see that they are consolidated and protected as far as possible from the infiltration of water. Water is a major cause of damage, not only to the foundations, but to the superstructure as well. All stones suffer slow deterioration on continued exposure whether it be to capillary moisture from the ground or to occasional heavy rainstorms. Water dissolves soluble matter from stones and by collection in cracks breaks them up. When present in quantity in the ground, soluble salts cause more damage to a monument than perhaps any other natural agency. Ground water almost always contains salts in solution or in suspension. Examples of this are sodium chloride (near the sea), sodium carbonate and sodium sulphate (gypsum) and many other constituents of soil rock which may have been transported from afar by floods. During the dry seasons the salty water gradually moves to the outer layers of wells and structures, evaporates and finally leaves saline deposits (efflorescences) on or near the surface (UNESCO, 1979). Elevated pH value occur in the water whose chemistry is dominated by minerals, most of which, are salts of a strong base and weak acids. The mineral carbonate and aluminosilicate and aluminosilicate minerals tend to increase the pH to value of 9 to 10 (Langmuir, 1997). The divalent metal carbonates typically occur as a solid solution and so contain trace to major amounts of one or more secondary metal cations (Reeder, 1983). Analysis of total element concentration in sediment can quantify the degree of trace element enrichment. Total element content does not provide information on transformation and mobilization of trace elements. Speciation studies can: (1) provide an insight into element distribution patterns; (2) identify metal bioavailability and toxicity in ecosystems; and (3) explain transformation and mobility of metal species (Guo, 1997). Surface of clays, organic matter, and iron oxides in sediment will absorb or desorb heavy elements when the ionic composition or Eh-pH changes (Keller, 1994).

The availability of trace metals for plant metabolism is related to their chemical forms in superficial and pore water, and to their availability in particulate matter. For this reason, material availability in both water and sediment is considered (Guilizzoni, 1991). Marsh of the Fatimid cemetery is situated to the south from the Aswan City (in front of Nubian Museum) represents a damage for the monuments at this region. The source of marsh water is unknown (ground water or drainage). In the present study the content and the level of metals, nonmetals in the water, sediment, soil and plant samples of marsh and the

surrounding area have been characterized to know the source of marsh water, interrelationship between the different elements in marsh content, and ability of the emergent weed growing in this region to accumulate the metals in aerial parts.

1 Material and methods

1.1 Study area

Marsh of the Fatimid cemetery is located at south Aswan City (24°1'N and 32°9'E), Egypt, in front of Nubian Museum (1 km south of the city center). It has a surface area of 0.1 km² (less than 0.5m deep), whereas the most area full with water (its source is unknown) as a result of land ozone and covered with emergent weed (*Phragmites australis*). The level of marsh water is decrease at summer months (temperature of Aswan > 45 °C) and leaves a part of dry land with salty topsoil.

1.2 Samples collection

At July 1999, water, sediment, and emergent weed samples were collected from different sites of the marsh (5 samples for each kind). In addition, topsoil, subsoil, metal (nonmetal-bearing salt, and emergent weed samples were collected from the dry land of the marsh. To know the source of the element in these samples, soil, emergent weed samples were collected from the surrounding highland of marsh (control samples), which it has a same soil structure. To detection of marsh water source, Nile River water, and wastewater (drainage) samples were collected at five sites in Aswan City.

Water samples were collected in 1L polyethylene sample bottle and filtered immediately using 0.45 µm filter paper. Portion from these samples were acidified to pH 2 for trace element analyses. Sediment samples were collected by means of a spring-loaded Ekman dredge sediment sampler made of stainless steel. Soil samples were collected from topsoil, subsoil of the dry land of marsh and the surrounding highland (control samples). Collected sediment and soil samples left to dry in air, then heated in an electrical oven at 105 °C till constant weight and then powdered using an agate mortar. Metal and nonmetal bearing salt samples (resulting from removing or scavenging dissolved components from aqueous phase) were collected from the surface of marsh dry land and then dried at 105 °C till constant weight.

The foliage part of *Phragmites australis* weed samples were collected from the same sites of sediment and soil samples and then washed several times using tap and bidistilled water. The weed samples were dried for 48h at 80 °C and then powdered in an agate mortar. The powdered samples of sediment, soil, metal and nonmetal bearing salt, and weed were kept in polyethylene bottles for analysis.

