

Evaluation of commonly used filter substrates for the measurement of aerosol trace element solubility

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Abstract

The published literature describing aerosol trace element fractional solubility measurements is characterized by a wide range of observed fractional solubilities. Whereas some of this variability is derived from natural differences in the chemical characteristics of the aerosol source material, the use of different sample collection and processing protocols by the scientific community has also confounded efforts to understand aerosol solubility. Bulk aerosol samples were collected at a coastal site over a nine-month period and used to assess the influence of filter material on aerosol solubility measurements. Two hundred samples were extracted with ultrapure deionized water and focused on the solubility of ten trace elements (Al, P, Ti, V, Mn, Fe, Ni, Cu, Zn, and Pb) of interest to the GEOTRACES program. Aerosol samples were collected on eight different filter types and extracted using a flow-through “instantaneous” extraction method. In many cases, the operationally defined aerosol trace element solubility differed depending on filter type. Major anion concentrations and trace element fractional solubility were found to differ 58% and 60% of the time, respectively. Filter blank concentrations are also reported for the various filter types. This work, in conjunction with the 2008 GEOTRACES Aerosol Intercalibration study, should aid the design of future research efforts by the wider marine aerosol community and allow better comparisons among published data.

The mission of GEOTRACES is to improve our understanding of the processes and fluxes that control the distributions of trace elements and isotopes (TEIs) in the ocean. An important component of this effort is to better quantify and characterize the flux of TEIs to the surface ocean via the atmospheric deposition of aerosols (SCOR Working Group 2006). Inherent to this mission is assessing the fractions of these aerosol TEIs that are soluble in seawater. Aerosols are produced by several

mechanisms including, but not limited to, uplift of continental material, high-temperature combustion activities, biomass burning, and volcanic emissions (Duce and Tindale 1991; Prospero et al. 1996; Jickells et al. 2005; Olgun et al. 2011). Aerosol deposition to the open ocean supplies important macronutrients, such as nitrate and phosphate, as well as micronutrients, particularly highly insoluble iron. Deposition of these nutrients can support primary productivity thereby linking aerosol TEIs to the biogeochemical cycling of carbon (Jickells et al. 2005).

It has long been thought that insufficient concentrations of bioavailable Fe limit the complete use of available macronutrients by phytoplankton creating high nutrient, low chlorophyll (HNLC) regions (Martin et al. 1990; Coale et al. 1996; Boyd et al. 2000). Iron availability can also regulate nitrogen fixation (Capone and Carpenter 1982; Falkowski et al. 1998; Morel and Price 2003; Mills et al. 2004; Sohm et al. 2011). Macronutrients, particularly nitrate and phosphate, from atmospheric deposition can support a substantial fraction of new production in oligotrophic areas of the ocean (Bergametti et al. 1992; Herut et al. 1999; Chen et al. 2007; Krishnamurthy et al. 2007; Mackey et al. 2007; Duce et al. 2008). Additionally, atmospheric deposition can introduce potentially toxic elements, e.g., copper, which may have deleterious effects on phytoplankton (Paytan et al. 2009) in oceanic regions signifi-

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cantly impacted by the deposition of anthropogenic aerosols (Sholkovitz et al. 2010).

Laboratory experimentation on both natural samples and reference materials using a variety of extraction methods has resulted in a wide range of operationally defined aerosol Fe fractional solubilities (Mahowald et al. 2005; Mahowald et al. 2008). We spotlight Fe as an example due to the relatively large number of published aerosol Fe solubility datasets, however it is likely that similar solubility ranges exist for many other elements (e.g., P). Baker and Croot (2010) suggest, "...some of this variability in reported estimates must also be due to the diverse experimental approaches used for determination of aerosol iron solubility." These approaches may include the use of different extraction solutions, solvent pH, solution to particle ratio, and exposure time with each of these variables potentially influencing the operationally defined fractional solubility estimate. In their review, those authors go on to rightly put forth surface seawater as the most "obvious" extraction media for assessing aerosol solubility in the ocean. However, as they point out and as is discussed in Buck et al. (2010) and Sholkovitz et al. (2012), the use of seawater complicates interpretation of the results and increases the complexity of subsequent analyses. Recent research has striven to offer alternative extraction solutions, and several studies have compared the solubility of aerosol Fe in both 18.2 m Ω ultrapure deionized water and 0.2 μ m filtered surface seawater both from marine and coastal aerosols (Buck et al. 2006; Chen et al. 2006; Aguilar-Islas et al. 2010; Buck et al. 2010). In one case, the fractional solubility was greater in seawater than in UHP (Aguilar-Islas et al. 2010).

