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Atmospheric nutrient inputs to the northern levantine basin from a long-term observation: sources and comparison with riverine inputs

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Abstract. Aerosol and rainwater samples have been collected at a rural site located on the coastline of the Eastern Mediterranean, Erdemli, Turkey between January 1999 and December 2007. Riverine sampling was carried out at five Rivers (Ceyhan, Seyhan, Göksu, Berdan and Lamas) draining into the Northeastern Levantine Basin (NLB) between March 2002 and July 2007. Samples have been analyzed for macronutrients of phosphate, silicate, nitrate and ammonium (PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+). Phosphate and silicate in aerosol and rainwater showed higher and larger variations during the transitional period when air flows predominantly originate from North Africa and Middle East/Arabian Peninsula. Deficiency of alkaline material have been found to be the main reason of the acidic rain events whilst high pH values (>7) have been associated with high Si_{diss} concentrations due to sporadic dust events. In general, lowest nitrate and ammonium concentrations in aerosol and rainwater have been associated with air flow from the Mediterranean Sea. Comparison of atmospheric with riverine fluxes demonstrated that DIN and PO_4^{3-} fluxes to NLB have been dominated by atmosphere (∼90% and ∼60% respectively) whereas the input of Si was mainly derived from riverine runoff (∼90%). N/P ratios in the atmospheric deposition (233); riverine discharge (28) revealed that NLB receives excessive amounts of DIN and this unbalanced P and N inputs may provoke even more phosphorus deficiency. Observed molar Si/N ratio suggested Si limitation relative to nitrogen might cause a switch from diatom dominated communities to non-siliceous populations particularly at coastal NLB.

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1 Introduction

The Mediterranean Sea has one of the most oligotrophic surface wasters in the world with Low Nutrient and Low Chlorophyll (LNLC). The average annual productivity in the Mediterranean Sea is half of the amount observed in the ultra-oligotrophic Sargasso Sea (Krom et al., 2004; Pitta et al., 2005). The main reason for this ultra-oligotrophic status is that the Mediterranean has an anti-estuarine (reverse thermohaline) circulation in which nutrient poor surface waters incoming from the Atlantic is balanced by outgoing relatively nutrient rich deep waters of the Mediterranean Sea through the Strait of Gibraltar (Hamad et al., 2005 and references therein). Most of the nutrient inputs to the Mediterranean Sea are originated from the atmosphere (including dry and wet) deposition and riverine runoff (Krom et al., 2004, 2010).

The Eastern Mediterranean Sea has a uniquely high N/P ratio raging from 25 to 28, compared to the Western Mediterranean (22) and the "normal" oceanic Redfield ratio of 16 (Krom et al., 1991; Yılmaz and Tuğrul, 1998). Thus the primary productivity in the Eastern basin is phosphorus limited (Thingstad et al., 2005). In their recent study, Krom et al. (2004) budgeted fluxes of N and P for the Eastern Mediterranean and concluded that the high N/P ratio is due primarily to the high biologically available N/P ratio in all of sources but for those particularly from the atmosphere (117:1) combined with regionally low denitrification rates (Krom et al., 2010). Ludwig et al. (2009) suggested that decrease in the dissolved Silica concentrations were due to a substantial reduction in the fresh water discharges. These authors have hypothesized that Si may not necessarily reduce the productivity in the Mediterranean however it can provoke a switch from diatom dominated communities to non-siliceous populations.

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The Mediterranean has one of the highest concentrations of airborne mineral dust owning to its close proximity to arid regions, in particular the Saharan, Middle Eastern and Arabian Deserts (Loÿe-Pilot et al., 1986; Guerzoni et al., 1999; Kubilay et al., 2000; Koçak et al., 2004a). Atmospheric deposition of desert dust over the Mediterranean supplies soluble or bioavailable macro (P, N) and micro nutrients (Fe) which influence ocean biogeochemistry (Herut et al., 1999, 2002, 2005; Guieu et al., 2002; Ridame and Guieu, 2002; Markaki et al., 2003, 2010; Bonnet et al., 2005; Carbo et al., 2005).

Atmospheric inputs of nutrients to the coastal system and the open ocean can take place through dry and wet (i.e. rain) deposition. According to Guerzoni et al., (1999), atmospheric input of inorganic nitrogen species is sufficient to the nitrogen requirement in 60% of the total nitrogen entering the Mediterranean from continental origin, 66% of which is via wet deposition. Kouvarakis et al. (2001) suggest that the input of inorganic N species in atmospheric deposition is enough to explain nitrogen needs in the eastern Mediterranean Sea. Unlike N compounds which have dominant anthropogenic sources (Spokes and Jickells, 2005) the aerosol P content and Si are of continental/natural origin (e.g. rock and soil) (Herut et al., 1999; Markaki et al., 2003; Baker et al., 2007).

A great number of data on atmospheric nutrient fluxes in Eastern Mediterranean have been published (Guerzoni et al., 1999; Herut et al., 1999; Kouvarakis et al., 2001; Kubilay et al., 2000; Markaki et al., 2003; Krom et al., 2004; Carbo et al., 2005). However, there is no available data on riverine fluxes of nutrients except that published Ludwig et al. (2009) while possible impact of both atmospheric and riverine inputs onto the Northeastern Levantine waters have not been evaluated yet. The present study is based on a long term aerosol, rainwater and riverine data collection in the Northern Levantine Basin of the Eastern Mediterranean. The main aim of the current study is to enhance our knowledge of atmospheric (dry and wet) deposition to the surface waters of the Northern Levantine Basin. Aerosol, rainwater and riverine samples collected from the Northern Levantine Basin, will allow us to (i) define temporal variability of nutrient concentrations in aerosol and rainwater, (ii) assess the influence of air mass back trajectories on nutrient composition and (iii) assess and compare the atmospheric and riverine inputs of nutrients to the Northern Levantine Basin.

2 Materials and methods

2.1 Sites description and sample collection

The Mediterranean climate is characterized by mild, humid winters and dry summers. Winter months are dominated by rainfall (November–February) whereas the summer months (June–September) are characterized by the lack of wet precipitation. The transition seasons, spring and autumn are of very different lengths. The relatively long spring season (March–May) is characterized by unsettled winter type weather, associated with North African cyclones; the rest of this period is very similar to that in the summer. Autumn usually lasts one month (October) and is characterized by an abrupt from the summer to the unsettled weather of winter (Brody and Nestor, 1980). Therefore, within the annual period three seasons were defined; winter, transitional, and summer. The winter period included the months November, December, January and February whereas the transitional season included the months March, April, May and October. The summer season included the months June, July, August and September.

Aerosol and rainwater sampling was carried out at a rural site located on the coastline of the Eastern Mediterranean, Erdemli (36°33′54″ N and 34°15′18″ E), Turkey (Fig. 1). The rural sampling site is not under direct influence of any industrial activities. Its immediate vicinity is surrounded by lemon trees, cultivated land and greenhouses. The city of Mersin (population ∼800 000) is located 45 km to the east of the sampling site. The samplers were positioned on a sampling tower (at an altitude of ∼22 m) which is situated at the Institute of Marine Sciences, Middle East Technical University (for more details see Kubilay and Saydam, 1995; Koçak et al., 2004b). Samples were collected from January 1999 to December 2007.