All chemical were purchased from BDH, Sigma, Aldrich, Redel de Haen, and E. Merck (A.R., 99.9 %). The various parameters for water and salt samples were determined using standard procedures (APHA, 1992). The soil and sediment samples were determined according to A textbook of soil analysis (Baruch, 1997), in addition, the weed samples were determined using chemical analysis of ecological material (Allen, 1989). The pH (pH meter, orion research, Model SA520, U.S.A), the conductivity (conductivity meter, HANNA Instruments, HI 8033, Italy) were measured *in situ* for water samples and in laboratory for soil, sediment and salt samples according to standard methods. 100g of each soil and sediment sample were extracted by 500 ml of bidistilled water, by shaking for 30 min. The solution was filtered off through Whatman No.42 filter paper and then used for analysis (soluble water salts) 1g of each metal and nonmetal bearing salt sample was dissolved in 250 ml bidistilled water and then used after its filtration for the analysis. The CO₃²⁻, HCO₃⁻ (titrimetrically), Cl⁻ (Mohr's method), SO₄²⁻ (turbidimetry), PO₄³⁻ (molybdenum blue method), SiO₂ (molybdosilicate method), NO₂⁻ (modified Griess-Ilosvay method), NO₃⁻ (chomotropic acid method), Ca, Mg, and TH (complexometric titration) were determined in water samples, as well as in soluble water salts of soil, sediment, and metal and nonmetal bearing salt samples. TDS in water samples and total organic matter for all samples were also determined

according to standard methods (APHA, 1992; Baruah, 1997).

Cd, Co, Cu, Fe, K, Mn, Na, Ni, Pb and Zn were determined in water, soluble water salt, and completely digested (conc. HNO_3 -HCl-HF acids) samples (weed, sediment, soil and USGS-GZ geological standards) using a Sp 1900 Pye Unicam recording flame atomic absorption spectrophotometer at their respective wavelengths with hollow cathode lamps (air-acetylene burner was used). The precision of the measurements was checked taking three replicates from sample and including a blank in each batch.

2 Results and discussion

Chemical composition of the marsh water, Nile River water and wastewater samples (mean of five samples) was recorded in Table 1.

The accuracy of analyses (Table 1) were obtained from the ion-balance error (Matthess, 1982) according to the following equation:

$$e = \frac{(rc - ra)}{(rc + ra)} \times 1000,$$

where: rc = cation sum as meq/L, ra = anion sum as meq/L and e = error percent. Applying this equation on the present analyses indicate that the e values (ranged from 0.13% to 3.31%) less than permissible limit (5%). The result means showed that the marsh water is alkaline ($\text{pH} = 8.12$) with high ionic content (conductivity = 10000 $\mu\text{S}/\text{cm}$). The ionic composition of the marsh water is dominated by chloride, sulphate, bicarbonate, sodium, calcium, and magnesium. The marsh water is poor with nitrite (0.013 mg/L), nitrate (0.2 mg/L) and it has relatively low amount of phosphate (0.34 mg/L). The ionic composition of the Nile River is dominated by bicarbonate, sulphate, chloride, calcium, sodium and magnesium, respectively. From the other side, the wastewater samples characterized by the following ionic dominance order: $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{PO}_4^{3-}$: $\text{Na} > \text{Ca} > \text{Mg}$. The wastewater samples were distinguished for the other samples (river and marsh waters) with high concentrations of organic matter (36.4 mg/L), phosphate (7.64 mg/L), and nitrate

Table 1 Chemical composition (mg/L) of the water samples* (marsh, river and waste) at Aswan City, Egypt

Parameters	Marsh water	Samples Nile water	Wastewater
Cond., $\mu\text{S}/\text{cm}$	10000	260	475
pH	8.12	7.8	7.25
HCO_3^- , as CaCO_3	731.3	128	280
CO_3^{2-} , as CaCO_3	0.0	0.0	0.0
Cl^-	1935.5	8.3	88.29
SO_4^{2-}	1000	11.2	33.8
PO_4^{3-}	0.34	0.044	7.64
NO_2^-	0.013	0.009	0.05
NO_3^-	0.2	0.15	3.5
SiO_2	4.5	6.6	9.4
Na	1495	11	98
K	24	5	13
Ca	200.4	30.46	42.6
Mg	145.9	7.8	14.59
Co	0.02	0.003	0.02
Ni	0.03	0.002	0.01
Fe	0.24	0.03	0.39
Mn	0.13	0.02	0.06
Cu	0.05	0.003	0.02
Zn	0.09	0.01	0.15
Cd	0.04	0.001	0.052
Pb	0.4	0.007	0.05
DOM**	10	1.2	36.4
TDS	5820	132	300
Error percent, %	0.13	3.31	1.32

