

Comparison between pure-water- and seawater-soluble nutrient concentrations of aerosols from the Gulf of Aqaba

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Abstract

Seawater-soluble nutrient fractions of aerosols better represent the contribution of aerosol dry deposition to the nutrient load from this source to the ocean than any estimates based on aerosol nutrients leached in pure water or acidic solutions. To understand the solubility difference between seawater and pure water, 31 pairs of aerosol samples collected from the Gulf of Aqaba were extracted in Sargasso seawater and pure water under consistent experimental conditions and procedures. Major inorganic N species (NO_3^- and NH_4^+) in the aerosols show similar solubilities in Sargasso seawater (average 44 and 23 nmol m^{-3}) and pure water (average 41 and 23 nmol m^{-3}). Seawater-soluble PO_4^{3-} concentrations (average 0.4 nmol m^{-3}) are slightly lower than the purewater concentrations (average 0.5 nmol m^{-3}). Total soluble N and P, which include dissolved organic compounds, extracted from the aerosols into the seawater (average 65 and 0.4 nmol m^{-3}) are significantly lower than those extracted by pure water (average 75 and 0.7 nmol m^{-3}). It was found that the dissolution of crustal-dominated trace metals (e.g. Fe and Al) strongly decrease in the seawater compared to that in pure water, while similar amounts of aerosol Zn are leached in both seawater and pure water. The percentage solubilities of non-crustal trace metals (Cu, Ni and Zn) are about one or two orders of magnitude higher than those of Fe and Al in the seawater. Our comparison experiments suggest that some previous reports may have overestimated the dry deposition inputs of aerosol P, Fe, Al, Cu, and Ni to the ocean as a result of the use of solubility estimates obtained from pure water extractions. The estimated dry deposition fluxes of soluble nutrients showed that the atmospheric nutrient input could increase the possibility of P limitation in the Gulf of Aqaba and also contribute a significant fraction of dissolved nutrients to the euphotic zone during stratification period (April to October).

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1. Introduction

Nutrient elements nitrogen, phosphorus and iron can be transported on aerosols and delivered to the surface ocean through atmospheric dry and wet depositions

(Duce et al., 1991; Jickells, 1995; Prospero et al., 1996; Mahowald et al., 2005). Atmospheric deposition may be particularly important in oligotrophic oceanic settings (Fanning, 1989; Owens et al., 1992). Specifically, the dry deposition of atmospheric nutrient elements to the Gulf of Aqaba may support a large fraction of new production in the euphotic zone due to negligible river runoff and precipitation (Ganor and Foner, 1996). As aerosol particles deposit directly to the sea surface, the

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amount of bioavailable trace metals is constrained by the degree to which they are soluble in seawater (Chester et al., 1993). Many investigations have been conducted on the chemical composition of aerosols (e.g. Johansen et al., 2000; Sellegri et al., 2001; Nair et al., 2001; Sasakawa and Uematsu, 2002; Dibb et al., 2003) and the solubility of various aerosol species in different waters (e.g. Zhu et al., 1992; Chester et al., 1997; Ridame and Guieu, 2002). Soluble nitrogen (N) species such as NO_3^- and NH_4^+ in the aerosol are often measured along with other exchangeable ions using a pure water extraction (Savoie et al., 1989; Huebert et al., 1998). Soluble phosphorus (P) in the aerosol has been leached out and analyzed in both pure water (Ridame and Guieu, 2002) and seawater (Herut et al., 1999a; Ridame and Guieu, 2002), and soluble iron (Fe) extracted in various acidic solutions (e.g. Zhu et al., 1993; Siefert et al., 1999; Chen and Siefert, 2004; Chester et al., 1997) as well as in seawater (Hodge et al., 1978; Crecelius, 1980; Moore et al., 1984; Chester et al., 1997). It has been suggested that the solubility of aerosol iron in an aqueous solution is strongly affected by the solution's pH and ionic strength as well as by iron complexation and change in its oxidation state (Zhu et al., 1992). It is important to note that nutrient element solubility in seawater should better represent the nutrient input through dry deposition mode than any estimates based on aerosol nutrients leached in pure water or acidic solutions (Chester et al., 1994; Ridame and Guieu, 2002). However, in many studies the latter is used. Moreover, very few studies (if any) have directly compared the solubility of natural aerosol samples collected simultaneously at the same site in both seawater and pure water to evaluate the respective extractions while excluding other compositional, source, and treatment effects.

This study aims to compare the soluble nutrient and selected trace metal concentrations extracted from aerosol particles by pure water and by filtered Sargasso seawater. Such a comparison using aerosol samples collected simultaneously thus reducing any variability associated with the aerosol composition and history has not been thoroughly examined before. Aerosol filter samples collected in the Gulf of Aqaba were used for these experiments. Concentrations of NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} , total soluble N (TSN), total soluble P (TSP), total soluble Fe (TSFe) and a few other trace metals (Al, Cu, Ni and Zn) in pure water and in seawater extracts were analyzed. Pure-water- and seawater-soluble nutrient concentrations are compared with each other graphically and statistically, and the solubility differences of nutrients and trace metals between pure water and seawater and

some of the possible causes for these differences are addressed.

2. Methods

2.1. Aqueous extractions of samples

Sargasso seawater was collected at the Bermuda Atlantic Time-Series (BATS) location (31°40'N, 64°10'W) through a towed "fish" deployed at 2 m depth on 27 August 2003. The seawater was pumped through acid-cleaned Teflon tubing and filtered through an acid-cleaned polypropylene cartridge filter (0.22 μm , MSI, Calyx®). The seawater has a salinity of 36.17 and pH of 8.16. The measured nutrient concentrations for this water are 0.2, 0.02 and 0.002 $\mu\text{mol L}^{-1}$ of dissolved NO_3^- , PO_4^{3-} and Fe, respectively (Gregory A. Cutter, unpublished data). These low concentrations are favorable as they are expected to be lower than those that will be added to the seawater from the aerosol source. Moreover, the Sargasso seawater is from an oligotrophic area that has been well studied (see BATS study website) and it is also relatively easy to be obtained due to frequent research cruises in this region. This water was used rather than the seawater from the Gulf of Aqaba for the extraction of aerosol species during this study since the trace metal concentrations in the Gulf of Aqaba are high (Chase et al., submitted for publication).

