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# On the importance of atmospheric inputs of inorganic nitrogen species on the productivity of the eastern Mediterranean Sea

G. Kouvarakis and N. Mihalopoulos
Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, Heraklion, Greece

A. Tselepides
Institute of Marine Biology of Crete, Heraklion, Greece

S. Stavrakakis
National Centre for Marine Research, Ag. Kosmas, Athens, Greece

**Abstract.** To assess the importance of the atmospheric deposition of nitrogen (N) on the productivity of the eastern Mediterranean Sea, measurements of both wet and dry deposition of dissolved inorganic nitrogen (DIN) have been performed at a remote coastal area in the island of Crete (Finokalia) during a 3-year period (1996–1999). The estimation of dry deposition of DIN is based on measurements of both gaseous ($HNO_3$ and $NH_3$) and particulate phase ($NO_3^-$ and $NH_4^+$) nitrogen compounds. The results of the wet and dry deposition obtained at Finokalia have been compared with data of particulate organic nitrogen (PON) obtained during two yearly (1994–1995 and 1997–1998) surveys (CINCS and MATER) in the Cretan Sea by using sediment traps deployed at 200 and 500 m depths. 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 basis of the primary productivity induced by the imported DIN and the productivity of the southeastern Mediterranean derived from in situ measurements a mean *f* ratio of 0.24 is calculated indicating that from the N point of view, the eastern Mediterranean can no longer be considered as among the most oligotrophic seas of the world. Other elements, most probably phosphorus (P), can account for the oligotrophic character of the eastern Mediterranean Sea. To our knowledge this is the first attempt to understand the role of the atmospheric input of nitrogen on the productivity of the eastern Mediterranean Sea.

## 1. Introduction

Atmospheric deposition is recognized 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 seawater [*Paerl*, 1985; *Jickells*, 1998]. 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. Recent estimates suggest that on a global basis, riverine and atmospheric inputs of dissolved inorganic nitrogen (DIN) are of similar significance [*Duce et al.*, 1991; *Jickells*, 1998].

The potential role of atmospheric N deposition on the productivity of oceanic areas has been estimated during two studies performed in Sargasso Sea and eastern Atlantic Ocean [*Knap et al.*, 1986; *Owens et al.*, 1992, *Michaels et al.*, 1993, *Spokes et al.*, 2000]. In the Sargasso Sea, by comparing atmospheric wet deposition to concurrent measurements of the ocean nitrogen cycle, it was concluded that wet deposition of nitrogen is a relatively unimportant process in affecting upper ocean nitrogen cycling in the Sargasso Sea [*Michaels et al.*, 1993]. However, Michaels et al. pointed out that additional information on dry deposition is needed to obtain a more complete picture. In the eastern Atlantic, on the other hand, although measurements of both dry and wet deposition of DIN have been performed, no concurrent data of nitrogen cycling exists. Still, the authors using estimates from the literature found that during May of 1997, ~30% of the new production in eastern Atlantic surface waters off Ireland can be supported by atmospheric inputs [*Spokes et al.*, 2000].

*Loye-Pilot et al.* [1993] estimated that wet deposition of DIN can account for 10–20% of the new production in the western Mediterranean. When dry deposition of aerosol $NO_3^-$ and $NH_4^+$ is taken into account, then the total DIN accounts for 15–30% of the new production in the northwestern Mediterranean.

The aim of this paper is to access the importance of atmospheric pathway as a source of DIN 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; *Berthoux et al.*, 1998; *Psarra et al.*, 2000; *Tselepides et al.*, 2000]. In addition, the eastern Mediterranean Sea presents an anomalous high nitrogen to phosphorus ratio (N/P ratio ranging from 20–27, compared to Redfield's ratio of 16), and it is not clear if it results from an increased N fixation [*Berthoux et al.*, 1998] or an important



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phosphorus leaching induced by dust [*Krom et al.*, 1991]. The eastern Mediterranean is also distinctive for several reasons [*Krom*, 1995, *Eijsink et al.*, 2000]. It is almost entirely enclosed, with a single outlet through the Straits of Sicily. It has an unusual antiestuarine circulation, which results in a net export of nutrients via the outgoing intermediate waters. 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 DIN on the productivity of the eastern Mediterranean, even though this pathway could be the most effective external source of DIN since riverine inflow is very low in this area [*Martin et al.*, 1989; *Herut et al.*, 1999].

Therefore measurements of both wet and dry deposition of inorganic N have been performed in a remote site on the island of Crete (Finokalia) during a 3-year period (1996–1999). The estimation of dry deposition is based on both gaseous ($HNO_3$ and $NH_3$) and particulate phase ($NO_3^-$ and $NH_4^+$) DIN measurements. The results of both wet and dry deposition obtained at Finokalia have been compared to data of particulate organic nitrogen (PON) obtained during two yearly surveys (1995 and 1997–1998) in the Cretan Sea using sediment traps deployed at 200 or 500 m.

## 2. Experiment

### 2.1. Sampling

The sampling sites where both the atmospheric deposition and sediment trap data sets were collected are depicted in Figure 1.

**2.1.1. Wet deposition.** Rainwater was collected on an event basis using wet-only collectors installed at two areas in Crete: at the University of Crete, situated 6 km south of the city of Heraklion, and at Finokalia (25°60′E, 35°24′N), a small village on the northern coast of Crete (Figure 1). The station at Finokalia is situated at an elevation of 130 m and faces the sea within the sector 270°–90°. No human activities occur within a range of 20 km. Details about Heraklion and Finokalia can be found elsewhere [*Mihalopoulos et al.*, 1997; *Kouvarakis et al.*, 2000]. After collection of the rain sample, 50–100 μL of chloroform were added as a biocide, and the sample was stored in the refrigerator until further analysis that was performed within a month.

**2.1.2. Dry deposition.** Dry deposition of DIN was estimated in two ways: (1) The first method was based on the collection of particles on a flat surface covered by glass beds, positioned on a funnel, and situated 3 m 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 ultrapure water, which was then filtered and proceeded as the rainwater sample. (2) The second method was based on the concentrations of the main gaseous ($HNO_3$ and $NH_3$) and particulate phase ($NO_3^-$ and $NH_4^+$) DIN compounds and their deposition velocities obtained from the literature.

Gas phase $HNO_3$ and $NH_3$ were collected using annular denuder tubes coated with $Na_2CO_3$ and citric acid, respectively. The sampling covers the November 1996 to March 1998 and April to September 1999 periods, respectively. The denuder tubes were 24.2 cm overall length, 2.2 cm inner cylinder diameter, and 0.1 cm annulus thickness [*Lawrence and Koutrakis*, 1994]. The day before use, they were filled with 10 mL of the coating solution, dried using purified air, and capped with Teflon fittings. Approximately 10% of the coated denuders were used as field blanks. Ambient air was drawn through the denuder tube at a rate of 15 sL $min^{-1}$. Exposure times varied between 3 and 48 hours. Following exposure, the tubes were extracted with 10 mL of Milli-Q water, and ~50 μL of chloroform were added immediately to the extract to preserve it against bacterial decomposition. The extracts were stored in Nalgene opaque polyethylene bottles in +4°C and analyzed for $NO_3^-$ and $NH_4^+$ using ion chromatography. More details about the collection efficiency and capacity of the denuders are given by *Lawrence and Koutrakis* [1994].

Aerosol particles were collected on 0.45 μm Gelman Zefluor PTFE filters. Flow rate was of 20 sL $min^{-1}$, and sampling efficiency was reported to be higher than 99.99%. The filters were extracted with 20 mL Milli-Q water, for 45 min in ultrasonic bath. The extraction efficiency of this method is higher than 98% for all compounds of interest. Chloroform (50–100 μL) was added as a biocide in the sample extracts, and all extracts were analyzed within a week.