As noted in Aguilar-Islas et al. (2010), it is possible that experimental artifacts are less likely to influence observational variability than aerosol source and together these factors explain the range of published aerosol Fe fractional solubilities in the literature. Regardless of the source of the variability, this range in solubilities complicates the effort to produce a widely applicable estimate of aerosol solubility, limits study comparability, and ultimately hinders our understanding of the factors controlling solubility. One of the specific GEOTRACES objectives is to "establish the range of fractional solubility of key atmospheric components and the process that underlie that variability" (SCOR Working Group 2006). To meet this goal, it is necessary to assess and reduce the impact of analytical variability related to sample collection and processing on solubility estimates. Ideally, a standardized method for measuring aerosol TEI solubility would be adopted by the research community allowing for the straightforward intercomparison of analytical results. The work presented here was designed to examine the impact of filter substrate on measured fractional solubility. Eight filter substrates were compared to assess analytical variability introduced by filter composition. The TEI blank of each filter type was characterized to aid researchers in determining which filter substrate is best suited for their specific analytical needs.

Aerosol solubility was estimated from measurements of the soluble and insoluble aerosol fractions. The soluble fractions of the major anions nitrate, sulfate, and oxalate were also measured. Sample handling was conducted following strict trace element clean protocols. The focus of this study was to determine the relative differences in aerosol solubility observations based on filter type and not to make determinations on the influence of environmental factors, both preceding and following deposition, on the respective solubilities of the elements and anions.

Materials and procedures

Materials

ACS Plus grade HNO₃ (70%) and HCl (38%) were purchased from Fisher Scientific and sub-boiling Teflon-distilled before use. HF (48%) was purchased in trace-metal grade. All references are to these acids at full concentration unless otherwise noted. All deionized water was ultrapure (pH ~5.5; \geq 18.2 M Ω) produced from a NANOpure water system (Barnstead/Thermolyne). All calibration standards were made from SPEX multi-element and single element standards designed for mass spectrometry and were diluted in ultrapure water (UHP) to appropriate concentrations. All ion chromatograph (IC) standards were made from SPEX multi-anion standards and diluted in UHP to appropriate concentrations.

Membrane filters were acid cleaned following two regimes. Polycarbonate and polytetrafluoroethylene filters were soaked for 1 week each in 4M HNO₃, 3M HCl, and 0.5M sub-boiling distilled HCl. The filters were rinsed with UHP between each step. After the final acid washing, individual filters were rinsed again with UHP. The polyethersulfone and Metrical filters were acid washed following a similar protocol with the exclusion of the initial HNO₃ wash. The GF/F and quartz filters were baked at 450° for 5 h, then placed in 3M HCl for 1 week. Following rinsing in UHP, the filters were soaked in 0.5M sub-boiling distilled HCl for an additional week followed by rinsing in UHP and drying. All drying was conducted in a Class 100 laminar flow hood. Blank filters of each type were processed in the same fashion as sample filters with the exception of field deployment.

Aerosol collection

Aerosol samples were collected using a total suspended particle (TSP) aerosol sampler located on the roof of the Interuniversity Institute of Marine Sciences in Eilat, Israel ~10 m off the northwest coast of the Gulf of Aqaba (29.5°N, 34.9°E). The aerosols were collected continuously over a 72-h period with an air flow of 1.2-1.5 m³ h⁻¹. The sampler has four 47-mm filter cartridges connected to dedicated flow meters thereby collecting replicate samples simultaneously and allowing for the samples to be normalized by their respective volumes of filtered air. The four parallel samples are collected at slightly different flow rates but should be similar in composition because they are sampling the same air masses. The airflow path of the sampler and filter holders are made entirely of plastic to min-

imize contamination for TEIs. After collection, the aerosol samples were stored frozen and in the dark. Frozen samples were shipped to California on a regular basis to minimize storage time and avoid possible changes in aerosol solubility (Buck et al. 2006).