Notes: * mean of five samples; ** dissolved organic matter

(3.5 mg/L), resulting from the sanitary discharge, sewage from domestic uses (Soltan, 1995). The low concentration of nitrite (0.013 mg/L), nitrate (0.2 mg/L) and phosphate (0.34 mg/L) in marsh water, in opposition to suppose the marsh water resulting from wastewater source. To know the source of marsh water, type of water samples (Nile water, wastewater and marsh water) were distinguished according to base exchange equation (Matthess, 1982). Applying this equation on the present analysis (Table 2) indicating that the type of marsh water (Na-SO_4 water) differ the type of wastewater (Na-HCO_3 water) and Nile River water (Na-HCO_3 water). Also, based on total dissolved solids (TDS), the class of marsh water is brackish water, while river water and wastewater are fresh waters (Table 2). Similarity of the water types

between wastewater and Nile River water indicate that the Nile River water is the main source for different uses at Aswan City. From the ionic dominance orders for different water samples, the dominance salts for marsh water, river water and wastewater are NaCl, $\text{Ca}(\text{HCO}_3)_2$ and NaHCO_3 , respectively (Table 2). The presence of Na instead of Ca as a main cation in wastewater resulting from the domestic discharge which it is rich with Na. The above differences between the marsh water quality and the other samples, increase the probability of ground water responsibility for the marsh seepy. The hydrochemical parameters $r\text{K}/r\text{Cl}$, $r\text{Na}/r\text{Cl}$, $r\text{Mg}/r\text{Cl}$, $r\text{Ca}/r\text{Cl}$ and $r\text{SO}_4/r\text{Cl}$ (where r = equivalent per million "epm") in the marsh water are calculated to define the genesis of ground water.

The standard values for sea water (for hydrochemical parameter, epm) are 0.0181, 0.8537, 0.1986, 0.0385 and 0.103, respectively. The calculated hydrochemical parameter for the marsh water were found to be greater than the standard values of normal sea water. This is an indication of the meteoric genesis of ground water in these area, this is also indicated that the leaching processes by meteoric water percolation to rocks are mainly responsible for the hydrogeochemical formation of this water. The meteoric water percolation according to the following relation:

$$\frac{(\text{K}^+ + \text{Na}^+) - \text{Cl}^-}{\text{SO}_4^{2-}} < 1, \quad (\text{deep meteoric})$$

where, the concentrations are in equivalent per million(epm).

Table 2 Classification of water samples(marsh, river and waste) according to different criteria

Criteria samples	TDS	Base exchange		Hypothetical salt combination		
	mg/L	Class	r^* , meq/L	Type	Ionic dominance order	Dominance salt
Marsh water	5820	Brackish water	0.52	$\text{Na} - \text{SO}_4$	$\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} : \text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^-$	NaCl
River water	152	Fresh water	1.08	$\text{Na} - \text{HCO}_3$	$\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} : \text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^-$	$\text{Ca}(\text{HCO}_3)_2$
Wastewater	300	Fresh water	2.58	$\text{Na} - \text{HCO}_3$	$\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} : \text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$	NaHCO_3

Notes: $r^* = \frac{\text{Na}^+ - \text{Cl}^-}{\text{SO}_4^{2-}}$ meq/L., where, $r > 1$ (Na- HCO_3 type), $r < 1$ (Na- SO_4 type)

3 Characterization of the highland surrounding the Fatimid cemetery marsh

The marsh surrounding by highland which consists of separate blocks from felsic rocks (rose granite) and fine sandy soil covering by little groups of emergent weeds (*Phragmites australis*). Highland soil and weed are considered as control samples because they for from the effect of marsh. The highland soil (Table 3) characterize by alkaline pH(8.9) and relatively large quantity of ions (conductivity = 5020 $\mu\text{S}/\text{cm}$) and have ionic (soluble-water salts) dominance order of $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} : \text{HCO}_3^- > \text{Cl}^- > \text{NO}_3^- > \text{CO}_3^{2-}$. The obvious low phosphate (2 $\mu\text{g}/\text{g}$) contents due to the relative immobility of phosphorus in soil (APHA, 1992). Relative low solubility for metals (conc. of metals in soluble-water salts/its conc. in complete attack system) in highland soil (Table 6) due to the composition of soil (fine sandy soil) minerals. Silicate and aluminosilicate rocks and their minerals are generally either less soluble or their rates of dissolution are slower than dissolution rates of carbonates, gypsum, or halite (Langmuir, 1997). On the other hand, the low contents of organic matter (40 $\mu\text{g}/\text{g}$) in the highland soil leads to decrease the soluble trace metals. Organic matter generally interacts strongly with trace metals, probably through formation of chelate type complex. Thus complexation by dissolved organic matter can leads to unexpectedly high concentrations of metals in solution (Drever, 1997). The emergent weeds growing in the soil of highland (control weed) were exhibited moderate concentration (Table 4) of the metals related to weeds growing in the marsh water and its dry land. The weeds of highland accumulate high quantites of metals than weeds growing in the dry land, whereas the soluble metals in dry land higher than their concentrations in the