### 2.2. 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. The reproducibility of the measurements was better than 2%, and the detection limits corresponded to 40 pmol $m^{-3}$ of air for a mean volume of 50 $m^3$. Blanks were below the detection limits.

### 2.3. Sediment Traps

Sediment traps have been deployed during two yearly surveys performed in the framework of two European funded projects, CINCS and MATER. During the first project (CINCS), traps were deployed from November 1994 to November 1995 at site D7 (Figure 1), and during the second (MATER), traps were deployed from April 1997 to March 1998 at both sites MST-1 and MST-2 (the same as D7; Figure 1).

All moorings were deployed in the open sea, as can be seen from the depth of the area (Figure 1). The traps (PPS3/3 Technicap, 0.125 $m^2$ collecting area, 12 receiving cups) were associated with current meters and were positioned at 200 m depth during the CINCS experiment and at 500 m depth during the MATER experiment. The sampling interval was 15–16 days, i.e., the first and the sixteenth days of every month. Upon recovery the samples were stored in the dark at +2°C until further processing, which includes removal of swimmers, subsampling, and preparation of filtration for various analyses. Details about the sediment trap preparation, deployment, and laboratory processing of the samples are given by *Heussner et al.* [1990] and *Stavrakakis et al.* [2000]. Particulate organic carbon and nitrogen determination (POC and PON) was performed at each sample using a Perkin Elmer (CHN 2400) or FISON Instrument (CHN EA1108) analyzer according to *Hedges and Stern* [1984].

## 3. Results and Discussion

To understand the distribution and the concentration of DIN in gas phase, aerosol, and rainwater, a quick outlook of the meteorological situation encountered in the east Mediterranean is presented below. The area is characterized by the existence of two well-distinguished seasons equally distributed throughout the year: The dry season (from April to September) and the wet season (from October to April). On the basis of a classification of 5-day backward trajectories performed for an 8-year period (1990–1997) the dry season is mainly characterized (up to 90%) by winds of N/NW direction (central and eastern Europe and Balkans) and high speed. During the wet season the prevalence of the N/NW sector is less

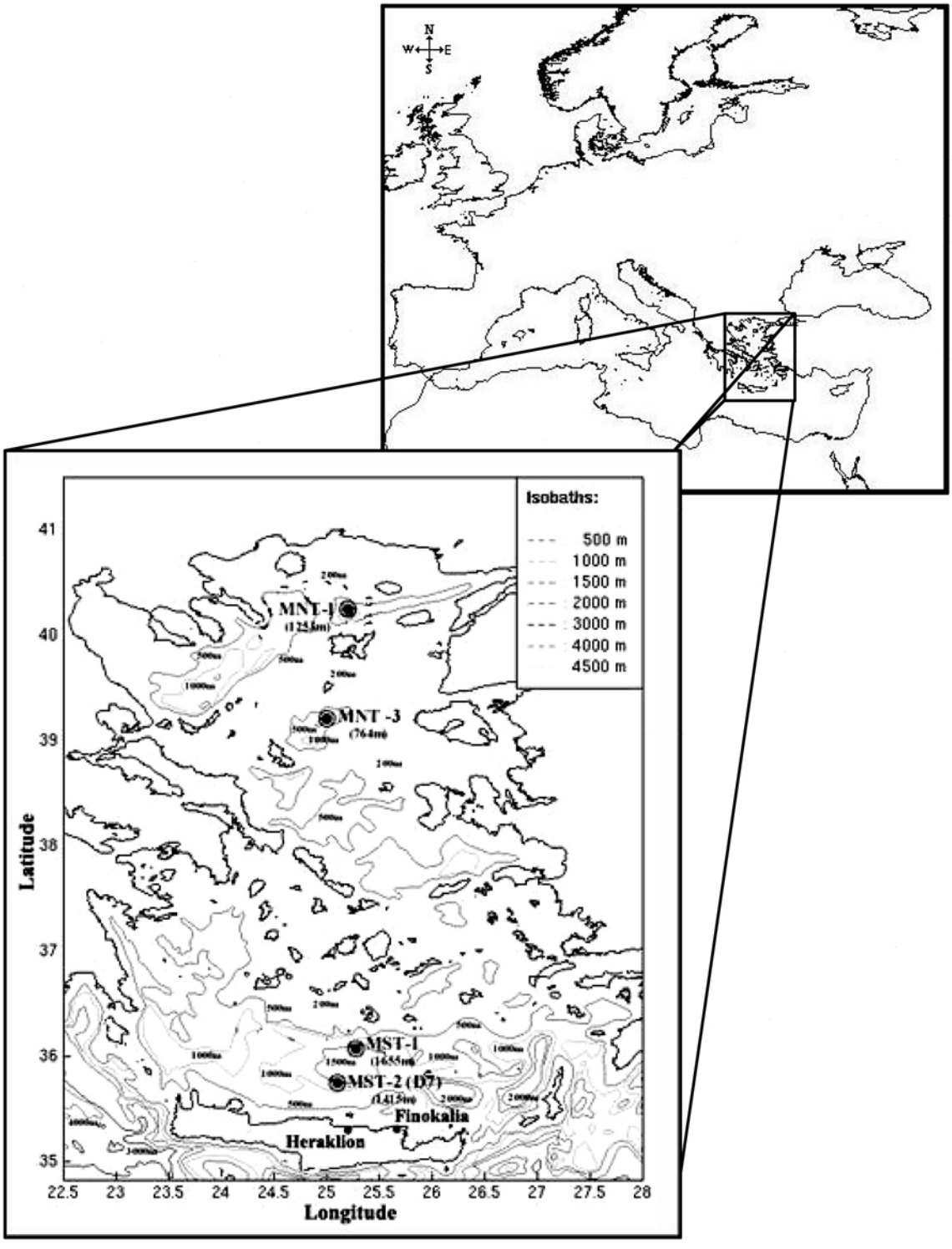


**Figure 1.** Map indicating the location of the sampling sites referenced in the text.

pronounced, while important transport from Sahara (S/SW winds; occurrence up to 20%) takes place. Details on the meteorological conditions encountered at Finokalia are given by *Mihalopoulos et al.* [1997] and *Kouvarakis et al.* [2000].

Table 1 presents the location, type of measurements, sampling period, and number of samples as well as a statistical analysis (average, median, and range) of all data obtained during this work. section 3.1 gives a detailed presentation of each parameter measured.

### 3.1. Wet Deposition of DIN

At both sampling sites, rainwater has been collected using automatic collectors. Figures 2a and 2b present the per event deposition of DIN at both locations during the whole period.

**Table 1.** Location, Type of Measurements, Sampling Period, Number of Samples, and Average, Median, and Range (Minimum to Maximum) of All Data Obtained During This Work