Five day air mass back-trajectories (AMBTs) were simulated using the NOAA Air Resources Laboratory Hybrid Single-Particle Lagrangian Integrated Trajectory Model (HYSPPLIT, FNL data set) (Draxler and Rolph 2003; Rolph 2003). Arrival heights were set at 20, 500, and 1500 m.

Filter comparison study

Eight filter types were deployed over the course of the study period to compare results from samples collected on a variety of filters. Four comparable samples were collected simultaneously during each sampling period allowing for the isolation of filter type effects from natural aerosol variability. Sampling was divided into four periods consisting of different combinations of filter types. Samples were collected over fifty 72-h intervals from 12 Mar 2009 to 6 Dec 2009 (Table 1). The filter types were chosen to be representative of commonly used substrates found in the literature (e.g., Herut et al. 2001; Chen and Siefert 2004; Pekney and Davidson 2005; Buck et al. 2006; Huang and Yang 2006; Karthikeyan et al. 2006; Sedwick et al. 2007; Wagener et al. 2008; Shelley et al. 2012). Whatman-41 filters were not included in this experiment but are extensively discussed in Morton et al. (in press).

Period A (12 Mar 2009–10 May 2009), B (14 May 2009–25 Jun 2009), and D (27 Aug 2009–06 Dec 2009) produced trace element data for each of the four filter types deployed during the respective periods (Table 1). Period C (28 Jun 2009–23 Aug 2009) included GF/F and quartz filters, which were not digested because of the large analytical blanks and complicated matrices inherent to digestions of these filter types

(Upadhyay et al. 2009), therefore only two solubility datasets from period C, PC, and PTFE, were available for statistical analysis. Major anions were measured on all filter types. Aerosol solubility was calculated based on the soluble and total aerosol (or soluble + insoluble) fractions by the equation:

$$\text{Aerosol M\%} = (\text{Soluble M}) \times (\text{Total M})^{-1} \times 100 \quad (\text{Eq. 1})$$

Extraction of the soluble aerosol fraction

Ultrapure deionized water (UHP) was the solvent of choice because the resulting solutions provided the flexibility to analyze a wide variety of soluble chemical species. Extraction by UHP is widely used in the community (e.g., Yeatman et al. 2001; Buck et al. 2006; Chen et al. 2006; Sedwick et al. 2007; Aguilar-Islas et al. 2010; Buck et al. 2010; Hsu et al. 2010) and is not subject to the solubility constraints that plague seawater extractions as described in Baker and Croot (2010).

We employed a rapid exposure, flow-through technique that measures the “instantaneous” solubility of aerosols (Buck et al. 2006). Sample filters were individually loaded into an acid-washed polysulfone filter holder (Nalgene) attached to a vacuum pump (Air Cadet). Filters were carefully handled using two sets of plastic tweezers to ensure that the filter remained flat and the potential for particles loss was minimized. The vacuum rapidly draws the extraction solution (100 mL UHP) through the filter in a process that is completed in less than 10 s. Care was taken to slowly pour the UHP onto the aerosol filter to minimize the head space over the filter and reduce the chance that aerosol particles would be suspended in the solution. An important aspect of this procedure is that it minimizes the possibility for hydroxide precipitation because the aerosol particles are constantly exposed to fresh solvent. Following extraction, the sample solution was divided into a 25-

Table 1. Filter types deployed during the comparison study.

