

Impact of atmospheric deposition on N and P geochemistry in the southeastern Levantine basin

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Abstract

Aeolian dust was collected from 2001 to 2003, as part of a longer-term study, to estimate the nutrient input to the Levantine basin from atmospheric deposition. Adsorption experiments, using dust samples from six individual dust storms, showed insignificant adsorption of phosphate onto dry deposited Saharan dust. Thus adsorption onto dust can be discounted as a reason for the high nitrogen:phosphorus (N:P) ratio in the deep water of the eastern basin. A single dust storm sample from the Western Mediterranean was able to adsorb some phosphate from seawater, and it is speculated that this may be linked to the action of acid aerosols on the dust during cloud formation, or to the varying chemical composition in different sources of dust.

Dry atmospheric deposition is an important net supplier of both N and P to the eastern basin. Leachable inorganic nitrogen concentrations and fluxes are higher in background (non-storm) samples than in storm samples, probably due to the smaller grain size and aerosol source. Total P is supplied naturally with the dust, as shown by the close correlation between total P and Al ($r^2 = 0.95$). However, there is a poor correlation between leachable inorganic P (LIP) and Al ($r^2 = 0.20$), which may be related to grain-size effects and/or recycling processes in the atmosphere. Even so, the supply of LIP to surface waters is greatest during dust storms due to comparatively high deposition of aerosol material. While atmospheric input of P during dust storms does not produce significant in situ increases in chlorophyll, probably due to rapid microbial grazing, it does represent an important proportion of the long-term nutrient input to the basin. This may be increasing as the frequency of dust storms increases.

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1. Introduction

The Eastern Mediterranean has one of the highest fluxes of aeolian dust because of its close proximity

to the Sahara desert (Chester et al., 1977; Guerzoni et al., 1999). Previous studies have shown that atmospheric inputs are an important source of nutrients (N and P) to the Mediterranean Sea and, in particular, to the eastern basin (Duce et al., 1991; Guerzoni et al., 1999; Herut et al., 1999a; Kouvarakis et al., 2001; Herut et al., 2002; Markaki et al., 2003). Indeed the primary inputs of N and P to the

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eastern basin are from atmospheric deposition, accounting for 60–70% of the bioavailable N and 30–50% of the bioavailable P, of which dust is a major source (Krom et al., 2004).

It is known that there are frequent dust storms that pass over the eastern basin, particularly in spring and autumn (Koçak et al., 2004). Ganor and Foner (1996) estimate the number of storms to range from five to 35 per year. It is generally assumed that these dust storms provide the majority of particulate matter that ultimately accumulates in the sediment. Such storms are responsible for the great variability that is characteristic of long term atmospheric flux records. Variations of up to four orders of magnitude are possible (Jickells and Spokes, 2001). It is known that nutrients are leached from aerosol material deposited into surface waters (Herut et al., 1999b; Herut et al., 2002). The current work presents an expanded dataset that includes a series of dust storm events, one of which was sampled at sea during the 2001 CYCLOPS cruise. The chemical characteristics of the dust samples collected during storms was determined and compared with background (non-storm) samples. Such data are necessary to enable data on storm frequency obtained by remote sensing to be converted into nutrient flux estimates.

The Eastern Mediterranean has a uniquely high nitrate:phosphate ratio in its deep water (~28:1), which results in the primary productivity in the basin being phosphorus-limited (Krom et al., 1991). Since it also has one of the highest dust fluxes anywhere in the world and it is known that this dust contains significant amounts of reactive iron and calcium carbonate, both of which are known to adsorb phosphate but not nitrate from seawater, Krom et al. (1991) hypothesized that adsorption of phosphate onto Saharan dust might be the reason for the high N:P ratio and hence phosphorus-limitation in the basin. The dust adsorption hypothesis has been investigated in three previous studies (Herut et al., 1999b; Pan et al., 2002; Ridame et al., 2003). These studies concluded that the extent of adsorption of P by Saharan dust was insufficient to explain P-limitation. However, the dust samples were not taken from, or not typical of, the actual aeolian dust that is deposited in the sea. Herut et al. (1999b) used a loess sample from the Negev desert. Ridame et al. (2003) used soil samples from the Sahara desert. Pan et al. (2002) used a single sample of

aeolian Saharan dust, which was subsequently found to be contaminated with wind-borne P fertilizer from loading operations in a nearby port. In this study, we carried out a series of adsorption experiments using six representative Saharan dust storm samples, thus reducing the uncertainty caused by using potentially atypical samples. These dust storm samples were used to test the hypothesis of Krom et al. (1991).

The results of this study, together with previous long-term studies on atmospheric inputs to the Eastern Mediterranean, have enabled estimates to be made of the relative importance of atmospheric supply to the total annual input of nutrients to the basin (Krom et al., 2004). The total annual externally supplied nutrient budget has been calculated and compared to the measured annual primary productivity (Antoine et al., 1995; Psarra et al., 2000; Turley et al., 2000; Bosc et al., 2004). From this comparison it is possible to examine the relative importance of recycling processes such as grazing in driving the overall primary productivity in this ultra-oligotrophic system.

2. Methods

2.1. Dust and seawater sample collection

Atmospheric dust samples were collected between 4 January 2001 and 13 April 2003 on 20 × 25 cm Whatman 41 filters, using a high-volume sampler (flow rate: 42 m³ h⁻¹). The sampler was positioned on the roof of the National Institute of Oceanography building at Tel Shikmona, Haifa, Israel, with the exception of May 2001 and May 2002, when samples were collected on board RV Aegaeo during the CYCLOPS cruises. Sampling frequency ranged from one to 19 days per month, with an overall average of 11 days (Table 1). Sampling time was from six to 77 h per filter, with a mean of 57 h. This sampling represents a continuation of long-term data set that began in 1992.