A total of 1525 bulk aerosol filter samples were collected using a high volume sampler with flow rates of around $1\,m^3\,min^{-1}$ on Whatman-41 cellulose fiber filters (20 cm×25 cm). Individual bulk aerosol samples were collected for typically 24 h (occasionally 48 h), unless interrupted by equipment failure (which occurred during July–December 2000, 2004 and 2005). Samples and blanks ($n = 110$) were kept cool at 4 °C until analysis conditions that our test showed no significant change in their composition for more than a year period. Gent type PM_{10} stacked filter unit (SFU) sampler was used in order to collect atmospheric particles in two size ranges namely, coarse and fine. Twenty daily samples were collected in June 2007. Upstream of the first holder is a preimpaction stage which intercepts particles larger than 10 µm equivalent aerodynamic diameter (EAD). The sampler operates at a flow rate of $16\,L\,min^{-1}$. It collects particulates which have an EAD of less than 10 mm in separate coarse (2.5–10 µm EAD) and fine (<2:5 µm EAD) size fraction on two sequential (for more details see Koçak et al., 2007a). It has been shown that results from SFU are in good agreement with other sampler types (Hitzenberger et al., 2004; Wieprecht et al., 2004). A total of 235 rain water samples were collected on an event specific basis by using an automatic Wet/Dry sampler, Model ARS 1000, MTX Italy (for more details see Özsoy and Saydam, 2000). After each specific event, the rain water sample was immediately transferred into the laboratory for filtration (0.45 µm, MFS, cellulose acetate, 47 mm diameter) and pH measurements.

Table 1. Summary of statistics of the nutrients PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+ of aerosol and rainwater at Erdemli during the period January 1999 and December 2007.

	P-PO_4^{-3}	Si_{diss}	N-NO_3^-	N-NH_4^+
Aerosol (nmol m^{-3})				
Mean ± Std	0.45 ± 0.43	1.08 ± 1.53	65.3 ± 35.1	121.6 ± 63.2
Min–Max	0.03–6.40	0.04–26.57	0.2–258.8	0.1–473.2
Median	0.37	0.52	62.6	113.8
G. M.[a]	0.34	0.51	50.0	95.8
N[b]	1525	1525	1525	1525
Coverage (%)	52	52	52	52
Rainwater (µmol L^{-1})				
WVM[c]	0.7	1.9	44	46
N[b]	235	235	235	212
Coverage (%)	50	50	50	45

[a] Geometric mean, [b] Number of samples, [c] Volume weighted mean. Average sampling coverage is calculated using the formulas $Coverage_{aerosol} = \frac{NS_{aerosol}}{ND} x100$ and $Coverage_{rain} = \frac{NS_{rain}}{NRE} x100$. $NS_{aerosol}$ and NS_{rain} refer to number of samples for aerosol and rain; ND and NRE denote number of days and rain events during sampling period.

Subsamples of rain waters were kept frozen (−18 °C) until nutrient analysis (not more than two weeks). The percentage of sampling coverage is highlighted in Table 1. Sampling coverage was around 50% (except NH_4^+ in rainwater ∼45%) between January 1999 and December 2007.

To complement the atmospheric samples, riverine samples for nutrient analyses were collected from five rivers (Ceyhan, Seyhan, Göksu, Berdan and Lamas; see Fig. 1) flowing into the Northeastern Levantine Basin of the Eastern Mediterranean. Seasonal sample collection was carried out between March 2002 and November 2007. It should be noted that nutrient measurements from 2000 to 2003 were very limited; dissolved ammonia was not measured, reactive phosphate, silicate, nitate+nitrite were measured merely in this period. For reliable estimation of the nutrient fluxes data obtained between 2004 and 2007 will therefore be used. A total of 103 river water samples were collected from the middle of the river bed at point near the river mouths, depending on transportation facilities from land to the river mouths. There are no domestic and/or industrial waste discharges further down the sampling points other than surface runoff during heavy rains. Nutrients samples were taken in high density polyethylene bottles stored at 4 °C for a few hours during transport and then kept frozen until analysis.

2.2 Sample analysis

The pH in rain waters was measured immediately using a Microprocessor pH meter (WTW-Model pH537) after each specific event. Calibration of the pH meter was carried out using N.B.S buffers at pH values of 4.00 and 7.00.

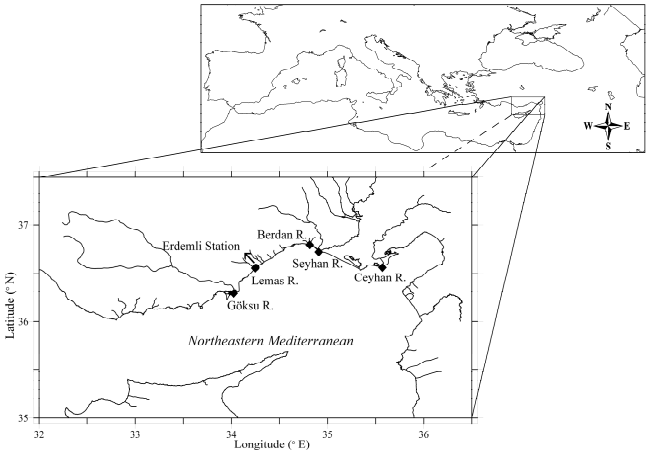

Fig. 1. Locations of atmospheric and riverine sampling sites. R refers to river.

The soluble nutrient measurements in aerosol, rainwater and river samples were carried out by a Technicon Model, four-channel Autoanalyzer (for more details see Yılmaz and Tuğrul, 1998). In general, blanks were found to be less than detection limit of the instrument. The detection limits of Autoanalyzer were 0.02, 0.10, 0.02 and 0.04 µm for phosphate, reactive silicate, nitrate and ammonium, respectively. Since this method determines reactive silicate (not polymeric silicates) obtained Si values will be presented as dissolved Silicate (Si_{diss}). The accuracy of the nutrient measurements was verified against Quasimeme (Quality Assurance of Information for Marine Environmental Monitoring in European Laboratory Performance Studies) intercalibration program samples. The precisions were found to be 7.3%, 7.4%, 8.9% and 3.3% for PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+, respectively.

Three-cm^2 of subsamples of the aerosol filters and blanks were shaken for 36 h in the dark at room temperature in precleaned centrifuge tubes containing 15 ml MilliQ (18.2 Ω; pH∼5.6) and 50 µL chloroform (Herut et al., 2002). Samples were immediately analyzed for nutrients after centrifuging at 3500 rpm for 15 min. The homogeneity for the subsamples was tested by applying historical data; one-eighth of each sample extracted for 45 min using 20 ml of nanopure water and 100 µL chloroform. (Koçak et al., 2004b). Figure 2 shows the regression line for two nutrients (NO_3^- and NH_4^+) which were obtained from different amount of filter and instruments. The slopes of the regression lines for NO_3^- and NH_4^+ were found 0.91 ($R^2 = 0.97$) and 0.94 ($R^2 = 0.98$), respectively. Obtained slopes suggested that NO_3^- and NH_4^+ values from Autoanalyzer (area = 3 cm^2) were 9 and 6% higher than those from Ion Chromatography (area = 62.5 cm^2). However, application of Wilcoxen signed-rank test showed that there were no statistical differences between two approaches for nitrate and ammonium, within 95% confidence level. Furthermore, relationship between

