

Phosphorus fluxes in the Southeastern Mediterranean waters

M.A.R. ABDEL-MOATI*, M. SAID* and N.M. DOWIDAR*

*Oceanography Dept., Faculty of Science, University, ALEXANDRIA (Egypt)
 †National Institute of Oceanography & Fisheries, ALEXANDRIA (Egypt)

The consideration of phosphorus in the marine environment is due to its double existence sometimes as a pollutant and others as an important nutrient element. Elevated phosphorus concentrations cause eutrophication problems while phosphorus absence may be in most cases a limiting factor for biological production.

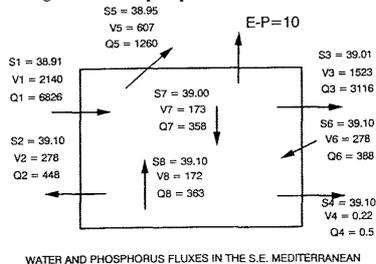
In the post High Dam period, the biological productivity of the S.E. Mediterranean has greatly declined due to the cessation of the Nile flood and the subsequent drop in the nutrients levels, especially phosphorus. The N:P ratio in the area is always over 20:1 indicating that phosphorus is a limiting nutrient in this basin. This peculiarity must be linked with physical and biological processes in the S.E. Levantine Basin. Direct current measurements are scarce and their use for water exchange is a complicated task due to existence of inshore counter currents and high variability due to wind. However, water circulation is a principal factor affecting the phosphorus cycle in the basin. Several biological and chemical transformations took place in the surface layer, while phosphorus is supposed to be more conservative in the intermediate and deep waters.

The present study is an attempt to compute the balance of phosphorus in the S.E. Mediterranean Basin based on the study of the movement of major water masses in the area. Data used in this study are a result of 10 oceanographic seasonal cruises carried out in the S.E. Mediterranean Basin during 1982/86, covering the area between longitudes 29°45' E & 32°40' E and extending over the continental shelf off the Egyptian coast. The geographical variations of salinity and temperature in this area were previously published by ABDEL-MOATI and SAID (1987). On the basis of water and salt budgets and in condition that there is no eustatic changes of bottom configuration, no fluctuations in sea level and that the bottom water layer has a more or less uniform thickness and depth, it is possible to write the mass balance equations:

$$V1+V6=V3+V4+V2+V5+(E-P); V2+V4-V6=V7+V8; P2S2V2+P4S4V4=P6S6V6 \text{ and } P6S6V6-P2S2V2-P4S4V4=P8S8V8-P7S7V7 \text{ where } (E-P)=10 \times 10^9 \text{ m}^3 \text{ y}^{-1} \text{ (see diagram).}$$

The coastal waters of the area receives about $16.1 \times 10^9 \text{ m}^3/\text{y}$ of fresh and brackish water from the different landbased sources. About 20% of this amount is discharged from the River Nile while the rest is being discharged through the Nile delta lakes. Through this route about 371 T of phosphorus are conveyed yearly to the S.E. Mediterranean waters. About 32% of this amount is discharged from Lake Manzalah, the largest Nile delta lake, while about 26% is conveyed through the functioning branch of the Nile. Upon mixing with sea water, huge amounts of this discharge are lost through sedimentation in the coastal waters. This is evidenced from the remarkably low phosphorus concentrations (average $0.088 \mu\text{M}$) observed at points located about 8 Km opposite to the major sources compared with $6 \mu\text{M}$ levels recorded near the hot discharge points. The contribution of rain water ($3.4 \times 10^9 \text{ m}^3/\text{y}$) to the phosphorus balance is considered insignificant (about 4.2 T/y) compared to that discharged by landbased sources.

