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Long-term atmospheric nutrient inputs to the Eastern Mediterranean: sources, solubility and comparison with riverine inputs

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Abstract

Aerosol and rain samples were 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 were 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 variation during the transitional period (March–May, September) when air flows predominantly originate from North Africa and Middle East/Arabian Peninsula. Deficiency of alkaline material were found to be the main reason of the acidic rain events whilst high pH values (>7) were associated with high Si_{diss} concentrations due to sporadic dust events. In general, lowest nitrate and ammonium concentrations in aerosol and rainwater were associated with air flow from the Mediterranean Sea. Unlike NO_3^- and NH_4^+ (Dissolved Inorganic Nitrogen, DIN), there were statistical differences for PO_4^{3-} and Si_{diss} solubilities in sea-water and pure-water. Solubilities of PO_4^{3-} and Si_{diss} were found to be related with air mass back trajectories and pH. Comparison of atmospheric with riverine fluxes demonstrated that DIN and PO_4^{3-} fluxes to NLB were dominated by atmosphere (~90% and ~60% respectively) whereas the input of Si was mainly derived from riverine runoff (~90%). N/P ratios (atmosphere~233; riverine~28) revealed that NLB receives excessive amounts of DIN and this unbalanced P and N inputs may provoke even more phosphorus deficiency. Molar Si/N ratios (atmosphere + riverine) suggested Si limitation which might cause a switch from diatom dominated phytoplankton communities to non-siliceous populations in 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 almost half that of 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, (Krom et al., 1991; Turley, 1999). As a result of this peculiarity, most of the nutrient inputs to the Mediterranean Sea are mainly originated from the atmosphere (including dry and wet depositions) and riverine runoff. Over the last four decades, the freshwater discharge from rivers to the Mediterranean rivers has suffered a substantial decrease owning to both climate change and dam constructions (Ludwig et al., 2009) therefore the relative importance of atmospheric inputs of nutrients to the Mediterranean surface waters will have increased.

The Eastern Mediterranean Sea has a uniquely high N/P ratio raging from 25 to 28, higher values compare 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 the input sources but for those particularly from the atmosphere (117:1). Ludwig et al. (2009) suggested that decreases in the dissolved Silica concentrations were due to a substantial reduction in the fresh water discharges. These authors have hypnotized 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 fluxes 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, 2005; Koçak et al., 2004a). Atmospheric deposition of desert dust over the Mediterranean supplies soluble or bioavailable macro (P, N) and trace 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), the atmospheric input of inorganic nitrogen represents 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).

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) to the surface waters of the Northern Levantine Basin. The extensive library of aerosol, rainwater and riverine samples collected from the region, will allow to (i) define temporal variability of nutrient concentrations in aerosol and rainwater, (ii) assess the influence of air masses back trajectories on nutrient composition, (iii) compare sea-water and pure-water solubilities of nutrients for selected aerosol samples and (iv) assess and compare the atmospheric and riverine inputs of nutrients to the Northern Levantine Basin.

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2 Materials and methods

2.1 Sites description and sample collection

Aerosol and rain water 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 sampling site is not under direct influence of any industrial activities. 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 form 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. 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. 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 1997 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. Monthly sample collection was carried out between March 2002 and November 2007. Sampling coverage was better than 30% for nutrients PO_4^{3-}, Si_{diss} and NO_3^- where it was around 20% for NH_4^+ during sampling period.

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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.

The soluble nutrient measurements in aerosols, rain waters and river samples were carried out by a Technicon Model, four-channel Autoanalyzer (for more details see Yılmaz and Tuğrul, 1998). The detection limits achieved using low concentration samples were 0.02, 0.10, 0.02 and 0.04 µM for phosphate, reactive silicate, nitrate and ammonium, respectively. 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) and 50 µL chloroform. In order to compare solubilities, the same extraction procedure was adopted using Northeastern Mediterranean surface Seawater (filtered with 0.2 µm, Herut et al., 2002) as the extraction medium. Samples were immediately analyzed for nutrients after centrifuging at 3500 rpm for 15 min.

2.3 Air mass back trajectories and cluster analysis

Air masses back trajectories arriving at the sampling site were computed by the Hysplit Dispersion Model (Hybrid Single Particle Langrangian Integrated Trajectory; Draxler and Hess, 1998) and were illustrated by one-hour endpoint locations in term of latitude and longitude. Daily back trajectories between January 1999 and December 2007 were evaluated for 3 days for three different heights above the starting point at ground level (1, 2 and 3 km a.g.l.). Cluster analysis was applied to categorize air masses back trajectories using the method described by Cape et al. (2000).

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2.4 Calculation of nutrient fluxes

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) and the volume weighted mean concentration (C_w) of the substance of interest (Eq. 1).

$$F_w = C_w \times P \tag{1}$$

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 μmol m^{-2} yr^{-1}, C_d in units of μmol m^{-3} and V_d in units of m yr^{-1} (for more details see Sect. 3.5.1).

$$F_d = C_d \times V_d \tag{2}$$

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

$$C_{dw} = \frac{\sum_{i=1}^{n} C_i \times Q_i}{\sum_{i=1}^{n} Q_i} \tag{3}$$

$$F_r = C_{dw} \times Q_{annual} \tag{4}$$

The discharge weighted mean concentration (C_{dw}, Eq. 3) 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 latest provided from General Directorate of State Hydraulic Works, Turkey.

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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 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 Eliat, Israel (Chen et al., 2007). Although phosphate concentrations were measured in seawater, highest levels over the Eastern Mediterranean was reported for Tel Shikmona and this might be attributed 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.,

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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 Eliat, 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 Eliat 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 (n=158; Koçak, 2006). 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 be those of total inorganic NO_3^- and NH_4^+ plus gaseous HNO_3 and NH_3.

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 (Markakie 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.

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

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presented in Fig. 2. 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. 2a–d).