Aerosol samples (collected on 47-mm polycarbonate membranes, Isopore™) were collected between 20 August 2003 and 21 November 2004 using a Total Suspended Particle High Volume Sampler (HVS) located at the northwest coast of the Gulf of Aqaba (29°31'N, 34°55'E, Fig. 1). The HVS is designed to have four filter cartridges connected to separate flow meters thus collecting four filter samples simultaneously. The airflow path of the HVS and filter holders are made of all plastic to minimize contamination with respect to the measurement of trace metals. The polycarbonate filters were cleaned by soaking the filters in hydrochloride acids for over 24 h. The filters were soaked first in concentrated HCl (A.C.S plus) and then in the ultra-pure HCl twice and finally rinsed with milli-Q water. Samples were taken at least once a week over a 24 h period with an air flow of 2.4–2.7 $\text{m}^3 \text{h}^{-1}$. Two of the four filter samples collected simultaneously at a given date were used for pure water and seawater extractions, respectively. The two parallel samples could at times be collected at slightly different flow rates and efficiencies and thus may have dissimilar ratios of particle weight to air volume (g m^{-3}), which would result in slight differences between the two samples with

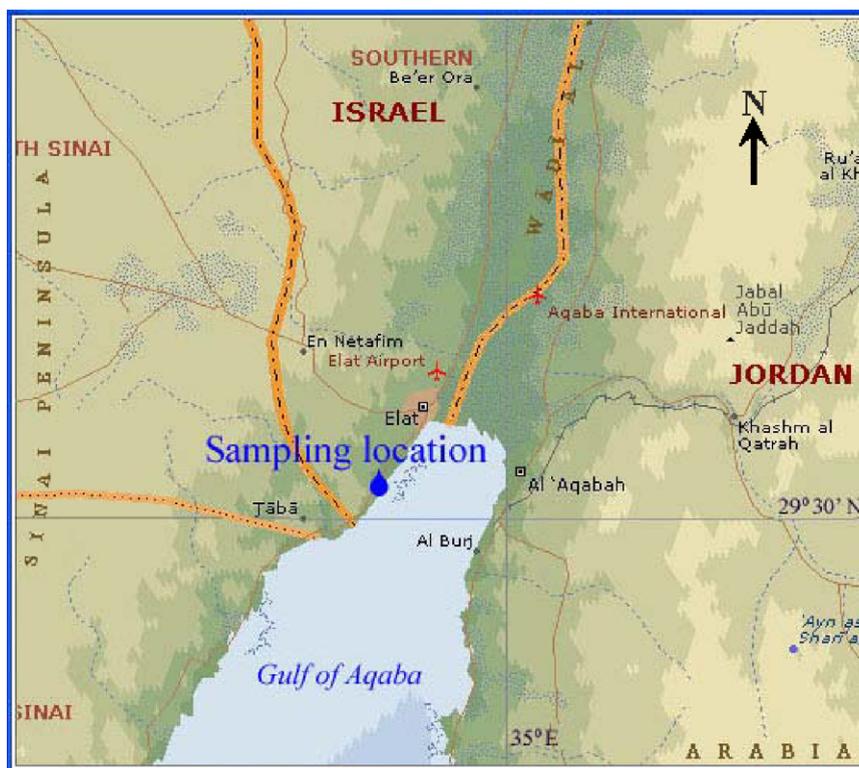


Fig. 1. Aerosol sampling location (29°31'N, 34°55'E) at the northwest coast of the Gulf of Aqaba.

respect to their species concentrations normalized by air volume (mol m^{-3}).

A total of 31 pairs of extractions were conducted under the same experimental conditions and procedures. We would like to emphasize that these extractions conditions are similar to previously used protocols (Chester et al., 1993; Ridame and Guieu, 2002) and are not designed to mimic the natural conditions but rather to compare the impact of using seawater versus pure water for extraction under otherwise similar protocols. The filter sample was placed in an acid-cleaned polypropylene jar (wide-mouth with unlined polypropylene screw cap, VWR®) with the dusty side facing up. 50 mL of 18.2 mΩ milli-Q water (pH 5.5) or Sargasso seawater was added to each jar, and the jar was covered using polypropylene screw cap and then sealed with parafilm. The filter sample was sonicated for 30 min to resuspend the aerosol particles into the solution. The choice to use 30 min sonication is a compromise between allowing enough contact time for dissolution process to reach a balance and keeping the sonication energy low enough not to break the particle aggregates and increase the solubility. The use of plastic rather than glass jars reduces the energy that impacts the

sample (Dr. Da-Ren Chen, personal communication). The extraction solution was then filtered through a 0.4 μm polycarbonate membrane and separated into several portions that were analyzed respectively for the concentrations of NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} , TSN, TSP, TSFe and selected soluble trace metals (Al, Cu, Ni and Zn). The 10 mL solution that was used for metals analysis was preserved in 2% ultrapure HNO_3 in an acid-cleaned 15 mL plastic centrifuge tube. 20 mL solution was stored in a 30 mL dark-brown Teflon bottle in the freezer (-20°C) for analysis of NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} . The rest of the solution was saved in a 30 mL plastic bottle at room temperature for TSN analysis.

Table 1 lists the particle loads in the pure water and seawater extractions for pairs of aerosol samples and the corresponding atmospheric concentrations of total P, Fe, Al, Cu, Ni and Zn in each sampling date. An average particle load of $\sim 70 \text{ mg L}^{-1}$ used in the aqueous extractions was chosen for analytical reasons although as stated previously it is not meant to represent the real aerosol concentration falling on the surface layer of the Gulf. Ridame and Guieu (2002) indicated that a particle concentration of 5 mg L^{-1} can be considered the highest value measured in the first meter of western

Table 1

Particle loads (mg L^{-1}) in the pure water and seawater extractions for pairs of aerosol samples and atmospheric concentrations (nmol m^{-3}) of total aerosol P, Al, Fe, Cu, Ni and Zn in each sampling date