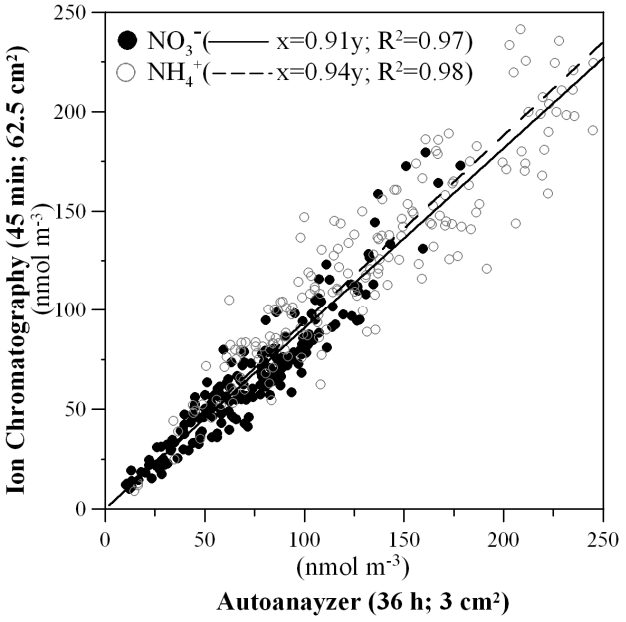

Fig. 2. Plot of NO_3^- and NH_4^+ concentration obtained from Autoanalyzer (3 cm^2) against the concentrations acquired from Ion Chromatography (62.5 cm^2).

two approached for ammonium reveals that bacterial consumption of NH_4^+ was efficiently prevented by the addition of chloroform during 36 h extraction period.

2.3 Air mass back trajectories and cluster analysis

3-day backward trajectories to the Erdemli sampling site were computed between January 1999 and December 2007 by the HYSPLIT Dispersion Model (HybridSingle Particle Langrangian Integrated Trajectory; Draxler and Hess, 1998) and illustrated by one-hour endpoint locations in terms of latitude and longitude. Recently, it has been shown that boundary layer in the region during winter (for example, December and January) was found to be as high as 1300 m and it ranged mostly between 700 and 800 m whereas, boundary layer in transition (for instance, March and April) reached up to 2500 m with values ranging mainly from 800 to 1400 m (Koçak et al., 2010). Furthermore, with increasing altitude, particularly the % influence of Saharan airflow increases in the region (Koçak et al., 2004a). For instance, from 1 km to 2 km its % influence increases around 10% while airflow from Europe remains constant. Consequently, 3-day backward trajectories of air masses at a height of 1000 m were selected to categorize air flow. Cluster analysis was applied to categorize air mass back trajectories using the method described by Cape et al. (2000).

2.4 Calculation of nutrient fluxes

The rain volume weighted average concentration (C_w) of nutrient species can be calculated as follow:

$$C_w = \frac{\sum_{i=1}^{n} C_i \times Q_i}{\sum_{i=1}^{n} Q_i} \quad (1)$$

where C_i is the nutrient concentration and Q_i is the rainfall for the ith precipitation event.

The wet and dry atmospheric fluxes of nutrients were calculated according to the procedure explained in Herut et al. (1999, 2002). The wet atmospheric deposition fluxes (F_w) were calculated from the annual amount of precipitation (P_{annual}) and the volume weighted mean concentration (C_w) of the substance of interest (Eq. 1).

$$F_w = C_w \times P_{annual} \quad (2)$$

The dry deposition (F_d) of nutrients can be calculated as the product of atmospheric mean nutrient concentrations (C_d) and their settling velocities (V_d), where F_d is given in units of mumol m^{-2} yr^{-1}, C_d in units of mumol m^{-3} and V_d in units of m yr^{-1} (for more details see Sect. 3.5.1).

$$F_d = C_d \times V_d \quad (3)$$

Annual riverine fluxes (F_r, Eq. 4) were calculated by the product of C_{dw} and Q_{annual} (Karakatsoulis and Ludwig, 2004).

$$C_{dw} = \frac{\sum_{i=1}^{n} C_i \times Q_i}{\sum_{i=1}^{n} Q_i} \quad (4)$$

$$F_r = C_{dw} \times Q_{annual} \quad (5)$$

The discharge weighted mean concentration (C_{dw}, Eq. 4) was determined on the basis of n samples of instantaneous concentrations (C_i, C_{i+1}) and discharge values (Q_i, Q_{i+1}). The water discharges data for flux calculations were provided from General Directorate of State Hydraulic Works, Turkey.

3 Results and discussion

3.1 Nutrient concentrations in aerosol and rainwater

The statistical summary for nutrients (PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+) measured in aerosol and rainwater samples collected from Erdemli between January 1999 and December 2007 were presented in Table 1. The water soluble PO_4^{3-} and Si_{diss} concentrations in aerosol ranged between 0.03–6.40 and 0.04–26.27 nmol m^{-3} with arithmetic mean values

Table 2. Comparison of nutrient concentrations in aerosol (nmol m^{-3}) and rainwater (μmol L^{-1}) samples for different sites of the Mediterranean.

Location	Si_{diss}	PO_4^{3-}		Reference
Aerosol (nmol m^{-3})				
Erdemli, Turkey	1.1 ± 1.5	0.5 ± 0.4	Jan 99–Dec 07 (1525)	This Study
Erdemli, Turkey	–	0.3	Jan 99–Jan 00 (194)	Markaki et al. (2003)
Finokalia, Crete	–	0.1	Sep 99–Sep 00 (85)	Markaki et al. (2003)
Tel Shikmona , Israel	–	0.8 ± 0.5	Apr 96–Jan 99 (41)	Herut et al. (2002)
Tel Shikmona, Israel	–	0.72	Jan 01–Apr 03 (71)	Carbo et al. (2005)
Eilat, Israel	–	0.4 ± 0.2	Aug 03–Sep 05 (137)	Chen et al. (2007)
Rainwater (μmol L^{-1})				
Erdemli, Turkey	1.9	0.5	Jan 99–Dec 07 (237)	This Study
Erdemli, Turkey	–		Feb 99–Dec 99 (16)	Markaki et al. (2003)
Heraklion, Crete	–	0.1	Sep 99–Sep 00 (41)	Markaki et al. (2003)
Tel Shikmona , Israel	–	0.6	Jan 92–Mar 98 (187)	Herut et al. (1999)
Ashdod, Israel	–	0.6	Nov 95–Mar 98 (67)	Herut et al. (1999)
Location	NO_3^-	NH_4^+		Reference
Aerosol (nmol m^{-3})				
Erdemli, Turkey	65 ± 34	121 ± 64	Jan 99–Dec 07 (1525)	This Study
Erdemli, Turkey	58	118	Jan 99–Jan 00 (194)	Markaki et al. (2003)
Finokalia, Crete	27 ± 13	53 ± 21	Oct 96–Sep 99 (496)	Kouvarakis et al. (2001)
Finokalia, Crete	16	24	Sep 99–Sep 00 (85)	Markaki et al. (2003)
Tel Shikmona , Israel	93 ± 29[a]	117 ± 88	Apr 96–Jan 99 (41)	Herut et al. (2002)
Tel Shikmona, Israel	106	108	Jan 01–Apr 03 (71)	Carbo et al. (2005)
Eilat, Israel	39 ± 19	25 ± 14	Aug 03–Sep 05 (137)	Chen et al. (2007)
Cap Ferrat, France	63	150	May–June 92	Loye-Pilot et al. (1993)
Rainwater (μmol L^{-1})				
Erdemli, Turkey	37	41	Jan 99–Dec 07 (237)	This Study
Erdemli, Turkey	46	–	Feb 99–Dec 99 (16)	Markaki et al. (2003)
Heraklion, Crete	18	21	Sep 99–Sep 00 (41)	Markaki et al. (2003)
Tel Shikmona , Israel	41	25	Jan 92–Mar 98 (187)	Herut et al. (1999)
Ashdod, Israel	57	45	Nov 95–Mar 98 (67)	Herut et al. (1999)

and standard deviations of 0.45 ± 0.43 and 1.08 ± 1.53, respectively. NO_3^- and NH_4^+ concentrations in aerosol samples was found to be ranged between 0.2–258.8 and 0.1–473.2 nmol m^{-3} with mean values and standard deviations of 65.3 ± 35.1 and 121.6 ± 63.2, respectively. On the other hand, volume weighted mean values for PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+ in rainwater samples were found to be 0.7, 1.9, 44 and 46 μmol L^{-1}, respectively.

