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Speciation of Some of Heavy Metals in Some Waters of Egypt

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CALCULATIONS have been performed to predict the various chemical species of four heavy metals (Zn, Fe ,Ni,Cd) in Nile water, ground water, and sewage effluent water which are considered the main sources of irrigation waters in Egypt. The levels of (Zn, Fe, Ni, Cd) in both Nile water and ground water are below the critical levels reported for these metals in waters for irrigation use. Meanwhile, the sewage effluent water contains measurable quantities of Zn (0.70 ppm), Fe (1.05ppm) , Ni (0.40 ppm), and Cd (0.12 ppm). Among the tested metals, only Cd concentration , as shown, is higher than the permissible limit for irrigation waters .

The predicted speciation of the tested metals indicated that the free ion (M^{2+}) is the major part of Zn, Fe ,Ni, and Cd in Nile water . This species accounts 82%, 92%, 98%, and 90% of their totals, respectively. The same situation also exists in ground water. Meanwhile, in sewage effluent water , the results reveal that Ni and Cd are the only metals exist as the free form. Ni constituted nearly, 87 % of dissolved Ni presents as Ni^{2+} , while Cd had about 97 % of (Cd_t) in that form . The data showed that the majority of Zn and Fe in sewage effluent water are complexed with phosphate ions. Approximately, 92% of (Zn) in sewage effluent water exists as $Zn_3(PO_4)_2$. Oppositely, this species was insignificantly contributed in either Nile or ground waters. The results also showed that an appreciable fraction of Fe is present as $FeSO_4$ (AQ) .This species contributes more than 93% in sewage effluent water and 47% of (Fe_t) in the ground water . The present data also referred that, Ni in sewage effluent water was the only metal complexed with carbonate ligands . This form amounts about 12% of (N_t) as $NiCO_3$(AQ).

Keywords : Speciation, Nile water, Heavy metals, Water quality.

It is generally agreed that water is one of the world's most precious resources, particularly in semi-arid and arid areas, as is the case with Egypt. The provision of irrigation water is one of the most important factors for the expansion of agricultural production. FAO Irrigation Paper No.29 stated that the River Nile is Egypt's sole source of surface water . But, under the pressing need for increasing of agricultural production, they used low quality waters for irrigation (*e.g.*, groundwater or/and sewage effluent water). These waters often contain some of trace metals, which enter from a variety of sources . Some of trace metals (*e.g.* Zn, Co, Cu, Mo , Fe) are nutrients and act as enzyme activators. Others are highly toxic (*e.g.*, Cd, Pb, As). Some of the nutrient elements (*e.g.*,Zn,Cu) may be toxic at elevated concentrations (Cottenie *et al.*,1979; Aboulroos *et al.*,1991 and More & Gschwend ,1987). Therefore, these metals must be carefully monitored and tightly controlled.

Moreover, in order to assess the environmental impact of these metals in waters, it is necessary to examine the total concentrations . Furthermore, many authors have unequivocally that metal toxicity in aquatic system is controlled by free metal species and not the dissolved concentration (Mattigod and Page,1983; Verweij *et al.*,1992 and Cambell,1995). Also, the studies of Bell *et al.* (1991) ; Holm *et al.* (1995); Sauve *et al.* (1997) and Bipra (1997) demonstrated that the mobility and bioavailability of the trace metals can be more fully identified on the basis of speciation studies.

So, the objectives of the present study are to examine the concentrations of four trace metals (Zn, Fe ,Ni ,Cd) in water sources of Egypt (River Nile, ground water, and sewage effluent water) and to calculate the various chemical forms (speciation) of these metals using a geochemical speciation model.

Material and Methods

A-Water Sampling

Sample containers

Sample containers were made of polyethylene and washed with a non-ionic detergent and rinsed three times with distilled water.

Water samples

Three composite water sample were collected to examine the concentrations and speciation of four trace metals (Zn, Fe ,Ni ,Cd) .

1-Nile water sample : This sample was made by mixing a series of samples, with equal volume, collected from River Nile near Cairo Governorate . The sampling ran on June 2001, before flood event.

2-Groundwater sample : The composite ground water sample was made by combining a series of samples collected from wells beside Cairo-Alexandria desert road. All the tested wells were equipped with pumps and the samples obtained at the point of discharge. Before the collection ,the water allows to flow for several minutes until it has reached constant conductivity .

