Atmospheric deposition of inorganic phosphorus in the Levantine Basin, eastern Mediterranean: Spatial and temporal variability and its role in seawater productivity

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Abstract

Total and dissolved inorganic phosphorus (IP) was measured in both rainwater and aerosol samples collected from two remote coastal areas: on the island of Crete (Greece) and at Erdemli (Turkey). Particle size distributions of P, as well as total deposition were also measured. Wet and dry deposition of dissolved inorganic phosphorus (DIP) from Crete are compared with simultaneously obtained dissolved inorganic nitrogen (DIN) and with productivity data from the literature. Our results indicate that (1) in both wet and dry deposition, the DIN/DIP molar ratio ranges between 63 and 349, exceeding by a factor of up to 22 the N/P ratio observed in seawater (ranging from 25 to 28) and (2) 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).

Atmospheric deposition is recognized as a potential source of trace elements of continental origin to oceanic areas. Of particular interest are the inputs of elements such as N, P, and Fe, which are essential for the biological growth of oceanic biota (Duce et al. 1991; Prospero et al. 1996; Pearl 1997; Jickells 1998; Guerzoni et al. 1999).

The potential role of atmospheric deposition on the ocean's productivity is expected to be particularly important for oligotrophic oceanic areas (Fanning 1989; Owens et al. 1992) such as the Mediterranean Sea and especially its eastern basin (Loye-Pilot et al. 1990; Bergametti et al. 1992;

Guerzoni et al. 1999; Herut et al. 1999; Migon et al. 2001; Ridame and Guieu 2002). The eastern Mediterranean Sea has attracted the attention of many investigators who have characterized this area as one of the least productive in the world (Krom et al. 1992; Bethoux et al. 1998; Psarra et al. 2000; Tselepides et al. 2000). The eastern Mediterranean Sea has a number of unique characteristics.

1. Its waters have a high nitrogen to phosphorus ratio ranging from 25 to 28, compared to the standard N/P Redfield ratio of 16, resulting from either increased N fixation (Bethoux et al. 1998) or from inorganic removal of phosphorus onto particulate matter (Krom et al. 1991).
2. It is located at the southern edge of Europe and is mainly (>70% of the time) influenced by air masses from anthropogenic sources of Central and Eastern Europe (Mihalopoulos et al. 1997). 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).
3. Aeolian inputs of trace elements in the area are by far the most effective external source, since riverine inflow has declined during recent years from construction of the Aswan damn on the Nile and from changes in irrigation (Martin et al. 1989; Guerzoni et al. 1999).
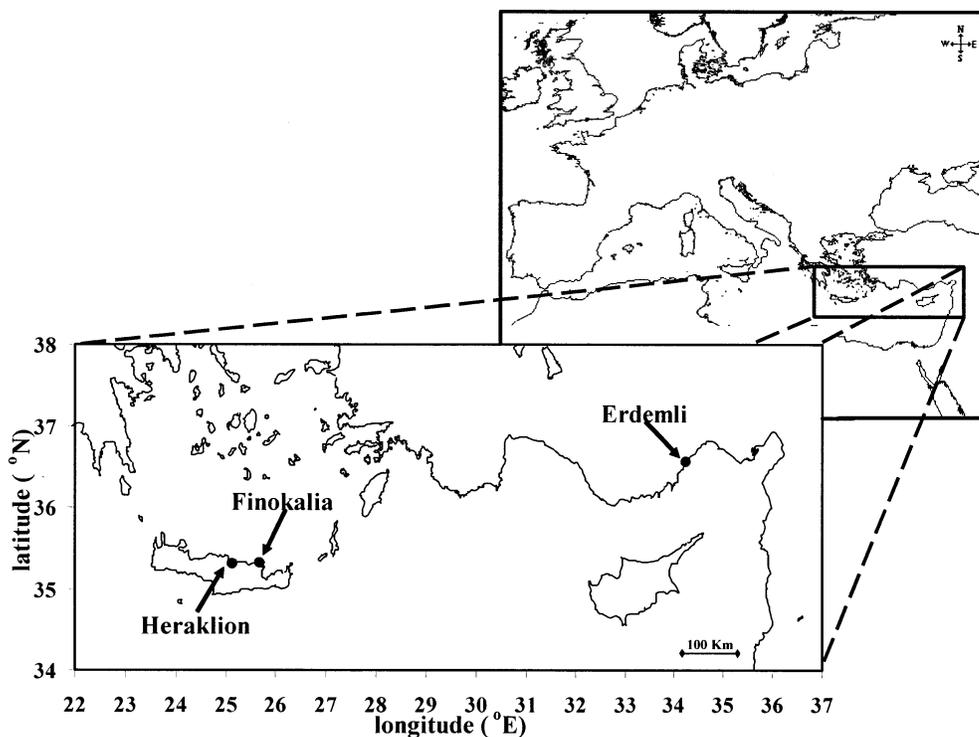
Fig. 1. Map indicating the location of the sampling sites referenced in the text.

Recently Kouvarakis et al. (2001) showed that airborne dissolved inorganic nitrogen (DIN) alone is more than sufficient to support new production in the southeast (SE) Mediterranean Sea because the sum of dry and wet deposition of DIN accounted for up to 370% of the particulate organic nitrogen (PON) measured using sediment traps. Kouvarakis et al. (2001) proposed that other elements (like P) might be responsible for the oligotrophic status of the eastern Mediterranean. Herut et al. (1999) reported the first estimate for total deposition of P to the SE Mediterranean by analyzing dissolved inorganic phosphorus (DIP) in rainwater, and inorganic phosphorus (IP) and leachable P in aerosols. Their work mainly focused on IP wet deposition, since only 20 aerosol filters were collected during the March–December 1996 study period. In a second study, Herut et al. (2002) performed leaching experiments for inorganic N and P on 41 aerosol samples. From these two studies they concluded that leachable fluxes of IP and inorganic nitrogen (IN, dry + wet) could support between 15 and 70% of the new production in the SE Mediterranean. This input might contribute significantly to the relatively high N/P ratios in the SE Mediterranean deep waters.

The current work presents and discusses results for inorganic P collected in aerosol and rainwater samples at two locations in the Levantine basin, eastern Mediterranean: (1) Finokalia, a coastal site in northern Crete, Greece, and (2) Erdemli, a coastal area in southeast Turkey. Samples were collected for an entire year at both sites. Therefore, an assessment of both the spatial and temporal variability of IP in the eastern Mediterranean atmosphere could be obtained. Compared to other coastal eastern Mediterranean sites, the island of Crete has the advantage of a central position in the SE Mediterranean far from Saharan and anthropogenic P emissions. Consequently, the data from Crete could be considered representative of the open SE Mediterranean sea.

The flux of DIP deposition is compared to DIN deposition at Finokalia in order to confirm for the whole eastern Mediterranean the existence of an unbalanced contribution of aeolian deposition of N and P to new production as reported by Herut et al. (1999). Finally the potential role of DIP on the productivity of the SE Mediterranean sea is discussed.

