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Long-term measurements of dissolved organic nitrogen (DON) in atmospheric deposition in the Eastern Mediterranean: Fluxes, origin and biogeochemical implications

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ABSTRACT

Atmospheric deposition of dissolved organic nitrogen (DON) was estimated in the Eastern Mediterranean by collecting and analyzing wet and dry deposition samples during a four year period (2003–2006). In wet deposition the annual volume weighted mean concentration of DON was estimated to be 23 μM and the annual mean flux was estimated to be 4.8 mmol/m^2. The average contribution of DON, NO_3^- and NH_4^+ to total dissolved nitrogen (TDN) was 22.7%, 45.7% and 31.6% respectively. On the other hand during the dry season the average annual flux of DON was estimated to be of 17.4 mmol/m^2 and those of NO_3^- and NH_4^+ were 25.3 mmol/m^2 and 2.4 mmol/m^2 respectively. The average contribution of DON, NO_3^- and NH_4^+ to TDN in dry deposition was 38.6%, 56.1% and 5.3 % respectively.

The contribution of anthropogenic emissions on DON levels was found to be of comparable importance with that of natural sources i.e. dust. Atmospheric deposition of DON was mainly governed by dry deposition as 78% of total DON is deposited through this pathway. Finally, 20–30% of the new production which could be stimulated by the atmospheric TDN deposition in the Eastern Mediterranean basin can be attributed to DON.

1. Introduction

Dissolved organic nitrogen (DON) contributes to the nitrogen budget of ecosystems and could influence atmospheric chemistry and air quality (Finlayson-Pitts and Pitts, 2000; Zhang et al., 2002). DON has long been recognized as an important component of aerosols and precipitation (Russell and Richards, 1919), however the difficulty of reliable chemical analysis and the absence of long-time series data prohibit a better understanding of its role in the biogeochemical cycle of nitrogen (N).

Organic nitrogen is incorporated in rainwater by direct dissolution of gaseous species, or by scavenging (in clouds or below clouds) of aerosols (Cornell et al., 2003; Calderon et al., 2007). The speciation of atmospheric DON is incomplete; available data indicate a variety of sources, both of natural and anthropogenic origin, such as plant degradation products (Likens et al., 1983) and biomass burning (Mukai and Ambe, 1986).

Several natural organic N-containing compounds in the atmosphere have been identified such as amino acids and peptides (Zhang and Anastasio 2003; Mace et al., 2003a,b; Matsumoto and Uematsu, 2005), urea (Cornell et al., 1998; Mace et al., 2003a) and aliphatic amines (Van Neste et al., 1987; Gorzelska et al., 1992; Gronberg et al., 1992; Angelino et al., 2001). Aromatic species such as Nitro-PAH, N-Heterocyclic compounds (Chen and Preston 2004; Tsapakis and Stefanou, 2007) and Nitro-Phenols (Schüssler and Nitschke, 2001) represent the main anthropogenic sources of DON. Additionally, peroxyacyl nitrates (PANs) (Roberts, 1990), amides (Cheng et al., 2006) and alkyl nitrates are photochemically produced in the atmosphere (Hauff et al., 1998; Chunk et al., 2002) contributing also to the anthropogenic fraction of DON. Recent studies have reported that humic like substances (HULIS), which are nitrogenous macromolecular organic compounds (Havers et al., 1998a,b; Graber and Rudich 2006) can also constitute an important fraction of organic N-containing compounds.

Despite the important role of DON in biogeochemical N cycling very few long-term studies have been performed in marine sites and especially in areas where atmospheric deposition of N can be of concern, such as the Eastern Mediterranean. Previous works have shown that Eastern Mediterranean is among the most oligotrophic ecosystems of the world (Sournia, 1973). Mediterranean seawater is also presenting an anomalous N/P molar ratio varying from 20:1 to 28:1 in the western and eastern basins respectively, which is significantly higher than the normal oceanic Redfield ratio (16:1) (Kress and Barak, 2001; Krom et al., 1991). Atmospheric deposition measurements (Herut and Krom, 1996; Kouvarakis et al., 2001; Markaki et al., 2009) as well as mass-budget calculations (Krom et al., 2004) indicate that atmospheric deposition of N can account for about

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70% of the N budget in seawater and substantially contribute to the anomalous seawater N/P ratio.

Most estimations of atmospheric N deposition to date only consider the inorganic forms of N (ammonium (NH_4^+) and nitrate (NO_3^-)), which are known to be bioavailable by the aquatic organisms. On the other hand several works pointed out that particulate or organic forms of N can be utilized by many organisms (Downing, 1997). This implies that the N/P ratio of the atmospheric deposition may be even higher than currently thought. It is clear that to obtain a more representative picture of marine ecosystem productivity both organic and inorganic forms of N should be considered.

