

## Speciation of Fe, Mn, Zn, Cu and Pb in the Inner-Shelf Sediments off Alexandria

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A chemical speciation study for the bottom sediments of the coastal belt off Alexandria has been conducted for iron, manganese, zinc, copper and lead. The purpose of the search is to demonstrate in which forms these metals are chemically associated, as well as, to differentiate between the residual metals (natural background) and non-residual ones (man-made sources of pollution). To achieve these objectives, twelve bottom samples were collected along the coastal water off

Table(1): Ranges and averages for different metal extracts(ppm)

Fraction	Exchangeable (EXCH)		Carbonate (CARB)		Easily reducible (EASR)		Organic matter (ORGS)		Residual (RESID)	
	range	aver.	range	aver.	range	aver.	range	aver.	range	aver.
Fe	0.07-22.2	12.97	0.09-37.72	24.65	16.29-33.05	25.24	15.20-36.95	25.24	997.59-1981.95	1482
Mn	N.D.-2.2	1.48	6.5-14.3	9.79	3.0-18.0	4.77	N.D.-4.05	1.85	85-166.3	125.58
Zn	1.0-2.2	1.79	4.90-21.1	9.05	N.D.-4.35	2.77	N.D.-4.35	2.87	25.83-93.73	48.83
Cu	N.D.-3.56	1.31	3.0-5.88	4.04	N.D.-2.2	0.43	N.D.-5.75	1.46	5.73-39.85	14.11
Pb	N.D.-7.52	2.69	6.25-22.5	11.82	N.D.-12.5	4.89	N.D.-7.58	1.34	27.29-65.0	48.5

\* Not Detected.

Alexandria city. Following the procedures described by Tessier et al. (1979) and Rapiñ and Forstner (1983), the suspensions of fine fraction sediments (0.250-0.125 mm) were sequentially fractionated to determine the levels of different metals in the following geochemical fractions: exchangeable (EXCH), carbonate (CARB), easily reducible (EASR), organic matter including sulphides (ORGS) and residual (RESID). The total metal contents in sediments (TOT) was determined after digesting the sediments with concentrated HNO<sub>3</sub>, pH, organic carbon, total carbonate and Fe-Mn oxides were estimated for correlation with the different forms of

Table(2): Ranges and averages for the total concentrations(TOT) of investigated metals(ppm).

Metal	Range	Average
Fe	1457.0-3813.4	2296.4
Mn	125 - 288	182.29
Zn	48.93-148.23	74.56
Cu	16.88-62.88	29.42
Pb	43.23-127.2	71.52

metal associations. This study revealed that the recorded high levels of metals observed in the investigated area are due to natural phenomena, as well as anthropogenic inputs. The levels of different metal extracts, and the total metal concentrations are shown in tables 1 and 2. Results showed that the recorded levels of the examined metal fractions are represented in the following sequence: RESD>EASR>ORGS>CARB>EXCH for iron,

RESD>CARB>EASR>ORGS>EXCH for manganese,  
RESD>CARB>EASR>ORGS>EXCH for zinc,  
RESD>CARB>ORGS>EXCH>EASR for copper  
RESD>CARB>EASR>EXCH>ORGS for lead.

and finally  
The characteristic high content in the residual fractions for the different metals emphasizes the strong influence of water discharge and sediment influx from the river Nile into the Mediterranean Sea (UNEP, 1984). This means that, considerable amounts of heavy metals are transported naturally into the Mediterranean as background contributions. Among the non-residual metal fractions, the carbonate associated metals showed noticeably high concentrations of Fe, Mn, Zn, Cu and Pb in comparison with the other extractions. This could be attributed to the prevalence of carbonate materials in the investigated area (El-Wakeel and El-Sayed, 1978; Nasr et al. 1988 and 1989) which offer favourable conditions for the heavy metals to be associated with them. The non-residual metal forms (man-made sources) represent 5.88% of the total extractable fractions for iron, 12.85% for manganese, 25.44% for zinc, 38.98% for copper and 31.06% for lead. These figures reflect a quite evident pollution with zinc, copper and lead in the investigated area. Correlation matrix has been carried out to highlight the interrelationship among different studied parameters.

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## Redox Distribution of Uranium Species in Suboxic Marine Environments

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Uranium is a member of the 5f (actinide) series of elements, all of which have a pronounced inherent sensitivity to the redox state of the environment. There are six well defined oxidation states of uranium which occur in nature. In the marine environment, including the complete vertical water column from the surface layer of the ocean down to the bottom sediments, three oxidation states of uranium - U(IV), U(V) and U(VI) - can coexist. In oxygenated seawater uranium is associated with the carbonate ion forming the very stable  $UO_2(CO_3)_3^{4-}$  complex. This results in the rather high dissolved uranium concentration in the ocean, the average values being  $3.3 \mu g L^{-1}$  (Chen et al., 1986). In the euphotic zone of the ocean, mixed complexes between uranium, carbonate and peroxide may be significant (Djogic and Branica, 1990).

In sedimentary processes the uranyl species are reduced to lower oxidation states and are incorporated into insoluble uranium minerals or bound to particulate organic matter. The problem of the solid(s) limiting the solubility of uranium in seawater, and thus also its concentration, remains unsolved and minerals such as uraninite, schoepite, halweiteite and others have been deemed responsible as the solubility controlling solids. Under all circumstances, the oxidation state of uranium depends on the stability of reduced uranium species, which involves complex redox equilibria and processes sensitive to system parameters such as Eh-pe, pH, concentration of dissolved and particulate organic matter, free radical activity and degree of anoxia.

In the transitional suboxic/anoxic layers of the water column, particularly if the oxygen/hydrogen sulfide interface is involved, uranium(V), i.e.  $UO_2^+$  species are thermodynamically stable (Langmuir, 1978; Kniewald and Branica, 1988). However, at the pH of seawater, the disproportionation reaction of U(V) into the (IV) and (VI) oxidation states is a feedback process resulting in a "dynamic disequilibrium" between dissolved U(VI) and U(V) species and U(V) precipitation.

The geochemical equilibrium computer code MINTEQ (Felmy et al., 1984) was used to evaluate the thermodynamic likelihood of various uranium redox reactions under conditions of low Eh prevailing in reducing marine environments. The two probable mechanisms of reduction are:

a) reduction of dissolved  $UO_2^{2+}$  to dissolved  $UO_2^+$  involving a kinetic equilibrium between the disproportionation reaction and the precipitation of insoluble U(V) and U(IV).

Preliminary investigations of  $UO_2^+$  formation in seawater, using visible and ultraviolet spectrophotometry yielded encouraging results and provide evidence that even dissolved U(V) species (the  $UO_2^+$  cationic complex) is a probable redox species to be encountered in suboxic marine milieu, because the reduction from  $UO_2^{2+}$  to  $UO_2^+$  involves no structural changes of the  $UO_2^{n+2}$  ( $n = 1$  or  $2$ ) ion.

b) binding of U(VI) to particulate/suspended organic matter (such as humic material) and its subsequent reduction to the less soluble redox species of U(V) and U(IV) during early diagenetic stages. This reduction process may take place at the solid/liquid interface, either in suspension or in the sediment proper.

Nonetheless, a combination of these mechanisms is also possible and will obviously depend on the prevailing redox potential of the environment, supply of DOM and POM, structure and texture of the sediment, dynamics of water exchange as well as the activity of anaerobic microorganisms.

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