Six larger samples of Saharan dust from storm events used in the adsorption experiments were collected in April 2000 and April and May 2001. These were sampled from the top of a glass panel at Beit Yannay, Israel, a coastal location about 20 m above sea level and 300 m from the shoreline. The dust was collected in acid cleaned (10% HCl) 15-ml scintillation vials. In addition the storm dust sample used by Pan et al. (2002), which was collected on 28 May 1997 from a plastic surrogate

Table 1
Number of sample days per month for dust collected at Tel Shikmona and on R/V Aegaeo (marked with*) from January 2001 to April 2003

	2001	2002	2003
January	13	–	–
February	8	16	6
March	14	13	9
April	9	15	10
May	19*	13*	–
June	18	16	–
July	17	12	–
August	8	5	–
September	12	1	–
October	10	18	–
November	–	15	–
December	–	–	–
Average	13	12	8

collector at Eilat (Gulf of Aqaba), was re-analysed in this study. A single large sample from the Western Mediterranean (38°N; 06°E) was collected during a dust storm at sea, in a plastic bucket on board RV Meteor. Analysis of the air-mass back trajectories for all the examined dust events showed the Sahara desert as their primary source. The operational trajectory model developed by the European centre for medium-range weather forecasts (ECMWF) in Reading, UK, was applied to three-dimensional wind fields acquired from the archives of ECMWF. Mediterranean seawater (MSW) used for the leaching and adsorption experiment was collected from RV Aegaeo at 5 m depth using a multi-sampler/carousel system during the CYCLOPS cruise in May 2002.

2.2. Nutrients and aluminium in filter samples

Seawater leachable inorganic N and P (LIN, LIP) was determined for dry deposition samples collected on filters. Preliminary experiments showed that the leaching process reached equilibrium after approximately 3 h (Pan et al., 2002). One-cm² subsamples of dust filters and blanks were shaken for 30 h in the dark at room temperature in pre-cleaned centrifuge tubes containing 15 ml of filtered 0.2 µm SE Mediterranean surface seawater and 50 µL chloroform. After leaching, the samples were centrifuged at 4000 rpm for 10 min. Subsamples were pipetted and stored frozen in pre-cleaned (10% HCl) plastic vials for nutrient analysis. Nitrate + ni-

trite, phosphate and ammonium determination was performed by a photometric segmented flow method using Skalar SAN^{plus} Systems and the procedures described in Kress and Herut (2001). The precisions were 0.02, 0.003 and 0.02 µM for nitrate + nitrite, phosphate and ammonium, respectively. The limit of detection was 0.075 µM for nitrate + nitrite and ammonium, and 0.008 µM for phosphate. All analytical results were corrected for filter blanks. The precisions of the blanks were ±11% for P, ±12% for nitrate and ±10% for ammonium. The blanks accounted in average for 15%, 3% and 18% of the leachable concentrations of phosphate, nitrate + nitrite and ammonium, respectively, and ~1% of the total inorganic P concentrations.

Total inorganic P determination was carried out using 9 cm² sub-samples of dust filters by the addition of 2 ml 1 N H₂SO₄ and 3 ml 1 N HCl into 50-ml pre-cleaned bottles. The sample was shaken for 24 h, filtered, and diluted to 50 ml.

Aluminium was measured on a second subsample, 35 cm², after total digestion with HF (ASTM, 1983). Aluminium concentration was measured on a Varian Spectra AA220 atomic absorption spectrometer equipped with graphite furnace. The accuracy of the Al concentrations were evaluated on the basis of analyses of Certified Reference Materials (Estuarine Sediment 1646a (NIST), MESS-2 Sediment (NRCC)). Nutrient and Al particulate concentrations in air were calculated considering the known volume of air per filter.

2.3. Determination of total P, inorganic P, and organic P in non-filter dust samples

The following method was adapted from Aspila et al. (1976). Approx. 0.01 g of each dust sample was weighed into a 10-ml platinum crucible (total P) and a 50-ml centrifuge tube (inorganic P). The crucibles were placed in a pre-heated furnace at 550 °C for 2 h, then cooled. The dust was then transferred to a 50-ml centrifuge tube. 10 ml of 1 N HCl was added to both the total P and inorganic P samples in the 50 ml tubes, which were shaken overnight. The samples were spun for 10 min at 2800 rpm. 2 ml of the supernatant was drawn off by pipette and diluted × 10 with MilliQ to give a concentration of 0.1 N HCl. P was determined in the resulting solution by an automated method (Krom et al., 1991). Organic P was calculated by subtracting inorganic P from total P.

2.4. Iron speciation

Iron speciation was determined using a three-stage extraction procedure, as described in Poulton and Raiswell (2002). A citrate buffered sodium dithionite solution was used to extract amorphous and crystalline iron oxides, and Fe at exchange sites (Canfield, 1989; Raiswell et al., 1994). This is referred to as highly reactive Fe (Fe_{HR}). Boiling 12 N HCl was used to extract the same oxides, plus magnetite and some silicate Fe, and any Fe associated with organic carbon (Berner, 1970; Raiswell et al., 1994). To calculate the second fraction, partially reactive Fe (Fe_{PR}), Fe_{HR} is subtracted from the concentration of Fe in the HCl extract. The third fraction, unreactive Fe (Fe_U), is determined when the concentration of Fe in the HCl extract is subtracted from the total Fe. Total Fe was determined using an HF–HClO₄–HNO₃ extraction (Walsh, 1980).

2.5. Flux calculations

The dry deposition flux, F , was calculated by multiplying the concentrations of the analyte in air, C , by a depositional velocity, V_d , using the following equation:

$$F = CV_d.$$

Physical processes determining the dry-deposition velocity include gravitational settling, impaction and diffusion (Jickells and Spokes, 2001). In this study fluxes were calculated using V_d depending on the nutrient, since the nutrients are known to be associated with different particle fractions. V_d values used for phosphate, nitrate and ammonium, 2.0, 1.2 and 0.6 cm s⁻¹, respectively (Duce et al., 1991; Prospero et al., 1996; Spokes et al., 2000), were those used previously in similar flux calculations by Herut et al. (2002).