3.2.1 Aerosol

Although, particles are efficiently scavenged by wet deposition (26% of the annual amount, 39% of the total events, one rain event per 5 day) 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 on 18–20 October 2002 and 4–5 April 2003 will be used. The first is an example of a dust event was 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 19 October with values of 2.6 and 26.6 nmol m^{-3}. Figure 3a shows air mass back trajectories for three levels (1, 2 and 3 km) along with TOMS-AI (Total Ozone Mapping Spectrometer Aerosol Index) for 19 October 2002. All air masses back trajectories for 19 October indicated air flow originating from the Middle East while TOMS exhibits particularly a large plume of dust from the Middle East region into the eastern Mediterranean with AI values ranging between 1.2 from 3. The second example was observed from 4 April to 5 April 2003 with mean PO_4^{3-} and Si_{diss} concentrations

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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 3b presents air masses 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% of the annual amount, 55% of the total events, one rain event per 3 day). 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).

3.2.2 Rainwater

In general, PO_4^{3-} and Si_{diss} 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 and which had a red "mineral dust" had pH values as high as 7 as a result of the dissolution of calcium carbonate originated 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 lower than those calculated for transition period. Therefore acid events (80% was observed in winter) might be attributed to the deficiency of alkaline material

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which was not sufficient to neutralize the acidity due to damp soil around vicinity and less frequent mineral dust transport to the region. 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 November 30 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 Si_{diss} since crust originated particles removed from atmosphere efficiently and resulted in a 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 3c 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 masses 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 airflow on nutrients

During the application of cluster analysis 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; 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 contributing to 9.1% of the trajectories. The third and fourth clusters show short trajectories originating from the north-west (Cluster 3; NWT) and northern Turkey (Cluster 4; NT) and they represent 41.4% and 19.6% of the airflow, respectively. The fifth cluster represents trajectories traveling at high speeds, being maritime air masses from the western Mediterranean Sea, representing 7.1% of the airflow (hereafter MEDS).

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Air masses originating from the Middle East/Arabian Peninsula (Cluster 6; MEAP) and Eastern Saharan (Cluster 7: SAH) represent 10.1% and 10.6% of the trajectories.

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 for aerosol and rain samples were found to be higher in the SAH and MEAP than those observed for remaining air flows. For instance, mean concentrations of PO_4^{3-} and Si_{diss} for aerosol (rain) were found approximately 1.5 (1.6) and 3 (2) times higher than remaining air flows, respectively. These two air flows are 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 flow origination from Europe (EU) and Mediterranean Sea (MEDS) whereas concentrations for the remaining air masses were found to be comparable. For aerosol ammonium concentrations were found statistically higher when air flows originating from Turkey (NWT and NT) 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 remaining air flows. It can be suggested that relatively cleaner air masses associated with Mediterranean Sea during rainy seasons.

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3.4 Comparison between sea-water and pure-water solubility of nutrients

There are few studies which have directly compared the dissolution of nutrients in sea-water and pure-water. For instance, Markaki et al. (2003) compared sea-water (SW) and pure-water (PW) solubility of P after extracting samples from Finokalia for 45 min. Results from the comparison did not reveal any statistical difference for solubility of P in sea-water and pure-water (slope = 0.99, R^2=0.80). Similarly, Chen et al. (2006) studied the dissolution of PO_4^{3-}, NO_3^- and NH_4^+ in sea-water and pure-water, after extracting aerosol samples from Gulf of Aqaba for 30 min. Dissolution of NO_3^- and NH_4^+ was found to be statistically not different while PO_4^{3-} was found to be 11% lower in sea-water than those observed for pure-water.

PO_4^{3-} and Si_{diss}: Non-parametric Wilcoxon matched pairs test was applied to compare nutrient solubilities in sea-water and pure-water. Figure 4a shows concentrations of PO_4^{3-} and Si_{diss} in pure-water and sea-water. The Wilcoxon test showed that there were statistical difference in the dissolutions of PO_4^{3-} and Si_{diss} in pure-water and sea-water. The mean concentrations of sea-water PO_4^{3-} and Si_{diss} (0.18 and 1.16 nmol m^{-3}) were found to 43% and 67% lower than those for pure-water (0.31 and 3.48 nmol m^{-3}), respectively. This difference might be attributed to pH and ionic strength of sea water and association of phosphate (Chen et al., 2006), silicate aerosols with less soluble compounds (such as calcium phosphate, kaolinite, opal and quartz) and origin of the aerosol species (Koçak et al., 2007a; Baker et al., 2007).

In order to assess influence of the origin of the aerosol species, air mass back trajectories were simply classified into three categories namely Turkey (T: NT+NWT) and Europe (E) and Southerly (S: SAH+MEAP) flows. Mean concentrations of PO_4^{3-} and Si_{diss} in pure-water and sea-water for the three air flow categories are presented in Table 4. As expected, highest concentrations of PO_4^{3-} and Si_{diss} for pure-water and sea-water were found to be associated with Southerly air flow, being 1.5 to 3 times higher than those observed for air flow from Europe and Turkey. The SW/PW (%) ratio

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for PO_4^{3-} and Si_{diss} showed values decreasing in the order E (80%)>T (57%)>S (48%) and T (48%)>S~E (25%), respectively. Observed difference for PO_4^{3-} might be attributed to higher anthropogenic character of the aerosol particles originating from Europe and Turkey compare to arid/semi-arid source regions. On the other hand, highest Si solubility were identified in air masses originating from Turkey, two time higher than those calculated for remaining air flows. It is possible that local and/or region crustal dust particles have a different solubility character compared to European and Southerly crustal material. Further studies (such as solid state speciation) are required to investigate the solubility of Si originating from different crustal materials.

