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Limnol. Oceanogr., 47(3), 2002, 870–878

The role of dust in supplying nitrogen and phosphorus to the Southeast Mediterranean

Abstract—This study assesses the role of the atmospheric dry fallout as a source of new nitrogen and phosphorus to the surface Levantine seawater. Leaching experiments of inorganic nitrogen ($LINO_3^-$, $LINH_4^+$) and phosphorus ($LIPO_4$), using SE Mediterranean surface seawater, were performed on 41 aerosol (hereafter dust) samples collected on Whatman 41 filters between April 1996 and January 1999 at Tel Shikmona, Israel and on four desert-event dust powder samples. A geometric mean of 2.8 and 3.2 mmol NO_3^- and NH_4^+ per gram of dust was leached by seawater from normal (background) dry deposition captured by the filters. Significantly lower amounts of IN with lower $NH_4^+ : NO_3^-$ ratios were leached from both the filters and the dust powder sampled during dust events (mean of 0.18 and 0.02 mmol NO_3^- and NH_4^+ per gram of dust). Similarly, relatively lower values of $LIPO_4$ were measured in desert type events, attributed to systematic decrease in IP solubility with increased rock/soil component. The calculated $LINO_3^-$ and $LINH_4^+$ fluxes were 34 and 20 mmol m^{-2} yr^{-1} from normal dry deposition, 2.5 higher than the wet IN deposition, and twice the riverine input (23 mmol m^{-2} yr^{-1}, Guerzoni et al.). This high ratio is due to the semiarid climate in this basin. The estimated flux of total dry IP was 1 mmol P m^{-2} yr^{-1}, approximately 3 times higher than the input of wet IP and somewhat lower than the estimated riverine input (1.4 mmol m^{-2} yr^{-1}, Guerzoni et al. 1999). The similarity of atmospheric and burial fluxes of P in the Levantine basin reinforces the hypothesis that the atmosphere is the dominant source of P to the sediments in the deeper parts of the basin. It was estimated that the leachable fluxes of IP and IN (dry + wet) can support between ~15 or ~70% (1–4 g C m^{-2} yr^{-1}) of the new production in the SE Mediterranean, effective mainly during dust events and stratification. This input may contribute significantly to the relatively high N : P ratios in Levantine deep water (~27).

Atmospheric deposition is an important route through which many elements are delivered to surface seawater. While water column profiles can help to measure this process for certain elements (e.g., Al), it is not suitable for nutrients, where the atmospheric input is masked by biogeochemical processes. Nevertheless, it has been suggested that atmospherically derived nutrients are an important component of bioavailable nutrients to the upper water column, particularly (1) during large sporadic events of deposition, either of anthropogenic or natural character (Paerl 1997; Prospero et al. 1996; Spokes et al. 2000); (2) in oligotrophic seas; and (3) during seasons of low vertical mixing.

The eastern Mediterranean has one of the highest fluxes of atmospheric dust to the sea surface (Guerzoni et al. 1999 and references therein; Herut et al. 2001). It is a very oligotrophic sea with low levels of nutrients even in the deep water (Kress and Herut 2001). Thus, in this particular basin, the atmospheric deposition may play a particularly important role in the supply of bioavailable nutrients to surface waters. Indeed, recent studies have suggested that significant input of nutrients to the Mediterranean basin at present is via the atmosphere (Martin et al. 1989; Guerzoni et al. 1999; Kouvarakis et al. 2001).

Although it has been shown previously that phosphate is leached from dry fallout into nutrient-depleted surface waters (Lepple 1975; Graham and Duce 1979; Herut et al. 1999*a*,*b*), almost no studies have previously examined N leachability in surface seawater and its dependence on aerosol sources (composition). In this study we provide estimates of seawater leachable (bioavailable) inorganic nitrogen (IN) and phosphorus (IP) from dry aerosols and their flux into the SE Mediterranean. Samples have been taken routinely over a period of two and one half years, which allows the background normal dry deposition to be characterized. In addition samples were taken during some desert dust events (Sahara, Sinai, and Negev), which is when most of the total particulate flux was supplied. These data are used to develop a clearer understanding of the role of atmospheric dry fallout as a source of new nitrogen and phosphorus in the Levantine basin, particularly in spring and summer when there is no deep mixing and the surface mixed layer is nutrient depleted.

The eastern Mediterranean contains deep waters with high $NO_3^- : PO_4^{3-}$ ratios (25–28 : 1; Krom et al. 1991, 1993; Herut et al. 2000*a;* Kress and Herut 2001), significantly higher than the normal oceanic Redfield ratio of 16 : 1. It has been hypothesized that this unusually high $NO_3^- : PO_4^{3-}$ ratio might result from one or a combination of the following processes: (1) nitrogen fixation (Bethoux et al. 1998); (2) inorganic removal of phosphate onto particulate matter, particularly in the deep-water column (Krom et al. 1991; Eijsink et al. 2000); (3) contribution of atmospheric precipitates with relatively high $NO_3^- : PO_4^{3-}$ ratios (~25) (Herut et al. 1999*a*); and (4) formation of NO_3^- enriched deep eastern Mediterranean waters of Adriatic origin (Civitarese et al. 1998). The results reported here enable a better evaluation of the importance of dry atmospheric deposition on the unusual N : P ratios in this basin.

Sampling and leaching experiments—The atmospheric sampling of total suspended particles (TSP) in air was performed on the roof of the National Institute of Oceanography (NIO) at Tel-Shikmona (TS) (located on the shore and inside the sea, 22 m above sea level). A total of 41 filter samples, collected between April 1996 and January 1999, were used for the leaching experiments. This site is on a headland