Methods

Sampling—The sampling sites where atmospheric deposition measurements were performed are depicted in Fig. 1.

Wet deposition: Rainwater was collected at both locations on an event basis using wet-only collectors with a lid activated by the rain sensor. Rain events were considered separate when they differed by >6 h. At Erdemli, samples were collected using an Andersen standard "acid rain sampler," whereas at Heraklion, a van Essen collector was used. Since IN and IP are both biologically labile, rainwater samples had to be treated immediately at the end of the rain event. For that reason, the collector on Crete was installed at the University 6 km south of the city of Heraklion, and the collector at Erdemli was installed on the roof of the laboratory 45 km west of the city of Mersin. After collection, 100–200 μl of chloroform were added as a biocide (Galloway et al. 1982), and the samples were stored in the freezer until analysis, performed within a month.

Aerosol sampling: On Crete, the aerosol samples were collected at Finokalia (25°60′E, 35°24′N), a small village on the northern coast of Crete 70 km east of Heraklion, between September 1999 and September 2000 (Fig. 1). Aerosol particles were collected on 47-mm-diameter, 0.45-μm-porosity Gelman Zefluor PTFE filters during a sampling duration of 2–3 d. The flow rate was 1.2 m^3 h^{-1} and the sampling efficiency was reported to be >99.99%. At Erdemli, the aerosol samples were collected on Whatman-41 filters (20 × 25 cm) using a high-volume sampler operating at a flow rate of 50 m^3 h^{-1} between January and December 1999 with sampling efficiency >95%. The aerosol collector was installed on a 21-m-high atmospheric collection tower a few meters from the rainwater sampler. Aerosol samples were collected daily except during weekends and holidays when multiday samples were taken. No size-specific cut-off was applied for either the Finokalia or Erdemli aerosol sampling. Therefore, all samples contained bulk aerosol. A comparison between the low-volume sampler used at Finokalia against the high-volume sampler used at Erdemli shows an agreement for the species distributed in the coarse mode (case of DIP, Ca^{2+} and NO_3^-) on the order of 20%. This agreement is satisfactory considering that it includes analytical errors, errors because of different sampling media, and so on. For the species distributed in the fine mode (i.e., NH_4^+) the agreement is better than 10%.

To calculate deposition velocities of DIP, the particle size distribution has to be taken into account because dry deposition is size dependent. Measurements for the particle size distribution of P were performed on nine samples at Finokalia using 6- (Sierra Andersen), 11- (Moudi), or 13-stage (Decati) impactors.

Dry deposition: Dry deposition of DIN and DIP was estimated based on the collection of particles on a flat surface covered by glass beads, positioned on a funnel, and installed 3 m above the ground as described by Kouvarakis et al. (2001). The glass bead system was situated at Finokalia close to the aerosol samplers and was exposed to the atmosphere for 1 to 2 weeks. After that period, the system was washed with ultrapure water (300 ml). The water was filtered through a 0.45-μm membrane filter and processed as a rainwater sample. Although this approach could have several limitations, it might provide useful information for the estimation of the deposition of aerosols. It should be noted that there is no well-established and accepted technique for the direct determination of dry deposition. The advantage of this technique compared to others using funnels or flat surfaces is that the multiple layers of glass beads can trap larger particles, thus avoiding resuspension.

More details on sample collections and local conditions of the sampling sites can be found in Mihalopoulos et al. (1997), Kubilay et al. (2000), Ozsoy et al. (2000), and Kouvarakis et al. (2001).

Chemical analysis—Sample pretreatment: A part (usually 1/8) of the Whatman-41 filters or a whole Teflon filter was cut in two equal sections. Each section was extracted in an ultrasonic bath with 50 ml of Milli-Q water for 45 min. The extraction efficiency of this method is >98% for all com-

pounds of interest as determined by a second extraction of the same sample. This result is in agreement with the dissolution experiments of P performed by Ridame and Guieu (2002), who reported that after a contact time of 10 min, the greater part of the dissolvable P was released. Chloroform (5–10 μl ml^{-1} sample) was added as a biocide in the sample extracts. One extract was used for total reactive P (TRP) determination and the other was filtered through a 0.45-μm membrane filter for ionic and DIP analysis.

Immediately after collection, the rainwater sample was split in three aliquots: One aliquot was used for pH determination, the second was filtered through a 0.45-μm membrane filter for ionic and DIP analysis, and the third was used for the TRP determination. All glassware and filters were pretreated and washed following the recommendations described in the Standard Methods for the Examination of Water and Wastewater (Eaton et al. 1995).

Analytical techniques: A Dionex AS4A-SC column with ASRS-I suppressor in autosuppression mode of operation was used for the analysis of the dissolved fraction of anions (including NO_3^- and PO_4^{3-}) and cations (including Na^+, Ca^{2+}, and NH_4^+). For cations, a CS12 column was used with a CSRS-I suppressor. The reproducibility of the measurements was better than 2%, and the detection limits were 0.1 μmol L^{-1} for NH_4^+, 0.05 μmol L^{-1} for PO_4^{3-}, and 0.02 μmol L^{-1} for NO_3^-.

Phosphorus was also determined spectrophotometrically as PO_4^{3-} using the stannous chloride method described in detail in the Standard Methods for the Examination of Water and Wastewater (Eaton et al. 1995). The detection limit was better than 0.05 μmol L^{-1} of P, and the reproducibility was better than 5%. The stannous chloride method compared successfully in the Crete laboratory to ion chromatography (slope $P_{IC}/P_{colorimetry}$ = 0.93, r^2 = 0.9, n = 47). The PO_4^{3-} results reported here were obtained using the stannous chloride method.

To examine the role of the extract medium in the dissolution of P and consequently on the levels of DIP, 47 aerosol samples with various ionic concentrations and various acidity levels (pH between 5.0 and 8.4) were extracted in an ultrasonic bath in both MQ-water and filtered P-free seawater for 45 min. PO_4^{3-} concentrations in the seawater extracts were in excellent agreement with those found in the MQ-water extracts (slope = 0.99, r^2 = 0.8, n = 47), indicating that the extraction medium (at least for our aerosol samples) had no significant influence on the reported DIP levels.

Phosphorus was also determined in the nonfiltered part of rainwater and aerosol extracts. This part of P is often reported in the literature as total reactive phosphorus (TRP; Eaton et al. 1995). To compare the TRP with the total inorganic phosphorus levels (TIP), 78 aerosol samples already analyzed for TRP were acid hydrolyzed using a mixture of H_2SO_4 (11 N) and HNO_3 (0.1 N) for TIP determination (Eaton et al. 1995). PO_4^{3-} levels were then measured in the TIP fraction. The aerosol samples used for that test (1/16 of the original Whatman-41 filter) were extracted in 25 ml of MQ, 0.25 ml of the acidic mixture described above were added, and the total was hydrolyzed at 100°C for 1.5 h. A good

Table 1. Details of the wet deposition measurements of DIP, TRP, and DIN at both locations.