To test the influence of pH on PO_4^{3-} and Si_{diss} solubilities, dissolution experiments were performed for 1, 3, 6 and 36 husing same sample set and pure-water. Measured Si concentrations at the end of 3, 6 and 36 (0.56, 0.70 and 3.48 nmol m^{-3}) h showed 1.2, 1.5 and 7.4 time increase compare to values obtained for 1 h (0.47 nmol m^{-3}). It should be worth to note that on average concentrations obtained from 1, 3 and 6 h dissolution experiments were found to be 2.5, 2.1 and 1.7 times less than sea-water solubility (1.16 nmol m^{-3}). Therefore, it might be suggested that solubility of Si was mainly constrained by pH of the pure-water. However, pH effect on PO_4^{3-} solubility was found to be much less pronouncing compare to Si. There was no statistical difference for 1 and 3 h solubilities whilst there was a statistical difference for concentrations obtained from 1 and 6, 36 h dissolution experiments with increase of 8% and 16% respectively. In addition to pH observed solubility difference of PO_4^{3-} for sea-water and pure-water might be affected by ionic strength.

NO_3^- and NH_4^+: Fig. 4b exhibits concentrations of NO_3^- and NH_4^+ in pure and sea water. The mean concentrations of NO_3^- and NH_4^+ (63.2 and 115.7 nmol m^{-3}) in sea-water were found to be similar to values obtained for pure-water (63.9 and 111.9 nmol m^{-3}). Unlike PO_4^{3-} and Si_{diss} there were no statistical differences for nitrate and ammonium solubilities in pure and sea water. Therefore, obtained results for nitrate and ammonium implies that sea water does not influence the solubilites of these nutrients considering

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high pH and ionic strength of sea water. This peculiarity suggests that aerosol nitrate and ammonium are almost exclusively associated with highly soluble chemical forms such as NH_4NO_3, $Ca(NO_3)_2$, $NaNO_3$ $(NH_4)_2SO_4$ and NH_4HSO_4 (Bardouki et al., 2003; Koçak et al., 2007b).

3.5 Nutrient fluxes

3.5.1 Atmospheric nutrient fluxes

Dry deposition of the particles is size dependent; therefore, 20 samples were collected by stack filter unit in two size fraction namely coarse (10–2.5 µm; <d<2.5 µm) and fine (d<2.5 µm) (for more details see Koçak et al., 2007c). 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%). An Approach adopted by Spokes et al. (2001), after Ottley and Harrison (1993) were used to estimate the settling velocities of nutrients. The V_d's of nutrients for the current study was based on assumption of V_d's are 0.1 cm s^{-1} and 2.0 cm s^{-1} for fine and coarse particles (Duce et al., 1991). Settling velocities of nutrient for Eastern and Western Mediterranean are presented in Table 5. 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 and 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

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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 a factor of two (Duce et al., 1991; Herut et al., 2002).

The atmospheric dry and wet deposition fluxes calculated for each nutrient are presented in Table 6. The dry deposition flux of PO_4^{3-} (0.35 mmol m^{-2} yr^{-1}) was found to be comparable with the wet deposition flux (0.34 mmol m^{-2} yr^{-1}). Whereas the Si_{diss} and NH_4^+ fluxes were found to be dominated by wet deposition (0.92 and 23 mmol m^{-2} yr^{-1}) with dry deposition contributed amounting to 35% (0.51 mmol m^{-2} yr^{-1}) and 40% (15 mmol m^{-2} yr^{-1}) of their total deposition, respectively. In contrast dry deposition accounted for 83% (103 mmol m^{-2} yr^{-1}) of the total nitrate flux. 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.

3.5.2 Comparison between atmospheric and riverine nutrient fluxes

Table 7 shows discharge weighted mean nutrient concentrations and discharges for 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 7 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 remaining rivers imply that these fresh water sources are substantially influenced by industrial, domestic and agricultural activities.

Using the nutrient deposition fluxes (dry + wet), total inputs (tons yr^{-1}) to the Northern Levantine Basin (NLB; bordered by Turkey, Cyprus, Syria and Lebanon, having a surface area of 111 000 km^2; Ludwing and Maybeck, 2003) was calculated.

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Within the annual period three seasons were defined; winter, transitional, and summer. The winter period included the months, December, January, and February, whereas the transitional season included the months March, April, and May. The summer season included the months June, July, August and September. On the basis of annual and seasonal atmospheric and riverine inputs (see Table 8) the following general observation might be made:

(a) Seyhan and Ceyhan Rivers 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 made by 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 Northern Levantine Basin.

(b) Seasonal riverine inputs of nutrients exhibited a decrease in values in the order of Transitional > Summer > Winter. During the transition period nutrient inputs were found to be two to five times higher than those calculated for winter and summer, respectively. This of course is not unexpected owing to the higher discharges of rivers in transition period.

(c) 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

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exclusively found to be originated from dry deposition in summer due to the lack of precipitation.

(d) 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 (36%) 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 64%. 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.

(f) Riverine molar N/P ratios ranged from 18 to 279 with a mean value of 28, 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; more than is 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 where riverine inputs limited.

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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 for Northeastern Levantine Basin of the Eastern Mediterranean have been investigated.

Nutrient concentrations in aerosol and rainwater samples exhibited substantial temporal variability and their values changed up to an order of magnitude from day to day. PO_4^{3-} and Si_{diss} in aerosol and rainwater exhibited higher and larger variations during the transitional period since their concentrations are heavily 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. Aerosol NO_3^- and NH_4^+ concentrations demonstrated higher values in summer 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.

Unlike NO_3^- and NH_4^+, there were statistical differences for PO_4^{3-} and Si_{diss} solubilities in sea-water and pure-water. Higher SW/PW (%) ratios for PO_4^{3-} were found in European (80%) and Turkey (57%) compare to Southerly (48%) air flows due to higher anthropogenic character of the aerosol particles originating from former air flows. The highest Si solubility was identified in air masses flowing from Turkey and attributed to different solubility character crustal materials. Solubility of Si was mainly constrained by the pH of the pure-water whereas, PO_4^{3-} solubility was found to be less effected by pH of the pure-water.

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

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a main source of nitrate flux (~80%). Seyhan and Ceyhan were found to be main fresh water sources of the region with nutrient contributions more than 85%. 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 is required by autotrophic organisms and this unbalanced P and N inputs may provoke even more phosphorus deficiency. Atmospheric and total 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 riverine input is limited.