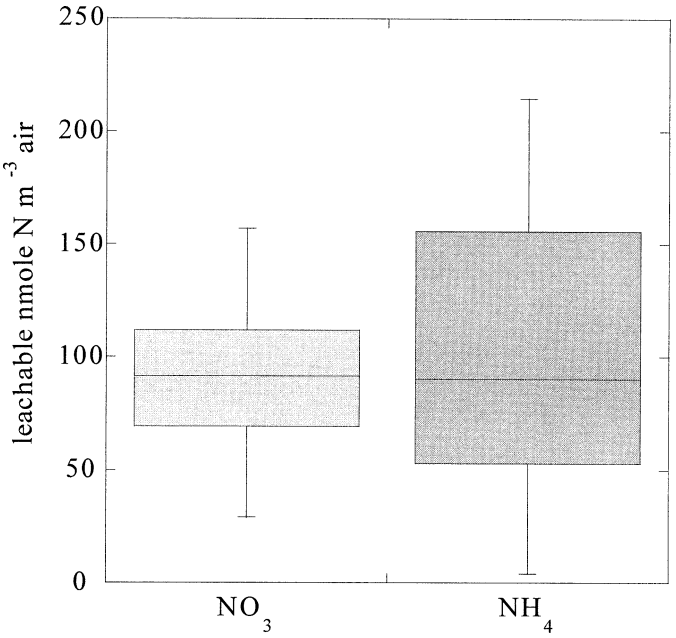

Fig. 1. Box plots of seawater leachable particulate NH_4^+ and NO_3^- concentrations in m^3 air. The bottom and the top edge of each box are located at the sample 25 and 75 percentiles. The central horizontal line is drawn at the sample median.

pointing into the sea, which has only minor amounts of local contamination. Indeed, contemporaneous samples from TS and another station along the Mediterranean coast of Israel showed similar variability of Al (and other metal) concentrations in air (Herut et al. 2001). In addition, a comparison with contemporaneous samples collected at Erdemli, Turkey, revealed a significant linear correlation ($r = 0.71$, $P < 0.05$, $n = 50$) of Al concentrations in air, excluding dust storm events (N. Kubilay pers. comm.). Suspended particles were collected on Whatman 41 filters (20 × 25 cm) by a high volume sampler at a flow rate of 42 $m^3\ h^{-1}$ for approximately 60 h for 75% of the samples and in the range of 19 to 114 h. After collection the filters were dried in a desiccator for 24 h before being reweighed. Nevertheless, the filter weights were inaccurate due to their tendency to immediately adsorb humidity. The error in weight accuracy (for filters with <120 mg dust) is estimated at approximately 30%, calculated from the standard error of the significant linear correlation ($P < 0.05$) between dust and Al concentrations in air. Dust powder samples (dry deposited material) were collected during major dust events (Table 1) from the top of a glass panel collector at Beit Yannay (BY, located on the roof of a building 300 m from shoreline), Israel, and from a plastic surrogate collector at Eilat (Gulf of Aqaba, located on the roof of a building 500 m from the shore), Israel. Following the dust storm, the dust powder was scraped from the panels by a clean plastic knife into prewashed (10% hydrochloric acid) 15-ml scintillation vials.

Leaching experiments were performed to evaluate the amount of seawater leachable nitrate, ammonium, and phosphate from the TSP. Subsamples of one cm^2 of dust filter and blanks were shaken in Teflon centrifuge vials for 30 h (constant room temperature and small pH variations of 8.12 ± 0.06 for both initial and final values) containing 30 ml of 0.2-μm filtered SE Mediterranean surface seawater (collected with the R/V *Shikmona* on 4 November 1998, 20 km off the Israeli coast). Preliminary experiments showed that the leaching process reached equilibrium after 3 h. After leaching, samples were centrifuged at 8,000 rpm for 10 min. Subsamples were pipetted and stored (frozen) in precleaned (10% HCl) 15-ml plastic vials for nutrient analyses. Aluminum, iron, and calcium concentrations were measured on a second subsample (35 cm^2) by total digestion with HF following the procedure of the American Society for Testing and Materials (ASTM 1983).

For the dust powder samples, the leachability experiments were similar to those of the filters, only differing in that (a) different amounts of the same dust sample was used (Table 1), (b) seawater leachates were shaken for 70 h, and (c) total IP leachates were done by the addition of 2 ml HF and 2 ml HCl (both suprapure and distilled) to the weighed dust samples. After four evaporation cycles with HCl additions (to drive off excess HF), 8 ml of Milli-Q water were added. After centrifugation, the top 7 ml were pipette for PO_4^{3-} analyses.

All analytical results were corrected for the blanks. The blanks for the experiments on filters were 0.08, 0.12, and 0.96 μmol L^{-1} for PO_4^{3-}, NO_3^-, and NH_4^+, respectively. The precisions of the blanks were ±11% for P, ±12% for nitrate, and ±10% for ammonium. The blanks accounted in average for 36%, 0.7%, and 6% of the mean leachable concentration, and 5% of the total IP concentrations. For the powder dust leaching experiments, the bottle blanks were 0.01, 0.12, and 0.17 μmol L^{-1} for PO_4^{3-}, NO_3^-, and NH_4^+, respectively. The blanks were calculated to be 20% and 25% of the mean leachable PO_4^{3-} and NO_3^- and 5% of total IP concentrations. The leachable concentrations of NH_4^+ were relatively low for the dust powder samples because relatively small amounts were used and the resultant signal was indistinguishable from the blank (Table 1).

Analyses for ortho-PO_4^{3-}, $NO_3^- + NO_2^-$, and NH_4^+ leached by seawater were performed using hybrid Alpkem RFA 300 (nitrate) and Technicon AA-II (phosphate and ammonium) autoanalyzers. Analytical methods followed the Joint Global Ocean Flux Study/World Ocean Circulation Experiment (JGOFS/WOCE) nutrient protocols (Gordon et al. 1994). The short-term precisions of the nutrient analyses were: phosphate, 0.4%; nitrate, 0.3%; and ammonium, 0.3% (Jennings et al. unpubl. data 1990–2001). The limit of detection was 0.005 μM for phosphate and 0.05 μM for nitrate and ammonium. Total N was measured on the dust powder samples using a Carlo-Erba CHN analyzer (L-cystein standards, precision of 0.3%; Keil et al. 1994). Al, Fe, and Ca concentrations were measured on a Perkin Elmer 1100B atomic adsorption spectrometer equipped with graphite furnace. The accuracy of the Al and Fe 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, which gave results within 5% of the certified values.

Several previous studies have used detailed sampling from coastal sites and extrapolated the results to the adjacent marine areas (Martin et al. 1989; Spokes et al. 2000). The dry

Table 1. Seawater leachable phosphate ($LIPO_4$), ammonium ($LINH_4^+$), nitrate ($LINO_3^-$), total inorganic P (total IP), and total N (total N) in dust samples during desert dust events and from total suspended particles (TSP) collected on 34 filters (statistical summary) representing normal (background) values. LS = low signal that is indistinguishable from the blank. na = not analyzed (not enough material left).