The aim of the present study is to quantify the role of atmospheric deposition of DON in the biogeochemical nitrogen cycle at a remote site in the Eastern Mediterranean by collecting and analyzing wet and dry deposition samples during a four year period (2003–2006). Both organic and inorganic forms have been analyzed and the factors controlling their concentration levels have been examined. Finally, the possible role of organic nitrogen on new production in the Eastern Mediterranean Sea has been investigated. To our knowledge, this is the first effort to quantify the contribution of atmospheric deposition of DON in total dissolved nitrogen (TDN) deposition and seawater productivity in the Eastern Mediterranean.

2. Experimental methods

2.1. Wet and dry deposition sampling

Rainwater and dry deposition samples were collected at the Finokalia monitoring station (25°60′E, 35°24′N) close to a small village on the northern coast of Crete (Fig. 1). Details about Finokalia station can be found elsewhere (Mihalopoulos et al., 1997; Gerasopoulos et al., 2005). The island of Crete is located at a central position in the Eastern Mediterranean Basin. Measurements of aerosols and gases simultaneously performed at our sampling site and airborne, ships, land-based stations during numerous campaigns (Kouvarakis et al., 2002; Lelieveld et al., 2002; Markaki et al., 2009) show that measurements at Finokalia are representative of the background Eastern Mediterranean atmosphere. This is due both to the location of Crete island in the Eastern Mediterranean (crossroad of the main air masses and fronts influencing the area), as well as to the location of our site (upwind and far from the main cities and touristic resorts of the island).

Wet deposition samples in this study were collected on an event basis. Bulk deposition samples were collected in parallel with the wet deposition samples. The estimation of bulk deposition is based on the collection of particles on a flat surface covered by multiple layers of glass beads, which can trap larger particles and avoid resuspension. The glass beads were placed in a funnel installed 3 m above the ground (Kouvarakis et al., 2001) and exposed to the atmosphere for 1 to 2 weeks. Then the system was washed with ultrapure water (300 ml). A detailed description of the technique is provided in Kouvarakis et al. (2001).

Wet and bulk deposition samples were filtered immediately after collection, through a pre-weighed 0.45 μm cellulose filter. From this solution, three aliquots were obtained. The first was immediately used for pH determination, in the second, 50–100 μl of chloroform was added as a biocide and stored in the refrigerator at 0 °C until further analysis for NO_3^- and NH_4^+. The third aliquot, after addition of 50–100 μl chloroform, was stored in the freezer at −18 °C until analysis for TDN. All analyses have been performed within a month of collection.

2.2. Total dissolved nitrogen

Determination of TDN was performed using the Persulfate Oxidation Method (PO), in which all nitrogenous compounds are oxidized to NO_3^- under alkaline conditions at 100 °C to 110 °C. The NO_3^- generated is then reduced to nitrite (NO_2^-) by passing through a