2.6. Adsorption experiments

The procedure used for adsorption of phosphate on particles was based on previous work by Pan et al. (2002). In order to mimic the conditions found in Eastern Mediterranean surface water, the dust samples were leached with nutrient-depleted surface seawater prior to the adsorption experiments. For each sample, 4 mg of dust and 40 ml Mediterranean surface seawater (MSW) were shaken in a 50-ml sterile polypropylene centrifuge tube. This gave a

particle concentration of 100 mg l⁻¹. The tubes were shaken in the dark for three days, after which they were spun in a centrifuge for 20 min at 3000 rpm. The supernatant was removed, a portion was filtered through a 0.2- μ m polycarbonate membrane before P determination. The leached dust was then used for the adsorption experiment. 40 ml of phosphate-spiked MSW was added to the leached dust sample. Four different phosphate concentrations were used: 0.25, 0.5, 1.0 and 1.5 μ M. The dust suspension was shaken in the dark for seven days, then filtered through a 0.2- μ m polycarbonate membrane before phosphate determination. All procedures were carried out in triplicate.

Blanks were prepared for both desorption and adsorption experiments. New, sterile tubes were filled with 40 ml of MSW that were spiked with a range of P additions (0.05, 0.1, 0.3, 0.5 μ mol L⁻¹ P initial concentrations). The same tubes were then emptied and refilled with fresh MSW spiked with the range of P concentrations used in the adsorption experiments (0.25, 0.5, 1.0 and 1.5 μ mol L⁻¹) and shaken for seven days. Samples were then filtered for subsequent phosphate determination. The tube walls adsorbed 3 nmol P per tube for the desorption experiments, and 5 nmol per tube for the adsorption experiments, irrespective of solution concentration.

2.7. Scanning electron microscopy

Samples were imaged using a high-resolution field emission scanning electron microscope (FEG-SEM, LEO 1530) or a CamScan 4 scanning electron microscope equipped with an Oxford MicroAnalysis 10/25S energy dispersive spectrometer. Aliquots of the dust or filters were deposited on a double sticky carbon pad on standard SEM stubs. They were subsequently coated with a 2-nm platinum layer and examined at 1 to 3 keV at a working distance of 2 to 4 mm and using the in-lens secondary electron detector. Energy Dispersive X-ray analyses was performed at 20 keV.

3. Results

3.1. Phosphorus and iron characteristics of Sahara dust

Total P in Saharan storm dust samples from the Eastern Mediterranean ($n = 4$) ranged from 31 to 42 μ mol g⁻¹ (0.09–0.13%). Organic P accounted for 13–19% of total P while leachable P ranged from

4–13%. The single sample from the Western Mediterranean contained approximately half the total P of those from the Eastern Mediterranean ($18 \mu\text{mol g}^{-1}$), and a higher organic P content (38% of total P) (Table 2).

Total Fe (Fe_T) in Eastern Mediterranean samples ($n = 3$) was approximately 3–3.5%, with $\sim 1\%$ of that in the ‘highly reactive’ fraction (Fe_{HR}) and 0.5–0.6% in the ‘partially reactive’ fraction (Fe_{PR}). Reactive Fe in this analytical scheme consists mainly of Fe oxides (Poulton and Raiswell, 2002). There was little variation between samples from the Eastern Mediterranean. The single sample from the Western Mediterranean had a slightly higher percentage of Fe_T and Fe_{HR} , and slightly less Fe_{PR} . The ratio of $\text{Fe}_{HR}/\text{Fe}_T$ was similar to the Eastern Mediterranean samples (Table 3).

3.2. Adsorption of phosphate by Saharan dust

Adsorption was tested over a range of dissolved phosphate concentrations including those typical of Eastern Mediterranean deep water, which is around $0.3 \mu\text{M}$ (Kress and Herut, 2001). The degree of adsorption for each dust sample can be seen from the adsorption isotherms (Fig. 1). All six samples of Saharan dust did not adsorb any phosphate from

seawater over the entire concentration range of 0.25 to $1.5 \mu\text{M}$ P. Indeed, there was a small amount of additional phosphate released by the dust, in most cases even though the samples had been pre-leached for three days in surface seawater before the adsorption experiment. By contrast, Saharan dust collected in the Western Mediterranean adsorbed P

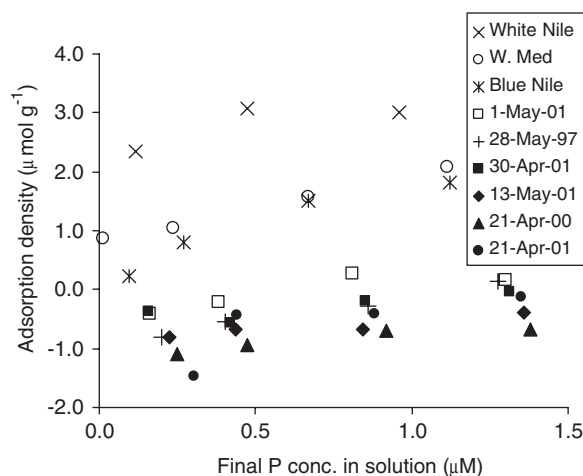


Fig. 1. Comparison of adsorption isotherms for Nile particulate matter and for Mediterranean dust-storm samples (five from the E. Mediterranean, marked by date in the legend, and 1 from the W. Mediterranean, marked as W. Med).