highland soils. This fact correlative with the osmosis. The high salinity of dry land minimize the absorption of soluble metals and nonmetals by weed growing at this area (Table 4).

4 Distribution of the elements in the marsh ecosystem

The ecosystem of marsh consists of water, sediment, emergent weed, topsoil and subsoil of dry land, and metal and nonmetal-bearing salts. Marsh water characterize by high concentration of dissolved soils (5820 mg/L) resulting from the presence of large amounts of Na^+ (1945 mg/L), Cl^- (1935 mg/L), sulphate (1000 mg/L), and bicarbonate (731.3 mg/L). In addition, considerable amount of Ca^{2+} (200 mg/L) and Mg^{2+} (145.9 mg/L) were associated in the highness of dissolved solids (Table 1). The water of marsh may be draining sandstone according to its composition, in addition, the lithologic composition of Aswan governorate is composed mainly from Nubian sandstone (Ahmed, 1997). Sandstone and, particularly shales are more complex. Shales commonly contain pyrite, which contributes sulphate to solution after oxidation, and calcite, which contributes

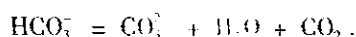
Table 3 Concentration of major elements (soluble water salts) in soil, sediment, and metal and nonmetal-bearing salt samples in marsh and surrounding area (control soil), Aswan, Egypt

Parameters *	Samples				
	Marsh samples				Highland samples
	Topsoil	Subsoil	Sediment	Salt	Control soil
Cond., $\mu\text{S}/\text{cm}$	174700	173200	6880	595000	5020
pH	8.2	8.27	9.73	9.1	8.9
CO_3^{2-} as CaCO_3	0.0	0.0	0.39	980	480
HCO_3^- as CaCO_3	3900	2930	290	2930	1460
Cl^-	33370	53390	1130	133500	870
SO_4^{2-}	6300	900	2300	94500	300
PO_4^{3-}	18	26	6	79	2
NO_2^-	1	2	1	18	1
NO_3^-	7270	7270	18	6580	53
SiO_2	160	10	70	0.0	45
Ca	29650	10020	160	24000	400
Mg	1950	1220	70	4860	100
Na	7500	1540	440	48400	700
K	1600	480	70	1200	200
Dissolved organic matter	560	160	80	1600	40

Note: * Concentration of elements: $\mu\text{g}/\text{g}$

calcium. Water draining shales also often contain chloride and sodium. These are through to originate from sea. Water trapped in the shale at the time of deposition, but the form in which these ions are stored in shales are highly variable in composition. They usually have sulphate or chloride as major anions, and lower silicate, in addition, the TDS values are highly variable (Drever, 1997). Also, the high ionic contents in the marsh water due to concentration of these contents as a result of the evaporation by the sunlight (temperature of Aswan City $> 45^\circ\text{C}$ during the summer season). In spite of the evaporation effect, relative decrease of K^+ (24 mg/L), NO_2^- (0.013 mg/L), NO_3^- (0.2 mg/L), PO_4^{3-} (0.034 mg/L), and organic matter (10 mg/L) contents in comparison with other components. This due to the geological composition of the sandstone rock, which is poor with these contents. Also, the weeds growing in this marsh leads to consumption an amount of macronutrients (N, P, K) which they essential to their life. Dissolved trace metals in marsh water exhibited relatively low concentrations (Table 1) in comparison with soluble concentrations (soluble water salts) in all investigated soil and sediment samples (Table 3). This explainable by adsorption phenomenon and effect of pH. The high concentrations of insoluble iron (ranged from 5737 to 6475 $\mu\text{g}/\text{g}$) and manganese (in the range 240 – 287.5 $\mu\text{g}/\text{g}$) at the marsh water ecosystem (Table 5) represents a solid phase for trace metals adsorption. Adsorption occurs when a dissolved ion or molecule becomes attached to the surface of a preexisting solid substrate (Drever, 1997). Hydrous manganese and iron oxides have extremely high adsorption capacity and high adsorption affinities for heavy metals (Jeme, 1997). Iron and manganese oxides are used as scavengers in wastewater treatment and may be very important in retarding the migration of pollutants in the subsurface (McKnight, 1990). Also, at high pH values (pH for sediment, 9.37; water, 8.12; topsoil, 8.2; metal and nonmetal-bearing salts,

