

Organic nitrogen in rain and aerosol in the eastern Mediterranean atmosphere: An association with atmospheric dust

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[1] From March through early May of 2000, rain and bulk aerosol samples were collected at a coastal site on the eastern Mediterranean Sea at Erdemli, Turkey, and analyzed for nitrogen (N) species, including nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), water-soluble organic N, urea, and dissolved free amino acids. Other ions were also analyzed, including Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , and SO_4^{2-} . Water-soluble organic N was found to contribute $\sim 17\%$ and $\sim 26\%$ of the total water-soluble N in rain and aerosols, respectively. Organic N concentrations within rain and aerosols exhibited statistically significant linear relationships to Ca^{2+} ion ($R_{\text{sqr}} \sim 0.75$, $P < 0.05$), suggesting a relationship to calcite (CaCO_3) in atmospheric dust. Kinematic trajectory analyses indicated the origin of winds from arid regions, mainly in northern Africa, in 70% of the aerosols sampled. Earth Probe/Total Ozone Mapping Spectrometer aerosol index data also confirmed the influence of atmospheric dust in the region on days when Ca^{2+} concentrations were elevated, and trajectory analyses suggested northern Africa as a source region. The combined ion, trajectory, and aerosol index data suggest that organic N is associated with atmospheric dust in this region. Urea N and amino N represented a small percentage of the organic N fraction. In rain and aerosols, urea represented $\sim 11\%$ and $< 1\%$, respectively, of the total organic N. While amino N contributed minimally to organic N totals ($\sim 1\%$ of total organic N in aerosols), the individual amino acids contributing $\sim 75\%$ of amino N were indicative of biological organisms. Further research is needed to decipher the influence from biology and gas phase adsorption of anthropogenically derived water-soluble organics on organic N totals.

INDEX TERMS: 0315 Atmospheric Composition and Structure: Biosphere/atmosphere interactions; 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; **KEYWORDS:** atmospheric dust, organic nitrogen, nitrogen cycling, Mediterranean Sea, Sahara

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1. Introduction

[2] Inputs of fixed nitrogen from atmospheric deposition can represent a significant proportion of the total N entering the Mediterranean Sea. As indicated by *Guerzoni et al.* [1999, and references therein] the atmospheric input of inorganic N represents $\sim 60\%$ of the total N entering the Mediterranean Sea from continental inputs, with wet

deposition representing $\sim 66\%$ of the total atmospheric flux. *Kouvarakis et al.* [2001] suggest that the input of inorganic N species in atmospheric deposition is enough to explain new production in the eastern Mediterranean Sea. While inorganic N species such as NO_3^- and NH_4^+ have received the most attention in atmospheric wet deposition studies, water-soluble organic N (as total N - inorganic N) has not been extensively investigated in atmospheric deposition in the Mediterranean or in other oceanic locations; although it may represent a significant proportion of the total N delivered to oceanic ecosystems via the atmosphere [*Cornell et al.*, 2001, 1995]. Additionally, the sources for the organic N fraction of atmo-

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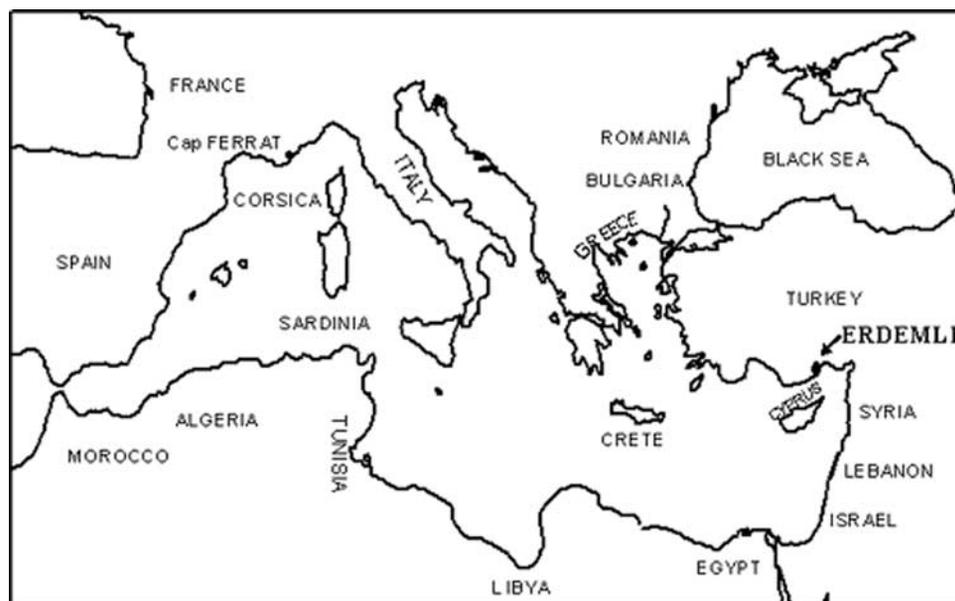


Figure 1. Map of the sampling location.

pheric N and its potential impacts on oceanic ecosystems are currently not well characterized. A few studies have analyzed individual water-soluble organic N species in the atmosphere in coastal areas [e.g., *Timperley et al.*, 1985; *Cornell et al.*, 1998; *VanNeste et al.*, 1987], and recent research suggests the bioavailability of dissolved organic N in rainwater [*Seitzinger and Sanders*, 1997; *Peierls and Paerl*, 1997]. However, very few studies have attempted to measure individual water-soluble organic N species in the context of total organic N. To add further insight regarding the sources for organic N in the global atmosphere and the species comprising the total organic N fraction, rain and bulk aerosol samples were collected from an atmospheric sampling tower located on the eastern Mediterranean Sea at Erdemli, Turkey (Figure 1), during the months of March through mid-May, 2000.

[3] As previously documented, the eastern Mediterranean Sea is capable of receiving atmospheric dust inputs from neighboring regions including the Sahara in northern Africa and the Middle East from the Arabian Peninsula and Syria [*Kubilay et al.*, 2000; *Kubilay and Saydam*, 1995]. In the eastern Mediterranean, the annual deposition of aerosol material delivered from the Sahara is estimated to be $\sim 14 \text{ g/m}^2$, a value higher than any other oceanic area affected by the Sahara except those off the western coast of Africa [*Goudie and Middleton*, 2001]. During the collection period transport from northern Africa is most likely, given the current climatology known for the region [*Kubilay et al.*, 2000, and references therein]. Since the Sahara is estimated as the world's largest source of aeolian soil dust and a large supplier of aeolian material to the oceans [*Goudie and Middleton*, 2001], the atmospheric sampling at Erdemli provided an opportunity to investigate the influence of atmospheric dust on organic N totals. Atmospheric sampling at Erdemli is also influenced by local agricultural sources and industrial pollution [*Kubilay and Saydam*, 1995]. Therefore the timing of the sampling included an opportunity to investigate the influence of mineral matter

derived from neighboring desert regions as well as the influence of local sources.