3- Sewage effluent water sample : This sample was made of mixing equal volumes of waters collected from sewer stations namely; Al Gabal El-Asfer, Abu Rawash and Helwan Stations.

All the bottles used for the study were rinsed several times with portions of sample before being filled.

Sample preservation

The collected samples were transferred to a refrigerator at about 4C°.

B-Chemical Analysis

Measurement of pH and conductivity

pH and conductivity values of the tested water samples were measured in separate portions of the sample.

Routine chemical analysis

The major cations and anions in the tested waters were determined according to Black (1965).

NO_3^- concentrations were measured using a standard autoanalyzer .

The concentrations of Fe ,Cu, Mn, Zn, Co, Cd, Pb, Ni ,B, and P were determined by Inductively Coupled Spectrometer Plasma (ICP), Plasma 400. The obtained results are listed in Table 1.

C- Data Treatment

The distribution of aqueous species was calculated using the geochemical speciation program MINTEQA2 ver 3.11 (Allison *et al.*,1991). The calculated data were listed in Table 2.

Results and Discussion

Values of concentrations of zinc in the tested waters are listed in Table 1. The present data reveal that the sewage effluent water had the highest level of Zn (0.70 ppm) ,followed in decreasing order by ground water (0.19 ppm)and finally

TABLE 1. Chemical composition of the tested waters caculated as pM = (-log ML $^{-1}$).

	Nile water		Well water		Sewage effluent water	
PH	7.15		7.82		7.03	
Ionic Strength	0.57		4.48		2.02	
Cations						
Na	2.97		1.77		1.98	
Ca	3.01		2.20		2.69	
Mg	3.08		2.30		2.79	
K	4.39		2.98		3.42	
Trace Metals						
Zn	6.73	(0.012 ppm)	5.53	(0.19ppm)	4.97	(0.7 ppm)
Cd	8.05	(0.001 ppm)	6.44	(0.04ppm)	5.97	(0.12ppm)
Pb	6.52		5.79		3.78	
Co	7.00		6.04		3.93	
Ni	7.76	(0.001 ppm)	5.62	(0.14ppm)	5.16	(0.4 ppm)
B	6.00		3.86		2.74	
Mn	6.39		5.85		4.34	
Fe	6.44	(0.02 ppm)	5.44	(0.20ppm)	4.72	(1.05 ppm)
Cr	6.30		5.49		3.58	
Cu	7.00		5.92		3.78	
Anions						
HCO3 (-1)	4.44		3.72		3.80	
Cl (-1)	4.49		3.23		3.77	
SO_4 (-2)	4.85		4.09		4.63	
NO_3 (-1)	4.53		4.40		3.02	
PO_4 (-3)	3.35		3.48		2.51	

by Nile water (0.012 (ppm). A glance in the levels of Zn in the tested waters showed that its concentrations were under the critical limit reported for Zn in irrigation waters , which set as 2.00 ppm (FAO,1976),(Table 1).

The various species of Zn in the tested waters calculated as percentages of their totals are listed in Table 2. The free ion species (Zn^{2+} (is the predominant form in ground water. It accounts (>95% of Zn_t) . The same situation also existed in Nile water whereas Zn^{2+} constitutes about 82% of total Zn (Zn_t) . The same results were also obtained by Tipping *et al.* (1998). They reported that the free aquo (Zn^{2+}) is the dominant species in three surface waters (riverine , estuarine, and marine surface waters).

Table 2 also showed that in sewage effluent water the free form of Zn do not contribute to the various species of Zn (5.6% of Zn_t). Their findings may be contributed to the positive relation between pH value and concentration of free form of a metal (M^{2+}) in solution. In the present study, the data of Table 1 show that the concentration of (H^+) ions in sewage effluent water is higher by one fold and six fold more than the concentration of that ion in Nile water and ground water , respectively. Lindsay (1979) referred to the association of level of Zn^{2+}

species with pH value . His results stated that as pH values increased, the free ions of Zn^{2+} increased. Moreover, El-Gendi (1998) mentioned that the presence of inorganic and organic ligands in sewage effluent water create web of reactions in the system resulting in decreasing the percentage of the free portion. Therefore, the presence of phosphate ligands with high level in sewage water (Table 1), causing the complexation of Zn with phosphate ions becomes the predominant species. This species amounts 91.6% of Zn_t as $Zn_3(PO_4)_2$ while the free portion is negligible (Tables 1 and 2).

