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Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: Sources, fluxes, and possible impact

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Abstract

Estimates of the sources and wet deposition fluxes of inorganic nutrients (PO_4^{3-}, NO_3^-, NO_2^-, NH_4^+) have been made using a long-term wet atmospheric deposition measurement at three sites along the Mediterranean coast of Israel. The nutrient composition in rainwater indicated a dominant anthropogenic source for NO_3^- and NH_4^+ and a continental, natural, and anthropogenic, rock/soil source for PO_4^{3-}. The calculated long-term dissolved inorganic N (IN) and inorganic P (IP) fluxes were 0.28 and 0.009 g m^{-2} yr^{-1} to the coastal zone and estimated as 0.24 and 0.008 g m^{-2} yr^{-1} to the Southeast (SE) Mediterranean, with a possible increasing pattern of the annual dissolved IN fluxes. Concentration of total and seawater leachable IP (LIP) from dust was examined on 20 Whatman 41 filters collected during 1996. The mean total IP concentration in dust was 0.13 ± 0.11% (geomean = 0.09%), with a mean of 387 ± 205 μg IP per g of dust leached by seawater. LIP from dust varies between 6 and 85% (mean of 38%) of the dry total IP. Dust of desert-type (Saharan) events exhibited lower LIP solubility in seawater (~25%, median) than air masses of European origin (~45%, median). The calculated ratio of wet deposition to total (wet and dry) deposition here of 0.2 showed the importance of dry deposition of P in the SE Mediterranean basin compared to atmospheric inputs into the northwestern basin. The total IP and seawater LIP fluxes from dry deposition were estimated as 0.04 and 0.01 g m^{-2} yr^{-1}, respectively. Atmospheric inputs of bioavailable N and P represent an imbalanced contribution to the new production of 8–20 and 4–11%, respectively, and reinforce the unusual N : P ratios (~27) and possible P limitation in the SE Mediterranean.

Transport via the atmosphere is recognized as an important route by which nutrients and particles are delivered to the sea surface. Estimates of the atmospheric fluxes of metals and nutrients to the oceans suggest that the atmosphere can be a major source in terms of mass (Duce et al. 1991; Prospero et al. 1996) and plays a major role in the oceanic biogeochemical cycling (Jickells 1995; Paerl 1997). The effect of such atmospheric input is expected to be particularly important in oligotrophic oceanic areas (Fanning 1989; Owens et al. 1992) and semienclosed seas such as the Eastern Mediterranean, which is bordered to the north by industrialized European countries and to the south by the North African desert belt. The principle available data on atmospheric inputs into the Mediterranean have been reviewed by GESAMP (1989) and recently by Guerzoni et al. (in press). Most of these data refer to the western basin (Loye-Pilot et al. 1990; Begametti et al. 1992; Migon and Sandroni in press), and almost no information is available on the eastern basin (Herut and Krom 1996). Large amounts of desert dust are exported from the Sahara and surroundings to the North Atlantic Ocean and the Mediterranean Sea (Moulin et al. 1997). Moreover, the area around the Mediterranean is now used extensively for agriculture. The process of ploughing has increased the amount of topsoil exposed to the atmosphere and thus available to be carried into the air as dust (Prospero et al. 1996). There has also been widespread use of chemical fertilizers that contain both N and P. This input, together with the long-range transport of anthropogenic substances from Europe, is expected to be particularly important in geochemical cycling in the Mediterranean (Martin et al. 1989).

Studies have shown that the contribution of nutrients from the atmosphere has increased as a result of anthropogenic activities (Cornell et al. 1995; Galloway et al. 1996). These anthropogenic increases in nutrient input are thought to increase the total amount of carbon fixed in the upper ocean and thus balance in part the global atmospheric increase in carbon dioxide. It has been suggested that atmospheric deposition of anthropogenic nitrogen to those areas of the ocean located downwind of populated and urbanized regions can lead to or shift toward greater phosphorus limitation (Fanning 1989). Atmospheric inputs of nutrients can result in a significant contribution to the new (export) production in oceanic surface waters, especially in oligotrophic areas such as the Eastern Mediterranean. Although rainfall events in the Eastern Mediterranean occur only in winter, it has

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been shown that there is sufficient light even in January–February for the annual phytoplankton bloom to occur (Krom et al. 1992). Regardless of the nutrient source, their depletion and dilution in the Eastern Mediterranean Basin results from the following main factors (Berman et al. 1984; Salihoglu et al. 1990): (1) its general west–east antiestuarine circulation with an inflow of nutrient-depleted surface waters from the Atlantic and a counterbalancing outflow of relatively nutrient-enriched Levantine intermediate and deep waters; (2) an arid climate with little natural freshwater (nutrient-rich) run-off, most of which is now intercepted for use by man; and (3) a narrow continental shelf capable of only limited benthic-pelagic recycling of nutrients.

In the present study, wet atmospheric deposition was sampled at three sites along the Mediterranean coast of Israel. The samples were analyzed for nutrients and major elements and the results used to identify sources of the rainwater and wet deposition fluxes of inorganic nitrogen and phosphorus. The additional contribution of dry fallout to the total atmospheric flux of P was estimated based on seawater leachable and total inorganic phosphorus measurements, and the impact of atmospheric nutrients on new production in the Southeast (SE) Mediterranean was assessed. These data may be used as a baseline for future work aimed at quantifying anthropogenic changes to this most sensitive ocean basin and reassessing its nitrogen and phosphorus budget (Bethoux et al. 1998).