Dates	Particle loads (mg L^{-1})		Total concentrations (nmol m^{-3})					
	PW	SW	P	Al	Fe	Cu	Ni	Zn
2003-8-20	32	28	0.9	14	4.9	0.05	0.03	0.1
2003-9-3	36	31	2.8	33	9.4	0.04	0.05	0.2
2003-9-16	36	30	4.1	27	8.4	0.06	0.04	0.2
2003-10-7	66	62	9.9	29	9.7	0.06	0.05	0.3
2003-10-27	38	34	0.4	16	5.1	0.02	0.02	0.07
2003-11-3	127	124	5.7	61	20	0.1	0.09	0.3
2003-11-24	88	69	9.1	93	28	0.08	0.1	0.4
2003-12-8	44	42	5.8	18	6.6	0.07	0.04	0.2
2003-12-15	101	99	8.1	122	34	0.1	0.1	0.8
2004-1-11	43	41	1.1	14	3.8	0.01	0.02	0.03
2004-1-18	59	58	4.4	16	4.3	0.06	0.03	0.2
2004-2-24	96	96	5.3	77	20	0.1	0.1	0.4
2004-3-8	50	38	1.3	16	4.6	0.07	0.04	0.2
2004-3-19	32	30	1.2	16	5.1	0.04	0.03	0.1
2004-3-23	54	30	3.2	34	12	0.04	0.04	0.1
2004-3-31	94	80	2.5	131	34	0.05	0.08	0.1
2004-4-25	34	33	2.3	100	29	0.03	0.07	0.1
2004-5-2	126	122	2.0	23	7.2	0.05	0.04	0.2
2004-5-10	418	415	12	547	145	0.2	0.3	0.5
2004-5-16	26	23	2.2	23	6.6	0.02	0.02	0.06
2004-5-30	127	98	3.7	113	29	0.04	0.09	0.2
2004-6-13	28	21	2.8	9.1	2.7	0.03	0.01	0.09
2004-6-27	32	22	2.7	12	4.0	0.03	0.02	0.1
2004-7-19	51	47	9.8	43	14	0.06	0.06	0.3
2004-8-2	27	24	1.2	11	3.3	0.03	0.01	0.08
2004-8-29	48	47	6.8	61	17	0.06	0.06	0.2
2004-9-21	58	49	11	37	11	0.08	0.07	0.3
2004-9-26	76	71	32	30	8.9	0.1	0.05	0.3
2004-10-19	102	90	10	75	23	0.1	0.1	0.6
2004-11-3	59	50	3.0	47	14	0.06	0.05	0.1
2004-11-21	50	46	2.6	30	9.9	0.03	0.03	0.02
Average	73	66	5.5	61	17	0.06	0.06	0.2
Median	51	47	3.2	30	9.7	0.06	0.05	0.2

Mediterranean Sea after a Saharan dust storm event of high magnitude. With a normal aerosol density of 0.05 mg m^{-3} over the Gulf, the particle loads used in our extraction were about 2 to 3 orders of magnitude higher than those in the surface seawater. Such high particle loads may have reduced the percentages of aerosol species dissolved into the solutions compared to low particle concentration in the real ocean. However, data with respect to the relative differences between the solutions used is what we emphasize here.

2.2. Chemical analysis

NO_2^- , NO_3^- , NH_4^+ and PO_4^{3-} extracted in pure water were measured by Ion Chromatography using a

DIONEX DX-500 system. Anions (e.g. NO_2^- , NO_3^- and PO_4^{3-}) were separated and eluted using an AS9-HC anion column (Dionex) using a Na_2CO_3 eluent, and cations (e.g. NH_4^+) separated and eluted using a CS12A cation column (Dionex) using a methanesulfonic acid (MSA) eluent. NO_2^- , NO_3^- , NH_4^+ and PO_4^{3-} extracted in Sargasso seawater were measured by a continuous segmented flow system consisting of components of a Technicon Autoanalyzer IITM and an Alpkem RFA 300TM. TSP, TSFe and soluble trace metal (Al, Cu, Ni and Zn) concentrations were determined by Inductive Coupled Plasma Optical Emission Spectroscopy (ICP-OES) in a matrix of 2% HNO_3 . Total soluble N (TSN) was analyzed using a modified persulfate digestion procedure (Delia et al., 1977) followed by Continuous-Flow Autoanalyzer (Alpkem Flow Solution IV) analysis. Standard stock solutions for cations (in 2% HNO_3), anions (in H_2O) and multiple elements (in 5% HNO_3) were obtained from SPEX CertiPrep, Inc. The detection limits calculated as three times of the standard deviation of blanks for the soluble NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} , TSP, TSFe, Al, Cu, Ni, Zn and TSN in the purewater (seawater) extracts are 0.1(0.1), 0.1(0.5), 0.01(0.01), 0.03(0.01), 0.3(0.3), 0.06(0.01), 0.1(0.03), 0.03(0.01), 0.008(0.003), 0.02(0.007) and 0.05(1) $\mu\text{mol L}^{-1}$, respectively. The lowest concentrations of these components measured in the extracted samples were over a factor of 3 higher than their detection limits except for the total soluble Al, Fe, Cu and Zn in the seawater extracts. The undetectable samples for the seawater-soluble Al, Fe, Cu and Zn were 32%, 39%, 16% and 13% of the total 31 samples, respectively. Only the real measured species data (above detection limits) were used for statistical analysis and comparison. An experimental blank was handled and analyzed with the samples, and its concentrations for all components were below the detection limits. The experimental and seawater blanks have been subtracted for the data reported below.

3. Results and discussion

3.1. Nitrogen species

Atmospheric concentrations of major nitrogen species (NO_3^- and NH_4^+) extracted by pure water and Sargasso seawater from aerosol samples are shown in Fig. 2. No significant differences between seawater and pure-water extractions were observed (paired *t*-test, $p > 0.05$, $n = 31$). Pure-water- and seawater-soluble NO_3^- concentrations are almost identical for the majority of sample pairs with the exception of a few samples (Fig.