Table 2 also showed that the complexation of Zn with carbonate ligands (HCO_3^- ,CO^{2-}) are relatively unimportant in the tested waters, even in the ground water where the concentration of carbonate ions (calculated as pM) is about 3.72 (Table 1). Alternately, Jensen *et al.* (1999) studied the speciation of heavy metals in polluted ground waters in Denmark. They concluded that Zn was present as carbonate complexes and free divalent Zn.

Fe concentrations in the tested waters are listed in Table 1 . The data showing concentrations in the tested waters are listed in Table 1 . The data showed that the highest value of Fe was recorded in sewage effluent water (1.05 ppm) , followed by ground water (0.2 ppm), while the Nile water had the lowest value (0.02 ppm) . These results refer that Fe concentrations in the waters are below the permissible limit for Fe in irrigation waters, which established as 20 ppm (FAO,1976).

The speciation of Fe in the tested waters is shown in Table 2. The data show that the majority of Fe form presents as free ions Fe^{2+} in Nile water (92% of Fe_t), followed by ground water (52%), while .in sewage water .this species was not important (Table 2). Table 2 also showed that the complexation of Fe with SO_4^{2-} ligands becomes significantly in both Nile and the ground waters . $FeSO_4$(AO) constitutes about 94% and 46% of Fe_t ,respectively.

Ni concentrations in the tested waters are listed in Table 1. The data showed that Ni concentrations in the waters followed the order: sewage water (0.40ppm) > ground water (0.14 ppm)> Nile water (0.001ppm). It is cleared from the present data that all the tested waters except sewage water sample , Ni level is under the acceptable limit which mentioned as 2.00ppm for irrigation water (FAO.1976).

The various Ni species in the tested waters are listed in Table 2. The data showed that an appreciable fraction of Ni is present as free aquo ion (Ni^{2+}) . The

TABLE 2 . Speciation of Zn, Fe, Cd, nd Ni in the tested waters (calculated as percentages of their sums).

Metal	Nile Water	Well water	Sewage effluent water
Zinc			
Zn(2+)	82.3 %	95.6 %	5.6 %
ZnHCO3(+1)	......	1.50 %	...
ZnCO3(AQ)	......	...	...
ZnHPO4	17.0 %	...	2.6 %
Zn3(PO4)2	...	...	91.6 %
Iron			
Fe(2+)	92.9 %	52.5 %	5.6 %
Fe3(PO4)2	...	...	...
FeH2PO4	6.90 %	...	...
FeSO4 (AQ)	...	46.9 %	93.5%
Cadmium			
Cd (2+)	98.7%	91.3 %	97.1 %
CdBr (+1)	...	...	...
CdHCO3 (+1)	...	1.50 %	...
CdCl (+1)	...	5.10 %	1.3%
CdCO3 (AQ)	...	1.50 %	...
Nickel			
Ni(2+)	90.7 %	66.7%	87.3 %
NiHCO3 (+1)	...	1.30 %	...
NiCO3 (AQ)	8.70 %	31.6 %	11.9 %
Ni3(PO4)2	...	...	...

highest value was obtained in Nile water (90% of Ni_t) , followed by sewage effluent water (87.3% of Ni_t) , while the ground water sample had the lowest level (66.7% of Ni_t) . Table 2 also refers that Ni also complexes with CO_3^{2-} ligands . NiCO3 species exists in all the tested waters . This species is ranged from 8% to 31% of Ni_t . The highest level was recorded in ground water sample, which had the highest level of carbonate concentration (Table 1). These results are in agreement with the findings of Tipping *et al.* (1999) who stated that complexation of Ni with carbonate ions (HCO^{3-}, CO_3^{2-}) were found in all waters. Also, Jensen *et al.* (1999) fractionated some of heavy metals in leachate polluted ground water . They concluded that a minor portion of Ni was found as free ion (not more than 10%). Meanwhile, the dominant fraction was presented complexes with carbonate ligands .