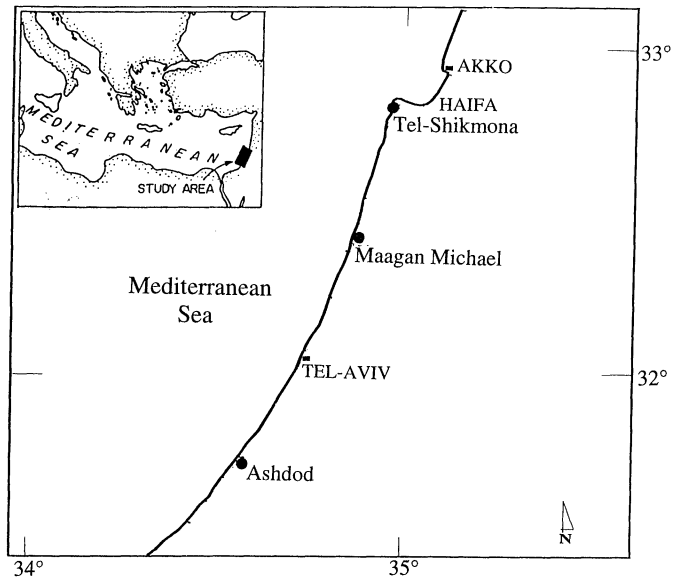

Fig. 1. Location of sampling stations along the Mediterranean coast of Israel.

Methods

Sampling and leaching experiments—The atmospheric sampling of the rainfall was performed on the roof of the National Institute of Oceanography at Tel-Shikmona (TS) (located on the shore, 22 m above sea level), at Ashdod (ASH, ~2.5 km from shore, ~30 m above sea level) and at Maagan Michael (MM, ~900 m from shore, 13 m above sea level). These sites provided samples in a north–south transect along the Mediterranean coast of Israel (Fig. 1). In TS and ASH, rain was collected on an event basis, while in MM rainwater samples were retrieved on a weekly basis. Rainwater samples were collected at TS from 1992 until March 1998, at MM from January 1996 until March 1998, and at ASH from November 1995 until March 1998. A total of 187, 36, and 67 rainwater samples were collected at each site, respectively.

Rainwater samples were collected using plastic funnels (25-cm diameter) and bottle-type collectors (100-cm height) as recommended by UNEP (1992). At ASH station, the rain was collected using a Graseby automatic collector. Subsamples were immediately frozen for nutrient determination, and pH was measured on a further subsample. The samples for nutrients were collected in 15-ml plastic scintillation vials that had been prewashed with 10% hydrochloric acid and rinsed thoroughly with double distilled water. The total amount of rain collected in each event was measured. The remaining rainwater samples were then filtered (through Whatman 42) and stored in a refrigerator at 4°C for major element analyses (Na^+, Ca^{2+}, Cl^-, SO_4^{2-}).

Leaching experiments were performed to evaluate the amount of seawater leachable inorganic P (LIP) and total inorganic P (IP) from total suspended particles (TSP) collected on Whatman 41 filters by high-volume sampler at TS between March and December, 1996. After collection, the filters were dried in a desiccator for 72 h before being reweighed. The filter weights were inaccurate due to their tendency to immediately adsorb humidity. Twenty dust filter subsamples (2 cm^2) were soaked and shaken for 3 h in 15 ml of 0.2-μm filtered SE Mediterranean surface seawater (collected by the R.V. Shikmona during 1997, 20 km off the Israeli coast). Another subsample (2 cm^2) was shaken for 4 d with 15 ml 1N HCl to estimate total IP and Ca content. Al concentrations were measured on a third subsample (10 cm^2) by total digestion with HF following the procedure of ASTM (1983). The filter blank and bottle adsorption effect were calculated as <5% of the total IP concentrations and insignificant (undetected) in the seawater LIP. Prior to the experiments, it was estimated that the leaching process (kinetics) reach close to equilibrium after 2 h.

Total IP concentrations were also measured on an additional 22 Whatman Ultra-pure Quartz Microfibre (QMA) filters collected by the same high-volume sampler at TS during February 1995–November 1996. Fifteen of the filters were collected together with the Whatman 41 filters (during 1996) but at different dates. The weights of TSP for the QMA filters were measured as given above and were found accurate. The total IP measurements were performed on subsamples (2 cm^2) that were shaken for 4 d with 15 ml 1N HCl. The filter blanks were found too high to perform the seawater LIP measurements. The filter blanks in the HCl digestion procedure for the determination of total IP were approximately 50% of the total IP concentrations.

Surface (1000 mb) air mass back trajectories (3–5 d) for the TS high-volume samples, both Whatman 41 and QMA, were calculated using the software Trajplot (Canadian At-

mospheric Environmental Agency). We classified the air masses into two geographical categories: (1) West–East European and (2) North African and Saudi Peninsular.

Chemical determinations—pH in rainwater was determined immediately after retrieving the sample using a Radiometer pH Meter. Dissolved nutrients (PO_4^{3-}, NO_3^-, NO_2^-, NH_4^+) were determined by a segmented flow Technicon System II autoanalyzer (Krom et al. 1991). The precisions for NO_3^-, NO_2^-, NH_4^+, and PO_4^{3-} were 0.04, 0.04, 0.7, and 0.01 μM, respectively. Cations (Na^+ and Ca^{2+}) were measured after suitable dilution using an ICP-EAS. Anions (Cl^- and SO_4^{2-}) were analysed using a Dionex DX100 Ion Chromatograph with AS14 column, AS3500 autosampler, and AI450 computer interface and software. Precision was 1.7% for Cl^-, 0.6% for SO_4^{2-}, 8.6% for Ca^{2+}, and 2.2% for Na^+. Accuracy was checked using IAPSO standard seawater stock solution, which gave results within 0.5% of the expected values. Al concentrations were measured on a Perkin Elmer 1100B atomic adsorption spectrometer equipped with graphite furnace. The accuracy and precision of the Al method were evaluated on the basis of analyses of international standard reference materials: Estuarine Sediment 1646 (NIST), MESS-2 sediment (NRCC), and Coal Fly Ash, with results within 5% of the certified values.