2. Sample Collection and Analysis

2.1. Sample Collection

[4] Rain and bulk aerosol samples were collected from a 21 m atmospheric sampling tower located on the Turkish Mediterranean coast at Erdemli, Turkey ($34^{\circ}15'18''\text{E}$, $36^{\circ}33'54''\text{N}$, Figure 1), during the months of March through mid-May of 2000. Rain samples were collected on an event basis using a standard wet/dry collector, transferred to pre-cleaned polyethylene sample bottles, and shipped frozen to College Station, Texas, United States, for analysis. Aerosol samples were collected using a high-volume aerosol collection system, sampling at a rate of $\sim 60 \text{ m}^3$ of air per hour, on pre-combusted (5 hours at 450°C in a muffle furnace) glass fiber filters. Collected filters containing atmospheric aerosols were stored at -20°C in pre-combusted aluminum (Al) foil, placed in separate polyethylene bags, and shipped frozen by express courier to College Station, Texas, United States, for analysis. In studies involving mineral aerosol, iron (Fe) and Al concentrations are normally determined to assess the importance of mineral matter on atmospheric samples. However, because of collection procedures involving the use of Al foil (to assure no loss of organic N during storage) and the limited amount of sample collected (i.e., small volumes of rain and only one available bulk aerosol collector) trace metal analyses for Fe and Al could not be performed on the collected samples. Blanks for rain and aerosol analysis consisted of purified water ($>17.9 \text{ M}\Omega\text{-cm}$) filtered and treated as rain samples, and pre-combusted glass fiber filters exposed to the atmosphere at the tower (i.e., no aerosol collection), respectively. Blanks are discussed in section 2.2.

2.2. Sample Analysis

[5] Upon arrival in College Station, Texas, rain and aerosol samples were analyzed for inorganic ions (NO_2^- , NO_3^- ,

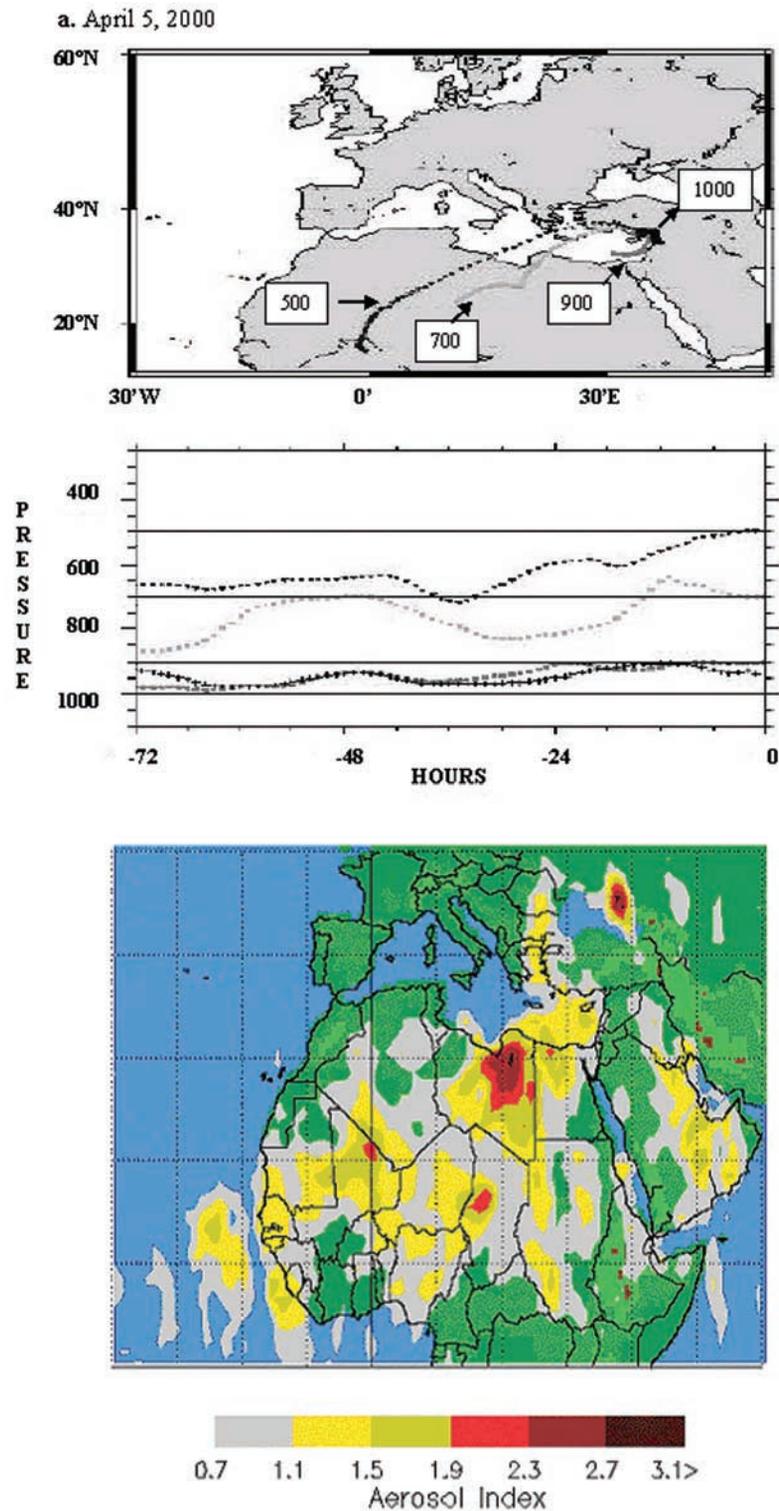


Figure 2. Kinematic trajectories and the corresponding aerosol index (courtesy of NASA/GSFC/TOMS group as described by *Torres et al.* [2002] and *Herman et al.* [1997]) for aerosol samples collected on (a) 5 April 2000 and (b) 15 April 2000. The lower panel in each trajectory diagram shows atmospheric levels for air masses arriving at 500-, 700-, 900-, and 1000-hPa in Erdemli, at the end of the 3 day trajectory period. Aerosol index plots represent the mean composite for satellite coverage on the individual dates indicated.