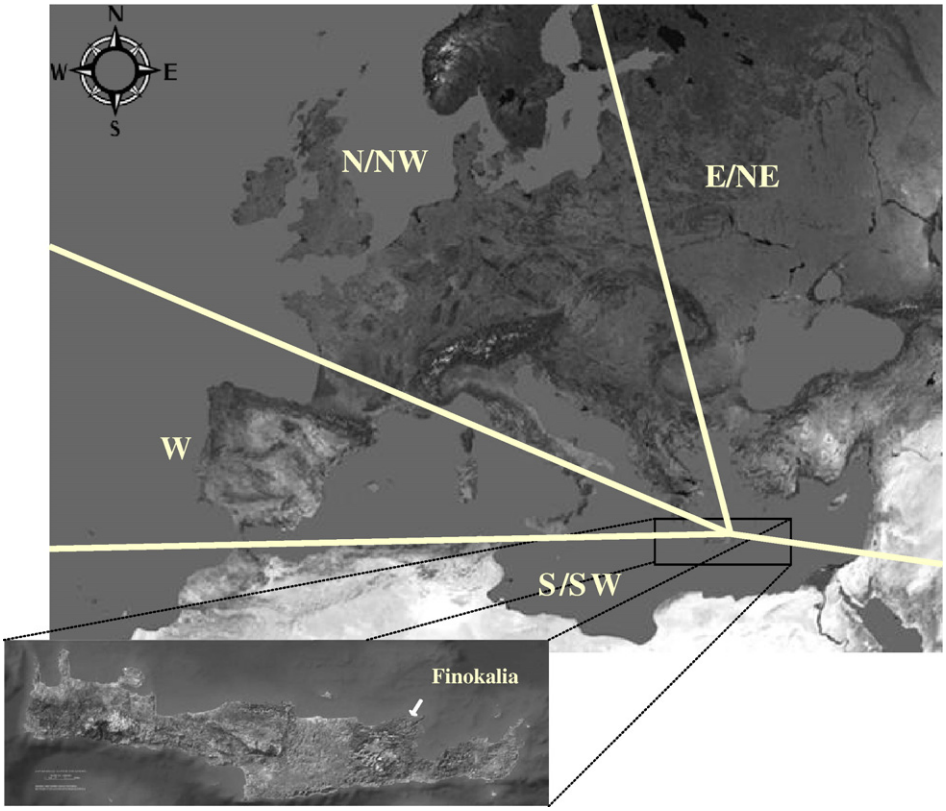

Fig. 1. Finokalia station (Crete) and representative air masses sectors.

Cu–Cd reduction column, and diazotized with sulfanilamide and N-(1-naphthyl)-ethylenediamine. The resulting azo dye and its concentration are measured by a spectrophotometer at 543 nm (Standard Methods for the Examination of Water and Wastewater, 1998).

Several modifications of the "standard" protocol were required to maximize the efficiency of the PO Method. First the reduction column is flushed with NH_4Cl–EDTA solution before and after each sample, to reduce random sample to sample error and ensure stability in the reduction column efficiency. Then, each sample is separated in three aliquots, which are sequentially passed through the column. This is due to minimize the interference of TDN from NH_4Cl–EDTA flush. The concentration of TDN is estimated as an average value of the last two aliquots as they are the last interfered by the previous sample and the NH_4Cl–EDTA solution. Finally, to minimize fluctuation in coloured azo dye from pH changes, the volume of the borate buffer solution is doubled (2 instead of 1 ml per 10 ml of sample) compared to the levels reported at the Standard Method (Standard Methods for the Examination of Water and Wastewater, 1998).

Calibration of the system was done using TDN stock solutions prepared by dissolving equal amounts (in terms of N) of analytical grade sodium nitrate (Merck#6537.0500), ammonium chloride (Merck#1.01145.1000), glutamic acid (Riedel-de Haen #27647) and urea (Sigma-Aldrich#U5128). Addition of chloroform as biocide ensures that the stock solution is stable for at least six months. Blank solutions are prepared with Milli-Q water and they are treated as the deposition samples. The average concentration of twenty blank solutions measured during the analysis period is 7.7 ± 1.1 μM N. The detection limit, estimated as three times the standard deviation (SD) of the blank, is found to be 3.2 μM N (0.045 ppm N).

To check possible matrix interferences, standard addition tests have been performed in natural rain samples. No matrix influence has been found as the slope of the calibration curves (absorption = *f*(mass of TDN)) did not change between MQ-Standards and natural rain solutions. Recovery of the added nitrogenous compounds was also found to be of the order of 105% with SD of 6%.

2.3. Dissolved inorganic and organic nitrogen

Dissolved inorganic nitrogen (DIN) is determined with ion chromatography. A Dionex AS4A-SC column with ASPS-I suppressor is used for the analysis of NO_3^-, while NH_4^+ is measured using a CS10-SC column with a CSRS-I suppressor. The reproducibility of the measurements is less than 2% and the detection limits are 0.15 μM and 0.5 μM for NO_3^- and NH_4^+, respectively. Blanks were always below the detection limits. Dissolved organic nitrogen (DON) is determined by subtracting dissolved inorganic nitrogen (DIN) from the TDN (DON = TDN − DIN). It should be kept in mind that the thus derived DON may include inorganic N that is not measured in DIN such as N_2O but given its very low levels in the atmosphere, it cannot influence our results.

3. Results and discussion

3.1. Wet deposition measurements

3.1.1. Nitrogen speciation

Samples from a total of 74 rain events were collected over four years from January 2003 to December 2006. DON concentrations ranged from below detection to 169.8 μM with an average value of 18.6 ± 26.9 μM (Median value: 9.6 μM) and volume weighted mean (VWM) of 23 μM. Fig. 2 presents the monthly VWM DON during the studied period; significant interannual and seasonal variabilities seen results from several factors. NO_3^- concentrations range from below detection to 156.7 μM with an average of 33.6 ± 29.1 μM (Median: 23.6 μM), NH_4^+ concentrations range from below detection to 72.3 μM with an average of 19.2 ± 14.6 μM (Median: 15.3 μM). DON contributes from 17% to 54.5% to the TDN pool with the highest contribution observed in June and October (54.5% and 42.3%, respectively, Fig. 3). Note however, that in June a single rain sample has been collected and the low precipitation frequency observed in June results in high DON (see discussion of Fig. 4). Concerning the inorganic pool of N, NO_3^- contributes 29 to 53% to the TDN with the highest contribution observed during May; NH_4^+ contributes 16 to 35% of TDN maximizing in March. The average contribution of DON, NO_3^- and NH_4^+ to TDN throughout the measured period is 22.7%, 45.7% and 31.6% respectively (Table 1).