Parameter	Location	Period	n	VWM (μmol L^{-1})	Flux*
DIP	Heraklion	Sep 99–Sep 00	41	0.13	64.6
TRP	Heraklion	As above	38	0.24	119.3
NO$_3^-$	Heraklion	As above	41	17.9	9.0
NH$_4^+$	Heraklion	As above	41	21.3	10.7
H$^+$	Heraklion	As above	41	5.0	
TRP	Erdemli	Feb 99–Dec 99	16	0.48	167.9
NO$_3^-$	Erdemli	As above	16	46.3	16.2
H$^+$	Erdemli	As above	41	1.0	

* In μmol m^{-2} yr^{-1} for P and mmol m^{-2} yr^{-1} for N species.

correlation was apparent between the two data sets ($r^2 = 0.9$, $n = 78$ with a mean TIP/TRP ratio = 1.49 ± 0.29), which allows for an extrapolation of the TRP values measured in the nonfiltered aerosol extracts to TIP with an error of 20%. Acid-hydrolyzed P could exist in the aerosols mainly as polyphosphate (Eaton et al. 1995).

All analyses, except on the rainwater samples collected at Erdemli, were preformed at the University of Crete using the techniques reported above. At Erdemli, PO$_4^{3-}$ and NO$_3^-$ determinations were performed using a segmented flow Technicon System II autoanalyzer. The subtracted blanks were <1% of the mean sample concentration for NO$_3^-$ and below the detection limit for PO$_4^{3-}$. Analytical accuracy was tested by comparison with QUASIMEME (Quality Assurance of Information for Marine Environmental Monitoring in Europe Laboratory Performance Studies) intercalibration program samples. The analytical precision was 7% for PO$_4^{3-}$ and 8% for NO$_3^-$, with a detection limit of 0.02 μmol L^{-1} and 0.05 μmol L^{-1} for PO$_4^{3-}$ and NO$_3^-$, respectively.

Filter blanks ranged from below the detection limit for all elements collected with the Gelman Zefluor PTFE filters to 0.2 μmol L^{-1} for PO$_4^{3-}$, 0.1 μmol L^{-1} for NO$_3^-$, and 8 μmol L^{-1} for NH$_4^+$ for the Whatman-41 filters. The reproducibility of the blank determination was 10–15%, and blank levels for Whatman-41 filters corresponded to 0.4, 2, 5, and 20% of the reported NO$_3^-$, NH$_4^+$, DIP, and TIP levels, respectively. All results reported in the manuscript have been corrected for blanks.

In the discussion below, the following terms will be used: DIP for the dissolved P of both rainwater and aerosol extracts, TIP for the total inorganic P of filters, and TRP for the total reactive inorganic P of the nonfiltered rainwater samples.

Results

Wet deposition measurements—Table 1 summarizes the wet deposition measurements at both locations.

Wet deposition of DIP and TRP: At Heraklion, 41 rainwater samples were collected during the same period of the aerosol sampling (September 1999–September 2000) and accounted for >95% of the annual precipitation amount (Heraklion meteorological office). The monthly volume weighted mean (VWM) of DIP ranged from 0.07 to 0.82 μmol L^{-1} (with an annual VWM of 0.13 μmol L^{-1}).

Taking into account the annual rainfall of 50 cm yr^{-1} at Heraklion, the annual wet deposition of DIP is estimated to be 64.6 μmol P m^{-2} yr^{-1}. This value is compared to 95 (63 for the reactive DIP fraction) and 258 μmol P m^{-2} yr^{-1} reported for the SE France (NW Mediterranean; Migon and Sadroni 1999) and Israeli coast (E Mediterranean; Herut et al. 1999), respectively.

TRP was determined in the rainwater both at Heraklion and Erdemli (Table 1). At Heraklion, the VWM of the TRP was found to be 0.24 μmol L^{-1}, (i.e., about two times higher than the DIP). However, the DIP/TRP ratio was not constant. Rainwater pH was found to be a key parameter influencing the DIP/TRP ratio. For pH between 4 and 6, the mean DIP/TRP ratio was 0.88 ± 0.15. A clear decrease was then observed, as a function of pH, reaching a minimum value of 0.32 ± 0.19 for pH between 8 and 9, a characteristic of Saharan-influenced rains. This trend could be explained either by the higher dissolution of P at lower pH or by the existence of more soluble P species associated with anthropogenic-influenced air masses (biomass burning, incineration of waste, fertilizers, etc.). The last explanation is the most likely as concluded by Herut et al. (1999).

At Erdemli, 16 samples were collected in parallel with the aerosol sampling (February 1999–December 1999) and accounted for 70% of the total precipitation amount (35 cm) during that period. The annual VWM of TRP was 0.48 μmol L^{-1}, two times higher than TRP measured at Finokalia. As indicated below, the much higher concentrations of TIP in aerosol samples (by a factor of 2.5) observed at Erdemli compared to Finokalia during the wet period could account for the difference in TRP levels observed in rainwater.

Wet deposition of DIN: In the rainwater samples collected at Heraklion, NO$_3^-$ and NH$_4^+$ were also determined. The VWM of NO$_3^-$ and NH$_4^+$ was 17.9 and 21.3 μmol L^{-1}, respectively, leading to an annual DIN wet deposition of 19.7 mmol N m^{-2} yr^{-1} (9 and 10.7 mmol N m^{-2} yr^{-1} for NO$_3^-$ and NH$_4^+$, respectively), in good agreement with the values of 22–27 mmol N m^{-2} yr^{-1} reported in the earlier work of Kouvarakis et al. (2001).

At Erdemli, only NO$_3^-$ was determined in rainwater samples. The VWM of NO$_3^-$ was 46.3 μmol L^{-1}, leading to an annual NO$_3^-$ wet deposition of 16.2 mmol N m^{-2} yr^{-1}, a factor of two higher than that reported at Heraklion.