9.1), metals are strongly adsorbed (McKnight, 1990). Elevated pH(9.37) value was measured in the marsh sediment resulting from the precipitation of calcite. Carbonate species are removed from solution over the entire the concentration range. The main removal process is precipitation of calcium carbonate and magnesium carbonate or silicate. During the intermediate stages, HCO_3^- is converted to CO_3^{2-} in response to rising pH, and CO_2 is lost as follows:



The soluble water salts of sediment (Table 3) exhibited considerable amounts of carbonate (390 $\mu\text{g/g}$) less than sulphate (2300 $\mu\text{g/g}$), moderate amounts of calcium (160 $\mu\text{g/g}$) and little amounts of magnesium (70 $\mu\text{g/g}$). This due to precipitation of calcium and magnesium as calcite and dolomite. Depending upon the extent of evaporation and the amounts and composition of inflowing waters, the first precipitates are calcite (CaCO_3), and perhaps, dolomite ($\text{CaMg}(\text{CO}_3)_2$), which may be followed by gypsum (CaSO_4), then halite (NaCl), and finally more complex sulphate, carbonate and halide salts (Faure, 1991; Berner, 1987). Relative high concentrations of chloride (1130 $\mu\text{g/g}$) and sodium (440 $\mu\text{g/g}$), due to precipitation of these elements as salts from the marsh water as a result of their high concentrations (Cl^- , 1935.5 mg/L and

Na^+ , 1495 mg/L) and to the evaporation effect. Cl^- is not precipitated as a salt until very high salinities are reached (Jones, 1977). Nitrate (18 $\mu\text{g/g}$), nitrite (1 $\mu\text{g/g}$) and phosphate (6 $\mu\text{g/g}$) gave low concentrations in sediment (soluble water salts), this is due to the fact that these elements are consumed as macronutrient for microorganisms and plants growing at sediment of marsh. The soluble trace metals (Table 5) of marsh sediment were exhibited low percentage (0.11%—4%) related to the total concentration (Table 6) of these metals (complete attack with conc. acids of HF, HNO_3 and HCl) except Cd (34.5 %). Low solubilities of trace metals can be explained with the strong adsorption of these elements onto a solid phase at high pH, in addition, their solubilities at higher pH are limited (Soltan, 1999). The relative high solubilities of Cd (34.5%) may be resulting from the complexation by dissolved organic matter (80 $\mu\text{g/g}$), whereas organic matter generally interacts strong with trace metals, probably through formation of chelate type complex. This complexation by dissolved organic matter can leads to unexpectedly high concentrations of metals in solution (Drever, 1997). Also, Cd may be present as complexed from with Cl^- which present as a main anion in the marsh water (1935.5 mg/L). CdCl_2 has a high solubility than the CdCO_3 , CdS and $\text{Cd}(\text{OH})_2$ in water. A ligand is an anion or neutral molecule that can combine with a cation to form complex. This leads to a high concentration of the species that forms the complex in solution (Langmuir, 1997). Generally, the most total concentration (Table 5) in the marsh sediment exceeds than their concentrations in the control soil (highland) with the factor 1.5, approximately. Increase the total metal concentrations in the marsh sediment as a result of precipitation their salts as carbonate or their adsorption on the solid phase of the sediment.

Table 4 • Accumulation and bioaccumulation coefficient of metals in *Phragmites australis* (aerial parts) samples growing at different sites in marsh and surrounding area (mean of 5 samples)

Metals	Sites					
	Marsh		Dry land		Highland (control)	
	A	B	A	B	A	B
Na	995	2.26	258	0.21	400	0.57
K	948	13.54	500	1.04	925	1.93
Co	2	10	0.15	0.06	0.25	2.5
Ni	7.5	6.25	0.1	0.06	0.15	0.75
Fe	540	73	81	30	171.75	42
Mn	750	1153	100.5	47	178.75	275
Cu	32	71	18.5	46	20	133
Zn	79.5	83	20	25	33.5	60
Cd	7.25	7.8	1.5	0.96	0.25	12.5
Pb	30.5	18	7.75	2	10.5	10.5