| Location | Measurement | Period | Number | Average | Median | Range | Units |
|---|---|---|---|---|---|---|---|
| Heraklion | wet dep. ($NO_3^-$) | March 1995 to May 1999 | 352 | 126 | 79 | 1–1186 | μmol N ($m^2$ event)$^{-1}$ |
| Heraklion | wet dep. ($NO_3^-$) | March 1995 to May 1999 | | 11.1 | | 10.5–12.0 | mmol N ($m^2$ yr)$^{-1}$ |
| Heraklion | wet dep. ($NH_4^+$) | March 1995 to May 1999 | 352 | 155 | 95 | 2–2032 | μmol N ($m^2$ event)$^{-1}$ |
| Heraklion | wet dep. ($NH_4^+$) | March 1995 to May 1999 | | 12.9 | | 11.2–15.2 | mmol N ($m^2$ yr)$^{-1}$ |
| Finokalia | wet dep. ($NO_3^-$) | Sept. 1996 to May 1999 | 128 | 199 | 171 | 11–1158 | μmol N ($m^2$ event)$^{-1}$ |
| Finokalia | wet dep. ($NO_3^-$) | Sept. 1996 to May 1999 | | 11.0 | | 9.7–12.3 | mmol N ($m^2$ yr)$^{-1}$ |
| Finokalia | wet dep. ($NH_4^+$) | Sept. 1996 to May 1999 | 128 | 123 | 70 | 1–1053 | μmol N ($m^2$ event)$^{-1}$ |
| Finokalia | wet dep. ($NH_4^+$) | Sept. 1996 to May 1999 | | 6.1 | | 4.4–7.8 | mmol N ($m^2$ yr)$^{-1}$ |
| Finokalia | $HNO_3$ | Nov. 1996 to Sept. 1999 | 326 | 29.6 | 26.1 | 0.5–106.1 | nmol N $m^{-3}$ |
| Finokalia | $NO_3^-$ | Oct. 1996 to Sept. 1999 | 496 | 26.3 | 24.0 | 1.1–71.9 | nmol N $m^{-3}$ |
| Finokalia | $NH_3$ | Nov. 1996 to Sept. 1999 | 329 | 18.2 | 15.63 | 1.2–56.6 | nmol N $m^{-3}$ |
| Finokalia | $NH_4^+$ | Oct. 1996 to Sept. 1999 | 496 | 56.2 | 49 | 1.2–170.9 | nmol N $m^{-3}$ |
| Finokalia | dry dep.[a] | April 1997 to Sept. 1999 | 71 | 154 | 137 | 18–390 | μmol N ($m^2$ d)$^{-1}$ |
| Finokalia | dry dep[b] | Oct. 1996 to Sept. 1999 | 496 | 64.9 | 63.1 | 4.4–192.5 | μmol N ($m^2$ d)$^{-1}$ |
| CINCS | PON | Nov. 1994 to Nov. 1995 | 23 | 32.5 | 25.1 | 2.8–129.7 | μmol N ($m^2$ d)$^{-1}$ |
| MATER | PON | April 1997 to March 1998 | 23 | 29.5 | 19.6 | 3.7–80.3 | μmol N ($m^2$ d)$^{-1}$ |

[a] Using glass beds and only during the dry period (April 1 to September 30); see text.
[b] Using deposition velocities from the literature.