Estimate of fluxes—The wet atmospheric deposition fluxes (F_w) were calculated from the annual amount of precipitation (P) and the volume-weighted mean concentration (C) of the substance of interest (Eq. 1). Samples from MM had a longer exposure time and contained dry fallout as well as rainwater. These samples were not used for the wet flux estimates. We will use these samples to examine the influence of dry fallout on the nutrient content in the rain. Similar results were obtained calculating the flux for all individual rain events and correcting it for the annual amount of precipitation (60–89% of the total annual amount was collected).

$$F_w = C \times P. \quad (1)$$

The dry atmospheric deposition fluxes (F_d) were calculated from the concentration of total particulate phosphorus in the air (P_p, geometric mean) times the deposition velocity (Eq. 2).

$$F_d = P_p \times V_d. \quad (2)$$

The term V_d varies with particle size from gravitational settling of large particles to impaction and diffusion of small particles (submicrometer) and is dependent on climatological and physical conditions in the troposphere. Owing to the absence of measured deposition rates, the values used here follow the mean values given by Duce et al. (1991). Phosphorus is present primarily in the coarse fraction (Duce et al. 1991; Prospero et al. 1996), and a mean value of 2 cm s^{-1} was used. These estimates might be uncertain by a factor of 2–3. In order to evaluate the flux of seawater LIP we substitute the mean P_p concentration with the geometric mean of seawater LIP concentration.

Results and Discussion

Rainwater—The chemical composition of the rainwater is similar at all three sites and is mainly Na-Cl. This is typical for the Israeli coastal zone area (Herut et al. in press). The rainwater salinity is higher at TS compared to MM and ASH. This is attributed to a higher input of seaspray (SS) components (e.g., Na and Cl) due to its close proximity to the sea. In most of the rains, Na^+ versus Cl^- showed a clear marine ratio (0.87) as presented in Fig. 2. The amount of SS and nonseaspray (NSS) for each ion was calculated from the

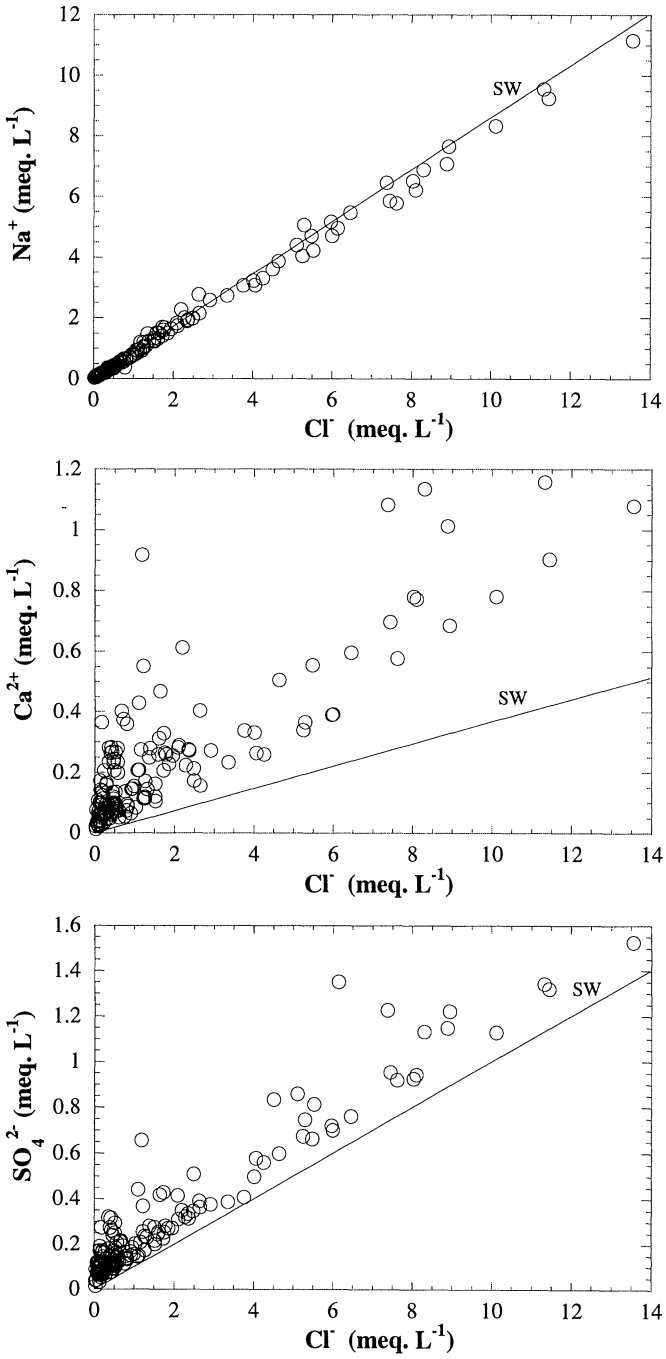

Fig. 2. Relationship between Na^+, Ca^{2+}, SO_4^{2-}, and Cl^- in rainwater. Cl^- versus Na^+ display a clear marine ratio (seawater [SW] line) indicating their introduction into all rain samples as seaspray while Ca^{2+} and SO_4^{2-} display a large nonseaspray fraction.