Table 2 shows the soluble nutrient concentrations in aerosol and rainwater samples obtained from different sites located around the Mediterranean. Although the values from this study and those in the literature cover different collection periods (and might have different sampling and analytical methodologies), comparison will be useful to evaluate spatial trends.

To our knowledge, no data of water soluble Si_{diss} in the aerosol over the Mediterranean and Si_{diss} in rainwater over the Eastern Mediterranean have been reported previously. Since Bartoli et al. (2005) reported only wet deposition inputs of Si_{diss} for the Western Mediterranean and hence would not be appropriate to compare these with the present Si_{diss} values. The mean aerosol phosphate concentration at Erdemli was comparable to levels reported for Eilat, Israel (Chen et al., 2007). Although phosphate concentrations were measured in seawater, highest levels over the Eastern Mediterranean were reported for Tel Shikmona (Herut et al., 2002) and Israeli coast (Carbo et al., 2005) due to the closer proximity of the sampling site to arid regions (Koçak et al., 2004a). Aerosol nitrate and ammonium concentrations are in agreement with the values reported for Erdemli (Koçak et al., 2004b). Observed mean aerosol nitrate and ammonium concentrations were found to be two to four times higher than

those reported for Finokalia, Crete (Kouvarakis et al., 2001, Markaki et al., 2003) and Eilat, Israel (Chen et al., 2007) whereas values were comparable levels reported for Tel Shikmona, Israel (Herut et al., 2002) and Cap Ferrat (Loÿe-Pilot et al., 1993). It should be noted that Erdemli and Tel Shikmona aerosol samples were collected on Whatman 41 cellulose fiber filters whilst Finokalia and Eilat aerosol were collected on Teflon and polycarbonate filters, respectively. It has been reported that positive nitrate and ammonium artifact can result the adsorption of gaseous HNO_3 and NH_3 on filter surfaces (mainly glass fiber and cellulose) or on already collected particles (Wieprecht et al., 2004 and references therein). For instance, Keck and Wittmaack (2005) showed that the retention efficiencies of HNO_3 and NH_3 are very high up to 100 %, if the gases are presented in equimolar concentrations. In order to clarify this difference, aerosol samples were simultaneously collected on Whatman 41 and polycarbonate filters. Comparing nitrate and ammonium results from different substrates it has been shown that NO_3^- and NH_4^+ values for Whatman 41 were 42% and 50% higher than those concentrations observed for polycarbonate filters. Therefore, it can be assumed that the measured nitrate and ammonium concentrations for the current study are equivalent to those of total inorganic NO_3^- and NH_4^+ plus gaseous HNO_3 and NH_3. In addition to dry depositions of nitrate and ammonium, alternative dry depositions will also be presented in parenthesis after multiplying by 0.58 and 0.50.

Rainwater volume weighted mean phosphate, nitrate and ammonium concentrations at Erdemli were found to be comparable to values reported for Israeli coastal sites (Herut et al., 1999) whereas lowest values were observed at Finokalia (Markaki et al., 2003) since this site is categorized by natural background (distance from large pollution sources >50 km) and its proximity to arid regions located at the Middle East/Arabian Peninsula.

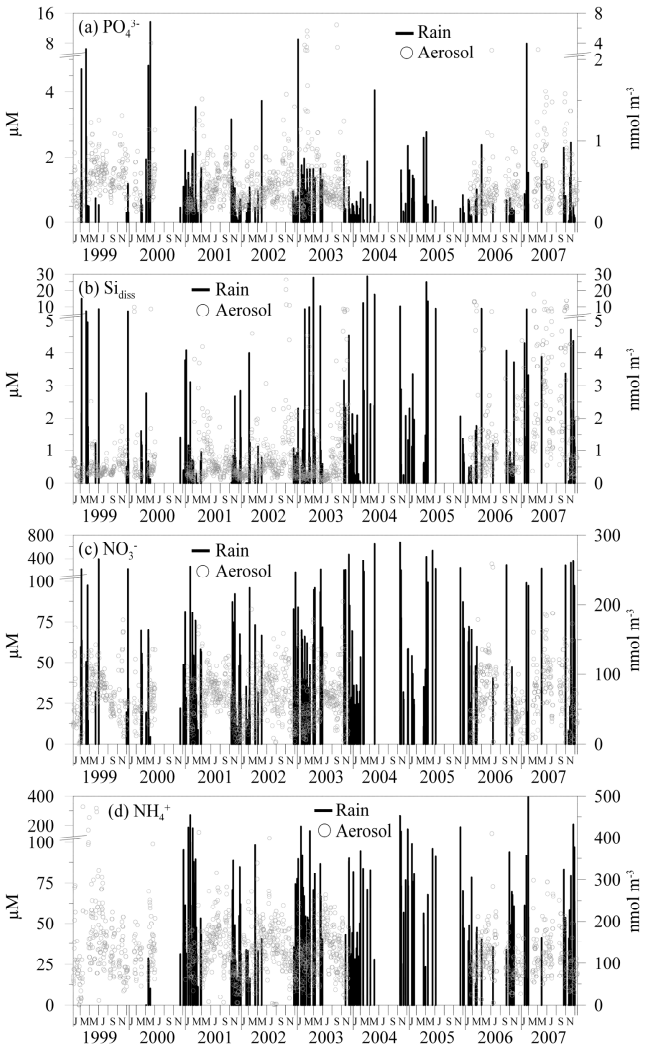

Fig. 3. Temporal variability of nutrient concentrations in aerosol (grey dots) and rain (black bars) samples collected from Erdemli site PO_4^{3-} **(a)**, Si_{diss} **(b)**, NO_3^- **(c)** and NH_4^+ **(d)**.

3.2 Variability of nutrient levels in aerosol and rainwater

The temporal variations in the concentrations of nutrients (PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+) between January 1999 and December 2007 for aerosol and rainwater samples are presented in Fig. 3. Nutrient concentrations in aerosol and rainwater samples demonstrated substantial temporal variability in agreement with earlier studies carried out in the Mediterranean (Loÿe-Pilot and Morelli, 1988; Herut et al., 1999, 2002; Markaki et al., 2003). Concentrations of nutrient species were highly variable on a daily time scale and their concentrations may change an order of magnitude from day to day (see Fig. 3a, b, c, d).