Table 2
P speciation in Mediterranean Saharan dust-storm samples

Location	Date of collection	Total-P ($\mu\text{mol g}^{-1}$)	Organic P ($\mu\text{mol g}^{-1}$)	Organic P (% of total P)	Leachable P (% of total)
E. Med.	21 Apr 2000	32.1	6.1	19	13
	30 Apr 2001	42.2	5.6	13	6
	1 May 2001	34.2	5.9	17	4
	13 May 2001	30.6	4.4	13	8
W. Med	20 Oct 2001	17.6	6.9	38	4

Table 3
Fe speciation in Mediterranean Saharan dust-storm samples

Location	Date of collection	Fe_{HR}^1 (Wt%)	Fe_{PR}^1 (Wt%)	Fe_U^1 (Wt%)	Fe_T^1 (Wt%)	$\text{Fe}_{HR}/\text{Fe}_T$ ratio
E. Med	30 April 2001	0.96	0.60	1.42	2.98	0.32
	1 May 2001	1.07	0.57	1.81	3.45	0.31
	13 May 2001	0.98	0.47	1.55	3.00	0.33
W. Med.	20 Oct 2001	1.29	0.40	2.10	3.79	0.34

¹ Fe_{HR} = highly reactive Fe, Fe_{PR} = partially reactive Fe, Fe_U = unreactive Fe, Fe_T = total Fe.

from seawater throughout the range of P concentrations used (0.25–1.5 μM), with uptake of P increasing with solution concentration and ranging from 0.9 to 2.1 $\mu\text{mol P g}^{-1}$ dust. The capacity to adsorb P was also seen in River Nile particulate matter, with a range of 0.2–1.8 $\mu\text{mol P g}^{-1}$ dust (Blue Nile) and 1.1–3.0 $\mu\text{mol P g}^{-1}$ dust (White Nile).

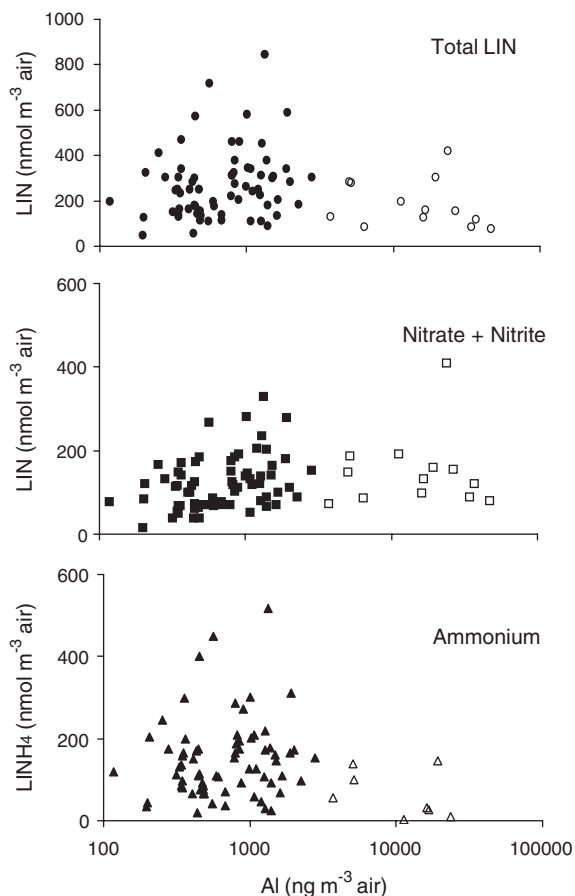


Fig. 2. The relationship between dust-borne leachable nitrogen and dust load (Al concentration) in air. Empty symbols—storm samples, full symbols—background samples. LIN—leachable inorganic nitrogen.

Table 4

Geomeans of leachable inorganic nitrogen (LIN) and phosphorus (LIP), and Total P concentrations in air, from storm, background and total dust filter samples from the Eastern Mediterranean basin

Sample type	LINH ₄ (nmol m ⁻³)	LI(NO ₃ + NO ₂) (nmol m ⁻³)	Total LIN (nmol m ⁻³)	Total P (nmol m ⁻³)	LIP (nmol m ⁻³)	LIP (% of total)
Storm (<i>n</i> = 12)	36	120	146	6.57	1.45	22
Background (<i>n</i> = 54)	119	101	227	0.80	0.60	73
Total (<i>n</i> = 71)	108	106	215	1.21	0.72	58

3.3. Nutrient input from dry deposition

Nutrient input was calculated from the dust filter samples (Table 1), were subsequently divided into two categories: ‘storm’ or high-desert dust events and ‘background’ deposition. The categories are based on aluminium (Al) concentration in air, with storm samples defined as containing $>3.6 \mu\text{g m}^{-3}$ (Herut et al., 2002). Using this definition, 14 of the total 86 filter samples were classified as storm deposition.

3.3.1. Seawater leachable inorganic nitrogen (LIN)

The overall mean LIN concentration in air during the 2001 to 2003 study period, based on both storm and background samples together, was $215 \pm 147 \text{ nmol m}^{-3}$, which is similar to the 210 nmol m^{-3} reported for the 1996 to 1999 subset (Herut et al., 2002). The LIN content of dust is variable in background deposition, with higher values in general for higher concentrations of background dust. The storm samples show a constant or slightly decreasing amount of LIN as the amount of dust increased (Fig. 2). Thus the relative amount of LIN carried in background deposition is greater than that of storms, even though the total dust load is much lower (geomean $146 \pm 109 \text{ nmol m}^{-3}$ for storms compared to the background load of $227 \pm 149 \text{ nmol m}^{-3}$) (Table 4). Systematic differences between the chemical composition of storm and background dust are apparent when the two main N groups, ammonium and nitrate + nitrite, are considered separately (Fig. 2). On average, background dust carried slightly more ammonium than nitrate + nitrite, while storm dust contained 3.5 times the amount of nitrate + nitrite compared to ammonium.