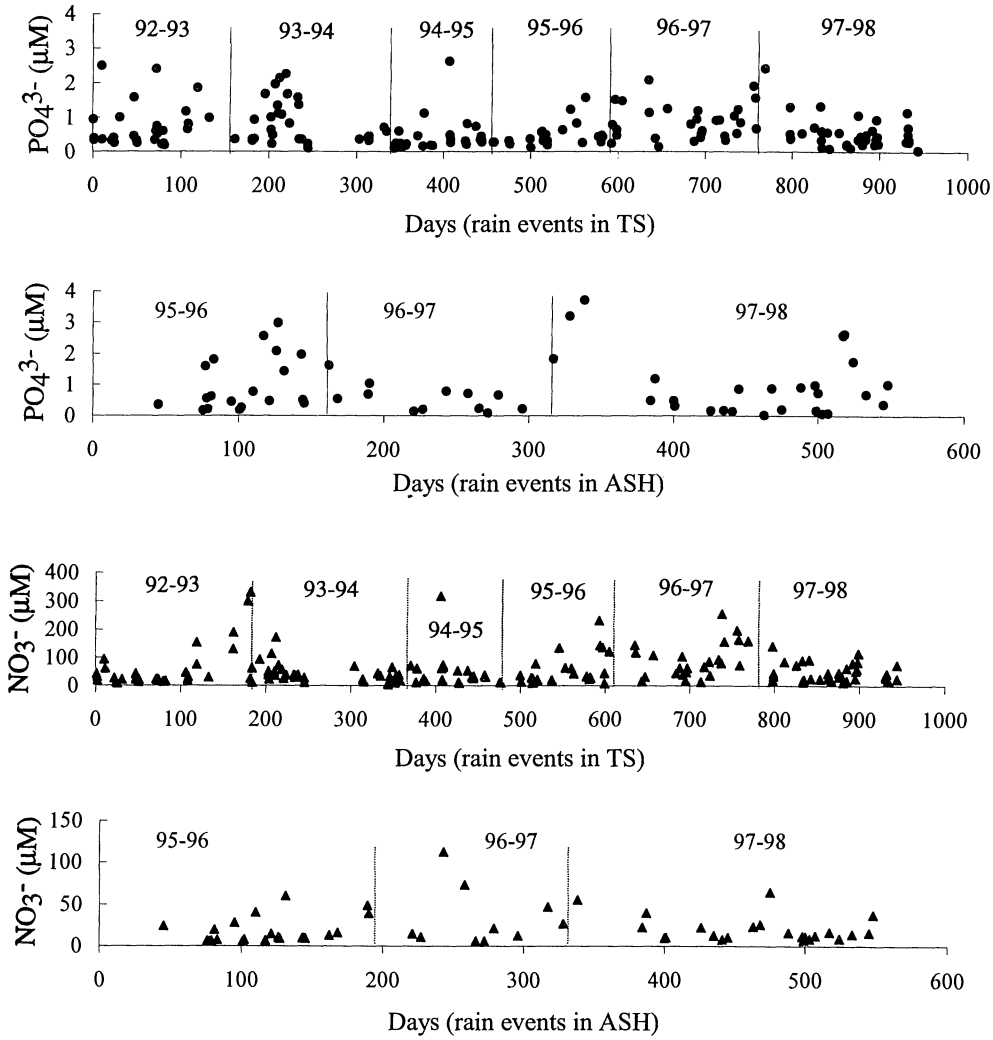

Fig. 3. Temporal variability of PO_4^{3-} and NO_3^- concentrations (μM) in rainwater samples collected at Tel-Shikmona (TS) and at Ashdod (ASH). Data points of five rain events from TS, which had PO_4^{3-} concentrations >4 μM, are out of scale (not marked by a symbol).

major ion to chloride ratio assuming no fractionation alters the seawater ratios during or after the injection of seaspray into the atmosphere. Ca^{2+} and SO_4^{2-} showed the most significant enrichment relative to the marine ratio, having significant NSS contribution (Fig. 2).

pH values in the rainwater samples ranged from 3.6 to 8.2, with volume-weighted mean value of 5.2. The relative contribution of NO_3^- versus $SO_4^{2-}{}_{NSS}$ to the rainwater acidity based on their volume-weighted mean concentration was approximately 1:4. A similar contribution for nitrate (of ~20%) was estimated in European precipitation (Berner and Berner 1996). However, no significant correlation was found in this study between H^+ and NO_3^- or NO_3^--NH_4^+ concentrations or between H^+ and $SO_4^{2-}{}_{NSS}$.

No correlation was found between the nutrients (PO_4^{3-}, NO_3^-, NH_4^+) and Na^+ or Cl^- concentrations ($r^2 < 0.046$), indicating a nonmarine origin for the nutrients. The SS contribution to the dissolved nutrients in the rainwater samples has been calculated to be insignificant. Less than 0.05% of the dissolved inorganic phosphorus (DIP) and 0.09% of the dissolved inorganic nitrogen (DIN) in the rainwater could be attributed to SS assuming that no fractionation occurred during the passage from seawater to SS. Even if the P was enriched by 150 in the surface microlayer (Graham and Duce 1979), the fraction of marine-derived phosphate would still be <10% of the total amount in the rain.

In general, high temporal variability of the nutrient concentrations was observed (Fig. 3). A dim seasonal pattern exists in the PO_4^{3-} behavior at ASH and TS with high concentrations occurring predominantly in the beginning and the end of each winter, while no seasonal pattern was exhibited by the NO_3^- (or NH_4^+, not shown) concentrations. This PO_4^{3-} seasonal pattern is probably related to higher concentrations of local dust being washed out of the air with the first rains in the autumn and to dust storms moving from North African and surrounding deserts, which occur mostly in spring (Ganor and Mamane 1982). There was a positive correlation between PO_4^{3-} and $Ca^{2+}{}_{NSS}$ concentrations for

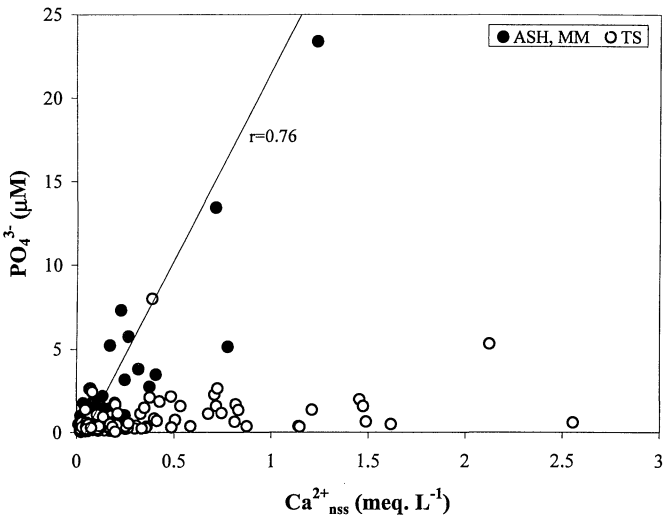

Fig. 4. PO_4^{3-} versus $Ca^{2+}{}_{NSS}$ concentrations in rainwater samples collected at Tel-Shikmona (TS), Maagan Michael (MM), and at Ashdod (ASH). The linear regression line calculated from ASH and MM data is included ($p < 0.05\%$).

rainwater samples from ASH and MM (Fig. 4). The relatively lower PO_4^{3-} : $Ca^{2+}{}_{NSS}$ ratios in TS rains indicate lower dissolution of phosphate from the dust (by rainwater) at this site. These differences might be attributed to the longer exposure time of the MM samples to dust particles and higher dust concentrations in the air at ASH (Herut 1998). However, without simultaneous measurements of dust concentrations in air it is difficult to assess the relationship between the nutrient concentrations and the latter.