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References

Avila, A., Alarcon, M., and Queralt-Mitjans, I.: The chemical composition of dust transported in red rains its contribution to the biogeochemical cycle of a holm oak forest in Catalonia, Spain, Atmos. Environ., 32, 179–191, 1998.

Baker, A. R., Weston, K., Kelly, S. D., Voss, M., Streu, P., and Cape, J. N.: Dry and wet deposition of nutrients from the tropical Atlantic atmosphere: Links to primary productivity and nitrogen fixation, Deep-Sea Res Pt. II, 54, 1704–1720, 2007.

Bardouki, H., Liakakou, H., Economou, C., Sciare, J., Smolik, J., Zdimal, V., Eleftheriadis, K., Lazaridis, M., Dye, C., and Mihalopoulos, N.: Chemical composition of size resolved atmospheric aerosols in the eastern Mediterranean during summer and winter, Atmos. Environ., 37, 195–208, 2003.

BGD
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Bartoli, G., Migon, C., and Losno, R.: Atmospheric input of dissolved inorganic phosphorus and silicon to the coastal northwestern Mediterranean Sea: Fluxes, variability and possible impact on phytoplankton dynamics, Deep-Sea Res Pt. I, 52, 2005–2016, 2005.

Bonnet, S., Guieu, C., Chiaverini, J., Ras, J., and Stock, A.: Effect of atmospheric nutrients on the autotrophic communities in a low nutrient, low chlorophyll system, Limnol. Oceanogr., 50(6), 1810–1819, 2005.

Cape, J. N., Methven, J., and Hudson, L. E.: The use of trajectory cluster analysis to interpret trace gas measurements at Mace Head, Ireland, Atmos. Environ., 34, 3651–3663, 2000.

Carbo, P., Krom, M. D., Homoky, W. B., Benning, L. G., and Herut, B.: Impact of atmospheric deposition on N and P geochemistry in the southeastern Levantine basin, Deep-Sea Res. Pt. II, 52, 3041–3053, 2005.

Chen, Y., Street, J., and Paytan, A.: Comparison between pure-water and seawater-soluble nutrient concentrations of aerosols from the Gulf of Aqaba, Mar. Chem., 101, 141–152, 2006.

Chen, Y., Mills, S., Street, J., Golan, D., Post, A., Jacobson, M., and Paytan, A.: Estimates of atmospheric dry deposition and associated input of nutrients to Gulf of Aqaba seawater, J. Geophys. Res., 112, D04309, doi:10.1029/2006JD007858, 2007.

Draxler, R. R. and Hess, G. D.: An overview of the HYSPLIT 4 modeling system for trajectories, dispersion and deposition, Aust. Meteorol, Mag., 47, 295–308, 1998.

Duce, R. A., Liss, P. S., Merrill, J. T., Atlas, E. L., and Buat-Menard, P.: The atmospheric input of trace species to the world ocean, Global Biogeochem. Cy., 5, 193–259, 1991.

Guerzoni, S., Molinaroli, E., and Chester, R.: Saharan dust inputs to the western Mediterranean Sea: depositional patterns, geochemistry and sedimentological implications, Deep-Sea Res Pt. II, 44(3–4), 631–654, 1997.

Guerzoni, S., Chester, R., Dulac, F., Herut, B., Loÿe-Pilot, M. D., Measures, C., Migon, C., Molinaroli, E., Moulin, C., Rossini, P., Saydam, C., Soudine, A., and Ziveri, P.: The role of atmospheric deposition in the biogeochemistry of the Mediterranean sea, Prog. Oceanogr., 44, 147–190, 1999.

Guieu, C., Loye-Pilot, M.-D., Ridame, C., and Thomas, C.: Chemical characterization of the Saharan dust end-member: Some biogeochemical implications for the western Mediterranean Sea, J. Geophys. Res., 107(D15), 4258, doi:10.1029/2001JD000582, 2002.

Herut, B., Krom, M. D., Pan, G., and Mortimer, R.: Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: sources, fluxes and possible impact, Limnol. Oceanogr., 44, 1683–1692, 1999.

BGD

7, 5081–5117, 2010

Herut, B., Collier, R., and Krom, M. D.: The role of dust in supplying nitrogen and phosphorus to the Southeast Mediterranean, Limnol. Oceanogr., 47, 870–878, 2002.
Herut, B., Zohary, T., Krom, M. D., Mantoura, R. F. C., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T., and Thingstad, T. F.: Response of east Mediterranean surface water to Saharan dust: On-board microcosm experiment and field observations, Deep-Sea Res. Pt. II, 52, 3024–3040, 2005.
Karakatsoulis, P. and Ludwig, W.: Guidelines for River (including estuaries) pollution monitoring programme for the Mediterranean region, UNEP/MAP Technical report Series 151, UNEP/MAP Athens, 2004.
Keck, L. and Wittmaack, K.: Laboratory studies on the retention of nitric acid, hydrochloric acid and ammonia on aerosol filters, Atmos. Environ., 39, 2157–2162, 2005.
Koçak, M., Nimmo, M., Kubilay, N., and Herut, B.: Spatio-temporal aerosol trace metal concentrations and sources in the Levantine basin of the eastern Mediterranean, Atmos. Environ., 38, 2133–2144, 2004a.
Koçak, M., Kubilay, N., and Mihalopoulos, N.: Ionic composition of lower tropospheric aerosols at a northeastern Mediterranean site: implications regarding sources and long-range transport, Atmos. Environ., 38, 2067–2077, 2004b.
Koçak, M.: Comprehensive chemical characterization of aerosols in the Eastern Mediterranean: Sources and Long range transport, Ph. D. thesis, Middle East Technical University, Institute of Marine Sciences, Erdemli, Turkey, 2006.
Koçak, M., Kubilay, N., Herut, B., and Nimmo, M.: Trace Metal Solid State Speciation in Aerosols of the Northern Levantine Basin, East Mediterranean, J. Atmos. Chem., 56, 239–257, 2007a.
Koçak, M., Mihalopoulos, N., and Kubilay, N.: Chemical composition of the fine and coarse fraction of aerosols in the northeastern Mediterranean, Atmos. Environ., 41(34), 7351–7368, 2007b.
Koçak, M., Mihalopoulos, N., and Kubilay, N.: Contributions of natural sources to high PM_{10} and $PM_{2.5}$ events in the eastern Mediterranean, Atmos. Environ., 41(18), 3806–3818, 2007c.
Kouvarakis, G., Mihalopoulos, N., Tselepides, A., and Stavrakaki, S.: On the importance of atmospheric inputs of inorganic nitrogen species on the productivity of the eastern Mediterranean Sea, Global Biogeochem. Cy., 15, 805–817, 2001.
Krom, M. D., Kress, N., Brenner, S., and Gordon, L. I.: Phosphorus limitation of primary productivity in the eastern Mediterranean, Limnol. Oceanogr., 36, 424–432, 1991.