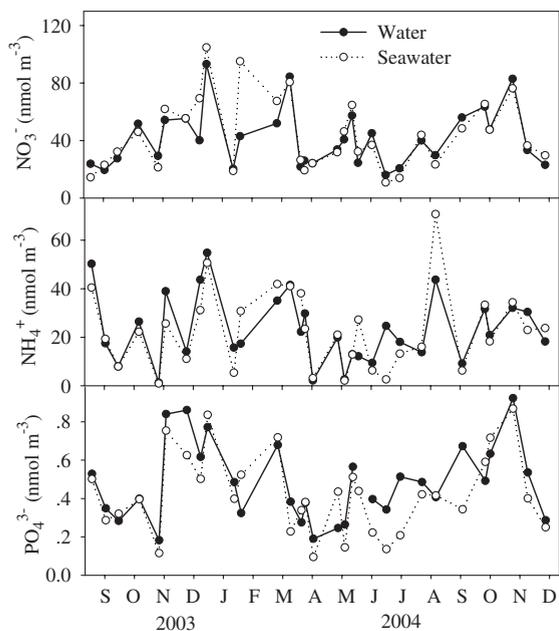


Fig. 2. Atmospheric concentrations of nitrate, ammonium and phosphate (nmol m^{-3}) extracted by pure water (black dots and solid line) and Sargasso seawater (white dots and dashed line) from aerosol samples ($n=31$) collected between 20 August 2003 and 21 November 2004 in the Gulf of Aqaba.

2a). These offsets may be due to small differences between the two filter samples collected side by side and used for comparing extractions. Concentrations of seawater-soluble NH_4^+ are also in general good agreement with the pure-water concentrations (Fig. 2b). Discrepancies found between NH_4^+ in the seawater and pure water are somewhat more frequent than for NO_3^- (Fig. 2a and b). This is probably because of the more volatile nature of the NH_4^+ ion which may result in loss during sample storage or processing (see Methods section). The mean concentrations of seawater-soluble NO_3^- and NH_4^+ are 44 and 23 nmol m^{-3} , respectively, which are comparable to the mean soluble NO_3^- (41 nmol m^{-3}) and NH_4^+ (23 nmol m^{-3}) in pure water (Table 2).

Although NO_3^- and NH_4^+ ions are the major components of soluble N in the aerosol (represent together over 85% of TSN). TSN concentrations, which include dissolved organic compounds in addition to NO_3^- and NH_4^+ , extracted in Sargasso seawater are significantly lower than those extracted in pure water (paired t -test, $p < 0.01$, $n=31$, Fig. 3). The mean concentration of TSN in the seawater (65 nmol m^{-3}) is about 12% lower than that of pure water extractions (75 nmol m^{-3} , Table 2). The lower TSN extraction yield could be a result of partial loss of NH_4^+ in an alkaline environment (pH around 8) during the 10-day storage of

seawater-extracts at room temperature before they were analyzed for TSN. However, in sealed sampling tubes the diffusion of NH_3 from seawater should be small (Genfa et al., 1998). Alternatively, the lower TSN in seawater extracts may be due to negligible organic N concentrations extracted in the seawater (the organic fraction is close to zero; see Table 2); while in pure water soluble organic N (SON) concentrations account on average for 13% of TSN (Table 2). SON in these aerosol samples has been found to be significantly correlated with non-sea-salt Ca^{2+} (Ying Chen, unpublished data), and therefore may be associated with the mineral dust component of the aerosol (Mace et al., 2003). Mineral particles are less soluble and may adsorb SON more tightly in seawater compared to pure water which may explain the observed decrease of organic N leaching in seawater.

3.2. Phosphorus species

Concentrations of PO_4^{3-} dissolved in seawater are slightly lower than the soluble PO_4^{3-} in pure water

Table 2

Atmospheric concentrations (nmol m^{-3}) of soluble nutrients (NO_2^- , NO_3^- , NH_4^+ , PO_4^{3-} , SON and SOP) and total soluble N (TSN), P (TSP), Fe (TSFe) and trace metals (Al, Ni, Cu, and Zn) and ratios between soluble inorganic N (SIN) and TSN and between phosphate and TSP extracted by pure water (PW) and Sargasso seawater (SW) from aerosol samples (31 pairs of samples) collected in the Gulf of Aqaba

Soluble species	PW-extracted nmol m^{-3}	SW-extracted nmol m^{-3}	Conc. change (%)	Sig. coefficient
NO_3^-	41±20	44±25	+7	0.212
NH_4^+	23±14	23±16	-2	0.788
NO_2^-	1±1	1±0.5	-22	0.476
PO_4^{3-}	0.5±0.2	0.4±0.2	-11	0.026
SON	10±0.5	0.01±4	-100	<0.001
SOP	0.2±0.5	0.02±0.2	-90	<0.001
TSN	75±34	65±35	-12	0.005
TSP	0.7±0.5	0.4±0.2	-40	0.002
TSFe	0.5±0.3	0.06±0.02	-88	<0.001
Al	4±2	0.8±0.6	-80	<0.001
Ni	0.04±0.02	0.03±0.008	-34	0.001
Cu	0.04±0.02	0.03±0.03	-22	0.052
Zn	0.1±0.08	0.1±0.08	0	0.305
SIN/TSN	0.9	1	-	-
PO_4^{3-} /TSP	0.7	1	-	-

Percent changes of soluble-nutrient concentrations in the seawater relative to pure water and significant coefficients from paired t -test are also list in the table (in bold those which indicate significant differences). The mean concentrations and standard deviations of seawater-soluble Fe, Al, Cu and Zn were based on their real measured data (above detection limits) which were 19, 21, 26 and 27 samples, respectively.

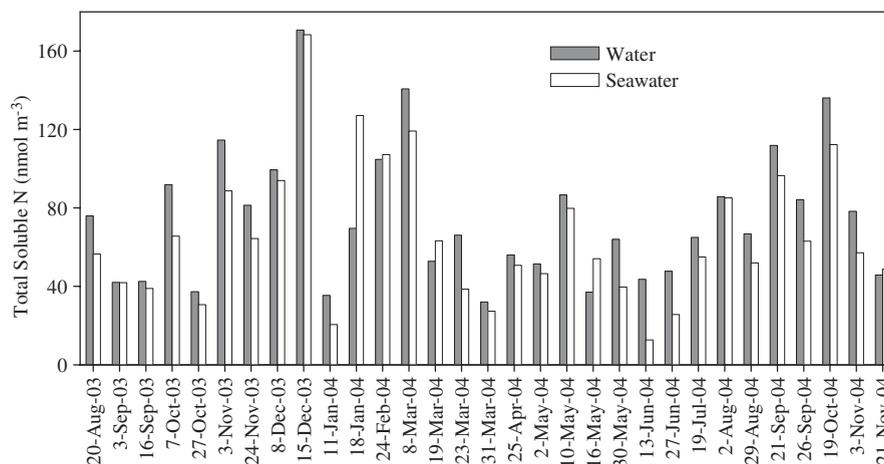


Fig. 3. Atmospheric concentrations of total soluble N (nmol m^{-3}) extracted by pure water (dark bars) and Sargasso seawater (white bars) from aerosol samples ($n=31$) collected in the Gulf of Aqaba.