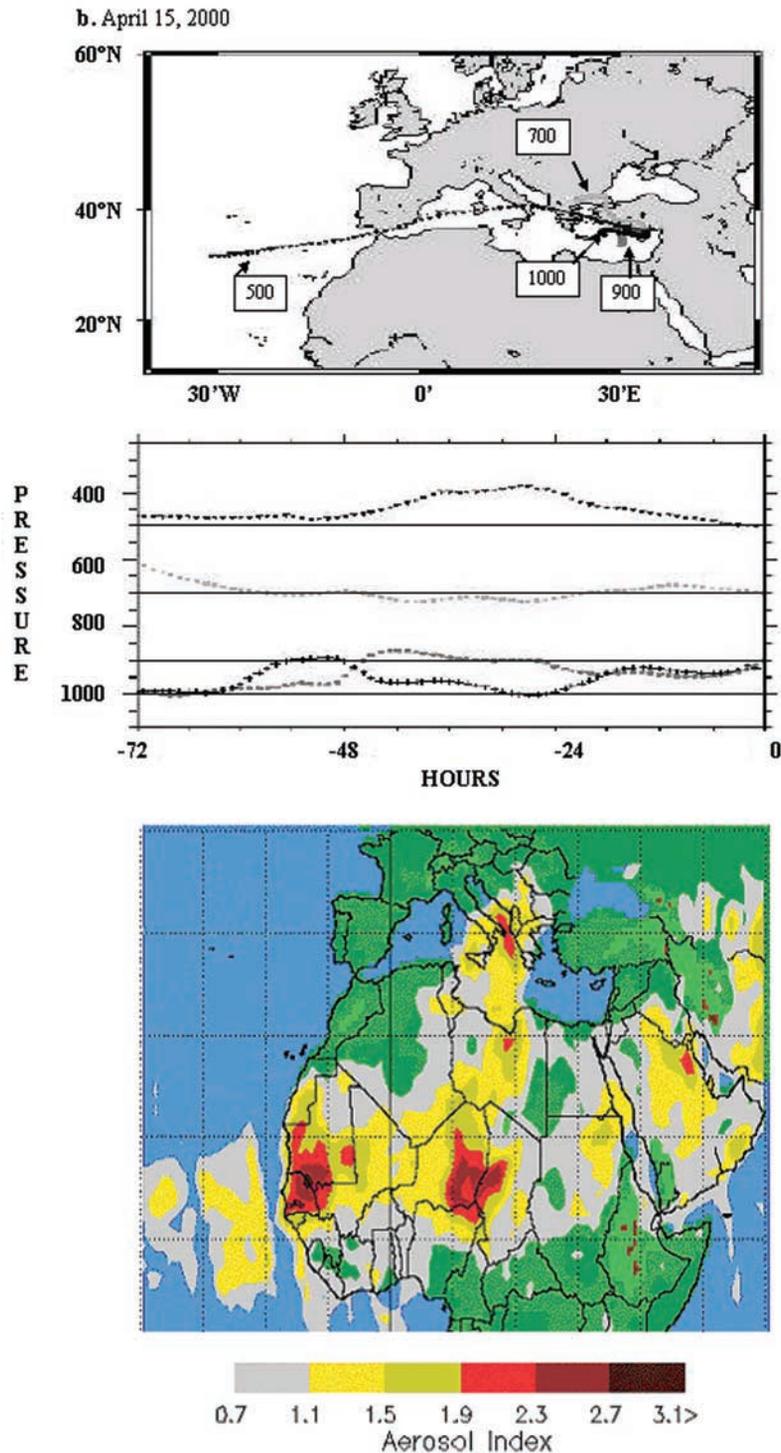


Figure 2. (continued)

NH_4^+ , Ca^{2+} , Mg^{2+} , K^+ , Na^+ , Cl^- , SO_4^{2-}), total N, urea, and 17 dissolved free amino acids - including aspartic acid, glutamic acid, serine, threonine, glycine, alanine, arginine, proline, valine, methionine, isoleucine, leucine, phenylalanine, cystine, lysine, histidine, and tyrosine. Rain samples were filtered through a $0.45\ \mu\text{m}$ Nuclepore polycarbonate filter prior to all the analytical analyses. The aerosol extracts consisted of 1/4 of a glass fiber filter extracted in $\sim 30\ \text{mL}$ of purified water, sonicated for 30 min in an ambient water bath,

and filtered through a $0.45\ \mu\text{m}$ Nuclepore polycarbonate filter.

[6] Inorganic ions were measured using a Dionex (Sunnyvale, California, United States) DX 300 ion chromatograph equipped with a Rheodyne (Cotati, California, United States) 9126 rear-loading valve and Dionex AI450 chromatography software. Cations were analyzed with a Dionex CS12A cation exchange column guarded with a CG12A guard column. A solution of methanesulfonic acid (MSA)

Table 1. Nitrogen in Erdemli Rain^a

Sample	Date	Local Time	NO ₃ ⁻ -N	NH ₄ ⁺ -N	Organic N	Urea N
1	1 March	0800–1400	28.6	38.5	b.d.	3.2
2	4 March	0300–0800	33.0	28.5	9.1	b.d. ^b
3	4 March	0800–1700	15.4	17.9	13.1	b.d.
4	18 March	0330–0800	0.3 ^c	50.6	29.6	3.9
5	19 March	1100–1630	66.9	75.3	3.0	3.8
6	19 March	2000–2400	23.2	34.0	3.2	2.0
7	23 March	0230–0830	71.6	72.5	0.04	3.4
8	23 March	0830–1600	57.5	49.9	b.d.	1.0
9	19–20 April	1730(19th)–0830(20th)	17.9	22.0	1.5	0.4
10	20 April	0830–1110	9.0	19.7	9.98	0.7
11	20 April	1110–1640	22.7	39.8	b.d.	0.7
12	20–21 April	1640(20th)–0800(21st)	18.9	43.9	11.5	b.d.
13	29 April	2000–2100	282.8	11.6	135	3.1
14	4–5 May	2030(4th)–0830(5th)	228.6	76.1	26.3	5.8
15	5 May	0830–1640	57.5	17.8	11.7	1.3
16	5–6 May	1640(5th)–0830(6th)	12.3	22.5	b.d.	b.d.
17	6 May	0830–1715	15.2	27.1	15.3	b.d.
18	17 May	1130–1300	35.9	77.0	b.d.	0.3
Average			32.4	40.3	15.0	1.6
Standard deviation			21.0	22.2	31.3	1.8
% organic N of total N			~17 ± 30			
% urea N of organic N			~11 ± 29			

^aUnits are μMN for all species.

^bValues reported as b.d. have been included in the calculation of the average as 0.

^cValue not included in calculation for average.

served as the eluent. Anions were analyzed with a Dionex AS12A anion exchange column guarded with an AG12A guard column. A solution of sodium bicarbonate and sodium carbonate served as the eluent. Both cation and anion analyses were performed according to column specifications in eluent recycle mode with an appropriate self-regenerating suppressor. The error for all the ion analyses was <6%, as indicated by 2 sets of standards cross-referenced to the National Institute of Standards and Technology (NIST), United States.