Phosphorus input and output fluxes due to water exchange, were calculated assuming that the phosphorus concentration observed in the western boundary is typical for the inflowing current while that of the eastern was characteristic for the outflowing current. The total phosphorus input to the S.E. Mediterranean Basin is 8589 T/y while the output reaches 4824 T/y, leading to a net gain of 3765 T/y. On the other hand, the standing stock of phosphorus in the basin is 3307 T. Of this amount 6% are present in the inshore waters (<20 m) while 44% and 50%, respectively, are present in the middle (20-100 m) and offshore waters (100-200 m). Between the input/output and the amount actually present, there is a surplus of 458 T of phosphorus. The difference between the calculated transport rates indicates a net loss from the water column. Comparing the estimated phosphorus recycled annually with the standing stock, it appears that the residence time of phosphorus is 0.4 ± 0.1 y. Incorporation with biological cycles and/or further sedimentation could explain this imbalance. Vertical water movements create an important role in phosphorus cycling in the S.E. Mediterranean Basin. Differences in concentrations between surface and bottom layers leads to a net phosphorus transport of about 5 T through the thermocline layer by down and upward fluxes. The upward flux is nearly negligible during summer time due to the trapping of regenerated phosphorus in the bottom water below the pycnocline. Using the formula of Hamilton-Taylor (1979) and an average sedimentation rate of 0.037 cm y^{-1} (ROSS & UCHUPI, 1977), the phosphorus sedimentary flux should be 61 T/y. The degree of accuracy of phosphorus loss depends on factors such as no organic phosphorus measurements were performed, particulate phosphorus data were not collected in continuous series and water circulation other than geostrophic were not considered. Based on in situ productivity measurements using labeled carbon-14 (DOWIDAR, 1984) the annual average primary production of the area was $55.5 \text{ g C m}^{-2} \text{ y}^{-1}$ corresponding to $527 \mu\text{g}$ at $\text{C m}^{-2} \text{ h}^{-1}$. Using Redfield ratio, the demand for phosphorus by phytoplankton amounted to $4.97 \mu\text{g}$ at $\text{P m}^{-2} \text{ h}^{-1}$ indicating that biological activity is a controlling factor in the phosphorus mass flux in the Levantine Basin.



* V1 TO V8 in $10^9 \text{ m}^3/\text{y}$ while Q1 TO Q8 in T/y

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Dissolved copper speciation in the coastal waters of Alexandria Region

M.A.R. ABDEL-MOATI* And C.M.G. VAN den BERG*

*Oceanography Dept., Faculty of Science, University of ALEXANDRIA (Egypt)
 †Oceanography Laboratory, University of LIVERPOOL (U.K.)

Speciation studies attempt to differentiate between the chemical forms and distribution of metal species in dissolved, colloidal and particulate phases. The distinction between dissolved and particulate forms by filtration through $0.45 \mu\text{m}$ is generally accepted. The dissolved fraction includes truly dissolved material plus colloidal fraction. Metals could also be classified according to their rate of reaction with a dissolved ligand as well as the extent of stability of their complex with this ligand. Metals bioavailability and biogeochemical cycles are influenced mainly by their interaction with dissolved organic matter which in turn is a reflection of the impact of man's activity on the environment.

The aim of the present study is to apply the cathodic stripping voltammetry (CSV) technique for the determination of dissolved copper species in several coastal marine environments differing in their exposure to the amount of metal discharged. The labile fraction of the metal is that species measured by CSV in untreated filtered sample including all inorganic complexes and a certain proportion of organically associated metal. The total dissolved metal is those species detected in U.V. irradiated (4 hours, 1 KW mercury lamp) and acidified (pH 2.5 ± 0.1) samples. This includes the summation of the metal present as free, inorganically complexed, organically complexed and colloiddally associated metal species.

Samples were collected during low and high landbased sources discharge periods from three different locations covering the coastal waters of Alexandria region. These environments are subjected to agricultural, industrial and sewage runoff. Samples were collected in pre-cleaned polyethylene bottles, filtered after collection by pressure and stored frozen between sampling and analysis. Analyses were carried out at pH 7.8 ± 0.4 using HEPES buffer and Oxine as a chelator (VAN den BERG, 1986). A PAR 174A Polarograph was used with a PAR 303A SMDE in conjunction with a Ag/AgCl reference and a platinum wire counter electrodes. Collection was performed at -1.0 V for 1 minute while scanning started from -0.3 V. Scanning parameters were : DPSCV, pulse rate 10 s^{-1} , scan rate 10 mV s^{-1} , pulse amplitude 25 mV . The reduction current was recorded on a x-y recorder. Calibration was achieved using the standard addition technique. Additional analyses for salinity, DOC and TSM were made.