(paired t -test, $p=0.026$, $n=30$, Fig. 2). The mean concentration of seawater-soluble PO_4^{3-} (0.4 nmol m^{-3}) is about 11% less than the mean PO_4^{3-} (0.5 nmol m^{-3}) in pure water (Table 2). Unlike NO_3^- and NH_4^+ ions which are almost completely soluble in an aqueous solution, much of the particulate PO_4^{3-} compounds (e.g. calcium phosphates) in the aerosol have low solubilities and their dissolution may be affected by water properties (e.g. pH and ionic strength). The dissolution of aerosol species may also depend on the nature of the particles such as grain size and chemical composition (Guieu et al., 1997) and the amount of particles introduced to the solution (Colin et al., 1990). However, aerosol samples used in our study for pure water and seawater extractions were collected simultaneously by one collector and had similar particle loads and features (dust sources and mineralogy). Accordingly, the slight decrease of soluble PO_4^{3-} concentration in the seawater media is mainly due to the change of water properties. Ridame and Guieu (2002) studied the dissolved inorganic phosphorus (DIP) in Saharan soil, and found that the percentages of DIP for a particle concentration of 5 mg L^{-1} were 21% in ultrapure water and 12% in seawater. In our experiments, the soluble PO_4^{3-} concentrations were around 16% (2 to 60%) and 12% (2.35%) of total aerosol phosphorus for pure water and seawater extractions, respectively. The percentage of PO_4^{3-} dissolved in the seawater is close to the range (3% to 11%) previously reported for particle concentrations of 60 to 90 mg L^{-1} (Lepple, 1975; Herut et al., 1999b; Ridame and Guieu, 2002). We also observe higher solubility of PO_4^{3-} in pure water (16%) compared to seawater (12%), consistent

with previous observations, suggesting that the pH of the solution or the ionic strength may play an important factor in the PO_4^{3-} solubility of aerosols.

TSP concentrations extracted in Sargasso seawater are found to be significantly lower than those extracted in pure water (paired t -test, $p<0.01$, $n=30$, Fig. 4). The mean concentration of TSP in pure water (0.7 nmol m^{-3}) decreases by about 40% when seawater is used (0.4 nmol m^{-3}) which is a more pronounced decrease than that of soluble PO_4^{3-} (Table 2). As a result, soluble organic phosphorus (SOP) concentrations, defined by subtracting soluble PO_4^{3-} from TSP, are over a factor of 4 higher in pure water than in seawater extractions. Organic P like organic N in these aerosols may also be associated with crustal metals such as iron and aluminum oxides (Bergametti et al., 1992), so enhanced leaching of crustal metal ions in pure water (compared to seawater) may reduce phosphorus sorption on the minerals and increase the SOP concentration in the pure water extracts (Sinaj et al., 2002). There are a few sampling dates for which the TSP concentrations leached in Sargasso seawater are higher than in pure water (Fig. 4, e.g. May 16 and Nov. 21, 2004). A common characteristic found for these dates is that their air mass back-trajectories cross the Mediterranean Sea and move towards the industrialized and semi-industrialized regions of Europe (Fig. 5a). These trajectories are different from other air masses that typically originate from the surrounding deserts and/or are transported mostly over land to the Gulf of Aqaba (Fig. 5b). Higher impact of anthropogenic sources and long transport path through the ocean can potentially remobilize phosphates and thus reduce or eliminate the discrepancy between P dissolution in

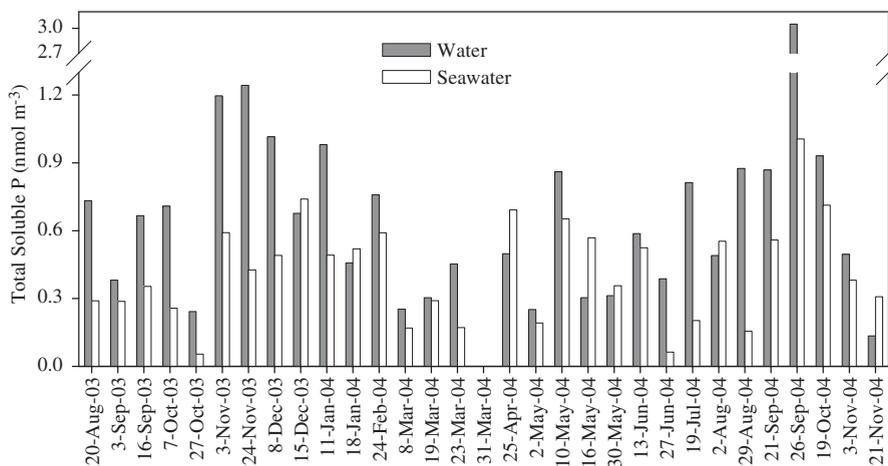


Fig. 4. Atmospheric concentrations of total soluble P (nmol m^{-3}) extracted by pure water (dark bars) and Sargasso seawater (white bars) from aerosol samples ($n=30$) collected in the Gulf of Aqaba.

the seawater and in pure water. Interestingly, the TSN concentrations in the seawater are also found to be greater than the respective pure-water concentrations for the sampling dates of May 16 and Nov. 21, 2004 (Fig. 3), which may also be explained by the increased component of anthropogenic aerosols which result in higher solubility of organic compounds in seawater.