Aerosol measurements—Aerosol levels of DIP and TIP: Figures 2 and 3 present the temporal variation and the var-
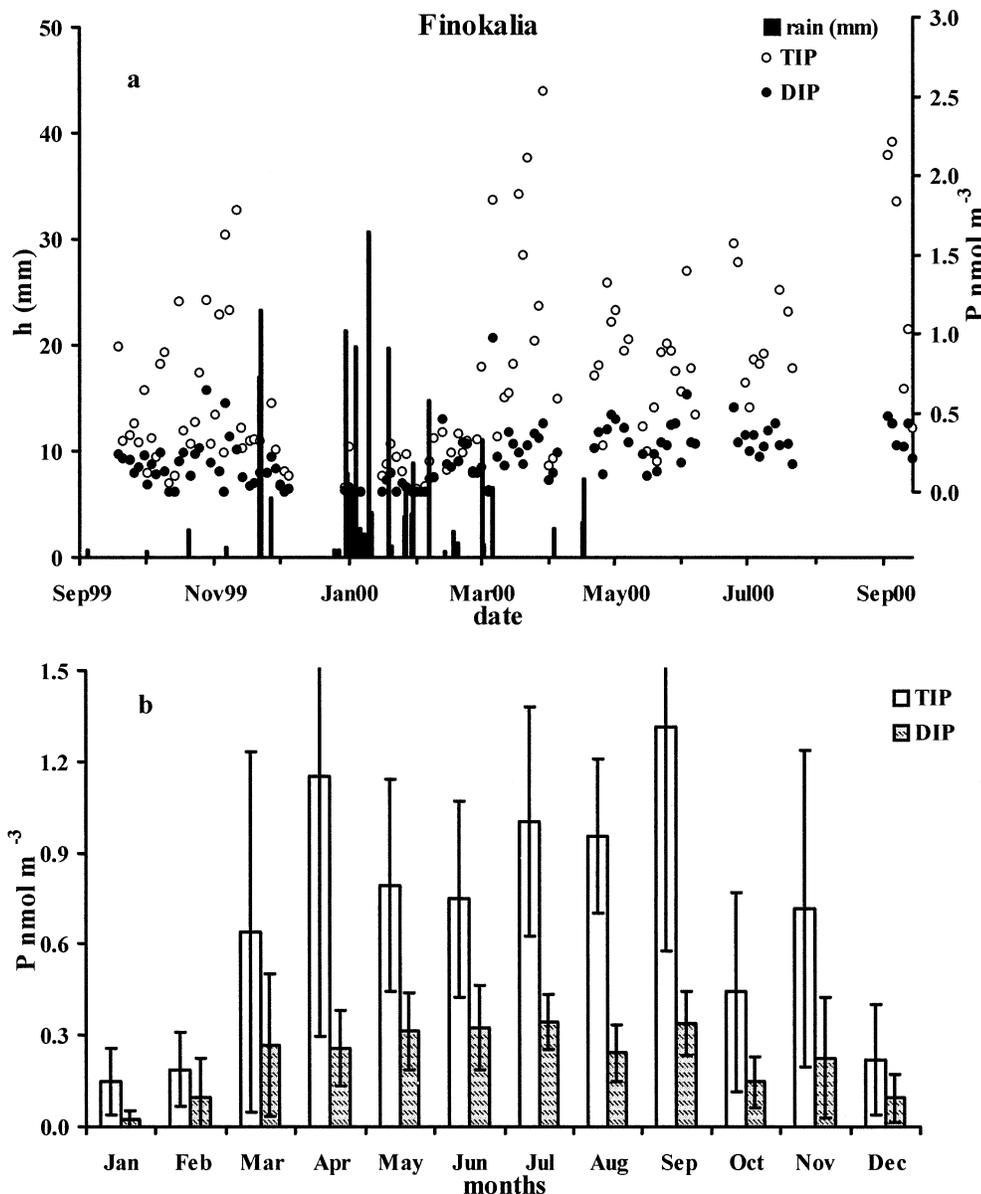
Fig. 2. Temporal variation of (a) aerosol TIP and DIP and rainfall and (b) monthly averaged aerosol TIP and DIP at Finokalia during the 1999–2000 period.

iation of monthly mean aerosol TIP and DIP concentrations during the whole period at Finokalia and Erdemli, respectively. The DIP and TIP levels measured at Finokalia range from below the detection limit (b.d.l.) to 0.97 nmol m^{-3} (geometric mean of 0.13 nmol m^{-3}; $n = 85$) and b.d.l. to 2.53 nmol m^{-3} (geometric mean of 0.43 nmol m^{-3}; $n = 85$), respectively (Fig. 2a,b). At Erdemli, the DIP and TIP levels range between 0.01 and 0.92 nmol m^{-3} (geometric mean of 0.26 nmol m^{-3}; $n = 195$) and 0.07 and 3.2 nmol m^{-3} (geometric mean of 0.77 nmol m^{-3}; $n = 194$), respectively (Fig. 3a,b).

Table 2 presents the TIP and DIP values at both locations as a function of season. At Finokalia, both DIP and TIP present a significant seasonal variation, with higher values being observed during the summer. On the other hand, no

clear seasonal trend for both DIP and TIP is observed at Erdemli, although lower values are evident during winter (Table 2).

The TIP and DIP values observed at Finokalia and Erdemli (Table 2) are comparable with the values reported in the literature. In the SE Mediterranean, Herut et al. (1999) reported TIP values averaging 0.65 and 2.91 nmol m^{-3} for samples collected under European and African/Arabian influence, respectively. However, no information on the seasonal trend of TIP can be derived from this data set. Bergametti et al. (1989, 1992) reported the most complete, up to date work on the seasonal variation of TIP in the western Mediterranean. Their values (geometric mean of 0.33 nmol m^{-3}) presented a clear seasonal trend (similar to that observed at Finokalia) and are in good agreement with our
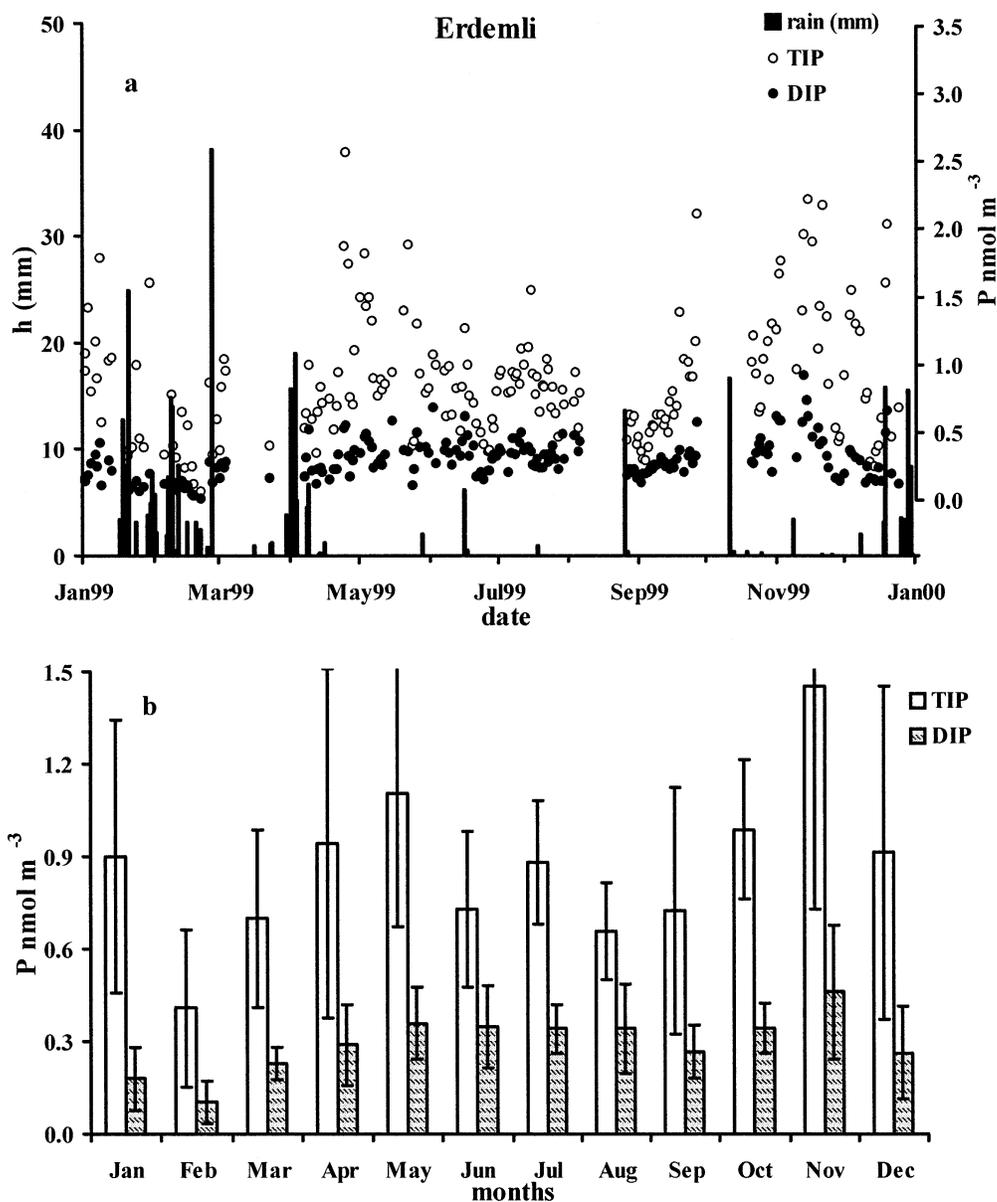
Fig. 3. Temporal variation of (a) aerosol TIP and DIP and rainfall and (b) monthly averaged aerosol TIP and DIP at Erdemli during the 1999 period.