DON concentrations in rainwater measured during this study are within the range of the literature reported levels observed at coastal sites (Table 2). Precisely, the VWM concentration of DON (18.6 ± 26 μM) measured at Finokalia is in good agreement to that reported by Mace et al. (2003a) for Erdemli, Turkey. In addition, the percentage contribution of DON to TDN obtained at Finokalia is within the range reported for urban and coastal areas (Cape et al., 2004; Kieber et al., 2005).

3.1.2. Fluxes of DON in wet deposition and factors controlling them

The Eastern Mediterranean is characterized by two well-distinguished meteorological seasons equally distributed within the year: The "dry" season (from May to September) and the "wet" season (from October to April). The dry season is mainly characterized by North/North-Eastern winds (originating from Central and Eastern Europe and Balkans), which from July to September correspond to 90% of the wind occurrences. During the wet season (October to April), the prevalence of N/NW sector is less pronounced, and especially in March/April and in October/November winds from the North/North-West, South/South-West (Africa) and West sectors (marine influence)

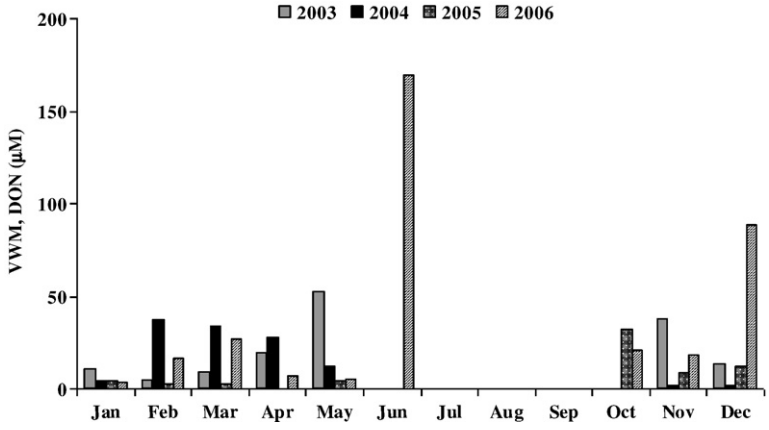

Fig. 2. Variation of VWM of DON during four years at Finokalia (Crete).

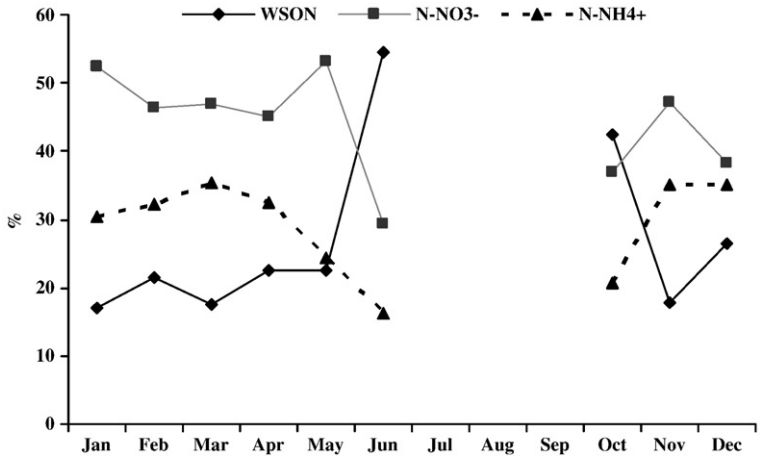

Fig. 3. Average monthly contribution of (%) nitrogen species to TDN in wet deposition during four years at Finokalia (Crete).