[7] For the total N analysis, filtered rain and aerosol extracts were diluted to an appropriate concentration and exposed to UV light, in a Metrohm Inc. (Switzerland) 705 UV digester, for 2 hours at a temperature of 85°C [Mace and Duce, 2002a]. Following UV exposure, samples were again analyzed for the inorganic N ions – NO₃⁻, NO₂⁻, and NH₄⁺. Organic N is defined as total water-soluble N minus inorganic N. UV blanks for rain ranged from 0–4 μM N, representing ~4% of total N. UV blanks for aerosols ranged from 0–9 μM N, representing ~2% of total N. The data presented have been corrected for blanks.

[8] Urea was analyzed using a new ion chromatography method developed in the laboratory at Texas A&M University [Mace and Duce, 2002b]. The method utilizes a Dionex CS12 cation exchange column, a CG12 guard column, an eluent consisting of 20 mM of methanesulfonic acid (MSA), and UV detection at 190 nm. A UV/Vis spectrophotometer (a part of the DX 300 ion chromatograph) provided the means for quantitative determination. For the analysis, filtered rain or aerosol extracts were injected onto the column without further preparation. A liquid urea standard purchased from Sigma (St. Louis, Missouri, United States, product 535–30) was utilized for the quantitative determination of urea within samples.

[9] Amino acids were analyzed using a modified 4-dimethylaminoazobenzene-4'-sulfonyl chloride (DABS-

Cl) method [Stocchi *et al.*, 1992]. Prior to analysis 10 mL of filtered sample were dried in a Savant speed-vac concentrator (Thermo Savant, Holbrook, New York, United States) and derivitized with DABS-Cl. A LC-DABS 15 cm \times 4.6 mm, 3 μm particle column, guarded with a LC-18-T guard column (Supelco, Bellefonte, Pennsylvania, United States), and a gradient of chromatography grade acetonitrile:methanol and a pH-neutral 25 mM potassium phosphate dibasic solution provided the means for amino acid separation. The DX 300 ion chromatograph, fitted with a Teflon switching valve and set to record absorbance at 436 nm using the UV/Vis detector, was a suitable system for this analysis. A liquid amino acid standard purchased from Sigma (product AA-S-18), containing the 17 amino acids listed above, was utilized for quantitative determinations of amino acids within samples.

2.3. Trajectory Analysis

[10] Three day kinematic (computed using the vertical velocity of the wind fields) air mass back trajectories were calculated at 4 levels of pressure ending at 1000-, 900-, 700-, and –500-hPa based on model results from the European Centre for Medium-Range Weather Forecasts (ECMWF) (Reading, England). Example trajectories arriving at Erdemli are shown in Figure 2 and will be discussed further in section 3.

2.4. Aerosol Index

[11] The aerosol index, the distribution of UV absorbing aerosol defined as the difference between the 331 and 360 nm radiances from the Earth Probe/Total Ozone Mapping Spectrometer (EP/TOMS) [Torres *et al.*, 2002; also see Herman *et al.*, 1997], was also utilized to judge the sources of the aerosols collected at Erdemli. As discussed by Torres *et al.* [2002], EP/TOMS retrieval techniques allow the separation of UV absorbing carbonaceous and mineral

Table 2. Nitrogen in Erdemli Aerosols^a

Sample	Date	Local Time	NO ₃ -N	NH ₄ ⁺ -N	Organic N	Urea N	Amino N
1	22–23 March	1040–1030	19	44	b.d.	0.12	0.36
2	23–24 March	1030–1010	13	53	b.d.	–	–
3	24–25 March	1010–0900	14	67	b.d.	b.d. ^b	0.47
4	25–26 March	0900–1323	24	80	11	–	–
5	26–27 March	1323–0910	31	62	31	b.d.	0.37
6	27–28 March	0910–0900	35	78	b.d.	–	–
7	28–29 March	0900–1111	44	109	79	0.47	–
8	29–30 March	1111–0900	5.6	123	–	b.d.	–
9	30–31 March	0900–1400	47	129	73	b.d.	0.16
10	31 March to 1 April	1400–0925	43	99	52	–	–
11	1–2 April	0925–1800	30	60	15	–	1.12
12	2–3 April	1800–0910	38	4.5	33	0.26	–
13	3–4 April	0910–0930	44	20	75	b.d.	0.39
14	4–5 April	0930–0900	60	20	116	b.d.	0.43
15	5–6 April	0900–1515	68	11	150	–	0.39
16	6–7 April	1515–0900	53	3.2	78	0.20	0.05
17	11–12 April	0900–0910	15	26	b.d.	–	0.28
18	12–13 April	0910–0900	28	46	b.d.	0.21	–
19	13–14 April	0900–0900	26	20	22	–	–
20	14–15 April	0900–1415	31	2.0	27	b.d.	–
21	15–16 April	1450–1700	42	56	b.d.	b.d.	0.41
22	16–17 April	1700–0940	83	39	150	–	–
23	17–18 April	0940–0940	30	19	20	0.13	–
24	18–19 April	0940–1330	28	37	6.1	–	–
25	19–20 April	1330–0830	42	2.9	35	0.14	0.06
26	20–21 April	0830–0910	112	1.3	–	–	–
27	22–23 April	0900–0920	21	1.5	16	b.d.	–
28	23–24 April	0920–0900	23	5.4	23	–	–
29	24–25 April	0900–0900	33	58	b.d.	b.d.	–
30	25–26 April	0900–0910	23	33	b.d.	–	–
31	26–27 April	0910–0900	26	70	b.d.	0.27	–
32	27–28 April	0900–0910	31	115	9.4	–	–
33	28–29 April	0908–1200	32	26	8.7	–	0.79
34	29–30 April	1200–0900	27	6.3	55	–	0.04
35	30 April to 1 May	0900–0830	22	23	b.d.	0.25	0.30
36	1–2 May	0830–1000	34	80	b.d.	–	–
37	2–3 May	1000–0900	43	103	b.d.	0.19	0.31
38	3–4 May	0900–0900	37	86	b.d.	–	–
39	4–5 May	0900–0900	37	77	b.d.	–	–
Average			36	49	29	0.11	0.37
Standard deviation			20	38	42	0.13	0.27
% organic N of total N			~26 ± 28				
% urea N of total N			~0.4 ± 0.3				
% amino N of total N			~1 ± 3				

^aUnits are nmol N/m³ for all species. Dashes represent no analysis for samples.

^bValues reported as b.d. have been included in the calculation of the average as 0.

aerosols from non-absorbing sulfate and sea-salt particles. Example aerosol index plots for the region are presented in Figure 2 and will be discussed in section 3.