At TS, the main (DIN) specie was usually NO_3^-, while at ASH NH_4^+ was dominant (Table 1). NO_2^- concentrations were negligible and constituted <2% of the DIN. Volume-weighted mean DIN concentrations were higher at TS than at ASH, mainly due to higher NO_3^- concentrations. Two possible hypotheses have been suggested to explain the markedly different NO_3^- : NH_4^+ ratios at TS and ASH. One possible explanation for this observation is that TS is more affected by occasional local anthropogenic contribution of NO_3^-, while ammonia derived from animal wastes and fertilizers is more dominant at ASH. TS is adjacent to the city of Haifa, while ASH is adjacent to areas of intensive agriculture. In this model, the NO_3^- flux at ASH plus the NH_4^+ flux at TS represent the total DIN flux of the European background rainfall. This more conservative model was chosen for the flux calculations carried out below. The alternative model is that the entire DIN in ASH comes from Europe and that there was no significant local input of NO_3^- or NH_4^+. This model requires that the European rain started off with a significant NH_4^+ content, part of which was subsequently transformed via atmospheric oxidation to NO_3^-. The more northerly rain then has undergone greater oxidation of NH_4^+ than the southerly rains. With the data available it is not possible to decide which of these hypotheses is correct.

Leachability of phosphorus from dry fallout by surface seawater—Leaching experiments using SE Mediterranean

Table 1. Estimates of wet nutrient fluxes (g m^{-2} yr^{-1}) and volume-weighted mean concentrations (μM) along the Israeli Mediterranean coast. All fluxes were calculated based on the annual or total (all years) volume-weighted mean concentrations (*see* text). NA = not analyzed; NC = not calculated due to partial NH_4^+ analyses; DIN = total dissolved inorganic N.

Site	Year	Precipitation (m)	Units	$P\text{-}PO_4^{3-}$	$N\text{-}NO_3^-$	$N\text{-}NH_4^+$	$N\text{-}NO_2^-$	DIN
Ashdod	1995–96	0.516	flux	0.015	0.069	0.217	0.002	0.284
Ashdod	1996–97	0.543	flux	0.006	0.107	NA	0.005	NC
Ashdod	1997–98	0.552	flux	0.009	0.108	0.301	0.004	0.413
Ashdod	all years	0.537	flux	0.009	0.097	0.269	0.004	0.364
			volume-weighted mean	0.56	12.94	35.80	0.48	48.47
			n	57	57	45	57	45
Tel Shikmona	1992–93	0.557	flux	0.008	0.161	NC	NA	NC
Tel Shikmona	1993–94	0.321	flux	0.010	0.339	0.076	NA	0.432
Tel Shikmona	1994–95	0.435	flux	0.008	0.183	0.144	0.002	0.325
Tel Shikmona	1995–96	0.620	flux	0.008	0.239	0.223	0.003	0.465
Tel Shikmona	1996–97	0.412	flux	0.011	0.470	0.211	0.003	0.684
Tel Shikmona	1997–98	0.647	flux	0.008	0.298	0.257	0.004	0.558
Tel Shikmona	all years	0.499	flux	0.009	0.284	0.177	0.003	0.482
			volume-weighted mean	0.58	40.62	25.40	0.44	69.04
			n	179	179	160	118	160

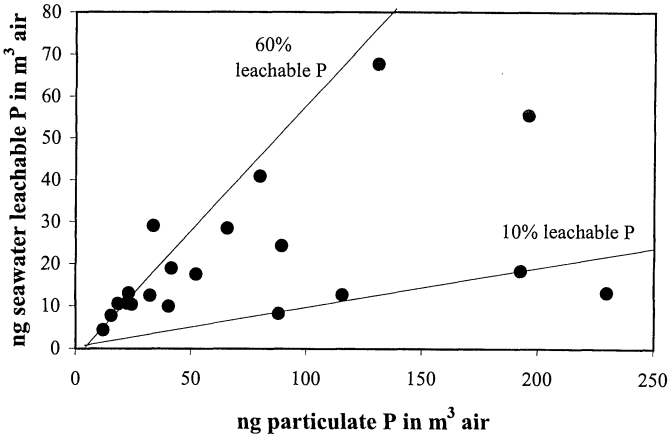

Fig. 5. Relationships between seawater leachable and HCl leachable (total) particulate inorganic P concentrations in m^3 air. Total and seawater leachable concentrations were measured in dust collected on Whatman 41 filters at Tel-Shikmona during 1996.

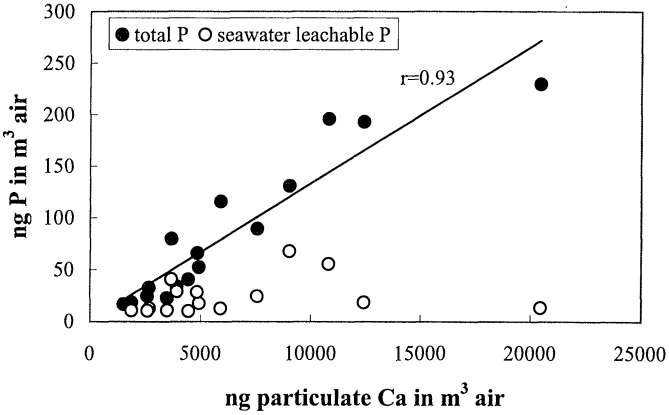

Fig. 6. Relationships between seawater leachable and HCl leachable (total) particulate inorganic P concentrations in m^3 air and particulate Ca concentrations in m^3 air. The linear regression line calculated for the total inorganic P data is included ($p < 0.05\%$).