3.3. Aerosol iron

Fig. 6 presents the TSFe concentrations extracted in pure water and Sargasso seawater for aerosol samples collected between 20 Aug. 2003 and 21 Nov. 2004 in the Gulf of Aqaba. About 39% of the TSFe concentrations

in the seawater-extracts are below the detection limits which were not presented in Fig. 6. A dramatic decrease of TSFe concentrations can be seen in the seawater extraction compared to those extracted in pure water (paired t -test, $p < 0.01$, $n=19$, Fig. 6). The mean concentration of TSFe in the seawater (0.06 nmol m^{-3}) is about an order of magnitude lower than that in pure water (0.5 nmol m^{-3} , Table 2). Such a significant drop of Fe solubility in seawater has been previously recognized by Zhu et al. (1992) base on theoretical calculation of ferric ion solubilities. The equilibrium solubilities of hematite, hydrous ferric oxide and goethite were calculated for aqueous solutions at various values of pH and ionic strength (Zhu et al., 1992). It was

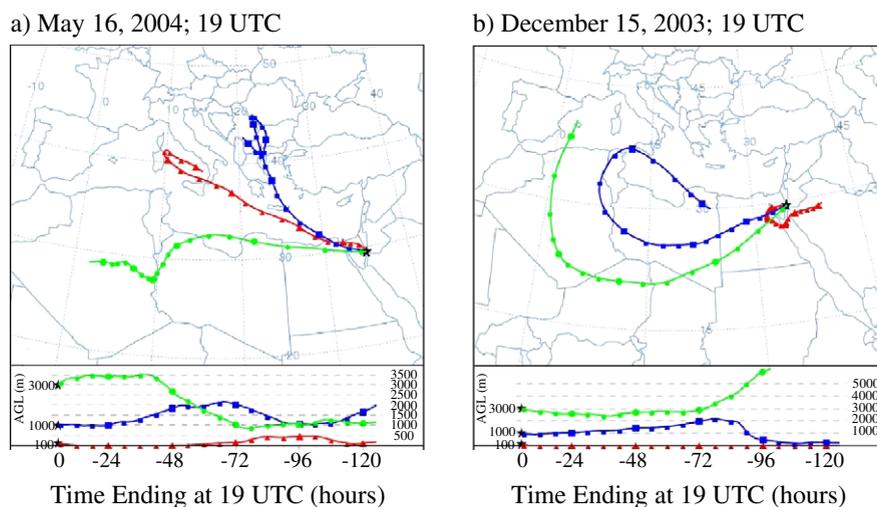


Fig. 5. Representative 5-day backward trajectories calculated for (a) 16 May 2004 and (b) 15 December 2004. The starting point is the northwest coast of the Gulf of Aqaba ($29^{\circ}31'N$, $34^{\circ}55'E$) at latitudes of 100, 1000 and 3000 m.

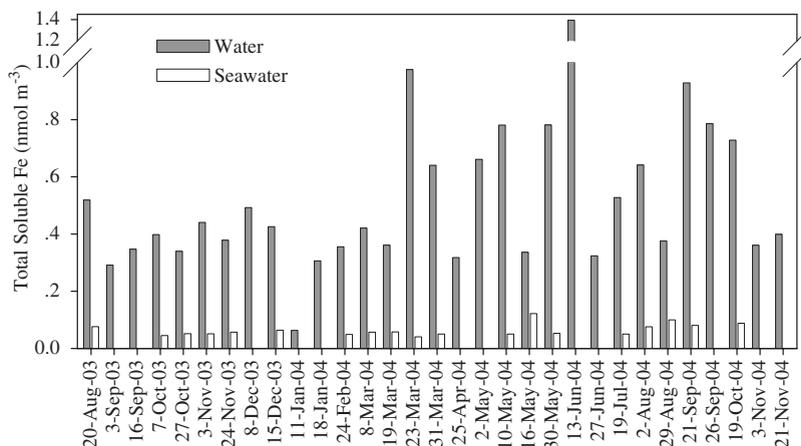


Fig. 6. Atmospheric concentrations of total soluble Fe (nmol m^{-3}) extracted by pure water (dark bars, $n=31$) and Sargasso seawater (white bars, $n=19$) from aerosol samples collected in the Gulf of Aqaba.

found that at a seawater condition (pH 8 and ionic strength 0.7 mol kg^{-1}) the soluble Fe^{3+} concentrations were one or two orders of magnitude lower than those in the rainwater (pH 5 and ionic strength $0.001 \text{ mol kg}^{-1}$). This is indeed consistent with our results; however, their calculation of the maximum Fe^{3+} solubility in seawater was 0.7 nM , which is approximately 60 times less than the mean TSFe concentration (43 nM) extracted in Sargasso seawater in this study. The measured high TSFe concentrations in our study compared to the theoretical calculations may be attributed to the existence of soluble species Fe^{2+} in the aerosol that can be oxidized rapidly to Fe^{3+} in seawater. Previous studies have shown that Fe^{2+} does exist in acidic leaching solutions and constitute 0.3% to 1.8% of total Fe in marine mineral aerosols (Zhu et al., 1993; Siefert et al., 1999; Johansen et al., 2000; Chen and Siefert, 2004). Moreover, our TSFe measurements are based on an operational definition of solubility that is the Fe fraction that can pass through a filter of $0.4 \mu\text{m}$ pore size. Under such conditions, the TSFe concentration would include truly dissolved Fe^{3+} as well as colloidal iron (extremely small particles) which may account for a major fraction of the TSFe concentration. Chelation of iron by natural ligands in seawater, lowering the free Fe^{3+} concentrations, may also explain these data.

Aerosols typically undergo about 10 condensation/evaporation cloud cycles during their transport in the atmosphere (Spokes et al., 1994). Chemical and photochemical reactions can occur after an aerosol particle is incorporated into a cloud droplet. Subsequent evaporation of the cloud droplet would result in a chemically processed particle that may contain a larger fraction of labile Fe than its initial state (Chen and

Siefert, 2003). Aerosols over the Gulf of Aqaba are transported primarily from the surrounding deserts (Ying Chen, unpublished data); however, their chemical properties may differ from desert soil. Bonnet and Guieu (2004) reported that the soluble Fe in seawater was 5 and 39 nM at a particle concentration of 10 mg L^{-1} for Saharan soil and urban particles, respectively. With a particle load of 70 mg L^{-1} (applied in this study), the soluble Fe leached from Saharan soil and urban particles could reach respectively 25 and 228 nM according to the linear relationships between the soluble Fe and the particle loads (Bonnet and Guieu, 2004). Saharan soil and urban aerosols represent two extremes in terms of labile Fe content, and thus our measurements of seawater-soluble Fe with a mean value of 43 nM fall within that range (although closer to the soil end-member) and are reasonable.