Aerosol: Although, particles are efficiently scavenged by rain (26% of the total annual amount of rain and 39% of the total rain events occur in transitional period) PO_4^{3-} and Si_{diss} demonstrated higher concentrations and larger variations during the transitional period (spring and autumn). As documented in the literature (Kubilay and Saydam, 1995; Avila et al., 1998; Moulin et al., 1998; Koçak et al., 2004a) intense sporadic dust events occur over the Eastern Mediterranean during the transitional period when the air mass trajectories originate predominantly from North Africa (but rarely from the Middle East/Arabian Peninsula). Higher concentrations and variations might be attributed to transport of PO_4^{3-} and Si_{diss} associated with mineral dust from arid desert areas. To illustrate, two distinct dust events observed 18–20 October 2002 and 4–5 April 2003 will be used. The first is an example of a dust event observed from 18 October 2002 to 20 October 2002 with mean PO_4^{3-} and Si_{diss} concentrations of 2.1 and 19.5 nmol m^{-3}, respectively. The highest PO_4^{3-} and Si_{diss} concentrations for this mineral dust episode were identified on October 19 with values of 2.6 and 26.6 nmol m^{-3}. Figure 4a shows air mass back trajectories

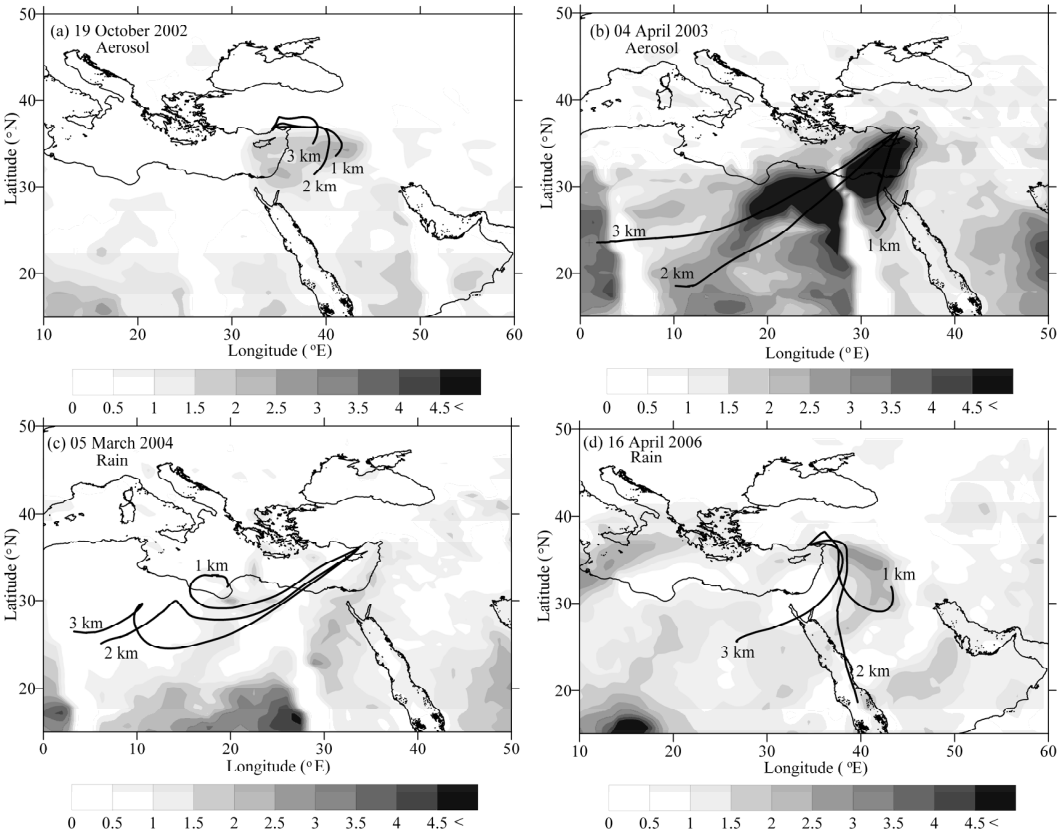

Fig. 4. Three day back trajectories for 1, 2 and 3 km altitude along with Aerosol Index on the 19 October 2002 (TOMS, **(a)**, 4 April 2003 (TOMS, **(b)**, 5 March 2004 (TOMS, **(c)** and 16 April 2006 (OMI, **(d)**).

for three levels (1, 2 and 3 km) along with TOMS-AI (Total Ozone Mapping Spectrometer Aerosol Index) for 19 October 2002. All air mass back trajectories for October 19 indicated air flow originating from the Middle East while TOMS exhibits particularly a large dust plume from the Middle East region into the eastern Mediterranean with AI values ranging between 1.2 from 3. The second example from 4 April to 5 April 2003 with mean PO_4^{3-} and Si_{diss} concentrations of 0.8 and 6.4 nmol m^{-3}, respectively. The highest PO_4^{3-} and Si_{diss} concentrations for this mineral dust episode were identified on 4 April with values of 1.0 and 6.6 nmol m^{-3}. Figure 4b presents air mass back trajectories along with TOMS-AI for 4 April 2003. Both air mass back trajectory (air flow from Egypt) and TOMS-AI (large dust plume from Egypt into eastern Mediterranean) demonstrated mineral dust transport to the sampling site from the Eastern Saharan region.

The lowest values for aerosol nutrient species were observed during the winter. Lower values of aerosol nutrients in winter can be attributed to efficient removal of particles from the atmosphere via frequent rain events (70% total annual amount of rain and 55 % of the total rain events occur in winter). Aerosol NO_3^- and NH_4^+ showed higher values in summer. This variability has mainly been attributed to the absence of precipitation and active photochemical formation under prevailing summer conditions in Mediterranean region (Mihalopoulos et al., 1997; Bardouki et al., 2003; Koçak et al., 2004b). For instance, it has also been shown that in the eastern Mediterranean, conversion rates of SO_2 to sulfate indicate a strong seasonal cycle with a winter minimum and a summer maximum (Erduran and Tuncel, 2001).

Rainwater: In general, PO_4^{3-} and Si_{diss} in rainwater showed higher concentrations in the transition periods due to dust transport from arid desert regions (e.g. North Africa and Middle East/Arabian Peninsula). It has been demonstrated that the pH of Western Mediterranean rains is strongly affected by the type of material scavenged from the atmosphere (Loÿe-Pilot et al., 1986). For instance, rain samples associated with air masses from North Africa (red rains) had pH values as high as 7 as a result of the dissolution of calcium carbonate from dust. The distribution of the pH at Erdemli indicated that the largest fraction ∼70% of all events had a pH greater than 5.6 whereas acidic rain events (pH<5.6; Guerzoni et al., 1997) accounted for 30% of all samples. Volume weighted mean values of PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+ in winter were 1.7, 2.1, 1.5 and 1.1 µm lower than those calculated for transition period. Therefore acid events (80% was observed in winter) might be attributed to the deficiency of alkaline material which was not sufficient to neutralize the

Table 3. Mean aerosol nutrient concentrations and volume-weighted mean (VWM) concentrations of nutrient in aerosol and rainwater, as a function of the categorized three-day air-mass back trajectories arriving at Erdemli.