3.3.2. Total P and seawater leachable inorganic phosphorus (LIP)

Concentrations of total P in air show a strong positive correlation with Al concentration in air,

which reflects the lithological source of P in atmospheric dust (Fig. 3). Leachable P also increased as dust load increased, but at a lower rate such that the fraction of LIP in storm dust as a function of total P is much less than that of background deposition (Fig. 3). In contrast to LIN, more LIP is present in the air, and enters the surface water, during storms than in background conditions. This is clear from the mean LIP concentration in storm aerosols ($1.45 \pm 0.66 \text{ nmol m}^{-3}$), compared to that of background aerosols ($0.60 \pm 0.41 \text{ nmol m}^{-3}$) (Table 4). The overall mean LIP concentration in air during the 2001 to 2003 study period, based on both storm and background samples, was $0.7 \pm 0.6 \text{ nmol m}^{-3}$, which is the same as that reported for the 1996 to 1999 subset (Herut et al., 2002).

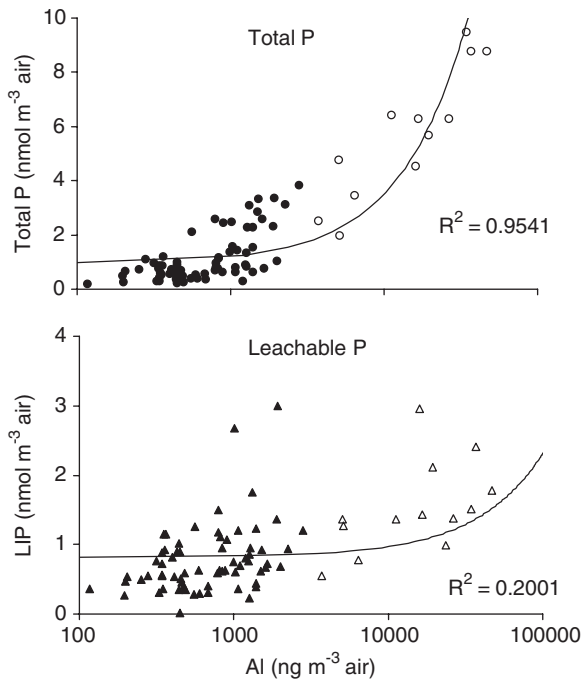


Fig. 3. The relationship between dust-borne phosphorus and dust load (Al concentration) in air. Empty symbols—storm samples, full symbols—background samples. LIP—leachable inorganic phosphorus.

3.3.3. Annual fluxes and Redfield ratios

The estimated annual flux of LIN input from dry deposition from January 2001 to April 2003 was $56 \text{ mmol m}^{-2} \text{ yr}^{-1}$. The estimated annual flux of LIP, which is the fraction that is known to be bioavailable, was $0.5 \text{ mmol m}^{-2} \text{ yr}^{-1}$ (Table 5). These figures are similar to the fluxes estimated for the period from 1996 to 1999 (Herut et al., 2002). Ratios of LIN:LIP in the calculated fluxes for each sample ranged from 8 to 436, with a geomean of 130, and were therefore almost always greater than, and usually much greater than, the Redfield ratio of 16:1. The storm samples had the lowest LIN:LIP ratios. A plot of LIN:LIP sample ratios vs. Al (Fig. 4) showed a simple relationship for storm samples vs. Al, with the lowest ratios in the most intense storms with the highest particle content. The relationship was much more diffuse at lower background particle concentrations. The flux of total inorganic P was $0.8 \text{ mmol m}^{-2} \text{ yr}^{-1}$, which resulted in an N:P ratio that was still far in excess of Redfield.

4. Discussion

4.1. Saharan dust and P adsorption

The purpose of this adsorption experiment was to test the hypothesis that Saharan dust removes

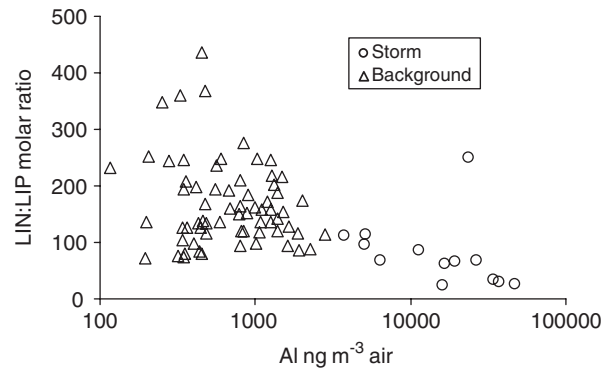


Fig. 4. LIN:LIP molar ratios calculated from fluxes, and plotted against Al concentration (representing dust load) in air.

Table 5

A comparison of annual fluxes of nutrients to the SE. Mediterranean, based on two studies (All units in $\text{mmol m}^{-2} \text{ yr}^{-1}$)

Study dates	Leachable IP	Total P	Leachable NH_4	Leachable $\text{NO}_3 + \text{NO}_2$	Total leachable IN
1996 to 1999 ($n = 41$) (Herut et al., 2002)	~0.4	1	20	34	54
2001 to 2003 ($n = 60$) (This study)	~0.5	0.8	16	40	56

significant amounts of phosphate but not nitrate from Levantine Deep water ($\sim 0.3 \mu\text{M}$) and thus caused the observed high nitrate:phosphate ratio. This study, using samples of dust from five Saharan storms, clearly showed that there was no adsorption of phosphate by Saharan dust. This result reinforces the conclusions of previous studies which used proxy materials, such as Negev loess (Herut et al., 1999b), and Saharan soil from southern Algeria (Ridame et al., 2003). Both these materials were shown to have low adsorption capacities of $0.13\text{--}0.2 \mu\text{mol P g}^{-1}$ (Table 6). Pan et al. (2002) carried out an adsorption isotherm study on a single aeolian dust storm sample from Eilat, and also found no adsorption of P. The Eilat sample however was atypical of Saharan dust as it had a total P content of $111 \mu\text{mol g}^{-1}$, which is approximately three times higher than other dust storm samples used in this study, and in the previous study by Herut et al. (2002). This high level is probably because of contamination caused by improper loading of phosphate fertilizers on ships in the nearby port of Aqaba. These results taken together show that, despite the relatively high content of reactive Fe in Saharan dust, adsorption of phosphate onto this dust is an insignificant process and can be discounted as a reason for the high nitrate:phosphate ratio found in the deep waters in the eastern basin (Krom et al., 1991). The most probable explanations still considered possible to explain the high N:P ratio is biological N fixation (Bethoux et al., 2002) or high N:P ratio in the input supply combined with low denitrification rates within the basin (Krom et al., 2004).