Sample	Type	Date sampled*	Sample weight (mg)	$LIPO_4$ (μmol g^{-1})	Total IP† (μmol g^{-1})	IP solubility (%)	$LINH_4^+$ (μmol g^{-1})	$LINO_3^-$ (μmol g^{-1})	Total N† (μmol g^{-1})
Desert type dust events									
BYDI	Dust powder	08 May 96	0.46	2.2	27	8	LS	LS	na
BYDI	Dust powder	08 May 96	0.62	4.3	27	16	LS	LS	
BYDI	Dust powder	08 May 96	1.54	2.5	27	9	15	19	
BYDII	Dust powder	15 Mar 98	0.13	2.1	96	2	LS	LS	164 ± 29
BYDII	Dust powder	15 Mar 98	0.40	7.7	96	8	LS	LS	
BYDII	Dust powder	15 Mar 98	1.00	8.0	96	8	0.6	199	
BYDIII	Dust powder	27 Mar 98	0.26	1.5	20	8	LS	LS	164 ± 29
BYDIII	Dust powder	27 Mar 98	0.40	3.5	20	17	11	175	
BYDIII	Dust powder	27 Mar 98	0.80	1.7	20	9	LS	LS	
ED	Dust powder	28 May 97	0.25	4.8	109	4	14	61	43 ± 7
ED	Dust powder	28 May 97	0.56	5.3	109	5	LS	LS	
140	TSP (filter)	11 Mar 98	0.18	10	55	17	761	1,070	LS
142	TSP (filter)	15 Mar 98	0.72	6.1	111	6	64	145	LS
143	TSP (filter)	27 Mar 98	0.76	7.2	140	5	LS	363	LS
161	TSP (filter)	14 Oct 98	1.03	7.5	37	20	20	494	LS
Geomean				4.2	52	8	20	181	
Median				4.8	55	8	15	188	
Average				5.0	66	10	127	316	
SD				2.7	43	5	280	341	
Normal (background) events (n = 34)									
Geomean	TSP (filter)	1996–1999	0.19	19	34	48	3,230	2,760	LS
Median			0.20	20	39	48	3,380	2,580	LS
Average			0.24	27	53	50	5,130	3,670	LS
SD			0.16	22	43	12	5,350	2,720	LS
Min			0.05	3	2	30	411	646	LS
Max			0.63	85	175	79	25,000	9,950	LS

* Initial sampling date.
† Measured on a separate subsample of dust.

atmospheric deposition flux (*Fd*) was calculated from the concentration of total particulate element or of the seawater $LIPO_4$ or LIN in the air (geometric mean, C) times the deposition velocity (V_d) ($F_d = C \times V_d$). Owing to the absence of measured deposition rates, the values used here for V_d are those 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. In coastal or marine environments, most nitrate occurs in the coarse fraction aerosols, whereas ammonium is predominant in the fine fraction (Li-Jones and Prospero 1998; Spokes et al. 2000). Thus, for nitrate and ammonium we used V_d values of 1.2 and 0.6 cm s^{-1}, respectively (Spokes et al. 2000). A similar value for nitrate (1 cm s^{-1}) and a lower value for ammonium (0.1 cm s^{-1}) was used by Duce et al. (1991). These estimates result in an uncertainty of a factor of 2–3 in the calculated flux (Duce et al. 1991).

Leachability of inorganic nitrogen from dry fallout by surface SE Mediterranean seawater—It was possible to describe the nutrients leachability and total flux data in terms of two populations of data: dust events, sampled as dust powder and filters on an event basis; and background values, which were sampled by the filters on a routine basis. Significantly higher concentrations of Al and Fe were observed in desert type air masses as compared to marine and European air sources (Herut et al. 2001). We classified the dust-event population to include only significant events with Al concentrations greater than 3,600 ng m^{-3} air, in order to better characterize this end member (Table 2). The normal background values include samples with Al concentrations lower than 1,700 ng m^{-3} air and probably reflects both crustal and anthropogenic inputs.

High variability with a geometric mean of 2.8 and 3.2 mmol NO_3^- and NH_4^+ per g of dust was leached by seawater from the filters (Table 1). This represents the amount of IN leached from the dry deposition during normal weather conditions. These estimated amounts might contain uncertainties related to the error in filter weights (*see sampling and leaching experiments*). Significantly lower amounts of IN were leached (*t*-test at 99% confidence interval or by nonparametric Mann–Whitney test) from both the filters and the dust powder sampled during dust events (geomean of 0.2 and 0.02 mmol NO_3^- and NH_4^+ per g of dust; Table 1). The sum of the seawater leachable IN species was similar to (though slightly higher than) the total N, suggesting that there is no significant organic N or other N phases in the dry deposition (i.e., during dust events).

The calculated geometric mean concentration of aerosol $LINO_3^-$ and $LINH_4^+$ in the normal air is 89 and 107 nmol m^{-3}, respectively (Table 2). The frequency distribution (Fig. 1) is similar to that observed elsewhere (e.g., Duce et al. 1991; Spokes et al. 2000), with significantly ($P < 0.05\%$) lower $LINH_4^+$ concentrations during desert type events (Table 2). In those previous studies the lower concentrations were considered typical of marine air masses while the higher concentrations were characteristic of polluted air masses. This distribution, however, might reflect possible variations

Table 2. Seawater leachable phosphate ($LIPO_4$), ammonium ($LINH_4^+$), nitrate ($LINO_3^-$), total inorganic P (total IP), and Al concentrations in air revealed from total suspended particles (TSP) collected on Whatman 41 filters at Tel-Shikmona (SE Mediterranean, Israel). The flux ratios between seawater leachable IN and IP (LIN/LIP) are included.

Parameter	Total IP (nmol m^{-3})	$LIPO_4$ (nmol m^{-3})	$LINH_4^+$ (nmol m^{-3})	$LINO_3^-$ (nmol m^{-3})	Al (ng m^{-3})	LIN/LIP* (molar)
Normal (background) events ($n = 34$)†						
Geomean	1.2	0.6	107	89	688	138
Median	1.2	0.6	126	95	717	150
Average	1.4	0.7	129	94	798	147
SD	1.0	0.5	90	28	416	52
Min	0.2	0.2	25	37	182	56
Max	5.5	2.4	524	157	1,670	288
Desert type dust events ($n = 4$)						
Geomean	12.1	1.2	18	66	16,250	37
Median	11.8	1.2	26	69	16,250	35
Average	18.2	1.4	29	70	33,610	44
SD	18.7	0.8	26	25	44,070	30
Min	4.0	0.7	4	42	3,612	18
Max	45.1	2.5	56	99	98,330	87
All filters ($n = 41$)						
Geomean	1.6	0.7	90	88	1,024	117
Median	1.4	0.6	98	94	857	145
Average	3.3	0.8	117	93	4,116	133
SD	7.5	0.5	88	29	15,570	58
Min	0.2	0.2	4	37	182	18
Max	45	2.5	524	157	98,330	288

* Flux ratios of $(LINO_3^- + LINH_4^+)/LIPO_4$.