Species	Aerosol (Mean, nmol m^{-3})					Rainwater (VWM, µMol L^{-1})				
	TUR	EU	MED	MEAP	SAH	TUR	EU	MED	MEAP	SAH
$P\text{-}PO_4^{-3}$	0.40 ± 0.34	0.39 ± 0.30	0.33 ± 0.15	0.62 ± 0.64	0.56 ± 0.70	0.38	0.32	0.29	0.68	0.61
Si_{diss}	0.59 ± 0.38	0.50 ± 0.32	0.45 ± 0.33	1.76 ± 3.08	1.98 ± 2.57	0.65	0.34	0.34	1.26	1.69
$N\text{-}NO_3^-$	65.6 ± 41.6	49.5 ± 31.6	51.5 ± 23.8	60.2 ± 30.9	68.1 ± 43.0	39.4	32.8	20.0	34.1	42.5
$N\text{-}NH_4^+$	133.0 ± 65.5	106.8 ± 60.5	92.9 ± 49.5	112.1 ± 51.4	104.8 ± 62.6	39.5	36.7	21.1	39.8	41.1

acidity due to damp soil around vicinity and less frequent mineral dust transport to the region. Furthermore, volume-weighted mean concentrations of Sidiss (1.8 µM) and PO_4^{3-} (0.8 µM) for non-acidic events were 6 and 3 times higher than those calculated for acidic events. Whereas, volume-weighted mean values for NO_3^- (50 µM) and NH_4^+ (46 µM) during non-acidic events were only 2.1 and 1.7 times higher than acidic events. For example, the most acid rain events were observed on 2 December and 3 December 2001, with the lowest pH value of 3.4. On 30 November pH was found around 5.8 with PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+ concentrations of 0.2, 0.1, 11 and 14 µM, respectively. Rain events on 2 and 3 December showed drastic decreases in pH (3.4) and Sidiss due to the higher anthropogenic influence (high NO_3 levels) and the deficiency of neutralizing agents such as calcium carbonate. In contrast, on 5 March 2004 and 16 April 2006 the pH of the rainwater were found to be 7.1 (PO_4^{3-} ~1; Si_{diss} ~12 µm L^{-1}) and 8.0 (PO_4^{3-} ~2; Si_{diss} ~9 µm L^{-1}). Figure 4c and d illustrate air mass back trajectories along with TOMS-AI (Total Ozone Mapping Spectrometer Aerosol Index) and OMI-AI (Ozone Monitoring Instruments Aerosol Index) for 5 March 2004 and 16 April 2006, respectively. Both air mass back trajectories and AI values indicated that on 5 March 2004 and 16 April 2006 the sampling site was under the influence of air flow from North Africa and Middle East/Arabian Peninsula, respectively.

3.3 Influence of airflows on nutrients

By applying the cluster analysis, the daily air mass back trajectories ($n > 3100$) for 1 km altitude were used covering the whole sampling period (1999–2007). First two clusters (Cluster 1 and 2; hereafter EU) shows north-westerly air flows: The first cluster includes trajectories with high wind speeds (long fetch) passing through Europe and accounting for 2.1 % of the airflow whereas the second cluster denotes relatively slower air flow and contributes to 9.1% of the trajectories. The third and fourth clusters show short trajectories originating from the north-west and northern Turkey and they represent 41.4% and 19.6% of the airflow, (Cluster 3 and 4; hereafter TUR) respectively. The fifth cluster represents trajectories travelling at high speeds, being maritime air masses from the western Mediterranean Sea and representing 7.1% of the airflow (hereafter MED). Air masses originating from the Middle East/Arabian Peninsula (Cluster 6; hereafter MEAP) and Eastern Saharan (Cluster 7; hereafter SAH) represent 10.1% and 10.6% of the trajectories, respectively.

The Kruskal–Wallis (K–W) test was applied to test for the presence of significant differences in nutrient concentrations. Consequently, if the nutrient concentrations are considered for each of the six air flow categories (Table 3) the following general observations might be made:

(a) The K-W test showed that there was a significant difference in the concentrations of PO_4^{3-} and Si_{diss} ($p < 0.01$). $PO_4^{3-}$and Si_{diss} concentrations in aerosol and rain samples were found to be higher in the SAH and MEAP than those observed for the remaining air flow. For instance, mean concentrations of PO_4^{3-} and Si_{diss} in aerosol (rain) were found approximately 1.5 (1.6) and 3 (2) times higher than the remaining, respectively. These two air flows were mainly affected by crustal aerosol population associated with dust events originating from North Africa and Middle East/Arabian arid regions occurring particularly during the transitional period.

(b) The K-W test indicated that there was a significant difference in the concentrations of NO_3^- ($p < 0.01$). Aerosol nitrate concentrations were found to be lower when air flows originated from Europe (EU) and Mediterranean Sea (MED) whereas concentrations for the remaining air masses were found comparable. For aerosol ammonium, the concentrations were found statistically higher when air flows originating from Turkey (TUR) and this might be mainly attributed to intense usage of ammonium containing fertilizers (Koçak et al., 2004b). Rainwater weighted mean values of nitrate and ammonium were found approximately two times lower when air flow originated from Mediterranean Sea than those observed for the remaining. It can be suggested that relatively cleaner air masses associated with Mediterranean Sea during rainy seasons.

Table 4. Summery of dry deposition velocities ($cm\,s^{-1}$) of the analyzed aerosol nutrients applied in the present study and the literature for different Mediterranean regions.

Location	PO_4^{3-}	NO_3^-	NH_4^+	Si_{diss}	Reference
Erdemli	1.56 ± 0.09	1.84 ± 0.03	0.14 ± 0.04	1.59 ± 0.12	This Study
Erdemli	2	2	0.2	–	Markaki et al. (2003)
Finokalia	2.3[a] (2[b])	2	0.2	–	Markaki et al. (2003)
Finokalia	–	1	0.2	–	Kouvarakis et al. (2001)
Tel Shikmona , Israel	2	1.2	0.6	–	Herut et al. (2002)
Eilat, Israel	2	1	0.1	–	Chen et al. (2007)
Cap Ferrat, France	–	1	0.1	–	Loye-Pilot et al. (1993)
Cap Ferrat, France	0.1–0.5	–	–	–	Migon et al. (2001)

[a] Calculated V_d from size resolved samples, [b] V_d value used during flux calculation.

3.4 Nutrient fluxes

3.5 Atmospheric nutrient fluxes

Results from stack filter unit showed that water-soluble PO_4^{3-}, NO_3^- and Si_{diss} were associated predominantly with coarse particles (>75%) whereas NH_4^+ was mainly found in the fine mode (>97%). Obtained results are in good agreement with previous studies conducted in the Eastern Mediterranean (Bardouki et al., 2003; Markaki et al., 2003; Koçak et al., 2007b) An Approach adopted by Spokes et al. (2001), after Ottley and Harrison (1993) were used to estimate the settling velocities of nutrients. Aforementioned estimates for Vd based on experimental and model results are $2.0\,cm\,s^{-1}$ for coarse particles and $0.1\,cm\,s^{-1}$ for fine (Duce et al., 1991). Settling velocities of nutrient can be calculated from relative two-sized aerosol fractions and modelled values (2.0 and $0.1\,cm\,s^{-1}$), where C_f and F_f are percentages of coarse and fine particles.

$$V_d = (C_f \times 2.0) + (F_f \times 0.1) \quad (6)$$

Settling velocities of nutrient to the Eastern and Western Mediterranean are presented in Table 4. Generally the V_d's value of 2 was applied to estimate dry deposition of PO_4^{3-} in the Eastern Mediterranean. Migon et al. (2001) applied settling velocity values between 0.1 and $0.5\,cm\,s^{-1}$ for dry deposition fluxes of P in the Western Mediterranean since 90% of the P was found to be associated with anthropogenic particles.