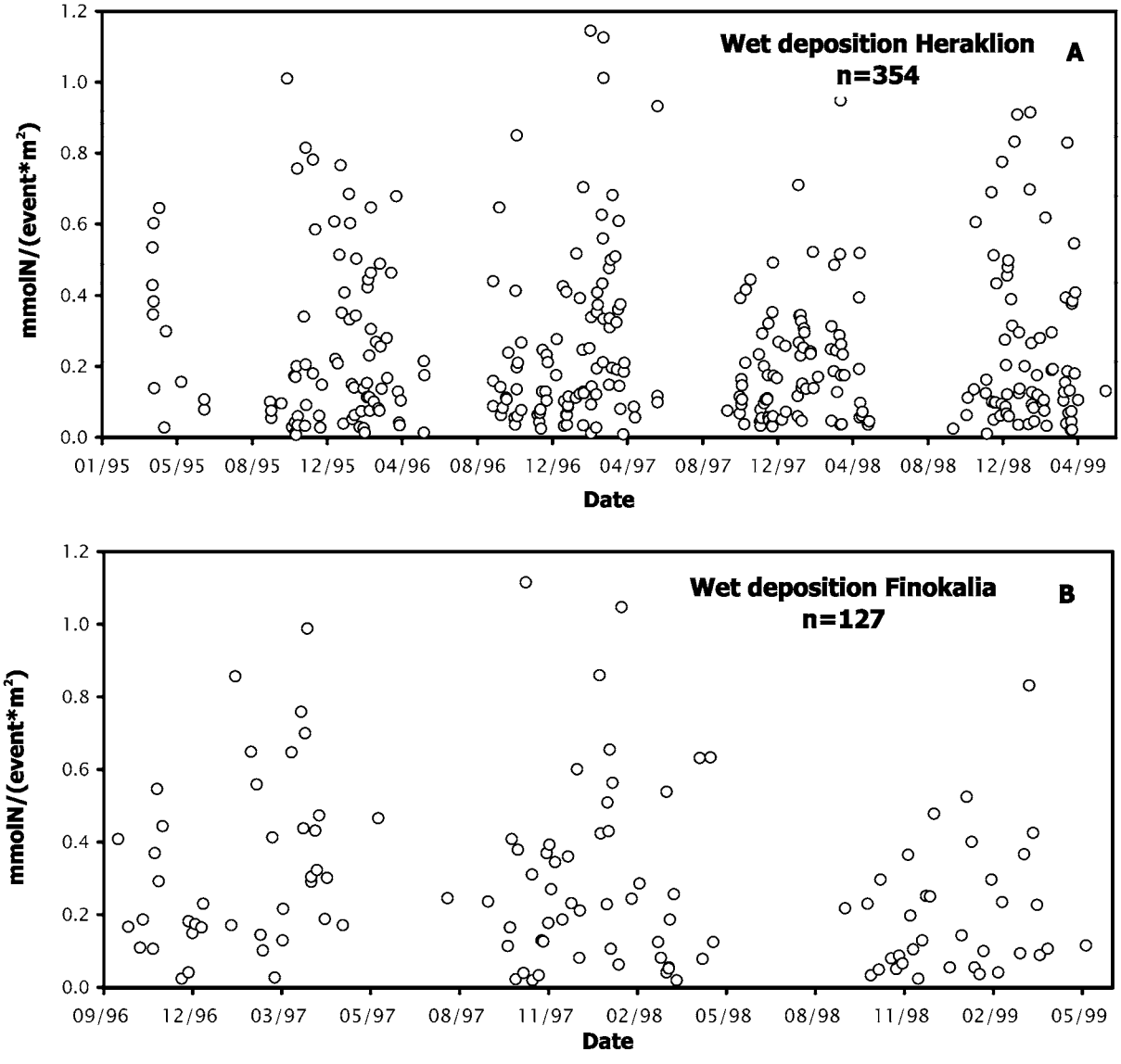


**Figure 2.** Variation of the per event wet deposition of DIN at (a) Heraklion and (b) Finokalia.

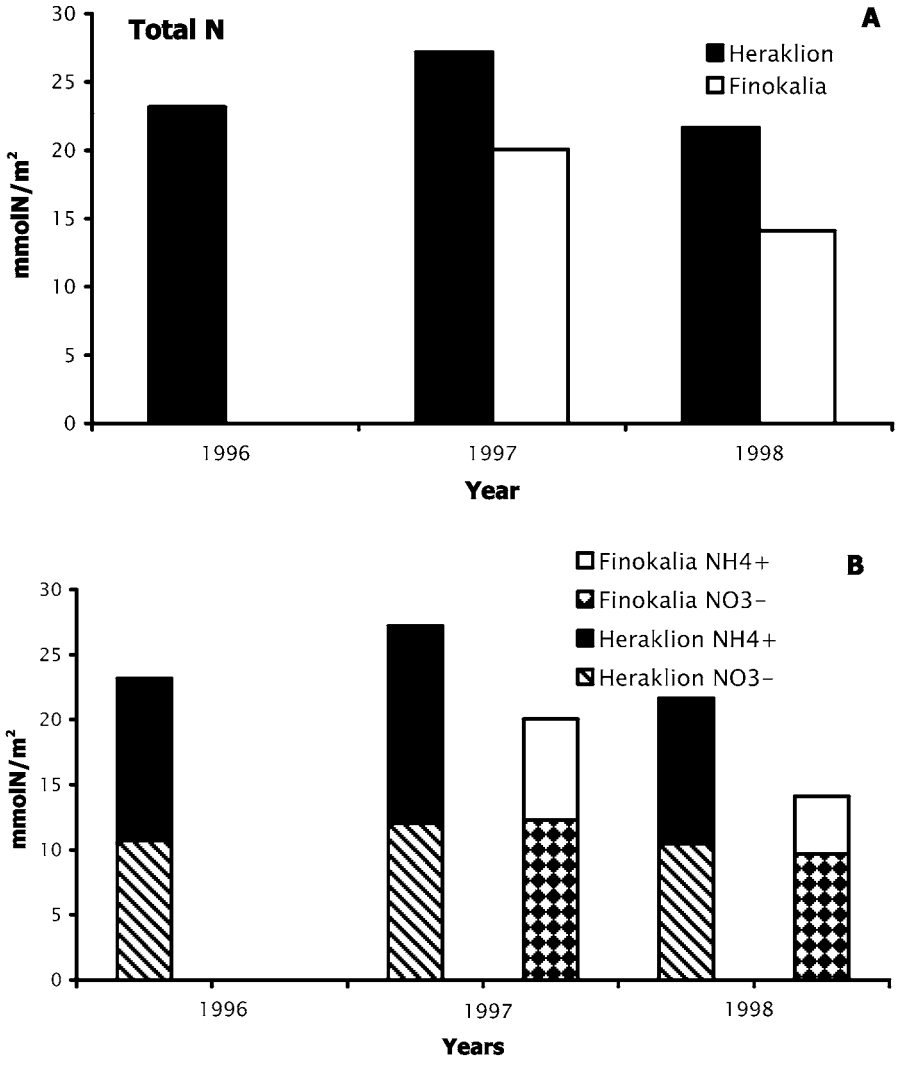


**Figure 3.** (a) Variation of annual wet deposition of DIN at Heraklion and at Finokalia during the 1996–1998 period and (b) relative contribution of $NO_3^-$ and $NH_4^+$ to the wet deposition of DIN at both sites.

Wet deposition of DIN ranges from 0.006 to 2.1 mmol $m^{-2}$ per event (median of 0.17 and 0.24 at Heraklion and Finokalia, respectively). At Heraklion, each rain separated from another by at least 2 hours was considered as a single event. At Finokalia, owing to its distance from Heraklion, rainwater collection was performed on a daily basis, which can explain the lower number of events compared to Heraklion. The slightly higher deposition at Finokalia is due to the lower precipitation at this area and thus to the lower dilution compared to Heraklion. However, when the annual wet deposition of DIN is considered, the tendency becomes completely different. This is clearly seen in Figure 3a, which presents total wet deposition of DIN at both locations. Total DIN deposition at Heraklion is ~40% higher compared to Finokalia. Local anthropogenic sources can account for this difference. Figure 3b presents the relative contribution of $NO_3^-$ and $NH_4^+$ to the wet deposition of DIN. At Heraklion, $NH_4^+$ is the main component of DIN since it contributes up to 55% to the total wet deposition of DIN, while at Finokalia, $NO_3^-$ is the main component since it contributes up to 63%. It is also clear that the difference in wet deposition of $NH_4^+$ between Heraklion and Finokalia is greater than that of $NO_3^-$, possibly denoting the presence of important local sources of $NH_3$ at Heraklion. The yearly wet deposition of DIN estimated from this work ranges from 22 to 27 mmol $m^{-2}$ for Heraklion and 14 to 20 mmol $m^{-2}$ for Finokalia. These figures are somehow lower compared to the 36.5 mmol $m^{-2}$ estimated by *Loye-Pilot et al.* [1990] for the NW Mediterranean but 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), indicating the existence of a W-E gradient. Note also that very few studies have been performed in sites far from big cities, as is our work at Finokalia.

### 3.2. Dry deposition of DIN

Dry deposition of DIN includes gaseous and particulate deposition. The measurement of the dry deposition of DIN is one of the major insights of this work since as pointed out by *Guerzoni et al.* [1999], only very few data exist for atmospheric particulate DIN for the whole Mediterranean. These are mainly given as annual averages, while measurements of its gaseous precursors are very scarce, originating exclusively from urban areas. To our knowledge, the simultaneously collected aerosol

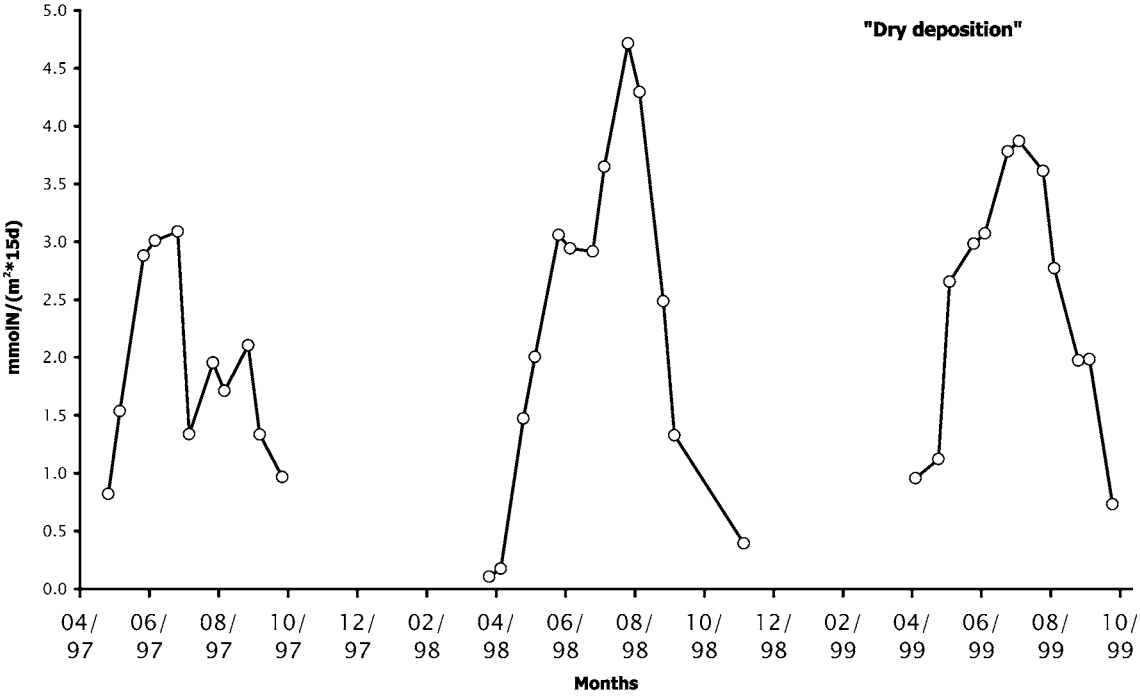


**Figure 4.** Variation of dry deposition of DIN at Finokalia during the 1996–1998 period using the glass beds covering only the dry period (April to September).

and gaseous data presented here are the first reported for a remote coastal location in the Mediterranean area. As mentioned in section 2, dry deposition has been estimated using two approaches.

**3.2.1. First estimate.** The first estimate is based on the collection of particles on a surface covered by glass beds. 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. Figure 4 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. To avoid bias from wet deposition, total deposition samples collected during periods with rain have been discarded. Thus the reported results cover the dry period from April to September. Since our sampler was situated only at 3 m above ground, resuspension of soil could be an additional source of DIN. To check this probability, several soil samples have been collected around the sampling area and from different depths. All these samples displayed DIN concentrations below the detection limit, indicating negligible contribution from local sources. The dry deposition calculated using this procedure ranges between 0.27 and 5.85 mmol $m^{-2}$ per 15 days 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.

**3.2.2. Second estimate.** On the basis of the concentrations of the main gaseous ($HNO_3$ and $NH_3$) and particulate phase ($NO_3^-$ and $NH_4^+$) DIN compounds and their deposition velocities, obtained from the literature and by using the equation $F_d = V_d C_d$, where $V_d$ and $C_d$ are atmospheric concentration and deposition velocity, respectively, the dry deposition $F_d$ is calculated. The main difficulty in this approach arises from the estimation of the deposition velocity. For gaseous species the model of *Hicks and Liss* [1976] has been used, suggesting that for readily water-soluble gases, such as $HNO_3$ and $NH_3$, the transfer velocity at the air-sea interface is a function of wind speed. Thus using the monthly mean wind speed data obtained at Finokalia, deposition velocities have been calculated for both gaseous compounds and for each month. Deposition velocities for the gaseous species thus range from 0.7 to 1.5 cm $s^{-1}$.