observations at Finokalia and Erdemli (mainly during summer). To our knowledge, the DIP values reported here are the first complete data set reported for the eastern Mediterranean.

In general, DIP followed TIP variation (r^2 = 0.59 and 0.52 for Finokalia and Erdemli, respectively) with a DIP/TIP ratio of 0.35. However, a closer examination of this ratio for samples influenced by Sahara dust showed much lower values (~0.1–0.3).

To investigate the role of the air mass origins on the measured TIP and DIP levels, 5-d trajectory analyses were performed on all samples collected at both Finokalia and Erdemli. Because local precipitation could strongly influence atmospheric P concentrations, we did not consider the samples collected when local precipitation occurred. Backward

trajectories were calculated using the HYSPLIT_4 (hybrid single-particle Langrangian integrated trajectory) model (http://www.arl.noaa.gov/ready/hysplit4.html). In Table 2, results of the classification of atmospheric TIP and DIP concentrations in relation to the origin of the sampled air masses are presented. At both sites, the SW sector, corresponding to the Sahara, represented TIP levels higher (by a factor of two) than the European (NE or NW) sectors. At Finokalia and Erdemli, no significant difference was observed between the NW and NE sectors. Of particular interest is the variation of the DIP and the DIP/TIP fraction as a function of the sectors (Table 2). The lowest values for the DIP/TIP ratio are associated with the SE and SW sectors, and the highest with the N sectors. This result is in good agreement with the observations of Herut et al. (1999) and with the rainwater

Table 2. Distribution of TIP, DIP, and DIN (geometric mean) as a function of sector and season in aerosol samples collected at both locations.

	TIP (nmol m^{-3})	DIP (nmol m^{-3})	DIP/TIP	NO$_3^-$ (nmol m^{-3})	NH$_4^+$ (nmol m^{-3})
Finokalia					
Season					
Winter	0.13	0.03	0.23	8.9	16.4
Spring	0.57	0.23	0.40	12.4	21.4
Summer	0.80	0.31	0.39	27.6	41.0
Autumn	0.50	0.18	0.36	15.0	17.2
Annual mean	0.43	0.13		16.0	24.0
Sector					
N/NE	0.63	0.24	0.37	15.3	36.6
NW	0.70	0.29	0.42	17.6	33.2
W	0.60	0.24	0.40	20.5	18.4
SW	1.18	0.26	0.22	17.2	10.7
Erdemli					
Season					
Winter	0.62	0.15	0.24	30.7	75.0
Spring	0.87	0.31	0.36	76.3	146.6
Summer	0.76	0.32	0.43	72.7	142.9
Autumn	0.87	0.29	0.33	51.2	108.5
Annual mean	0.77	0.26		57.7	118.3
Sector					
N/NE	0.84	0.34	0.40	64.7	133.4
NW	0.74	0.26	0.35	39.3	91.1
W	0.62	0.21	0.34	76.4	139.4
SW	1.66	0.38	0.23	106.2	129.9
SE	0.94	0.20	0.22	29.5	84.8

results presented earlier, indicating the lowest solubility of P in dust influenced air masses. Therefore, despite the fact that dust events can transport large amounts of P (up to a factor of two to three higher than in air masses from Europe), the low solubility of P in dust-influenced samples could decrease the potential role of dust as a source for DIP in seawater.

To better understand the factors controlling the distribution of TIP and DIP species in aerosols, a meteorological background is presented in the context of a 5-d backward trajectory, performed at both Finokalia and Erdemli. The SE Mediterranean region is characterized by the existence of two well-distinguished seasons equally distributed throughout the year. The dry season (from April/May to September/ October) and the wet season (from October to April). At both locations, the dry season is mainly characterized (up to 90%) by high-speed winds of N/NE/NW direction (central and eastern Europe and Balkans) (Mihalopoulos et al. 1997). Thus, it is not surprising that the TIP and DIP concentrations were very similar at both locations during the dry season. Indeed, the corresponding geometric means of TIP (DIP) values were 0.81 nmol m^{-3} (0.29) and 0.78 nmol m^{-3} (0.30) at Finokalia and Erdemli, respectively. Also during summer, the corresponding TIP and DIP values were similar (Table 2). However, a month-by-month comparison reveals some differences between the two sites (Figs. 2,3), which are likely due to different years in the comparison.