V_d values between 1 to 2 and 0.1 to 0.6 were applied to calculate the dry deposition fluxes of NO_3^- and NH_4^+ in the Mediterranean, respectively. Nitrate at Erdemli and Finokalia sites were mainly associated (>70%) with the coarse fraction due to reactions with alkaline sea salt and dust particles, whilst ammonium was almost exclusively found in fine fraction in the form of $(NH_4)HSO_4$ (Bardouki et al., 2003; Koçak et al., 2007b). Based on our knowledge, there is no reported V_d value for Si_{diss} in the literature for the Mediterranean region. Estimated mean V_d value of $1.59\,cm\,s^{-1}$ would be logical for Si_{diss} since it was found to be associated mainly in coarse fractions and predominantly originated from crustal material. However, it should be noted that the settling velocities used in the present study will still be a sources of uncertainty in the dry deposition calculations and the estimation might be subject to a bias of 40%.

Table 5 demonstrates dry, wet and total atmospheric depositions of nutrients obtained from different sites located at the Eastern Mediterranean. Estimated dry deposition for phosphate at Erdemli was comparable to value reported for Eilat, Israel, Israel (Chen et al., 2007) whereas (as expected) phosphate dry deposition at Erdemli was approximately two times lower than those calculated for Tel Shikmona and Israeli coast. Estimated NO_3^- dry depositions at Erdemli, Tel Shikmona, Israeli coast and Eilat were found to be similar, whilst the highest dry deposition for ammonium was estimated at Tel Shikmona (Herut et al., 2002) and Israeli coast (Carbo et al., 2005) on account of applied settling velocity ($0.6\,cm\,s^{-1}$). Calculated wet depositions for phosphate and nitrate at Erdemli and Tel Shikmona were two to four times higher than those of observed at Crete, respectively. Whereas, wet deposition of ammonium at Erdemli was two times higher that those estimated for Tel Shikmona. Taking into account the total atmospheric depositions, phosphate demonstrated decreasing fluxes in the order of Tel Shikmona > Erdemli > Crete while DIN showed declining fluxes in the order of Tel Shikmona ∼Erdemli > Crete.

At Erdemli, the PO_4^3, Si_{diss} and NH_4^+ fluxes were found to be dominated by wet deposition (0.34, 0.92 and $23\,mmol\,m^{-2}\,yr^{-1}$) with dry deposition contributions amounting to 40% ($0.22\,mmol\,m^{-2}\,yr^{-1}$), 35% ($0.54\,mmol\,m^{-2}\,yr^{-1}$) and 18% ($3\,mmol\,m^{-2}\,yr^{-1}$) of their total deposition, respectively. Whereas dry and wet deposition of nitrate was comparable with a value of $22\,mmol\,m^{-2}\,yr^{-1}$. In addition, fluxes of nitrate and ammonium via wet deposition were found to be similar whilst dry deposition flux of nitrate was an order of magnitude higher than those for ammonium owning to differences in their particle sizes and hence settling velocities.

Table 5. Dry and wet deposition depositions of the analyzed nutrients calculated for the present study and the literature for different Mediterranean regions.

Location	Si_{diss}	PO_4^{3-}	NO_3^-	NH_4^+	DIN	Reference
Dry Deposition (mmol m^{-2} yr^{-1})						
Erdemli, Turkey[b]	0.54	0.22	38 (22)	5 (3)	43 (25)	This Study
Winter[a]	0.15	0.05	9 (5)	1 (0.5)	10 (6)	This Study
Transition[a]	0.24	0.09	14 (8)	2 (1)	16 (9)	This Study
Summer[a]	0.15	0.07	15 (9)	2 (1)	17 (10)	This Study
Erdemli, Turkey[b]	-	0.16	36 (21)	8 (4)	44 (25)	Markaki et al. (2003)
Finokalia, Crete[c]	–	0.08	10	2	12	Markaki et al. (2003)
Tel Shikmona, Israel[b]	–	0.51	35 (20)	22 (11)	57 (31)	Herut et al. (2002)
Israeli Coast[b]		0.45	40 (23)	26 (13)	66 (36)	Carbo et al. (2005)
Eilat, Israel[c]	–	0.25	–	–	38	Chen et al. (2007)
Wet Deposition (mmol m^{-2} yr^{-1})						
Erdemli, Turkey	0.92	0.34	22	23	45	This Study
Winter[a]	0.54	0.18	13	16	29	This Study
Transition[a]	0.38	0.16	9	7	16	This Study
Erdemli, Turkey	–	–	16	–	–	Markaki et al. (2003)
Heraklion, Crete	–	0.07	9	11	20	Markaki et al. (2003)
Tel Shikmona, Israel		0.30	20	13	33	Herut et al. (1999)
Atmospheric Deposition (mmol m^{-2} yr^{-1})						
Erdemli, Turkey	1.46	0.56	60 (44)	28 (26)	88 (70)	This Study
Crete	–	0.15	19	13	32	Markaki et al. (2003)
Tel Shikmona, Israel	–	0.81	55 (40)	35 (26)	90 (76)	Herut et al. (1999, 2002)

[a] denotes seasonal fluxes, [b] and [c] show Whatman 41 and Teflon filter. Values in parenthesis indicate alternative dry depositions of nitrate and ammonium for Whatman 41 filters after multiplying 0.58 and 0.50, respectively.

Dry deposition inputs of PO_4^{3-} and Si_{diss} in the transition period were 1.2 to 1.6 times larger than those observed during the winter and summer. NO_3^- and NH_4^+ dry deposition inputs were found comparable for the transition period and summer, whilst the lowest input was observed in winter. During the winter period wet (P = 357 mm) deposition inputs of nutrients were 1.2 to 2 times higher than those calculated for the transition period (P = 133 mm) mainly due to the higher amount of precipitation. In winter, with the exception of nitrate, nutrient inputs were dominated by wet deposition compared to dry deposition. For example, inputs of PO_4^{3-}, Si_{diss} and NH_4^+ via wet deposition were found to be 2 to 3 times larger than their inputs via dry deposition. In addition, inputs of nutrients were exclusively found to be originated from dry deposition in summer due to the lack of precipitation.

3.5.1 Riverine nutrient fluxes

Table 6 shows discharge weighted mean nutrient concentrations and discharges for the studied rivers. Annual mean water discharge for Seyhan, Ceyhan, Göksu, Berdan and Lamas were found to be 168, 144, 45, 6 and 3 m^3 s^{-1}, respectively. Discharges of Rivers show similar seasonality with highest values during spring. Table 6 clearly indicates that Lamas River is a typical example for the least polluted rivers in the Northern Levantine Basin with very low ammonium and phosphate concentrations. On the other hand, concentrations of ammonium and phosphate for the remaining imply that these fresh water sources are substantially influenced by industrial, domestic and agricultural activities.

Table 6. Discharge weighted mean nutrient concentrations (μM) and discharges (m^3 s^{-1}) for studied Rivers.

River	Si_{diss}	PO_4^{3-}	NH_4^+	NO_3^-	Q
Seyhan	117	5.6	16	83	168
Ceyhan	161	1.9	19	105	144
Göksu	112	3.3	7	58	45
Berdan	91	4.8	34	85	6
Lamas	113	0.4	1	101	3

Seyhan and Ceyhan Rivers (Tables 6, 7) were found to be main fresh water sources and more than 85 % of the PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+ (DIN as well) originated from these two rivers. In addition, the contribution from the Göksü River was 10, 11, 8 and 5 % to PO_4^{3-}, Si_{diss}, NO_3^- and NH_4^+ fluxes, respectively. Although, ammonium inputs from rivers showed substantial contribution (15%), nitrate inputs were the primary component of the DIN pool (85%) to the

Table 7. Comparison of riverine and atmospheric nutrient inputs (10^9 mol km^{-2} yr^{-1}) to the Northeastern Levantine Basin of the Eastern Mediterranean and the literature for the Eastern Mediterranean region.