† Similar particulate AL concentrations were measured at TS during 1994–1997 (geomean = 865, n = 96) and at Erdemli, Turkey (Kubilay and Saydam 1995).

in removal processes and vertical mixing. The calculated $LINO_3^-$ and $LINH_4^+$ depositional fluxes are 34 and 20 mmol m^{-2} yr^{-1}, respectively. The total LIN flux is, therefore, approximately 50 mmol m^{-2} yr^{-1}, approximately twice the riverine input (23 mmol m^{-2} yr^{-1}, Guerzoni et al. 1999). These flux estimates contain uncertainties related to errors attributed to deposition velocity values (*see sampling and leaching experiments*) and the fact that samples were not collected continuously over a whole year, but follow the approach of several previous estimates (e.g., Duce et al. 1991). By use of the calculated wet IN deposition of 20 mmol m^{-2} yr^{-1} (Herut et al. 1999*a*), the estimated ratio of dry : total IN deposition is 0.7, in contrast to previous estimates of 0.25 (Martin et al. 1989) in the West Mediterranean and other oceanic sites (Duce et al. 1991). This unusually high ratio is probably because Tel Shikmona, Haifa, is in a semiarid location, whereas previous data were collected from more humid regions. In addition, several processes may shift volatile N species to the aerosol phases and enhance their dry deposition. These include the formation of submicron NH_4NO_3 or $(NH_4)_2SO_4$ and coarser $NaNO_3$ aerosols (Prospero et al. 1996). The presence and relationship of non–sea-salt sulfate and IN species in aerosols (Mihalopoulos et al. 1997) and rains (Herut et al. 2000*b*) at coastal sites in the Eastern Mediterranean Basin were reported previously.

Leachability and dry flux of inorganic phosphorus—The geomean of total IP concentration in the filters of normal events was somewhat lower than that found in the samples from dust events (~30 and 50 μmol g^{-1} dust, Table 1). It was found that the total IP concentrations for filter samples were linearly correlated with particulate Fe (or Al, Ca) (Fig. 2). This suggests that the total IP is derived from or associated with the soil/rock source.

A geomean of 19 μmol IP per gram of dust on the filters was leached by seawater in normal events (Table 1). By contrast the dust samples of desert type events showed considerably lower mean seawater leachable values of ~4 μmol IP per gram of dust (Table 1). This compares to a value of ~12 ± 7 μmol IP per gram of dust on 20 filters of both background dry deposition and dust events measured at Tel Shikmona during 1996 (Herut et al. 1999*a*). The seawater $LIPO_4$ varied between 5 and 79% of the total IP (Table 1, mean of ~50%). The fraction of P leached was highest in the filter samples with low concentrations of rock/soil-derived elements (e.g., Al, Fe, Ca) (Fig. 3). By contrast, in dust storm events, a geomean seawater solubility of both the filter and powder samples was 8% (Table 1). Previous studies showed a similar pattern with a lower fraction of total IP being leached in TSP samples collected during dust events in 1996 at Tel Shikmona (Herut et al. 1999*a*) and in remote loess particles (Eolian deposits used as dust proxy) collected at the Negev Desert (Israel) (Herut et al. 1999*b*). Over the NW Mediterranean, Bergametti et al. (1992) and Migon and Sandroni (1999) also found lower P solubility in rainwater during Saharan type events. Speciation of P in sample BYDI (Eijsink et al. 2000) suggested that most of the seawater $LIPO_4$ in the desert type samples was probably extracted from the exchangeable and loosely bound, and in part of the iron-bound P phases in the dust.

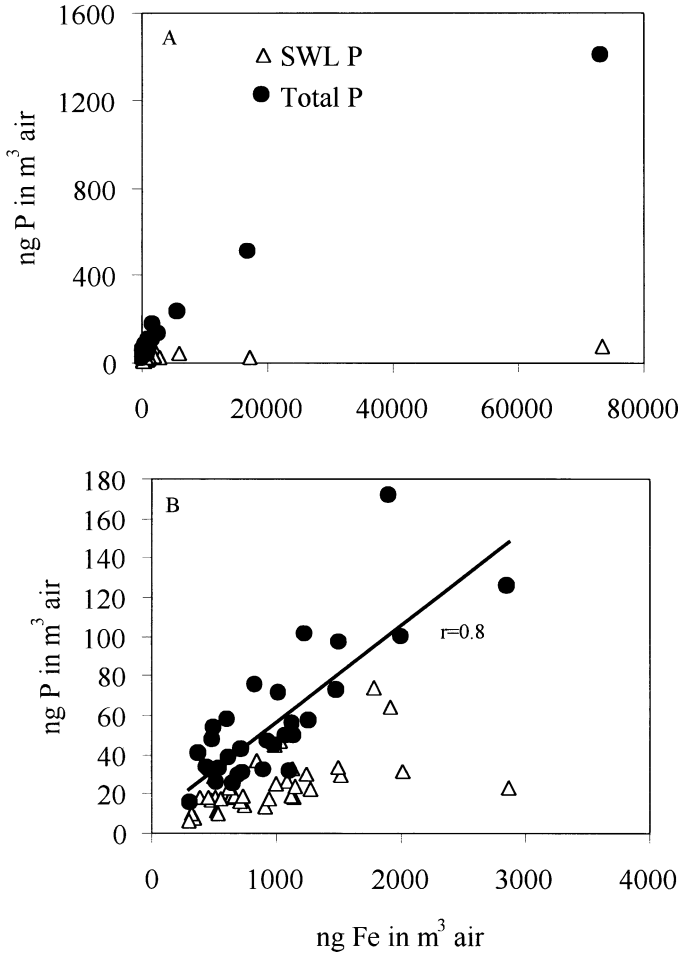

Fig. 2. (A) Relationships between seawater leachable (SWL) and total particulate inorganic P and Fe concentrations in m^3 air. (B) Expansion of lower left corner of panel A (low concentration range). Total and seawater leachable concentrations were measured in dust (aerosols) collected on Whatman 41 filters at Tel-Shikmona. The linear regression line that was calculated for the total inorganic P data (in panel B) is included ($p < 0.01\%$).