Figures 5a and 5b present the variation of the monthly mean concentrations of gaseous and particulate DIN species during the whole period. In both phases (gas and particulate), DIN species present a well-distinguished seasonal pattern with higher levels in summer than in winter. Changes in air mass origin and lack of removal via precipitation during summer can account for this pattern. More details on the factors controlling the variability of DIN species in the atmosphere will be presented in another paper.

The $NO_3^-$ and $NH_4^+$ levels measured at Finokalia range from 1.1 to 71.9 and 1.2 to 56.6 nmol $m^{-3}$, respectively (Figure 5a) and present a seasonal variation with higher values during summer. The $NO_3^-$ and $NH_4^+$ levels measured at Finokalia are in very good agreement with the values previously reported for the same place [*Mihalopoulos et al.*, 1997] and in reasonable agreement with the values reported for various coastal places in the eastern Mediterranean area (Table 2). The higher values reported for the NW Mediterranean (especially for $NH_4^+$) can be explained by the existence of a W-E gradient similar to that observed in the wet deposition of DIN.

The measured $HNO_3$ are comparable (Table 2) to the values reported by *Danalatos and Glavas* [1999] at a coastal site the western Greece, the only values reported by far for the eastern Mediterranean. On the other hand, $NH_3$ levels were a factor of 3–5 lower to those reported by *Danalatos and Glavas* [1999] and among the lowest reported in the literature for rural areas (Table 2).

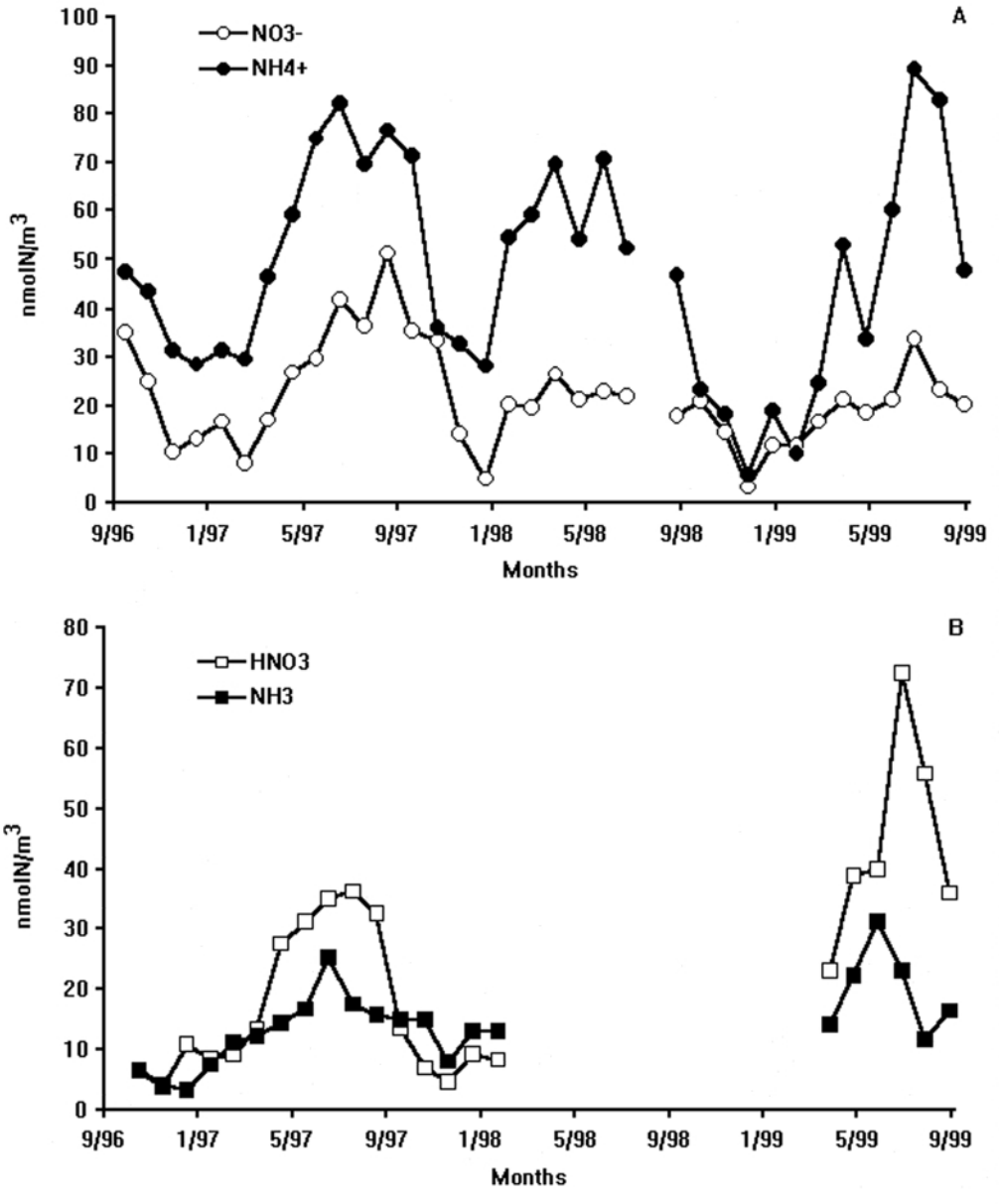


**Figure 5.** Temporal variation of monthly averaged (a) particulate $NO_3^-$ and $NH_4^+$ and (b) gaseous phase $HNO_3$ and $NH_3$ during the experimental period.

To calculate deposition velocities of aerosol species, the particle size distribution has be taken into account since dry deposition of particles is size dependent. Measurements of particle size distribution of $NO_3^-$ and $NH_4^+$ have been performed using six-stage impactors [*Kouvarakis et al.*, 2001]. From these 60 series of measurements, 75% of $NO_3^-$ and 11% of the $NH_4^+$ were found to be associated with the coarse particles ($d > 1$ μm) while the remaining part was found in fine particles ($d < 1$ μm). On the basis of this particle size distribution and assuming deposition velocities for fine and coarse particles of 0.075 and 1.25cm $s^{-1}$, respectively, the deposition velocities of $NO_3^-$ and $NH_4^+$ were calculated to be 1 and 0.21 cm $s^{-1}$, respectively. As pointed out by several authors [i.e. *Rendell et al.*, 1993, and references therein], the largest errors are likely to arise from the use of the theoretically derived values of $V_d$ as a function of size, since experimental validation is extremely difficult. Thus although our estimated $V_d$ for both fine and coarse particles are mean values derived from the best estimates reported in the literature [see, e.g., *Duce et al.*, 1991; *Rendell et al.*, 1993; *Sievering et al.*, 1989; *Spokes et al.*, 2000], they could easily be a factor of 2 higher or lower depending on these best estimates used. Figure 6a depicts the seasonal variation of dry deposition estimated for both gaseous and particulate phases and compared to dry deposition estimated using the glass beds (Figure 6b). The following remarks can be made: (1) Dry deposition of the gaseous phase DIN is at least comparable to that of the particulate phase since the annual values are 11.6 and 9.7 mmol $m^{-2}$, respectively. Thus omission of the gaseous phase can underestimate the total dry deposition of DIN by about a factor of 2. (2) Both estimates of dry deposition present the same pattern with higher values during summer and lower during winter. However, in absolute values the deposition estimated using the glass beds is higher by a factor of 1.6. Such agreement is quite good given the large uncertainties encountered in the estimation of $V_d$. (3) Finally, on an annual basis, total dry