River	Si_{diss}	PO_4^{3-}	NO_3^-	NH_4^+	DIN	N/P	Si/N
Seyhan	0.620	0.030	0.44	0.08	0.62	18	1.2
Ceyhan	0.730	0.009	0.48	0.09	0.73	65	1.3
Göksu	0.160	0.005	0.08	0.01	0.16	20	1.7
Berdan	0.020	0.001	0.02	0.01	0.02	25	0.8
Lamas	0.010	0.00004	0.01	0.0001	0.01	279	1.1
Winter	0.465	0.014	0.258	0.058	0.366	26	1.3
Transition	0.770	0.020	0.514	0.093	0.604	30	1.3
Summer	0.305	0.010	0.252	0.036	0.242	24	1.3
NLB-R[a]	1.54	0.04	1	0.2	1.2	28	1.3
NLB-A[a]	0.16	0.06	7	3	10	233	0.01
Total[a]	1.70	0.10	8	3.2	11	145	0.1
EMED-A[a]	2.44	0.93	100	47	147	145	0.1
EMED-A[b]	–	0.95	–	–	111	117	–
NLB-R[c]	2.77	0.12	–	–	5.5	46	0.5

[a] Current study, [b] Krom et al., 2004, 2010, [c] Ludwig et al., 2009. NLB: Northeastern Levantine Basin, Total: Riverine + Atmospheric inputs, EMED: Eastern Mediterranean, A: Atmospheric flux and R: Riverine flux.

Northern Levantine Basin. Seasonal riverine inputs of nutrients exhibited a decrease in values in the order of Transitional > Winter > Summer. During the transition period nutrient inputs were found to be two to five times higher than those in winter and summer, respectively. This of course is not unexpected owing to the higher fluvial discharge in the transitional period.

3.5.2 Comparison between atmospheric and riverine nutrient fluxes

Krom et al. (2004, 2010) and Ludwig et al. (2009) calculated the atmospheric and the riverine nutrient fluxes in Eastern Mediterranean, respectively. As can be deduced from Table 7, current atmospheric phosphorous and nitrogen fluxes are in good agreement with the values reported by Krom et al. (2004, 2010) for EMED. In spite of different approaches during the estimation of the riverine nutrient fluxes in NLB, the current riverine fluxes and reported fluxes by Ludwig et al. (2009) were found in the same magnitude. Our estimated riverine fluxes for silicate, phosphorous and nitrogen were 1.8, 3 and 4.6 times lower than those calculated by Ludwig et al. (2009) for NLB. This discrepancy might be attributed to difference in study period. As suggested by Ludwig et al. (2009) local patterns of rivers which are not sufficiently captured by their method might also be as a source of this difference.

On the basis of annual atmospheric and riverine inputs (see Table 7) the following general observation might be made:

(a) Comparison of the atmospheric and riverine fluxes (annual and seasonal) reveals that inorganic nitrogen species (DIN = NO_3^- + NH_4^+) fluxes to NLB were dominated by the atmospheric pathway with a mean contribution being more than 90%. Riverine phosphate flux (40%) had a substantial contribution to the phosphate pool in the NLB, however the atmosphere was found to be the main source to the surface waters with a mean contribution of 60%. Unlike inorganic nitrogen and phosphate, the NBL Si pool was almost exclusively dominated by riverine fluxes (90%) and only 10% of the Si was attributed to atmospheric source.

(b) Riverine molar N/P ratios ranged from 18 to 279 with a mean value of 28 and in contrast the molar Si/N ratios were found to range from 0.8 to 1.7, with a mean value of 1.3. Obtained riverine N/P and Si/N ratios suggested that riverine sources in the region are deficient in phosphate compare to DIN and Si. Atmospheric (dry and wet) molar mean N/P ratios were found to be order of magnitude higher than former ratio whereas riverine Si/N ratio was 100 times greater than those observed for atmospheric inputs. It appears that both sources were deficient in phosphorus compared to nitrogen. In other words, the Northeastern Levantine Basin of the Mediterranean Sea receives excessive amounts of DIN; higher than those required by autotrophic organisms. Considering N/P ratio it might be suggested that unbalanced phosphorus and nitrogen inputs may provoke even more phosphorus deficiency in NLB. Although Si inputs have no effect on phosphorus limitation, total Si/N ratio suggests that Si deficiency relative to nitrogen might cause a switch from diatom dominated phytoplankton population to non-siliceous communities particularly at coastal areas in NLB. It has been shown that coastal sites of the Cilician Basin are dominated by diatom population (Uysal and Köksalan, 2010). Recently, our seasonal

studies in this area have revealed that Si might be as important as P at coastal sites. For instance, in February and March Si/N ratios were found to be ranged from 0.2 to 0.8 during diatom bloom which imply Si deficiency proportionate to nitrogen is likely to influence on phytoplankton composition on seasonal basis.

4 Conclusions

In this study, factors controlling nutrient composition in aerosol and rainwater, differences in sea-water and pure-water solubilities of nutrients and atmospheric and riverine nutrient inputs to the Northeastern Levantine Basin of the Eastern Mediterranean have been investigated.

Nutrient concentrations in aerosol and rainwater samples exhibited substantial temporal variability, up to an order of magnitude on daily basis. PO_4^{3-} and Si_{diss} in aerosol and rainwater exhibited higher and larger variations during the transitional period since their concentrations are affected by sporadic dust events originating from North Africa and Middle East/Arabian Peninsula. Their mean concentrations were at least 1.5 times higher during airflows originating from the Saharan and Middle East/Arabian Peninsula than those observed for the remaining air flows. Deficiency of alkaline material were found to be the main reason of acidic rain events whereas, alkaline rain events were observed when air mass back trajectories originated from arid and semi-arid desert regions. Higher aerosol nitrate and ammonium concentrations in the summer were due to the lack of precipitation and active photochemical formation. In general, lowest nitrate and ammonium concentrations in aerosol and rainwater were associated with air flow from Mediterranean Sea.

Dry and wet deposition fluxes were found comparable for PO_4^{3-}. Si_{diss} and NH_4^+ fluxes were found to be dominated by wet deposition (∼60%) whilst dry deposition was a main source of nitrate flux (∼80%). Seyhan and Ceyhan were found to be the main fresh water over the study the region with nutrient contributions more than 85% of the total riverine nutrient inputs. Riverine DIN pool was found to be dominated by nitrate input (75%). Comparison of the atmospheric and riverine fluxes demonstrated that DIN and PO_4^{3-} fluxes to NLB were dominated by atmospheric pathway (∼90% and ∼60%). However, the Si pool in the NLB was almost exclusively originated from riverine runoff (∼90%). Considering molar N/P ratios from the atmosphere (236) and riverine (22) sources it is clear that the NLB of the Eastern Mediterranean Sea receives excessive amounts of DIN; more than the amounts required by autotrophic organisms and this unbalanced P and N inputs may provoke even more phosphorus deficiency. Observed molar Si/N ratio suggested that Si limitation relative to N and it might cause a switch from diatom dominated communities to non-siliceous populations particularly at coastal areas where in NLB.

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