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7, 5081–5117, 2010

Krom, M. D., Herut, B., and Mantoura, R. F. C.: Nutrient budget for the Eastern Mediterranean: implications for P limitation, Limnol. Oceanogr., 49, 1582–1592, 2004.
Kubilay, N. and Saydam, C.: Trace elements in atmospheric particulates over the Eastern Mediterranean: concentration, sources and temporal variability, Atmos. Environ., 29, 2289–2300, 1995.
Kubilay, N., Nickovic, S., Moulin, C., and Dulac, F.: An illustration of the transport and deposition of mineral dust onto the eastern Mediterranean, Atmos. Environ., 34, 1293–1303, 2000.
Loÿe-Pilot, M. D., Martin, J. M., and Morelli, J.: Influence of Saharan dust on the rain acidity and atmospheric input to the Mediterranean, Nature, 321, 427–428, 1986.
Loÿe-Pilot, M. D. and Morelli, J.: Fluctuations of ionic composition of precipitations collected in Corsica related to changes in the origin of incoming aerosols, J. Aerosol Sci., 19, 577–585, 1988.
Loÿe-Pilot, M. D., Klein, C., and Martin, J. M.: Major Inorganic elements in North Western Mediterranean Aerosols, Eros 2000 4th Workshop on the North Western Mediterranean Sea, Water Pollution Report, 30, 271–277, 1993.
Ludwig, W. and Maybeck, M.: Riverine transport of water, sediments and pollutants to the Mediterranean Sea, United Nations Environment Programme Mediterranean Action Plan (UNEP/MAP), MAP Technical Report Series #141, 111 pp., 2003.
Ludwig, W., Dumont, E., Meybeck, M., and Heussner, S.: River discharges of water and nutrients to the Mediterranean and Black Sea: Major drivers for ecosystem changes during past and future decades?, Prog. Oceanogr., 80(3–4), 199–217, 2009.
Markaki, Z., Oikonomou, K., Koçak, M., Kouvarakis, G., Chaniotaki, A., Kubilay, N., and Mihalopoulos, N.: Atmospheric deposition of inorganic phosphorus in the Levantine basin, eastern Mediterranean: spatial and temporal variability and its role in seawater productivity, Limnol. Oceanogr., 48, 1557–1568, 2003.
Markaki, Z., Loÿe-Pilot, M. D., Violaki, K., Benyahya, L., and Mihalopoulos, N.: Variability of atmospheric deposition of dissolved nitrogen and phosphorus in the Mediterranean and possible link to the anomalous seawater N/P ratio, Mar. Chem., 120, 187–194, 2010.
Migon, C., Sandroni, V., and Béthoux, J. P.: Atmospheric input of anthropogenic phosphorus to the northwest Mediterranean under oligotrophic conditions, Mar. Environ. Res., 52, 413–426, 2001.
Mihalopoulos, N., Stephanou, E., Kanakidou, M., Pilitsidis, S., and Bousquet, P.: Tropospheric aerosol ionic composition in the E. Mediterranean region, Tellus B, 49, 1–13, 1997.

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Moulin, C., Lambert, E., Dayan, U., Masson, V., Ramonet, M., Bousquet, P., Legrand, M., Balkanski, Y. J., Guelle, W., Marticorena, B., Bergametti, G., and Dulac, F.: Satellite climatology of African dust transport in the Mediterranean atmosphere, J. Geophys. Res., 103, 13137–13144, 1998.

Ottley, C. J. and Harrison, R. M.: Atmospheric dry deposition flux of metallic species to the North Sea, Atmos. Environ., 27A, 685–695, 1993.

Özsoy, T. and Saydam, C.: Acidic and alkaline precipitation in the Cilician Basin, north western Mediterranean sea, Sci. Total Environ., 352, 93–109, 2000.

Pitta, P., Stambler, N., Tanaka, T., Zohary, T., Tselepides, A., and Rassoulzadegan, F.: Biological response to P addition in the Eastern Mediterranean Sea: the microbial race against time, Deep-Sea Res. Pt. II, 52, 2961–2974, 2005..

Ridame, C. and Guieu, C.: Saharan input of phosphate to the oligotrophic water of the open western Mediterranean Sea, Limnol. Oceanogr., 47(3), 856–869, 2002.

Spokes, L. J., Jickells, T. D., and Jarvis, K.: Atmospheric inputs of trace metals to the northeast Atlantic Ocean: the importance of south-easterly flow, Mar. Chem., 76, 319–330, 2001.

Spokes, L. J. and Jickells, T. D.: Is the atmosphere really an important source of reactive nitrogen to coastal waters?, Cont. Shelf Res., 25, 2022–2035, 2005.

Thingstad, T. F., Krom, M. D., Mantoura, R. F. C., Flaten, G. A. F., Groom, S., Herut, B., Kress, N., Law, C. S., Pasternak, A., Pitta, P., Psarra, S., Rassoulzadegan, F., Tanaka, T., Tselepides, A., Wassmann, P., Woodward, E. M. S., Wexels Riser, C., Zodiatis, G., and Zohary, T.: Nature of phosphorus limitation in the ultraoligotrophic eastern Mediterranean, Science, 309, 1068–1071, 2005.