3. Results and Discussion

3.1. Organic Nitrogen in Rain and Aerosol

[12] Rain samples contained a mean organic N concentration of 15 μM N, representing ~17% of total N (Table 1). Aerosol samples contained a mean organic N concentration of 29 nmol N/m³, representing ~26% of total N (Table 2). Concentrations of organic N within both rain and aerosols were highly correlated with Ca²⁺ ion (R_{sqr} of ~0.75 and $P < 0.05$ for both rain and aerosols) (Table 3 and Figures 3 and 4). In both rain and aerosol samples the linear correlation for organic N with Ca²⁺ was higher than for any other ion (Table 3 and Figures 3 and 4). As outlined by *Loyé-Pilot et al.* [1986] high concentrations of Ca²⁺ in rain in the Mediterranean atmosphere can be attributed to the high concentration of calcite (CaCO₃) in Saharan dust. High concentrations of

organic N within our samples and its association with Ca²⁺ suggest that organic N is associated with atmospheric dust.

[13] Since statistically significant linear relationships were also found between organic N and other ions, the non-sea salt (NSS) components of K⁺, Na⁺, Ca²⁺, Mg²⁺ concentrations were calculated, using the standard procedure [*Arimoto et al.*, 1996, and references therein] to further investigate the potential influence of atmospheric dust on organic N totals. Non-sea salt (NSS) concentrations were calculated as follows:

$$[X]_{\text{NSS}} = [X]_{\text{total}} - \{ [Na^+]_{\text{seasalt}} * ([X]_{\text{seawater}} / [Na^+]_{\text{seawater}}) \}$$

where

[X]_{total} total [X] ion concentration;
[X]_{seawater} [X] ion concentration in seawater;
[Na⁺]_{seawater} [Na⁺] ion concentration in seawater;
[Na⁺]_{seasalt} seasalt [Na⁺] ion concentration (obtained by multiplying the total Cl⁻ concentration within aerosols and the ratio of Na⁺/Cl⁻ in seawater).

NSS results for aerosols are presented in Figure 4.

Table 3. Results of the Linear Regression Analysis^a

Species	Organic N (N = 18)	Urea N (N = 18)	Amino N	Ca ²⁺ (N = 18)
Rain				
Na ⁺	R _{sqr} = 0.04/P > 0.05	R_{sqr} = 0.54/P < 0.05	–	R _{sqr} = 0.20/P > 0.05
K ⁺	R_{sqr} = 0.25/P < 0.05	R_{sqr} = 0.52/P < 0.05	–	R_{sqr} = 0.45/P < 0.05
Mg ²⁺	R _{sqr} = 0.07/P > 0.05	R_{sqr} = 0.57/P < 0.05	–	R_{sqr} = 0.35/P < 0.05
Ca ²⁺	R_{sqr} = 0.72/P < 0.05	R _{sqr} = 0.20/P > 0.05	–	–
Cl [–]	R _{sqr} = 0.03/P > 0.05	R_{sqr} = 0.57/P < 0.05	–	R _{sqr} = 0.03/P > 0.05
SO ₄ ^{2–}	R_{sqr} = 0.57/P < 0.05	R_{sqr} = 0.37/P < 0.05	–	R _{sqr} = 0.15/P > 0.05
NO ₃ [–]	R_{sqr} = 0.59/P < 0.05	R_{sqr} = 0.35/P < 0.05	–	R_{sqr} = 0.66/P < 0.05
NH ₄ ⁺	R _{sqr} = 0.09/P > 0.05	R_{sqr} = 0.27/P < 0.05	–	R _{sqr} = 0.07/P > 0.05
Organic N	–	R _{sqr} = 0.09/P > 0.05	–	–
	Organic N (N = 38)	Urea N (N = 21)	Amino N (N = 16)	Ca ²⁺ (N = 41)
Aerosol				
Na ⁺	R_{sqr} = 0.16/P < 0.05	R _{sqr} = 0.05/P > 0.05	R _{sqr} = 0.07/P > 0.05	R_{sqr} = 0.20/P < 0.05
K ⁺	R_{sqr} = 0.29/P < 0.05	R _{sqr} = 0.02/P > 0.05	R _{sqr} = 0.01/P > 0.05	R_{sqr} = 0.41/P < 0.05
Mg ²⁺	R_{sqr} = 0.24/P < 0.05	R _{sqr} = 0.03/P > 0.05	R _{sqr} = 0.03/P > 0.05	R_{sqr} = 0.31/P < 0.05
Ca ²⁺	R_{sqr} = 0.75/P < 0.05	R _{sqr} = 0.02/P > 0.05	R _{sqr} = 0.06/P > 0.05	–
Cl [–]	R _{sqr} = <0.001/R > 0.05	R _{sqr} = 0.07/P > 0.05	R _{sqr} = 0.07/P > 0.05	R _{sqr} = 0.02/P > 0.05
SO ₄ ^{2–}	R _{sqr} = 0.05/P > 0.05	R _{sqr} = 0.02/P > 0.05	R _{sqr} = 0.12/P > 0.05	R_{sqr} = 0.13/P < 0.05
NO ₃ [–]	R_{sqr} = 0.69/P < 0.05	R _{sqr} = 0.02/P > 0.05	R _{sqr} = 0.03/P > 0.05	R_{sqr} = 0.36/P < 0.05
NH ₄ ⁺	R _{sqr} = 0.04/P > 0.05	R _{sqr} = 0.004/P > 0.05	R _{sqr} = 0.03/P > 0.05	R _{sqr} = 0.07/P > 0.05
Organic N	–	R _{sqr} = <0.001/P > 0.05	R _{sqr} = 0.04/P > 0.05	–
Urea N	–	–	R _{sqr} = 0.27/P > 0.05	–

^aR_{sqr} is the correlation coefficient. P is the level of significance at a level of $\alpha = 0.05$. Statistically significant correlations are shown in bold print. Dashes represent no analyses for species or comparisons that are not relevant.

[14] As seen in Figure 4, NSS Ca²⁺ concentrations are closely correlated with organic N concentrations. In several instances, NSS Na⁺, K⁺, Mg²⁺ are also elevated when organic N was elevated, although the correlations are not as pronounced as those for NSS Ca²⁺ (Figure 4). For African dust, concentrations of K⁺ and Mg²⁺ can be linked to the presence of illite (containing K⁺) and smectite, palygorskite, and dolomite (containing Mg²⁺) [Avila *et al.*, 1998]. Also, Saharan dust has been documented to contain sodium oxides (e.g., Na₂O) [Goudie and Middleton, 2001]. Thus elevated NSS base cation concentrations can be indicative of a Saharan dust source.

[15] As seen in Figure 4, one of the highest concentrations of organic N in aerosol samples, the sample from 5 April 2000 coincided with peaks in the enrichment of NSS Ca²⁺ as well as elevated NO₃[–] concentrations. The kinematic air mass back trajectory plot for this sample is shown in Figure 2a. Also shown in Figure 2a is the aerosol index. As seen in Figure 2a, the sample from 5 April 2000 was influenced by air masses originating in northern Africa, Syria, and along the coast of Israel. The air masses for this sample also originated or passed over regions where the aerosol index was elevated.