The average labile and total dissolved copper concentrations in the coastal waters of Alexandria, presented in Table 1, are higher than normal values expected in coastal waters. At the high salinity region i.e. offshore stations, labile Cu showed small changes (Figure 1). However, a significant increase in the non-labile Cu fraction was observed opposite to discharge points especially when salinity drops below 30 during high flow period. This increase coincided with the increase in DOC ($r=0.8755$, $p<0.001$) and suspended matter ($r=0.7301$, $p<0.01$) concentrations. Such a relation suggests the removal of Cu from solution through complexation by either organic matter and/or adsorption onto solids at the turbidity maximum zones. Agricultural rather than industrial and sewage discharges seemed to be the major source for dissolved Cu to the coastal waters. The use of copper sulphate in controlling algal blooms in the Nile delta lakes may be the possible explanation for this source. A high degree of copper complexation was observed at the dumping site for domestic and sewage discharge.

TABLE 1. Average labile and total Cu in Alexandria coastal waters.

Survey	Labile		Total		Non-labile	
	mean	range	mean	range	mean	range
High flow	30 ± 9	18.5-49.7	49 ± 17	24.0-83.5	19 ± 8	5.5-33.8
Low flow	15 ± 8	6.5-34.1	20 ± 11	9.0-40.2	5 ± 3	2.5- 6.1

From the TDCu and salinity regression : $\text{TCu} = -2.15 \text{ S} + 117.9$ (high flow) and $\text{TCu} = 0.0995 \text{ S} + 17.98$ (low flow), the extrapolated TCu concentrations at salinity zero would be 118 and 18 nM for high and low flow periods, respectively. Such values are inconsistent with those reported at the Nile delta lakes-sea mixing zone i.e. 66 and 10 nM, respectively.

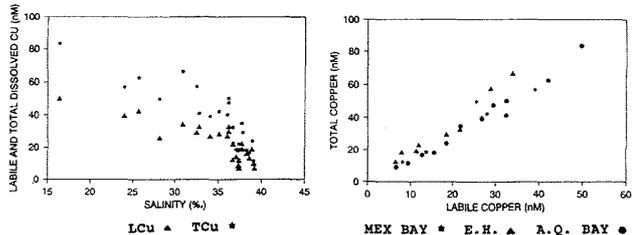


Figure 1. LCu and TCu vs. Salinity.

Figure 2. LCu against TCu.

The labile and total dissolved copper are linearly related (Figure 2). The LCu/TCu ratio was obtained for each zone from a plot of LCu values against those of TCu. The ratio ranged between 0.502 ± 0.03 and 0.608 ± 0.05 . This ratio indicated that a range of 89 to 96.4% of the TDCu would be organically complexed. Such a value emphasizes the importance of organic copper complexation in the coastal waters of Alexandria. Reported percentages of bound Cu of the total ranges from 30-50% (BATLEY & FLORENCE, 1976); 70-100% (SUGAI & HEALY, 1978); 94-98% (VAN den BERG, 1984) for coastal waters and <10-35% (DONAT *et al.*, 1986) for oceanic waters. The mean $\log \alpha_{\text{Cu}}$ determined in this study was 4.86 ± 0.97 , a value which is higher compared to previous studies ex: 3.14 for Irish Sea (VAN den BERG, 1984), 2.39-2.72 for Liverpool bay (NIMMO *et al.*, 1989) and 3.95 for Guanabara bay (VAN den BERG & REBELLO, 1986) indicating either high ligand concentration and/or high stability constant.

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