During the wet season, the prevalence of the N/NW sector is less pronounced, especially during the transitional periods (September–November and March–May), and important

transport from the Sahara (S/SW winds, occurrence up to 20–25%) takes place at both locations (Mihalopoulos et al. 1997; Kubilay et al. 2000). There are two reasons that could explain the differences in TIP and DIP levels observed at both locations during the wet season, as depicted in Figs. 2 and 3. First, during the December–February period, trajectory analysis showed that Erdemli was highly influenced by air masses originating in the arid areas of eastern Turkey and the Arabian Peninsula, which was not the case at Finokalia. This situation can explain the observed difference between the TIP and DIP levels at Finokalia and Erdemli during December 1999 (1–18 December), since >80% of the samples collected at Erdemli were associated with air masses coming from arid areas (mainly from the Arabian peninsula). Another important parameter was the difference in the precipitation amount. During the December period at Finokalia, the precipitation amount was 46 mm compared to only 5 mm at Erdemli. Also, in January 2000, the precipitation amount at Finokalia was 110 mm, while at Erdemli it was only 44 mm.

The TIP levels observed at both sites were significantly correlated with the non–sea salt Ca^{2+} (nss-Ca^{2+}) measured in aerosol samples (Fig. 4). Although the two data sets are in good agreement, the slope calculated for Finokalia was significantly higher (1.86×10^{-2}; $r^2 = 0.76$; $p < 0.0001$) than that for Erdemli (1.4×10^{-2}; $r^2 = 0.60$; $p < 0.0001$), thus indicating a smaller terrigenous influence at Finokalia than at Erdemli, a difference in the composition of P sources, or both. A similar correlation for TIP and nss-Ca^{2+} has been reported by Herut et al. (1999) (with a slope of 1.3×10^{-2}
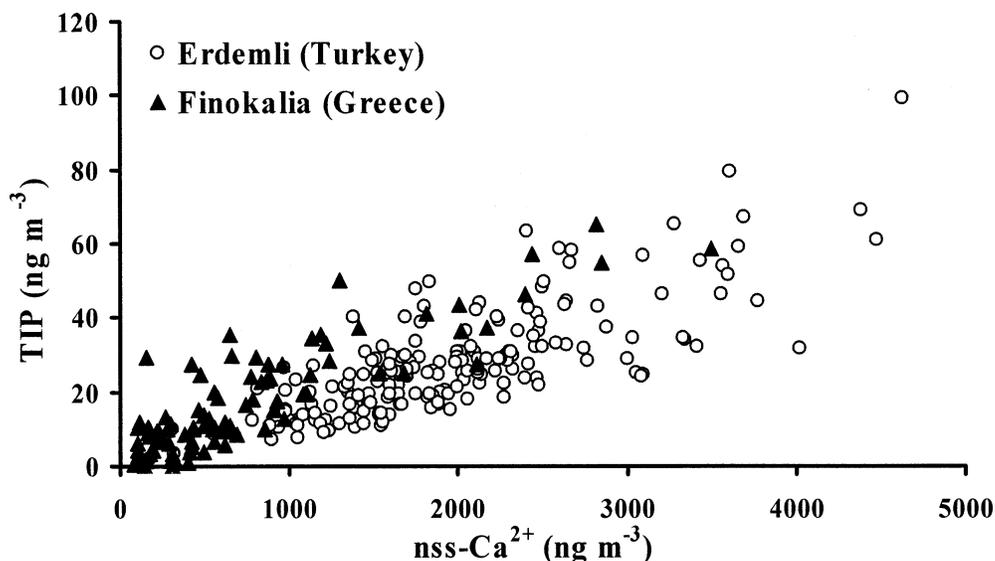
Fig. 4. Relationships between TIP and nss-Ca^{2+} for both Finokalia and Erdemli samples.

as derived from the curve reported in their fig. 6). A significant correlation, determined by filter weighting, was observed at Finokalia between TIP and total suspended particles (TSP) (TIP [nmol m^{-3}] = TSP [μg m^{-3}] × 0.77 − 6.67, $n = 83$, $r^2 = 0.67$, $p < 0.0001$). The long-term data for Finokalia resulted in a mean TSP value of 35 μg m^{-3}. Application of this TSP value to the above equation leads to an annual TIP mean of 0.65 nmol m^{-3}, in good agreement with our TIP observations, and supports the representativeness of the TIP data presented here. The validity of this equation to other Mediterranean locations needs further investigation.

To distinguish between soil-derived and anthropogenic phosphorus, several authors used Al as a crustal element tracer and a mean crustal P/Al ratio of 0.013 (*see,* for instance, Bergametti et al. 1992). At Erdemli, monthly mean Al concentrations ranged between 10.8 and 54.5 nmol m^{-3} (mean of 26.7 nmol m^{-3}). Al was not systematically measured in all of our samples at Finokalia. Thus, to obtain an idea of the relative contribution of terrigenous sources to P levels, we used monthly Al concentrations derived either from long-term data that exist for Finokalia (period 1996–1998, $n = 343$) or from the very significant correlation between Ca and Al observed during the 1996–1998 period and Ca measurements in the 1999 samples. Both procedures lead to similar results. Soil-derived phosphorus was thus found to contribute between 25 and 34% of the TIP levels at Finokalia and Erdemli, respectively. These values compare quite well (especially for Finokalia) with the Corsican value of 23% reported by Bergametti et al. (1992).

Aerosol concentrations of DIN: NO$_3^-$ and NH$_4^+$ concentrations also were determined for aerosol samples collected at Finokalia and Erdemli. The results are reported in Table 2 as a function of season and air mass origin. Several patterns emerge.

1. A clear seasonal variation is observed at both locations and for NO$_3^-$ and NH$_4^+$, with higher values being observed during summer. At Erdemli, high values of NO$_3^-$ and NH$_4^+$ are also observed during spring.

2. The levels of DIN reported at Finokalia are in good agreement with those reported by Kouvarakis et al. (2001) for the 1996–1999 period. The levels of DIN at Erdemli are higher by a factor of 3.5–5 compared to those at Finokalia and comparable to the levels reported by Herut et al. (2002) for Israel. Savoie et al. (1989) reported that Whatman 41 filters can collect HNO$_3$ in addition to NO$_3^-$ with an efficiency of >95%. This is not the case for Teflon filters. Considering that gaseous HNO$_3$ levels at Erdemli are comparable to NO$_3^-$ as in Finokalia (Kouvarakis et al. 2001), a significant part of the difference regarding the NO$_3^-$ levels can be explained. However, this could not be the only reason because annual NO$_3^-$ wet deposition at Erdemli was a factor of two higher compared to Heraklion. Local anthropogenic activities at Erdemli, like traffic and fertilizer use, as reported by Ozsoy et al. (2000), could also account for the high NO$_3^-$ and NH$_4^+$ levels.