[16] Individual kinematic trajectory plots as well as plots for the aerosol index were examined in further detail for each collected aerosol sample. Since each individual trajectory plot and aerosol index plot cannot be shown for all of the aerosol samples collected, the following discussion is utilized as an example regarding the process that was undertaken to glean information regarding organic N. In Figure 2b, the kinematic trajectories and the aerosol index plots for the aerosol sample collected on 15 April 2000 are presented. The sample from 15 April 2000 was not affected locally by washout from rain, see Table 1, causing less interference when interpreting aerosol ion concentrations. As indicated by Figure 2b, the aerosol sample from 15 April 2000 was not influenced by northern Africa (no North

African trajectory). This sample was also not influenced at the ground level by UV absorbing aerosols (i.e., the 500 mb trajectory passed over a UV absorbing region but it did not influence the ground level collection of aerosols); and this sample did not contain elevated concentrations of organic N, Ca²⁺, K⁺, Mg²⁺, and Na⁺ (as seen in Figure 4).

[17] Approximately 70% of the aerosol samples analyzed were influenced by desert regions surrounding Turkey, mostly in northern Africa. Aerosol samples collected from 22–27 March, 15 and 23–25 April, and 1 May 2000 were not influenced by desert regions. Samples from these days were found to have a low aerosol index for areas surrounding Erdemli in the Mediterranean Sea. These samples also contained low concentrations of organic N and generally low concentrations of major ions (Figure 4). Concentrations for urea and amino acids did not follow patterns similar to organic N on non-dust days. Potential sources and cycling for urea and amino acids are discussed in the following paragraphs.

[18] The scavenging ratio (S), a calculation for the removal of particles or gases during wet precipitation, is defined as follows:

$$S(\text{dimensionless}) = \frac{C_r \rho}{C_a}$$

where for this study, C_r is the concentration in rain in $\mu\text{mol N/kg}$, C_a is the concentration in air in $\mu\text{mol N/m}^3$, and ρ is the density of air at 20°C and 1013 hPa, 1.2 kg/m³.

[19] The scavenging ratio was calculated for samples when both rain and aerosol data from Erdemli were available. For multiple rain events in a single day, the average concentrations of organic N were utilized. Finally, the mean for both rain and aerosols was utilized to calculate a scavenging ratio. The mean scavenging ratio calculated for organic N using this procedure was $S = \sim 1100$ (~ 600 if the average concentrations for rain and aerosol organic N in Tables 1 and 2 are utilized). Values for the scavenging ratio in the range of 200–

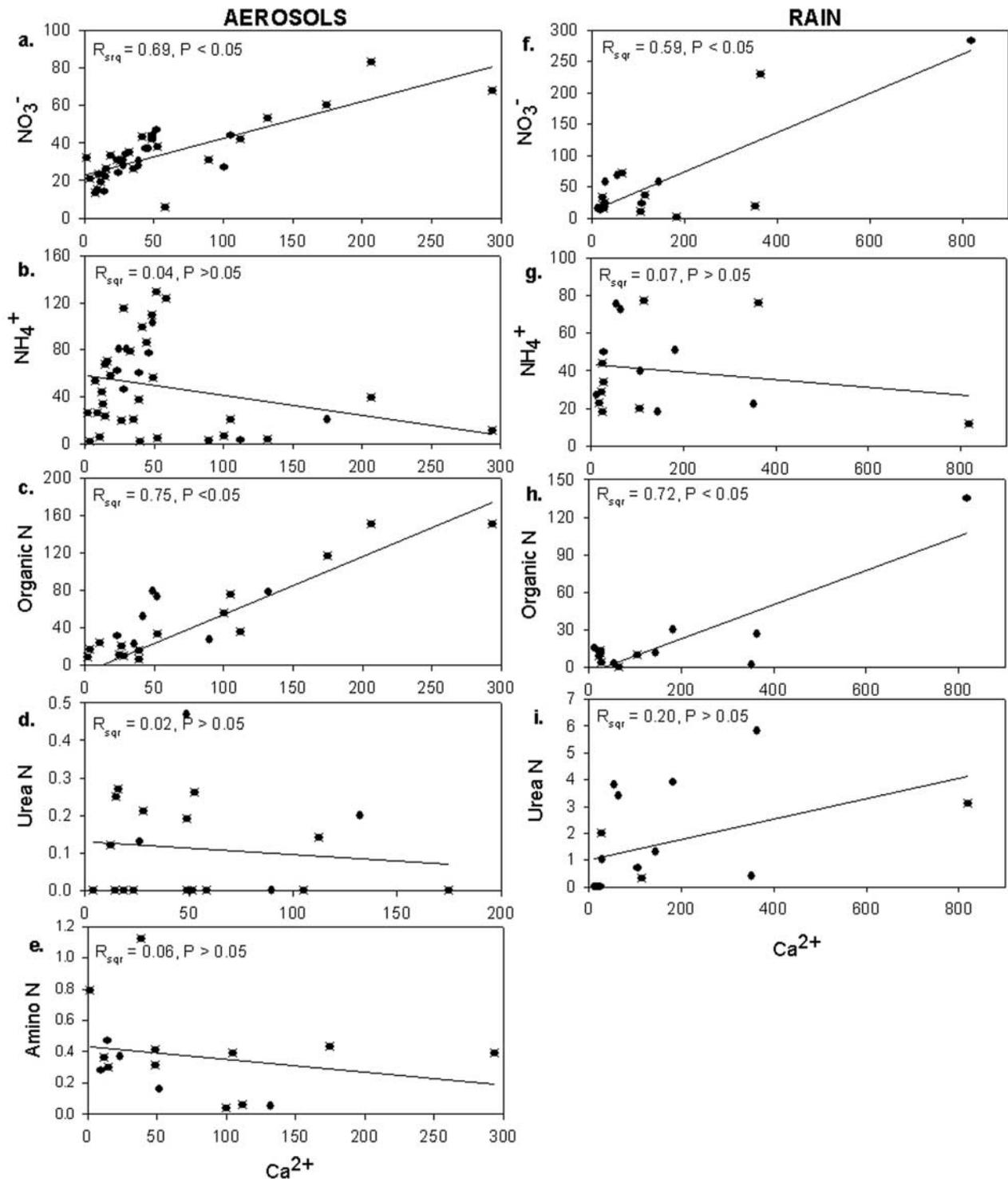


Figure 3. Linear regression results for N species in (a–e) aerosols and (f–i) rain in relation to Ca^{2+} concentrations. Units are nmol N/m^3 for all N species within aerosols (in Figures 3a–3e), and μMN for all N species in rain (in Figures 3f–3i). Ca^{2+} ion concentrations are given as $\text{nmol Ca}^{2+}/\text{m}^3$.

