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

Ying Chen *, Joseph Street, Adina Paytan

Geological and Environmental Sciences, Stanford University, Stanford, CA 94305, USA

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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).

Keywords: Seawater; Soluble; Nutrients; Aerosols; Gulf of Aqaba

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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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* Corresponding author. Tel.: +1 650 723 0841; fax: +1 650 725 0979.
E-mail address: ychen04@stanford.edu (Y. Chen).

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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 $\mu mol\ L^{-1}$ 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 $m^3\ h^{-1}$. 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