surface seawater were performed on 20 Whatman 41 dust filters from TS to evaluate the amount of seawater LIP. The mean total IP concentration in the dust was 0.13 ± 0.11% (geomean = 0.09%). A mean of 387 ± 205 μg IP per g of dust was leached by seawater. However, the concentrations of phosphate in the dust on the Whatman 41 filters may contain relatively large errors because the weight of the dust on the filters was inaccurate (*see* Methods). Similar leachable values (LIP per g of dust) were obtained using dust weights that had been estimated from the Al concentrations assuming that this element represents on average 4.5% by weight of the mineral aerosol (Herut 1998) or by using both Ca and Al concentrations assuming they represent the calcium carbonate and aluminosilicate fractions in each sample. A somewhat lower mean total IP concentration of 0.07 ± 0.04% was calculated in the dust samples collected by QMA filters (22 samples). Applying the average seawater leachable fraction of LIP (38% in the Whatman 41 filters; *see* below) to the mean total IP of the QMA filters, an average of 260 μg LIP per g of dust was leached by seawater. Figure 5 shows that the seawater LIP accounted for 6–85% of the total IP (mean of 38%), and it varied between samples and probably dust sources. While total IP concentrations in air were linearly correlated to the particulate Ca (or Al, not shown) concentrations, no such relationship was observed with seawater LIP (Fig. 6). Most of the total IP peaks (Fig. 7) represent desert-type dust events as estimated using air mass back trajectories for the TS high-volume samples. This conclusion was based on back-trajectory categorization of all the dry deposition samples into two air mass populations: (1) from North Africa and the Saudi Peninsula, and (2) from West and East Europe. While the desert-type events usually contain higher P and Ca concentrations in air (similar behavior was observed for the QMA filters), their IP solubility in seawater, expressed as a percentage of total IP, was usually lower (median value of ~25% as compared to ~45% in European-type events; Fig. 8). Although Saharan dust events exhibited lower IP solubility in seawater, such dust events may still contribute high amounts (load) of P to the surface waters owing to their relatively high deposition rates and high total IP concentrations (0.36–0.44%; Ganor and Foner 1996; Guieu and Thomas 1996). The solubility of IP in remote loess particles (aeolian deposits) collected at the Negev Desert (Israel) was approximately 11% in seawater (Herut et al. 1999), similar to the dust events here. Over the Northwest (NW) Mediterranean, Bergametti et al. (1992) and Migon and Sandroni (in press) observed a similar trend of lower P solubility in rainwater during Saharan-type events.

Fluxes and possible impact—The annual rainfall and the fluxes of PO_4^{3-} (DIP) and the various inorganic nitrogen species in rainwater are presented in Table 1. These flux estimates might contain uncertainties related to the analytical error of the volume-weighted mean concentrations (<±7% for PO_4^{3-}, NO_3^-, and NH_4^+ and 30% for NO_2^-) and to the fact that the latter were calculated based on 60–89% of the total amount precipitated (*see* Methods). The DIN flux in TS (~0.48 g N m^{-2} yr^{-1}) was higher than in ASH, and significant differences exist between the NO_3^- and NH_4^+ fluxes owing to their different concentrations in the rain (Table 1). Using the more conservative hypothesis to explain this observation (*see* above), we find that the NO_3^- fluxes in ASH (~0.10 g N m^{-2} yr^{-1}) and NH_4^+ fluxes at TS (~0.18 g N m^{-2} yr^{-1}) represent the total DIN flux of the European background (0.28 g N m^{-2} yr^{-1}). The average $NH_4^+ : NO_3^-$ ratio of this background flux (1.8) is in the range of ratios typically found in polluted air masses (1.1–2.8) and higher than those associated with African air masses (<0.9) in the NW Mediterranean (Loye-Pilot et al. 1990). The flux variations between years were not related to the amount of precipitation and were probably attributed to variations in air mass climatology as observed for the Western Mediterranean (Loye-Pilot et al. 1990). The increasing pattern of NH_4^+ fluxes at TS may indicate larger anthropogenic contributions over the past several years. However, because this is the first such estimate of DIN flux to the region, it is not possible to de-

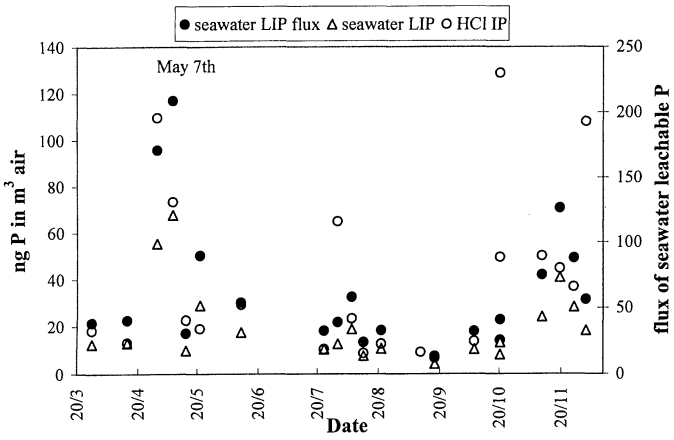

Fig. 7. Temporal variability of seawater leachable (LIP) and HCl leachable (total) particulate inorganic P (IP) in m^3 air and temporal variability of seawater LIP fluxes ($\mu g\ m^{-2}\ d^{-1}$).

termine conclusively whether this flux is increasing systematically with time and, if so, by how much.