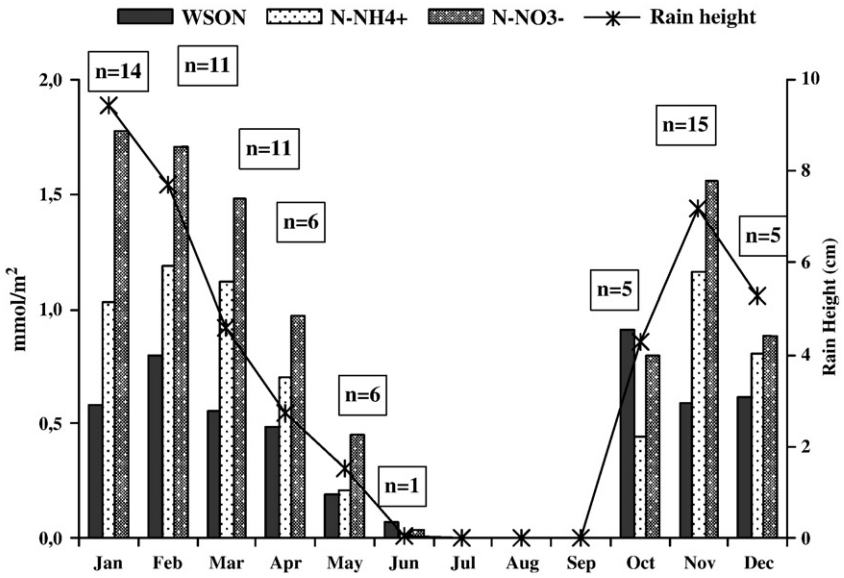

Fig. 4. Average monthly wet deposition of nitrogenous species during four years at Finokalia (Crete).

are roughly equally distributed. More details concerning the trajectories as well as their seasonality are described elsewhere (Gerasopoulos et al., 2005; Arsene et al., 2007). Comparing the annual wet deposition of nitrogen species in the whole dataset, higher deposition fluxes of all nitrogen species studied have been observed in 2003 and 2006, linked with the higher precipitation that occurred during those years. As can be seen in Fig. 4, the variation in deposition of the TDN species follows the amount of rain quite well.

Seasonality of DON deposition is depicted in Fig. 5. Seasons were defined as winter: December–February, spring: March–May, summer: June–August, and fall: September–November. Wet deposition of nitrogenous species closely follows rainfall patterns, (Fig. 5) presenting a winter maximum. Rainfall rate is not the only factor controlling DON fluxes; this is clearly seen during autumn and spring when rainfall is almost a factor of two lower compared to winter but the calculated DON fluxes are smaller by only 30%.

Pollen, spores and plant debris are abundant during spring time, which are considered as an important primary source of peptides, amino acids and other biological nitrogenous (Matthias-Maser et al., 1999). Additionally, during spring and autumn the atmosphere of Eastern Mediterranean is affected by African dust due to frequent South winds (Mihalopoulos et al., 1997). Dust is considered as an excellent adsorptive surface not only for nitrogenous compounds but also for living biological organisms (Griffin et al., 2001; Prospero et al., 2005).

To investigate the role of air mass origin on the concentration of DON in rainwater, rain samples have been classified into four classes corresponding to the winds sector of origin. Back trajectories calculated using HYSPLIT (Hybrid Single Particle Langrangian Integrated Model); 61 of the 74 rainwater samples remained within a sector for five consecutive days.

Representative back trajectories are depicted in Fig. 1. The average per event wet deposition flux within each wind sector for DON, NO_3^-

Table 1
Annual wet deposition of nitrogenous species during the studied period.

Wet deposition (mmol/m^2)					
	H (cm)	TDN	DON	N–NH_4^+	N–NO_3^-
2003	53.8	26.4	6.9	8.3	11.3
2004	37.8	14.5	2.7	5.1	6.7
2005	35.4	18.0	1.9	6.5	9.6
2006	44.2	25.5	7.7	6.8	11.0
Average		21.1	4.8	6.7	9.6
Percentage (%)			22.7	31.6	45.7

Table 2
Comparison of DON levels in rainwater measured during this work with those reported in the literature.

Location	Sampling period	DON (μM)	DON (%)	*n*	References
Rural					
Maraba (Amazonia)		22±4		6	Cornell et al. (1995)
Brazil (Recife)		3±1		11	Cornell et al. (1995)
N.England (Merlewood)	2000–2002	12	18	68	Cape et al. (2004)
E. Scotland (Bush)	2000–2002	15	33	54	Cape et al. (2004)
N.Scotland (Cairngorm)	2000–2002	2	5	30	Cape et al. (2004)
Venezuela (Calabozo)		24	76	17	Pacheco et al. (2004)
Remote					
Vermuda		16±7		18	Cornell et al. (1995)
Tahiti		13±2		16	Cornell et al. (1995)
Venezuela (Parupa)		24	92	24	Pacheco et al. (2004)
Tasman	Nov.2000	7.2±5.4	19	6	Mace et al. (2003b)
Urban					
N.England (Norwich)	2001–2002	30	24	25	Cape et al. (2004)
Venezuela (Valencia)		57	62	30	Pacheco et al. (2004)
Venezuela (Caracas)		58	61	9	Pacheco et al. (2004)
Coastal					
NE. America (Virginia)	1996–1999	3.1	6.5	83	Keene et al. (2002)
NE. America (Newark)	1997–1999	4.2	7.8	50	Keene et al. (2002)
Hawaii	1999–2000	0.4	16		Carrillo et al. (2002)
N. Carolina (Wilmington)	2002–2003	4.6±1.3	21	129	Kieber et al. (2005)
Florida (Tampa Bay)	2005	4.7±2.7	8.9±5.8	11	Calderon et al. (2007)
SW.Turkey (Erdemli)	2000(1/3–17/5)	15±31.3	17±30	18	Mace et al. (2003a)
Crete (E. Mediterranean)	2003–2006	18.6±26.9	22.7	74	This study