**Table 2.** Comparison Between the Results Obtained During This Work and Those Reported in the Literature for Mediterranean and European Areas Regarding Aerosol ($NH_4^+$ and $NO_3^-$) and Gaseous ($HNO_3$ and $NH_3$) DIN Measurements

| Value | Location | Period | Reference |
|---|---|---|---|
| | | *Aerosol $NO_3^-$, nmol $m^{-3}$* | |
| 26.9 ± 13.3 | Finokalia | Oct. 1996 to Sept. 1999 | this work |
| 24.4 ± 18.3 | Finokalia | March 1994 to April 1995 | *Mihalopoulos et al.* [1997] |
| 9.7–25.6 | Patra, Greece | Nov. 1995 to Aug. 1996 | *Danalatos and Glavas*. [1999] |
| 19.0 ± 13.5 | Antalya, Turkey | March 1992 to Dec. 1993 | *Gullu et al.* [1998] |
| 44.0 | Erdemli, Turkey | Oct. 1991 to Dec. 1992 | *Ozsoy et al.* [2000] |
| 51.6 | Corsica (Calvi) | May to June 1992 | *Loye-Pilot et al.* [1993] |
| | | *Aerosol $NH_4^+$, nmol $m^{-3}$* | |
| 53.17 ± 21.15 | Finokalia | Oct. 1996 to Sept. 1999 | this work |
| 53.7 ± 32.2 | Finokalia | March 1994 to April 1995 | *Mihalopoulos et al.* [1997] |
| 94.44–205.5 | Patra, Greece | Nov. 1995 to Aug. 1996 | *Danalatos and Glavas*. [1999] |
| 77.8 ± 61.1 | Antalya, Turkey | March 1992 to Dec. 1993 | *Gullu et al.* [1998] |
| 211.1 | Corsica (Calvi) | May to June 1992 | *Loye-Pilot et al.* [1993] |
| | | *$HNO_3$, nmol $m^{-3}$* | |
| 19.07 ± 12.23 | Finokalia | Nov. 1996 to Sept. 1999 | this work |
| 25.39–66.6 | Patra, Greece | Nov. 1995 to Aug. 1996 | *Danalatos and Glavas*. [1999] |
| 1.64 ± 2.57 | (maritime) Portugal coast | Nov. 1993 to Aug. 1994 | *Pio et al.* [1996] |
| 12.14 ± 8.57 | (continental) Portugal coast | Nov. 1993 to Aug. 1994 | *Pio et al.* [1996] |
| | | *$NH_3$, nmol $m^{-3}$* | |
| 13.36 ± 5.75 | Finokalia | March 1997 to June 1998 | this work |
| 117.6–258.8 | Patra, Greece | Nov. 1995 to Aug. 1996 | *Danalatos and Glavas*. [1999] |
| 9.29 ± 6.43 | (maritime) Portugal coast | Nov. 1993 to Aug. 1994 | *Pio et al.* [1996] |
| 25.0 ± 17.14 | (continental) Portugal coast | Nov. 1993 to Aug. 1994 | *Pio et al.* [1996] |

deposition of DIN is of the order of 21.3 mmol $m^{-2}$, thus being at least of equal importance to wet deposition.

### 3.3. 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]. Over annual timescales, the amount of material that leaves the euphotic zone will equal the nutrient supply from outside the euphotic zone (new production).

Figure 1 and Table 1 present information about the location of the moorings, the sampling depths, and the period of deployment. Figures 7a and 7b present the flux of particulate organic N (PON) during the two-year period. Figure 7a corresponds to the period November 1994 to November 1995 at the site D7 (Figure 1; project CINCS) while Figure 7b to the period April 1997 March 1998 at sites MST-1 and MST-2 (the same as D7; project MATER). There is an extensive literature available on the shortcomings regarding the use of sediment traps. Nonetheless, they are extensively used because an alternative approach does not yet exist.

Flux of PON ranges from 0.04 to1.95 mmol $m^{-2}$ per 15 days with distinct seasonal variation, with higher values occurring during the end of winter and beginning of spring. The Cretan Sea is dominated by a variety of mesoscale features, which could account for the variability observed between the two data sets collected during the MATER project. Note, however, that the overall PON flux estimation is not significantly affected by this variability since both data sets present similar seasonal patterns with very similar PON fluxes.

On a yearly basis the PON flux was estimated to vary between 9.6–11.2 mmol $m^{-2}$, i.e., a factor of 1.5–2 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 >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.

Figures 8a–8c compare the atmospheric inputs of DIN to the PON fluxes measured using the sediment traps. Figure 8a compares the PON fluxes with the wet deposition measured at Heraklion, Figure 8b compares the DON fluxes with both the dry and wet deposition estimated and measured, respectively, at Finokalia, and Figure 8c averages the PON data presented at Figures 8a and 8b and compares them with averaged deposition data from Finokalia. It is clear that even when the most conservative estimates are used (wet deposition from Finokalia instead of Herakion and dry deposition data estimated from the gaseous and particulate measurements instead of deposition data obtained using the glass beds), atmospheric inputs of DIN can account for the integrity of the measured PON fluxes. On a yearly basis, atmospheric DIN fluxes are 3.5 times higher compared to the PON fluxes indicating that atmospheric inputs of DIN can account for all the measured new production in the Cretan Sea.

At this stage an important question can be raised. Are the PON data measured in the Cretan Sea representative for the entire Aegean Sea? During the MATER program, PON measurements have been performed in two locations in the northern Aegean (Figure 1). Details about these measurements will be presented in another paper; here we will compare only the total PON fluxes measured in the northern Aegean with those measured in the Cretan Sea. Annual PON fluxes ranged from 32.5 to 53 mmol $m^{-2}$ for the MNT-3 and MNT-1 stations, respectively, and thus are a factor of 3–5 higher compared to the PON measurements performed in the Cretan Sea. Note, however, that both north Aegean stations are situated either on a plateau (MNT-3) or near to the exit of Black Sea waters (MNT-1), and thus contamination from continental sources is expected to be very important. However, even in this case, atmospheric DIN inputs measured at Finokalia can account for 72–120% of the new production estimated for these areas.