The original hypothesis, that Saharan dust was removing phosphate by adsorption, was based on the fact that iron oxides and hydroxides are known to adsorb phosphate (McBride, 1994; Cornell and Schwertmann, 2003). It is therefore relevant to ask the question, why is Saharan dust in the Eastern

Mediterranean so unreactive towards adsorption of phosphate? This is particularly relevant because the solitary sample from a Western Mediterranean dust storm behaved differently from those collected in the eastern basin. The Western Mediterranean sample had a moderate capacity (more than eastern dust but less than Nile particulates) to adsorb P throughout the range of P concentrations, with adsorption capacity increasing with solution P concentration. At typical deep water P concentration of $\sim 0.3 \mu\text{M}$ P, the dust adsorbed $\sim 1.5 \mu\text{mol g}^{-1}$ (Fig. 1). The Western Mediterranean proxy sample from Algeria (Ridame et al., 2003) also showed some capacity for adsorption ($0.13 \mu\text{mol g}^{-1}$), but this is an order of magnitude smaller than the adsorption by the true aeolian storm sample.

The main difference between dust deposition in the western and eastern basin is that the dust is associated with rain events more frequently in the western basin than in the eastern basin (Guerzoni et al., 1999). It is known that dust particles within clouds can be recycled many times at low pH, which is known to alter their Fe speciation (Jickells and Spokes, 2001). Saharan dust is formed in a hot arid climate which favours conversion of iron to haematite during mineral weathering. Haematite is known to be one of the least reactive of iron oxides to chemical reactions (Poulton et al., 2004). Thus any recycling reactions in the clouds are likely to convert iron to the more reactive iron oxides and/or Fe(II) (Jickells and Spokes, 2001).

It is hypothesised that the higher adsorption capacity and higher content of highly reactive Fe (1.3%) in the Western Mediterranean sample compared to the Eastern Mediterranean samples (1%) may be related to recycling in clouds. Some preliminary evidence to support the cycling of the Western Mediterranean dust through rain clouds comes from SEM images, which show spherical particles that look like the dust has adhered together

Table 6

Comparison of LIP and adsorbed P from this study and four similar studies. Adsorption data are taken from starting solution P concentrations representative of deep-water P concentration— $0.3 \mu\text{M}$ (Herut et al., 1999a), $0.25 \mu\text{M}$ (Pan et al., 2002) and $0.25 \mu\text{M}$ (This study)

	Herut et al. (1999a)	Pan et al. (2002), Herut et al. (2002)	Ridame et al. (2003)	This study
Leachable inorganic P ($\mu\text{mol P g}^{-1}$ dust)	1.3 (Negev loess, $n = 1$)	1.5 to 8.0 (storm dust, $n = 4$)	N/A	1.1 to 6.7 (storm dust, $n = 6$)
Adsorbed P ($\mu\text{mol P g}^{-1}$ dust)	0.2 (Negev loess)	None (storm dust)	0.13 (Saharan soil, S. Algeria)	None (storm dust)