Turley, C. M.: The changing Mediterranean Sea – a sensitive ecosystem?, Prog. Oceanogr., 44, 387–400, 1999.

Wieprecht, W., Brüggemann, E., Müller, K., Acker, K., Spindler, G., ten Brink, H. M., Hitzenberger, R., and Maenhaut, W.: INTERCOMP2000: Ionic constitution and comparison of filter and impactor samples and its analysis, Atmos. Environ., 38, 6477–6486, 2004.

Yılmaz, A. and Tuğrul, S.: The effect of cold- and warm-core eddies on the distribution and stoichiometry of dissolved nutrients in the northeastern Mediterranean, J. Mar. Syst., 16, 253–268, 1998.

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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.

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

Location	NO_3^-	NH_4^+		Reference
		Aerosol (nmol m^{-3})		
Erdemli, Turkey	65±34	121±64	Jan 1999–Dec 2009 (1525)	This Study
Erdemli, Turkey	58	118	Jan 1999–Jan 2000 (194)	Markaki et al. (2003)
Finokalia, Crete	27±13	53±21	Oct 1996–Sep 1999 (496)	Kouvarakis et al. (2001)
Finokalia, Crete	16	24	Sep 1999–Sep 2000 (85)	Markaki et al. (2003)
Tel Shikmona, Israel	93±29[a]	117±88[a]	Apr 1996–Jan 1999 (41)	Herut et al. (2002)
Eliat, Israel	39±19	25±14	Aug 2003–Sep 2005 (137)	Chen et al. (2007)
Cap Ferrat, France	63	150	May–June 1992	Loye-Pilot et al. (1993)
		Rainwater (µmol L^{-1})		
Erdemli, Turkey	37	41	Jan 1999–Dec 2007 (237)	This Study
Erdemli, Turkey	46	–	Feb 1999–Dec 1999 (16)	Markaki et al. (2003)
Heraklion, Crete	18	21	Sep 1999–Sep 2000 (41)	Markaki et al. (2003)
Tel Shikmona, Israel	41	25	Jan 1992–Mar 1998 (187)	Herut et al. (1999)
Ashod, Israel	57	45	Nov 1995–Mar 1998 (67)	Herut et al. (1999)
Location	Si_{diss}	PO_4^{3-}		Reference
		Aerosol (nmol m^{-3})		
Erdemli, Turkey	1.1±1.5	0.5±0.4	Jan 1999–Dec 2009 (1525)	This Study
Erdemli, Turkey	–	0.3	Jan 1999–Jan 2000 (194)	Markaki et al. (2003)
Finokalia, Crete	–	0.1	Sep 1999–Sep 2000 (85)	Markaki et al. (2003)
Tel Shikmona, Israel	–	0.8[a]±0.5	Apr 1996–Jan 1999 (41)	Herut et al. (2002)
Eliat, Israel	–	0.4±0.2	Aug 2003–Sep 2005 (137)	Chen et al. (2007)
		Rainwater (µmol L^{-1})		
Erdemli, Turkey	1.9	0.5	Jan 1999–Dec 2007 (237)	This Study
Erdemli, Turkey	–		Feb 1999–Dec 1999 (16)	Markaki et al. (2003)
Heraklion, Crete	–	0.1	Sep 1999–Sep 2000 (41)	Markaki et al. (2003)
Tel Shikmona, Israel	–	0.6	Jan 1992–Mar 1998 (187)	Herut et al. (1999)
Ashod, Israel	–	0.6	Nov 1995–Mar 1998 (67)	Herut et al. (1999)

[a] Indicates sea-water solubility of nutrient species.

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Table 3. Mean 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})					
	NWT	NT	EU	MED	MEAP	SAH	NWT	NT	EU	MED	MEAP	SAH
$P\text{-}PO_4^{-3}$	0.38	0.41	0.39	0.33	0.62	0.56	0.38	–	0.32	0.29	0.68	0.61
Si_{diss}	0.59	0.58	0.50	0.45	1.76	1.98	0.65	–	0.34	0.34	1.26	1.69
$N\text{-}NO_3^-$	67.8	63.3	49.5	51.5	60.2	68.1	39.4	–	32.8	20.0	34.1	42.5
$N\text{-}NH_4^+$	134.7	131.3	106.8	92.9	112.1	104.8	39.5	–	36.7	21.1	39.8	41.1

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Table 4. Mean concentrations of PO_4^{3-} and Si_{diss} in sea-water and pure-water (n=34) along with SW/PW (%) ratio as a function of the categorized three day air mass back trajectories arriving at Erdemli.

	Turkey (T)	Europe (E)	Southerly (S)
PW-PO_4^{3-}	0.28	0.16	0.55
DW-PO_4^{3-}	0.16	0.13	0.26
SW/PW (%)	57	80	48
PW-Si_{diss}	2.3	2.9	6.7
DW-Si_{diss}	1.1	0.7	1.7
SW/PW (%)	48	25	25

SW/PW (%) was calculated according to concentration in sea-water divided by concentration in pure-water and multiplies with 100.

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Table 5. Summery of the nutrient settling velocities (cm s^{-1}) applied in 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)
Eliat, 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)

[1] This Study (Erdemli), [2] Markaki et al., 2003, [3] Kouvarakis et al., 2001, [4] Herut et al., 2002, [5] Chen et al., 2007, [6] Loye-Pilot et al., 2000, [7] Migon et al., 2001.

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

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Table 6. Calculated Atmospheric Dry and Wet Depositions (as mmol m^{-2} yr^{-1}).

	Dry Deposition (mmol m^{-2} yr^{-1})	Wet Deposition (mmol m^{-2} yr^{-1})	Total
P-PO_4^{-3}	0.35[a] (0.61[b])	0.34	0.69
Si_{diss}	0.52[a] (1.54[b])	0.92	1.43
N-NO_3^-	103	22	125
N-NH_4^+	15	23	38
DIN	118	45	163

[a] Dry depositions calculated from sea-water solubilities of PO_4^{3-} and Si_{diss}.
[b] Dry depositions calculated from pure-water solubilities of PO_4^{3-} and Si_{diss}.