and NH_4^+, non-sea-salt calcium (nss-Ca^{2+}) and non-sea-salt sulfate (nss-SO_4^{2-}) is shown in Table 3. Nss-Ca^{2+} was used as an indicator of dust, whereas nss-SO_4^{2-} is used as an anthropogenic tracer. These two indicators were chosen given that DON can have both natural (Mace et al., 2003a) and anthropogenic contributions (Sandroni et al., 2007). Significant deposition fluxes of nss-Ca^{2+} are observed within SW/S sector, which are attributed to high levels of calcite ($CaCO_3$) from Sahara dust (Loÿe-Pilot et al., 1986). This result is in agreement with the observations of Mace et al. (2003a) at the Eastern Mediterranean site of Erdemli (Turkey) using rain samples from March to May 2000. High deposition values of nss-SO_4^{2-} and N-NO_3^- are associated with the NE/E sector, indicating the influence of anthropogenic emissions in agreement with the observations of Sandroni et al. (2007) in the Western Mediterranean. Comparing the average per event deposition of DON within each sector, comparable deposition fluxes are observed in NE/E and SW/S sectors. This is an indication that the influence of anthropogenic emissions on DON levels at Finokalia could be comparable to that from natural sources i.e. dust (Mace et al., 2003a; Sandroni et al., 2007).

No significant correlation has been found between wet deposition of DON and main ions with linear regression analysis performed on the whole dataset. However, significant correlation has been found between DON and nss-Ca^{2+} ($r^2=0.6$, $p<0.00005$) and DON and nss-SO_4^{2-} ($r^2=0.6$, $p<0.00005$) during spring and winter

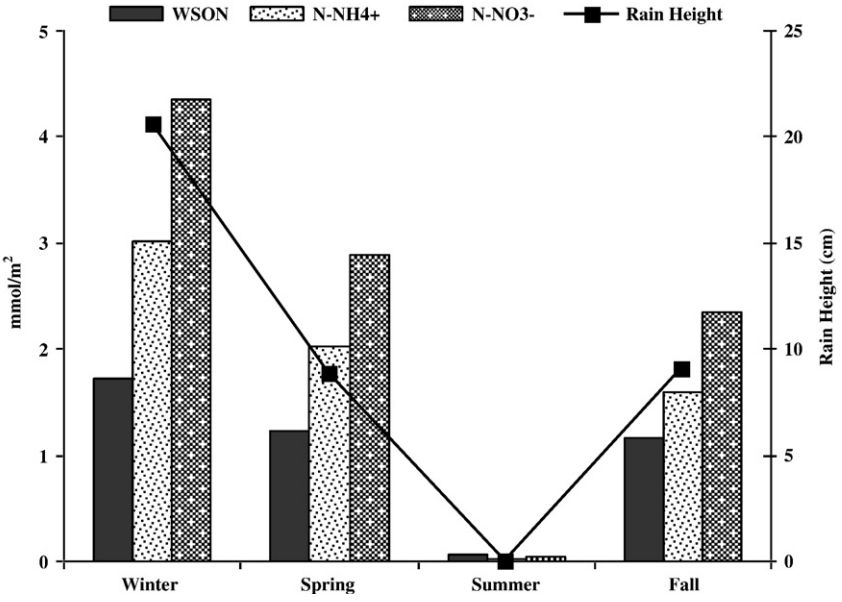

Fig. 5. Seasonal variation of nitrogenous species in wet deposition.

Table 3
Mean per event wet deposition within each sector of nitrogen species.

Per event wet deposition (μmol/m^2)						
	n	DON	N–NH_4^+	N–NO_3^-	nss-Ca^{2+}	nss-SO_4^{2-}
NW/N	23	119.1	482.4	669.4	1195.7	505.2
SW/S	26	316.1	278.7	432.9	2212.6	396.5
W	4	17.0	109.2	254.0	399.3	174.5
NE/E	8	335.0	429.1	599.3	1499.2	543.3

Table 4
Annual dry deposition of nitrogenous species.