2000 are typical for the scavenging of atmospheric mineral matter or other particles [Duce *et al.*, 1991].

[20] The combined ion, trajectory, and aerosol index data presented above suggest an association between dust and organic N. However, the nature of this association can not be determined with the data set presented. Since organic N and base cations are found in soils, the organic N contained

within rain and aerosols collected at Erdemli may result from the uplift and transport of dust from arid regions. However, organic N may also be the result of gas-phase adsorption of organics onto dust particles. Such a phenomenon has previously been suggested by Dentener *et al.* [1996], who noted that N and sulfur gases (e.g., SO_2 and N_2O_5) react with mineral aerosols thereby increasing the

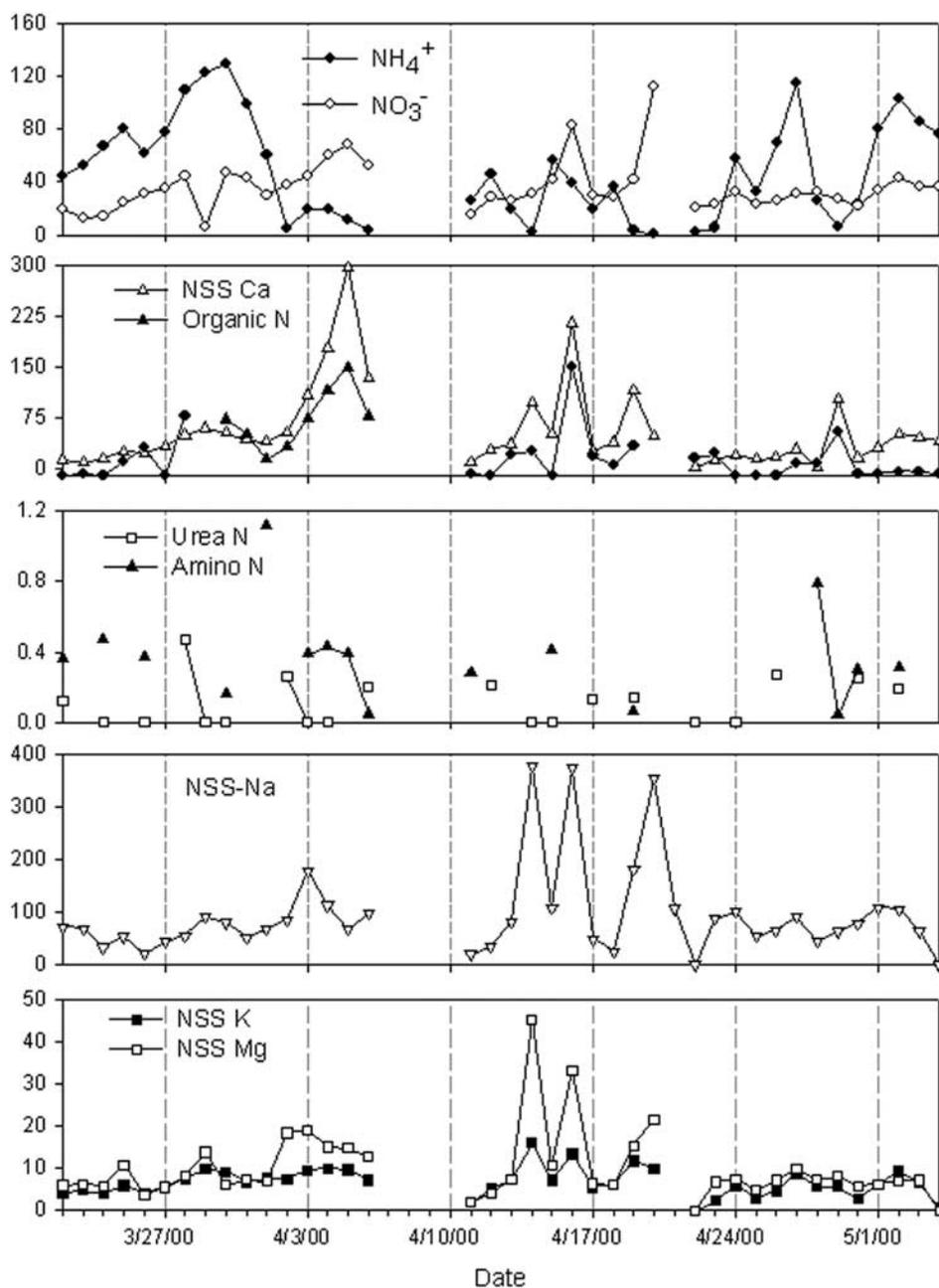


Figure 4. NSS (non-sea salt) ion, organic N, and urea N concentrations for aerosol samples. Units are nmol N/m^3 for NH_4^+ , NO_3^- , organic N, urea N, and amino N. Units are nmol ion/m^3 for Ca^{2+} , Mg^{2+} , K^+ , and Na^+ .

concentrations of SO_4^{2-} and NO_3^- in atmospheric dust samples. Future study where size-separated aerosols are collected for organic N analysis and where N isotopes are utilized will help answer questions regarding sources for organic N in the eastern Mediterranean atmosphere.

3.2. Urea Nitrogen in Rain and Aerosol

[21] Urea was present in 13 of 18 rain samples analyzed (a mean of $1.6 \mu\text{M N}$ as urea) and was found to contribute $\sim 11\%$ of the organic N fraction (Table 1). The remainder of the organic N in rain, $\sim 98\%$, was uncharacterized (since amino N analysis could not be performed on rain samples because of

volume limitations). In aerosols, urea N represented $\sim 0.4\%$ of organic N at a mean concentration of 0.11 nmol N/m^3 .

[22] As seen in Table 3 and Figure 3, urea exhibited statistically significant relationships to Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , NO_3^- , and NH_4^+ ion concentrations in rain, but not with Ca^{2+} or organic N. No statistically significant relationships were found for urea N or amino N within aerosols (Table 3). The association of urea N with other ions in rain and the lack of statistically significant relationships for urea N within aerosols suggests complex sources and/or cycling for urea and amino N within the eastern Mediterranean atmosphere.