Notes: A: accumulation, $\mu\text{g/g}$; B: bioaccumulation coefficient

Table 5 Concentration of trace metals (complete attack and soluble water salts) in soil, sediment, and metal and nonmetal-bearing salts at the marsh and surrounding area (mean of 5 samples)

Metals, $\mu\text{g/g}$	Samples									
	Marsh samples								Highland samples	
	Top soil		Subsoil		Sediment		Salts		Control soil	
	A	B	A	B	A	B	A	B	A	B
Co	2.5	12.5	1.05	15	0.2	3.3	1.8	18.75	0.1	3.75
Ni	3.5	25	1.5	25	1.2	30	1	6	0.2	25
Fe	3.15	6187.5	2.65	6462.5	7.35	6475	6.95	5737	4.05	5450
Mn	7.3	281.3	2.15	290	0.65	240	1.35	287.5	0.55	140
Cu	1	35	0.4	41.3	0.45	25	1.1	21.25	0.15	15
Zn	1.05	76.3	0.8	78.3	0.95	76.25	14.15	97.5	0.55	31.3
Cd	1.8	6.3	1.55	10	0.92	3.75	1.8	23.75	0.02	5
Pb	6.9	76.3	4	79.8	1.7	56.25	3.6	70	1	41.3

Note: A; concentration of metal (soluble water salts); B; concentration of metal (complete attack)

Topsoil of the dry land of marsh (in depth from 0—2 cm) characterize by blackish colour and very hygroscopic forming a separate scale for the subsoil. Very large quantities of ions (Table 3) were leached from the topsoil samples (cond. = 174000 $\mu\text{S}/\text{cm}$). The leachate was alkaline (pH: 8.2) and ionic dominance order of $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+ : \text{Cl}^- > \text{NO}_3^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. Subsoil of the dry land of marsh (in depth from 2—10 cm) characterized by brownish colour and relatively anhydrous. The ionic contents of the subsoil (Table 3) samples were very high (cond. = 173000 $\mu\text{S}/\text{cm}$), but less than the topsoil. On the other hand, slight increase of subsoil pH (8.27) than the topsoil. The subsoil leachate ionic dominance order of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ : \text{NO}_3^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. From the above results, we can indicate that the hydrous topsoil resulting from the CaCl_2 as dominance salt which characterize by its highly hygroscopic. The dominance salt of subsoil samples is NaCl . It is unhydrous in the pure form but little hydrous in the presence of impurities from magnesium salts (Issa, 1978). Highness of dissolved contents in topsoil than subsoil resulting from the high content of dissolved organic matter in the topsoil (560 $\mu\text{g/g}$) than subsoil (160 $\mu\text{g/g}$). Responsibility of the organic matter due to fulvic acid. Fulvic acid is present in all soils where it makes up roughly 25% to 75% of the total organic matter. Fulvic acid plays a major role in the transport and deposition of Fe, Al, and other metals in soils. The acid is produced by organic decay in top of the soils. A horizon-fulvic acid ligand can form soluble complexes with Fe^{3+} and Al^{3+} and other metals, which facilitates metal movement downward through the soil. Thus, as fulvic acids are destroyed by aerobic decay of other processes during downward percolation, the metals precipitate, typically in the soils B horizon (subsoil). Precipitation of Fe and Al (and also Mn) oxyhydroxides, in turn, leads to coprecipitation of trace metals such as Cu, Cd, Zn, Co, Ni, and Pb in the topsoil (Malcolm, 1985; Suarez, 1975). Obvious high concentrations of Ca^{2+} in topsoil (29650 $\mu\text{g/g}$) than subsoil (10020 $\mu\text{g/g}$) samples, can be interpretation that by the complexing of Ca^{2+} with high concentrations of HCO_3^- and SO_4^{2-} in topsoil. If sulphate and bicarbonate concentrate calcium concentration in equilibrium with calcite is increased ions are high enough so that significant amounts of complexes CaSO_4^0 and CaHCO_3^+ are formed, the total calcium concentration in equilibrium with calcite is increased, because:

$$\Sigma m\text{Ca} = m\text{Ca}^{2+} + m\text{CaHCO}_3^+ + m\text{CaSO}_4^0.$$

Where $\text{Ca} = K_{sp}/m\text{CO}_3^{2-}$ and is unchanged.