In order to calculate the flux of DIN to the SE Mediterranean Basin, it is necessary to allow for the lower rainfall amounts at sea (350–450 mm yr^{-1}; Martin et al. 1989) and probably lower DIN concentrations owing to local inland contribution. It was therefore assumed that the DIN fluxes over the SE Mediterranean Basin were attributed to the European background (as defined above) and were 15% lower due to reduced precipitation. The calculated DIN fluxes (~0.24 g N $m^{-2}\ yr^{-1}$) are much higher than estimates for remote clean areas or for the Southern Hemisphere oceans (0.03–0.04 g N $m^{-2}\ yr^{-1}$) (Duce et al. 1991). They are lower, however, than the fluxes calculated for areas such as the North and Baltic Seas (~1 g N $m^{-2}\ yr^{-1}$) (Duce et al. 1991) or the NW Mediterranean (0.51 g N $m^{-2}\ yr^{-1}$) (Loye-Pilot et al. 1990), which are immediately adjacent to areas of significant anthropogenic input. Assuming that the fluxes in the Southern Hemisphere represent the natural background level, nearly all of the DIN flux into the Mediterranean is of anthropogenic origin.

At present, no estimates are available of the IN content of dry fallout in the Eastern Mediterranean. The estimated ratio of the wet : total (i.e., both wet and dry) IN deposition in the West Mediterranean is approximately 0.75 (Martin et al. 1989; Guerzoni et al. in press), which is similar to that of other oceanic areas (Duce et al. 1991). Based on the latter, we estimated a total IN deposition of ~0.37 g N $m^{-2}\ yr^{-1}$ and ~0.32 g N $m^{-2}\ yr^{-1}$ to the Israeli Mediterranean coast and the SE Mediterranean, respectively. Higher total IN fluxes of 0.66–0.77 g N $m^{-2}\ yr^{-1}$ were estimated for the NW Mediterranean (Loye-Pilot et al. 1990; Guerzoni et al. in press, and references therein).

The calculated average DIP flux via rainfall into the Mediterranean coastal zone of Israel was estimated as 0.009 g P $m^{-2}\ yr^{-1}$ (Table 1) and somewhat lower in the SE Mediterranean (0.008 g P $m^{-2}\ yr^{-1}$). Applying Eq. 2, we calculated the total IP dry fluxes and the seawater LIP fluxes (Fig. 7). It was estimated that the average (geomean) dry total IP flux was 0.031 g P $m^{-2}\ yr^{-1}$ and the geomean dry LIP flux was

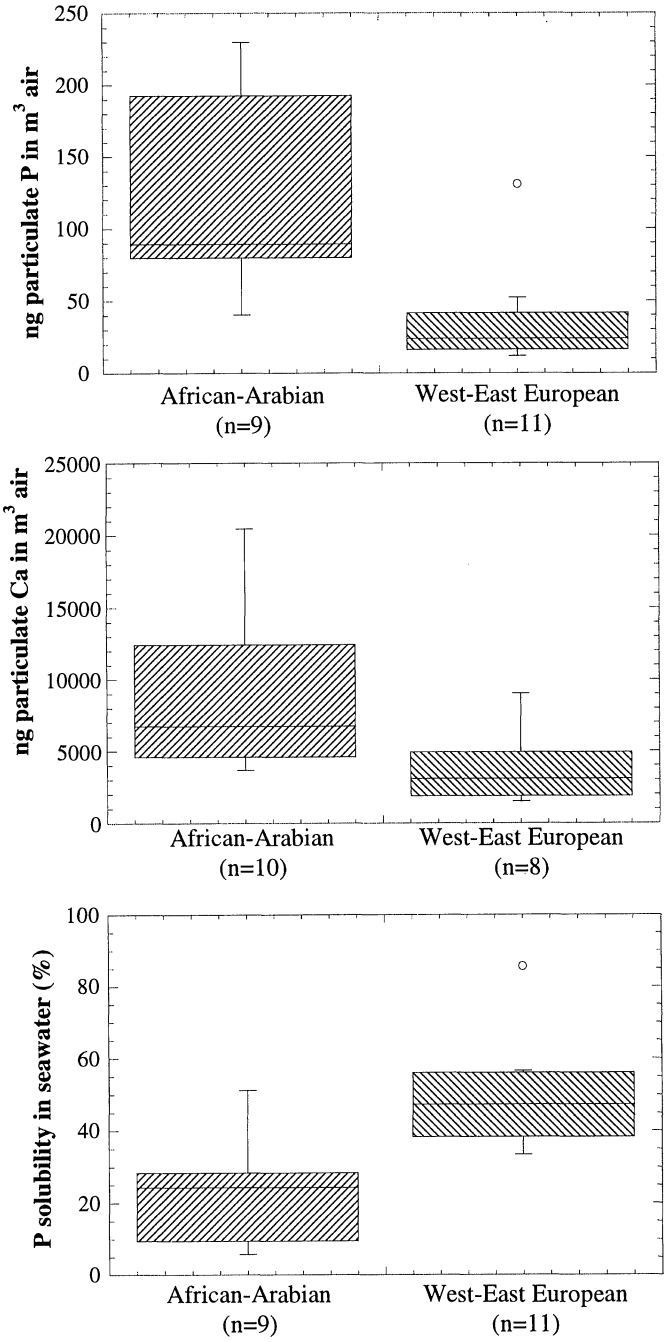

Fig. 8. Box plots of HCl leachable (total) particulate inorganic P (IP) concentrations in m^3 air, particulate Ca concentrations in m^3 air, and solubility of IP in seawater (seawater leachable IP/HCl leachable IP) according to the origins of the air masses. Two geographical sectors were classified, North–West European and African–Saudi Peninsular (Arabian) (*see* text). The bottom and the top edge of each box are located at the sample 25 and 75 percentiles. The central horizontal line is drawn at the sample median.

0.01 g P $m^{-2}\ yr^{-1}$. If we use an estimated deposition flux of 20 g $m^{-2}\ yr^{-1}$ for the Saharan dust over the SE Levantine Basin (Ganor and Mamane 1982) and a mean total IP and LIP as calculated in this study (0.13% and 387 ppm), similar fluxes of 0.008 and 0.026 g P $m^{-2}\ yr^{-1}$ are obtained. Using

Table 2. Calculated values of the flux of dissolved inorganic nitrogen and phosphorus in rainfall (DIN and DIP), seawater leachable from dry fallout (LIN and LIP), the total nutrient input (total dry and wet IN and IP) in units of g m^{-2} yr^{-1}, and their ratios over the Israeli Mediterranean coast (IMC), the SE Mediterranean (SEMED) and the NW Mediterranean (NWMED). The bioavailable IP (BIP) flux was estimated by DIP + LIP. Unknown data is marked by ?.

