# On the importance of atmospheric inputs of inorganic nitrogen and phosphorus on the productivity of the Eastern Mediterranean Sea

G. Kouvarakis[1], C. Economou[1], Z. Markaki[1], A. Tselepides[2], N. Kubilay[3] and N. Mihalopoulos[1]*

*Mihalo@chemistry.uoc.gr, ttse@imbc.gr, Kubilay@ims.metu.edu.tr*
*1:Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 1470, 71409 Heraklion, Greece, *Corresponding Author*
*2: IMBC, P.O. Box 2214, 71003 Heraklion, Crete, Greece*
*3: Institute of Marine Sciences, Middle East Technical University, P.O. Box 28, Erdemli 33731, Icel, Turkey*

**Abstract-** To assess the importance of the atmospheric deposition of nutrients on the productivity of the Eastern Mediterranean Sea, measurements of both wet and dry deposition of dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) have been performed at a remote coastal area on the island of Crete (Finokalia). The results of the wet and dry deposition of DIN obtained at Finokalia have been compared with data of particulate organic nitrogen (PON) obtained in the Cretan Sea by using sediment traps deployed at 200 and 500m depth. Our results show that the atmospheric deposition of DIN can account for up to 370% of the measured PON in the sediment traps indicating that atmospheric pathway alone can sufficiently account for the measured new nitrogen production. On the other hand even during the summer and autumn period, i.e when water stratification attains is maximum, atmospheric deposition of dissolved inorganic phosphorus (DIP) could account for only up to 40% of the observed new production. Thus atmospheric inputs of bioavailable N and P represent an imbalanced contribution to the new production which could account for the anomalous N/P ratio observed in surface seawater and P limitation in the SE Mediterranean.

**Keywords**-Atmospheric deposition, nitrogen, phosphorus, Eastern Mediterranean, seawater productivity.

## Introduction

Atmospheric deposition is recognised as a potential source of nutrients to many ecosystems and especially in coastal areas and enclosed seas where terrestrial inputs (rivers plus atmospheric deposition) have been proposed to play a crucial role in regulating the productivity of sea water (Jickells, 1998 and references therein). Nitrogen is usually considered as the limiting nutrient in the oceans, although phosphate or even trace metals may also play a role in regulating phytoplankton growth.



The aim of this paper is to assess the importance of atmospheric pathway as a source of nutrients (DIN and DIP) in the Eastern Mediterranean. The oligotrophic properties of the Mediterranean Sea and especially its Eastern basin have attracted the attention of many investigators who have characterized this area as one of the less productive of the world on the basis of its low nutrient levels and poor productivity (Krom et al., 1992; Ignatiades, 1998; Tselepides et al., 2000). The Eastern Mediterranean basin is located at the Southern edge of Europe receiving during most of the year (at least 70% of the time) air masses from Central and Eastern Europe. Atmospheric input of anthropogenic nutrients to areas located downwind of populated and urbanized regions can lead to or shift toward greater phosphorus limitation (Fanning, 1989). However, to our knowledge no attempt has been made so far to understand the role of the atmospheric input of nutrients on the productivity of the Eastern Mediterranean even though this pathway could be the most effective external source since riverine inflow is very low in this area (Martin et al., 1989). Therefore, measurements of both wet and dry deposition of DIN and DIP have been performed in a remote site on the island of Crete (Finokalia). The results of both wet and dry deposition of DIN obtained at Finokalia have been compared to data of particulate organic nitrogen (PON) obtained in the Cretan Sea using sediment traps deployed at 200 or 500m

## Experimental

***Wet deposition:*** Rain water was collected on an event basis using a wet-only collector installed at Finokalia (25°60'E, 35°24'N) a small village on the northern coast of Crete (Fig. 1). Details about Finokalia can be found elsewhere (Mihalopoulos et al., 1997; Kouvarakis et al, 2000).

***Dry deposition:*** Dry deposition was estimated based on the collection of particles on a flat surface covered by glass beads, positioned on a funnel and situated 3m above the ground. The deposition measured using this technique corresponds to the total deposition. However since from May to September no rain events occur, the measured total deposition during that period corresponds to the dry one. The glass-bed system was exposed to the atmosphere for a week and after that period it was washed with ultra pure water, which was then filtered and proceeded as the rainwater sample.