Carbonate, sulphate and fluoride complexes of metals are poorly adsorbed (Langmuir, 1997). Low concentration of soluble silicate in subsoil (10 $\mu\text{g/g}$) comparably with topsoil (160 $\mu\text{g/g}$) due to the precipitation of sepiolite ($\text{MgSi}_2\text{O}_6(\text{OH})_2$) during the metals movement downward through the soil. After only slight evaporation, calcite would start to precipitate. As evaporation proceeds, calcite would continue to precipitate until essentially all the calcium was removed from solution. The next mineral to precipitate

would be sepiolite. Precipitation of sepiolite would remove Mg^{2+} , SiO_2 and alkalinity (Jones, 1997). The above interpretation was indicated by the low concentrations of Mg^{2+} (1220 $\mu g/g$) and alkalinity HCO_3^- (2930 $\mu g/g$) in subsoil than the topsoil (1950 $\mu g/g$) and 3900 $\mu g/g$, respectively). Similar elevated concentration of NO_3^- (7270 $\mu g/g$) for topsoil and subsoil samples. The elevated concentration due to the effect of evaporation in concentrate the soluble nitrate in the soil samples (control soil contains 530 $\mu g/g$), but the similarity due to the high solubility of nitrate salts, whereas not leads to precipitate the nitrate salts in subsoil.

Metals and nonmetals-bearing salts of marsh resulting from the complete evaporation for marsh water at relatively high land of the marsh leaving the white crystalline salts at the surface of these sites. The soluble water salts have a highly concentrations (Table 3) of the anions and cations (cond. = 595000 $\mu s/cm$). Their ionic dominance order of $Na^+ > Ca^{2+} > Mg^{2+} > K^+ ; Cl^- > SO_4^{2-} > NO_3^- > HCO_3^-$ with elevated concentrations of organic matter (1600 $\mu g/g$). The soluble water salts characterized by high alkalinity pH (9.1) resulting initially from the presence of CO_3^{2-} ($CO_3^{2-} = 980 \mu g/g$ in soluble water salts) and HCO_3^- (2930 $\mu g/g$) as sodium salts ($Na^+ = 48400 \mu g/g$). Similarity of ionic dominance order (except NO_3^- instead HCO_3^- in the salts) for marsh water and soluble water salts (metal and nonmetal-bearing salts), indicated that the origin of metal and nonmetal-bearing salts are marsh water salts. Back dislodge of HCO_3^- order in the salts than its order in marsh water resulting from the precipitation of HCO_3^- and CO_3^{2-} from the marsh water during the evaporation process as a result of a small value of K_{sp} (K_{sp} for calcite = $10^{-8.48}$). Carbonate species are removed from solution over the entire concentration range (as a result of evaporation). Trace metals in soluble water form of metal and nonmetal-bearing salts (Table 5) exhibited low concentrations, this due to two main reasons; firstly, the presence of most these metals as carbonates; secondarily, the high alkalinity of soluble salts (pH = 9.1). The carbonates of divalent Fe, Mn, Cd, Co, and Pb are over 100 times less soluble (Glynn, 1990). High pH and high organic matter contents reduce the solubility and mobility of metals and the plant availability of most metals (Driel, 1988). High concentrations of trace metals resulting from complete attack on the solid salts indicate that the salts precipitated as carbonates or/and adsorbed on the solid phase. High soluble metal ratio (conc. of the metal in soluble water from/its concentration in complete attack form) was obtained (Table 6) in all samples for Co (5.3% – 20%), Cd (1.6% – 34.5%), Ni (4% – 10%), Pb (1.8% – 9%), this indicate that these metals present as complexes. Also, these metals interacts strongly with organic water, probally through formation of chelate type complex. Complexing of dissolved species that also occurs in a mineral tends to increase the solubility in the absence of aqueous complexing. This leads to a higher total concentration of the species that forms the complex in solutions saturated with respect to the mineral (Langmuir, 1997). For Co, Cd and Pb, the maximum soluble ratio is present in topsoil, this fact indicate the above interpretation, whereas the topsoil contains higher concentration of organic matter (560 $\mu g/g$) and ionic contents (conductivity = 174000 $\mu g/cm$) that other samples (except metal and nonmetal-bearing salts). In addition, the minimum soluble ratio was recorded for the above metals in control soil samples as a result of the low amounts of organic matter (40 $\mu g/g$) and ionic contents (conductivity = 5020 $\mu g/cm$) comparably with the other samples. Iron (0.041% – 0.120%) and manganese (0.27% – 2.6%) were exhibited low soluble ratios in all samples, this explains the presence of iron and manganese as oxyhydroxide which are used as scavenger in wastewater treatment, and may be very important in retarding the migration of pollutants in the subsurface (McKnight, 1990). In addition, the mobility is characteristically lowered for Mn and Fe under oxidizing conditions (Campbell, 1983).