Parameter	IMC*	SEMED†	NWMED‡
DIN	0.28	0.24	0.51†
LIN§	?	?	?
Total dry and wet IN	0.37‖	0.32‖	0.7¶
DIP	0.009	0.008	0.005# − 0.016¶ (avg. 001)
LIP§	0.01	0.01	0.01**
Total dry and wet IP	0.040	0.039	0.034 − 0.04†† (avg. 0.037)
Bioavilable IP (BIP)	0.019	0.018	0.02
Total dry and wet IN/IP (molar)	20	18	42
DIN/DIP (molar)	70	66	113
DIN/BIP (molar)	33	30	56

* This study.
† Extrapolation of 85% IMC fluxes for DIN and DIP (*see* text).
‡ Loye-Pilot et al. 1990; Migon et al. 1989.
§ Seawater IN and IP from dry fallout (bioavailable).
‖ Calculated assuming wet IN = 3 dry IN (*see* text).
¶ Guerzoni et al. 1999.
# Migon and Sandroni in press.
** Calculated assuming similar leachability (LIP/total IP ratio) as in IMC.
†† Bergametti et al. 1992.

these data, we find that the ratio of the wet : total IP (i.e., both wet and dry) deposition was calculated to be 0.2. This value is somewhat smaller than the estimate of 0.3 for the West Mediterranean (Martin et al. 1989) probably because the SE Mediterranean receives only ~450 mm yr^{-1} of rainwater distributed over sporadic 20–30 rain days. The total (wet and dry) IP flux over the Mediterranean coast of Israel was estimated to be 0.04 g P m^{-2} yr^{-1} and was probably somewhat lower over the SE Mediterranean Basin (0.039 g P m^{-2} yr^{-1}). Similar fluxes were estimated in the NW Mediterranean (0.034 g P m^{-2} yr^{-1}; Loye-Pilot et al. 1990) and in Corsica (0.04 g P m^{-2} yr^{-1}; Bergametti et al. 1992). Lower fluxes by a factor of 3 were estimated for the North Atlantic and Pacific (0.0056 and 0.0076 g P m^{-2} yr^{-1}, respectively) and by about a factor of 20 for the South Atlantic and Pacific (Duce et al. 1991).

Table 2 summarizes the estimated wet, dry, and leachable IN and IP atmospheric fluxes and their ratios over the SE and NW Mediterranean. It is reasonable to suggest that the dissolved IP plus seawater LIP fluxes represent the amount of phosphate that is bioavailable in the surface waters. This assumes that there is no significant adsorption onto or desorption from inorganic particles after they reach the surface waters. The DIN : DIP and the dissolved plus the seawater leachable IN : IP ratios in the atmospheric precipitates were well above Redfield ratio (N : P = 16 : 1) and higher than the measured N : P ratios in Levantine deep waters (N : P = 27 : 1; Krom et al. 1991). This estimated ratio may increase even further due to the unknown contribution of seawater leachable N from dry fallout. It is estimated that these ratios are higher in the NW Mediterranean as compared to the SE basin mainly due to higher total IN fluxes. These data suggest that the atmospheric input of nitrogen could potentially support higher amounts of productivity by a factor of approximately 2–3 than does the input of phosphorus. By using the N : C ratios of Redfield (16 : 106) or that evaluated by Takahashi et al. (1985) (16 : 122), we find that the atmospheric input of DIN estimated here (0.24 g N m^{-2} yr^{-1}) supplies 8% of the total new production (16.7–19.2 g C m^{-2} yr^{-1}; Krom et al. 1992) to the Eastern Mediterranean, but a minimum of 20% if the production recycled from the previous year (Krom et al. 1992) is removed. In comparison, the atmospheric total IN inputs account for 10–50% of the total new production in the Western Mediterranean Sea (Martin et al. 1989). By using the P : C ratios of Redfield (1 : 106), the total bioavailable IP flux of 0.018 g m^{-2} yr^{-1} (Table 2) accounts for 0.74 g C m^{-2} yr^{-1} (4–11% of the total new production), about half that of DIN. Thus, the atmospheric contribution to new production may be less than the above DIN assessment. However, because the surface waters are so oligotrophic, it is nevertheless possible that particular rainfall or dust storm events may still trigger measurable blooms of phytoplankton (Buat-Menard et al. 1989; Bergametti et al. 1992; Migon and Sandroni in press). For example, the dust event on 7 May 1996 contributed seawater LIP in the order of 117 ng m^{-2} d^{-1} (Fig. 7). This input is equivalent to 4.8 mg C m^{-2} d^{-1}, which corresponds to 96 μg Chl *a* m^{-2} d^{-1} (using C Chl a^{-1} = 50 [23–79] by weight; Parsons and Takahashi 1975). Although this amount constitutes <1% of the total integrated Chl *a* in the euphotic zone (0–120 m) during spring (12 mg Chl *a* m^{-2}; Herut unpubl. data), it represents a significant fraction (~8%) of the upper mixed layer (~20 m with mean Chl *a* concentration of 0.06 μg l^{-1}).

The calculated atmospheric N and P fluxes suggest that the atmospheric input to the basin causes an imbalance of N : P, which at the very least reinforces the possible P limitation (Krom et al. 1991; Zohary and Robarts 1998). More-

over, global atmospheric N fluxes have increased during the last 100 years (Galloway et al. 1995). It is likely that in this basin the anthropogenic sources of N to the atmosphere are increasing faster than those of P. This suggests that anthropogenic changes in the atmospheric nutrient flux will also reinforce the P-limited nature of the basin, as has been suggested for other oceanic areas (Fanning 1989). However, in coastal areas of N-limited waters it may enhance primary production (Paerl 1985) or trigger the development of harmful algal blooms (Paerl 1997).

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