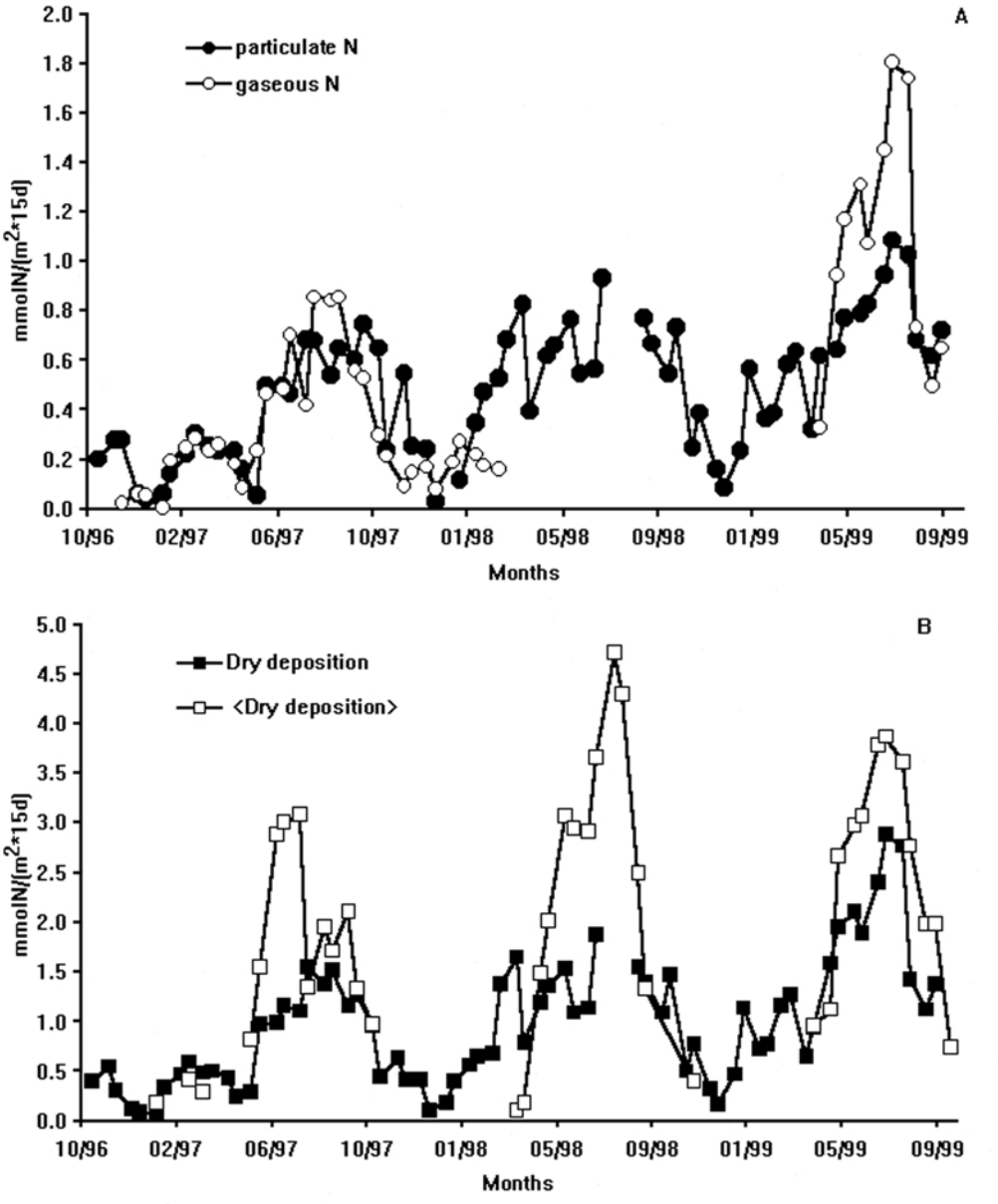


**Figure 6.** (a) Temporal variation of dry deposition of both gaseous and particulate DIN and (b) comparison with the dry deposition estimated using the glass beds. When gaseous DIN measurements were missing, dry deposition of gaseous DIN was estimated by using average values obtained for similar months during the sampling period.

On the other hand, the gaseous and/or particulate data measured at Finokalia and used for DIN estimation are in good agreement (even lower) compared to the scarce data reported for the Mediterranean area [*Danalatos and Glavas*, 1999, and references therein]. Thus, although additional measurements at other locations of the eastern Mediterranean area are clearly needed, the Finokalia DIN deposition data could be reasonably extrapolated for the whole Aegean Sea. Note also that this study does not consider the potential role of dissolved organic nitrogen (DON), which on the basis of recent estimates [*Cornell et al.*, 1995; *Scudlark et al.*, 1998; *Spokes et al.*, 2000], can account for 20–60% of the total DIN flux, nor does it consider the potential role of other nitrogen compounds like $NO_x$, peroxy acetyl nitrate (PAN) and organic nitrates which could also contribute to the total DIN flux. Thus the potential role of atmospheric nitrogen input on the new production could be even higher than that previously estimated if the role of DON and other $NO_y$ species is taken into account.

### 3.4. Atmospheric DIN Deposition and *f* Ratio

On the basis of the data obtained from Finokalia we estimated an annual deposition of DIN (both wet and dry) equivalent to 38.4 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 0.25 mol C $m^{-2}$. 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 3. 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

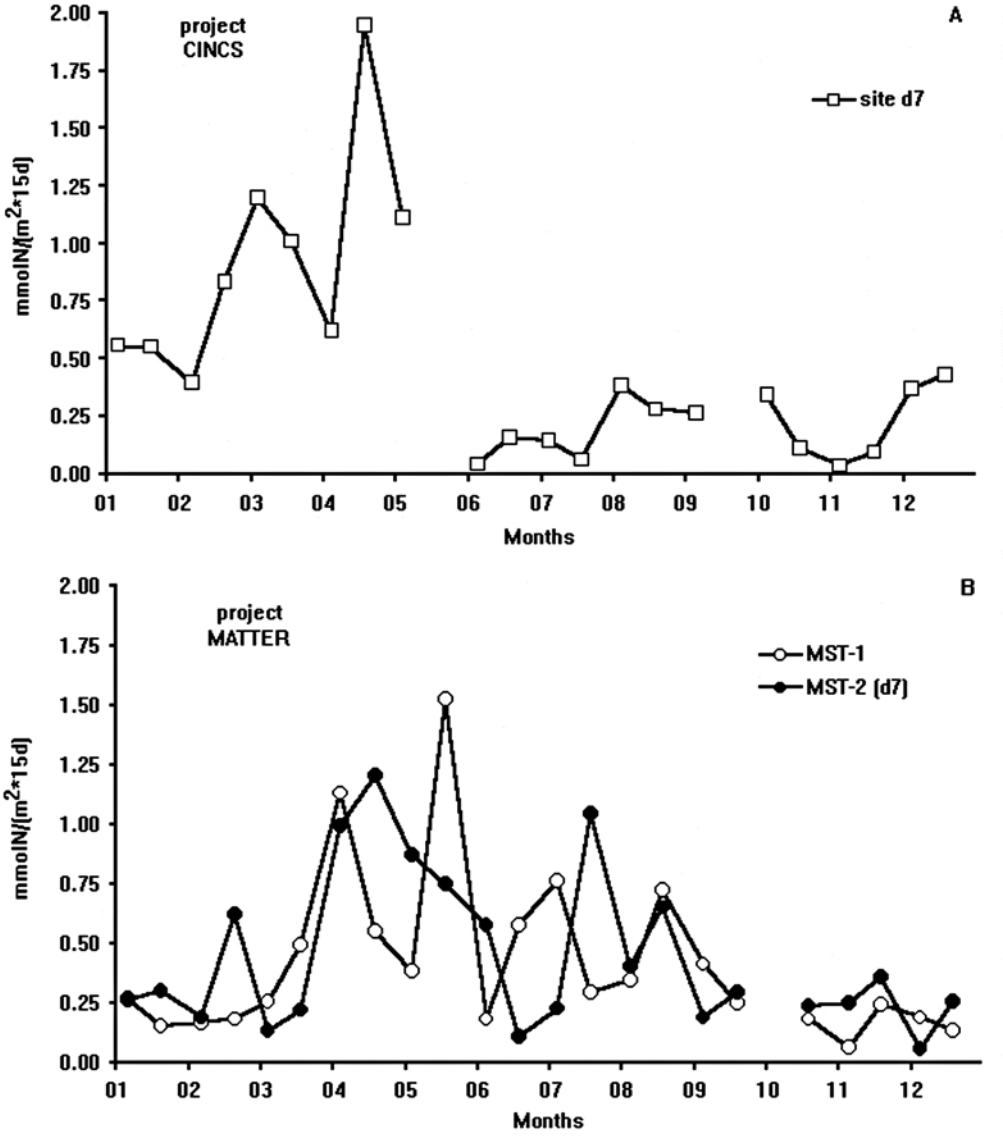


**Figure 7.** Flux of particulate organic N (PON) during 2-year periods using sediment traps (a) during the CINCS project (November 1994 to November 1995) and (b) during the MATER project (April 1997 to March 1998).

integrated at the level of the thermocline (20–50 m depending on season), is also reported in Table 3. From these two data sets an *f* ratio due to external input DIN at these depths can be deduced by dividing the primary production (PP) due to N to the PP estimated from the in situ measurements. The thus calculated *f* ratio has a mean value of 0.24, i.e., significantly higher than the value assigned to oligotrophic areas (0.05–0.2 [*Eppley and Peterson*, 1979]). It is worth noting that the calculated *f* ratio displays a seasonal trend with highest values during summer and autumn, i.e., when the water column is stratified and thus contribution of nutrients from deeper layers is reduced.