3. At Finokalia, no particular sector is significantly preferred for the NO$_3^-$ transport. At Erdemli, the NO$_3^-$ levels associated with the transport along the SW sector (Sahara desert) were higher by a factor of two to three compared to those associated with the transport along the N sectors (Europe plus Russia). These results are in very good agreement with the observations by Kouvarakis et al. (2002) and Ozsoy et al. (2000). These authors attributed this tendency to an uptake of HNO$_3$ by dust (Dentener et al. 1996), which suggests the important role of interactions between gaseous DIN species (mainly HNO$_3$) with dust or sea salt particles in the area. The lowest values of NO$_3^-$ at Erdemli were observed under the SE influence (Arabian peninsula and Anatolia), denoting a lower NO$_3^-$ source strength, but one must keep in mind that this sector occurs only during winter, thus possibly resulting in biased concentrations.
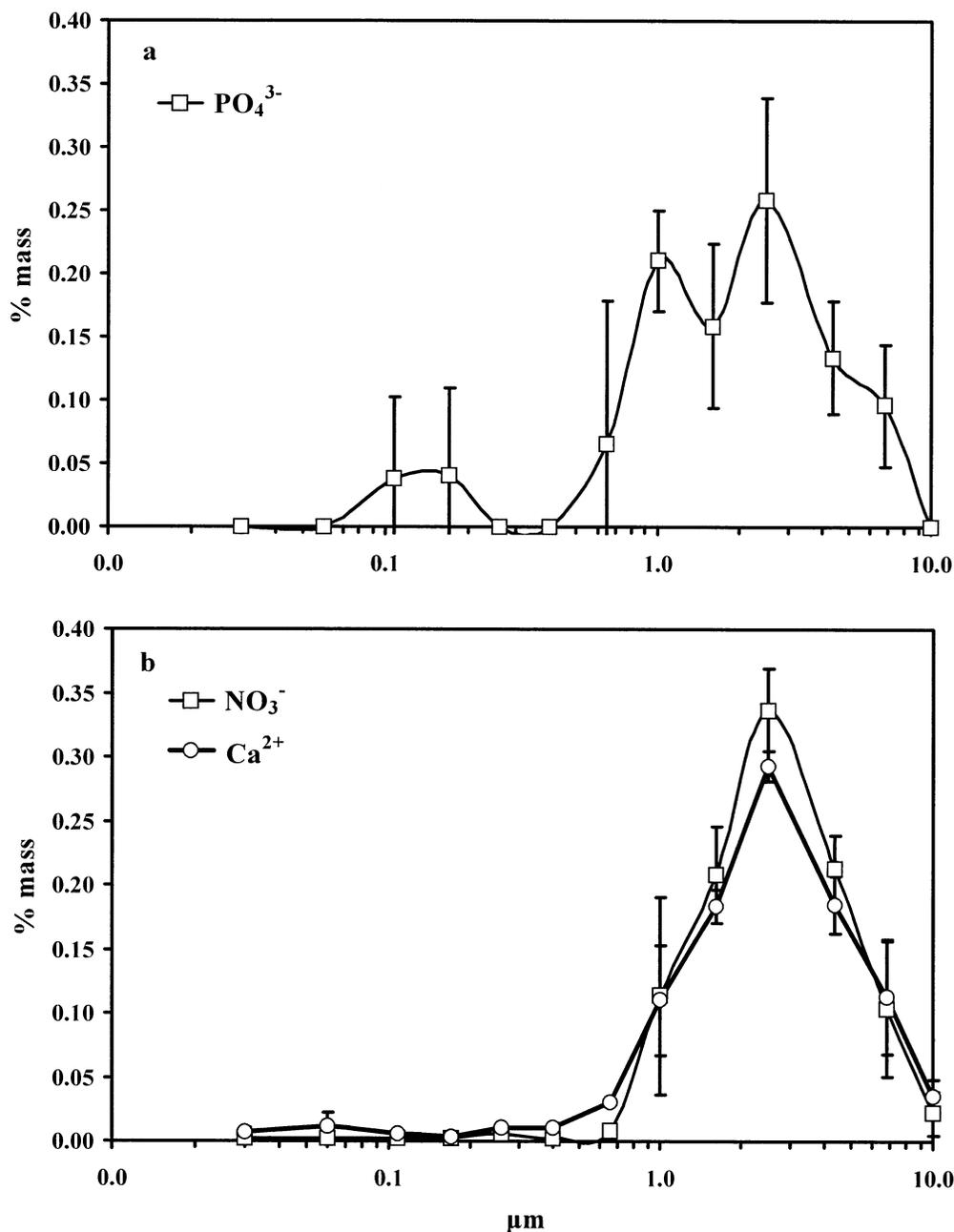
Fig. 5. Percent mass distribution of (a) PO_4^{3-} and (b) NO_3^- and Ca^{2+} at Finokalia as a function of diameter.

4. An interesting trend is obtained by calculating NH_4^+/NO_3^- ratios for different sectors and for both stations. The NH_4^+/NO_3^- ratio decreases from about 2 for the N sectors to 1 for the SW sector. This could be due to either lower NH_4^+ sources for SW sectors, increased uptake of HNO_3 by aerosols under SW sector influence because of their higher alkalinity, or both.

Total deposition of DIP and DIN in the eastern Mediterranean Sea—The dry deposition (F_d) of DIP can be calculated as the product of atmospheric DIP concentration (C_d) and its deposition velocity (V_d) obtained from the literature.

$$F_d = V_d \times C_d$$

Because dry deposition of particles is size dependent, measurements of particle size distribution of DIP were performed using 6- (Sierra Andersen), 11- (Moudi), or 13-stage (Decati) impactors. At Finokalia, nine size-segregated samples were collected during summer under absence of any dust events. The distribution of DIP shows bimodal characteristics with a small fine-mode aerosol fraction as well as a dominant coarse-mode component. In other words, more than ~85% of DIP was associated with the coarse particles ($d > 1 \mu m$; Fig. 5). It is interesting to note that DIP distri-

Table 3. Seasonal variation of dry and wet deposition of DIN and DIP species at both locations.

Season	Dry DIP (μmol m^{-2} d^{-1})	Wet DIP (μmol m^{-2} d^{-1})	Dry DIN (μmol m^{-2} d^{-1})	Wet DIN (μmol m^{-2} d^{-1})	Wet NO$_3$* (μmol m^{-2} d^{-1})	Dry DIN/DIP	Total DIN/DIP
Crete Island							
Winter	0.05	0.55	18.24	143.7	—	348.9	268.9
Spring	0.40	0.07	25.15	40.1	—	63.3	139.6
Summer	0.54	0	54.85	0	—	102.4	102.4
Autumn	0.31	0.13	28.87	31.3	—	92.8	136.4
Annual mean†	125	68.4	11.60	19.7	—	151.9	161.8
Erdemli							
Winter	0.26	n.d.	65.97	—	91.9	255.6	—
Spring	0.54	n.d.	157.19	—	57.0	293.8	—
Summer	0.56	n.d.	150.39	—	0	268.9	—
Autumn	0.49	n.d.	107.28	—	28.9	217.3	—
Annual mean*	167.9	n.d.	43.88	—	16.2	261.3	—

n.d., not determined (only TIP has been measured in rainwater, *see text*).
* Only NO$_3^-$ has been measured in the rainwater.
† Annual deposition in μmol m^{-2} yr^{-1} for P and mmol m^{-2} yr^{-1} for N species.

bution was found to be similar to that of NO$_3^-$ and Ca^{2+} (Kouvarakis et al. 2002). For nitrate, the reaction of gaseous HNO$_3$ with dust and NaCl in our coastal environments shifts nitrate from gas phase and fine-mode aerosol to the coarse mode through the formation of Ca(NO$_3$)$_2$ and NaNO$_3$. These reactions are expected not only to enhance dry deposition through more efficient gravitational settling of large particles but also to increase the efficiency of precipitation scavenging via inertial impaction (*see also* Spokes et al. 2000). Similar reactions could occur also for P.