Dry deposition (mmol/m^2)				
	TDN	DON	N–NH_4^+	N–NO_3^-
2003	37.1	15.7	1.9	19.5
2004	64.4	27.0	3.9	33.5
2005	38.0	11.4	2.2	24.4
2006	41.0	15.7	1.5	23.9
Average	45.1	17.4	2.4	25.3
Percentage (%)		38.6	5.3	56.1

respectively. As nss-Ca^{2+} and nss-SO_4^{2-} are indicators of natural (dust) and anthropogenic sources respectively, the above correlations highlight the relative importance of anthropogenic and natural sources in regulating DON levels during winter and spring respectively.

3.2. Dry deposition measurements

Besides wet, dry deposition is another pathway by which trace gases and particles are removed from the atmosphere. The factors that govern the dry deposition rate are: atmospheric turbulence, the nature of the surface and the chemical properties of the deposited compounds.

108 bulk deposition samples have been collected at Finokalia monitoring station, of which 39 are unaffected by wet deposition. In addition during the months of April, May, June and October with one or maximum two rain events, dry deposition has been calculated as the difference between bulk and wet deposition. Monthly average dry deposition fluxes of nitrogenous species are presented in Fig. 6. During the whole sampling period the average dry deposition of DON, NO_3^- and NH_4^+ is estimated to be 17.4, 25.3, and 2.4 mmol/m^2, respectively (Table 4). The average contribution of DON, NO_3^- and NH_4^+ to TDN in dry deposition is 38.6%, 56.1% and 5.3% respectively.

The dry deposition of DON measured at Finokalia is in very good agreement with the value of 14.6 mmol/m^2 reported by Sandroni et al. (2007) for the Western Mediterranean. For dry deposition of NO_3^- and NH_4^+ Sandroni et al. (2007) reported values of 25.5 mmol/m^2 and 0.4 mmol/m^2 are also in good agreement with our observations.

The dominance of NO_3^- over NH_4^+ in dry precipitation is mainly related to their association with coarse and fine particles, respectively. Indeed, fine particles are lost at a much lower deposition rate (deposition velocity $V_d = 0.075$ cm s^{-1}) than coarse ($V_d = 1.25$ cm s^{-1}) (Duce, 1991; Spokes et al., 2001). Very little is known on the size dependence of DON. To our knowledge the only work on size segregation of DON has been performed by Mace et al. (2003b) in the pristine Indian Ocean. Size segregated measurements have been performed at Finokalia using virtual impactors, separating aerosols in fine (<1.3 μm) and coarse (>1.3 μm) fractions. DON is found to exist in both coarse and fine mode with relative contributions of 49% and 51% respectively. Size segregated chemical composition measurements performed in the area (e.g. Lelieveld et al., 2002; Koulouri et al., 2008) showed that anthropogenically derived material is mainly confined in the fine fraction. Indeed the majority (greater than 85%) of sulfur, organic and elemental carbon (soot) is found in the fine fraction. On the other hand the coarse fraction is mainly composed of dust (even out of periods of Saharan dust influence). As DON exists in both fractions, we conclude that DON has both anthropogenic and natural origin. This behaviour is in-line with the conclusion derived from the rainwater samples study.

Furthermore, the double origin (natural and anthropogenic) of DON is supported when examining the periods with maximum dry deposition fluxes of DON, that are September (4.8 mmol/m^2) and August (4.2 mmol/m^2). These two months are typical cases of the contribution of both natural and anthropogenic sources on DON levels as derived from a long-term air masses climatology in the area (Mihalopoulos et al., 1997; Sciare et al., 2008). Indeed September is characterized by Sahara dust influence, while August by anthropogenic sources and biomass burning (Mihalopoulos et al., 1997; Sciare et al., 2008).

3.3. The role of DON deposition on seawater productivity

As part of DON is bioavailable, hence atmospheric deposition may influence the primary production of the euphotic zone of the Eastern Mediterranean seawater. DON bioavailability depends on a number of factors, including aerosol chemical composition, the microorganisms present, the ambient conditions and exposure time (Wedyan et al., 2007). The DON is being composed of at least two distinct "timescale" pools: a large refractory pool, which likely turns over on timescales of months to years (e.g., humic substances) and a less refractory fraction composed of e.g. amino acids and urea, that likely turns over in minutes to days (Bronk et al., 2007). A number of studies have attempted to quantify the bioavailability of organic nitrogen by collecting water samples from rivers and estuaries. Seitzinger and Sanders (1997) suggested that 40 to 72% of DON was consumed during 10 to 15 day dark bioassays, while Bronk (2002) suggested