***Chemical analysis:*** Analysis of DIN was performed by ion chromatography. A Dionex AS4A-SC column with ASRS-I suppressor in autosuppression mode of operation was used for the analysis of $NO_3^-$. For $NH_4^+$ a CS10-SC column was used with a CSRS-I suppressor. Analysis of DIP was performed using the stannous chloride method.

***Sediment traps:*** Sediment traps have been deployed during two yearly surveys performed in the frame work of European funded project MATER (from 4/1997-3/1998 at both sites MST1 and MST2 (Fig. 1).

All moorings were deployed in the open sea. The sampling interval was 15 to 16 days, ie the 1st and the 16th of every month. Details about the sediment trap preparation, deployment, and laboratory processing of the samples are given at Stavrakakis et al., (2000).

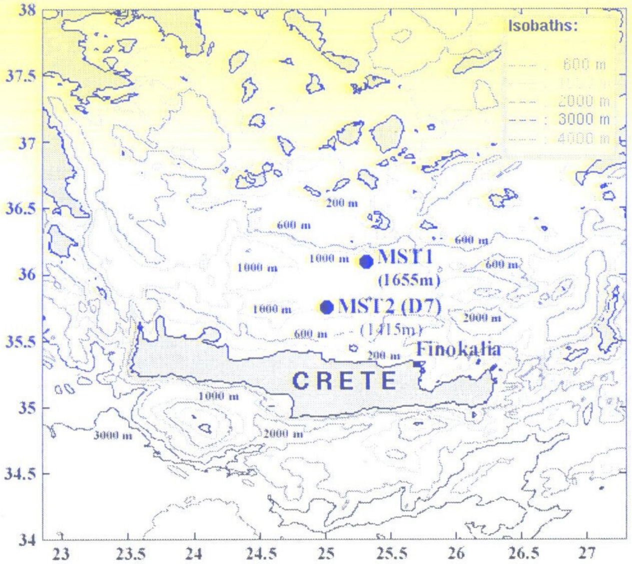


Fig. 1. Map indicating the location of the sampling sites referenced in the text.

## Results and Discussion

***Wet deposition of DIN***

Wet deposition of DIN ranges from 0.018–1.946 mmol/m$^2$/event (0.0–3.77 mmol/m$^2$ /15days, Fig. 2a). The yearly wet deposition of DIN estimated from this work ranges from 12.8-18.2 mmol/m$^2$. These Fig.s are in good agreement with the values of 15-20 mmol/m$^2$ reported by Le Bolloch and Guerzoni (1995) for the island of Sardinia (central Mediterranean) and the value of 22 mmol/m$^2$ estimated by Herut and Krom (1996) for the Israeli coast (Eastern Mediterranean). Note also that very few studies have been performed in sites far from big cities, as is our work at Finokalia.

***Dry deposition of DIN***

Dry deposition has been estimated based on the collection of particles on a surface covered by glass beads. Although this approach could have several limitations, it could provide useful information for total deposition estimation of gases and aerosols. Note also the absence of well-established techniques for the direct determination of dry deposition. Fig. 2a reports the variation of dry deposition of DIN. To facilitate the comparison with the sediment trap data, dry deposition is reported on a 15-day basis. The dry deposition calculated using this procedure ranges between 0.11 – 4.71 mmol/m$^2$/15days and presents a distinct seasonal variation with high values during summer. From April to September total



dry deposition is estimated to be of the order of 26 mmol/m$^2$, i.e. a factor of 1.3-2 higher than the annual wet deposition.

***Particulate Organic Nitrogen (PON) flux estimation using sediment trap deployments (exported N).***

Sediment traps were deployed to estimate new production in the area. New production is defined as the phytoplankton growth supported by nutrients supplied from outside the euphotic zone (Dugdale and Goering, 1967). Fig. 2a presents the flux of particulate organic N (PON). Flux of PON ranges from 0.055 to 1.204 mmol/m$^2$/15days with distinct seasonal variation, of higher values occurring during the end of winter, beginning of spring.