## 4. Conclusion and Further Questions

The results obtained during this study show that airborne DIN alone is more than sufficient to explain new production in the east Mediterranean Sea. Dry deposition alone accounts for about a factor of 2 of the collected PON, and both dry and wet deposition account for ~370% of the PON. A comparison between the primary productivity induced by the airborne DIN and the primary productivity derived from in situ measurements (integrated at the mixing layer; 25–50 m) indicates that from the N point of view the eastern Mediterranean is not oligotrophic since the mean calculated *f* ratio is of the order of 0.24. This result does not necessarily imply that other processes, such as advection and or nitrogen fixation, proposed by 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. If the contribution from the atmospheric organic N, which can account for up to 60% of the inorganic N, is also taken into account, the role of the atmospheric input becomes more important.

At this stage two important questions are raised.

1. What is the fate of the remaining N? By performing a simple N budget using the fluxes of N deposited through the atmosphere and collected in sediment traps (integrated at the depth of sediment traps) and assuming that the unused N remains in soluble phase, we calculate an annual increase of dissolved N (in forms of $NO_3^-$ and $NH_4^+$) of ~1–2%. A similar conclusion has been drawn for the

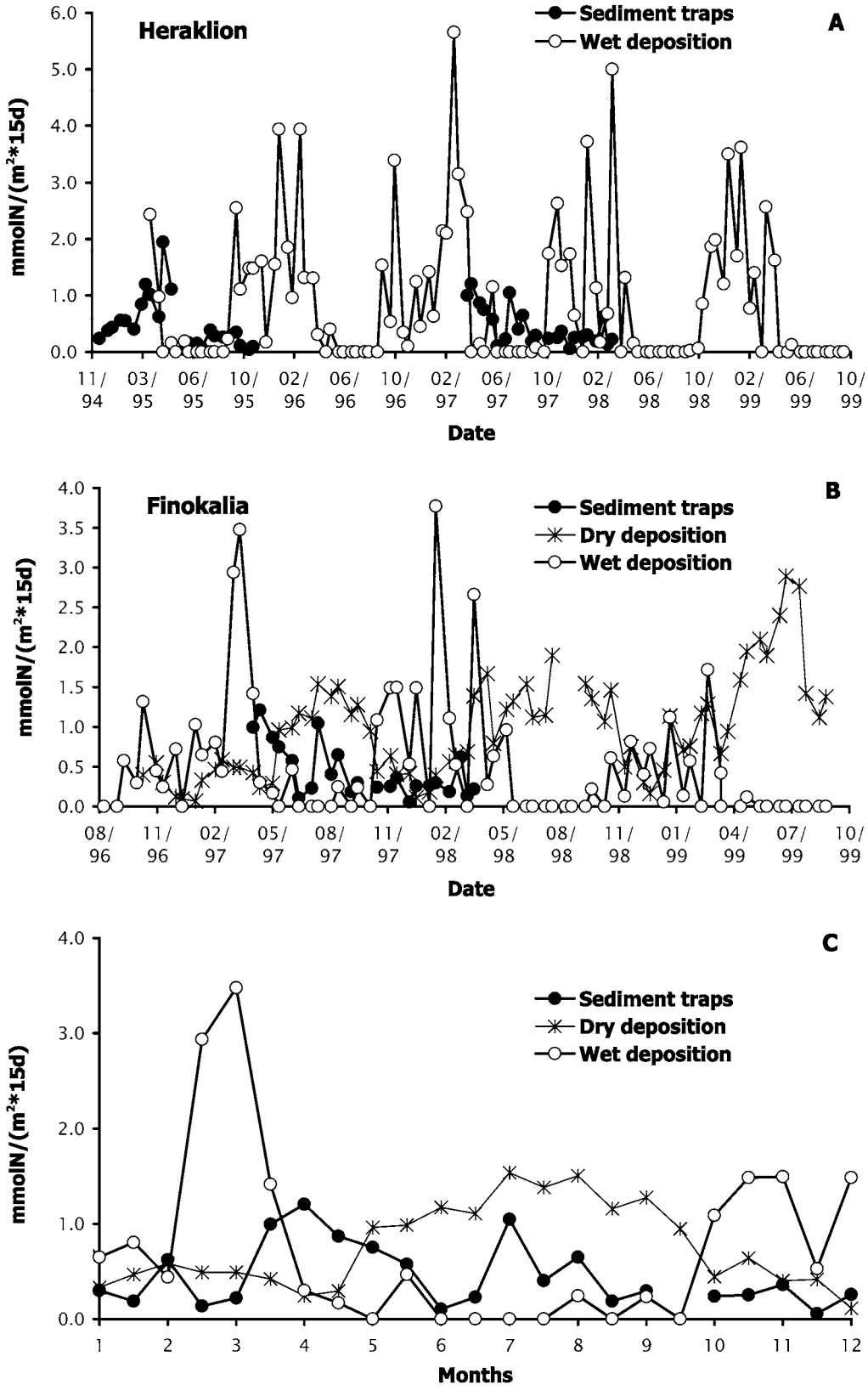


**Figure 8.** Comparison between (a) PON fluxes and the wet deposition at Heraklion, (b) PON fluxes with both dry and wet deposition estimated and measured, respectively, at Finokalia, and (c) monthly averaged PON and deposition data also from Finokalia.

**Table 3.** Seasonal Variation of Primary Productivity Deduced From In Situ Measurements, Primary Productivity Estimated From Atmospheric DIN Deposition, and *f* Ratio

| Season | PP In Situ, mg C $m^{-2}d^{-1}$ | PP (N), mg C $m^{-2}d^{-1}$ | *f* ratio |
|---|---|---|---|
| Winter | 76.8 | 6.95 | 0.091 |
| Spring | 50.4 | 10.46 | 0.21 |
| Summer | 27.6 | 8.35 | 0.30 |
| Autumn | 26.4 | 9.36 | 0.35 |
| Annual average | 45.3 | 8.8 | 0.24 |

western basin by using a completely different procedure [*Berthoux et al.*, 1998].

2. Why is the eastern Mediterranean still oligotrophic? Other elements (like P) should be responsible for the oligotrophy of the eastern Mediterranean. On the basis of the work by *Krom et al.* [1991] and *Zohary and Robarts* [1998], eastern Mediterranean is thought to be the largest body of water in the world that is P limited. The degree of P limitation increases from west to east across the entire basin [*Krom et al.*, 1991]. Given that the total Aeolian flux of P has been estimated to be 40–60 times lower compared to that of N [*Herut and Krom*, 1996; N. Mihalopoulos et al., unpublished data, 2001], the absence of a strong external P source (riverine and atmosphere) compared to DIN could explain the anomalous high N/P ratio (20–27) observed in the eastern Mediterranean Sea compared to the rest of the world's oceans.

Since anthropogenic sources contribute to the deposition of atmospheric nitrogen in the oceans and given the fact that anthropogenic $NO_x$ emissions have increased by almost 100% over the past three decades [*Knap et al.*, 1986] and will continue to increase in the future, anthropogenic induced DIN fluxes could further increase the already anomalous N/P ratio.

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G. Kouvarakis and N. Mihalopoulos, Environmental Chemical Processes Laboratory, Department of Chemistry, University of Crete, P.O. Box 1470, 71409 Heraklion, Crete, Greece. (mihalo@chemistry.uch.gr)

S. Stavrakakis, NCMR, Ag. Kosmas, Helliniko, 16604, Athens, Greece.

A. Tselepides, IMBC, P.O. Box 2214, 71003 Heraklion, Crete, Greece.

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