In the extraction experiments, the mean percentages of aerosol Fe dissolved in pure water and Sargasso seawater are 5% (0.5 to 19%) and 0.7% (0.003 to 2%), respectively. These percentages are consistent with the solubilities of aerosol Fe measured by other researchers (e.g. Hardy and Creelius, 1981; Moore et al., 1984; Chester et al., 1993; Guerzoni et al., 1999; Bonnet and Guieu, 2004). Guerzoni et al. (1999) leached aerosol filter samples in pure water and found a wide-range of Fe solubility from 1% at a particle concentration of 200 mg L^{-1} to 13% at a particle concentration of 5 mg L^{-1} . Bonnet and Guieu (2004) reported that the percentage of Fe released in seawater varied from 0.05% to 2.2% depending on the particulate load, the aerosol source and the contact time. In general, the soluble fraction of aerosol Fe in the seawater ranges from less than 1% to 10% (Jickells and Spokes, 2001).

The solubility of aerosol Fe decreases with an increasing particle load following a power law (Bonnet and Guieu, 2004). In our experiments, a mean particle load of 70 mg L^{-1} was used and therefore the solubility measurements are on the low end of the reported range.

3.4. Trace metals

A few other soluble trace metals (Al, Cu, Ni and Zn) were also analyzed along with the soluble Fe in pure water and Sargasso seawater extracts, and their concentrations are shown in Table 2. Similar to soluble aerosol Fe, the concentrations of soluble Al and Ni extracted in the seawater are significantly lower than those extracted in pure water (paired *t*-test, $p < 0.01$, Table 2). The soluble Cu concentrations are also found to be lower in the seawater than in pure water but show more scatter ($p = 0.05$, Table 2). No significant difference between the seawater- and pure-water-soluble Zn concentrations was detected ($p > 0.05$, Table 2). Our observations of the dissolution features of aerosol Cu and Zn in seawater and pure water are consistent with the findings reported by Chester et al. (1994). They found that very similar amounts of aerosol Zn were soluble in both seawater and the rainwater (pH around 4.0), and that the total Cu soluble in the rainwater was greater than that soluble in seawater (Chester et al., 1994). In our experiments, the average percentage of Al dissolution decreased significantly from approximately 13% (1 to 40%) in pure water to about 3% (0.1 to 9%) in the seawater. Both values are considerably lower compared to the average percentages of aerosol Cu, Ni and Zn dissolved in the seawater (49%, 48% and 44%) and pure water (66%, 62% and 44%). As suggested by several authors, trace metals that are crust-dominated in the aerosols such as Al and Fe are mainly refractory (e.g.

> 70% of the total Al and Fe is held in the refractory fraction; Chester et al., 1994) and have speciation signatures that are generally more soluble in acidic than in basic waters. Our mean Al solubility in pure water (13%) falls within the range (less than 1% at particle loads greater than 100 mg L^{-1} to around 30% at particle loads lower than 5 mg L^{-1}) reported by Guerzoni et al. (1999) for Mediterranean aerosols. The measured mean solubilities of aerosol Cu (49%) and Zn (44%) in the Sargasso seawater are also comparable to those (Cu: 34 to 40% Zn: 58 to 75%) previously reported for anthropogenic-rich aerosols collected at Liverpool (Chester et al., 1993) and the North Sea (Kersten et al., 1991; Chester et al., 1994). These results may suggest that the majority of Cu and Zn even in this desert region are of anthropogenic sources.

Significant anthropogenic component of the aerosols has been indicated by relatively low contents of total Al (average 3%, Fig. 7) in these aerosol samples. Al is often used as a representative crustal tracer and makes up about 8% of the upper continental crust (Taylor and McLennan, 1985). The Al concentrations normalized by aerosol particle weights (%) in our samples were about a factor of 2 lower than the crustal ratio, suggesting that the aerosols were influenced substantially by other sources (e.g. anthropogenic aerosols from Europe) besides the dust from surrounding deserts or that the specific mineral dust source has an Al concentration that is different from average crust. Total Al concentrations (%), representing the magnitude of soil dust component in aerosols, were found to be reversely correlated with the percentage solubilities of aerosol Al ($r = 0.78$) and Fe ($r = 0.64$) in the pure water (Fig. 7). These correlations suggest that (1) soil dust is the major source for Al and Fe and their soluble fractions in the aerosols and (2) aerosol Al and Fe contributed by anthropogenic sources

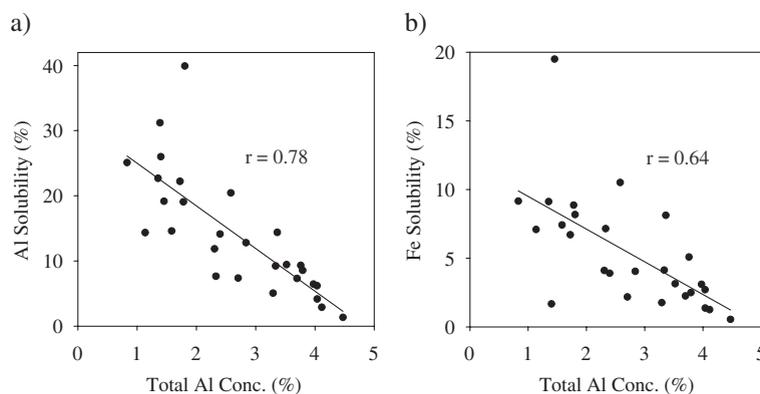


Fig. 7. The percentage solubilities (%) of aerosol Al (a) and Fe (b) in pure water versus the total Al content in aerosol particles (weight percentage) for the aerosol samples collected in the Gulf of Aqaba.