On a yearly basis the PON flux was estimated to vary between 10.44 – 11.87 mmol/m$^2$, i.e. a factor of 1.5 to 2 lower compared to wet deposition and up to a factor of 2 lower compared to dry deposition. To stress the important role of wet deposition, which although sporadic can bring considerable amounts of DIN to the sea surface, in more than 95% of the rain events the DIN wet deposition equaled the sinking particulate N flux and in 70% of the events this value was 5-times the corresponding PON value.

Figs 2a and b compare the atmospheric inputs of DIN to the PON fluxes measured using the sediment traps. Fig. 2a compares the DON fluxes with both the dry and wet deposition measured at Finokalia and Fig. 2b, averages the above data on a monthly basis. Dry deposition alone accounts for about a factor of two of the collected PON and both dry and wet deposition account for about 370% of the PON. Thus airborne DIN alone is more than sufficient to explain new production in the Eastern Mediterranean Sea.

***Atmospheric DIN and DIP deposition and seawater productivity***

Based on the data obtained from Finokalia we estimated an annual deposition of DIN (both wet and dry) equivalent to 45.25 mmol/m$^2$. If we assume that all of this DIN is available to the phytoplankton for new production we can convert this nitrogen flux into carbon uptake using a Redfield C:N ratio of 6.625. Atmospheric nitrogen can therefore fix on a yearly basis 30 molC/m$^2$. The seasonal variation in the amount of C that could be fixed by converting DIN flux into carbon uptake is determined according to the procedure described above and reported at Table 1. The seasonal variation of primary production deduced from measurements performed by Ignatiades (1998) in this area during 1994, in four stations during four seasons and integrated at the level of the thermocline (20-50meters dependingon season), is also reported in Table 1. From these two datasets a (f) ratio due to external input DIN at these depths can be deduced by dividing the PP due to N to the PP estimated form the "in situ" measurements. The thus calculated (f) ratio has a mean value of 0.29, i.e. significantly higher than the value assigned to oligotrophic areas (0.05-0.2; Eppley and Petterson, 1979). Thus from N point of view the E. Mediterranean is not oligotrophic. This result does not necessarily imply that other processes such as advection and or nitrogen fixation proposed by

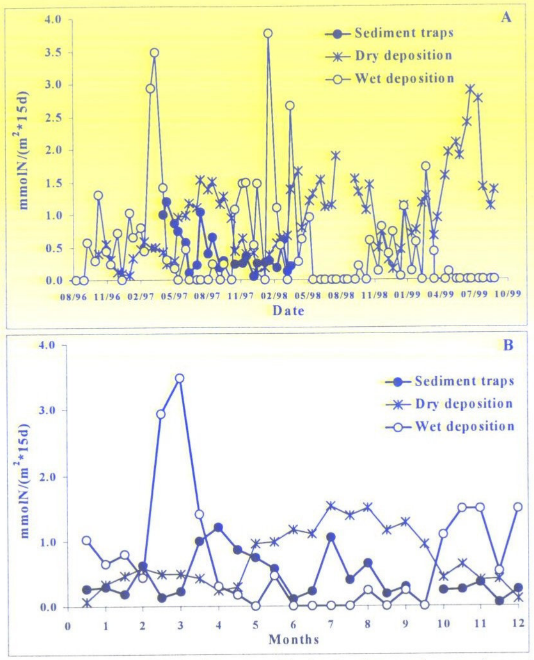


Fig. 2. Comparison between PON fluxes with both dry and wet deposition at Finokalia (a) and monthly averaged PON and deposition data (b).

several authors as possible sources of N are of minor importance. It simply shows that the atmosphere alone through DIN deposition can supply the entire required N, in 100% bioavailable form.

Other elements (like P) should be responsible for the oligotrophic status of the Eastern Mediterranean. To assess the spatial and temporal variation as well as the importance of the atmospheric deposition of inorganic phosphorus (IP) on the productivity, measurements of phosphorus (total and dissolved) were performed both in rain water and aerosols. Particle size distribution of P, as well as total deposition measurements were also performed at the Cretan site. The results of the wet and dry deposition of dissolved inorganic phosphorus (DIP) obtained from Crete are compared with data of dissolved inorganic nitrogen (DIN) obtained simultaneously and with productivity data from the literature. Our results show that: i) the DIN/DIP molar ratio in both wet and dry deposition ranges between 63 and 349, therefore exceeding by a factor of up to 22 the N/P ratio observed in seawater (ranging from 25 to 28) and ii) the atmospheric deposition of DIP could reasonably account for a significant part of the new production (up to 38%) observed during the summer and autumn period, i.e. when water stratification is at its maximum (Markaki et al., submitted manuscript). This result confirms the observations made by Herut et al. (1999) that amospheric input of bioavailable N



and P represent an imbalanced contribution to the new production and reinforce the unusual N/P ratios and possible P limitation in the SE Mediterranean.