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Table 7. 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

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Table 8. Comparison of riverine and atmospheric nutrient inputs (tons yr^{-1}) to the Northeastern Levantine Basin of the Eastern Mediterranean.

River	Si_{diss}	PO_4^{3-}	NO_3^-	NH_4^+	DIN	N/P[a]	Si/N[a]
Seyhan	17 389	917	6171	1170	7341	18	1.2
Ceyhan	20 383	269	6641	1225	7866	65	1.3
Göksu	4443	144	1162	146	1308	20	1.7
Berdan	494	29	231	91	322	25	0.8
Lamas	279	1	125	1	126	279	1.1
Total Rivers	42 988	1360	14 330	2633	16 963	28	1.3
Winter	12 927	434	4444	654	5098	26	1.3
Transition	21 412	611	7105	1303	8408	30	1.3
Summer	8484	317	2729	640	3369	24	1.3
Atmosphere	4538	2409	194 250	59 052	253 302	233	0.01
D* Winter	452	339	37 593	5752	43 345	283	0.005
D* Transition	723	449	59 371	7861	67 232	332	0.005
D* Summer	440	406	62 452	9025	71 477	390	0.003
W* Winter	1553	712	21 082	20 134	41 216	128	0.01
W* Transition	1199	443	11 853	8672	20 525	103	0.02
Total	47 526	3769	208 580	61 685	270 265	145	0.1

N/P[a] and Si/N[b] expressed as molar ratios.
D* and W* refer to Dry Deposition and Wet Deposition, respectively. Atmospheric inputs of PO_4^{3-} and Si_{diss} assessed considering their sea-water solubilities.

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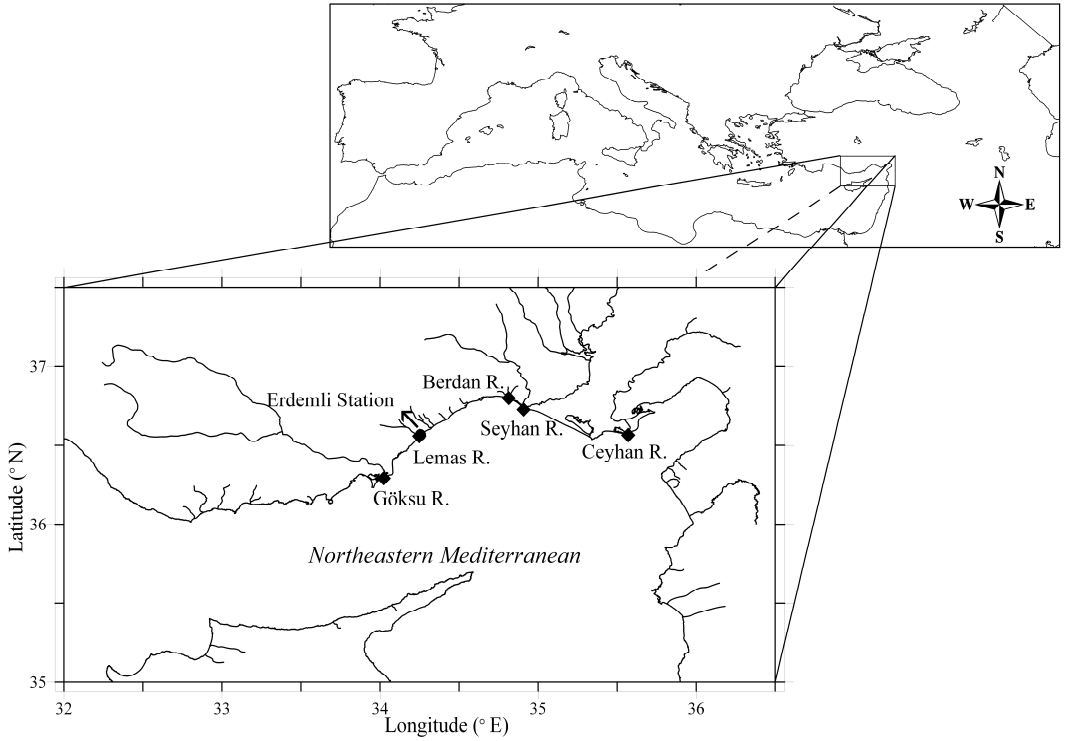

Fig. 1. Locations of atmospheric and riverine sampling sites. R refers to river.

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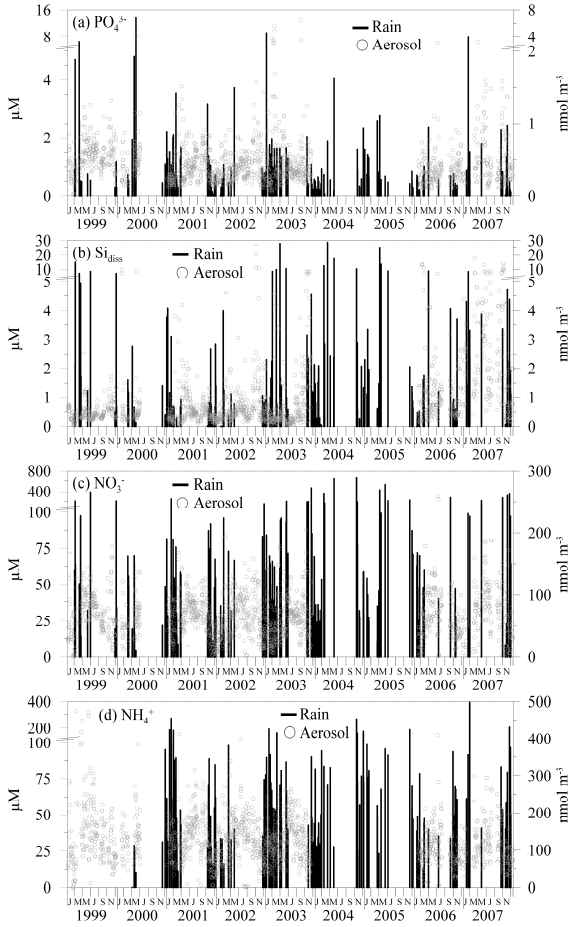

Fig. 2. Temporal variability of nutrient concentrations in aerosol (grey dots) and rain (black bars) samples collected from Erdemli site PO_4^{3-} **(a)**, Si_{diss} **(b)**, NO_3^- **(c)** and NH_4^+ **(d)**.