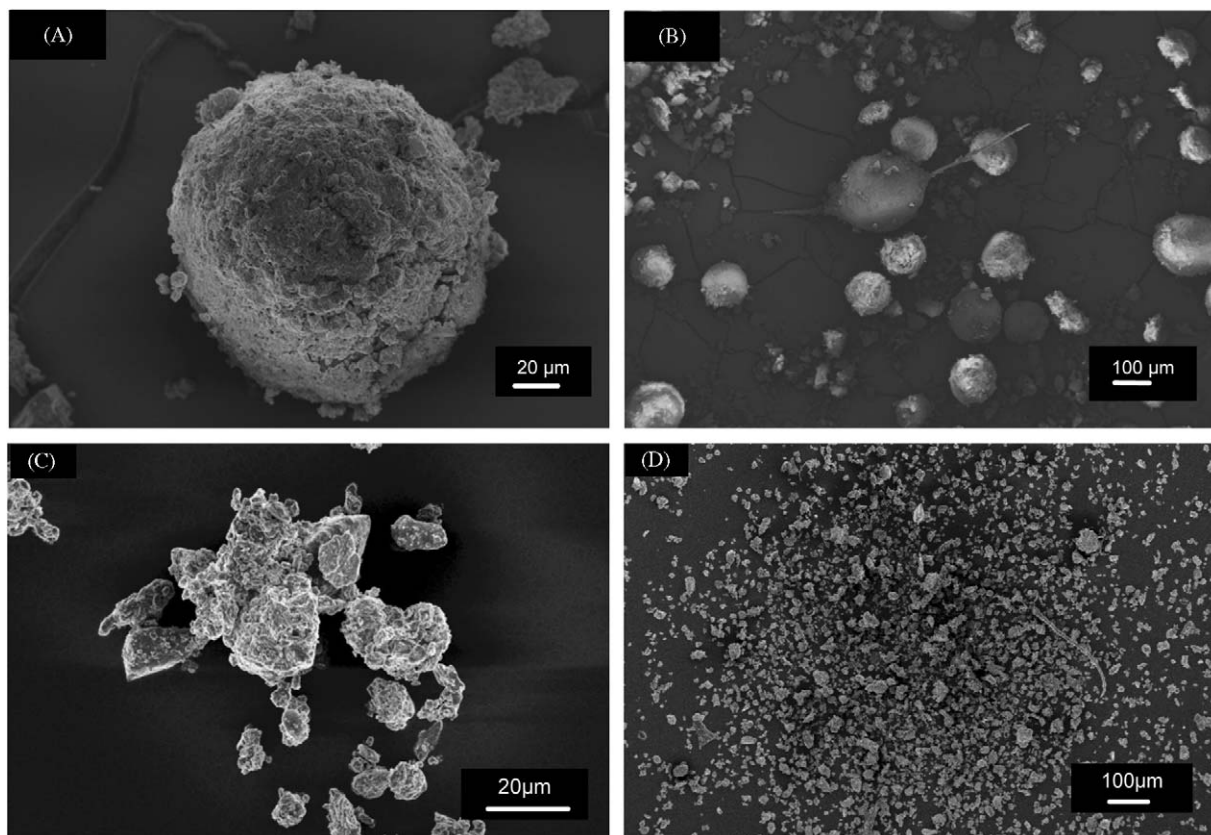


Fig. 5. Scanning electron micrographs of dust particles. (A) A large, aggregated dust particle from the Western Mediterranean sample, presumably aggregated through interaction with cloud moisture. Note that the particle is made of thousands of smaller particles, (B) as (A), but with lower magnification: an array of aggregates, (C) typical non-aggregated dust particles from an Eastern Mediterranean sample, (D) as (C), but with lower magnification.

on subsequently evaporated raindrops (Fig. 5A and B). The Western Mediterranean sample contains spherical aggregates $\sim 100\ \mu\text{m}$ in diameter that are composed of many small ($1\text{--}5\ \mu\text{m}$) clusters. These large spheres were very much less common in Eastern Mediterranean dust samples from the Israeli coast (Fig. 5C and D). Spectrometric analysis of both samples showed that the individual subgrains consisted primarily of clays, quartz and feldspar with minor calcite content showing major Al, Si, K, Na and Ca peaks and minor Fe and Mg peaks. Further experiments are necessary to investigate the chemical speciation and reactivity of this dust.

4.2. Nutrient input from dry deposition

4.2.1. Storm vs. background inputs

There are some clear chemical differences between the nutrient content of storm and background

dust, which are evident in both this study and that of Herut et al. (2002). It has been shown that the source of total P is the rock/soil content of dust without any additional input from atmospheric sources. This is confirmed in this study by the linear relationship between total P and Al as a measure of total particulate matter ($r^2 = 0.95$). Little is known about the source and nature of the LIP phase. In this study it was found that the leachable-P fraction in background samples is much greater than that of storm samples. Since the particle size of storm dust is coarser than that of background dust (Offer and Goossens, 2004) this may be related to the greater mean particle size, and therefore smaller surface area. Alternatively, it may be related, at least in part, to atmospheric recycling processes since the background samples have higher LIP and higher LIN. The processes that add N to background dust particles may convert some of the total P into leachable P in the atmosphere. It is well known that

cloud water tends to be acidic because acid gases dissolve in cloud water, typically forming sulphuric, nitric and carbonic acids (Seinfeld and Pandis, 1998).

By contrast LIN is not part of the rock/soil component, and accumulates by atmospheric processes en route. Differences in LIN load are linked to the trajectory from the source to the deposition area. In general the major source of NO_x in the atmosphere is transport related pollution, while ammonium is derived predominantly from agriculture (Galloway, 2003). Hanke et al. (2003) have demonstrated efficient uptake of gaseous nitric acid (HNO_3) onto mineral dust aerosol particles, and suggest that dust is an important sink for HNO_3 in the troposphere. Lelieveld et al. (2002) observed that anthropogenic aerosol pollution in the Eastern Mediterranean basin comes mainly from Eastern Europe. Our results suggest that background dust has a higher content of N than Saharan dust. The background dust has a higher proportion of fine grained particles and probably a different trajectory and residence time in the atmosphere than dust storms. Dust carried via northern trajectories will carry more nitrogen than dust carried along southerly trajectories, and this results in a higher LIN:LIP ratio. A large proportion of background samples in this study have a high LIN:LIP ratio, and it is possible that this reflects a northerly trajectory. On the other hand, storm dust is typically blown directly from the south (D'Almeida, 1986), which would explain the lower LIN load that results in lower LIN:LIP ratios (Fig. 4).

4.2.2. Atmospheric input of nutrients during CYCLOPS addition cruises

No blooms have yet been reported in the Eastern Mediterranean as a result of nutrient input from dust storms. The occurrence of a dust storm during the first CYCLOPS cruise in 2001 provided an opportunity to observe the ecosystem response directly. At the height of the storm, there was a 3- to 4-fold increase in LIP input, and a smaller increase in LIN over background values. The LIN:LIP from atmospheric deposition was greater than Redfield ratios throughout the cruise, including during the storm. In-situ measurements made during and immediately after the storm showed an increase in bacterial activity (but not biomass) and small measurable change in chlorophyll content (Herut et al., 2005) with a change in species composition.

The fertilizing effect of dust addition in Eastern Mediterranean surface water was investigated over a range of particle concentrations in a dust microcosm experiment, performed during the CYCLOPS cruise (Herut et al., 2005). These investigations showed that as soon as dust is added to the surface water in the microcosm, nutrients are released which are taken up by bacteria and phytoplankton. These result in increased chlorophyll content, bacterial activity, and primary productivity. In interpreting these results Herut et al. (2005) have noted that the dust input from the storm fell at the lower end of the range of dust additions in the experiment and thus it would not necessarily have produced a detectable increase in chlorophyll. However taken with other results obtained during the CYCLOPS addition experiment, it was concluded that any chlorophyll increase which might have been caused by dust fertilization would be expected to be immediately grazed out of the water column Thingstad et al., (2005), and therefore undetected by remote sensing.