The calculated geometric mean concentration of total particulate IP in air was 1.6 nmol m^{-3} (Table 2). The calculated corresponding flux of total IP via dry fallout was 1 mmol P m^{-2} yr^{-1}. This was approximately 3 times higher than the input of wet IP (0.3 mmol P m^{-2} yr^{-1}, Herut et al. 1999*a*), and somewhat lower than the estimated riverine input (1.38 mmol m^{-2} yr^{-1}, Guerzoni et al. 1999).

The Eastern Mediterranean Basin is extremely nutrient depleted and considered as limited by the availability of P (Krom et al. 1991; Zohary and Robarts 1998). In order to relate the possible atmospheric input of IP to the sediment and phytoplankton reservoirs in this basin we assumed that (1) in view of the P limitation across the basin, it is reasonable to assume that most of the bioavailable P is recycled in the water column and eventually will leave the basin through the straits of Sicily. The burial flux of organic P into the sediments is minor (Eijsink et al. 2000). (2) In this particular basin, the atmospheric deposition may play a particularly important role in the supply of new bioavailable nutrients to

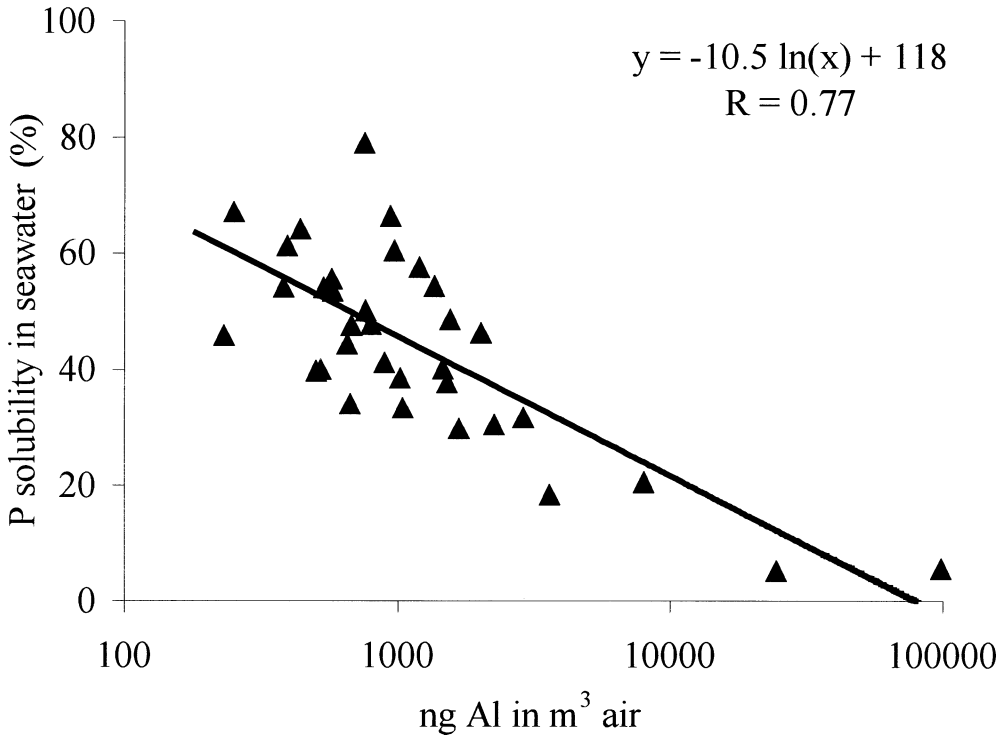

Fig. 3. Inorganic P solubility (%) in seawater versus particulate Al concentrations in m^3 air. The exponential regression line calculated from the data is included.

the open sea (deep basin) surface waters. (3) The phytoplankton nutrient uptake is in Redfield ratios. (4) Slightly less than half of the total dry IP is leachable. This semiqualitative estimate is because the annual estimate of supply of dry deposition by dust-type events is not well quantified and contains large interannual variability. However, based on our dataset and records of dry input in Erdemly (Turkey, Kubilay et al. 2000), dust events accounted for 30–40% of the annual input.

Considering the above assumptions, approximately 0.6 mmol P m^{-2} yr^{-1} settles directly to the sediment (slightly more than half of the total dry IP deposition). This calculation is similar to the estimate of the burial rate of P in sediment at stations across the pelagic zone of the Levantine basin (0.8 mmol P m^{-2} yr^{-1} estimated by Eijsink et al. 2000), but much lower than the burial rates determined at the Egyptian–Israeli shelf (~100 mmol P m^{-2} yr^{-1}). The similarity of atmospheric and burial fluxes in the Levantine basin reinforces the suggestion that the atmosphere is the dominant source of P to the sediments in the deeper parts of the basin.

To assess the amount of P deposited over the deep Eastern Mediterranean basin, we multiplied the total bioavailable (leachable + wet) atmospheric flux of IP (~0.7 mmol P m^{-2} yr^{-1}) by the area of the deep basin (~1.5×10^6 km^2, Eijsink et al. 2000). Following the above assumptions, the estimated atmospheric deposition is fueling the new production by ~1×10^{12} mmol P yr^{-1}. Studies that have examined the net outflux of phosphate through the straits of Sicily present estimates of 1.7×10^{12} mmol P yr^{-1} (Sarmiento et al. 1988) and 7.2×10^{12} mmol P yr^{-1} (Bethoux et al. 1992). The lower range implies that atmospheric deposition may contribute significantly to the total bioavailable P in the basin, whereas it is less important for the higher estimate.

By use of a similar approach for IN and multiplication of the total bioavailable (leachable—this study + wet—Herut et al. 1999*a*) atmospheric flux of IN (~70 mmol m^{-2} yr^{-1}) by the area of the deep basin, the estimated atmospheric deposition is ~10^{14} mmol IN yr^{-1}. The net outflux of IN through the straits of Sicily is not known. Multiplying the outflux of water from the Levantine Basin into the Western Mediterranean through Sicily straits (1–1.5 Sv, Astraldi et al. 1999) by their nitrate concentration range (Levantine intermediate water mass, Kress and Herut 2001) gives a flux in the same order of magnitude as the atmospheric deposition. Thus, the atmospheric deposition might be significant but needs to be further reassessed.