| | | |
|--------------------|--------|--|
| Period A | MCE | Millipore Mixed Cellulose Ester membrane; 0.45 μm . |
| 12 Mar-10 May 2009 | PCTE | GE Osmonics Polycarbonate Track-Etched membrane; 0.4 μm |
| <i>n</i> = 13 | GN-6 | Pall Gelman Metrical membrane; 0.45 μm |
| | HPWP | Millipore Polyethersulfone membrane; 0.45 μm |
| Period B | PC | Millipore Isopore Polycarbonate membrane; 0.4 μm |
| 14 May-25 Jun 2009 | PCTE | GE Osmonics Polycarbonate Track-Etched membrane; 0.4 μm |
| <i>n</i> = 12 | GN-6 | Pall Gelman Metrical membrane; 0.45 μm |
| | HPWP | Millipore Polyethersulfone membrane; 0.45 μm . |
| Period C | PC | Millipore Isopore Polycarbonate membrane; 0.4 μm |
| 28 Jun-23 Aug 2009 | GF/F | Whatman Borosilicate Glass; 0.7 μm |
| <i>n</i> = 13 | Quartz | Millipore Quartz Fiber |
| | PTFE | Millipore polytetrafluoroethylene membrane; 0.45 μm |
| Period D | PC | Millipore Isopore Polycarbonate membrane; 0.4 μm |
| 27 Aug-6 Dec 2009 | HPWP | Millipore Polyethersulfone membrane; 0.45 μm . |
| <i>n</i> = 12 | GN-6 | Pall Gelman Metrical membrane; 0.45 μm |
| | PTFE | Millipore polytetrafluoroethylene membrane; 0.45 μm |

n = sampling periods

mL aliquot stored frozen in a 60 mL acid-washed centrifuge tube and a 75-mL aliquot acidified to 0.024M HNO₃ in an acid-washed 125 mL LDPE narrow mouth bottle. The operationally defined soluble fraction is that which passes through a 0.4 μm filter. All of the filters were extracted using the flow through technique with the exception of the polytetrafluoroethylene membranes whose hydrophobic properties were not compatible with this technique. Those filters were extracted using 50 mL UHP and the batch leaching method described in Chen et al. (2006).

Chemical analyses

Filter digestion procedures

The insoluble aerosol fraction was measured following strong acid digestion of the residual material remaining after soluble extraction. The methods used were dependent on the filter type used to collect the sample and represent methods commonly used in the literature. Both hotplates and a CEM MDS-2100 microwave (CEM) equipped with Teflon digestion vessels were used. The Millipore quartz fiber and Whatman GF/F borosilicate glass filters were not digested because of the high blank of the resulting solution and the complicated solution matrix created by the large volume of HF required to fully digest these filter types.

The polycarbonate (PC), polycarbonate track-etched (PCTE), polyethersulfone (HPWP), and polytetrafluoroethylene (PTFE) filters were microwave digested following a variation of the method described in Chen and Siefert (2004). In each of these cases, the entire filter was digested with the exception of the PTFE filters, which were cut in half before soluble aerosol extraction. The digestion vessels were filled with 3 mL each of Teflon-distilled HNO₃ and HCl as well as 1 mL of trace metal grade HF. The vessels were heated to 180°C with a 30-min ramp time and held at temperature for 10 min. After cooling, 2 mL of 5% boric acid made in UHP was added and the vessels heated again to 100°C for more than 10 min. The procedure was run in batches of eleven with one temperature/pressure control vessel containing only the acid mixture. The resulting solutions were decanted into acid washed 60 mL LDPE wide-mouth bottles and placed on a hotplate inside a fume hood housed in UCSC's W. M. Keck Isotope Laboratory. The hotplate was set to 70°C, and the solution taken to near dryness. The residue was re-hydrated with 50 mL UHP and acidified to 0.024M HNO₃.

The mixed cellulose ester (MCE) and Pall/Gelman Metrical membrane (GN-6) filters were digested following the method of Sedwick et al. (2007). Following soluble aerosol extraction, each filter was cut in half using a ceramic blade. One half of the filter was placed in a 15 mL acid-washed Teflon digestion vial. The vial was filled with 8 mL UHP, 0.5 mL Teflon-distilled HNO₃, and 0.4 mL trace metal grade HF. The solution was taken to dryness by heating on a hotplate at 80°C inside a fume hood as described previously. After the first step, 2 mL UHP, 0.3 mL Teflon-distilled HNO₃, 0.3 mL Teflon-distilled HCl, and 0.1 mL trace metal grade HF were added and again