Table 1. Seasonal variation of primary productivity deduced from "in situ" measurements, primary productivity estimated from atmospheric DIN deposition and (f) ratio.

| Season | PP-"in situ" | PP- (N) | (f) ratio |
|---|---|---|---|
| | $mgCm^{-2}d^{-1}$ | $mgCm^{-2}d^{-1}$ | |
| Winter | 76.8 | 4.33 | 0.06 |
| Spring | 50.4 | 10.47 | 0.21 |
| Summer | 27.6 | 16.65 | 0.60 |
| Autumn | 26.4 | 7.79 | 0.29 |
| *Annual average* | 45.3 | 9.81 | 0.29 |

## References

Dugdale R.C., and J.J. Goering, Uptake of new and regenerated forms of nitrogen in primary productivity, *Limmol. Oceanogr.*, **12,** 196-206, 1967.

Eppley, R.W., and B.W. Peterson, Particulate organic matter flux and planktonic new production in the deep ocean, *Nature,* **282,** 677-680, 1979.

Fanning, K.A., Influence of atmospheric pollution on nutrient limitation in the ocean, *Nature*, **339**, 460-463, 1989.

Herut B., and M. Krom, Atmospheric input of nutrient and dust to the SE Mediterranean. In: *The Impact of Desert Dust Across the Mediterranean*, S. Guerzoni and R. Chester, editors, Kluwer Academic Publishers, **349**-358, 1996.

Herut, B., M.D. Krom, G. Pan, and R. Mortimer, Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: Sources, fluxes, and possible impact, *Limnol. Oceanogr.*, **44,** 1683-1692, 1999.

Ignatiades L., The productive and optical status of the oligotrophic waters of the Southern Aegean Sea (Cretan Sea), Eastern Mediterranean, *J. Plankton Res.*, **20,** 985-995, 1998.

Jickells T.D., Nutrient biogeochemistry of the coastal zone, *Sience,* **284**, 217-222, 1998.

Kouvarakis G., K. Tsigaridis, M. Kanakidou, and N. Mihalopoulos, Temporal variations of surface regional background ozone over Crete Island in southeast Mediterranean, *J. Geophys. Res.*, **105**, 4399-4407, 2000.

Krom M.D., S. Brenner, N. Kress, A. Neori and L.I. Gordon, Nutrient dynamics and new production in a warm-core eddy from the Eastern Mediterranean Sea, *Deep-Sea Research,* **39**, 467-480, 1992.

Le Bolloch O., and S. Guerzoni, Acid and alkaline deposition in precipitation on the western coast of Sardinia, Central Mediterranean (40° N, 8° E), *Water Air and Soil Pollution,* **85 (4)**, 2155-2160, 1995.

Martin, J.H., F. Elbaz-Poulichet, C. Guieu, M.D. Loye-Pilot, and G. Han, River versus atmospheric input of material to the Mediterranean: an overview, *Mar. Chem.*, **28,** 159-182, 1989.

Mihalopoulos N., E. Stephanou, M. Kanakidou, S. Pilitsidis, and P. Bousquet, Tropospheric aerosol ionic composition above the Eastern Mediterranean Area, *Tellus B,* 314-326, 1997.

Stavrakakis S., G. Chronis, A. Tselepides, S. Heussner, A. Monaco, A. Abassi, Downward fluxes of settling particles in the deep Cretan Sea (NE Mediterranean), *Progress in Oceanography,* **46,** 217-240, 2000.

Tselepides A., V. Zervakis, T. Polychronaki, R. Danovaro, G. Chronis, Distribution of nutrients and particulate organic matter in relation to the prevailing hydrographic features of the Cretan Sea (NE Mediterranean), *Progress in Oceanography,* **46,** 113-142, 2000.