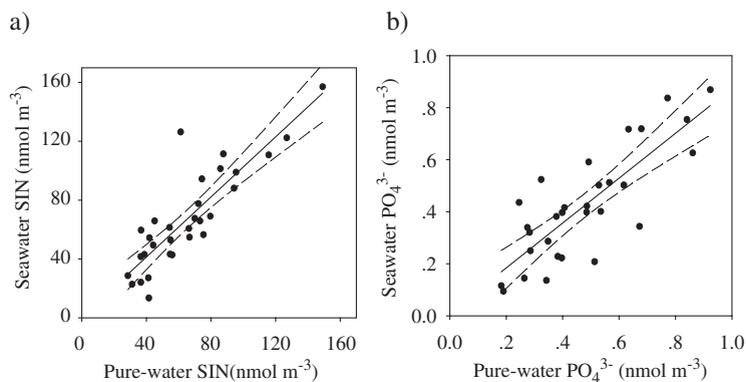


Fig. 8. Linear relationships between Sargasso seawater and pure water concentrations of (a) soluble inorganic nitrogen (SIN), slope 1 and (b) phosphate (PO_4^{3-}), slope 0.86, extracted from the aerosol samples ($n=31$) collected in the Gulf of Aqaba; the short dashed lines represent 95% confidence intervals.

are more soluble than those in the soil dust. However, such relationships have not been observed between the AI concentrations and the percentage solubilities of aerosol Cu, Ni and Zn. One possible reason for this lack of correlation could be the majority of these trace metals and their soluble fraction in these aerosol samples is in the anthropogenic component of the aerosols and not in the soil dust component. The major source of anthropogenic aerosols for these trace metals may also explain their relatively high solubilities measured. In fact, aerosol source is only one of many factors controlling the solubility of aerosol species. Ambient weather conditions, cloud processing and chemical and photochemical reactions during the particle transport all related to the “history” of the aerosols could also have important impacts on the soluble fraction of aerosol species.

3.5. Impact on the water column

We calculated dry deposition fluxes of soluble nutrients using the measured seawater-soluble nutrient concentrations times the dry deposition velocities previously reported for NO_3^- , NH_4^+ , PO_4^{3-} (1, 0.1, 2 cm s^{-1} , Duce et al., 1991) and Fe (1 cm s^{-1} , Jickells and Spokes, 2001). These are rough estimates of nutrient fluxes to the Gulf of Aqaba due to limited sampling dates and the simplified calculation (e.g. using fixed deposition velocities), but may still show the importance of atmospheric nutrient input to the water column. The calculated fluxes of soluble inorganic N, P and Fe are 41, 0.7 and 0.05 $\mu\text{mol m}^{-2} \text{d}^{-1}$, respectively. The N:P ratio (59:1) in the seawater soluble fraction of atmospheric dry deposition is well above Redfield ratio (N:P=16:1), suggesting that the atmospheric

input of nutrients to the Gulf preferentially adds new N to the euphotic zone, thus increasing the possibility of P limitation in this system. Obviously, the actual limiting nutrient will depend on the N:P ratios of all nutrient sources to the euphotic zone coupled with the specific demands by organisms. The water column of the Gulf of Aqaba is stratified with a mixing depth less than 100 m between April and October based on the nutrient profiles of the water column (Adina Paytan, unpublished data). During these seven months, atmospheric input of nutrients would finally cause an increase of 0.09 μM , 0.001 μM and 0.1 nM for soluble inorganic N, P and Fe, respectively in the up 100 m seawater (which is also euphotic zone) if neglecting any losses of nutrient species (e.g. biological uptake). Such atmospheric input of nutrients particularly SIN would be significant compared to the averaged concentrations of dissolved inorganic N, P (0.23 and 0.03 μM , Adina Paytan, unpublished data) and Fe (6 nM, Chase et al., submitted for publication) in the euphotic zone during the stratification period. However, the nutrient deposition from the atmosphere may not be important between November and March.

4. Conclusions

Nutrient element solubility in seawater should better represent the nutrient input through atmospheric dry deposition than any estimates based on aerosol nutrients leached in pure water or acidic solutions. From the comparison between pure water and Sargasso seawater extractions of the aerosols used in this study, we found that (1) similar concentrations of inorganic N (mainly NO_3^- and NH_4^+) are leached in both seawater (average 44 and 23 nmol m^{-3}) and

pure water (average 41 and 23 nmol m⁻³), (2) seawater-soluble PO₄³⁻ concentrations (average 0.4 nmol m⁻³) are only slightly lower than those in pure water (average 0.5 nmol m⁻³), and (3) Fe dissolution strongly decreases from an average of 0.5 nmol m⁻³ in pure water to an average of 0.06 nmol m⁻³ in the seawater.

Concentrations of both soluble inorganic N (SIN) and PO₄³⁻ in the seawater are significantly correlated with their pure-water concentrations following the equations below (Fig. 8).

$$\text{SW}(\text{SIN}) = (1.02 \pm 0.11) \times \text{PW}(\text{SIN}) + (0.51 \pm 7.9), r = 0.86$$

$$\text{SW}(\text{PO}_4^{3-}) = (0.86 \pm 0.12) \times \text{PW}(\text{PO}_4^{3-}) + (0.012 \pm 0.059), r = 0.82$$

where SW(SIN) and PW(SIN) represent atmospheric SIN concentrations (nmol m⁻³) derived from seawater and pure-water leaches, respectively. Similar abbreviations are used for PO₄³⁻. Uncertainties for both slopes and intercepts are given with “±SE” in the equations. Using these equations and assuming similar relations for aerosols in general it is possible to convert any pure-water SIN and PO₄³⁻ measurements to their respective seawater solubilities which would give better estimates for the atmospheric inputs of SIN and PO₄³⁻. No consistent relationship is found between the TSFe concentrations in the seawater and pure water. The mean solubility of aerosol Fe in the seawater (around 0.7%) along with the total aerosol Fe concentrations should therefore be used for the calculation of the atmospheric input of soluble Fe to the Gulf and this relationship may not be globally applicable.

We also found from the comparison experiments that: (4) total soluble N and P, which include dissolved organic compounds, extracted from the aerosols into the seawater (average 65 and 0.4 nmol m⁻³) are generally lower than those extracted in pure water (average 75 and 0.7 nmol m⁻³); (5) the concentrations of soluble aerosol Al, Cu and Ni in the seawater are significantly lower compared to those in pure water, while similar amounts of aerosol Zn are leached in both seawater and pure water. Our comparison suggests that when estimating the effect of dust deposition on marine ecosystems the solubility of nutrient and trace elements in seawater should be used, and attention to the aerosol history (e.g. air mass trajectory) should be given. It is likely that some previous reports have overestimated the input of aerosol P, Fe, Al, Cu, and Ni to the ocean as a result of the use of solubility estimates obtained from pure water.

Our estimates of dry deposition fluxes of nutrients based on their seawater solubilities show that atmospheric nutrient input contributes a significant fraction of dissolved nutrients to the Gulf of Aqaba euphotic zone during its stratification period (April to October). This may also be the case for other oligotrophic areas during dust events.

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