Possible support of new production by individual dust events—The ratio of seawater LIN : $LIPO_4$ decreases exponentially with increased rock/soil component (e.g., Al) from values close to 400 : 1 (Fig. 4). Even during dust events where the N : P ratio is at its lowest (Table 2), the ratio is still well above Redfield ratio (N : P = 16 : 1). Relatively high ratios (~70) were also recorded in wet deposition (Herut et al. 1999*a*), which suggests a potential contribution of relatively high N : P ratios of atmospheric input. Assuming that this atmospheric influx (wet + dry) is the major source of nutrients for new production in this basin and a Redfield ratio in the burial of N and P, this input may contribute significantly to the relatively high N : P ratios (~27) in Levantine deep water.

In oligotrophic seas like this basin, it is possible that in-

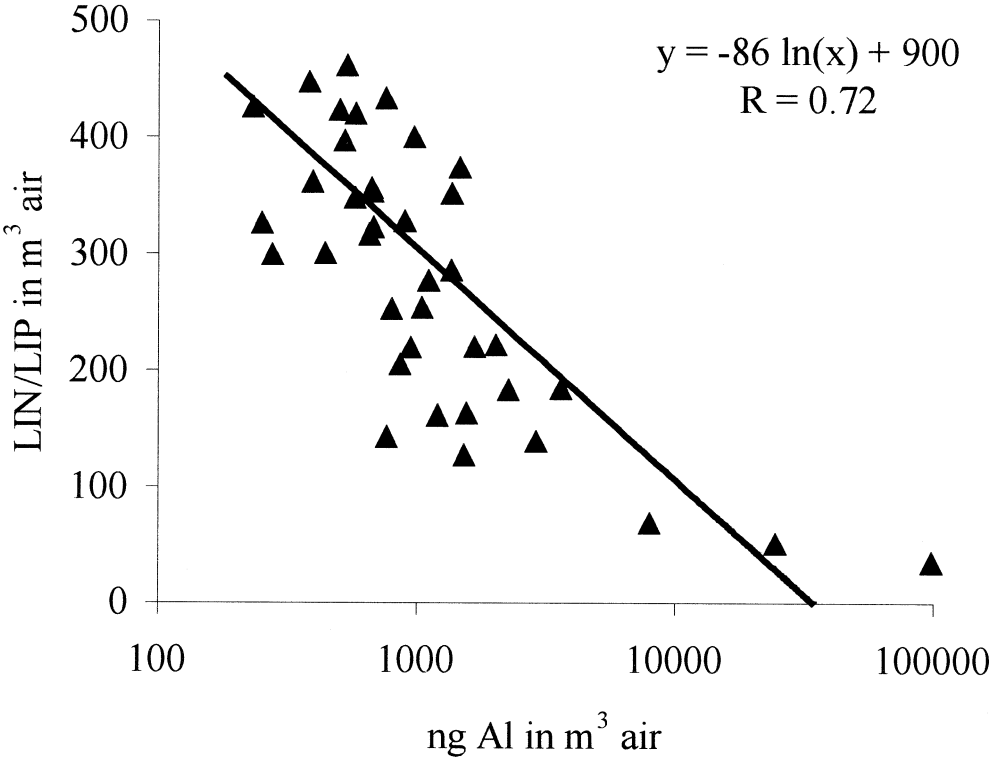

Fig. 4. The relationships between the ratios of seawater leachable inorganic N (LIN) and P (LIP), and particulate Al concentrations in m^3 air. The exponential regression line calculated from the data is included.

dividual dust or rain events may trigger a significant phytoplankton bloom (Buat-Menard et al. 1989; Bergametti et al. 1992; Migon and Sandroni 1999). Satellite data on desert aerosol events and marine phytoplankton blooming have been linked for cause-response interaction (Dulac et al. 1996; Saydam and Polat 1999). We consider here the possible impact of a major dust event, such as on 15 March 1998 (Table 1). In this event we measured a dust concentration of 406 μg in m^{-3} air, which gives a deposition flux of approximately 700 mg m^{-2} d^{-1} (406 μg m^{-3} × 2 cm s^{-1} V_d). This estimate was similar, though somewhat smaller, to modeled values of dust deposition over the SE Mediterranean (presented by Meduse Project, Mediterranean Research Centre, Erice, www.halo.is/meduse/sp14mar98.html) or in previous events (Ozsoy et al. 2001). This event contributed 2.5 nmol $LIPO_4$ in m^{-3} air, which produces a flux of approximately 4.3 μmol $LIPO_4$ m^{-2} d^{-1}. The calculated flux of leachable IN was 74 μmol m^{-2} d^{-1}. To convert this exogenous input of nutrients to potential carbon production, we used the C : N and C : P Redfield ratios (6.625 and 106). The leachable input could support 5–6 mg C m^{-2} d^{-1}. Compared to the annual bioavailable fluxes of IP and IN (*see below*) dust events have important (but not principal) contribution to IP deposition, and probably normal (background) events dominate the IN deposition. It should be mentioned that the stimulation of blooms by dust events might include iron as a possible nutrient or stimulant. In general, the atmospheric input of bioavailable IN (~50 mmol m^{-2} yr^{-1}) and IP (0.4 + 0.3 mmol m^{-2} yr^{-1}, from dry and wet deposition) can fix ~1 or 4 g C m^{-2} yr^{-1}, corresponding to 10–20 or 50–80% of the new production in the Levant basin (~8 g C m^{-2} yr^{-1}, Krom et al. 1992; ~5 g C m^{-2} yr^{-1}, Kress and Herut 2001). These values are similar to estimates of the support of new production by atmospheric inputs in the western Mediterranean Sea (3 g C m^{-2} yr^{-1}, Martin et al. 1989).

The results reported here demonstrate that atmospheric dry fallout may play a particularly important role in the supply of new nitrogen and phosphorus to surface water in the Levantine basin, particularly in spring and summer when there is no deep mixing. The nutrient leachability and total flux were assessed in terms of dust versus background (non-dust) events. To generalize these results across the basin further, regional studies and knowledge on the nutrients mass balance (magnitude of other sources and sinks) are required.

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Acknowledgments

The authors would like to express their gratitude to Y. Gertner and G. Fainstein for their technical assistance in the dust collection and analyses and Lou Gordon, Joe Jennings, and Andy Ross for

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References

ASTM. 1983. Designation—D3683-78. Standard test method for trace elements in coal and coke ash by atomic absorption, p. 472–475. American Society for Testing and Materials Publisher.