4.3. Is dust important in the nutrient budget and new production in the basin?

4.3.1. Fluxes and Redfield ratios

Flux estimates from the Tel Shikmona datasets, from 1996 to 1999 (Herut et al., 2002) and 2001 to 2003 (this study), show similar total nitrogen inputs (Table 5). Estimated LIN input from dry deposition was $56 \text{ mmol m}^{-2} \text{ yr}^{-1}$ during 2001–2003, compared to the 1996 to 1999 value of $54 \text{ mmol m}^{-2} \text{ yr}^{-1}$. The annual flux of total P (both leachable and insoluble) from dry deposition was estimated at $0.8 \text{ mmol m}^{-2} \text{ yr}^{-1}$, which is close to the $1 \text{ mmol m}^{-2} \text{ yr}^{-1}$ of the 1996 to 1999 dataset (Herut et al., 2002). Mean LIP is 58%, giving an estimated annual flux of $0.5 \text{ mmol m}^{-2} \text{ yr}^{-1}$ LIP. These results show that the total atmospheric flux estimates used in Krom et al. (2004) are also valid for this additional data set. As a result of the chemical differences observed in this study, it was found that dust storms contribute greater LIP to the surface water, while background inputs provide greater LIN. Since LIN:LIP ratios in the combined storm and background dataset are consistently above the Redfield ratio of 16:1 (Redfield et al., 1963), and the Eastern Mediterranean is primarily P-starved, LIP is the important factor to consider when calculating the effect of dust inputs on primary production.

Table 7

Table showing the calculated nutrient inputs into the Eastern Mediterranean basin as calculated in Krom et al. (2004)

Best estimate for nutrient fluxes into the basin		
Source:	N input	P input
Atmospheric input	111	0.95
Riverine input (Po and adjacent area of N. Adriatic)	20	0.9
Nile input	15	0.25
Riverine input from rest of basin	28	1.25
Black Sea	8	0
Total input to basin	180	3.4
Best estimate for nutrient fluxes out of the basin		
Straits of Sicily	142	4.4
Sediment deposition	27	1.0
Sediment denitrification	9	
Total output from basin	178	5.4

All values are given in 10^9 moles/yr.

New production is defined as the annual primary production in a given location supported by externally supplied nutrients (Dugdale and Goering, 1967). This concept and the related idea of export production have been used extensively for many purposes, including determining the amount of anthropogenic carbon dioxide uptake in the oceans. However in systems such as the Eastern Mediterranean, a significant fraction of the externally supplied nutrients is from organic matter recycled from the previous year's primary productivity. Krom et al. (1992) showed that a minimum of 60–70% of the nutrients supplied to the surface waters in the Cyprus warm-core eddy was actually derived from the previous year's primary productivity, which had dropped below the photic zone but was still within the depths affected by the following year's deep winter mixing.

Since the Eastern Mediterranean is essentially an isolated seawater lake, it is possible to determine the total annual nutrient supply, which represents the true externally driven new production (external production) within the basin. Krom et al. (2004) determined such a total nutrient budget for the Eastern Mediterranean (Table 7). This budget shows that atmospheric input, which is mainly from dry deposition, represents ~60% of the N input to the basin and ~30% of the P input. Using a C:N:P molar ratio of 106:16:1 (Redfield et al., 1963), the total external production for the eastern

basin deduced from the phosphate budget is $5.6 \text{ g C m}^{-2} \text{ yr}^{-1}$, and from the nitrate budget the corresponding value is $8.3 \text{ g C m}^{-2} \text{ yr}^{-1}$. The difference between these estimates is due mainly to the unusual N/P ratio in the region. These estimates are similar to those calculated by Bethoux et al. (1998) of 5.5 and $8 \text{ g C m}^{-2} \text{ yr}^{-1}$, respectively, which were calculated based on the outflow from the basin through the Straits of Sicily. Estimates have been made for the total basin-wide primary productivity using satellite images of sea colour. More than 2600 images were collected by CZCS aboard the NIMBUS-7 satellite from 1978 to 1986 (Antoine et al., 1995), resulting in an annual figure of $110 \text{ g C m}^{-2} \text{ yr}^{-1}$. A more recent estimate from 1998 to 2000 by the same research group (Bosc et al., 2004) gave an adjusted value of $121 \text{ g C m}^{-2} \text{ yr}^{-1}$. In situ measurements have produced estimates of $55 \text{ g C m}^{-2} \text{ yr}^{-1}$ for the eastern basin (Turley et al., 2000) and $59 \text{ g C m}^{-2} \text{ yr}^{-1}$ Cretan Sea slope (Psarra et al., 2000). These figures suggest that external production is ~5–10% of the total production within the system. This value is low even when compared to ultra-oligotrophic areas of the ocean, particularly since the Eastern Mediterranean has such a high flux of dust that acts as ballast and increases the flux of organic matter into deeper water (Hubner et al., 2004). This shows that in such ultra-oligotrophic systems, primary productivity is driven mainly by winter mixing and by very efficient recycling of nutrients within the system due to grazing. Nevertheless external supply processes such as atmospheric deposition are extremely important in controlling the total amount and nature of primary production.

4.4. Potential for change in dust storm effects

Global nitrogen fluxes have increased over the last 100 years due to anthropogenic activity (Galloway et al., 1996) and it is likely that the anthropogenic nitrogen input will increase, adding to P-limitation. However, since the Eastern Mediterranean has an exceptionally high N:P ratio of 25–28:1, increasing anthropogenic N inputs are unlikely to cause an increase in productivity. By contrast, an increase in P inputs is likely to enhance productivity. In this study, we have shown that most of the P supplied to the basin comes from Saharan dust storms. There is evidence that P inputs may be increasing, as a result of higher frequency and duration of Saharan dust storms over the last

few decades, coinciding with long term drought in the Sahelian zone (Middleton, 1985; Ganor, 1994; N'tchayi Mbourou et al., 1997). In the SE Mediterranean, storms increased from ~10 in 1958 to ~19 in 1991 (Ganor, 1994).

Long-term studies are vital in order to determine the response of this ultra-oligotrophic system to potentially increasing nutrient inputs.

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