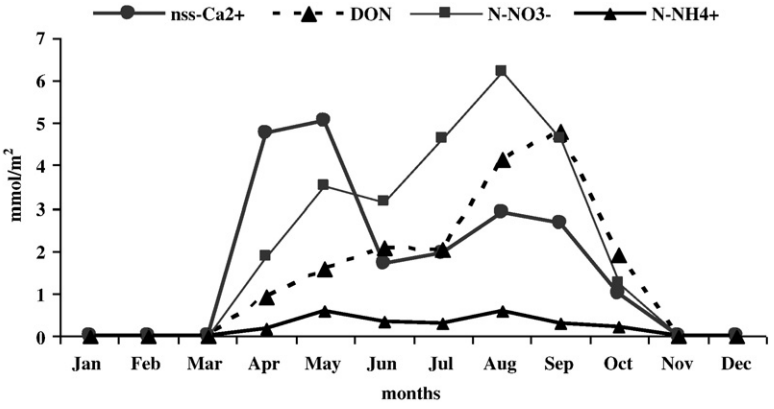

Fig. 6. Average monthly dry deposition of nitrogenous species and nss-Ca^{2+} during four years at Finokalia (Crete).

that 12 to 72% of the DON pool is bioavailable within few days to weeks. In addition, 19 to 55% of the bulk DON in two streams in Sweden was found to be bioavailable in short-term bioassays (Stepanauskas et al., 2000), while Wiegner et al. (2006) suggested that more than 40% of DON was consumed over a six-day incubation. Finally, the biological availability of DON in aerosol samples collected at the Gulf of Aqaba was found to range from 46 to 80% (Wedyan et al., 2007). Those findings indicate that DON is an important source of bioavailable nitrogen, especially for a sensitive oligotrophic ecosystem such as the Eastern Mediterranean basin.

Several important implications regarding the importance of atmospheric DON deposition in biogeochemical nitrogen cycle of the Eastern Mediterranean could arise from this study. Total deposition of DON (both wet and dry) is mainly governed by dry deposition as 78% of total DON is deposited through this pathway. Considering that during the summer, when lack of rainfall and water column stratification prevails, dry deposition path is predominant maximizing the impact of atmospheric deposition into the marine environment. The average annual DON total deposition during the four years sampling period was calculated to be 22.2 mmol m^{-2} y^{-1} (Table 5). Assuming that the bioavailability of DON ranges from 40% to 70% and converting the DON flux into carbon uptake by using the Redfield C/N ratio of 6.625, the DON is found to be responsible, on an annual basis, for the fixation of 0.06 mol C m^{-2} y^{-1} to 0.10 mol C m^{-2} y^{-1}.

The annual mean DIN deposition in the whole dataset period of 44.0 mmol m^{-2} y^{-1} supports fixation of 0.29 mol C m^{-2} y^{-1}, since it is 100% bioavailable. This value is in agreement with the 0.25 mol C m^{-2} y^{-1} reported by Kouvarakis et al. (2001) for the same region. Hence, 20–30% of the new production potentially stimulated by atmospheric deposition of TDN in the Eastern Mediterranean basin can be attributed to DON.

Krom et al. (2004) estimated that 70% of the nitrogen budget in the Eastern Mediterranean is due to atmospheric deposition of DIN. As DON can provide nitrogen in bioavailable form, atmospheric deposition of both DIN and DON can account for up to 90% of the nitrogen budget in areas far from the continental shelf; thus highlights the important role of atmospheric deposition in the biogeochemical nitrogen cycle in the Eastern Mediterranean.

4. Conclusions

Atmospheric deposition of DON has been measured in the Eastern Mediterranean during a four year period. DON is found to be a significant fraction of TDN, accounting for 23% and 38.6% of the wet and dry deposition fluxes respectively. The concentration of DON is associated strongly with the meteorological patterns encountered in the area. Furthermore, the estimated fluxes of DON depend not only on the amount of rain but also on the air mass origin since the influence of anthropogenic emissions on DON levels (E/NE winds) could be of comparable importance with the natural sources i.e. dust (SW/S winds).

Atmospheric deposition of DON was mainly governed by dry deposition as 78% of total DON is deposited through this pathway. Thus during summer when the water column stratification prevails, the impact of atmospheric deposition to the marine environment is maximized. Finally, 20–30% of the new production which could be stimulated by the atmospheric TDN deposition in the Eastern Mediterranean basin can be attributed to DON.

Table 5
Annual total deposition of nitrogenous species.

Total deposition (mmol/m^2)			
	DON	$N–NH_4^+$	$N–NO_3^-$
2003	22.5	10.2	30.8
2004	29.7	9.0	40.2
2005	13.3	8.7	34.0
2006	23.4	8.3	34.5

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