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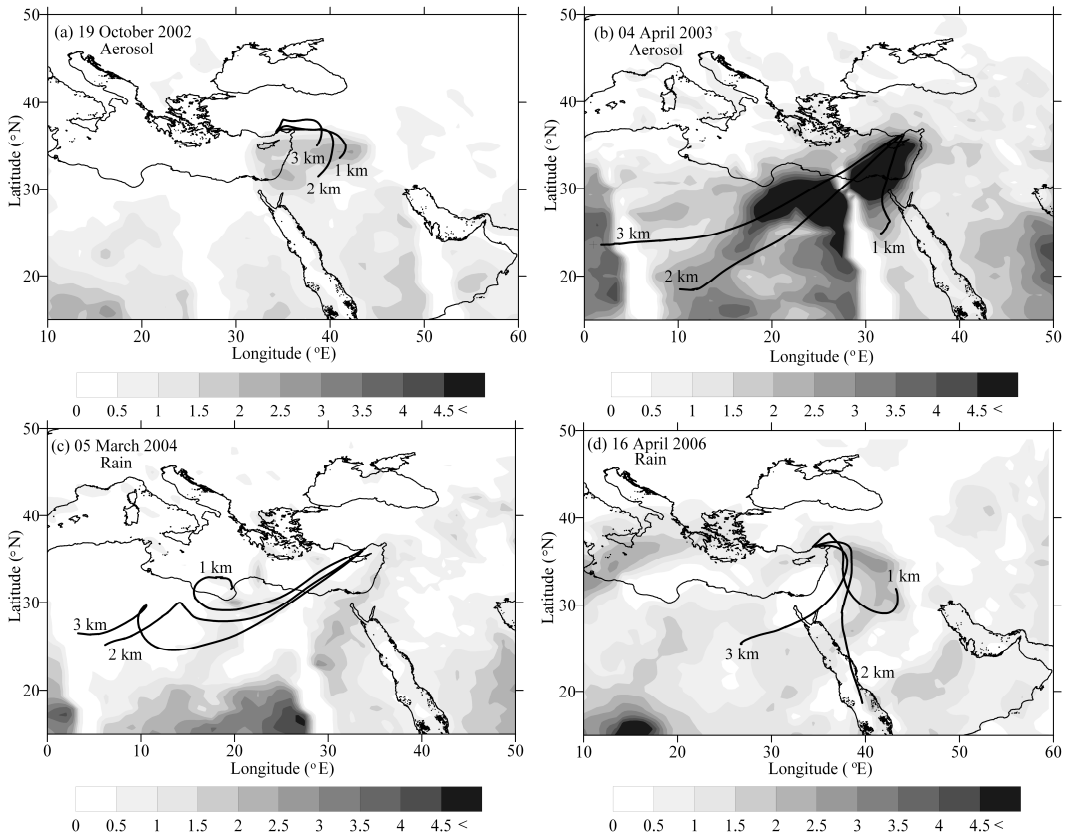

Fig. 3. Three day back trajectories for 1, 2 and 3 km altitude along with Aerosol Index on the 19 October 2002 – TOMS, **(a)**, 4 April 2003 – TOMS, **(b)**, 5 March 2004 – TOMS, **(c)** and 16 April 2006 – OMI, **(d)**.

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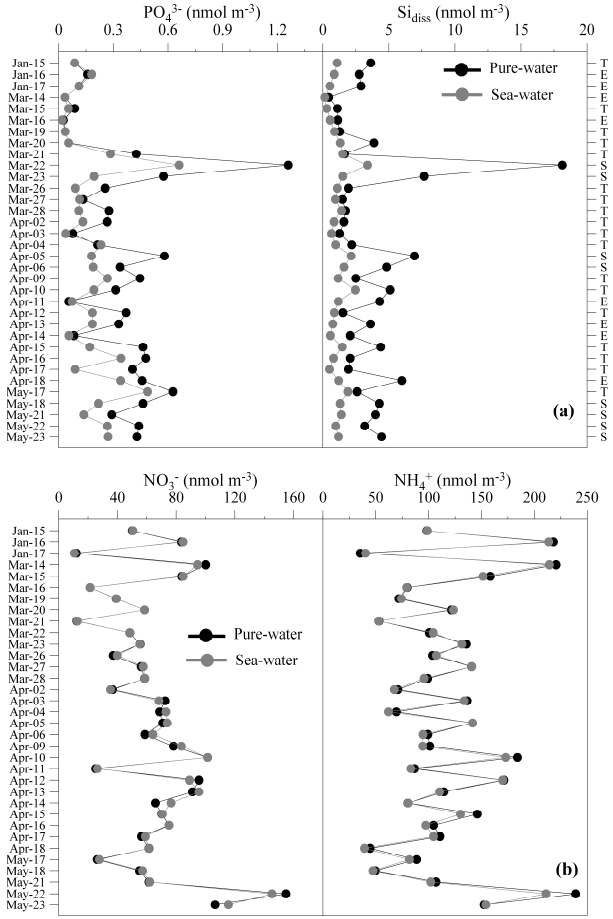

Fig. 4. Nutrient concentrations extracted by pure-water (black lines and dots) and surface Eastern Mediterranean sea-water (grey lines and dots) from aerosol samples (n=34) collected from Erdemli, PO_4^{3-} and Si_{diss} **(a)** and NO_3^- and NH_4^+ **(b)**.

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