5 Ability of *Phragmits australis* for metals accumulation

Emergent weeds (*Phragmites australis*) growing in different sites of marsh and surrounding area accumulate variable quantities of metals (Table 4) dependent on the soil characterization (soluble water salts). Generally, the emergent weed samples under study classified into three groups related to their metal contents. Firstly, the marsh weed characterized by high contents of metals with highly accumulation coefficient; secondly, the control weeds (highland weeds) were exhibited moderate bioaccumulation of metal; thirdly, the marsh dry land weeds showed a low contents of metals with low or no bioaccumulation coefficient. The presence

Table 6 Solubility percent of metals in different samples* (soil, sediment, and metal and nonmetal-bearing salts) at marsh and surrounding area (control soil)

Metals	Samples				
	Marsh samples				Highland samples
	Topsoil	Subsoil	Sediment	Salts	Control soil
Co	20	7	8.3	9.6	5.3
Ni	10	6	8	6.7	5.2
Fe	0.051	0.041	0.11	0.12	0.074
Mn	2.6	0.8	0.27	0.47	0.46
Cu	2.9	1	1.8	5.17	1
Zn	1.4	1.05	1.25	14.51	1.76
Cd	28.5	15.5	24.5	7.58	1.6
Pb	9	5.4	3.02	5.14	2.42

Note: * Mean of 5 samples

of metals as ions or natural molecules or as complexes in aqueous medium (marsh water) leads to increase the mobility of these metals and their bioavailability. When the concentration of a dissolved species is controlled or limited by the solubility of a mineral containing that species, the total concentration of the species will be higher in solutions in which it is complexed than in those in which it is not. The bioavailability of essential metals to plants is also a function of their metal speciation (Morel, 1993). Low metal contents in the marsh dry land due to the high salinity of the dry land soil (cond. for topsoil: 174700 $\mu\text{S/cm}$ and subsoil: 173200 $\mu\text{S/cm}$). At high substrate salinity growth depression may also originate from inhibited nutrient uptake, transport and utilization in the plants (Cramer, 1992). Increasing the salt concentrations and osmotic potential of the soil solution decreases water (rich in nutrient) availability to plants and can severely impair plant water relations (Schleiff, 1986). From the other side, high organic matter in the dry land soil (topsoil, 560 $\mu\text{g/g}$; subsoil, 160 $\mu\text{g/g}$) will diminish the absorbing of metals as a result of complex formation. Excretions of organic compounds by roots in terrestrial ecosystems are known. The absorbing surfaces of humic substances and clay particles will at least camouflage or neutralize their effect on metal speciation. Excretion of complexing agents to the surrounding water, will diminish the availability of metals to plants and thus reduce their toxicity (Butler, 1980). Low salinity (cond. = 5020 $\mu\text{S/cm}$) of control soil lead to moderate consumption of metal by weeds roots and their accumulation in the aerial parts. All weed samples showed a strong ability to accumulate Mn with bioaccumulation coefficient ranged from 47—1153. Weeds were also able to concentrate Cu, Zn and Fe in aerial parts with bioaccumulation coefficient reached up to 133, 83 and 73 respectively. The high concentration of Mn in aerial parts of weeds due to the Mn acts as cofactor, activating about 35 different enzymes (Burnell, 1988) and its particular role in photosynthesis (Kriedemann, 1985). The role of relation coefficient ranged from 0.06—6.25, 0.96—12.5, and 2—18, respectively.

6 Conclusion

Marsh water at Fatimid cemetery, Aswan City, Egypt resulting from the seepy of ground water at this low land. For protection the monuments must be taking all measures possible to lower the water-table. e. g., by introducing tube wells, shallow drains or land drain (as used by farmers). This involves making a careful survey for soil permeability in order to discover the most effective drainage areas. The alkaline pH of marsh ecosystem is diminish the metals solubilities, therefore, this factor minimize the side effect of toxic metals on water-table. The concentration of elements are very different for topsoil than subsoil as a result of the effect of organic matter content, difference of salt solubilities and complexes formation. The *Phragmites australis* exhibit high tolerance for Mn and Fe and it has ability to growth in wide range of

environments(normal and salty soils). The growth of emergent weeds in the marsh water leads to decrease the salinity according to its high bioaccumulation coefficients for metals.

Dedication: This work is dedicated to the memory of my Professor Dr. R. M. Awadallah(1943—1999). Professor Awadallah's live was dedicated to the science, his school member colleagues and social relationships.

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