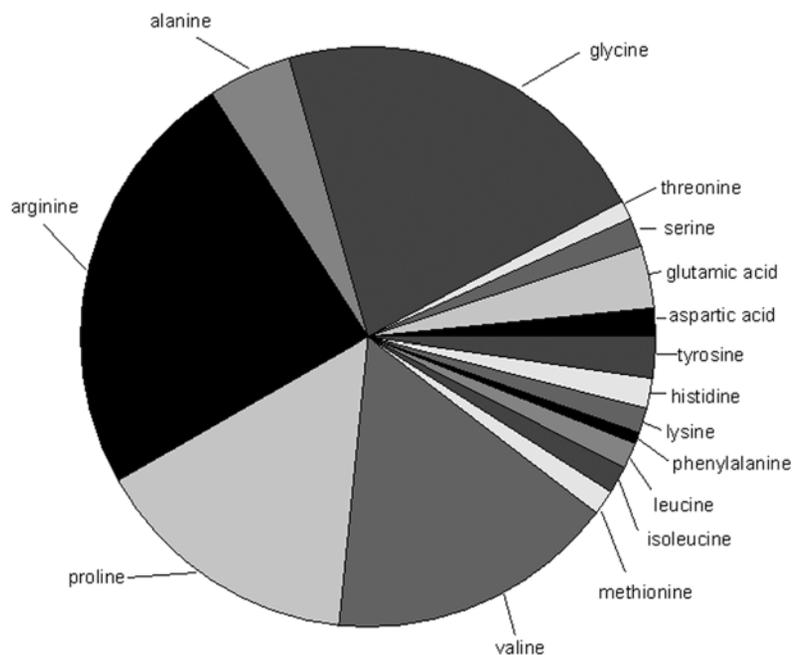


Figure 5. Mean percent contributions of individual amino acids contributing to amino N totals. All amino acids are presented as the percentage of N from individual amino acids.

[23] A mean scavenging ratio of $\sim 1.4 \times 10^4$ ($\sim 1.7 \times 10^4$ if averages in Tables 1 and 2 are utilized) was obtained for urea in rain. These values suggest the scavenging of gas phase urea and/or the formation or production of urea within rain samples. As mentioned above, urea concentrations exhibited statistically significant relationships to other ions within rain samples. Similar relationships were not found for urea within aerosol extracts. However, urea was only detected in 10 of the 20 aerosol samples analyzed. Therefore any significant relationships between urea N and other ions in the aerosols may have been lost because of analytical limitations or to post-depositional changes of urea. The association of urea with Na^+ and Cl^- ion concentrations (Table 3) in rain possibly indicates an association with atmospheric sea salt, as previously suggested [Mace *et al.*, 2003]. The correlation of urea with NH_4^+ could either be due to a dust/soil influence [Goudie and Middleton, 2001] or to the degradation of organic N compounds. The other ion correlations presented in Table 3 may result from an association with atmospheric dust. In order to determine the nature and sources for urea N, additional sampling, including bulk and size-separated aerosols, as well as bacterial numbers or production rates within rain samples will be needed.

3.3. Amino Nitrogen in Aerosol

[24] The average amino N concentration in aerosols was 0.37 nmol N/m^3 – representing $\sim 1\%$ of the total organic N (Table 2). The individual dissolved free amino acids contributing the largest percentages to amino N totals in aerosols were glycine, arginine, proline, and valine (Figure 5). (Volume limitations precluded the analysis of amino acids in rain.) These 4 amino acids contributed $\sim 75\%$ of the total amino N. As previously documented [Glavin *et al.*, 2001, and references therein; Nagata *et al.*, 2001], increased concentrations of glycine, proline, and valine can often be associated with a bacterial or a biological influence since primitive organisms,

such as bacteria, contain these amino acids in high concentration (e.g., in *E. coli* 6 amino acids, aspartic acid, glutamic acid, serine, glycine, alanine, and valine, represent $\sim 70\%$ of the total amino N). Arginine, an amino acid containing 4 N atoms, is produced by organisms during the urea cycle [Salway, 1999]. The concentration of N in individual amino acids possibly suggests that primitive biological organisms are a source of the amino acids detected in aerosol samples.

[25] The presence of bacteria and fungi has previously been reported for African dust events [Griffin *et al.*, 2001] further supporting the suggestion that living biological organisms contributed to the amino N fraction. Given the apparent persistence of microorganisms in desert dust, it is also likely that un-hydrolyzed amino acids exist in aerosol samples influenced by arid regions.

[26] However, amino N was also found to be present on non-dust days. For example, aerosol samples from 22, 24, and 26 March and 15 April 2000 (Figure 4) also contained amino N, although they were found not to be highly impacted by dust derived from arid regions (based on kinematic trajectory and aerosol index data). Only dissolved free amino acids were measured in the aerosol samples collected. In future work aimed at understanding organic N within aerosol samples, the measurement of both hydrolyzed and un-hydrolyzed (combined) amino acids should be measured. By examining the contribution of total amino acid N in aerosols it will be possible to better understand the influence of primitive organisms and local or long-range sources on the organic N fraction.

4. Conclusion

[27] Rain and aerosols collected from an atmospheric sampling tower located on the eastern Mediterranean Sea at Erdemli, Turkey, were analyzed for water-soluble organic N, amino N, and urea N as well as cations and anions.

Statistically significant linear relationships were found for total organic N and several ion species. Calcium ion exhibited the strongest relationship to the organic N fraction, likely because of the high concentration of calcite in desert dust, since trajectory analyses and aerosol index data revealed the persistent influence of mineral material derived from northern Africa (with minor contributions of mineral material from the Arabian Peninsula and Syria).

[28] While urea and amino N represented a small percentage of the total organic N in rain (urea ~11% of organic N) and aerosols (urea <1% of organic N, and amino acids ~1% of organic N), they exhibited interesting profiles. Urea N, as for total organic N, was correlated to several ion species in rain. Urea was not statistically correlated to other ions within aerosols. The association and non-association for these ions in rain and aerosols, respectively, suggest complex sources and cycling for urea, not understood to date.

[29] The individual amino acids contributing ~75% of the total amino N suggest the presence of primitive organisms in the aerosol samples analyzed. Since bacteria and fungi are thought to be associated with African dust [Griffin *et al.*, 2001], and since an atmosphere dominated by desert sources persisted during the sampling campaign, it is likely that individual amino acid totals within aerosol samples at Erdemli were influenced by these organisms. However, only dissolved free amino acids were analyzed in this study. To understand the full contribution of biological organisms to the total organic N fraction in this area, un-hydrolyzed (combined) amino acids should be analyzed in aerosols influenced by atmospheric dust. Given the significance of atmospheric N deposition on the eastern Mediterranean Sea it is also necessary to quantify the influence of atmospherically derived organisms and their organic molecules on nutrient totals.

[30] Furthermore, there is a need to investigate the adsorption of gas phase organic N compounds onto dust particles. A particle size-separated aerosol study along with measurements for associated soil derived elements (e.g., Al, Fe), and/or isotopic measurements could add insights regarding the findings in this study for elevated organic N concentrations in atmospheres containing large quantities of atmospheric dust. Such a study would help us to better understand whether the majority of the organic N associated with atmospheric dust is natural or anthropogenic in origin. Until future research is conducted the relationship between organic N and atmospheric dust in the eastern Mediterranean will remain unclear.

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