Duce et al. (1991) proposed a V_d of 2 cm s^{-1} for compounds primarily occurring in the coarse fraction like P. From the P aerosol measurements and the total deposition given by Bergametti et al. (1992) for the dry period, a mean V_d of 2.7 cm s^{-1} can be derived. Finally at Finokalia using the DIP aerosols measurements and the dry DIP deposition obtained using the glass bead system (data not shown), a mean V_d of 2.3 cm s^{-1} is estimated. In the following discussion and for comparison purposes, a V_d of 2 cm s^{-1}, similar to that used by Herut et al. (2002), will be used for DIP dry deposition estimates, keeping in mind that these estimates can result in uncertainty by a factor of two to three in the calculated flux (Duce et al. 1991).

Table 3 recapitulates the variation (on both a seasonal and annual basis) of DIP and DIN deposition (wet and dry) at both stations. The calculated annual dry deposition of DIP at Crete is estimated to be 125 μmol P m^{-2} yr^{-1}, which is a factor of two higher than the wet deposition of DIP. The dry deposition of DIP at Erdemli was 167.9 μmol P m^{-2} yr^{-1}.

The dry deposition of DIN was estimated using $V_d = 2$ cm s^{-1} and 0.2 cm s^{-1} for NO$_3^-$ and NH$_4^+$, respectively. For NO$_3^-$, this V_d is two times higher than that used by Kouvarakis et al. (2001) because NO$_3^-$ has a similar size distribution as DIP; thus, a similar V_d should be used. Moreover, Kouvarakis et al. (2001) pointed out that their V_d estimate gave results two times lower than obtained using the glass bead approach. The annual dry deposition of DIN is calculated to be 11.6 and 43.9 mmol N m^{-2} yr^{-1} for Finokalia and Erdemli, respectively. Kouvarakis et al. (2001) also cal-

culated that the dry deposition from gaseous HNO$_3$ and NH$_3$ species (not continuously measured during this work) could be as high as the dry deposition from aerosol DIN species (NO$_3^-$ and NH$_4^+$). Thus, the total dry DIN deposition considering aerosol and gaseous species should be higher by at least a factor of two than that calculated using only the aerosol phase.

Discussion

Atmospheric P deposition, atmospheric DIN/DIP ratio, and seawater productivity—It has been suggested that atmospherically derived nutrients are an important component of bioavailable nutrients to the upper water column, particularly in oligotrophic seas and during seasons of low vertical mixing (Prospero et al. 1996; Paerl 1997). In the Mediterranean, especially, studies have shown that the input of atmospheric nutrients by rain or dust can trigger phytoplankton growth during oligotrophic conditions (Martin et al. 1989; Ridame 2001).

Recently Kouvarakis et al. (2001) indicated that the sum of dry and wet deposition of DIN accounts for up to 370% of the PON measured using sediment traps. In the study presented in this manuscript, annual atmospheric DIN deposition in Crete ranged from 31.3 to 42.9 mmol N m^{-2} yr^{-1} (wet deposition + aerosol DIN deposition and wet deposition + aerosol and gaseous dry DIN deposition, respectively), assuming an equal contribution of the gaseous HNO$_3$ and NH$_3$ species to the total dry deposition as reported by Kouvarakis et al. (2001). Even if the lowest figure is considered, atmospheric DIN deposition is higher by a factor of three than the annual flux of PON measured (10.4 mmol N m^{-2} yr^{-1}) using sediment traps deployed in the Cretan Sea (Kouvarakis et al. 2001). A similar PON value was measured in the Cretan Sea (Tselepides pers. comm.) during the time of this study indicating that the SE Mediterranean was not N limited (at least from September 1999 to September 2000). This result is in agreement with Krom et al. (1991), who proposed that P could be responsible for the oligotrophic status of the eastern Mediterranean.

Because atmospheric deposition of DIN alone is more than sufficient to support new production in the SE Mediterranean Sea, the atmospheric source could cause (at least partially) the anomalously high N/P ratio in eastern Mediterranean seawater.

Of particular interest is the variability of the DIN/DIP ratio in rainwater and aerosols, since both DIN and DIP can be transported to seawater via wet and dry deposition. Table 3 presents the seasonal variation of DIN/DIP deposition ratio for both locations. The DIN/DIP ratio in aerosol samples ranges between 63 and 349 at Crete and 217 and 294 at Erdemli. Even when total deposition is considered at Crete, the DIN/DIP ratios range between 102 and 269, with no sector preference. Thus, DIN/DIP ratios are higher by a factor of 4–22 than the Redfield N/P ratio of 16. This result confirms the observations by Herut et al. (1999) that atmospheric inputs of bioavailable N and P represent an unbalanced contribution to new production and reinforce the unusual N/P ratios and possible P limitation in the SE Mediterranean.

Based on the results reported in Table 3, 193.4 μmol P m^{-2} yr^{-1} is estimated to be deposited annually by wet and dry deposition in the Cretan sea. If all of this DIP is available to phytoplankton for new production and if a Redfield C:P ratio of 106 is used, we estimate that the atmospheric DIP flux can support primary production of 20.5 mmol C m^{-2} yr^{-1}.

During summer and autumn, when the water column is stratified and the contribution of nutrients from deeper layers are reduced, the atmospheric influence on new production is maximized. Sediment traps deployed in the Cretan Sea during two yearly surveys (1995 and 1997–1998) revealed that during the summer–autumn period, new production ranged from 0.15 to 0.23 mmol C m^{-2} d^{-1} (Kouvarakis et al. 2001). By comparing these values to those supported by the atmospheric flux of DIP reported in Table 3 during summer and autumn, we estimate that atmospheric DIP deposition represents 20 to 38% of the P used for the new production. Thus, atmospheric deposition of DIP could act as a significant source of phosphorus input during the stratified period. The above result is in agreement with the conclusions by Bergametti et al. (1992) for the northwestern Mediterranean.

DIP concentrations observed in aerosols both at Crete and Erdemli during the summer–autumn period indicate that our conclusions on the role of atmospheric DIP deposition on new production in the Cretan Sea could have a more regional significance. Indeed, if the values of new production measured in the Cretan sea stand for the entire Levantine Sea, atmospheric DIP deposition at Erdemli during summer and autumn represents at least 22–40% of the P used for the new production.

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