Cd concentrations in the tested waters are presented in Table 1. Cd content in sewage effluent water is above the permissible limit of FAO (1976),who said that 0.01 ppm for Cd is the maximum limit for irrigation waters.

The speciation of Cd in the tested waters is listed in Table 2. The data showed that the free species of Cd (Cd2+) is the prevalent form in all tested waters.This form accounts 98.7, 97.1%, and 91.3% of total dissolved Cd (Cd_t) , respectively.

The Table also showed that complexation of Cd with Cl^- ions occurred only in ground water sample . $CdCl^+$ species amounts 5% of Ni_t. These results may be attributed to the high concentration of Cl^- ions in that water (Table 1). The same observations were also obtained by Garcia and Page (1976) who predicted that Cd would be complexed with chloride ions especially in solution had high Cl^- concentration.

Conclusion

The calculations reported here show good figures for Zn,Fe ,and Ni in all waters except for Cd in sewage effluent water. Also, the four metals considered vary in the extent of their interactions with inorganic ligands presented in the waters and this leads to substantial difference in their species distribution. It worth to mention that in all waters the majority portions of the toxic metal species (Ni, Cd) exist as a free form (M^{2+}). Many authors have shown unequivocally that metal toxicity in aquatic system is controlled by the free species (Verweij *et al.*, 1992 and Campbell ,1995) . Therefore, a comprehensive protection policy is needed for sustainable use of waters of Egypt and for the preservation of human health.

References

Aboulroos , A.S., Holah,Sh.Sh., El- Kerbawy, I.M. , and Badawy, H.E. (1991) Fractionation of some heavy metals in soils irrigated with sewage effluent for different years . *Egypt . J. Soil Sci.* **31**(1), 43.

Allison, J.D., Brown, D.S. and Novo Gradac, K.J. (1991) MINTEQA2/PRODEFA2. a Geochemical Assessment Model for Environmental System : *Version 3.0 User's Manual.* U.S. Environmental Protection Agency . EPA/600/3-91/021.

Bell, P.F., James, B.R. and Chaney , R. L. (1991) Heavy metals extractability in long-term sewage sludge and salt - amended soils. *J. Environ. Qual.* **20** .481.

Bipra , G. (1997) Speciation of Cu,Cd annd Pb in coastal waters of Kandla- Porbander Shelf region, west coast of India . *Indian Journal of Marine Sciences* , **26**, 227 .

Black, C.A. (Ed.). (1965) " *Methods of Soil Analysis*", Part. (1) Am. Soc. of Agron. Madison, Wisconsin .

Campbell , P.G.C. (1995) Interactions between trace metals and aquatic organisms : a critique of the free-ion activity model. In : *Metal Speciation and Bioavailability* in *Aquatic System*, A.Tessier and D.R. Turner (Eds.) pp.45-102. , John Wiley and Sons, Chichester, UK.

Cottenie , A. ,Camerlynck, A.,Verloo , M. and Dtasese , A. (1979) Fractionation and determination of trace elements in plants. *Pure Appl. Chem.* **52** , 45 .

El-Gendi , S.A.M. (1998) Ionic forms and solid phases formation of some heavy metals in sewage effluent- treated soil. *J. Agric. Sci. Mansoura Univ.* **23** (12), 5737.

FAO (1976) Water quality for agriculture. *Irrigation and Drainage*, Paper 29, FAO, Rome, 97p.

Garcia - Miragaya , J. and Page , A.L. (1976) Influence of ionic strength and inorganic complex formation of the sorption of trace amounts of Cd by montmorillionite. *Soil Sci. Soc. Am. J.* **40**, 658.

Holm , E.P., Christensen , H.T , Tjell,C. and McGarth, P.S. (1995) Speciation of cadmium ahd zinc with application to soil solutions. *J. Environ. Qual.* **24**, 183 .

Jensen , L.D., Ledin, A. and Christensen , H.T. (1999) Speciation of heavy metals in Landfill-leachate polluted ground water . *Water Res.* **33** (11), 2642 .

Lindsay, L.W. (1979) " *Chemical Equilibria in Soil* " . John Wiley & Sons, New York.

Mattigod, S.V. and Page, A.L. (1983) *Applied Environmental Geochemistry* . Academic Press., London .