ASTRALDI, M., AND OTHERS. 1999. The role of straits and channels for the comprehension of the Mediterranean circulation characteristics. Prog. Oceanogr. **44:** 65–108.

BERGAMETTI, G., E. REMOUDAKI, R. LOSNO, E. STEINER, AND B. CHATENET. 1992. Source, transport and deposition of atmospheric phosphorus over the northwestern Mediterranean. J. Atmos. Chem. **14:** 501–513.

BETHOUX, J. P., P. MORIN, C. MADEC, AND B. GENTILI. 1992. Phosphorus and nitrogen behavior in the Mediterranean Sea. Deep-Sea Res. I **39:** 1641–1654.

———, ———, C. CHAUMERY, O. CONNAN, B. GENTILI, AND D. RUIZ-PINO. 1998. Nutrients in the Mediterranean Sea, mass balance and statistical analysis of concentrations with respect to environmental change. Mar. Chem. **63:** 155–169.

BUAT-MENARD, P., AND OTHERS. 1989. Non-steady-state biological removal of atmospheric particles from Mediterranean surface waters. Nature **340:** 131–134.

CIVITARESE, G., M. GACIC, A. VETRANO, A. BOLDRIN, D. BREGANT, S. RABITTI, AND E. SOUVERMEZOGLOU. 1998. Biochemical fluxes through the Strait of Otranto (Eastern Mediterranean). Cont. Shelf Res. **18:** 773–789.

DUCE, R. A., AND OTHERS. 1991. The atmospheric input of trace species to the world ocean. Glob. Biogeochem. Cycles **5:** 193–259.

DULAC, F. AND OTHERS. 1996. Quantitative remote sensing of African dust transport to the Mediterranean, p. 25–49. *In* S. Guerzoni and R. Chester [eds.], The impact of desert dust across the Mediterranean. Kluwer.

EIJSINK, M. L., M. D. KROM, AND B. HERUT. 2000. Speciation and burial flux of phosphorus in the surface sediments of the eastern Mediterranean. Am. J. Sci. **300:** 483–503.

GORDON, L. I., J. C. JENNINGS, JR., A. A. ROSS, AND J. M. KREST. 1994. A suggested protocol for continuous flow automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE Hydrographic Program and the Joint Global Ocean Fluxes Study. WOCE operations manual, vol. 3. The observational programme. WHPO 91-1, WOCE report 68/91.

GRAHAM, W. F., AND R. A. DUCE. 1979. Atmospheric pathways of the phosphorus cycle. Geochim. Cosmochim. Acta **43:** 1195–1208.

GUERZONI, S., AND OTHERS. 1999. The role of atmospheric deposition in the biogeochemistry of the Mediterranean Sea. Prog. Oceanogr. **44:** 147–190.

HERUT, B., A. ALMOGI-LABIN, N. JANNINK, AND I. GERTMAN. 2000*a*. The seasonal dynamics of nutrient and chlorophyll *a* concentrations on the SE Mediterranean shelf-slope. Oceanol. Acta **23:** 771–782.

———, M. D. KROM, G. PAN, AND R. MORTIMER. 1999*a*. Atmospheric input of nitrogen and phosphorus to the SE Mediterranean: Sources, fluxes and possible impact. Limnol. Oceanogr. **44:** 1683–1692.

———, M. NIMMO, A. MEDWAY, R. CHESTER, AND M. D. KROM. 2001. Dry atmospheric inputs of trace metals at the Mediterranean coast of Israel (SE Mediterranean): Sources and fluxes. Atmos. Environ. **35:** 803–813.

———, A. STARINSKY, A. KATZ, AND D. ROSENFELD. 2000*b*. Relationship between the acidity and chemical composition of rainwater and climatological conditions along a transition zone between large deserts and Mediterranean climate, Israel. Atmos. Environ. **34:** 1281–1292.

———, T. ZOHARY, R. D. ROBARTS, AND N. KRESS. 1999*b*. Adsorption of dissolved phosphate onto loess particles in surface and deep Eastern Mediterranean water. Mar. Chem. **64:** 253–265.

KEIL, R. G., E. TSAMAKIS, C. FUH, C. BOR, J. C. GIDDINGS, AND J. I. HEDGES. 1994. Mineralogical and textural controls on the organic composition of coastal marine sediments: Hydrodynamic separation using SPLITT-fractionation. Geochim. Cosmochim. Acta **58:** 879–893.

KOUVARAKIS, G., N. MIHALOPOULOS, A. TSELEPIDES, AND S. STAVRAKAKIS. 2001. On the importance of atmospheric inputs of inorganic nitrogen species on the productivity of the eastern Mediterranean Sea. Global Biogeochem. Cycles **15:** 805–817.

KRESS, N., AND B. HERUT. 2001. Spatial and seasonal evolution of dissolved oxygen and nutrients in the Southern Levantine Basin (Eastern Mediterranean Sea). Chemical characterization of the water masses and inferences on the N:P ratios. Deep-Sea Res. I **48:** 2347–2372.

KROM, M. D., S. BRENNER, N. KRESS, A. NEORI, AND L. I. GORDON. 1992. Nutrient dynamics and new production in a warm-core eddy from the E. Mediterranean. Deep-Sea Res. **39:** 467–480.

———, ———, ———, ———, AND ———. 1993. Nutrient distributions during an annual cycle across a warm-core oceanic eddy from the E. Mediterranean sea. Deep-Sea Res. **40:** 805–825.

———, N. KRESS, S. BRENNER, AND L. I. GORDON. 1991. Phosphorus limitation of primary productivity in the Eastern Mediterranean Sea. Limnol. Oceanogr. **36:** 424–432.

KUBILAY, N., S. NICKOVIC, C. MOULIN, AND F. DULAC. 2000. An illustration of the transport and deposition of mineral dust onto the eastern Mediterranean. Atmos. Environ. **34:** 1293–1303.

LEPPLE, F. K. 1975. Eolian dust over the North Atlantic Ocean. Ph.D. thesis, Univ. Delaware.

LI-JONES, X., AND J. M. PROSPERO. 1998. Variations in the size distribution of non-sea-salt sulfate aerosol in the marine boundary layer at Barbados: Impact of African dust. J. Geophys. Res. **103:** 16073–16084.