Morel, F.M.M. and Gschwend, P.M. (1987) The role of coiloids in the partitioning of solutes in natural Waters. In : W. Stumm (Ed.), *Aquatic Surface Chemistry* . Wiley , New York , pp. 405-422.

Pratt, R.F. (1972) *Quality Criteria for Trace Element in Rirrigation Waters.* Calif. Agric. Exp. Sta.

Sauve, S., McBride, M.B. and Hendershot, W.H. (1997) Speciation of lead in contaminated soils. *Environmental Pollution*, **98** (2), 149 .

Tipping , E., Lofts , S. and Lawlor , J. A. (1998) Modeling the chemical speciation of trace metals in the surface waters of Humber system. *The Science of the Total Environment* , **210**,63.

Verweij, W., Glazewski, R. and de Hann , H. (1992) Speciation of copper in relation to its bioavailability. *Chemical Speciation and Bioavailability*, **4**,43.

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دراسة الصور الكيماوية المختلفة لبعض الفلزات الدقيقة في الموارد المائية في مصر

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أجريت دراسة لتقييم بعض الموارد المائية المتاحة للرى فى مصر والتى تشمل على نهر النيل - مياه الآبار - وكذلك مياه الصرف الصحى من خلال دراسة التركيزات الكلية لأربعة معادن وهى (Zn,Fe, Ni ,Cd) وكذلك التعرف على أهم المفصولات الكيماوية لتلك المعادن .

أوضحت نتائج الدراسة أن التركيزات المقاسة للمعادن المختبرة كانت اقل من الحد الحرج لتلك المعادن والمسموح به للاستخدام في الرى وذلك بالنسبة لمياه النيل وكذلك لمياه الآبار المختبرة . أما مياه الصرف الصحى فأوضحت النتائج أنها تحتوى على كميات محسوسة من الزنك (٧,. جزء فى المليون) - النيكل (٤, .جزء فى المليون) - الكادميوم (١٢,. جزء فى المليون) . ولقد كان عنصر الكادميوم هو العنصر الوحيد المتواجد بتركيز أعلى من الحد المسموح به للاستخدام فى مياه الرى .

تمت دراسة الصور الكيماوية المختلفة للمعادن المختبرة في عينات المياه المختلفة . أوضحت النتائج أن الصورة الايونية النشطة (M^{2+}) هي الصورة الكيماوية السائدة لمعادن Zn, Fe, Ni,,Cd وذلك في مياه النيل حيث بلغت هذه الصورة ٨٢ ٪ ، ٩٢٪، ٩٨ ٪، ٩٠٪ من الكمية الكلية للصور الايونية لتلك المعادن على الترتيب . كذلك أوضحت الدراسة أن نفس الاتجاه كان سائدا لحد كبير في مياه الآبار ، حيث بلغت الصورة الايونية الحرة اكثر من٥٠ ٪ من مجموع

الصور الكلية لتلك المعادن (كمتوسط عام) . أما في مياه الصرف الصحي فنجد فقط أن Ni وكذلك Cd يتواجدان بكمية محسوسة مقدارها ٨٧٪، ٩٧٪ من مجموع الصور الايونية) على صورة ايونية حرة ، على الترتيب .

أوضحت النتائج أن تكوين معقدات الفوسفات مع المعادن المختبرة كان واضحا في مياه الصرف الصحي مع Zn حيث بلغت النسبة المئوية للصورة الايونية $Zn_3(PO_4)_2$ حوالى٩٢٪ من الكمية الكلية الذائبة للزنك . وعلى عكس ذلك نجد أن هذه الصورة الايونية غير معنوية سواء في مياه النيل أو المياه الجوفية .

كذلك تشير النتائج المتحصل عليها أن Fe يتواجد على الصورة الايونية $FeSO_4$ (AQ) في كل من مياه الصرف الصحي (أكبر من ٩٣٪ من الكمية الكلية للحديد الذائب) وكذلك في المياه الجوفية (حوالى ٤٧٪).

كذلك وجد أن Niفي مياه الصرف الصحي كان هو المعدن الوحيد الذى يرتبط مع الكربونات . وهذه الصورة $NiCO_3$ (AQ)تمثل ١٢٪ من الكمية الكلية للنيكل الذائب .