MARTIN, J. M., F. ELBAZ-POULICHET, C. GUIEU, M. D. LOYE-PILOT, AND G. HAN. 1989. River versus atmospheric input of material to the Mediterranean Sea: An overview. Mar. Chem. **28:** 159–182.

analytical support on nutrients. This study was supported in part by the Israeli Ministry of Environment, UNEP/WMO (Medpol Program, project 13.181) and the Israeli Ministry of Infrastructure. This work was also supported by the European Commission (Research Directorate General-Environment Programme—Marine Ecosystems) through the CYCLOPS project (EVK3-1999-00037). The CYCLOPS project is part of the EC IMPACTS cluster. The College of Oceanic and Atmospheric Sciences, Oregon State University provided facilities during the sabbatical leave of B.H. and analytical assistance was provided by Bobbi Conard, Charlotte Meredith, and Pat Collier. We thank the reviewers for their comments, which helped to improve the manuscript.

MIGON, C., AND V. SANDRONI. 1999. Phosphorus in rainwater: Partitioning, inputs and impact on the surface coastal ocean. Limnol. Oceanogr. **44:** 1160–1165.

MIHALOPOULOS, N., E. STEPHANOU, M. KANAKIDOU, S. PILITSIDIS, AND P. BOUSQUET. 1997. Tropospheric aerosol ionic composition in the Eastern Mediterranean region. Telus, Ser. B **49:** 314–326.

OZSOY, E., N. KUBILAY, S. NICKOVIC, AND C. MOULIN. 2001. A hemispheric dust storm affecting the Atlantic and Mediterranean in April 1994: Analyses, modeling, ground-based measurements and satellite observations. J. Geophys. Res. Atmos. **106:** 18439–18460.

PAERL, H. W. 1997. Coastal eutrophication and harmful algal blooms: Importance of atmospheric deposition and groundwater as ''new'' nitrogen and other nutrient sources. Limnol. Oceanogr. **42:** 1154–1165.

PROSPERO, J. M., AND OTHERS. 1996. Atmospheric deposition of nutrients to the North Atlantic Basin. Biogeochemistry **35:** 27–73.

SARMIENTO, J. L., T. HERBERT, AND J. R. TOGGWEILER. 1988. Mediterranean nutrient balance and episodes of anoxia. Glob. Biogeochem. Cycles **2:** 427–444.

SAYDAM, A. C., AND I. POLAT. 1999. The impact of Saharan dust on the occurrence of algae blooms, p. 656–646. *In* P. M. Borrell and P. Borrell [eds.], Proceedings of EUROTRAC Symposium, Southampton WIT.

SPOKES, L. J., S. G. YEATMAN, S. E. CORNELL, AND T. D. JICKELLS. 2000. Nitrogen deposition to the eastern Atlantic Ocean. The importance of south-easterly flow. Tellus **52:** 37–49.

ZOHARY, T., AND R. D. ROBARTS. 1998. Experimental study of microbial P-limitation in the eastern Mediterranean. Limnol. Oceanogr. **43:** 387–395.

Received: 4 June 2001
Accepted: 31 December 2001
Amended: 13 February 2002

Limnol. Oceanogr., 47(3), 2002, 878–885

Calanoid copepods feed and produce eggs in the presence of toxic cyanobacteria *Nodularia spumigena*

Abstract—Feeding and fecundity of two calanoid copepod species (*Acartia bifilosa* and *Eurytemora affinis*) were studied in a food assemblage dominated by toxic cyanobacteria, to reveal whether mesozooplankton are able to obtain sufficient good quality food in different phases of a cyanobacteria bloom. Bloom conditions were simulated in a mesocosm by adding a high concentration of cultured hepatotoxic *Nodularia spumigena* to 100 μm filtered natural sea water. This seston was fed to copepods at days 1, 7, and 14 from the start of the mesocosm experiment, when it consisted of actively growing cyanobacteria (days 1 and 7) and increasing amounts of heterotrophic organisms and probably detritus (day 14). From bulk changes in chlorophyll and estimated ratios between chlorophyll and accessory pigments, it appears that both copepod species ingested large quantities of cyanobacteria in the first experiment but switched to ciliates when those became more abundant. Egg production of *A. bifilosa* was observed in all experiments, irrespective of the high concentration of nodularin in the mesocosm. The results demonstrate that the dominant copepod species of the Baltic Sea are able to feed, survive, and produce eggs in a plankton community dominated by toxic cyanobacteria.

Most studies of mesozooplankton grazing on natural plankton assemblages show avoidance of cyanobacteria (Meyer-Harms and von Bodungen 1997) and a negative correlation between secondary production and cyanobacteria abundance (Schmidt et al. 1998). Laboratory studies generally agree: even though some zooplankton species may sometimes have relatively high grazing and reproduction rates on cyanobacteria (Burns and Xu 1990; Engström et al. 2000), the majority of studies show low rates of ingestion and/or fecundity (e.g., Lampert 1987; Sellner et al. 1996; Koski et al. 1999). In general, besides often being toxic, cyanobacteria are likely to be poor-quality food for aquatic crustaceans. This is probably due to the lack of the long-chain polyunsaturated fatty acids 20:5ω3 and 22:6ω3 (Ahlgren et al. 1992), which are essential for mesozooplankton growth (Müller-Navarra et al. 2000).

The quality of cyanobacteria as copepod food may change because of aging or accumulation of an active microbial community on the algae (Hoppe 1981). First, toxicity of cyanobacteria blooms may decrease as the bloom ages (Kankaanpää et al. 2001); second, decomposing cyanobacteria filaments have been shown to be better-quality food than actively growing ones, probably because of attached bacteria (Repka et al. 1999). Decaying filaments and associated bacteria may also be consumed by ciliates and heterotrophic flagellates (Rolff 2000), which in turn can be consumed by copepods (Gifford 1991). Some protozoans improve the food quality for mesozooplankton by producing essential food components (e.g., long-chain polyunsaturated fatty acids and sterols) that are low in their algal prey (Klein Breteler et al. 1999). Therefore, aging, decreasing toxicity, colonization by bacteria, and biochemical ''upgrading'' by microzooplankton may improve the quality of cyanobacteria as food for mesozooplankton.

A study of mesozooplankton feeding and production in a cyanobacteria-dominated food assemblage was undertaken to reveal whether mesozooplankton are able to obtain sufficient good-quality food for egg production and survival in different phases of a cyanobacteria bloom and investigate whether the food quality of cyanobacteria improves as blooms age. A mesocosm experiment was conducted in which a natural plankton community was enriched with a high concentration of cultured toxic *Nodularia spumigena.* The development of the plankton community in this bloom