taken to dryness. The residue was then rinsed into an acid cleaned narrow-mouth 60 mL LDPE bottle with 50 mL UHP and acidified to 0.024M HNO₃. San Joaquin soil (NIST Standard Reference Material #2709) was initially used to assess digestion method efficiency; however this SRM, and others including MESS-3, require digestion of at least 250 mg of material to be certifiable. This mass is approximately two orders of magnitude greater than that of the samples collected during this study and would require adaptation of the acid recipe to achieve complete digestion producing certifiable results. This study was interested in analytical precision rather than accuracy, therefore, the use of SRMs was discontinued. All digestion series are assumed to have the same efficiency.

Major anion analysis

Extracts were analyzed using a Dionex ICS-2000 ion chromatograph equipped with the IonPac AS18 hydroxide-selective anion-exchange column for soluble nitrate, (detection limit = 0.6 μM; precision = 0.73%), sulfate (detection limit = 0.5 μM; precision = 0.63%), and oxalate (detection limit = 0.6 μM; precision = 1.31%). The eluant was 23 mM KOH with the temperature controlled at 30°C. Time of analysis was 14 min.

Trace element analysis

The soluble and insoluble aerosol fractions were measured in the acidified subsamples on a magnetic-sector high resolution inductively coupled plasma mass spectrometer (HR ICP-MS; Thermo Element XR) located in UCSC's Marine Analytical Laboratory. The ICP-MS provides several analytical advantages over other methods because of its ability to analyze small volume samples for multiple elements over a large dynamic range in a short amount of time (Upadhyay et al. 2009 and references therein). A calibration curve was constructed for each analytical run derived from the analysis of external standards. Elements were calibrated across a wide concentration range to allow for the analysis of both soluble aerosol extracts and insoluble aerosol digests during the same analytical run. Standards and blanks were measured multiple times during the runs and these repeat analyses were used to calculate analytical precision (RSD) and the detection limit (3σ). Analytical precision was generally less than 1%. All data were corrected using data from field blanks, which were blank filters washed and handled in the same manner as the sample filters.

Statistical analysis

The nonparametric Friedman test was used because it allows for the comparison of several independent sets of data without the requirement that those data be normally distributed (Miller and Miller 2000). The test was applied to the soluble concentration of anions per cubic meter of collected air and the trace element fractional solubility in percent values. The Friedman test is a two-way method that allows for the effects of two factors, the treatment and the block, to be tested. In this case, the treatment was the filter type and the block was the sampling interval. Variability in the data were introduced through differences in the filters as well as differences in the aerosols collected during each interval. By block-

ing the aerosol samples together by sampling interval, this noise is removed from the evaluation and only differences resulting from the filters remain. This “randomized block design” is equivalent to matching paired samples (Helsel and Hirsch 2002). The Friedman test requires a balanced design meaning there must be one observation per treatment-block. This requirement precludes the inclusion of any data from sampling periods wherein any one observation was less than the detection limit or a sample was lost for any reason. The null hypothesis for this method was that the filter types had no effect on solubility. In cases where the Friedman test rejected the null hypothesis when applied to all four filter types, multiple comparisons of the possible sample population combinations were made to determine which filter types were significantly different.

When applicable, the paired *t* test was used to assess whether a statistical difference existed between two popula-

tions of samples, e.g., trace element solubility from period C. This test requires that the differences between the paired values have a normal distribution. The exact form of the non-parametric sign test was used for non-normally distributed paired data. The Grubb’s test was used to test for outlier data from the four samples collected during a single 72-h sampling interval ($n = 4$). These outliers were not included in any statistical tests. All tests were run at the 95% confidence interval.

Assessment

Aerosol sources

In a previous study of Gulf of Aqaba aerosols, Chen et al. (2008) devised a six sector classification scheme to characterize air mass back-trajectories (AMBTs) reaching the study site. These sectors were defined as North Africa, Arabian Peninsula, local region, Western Europe, Eastern Europe, and Mediterranean Sea (Fig. 1). The general

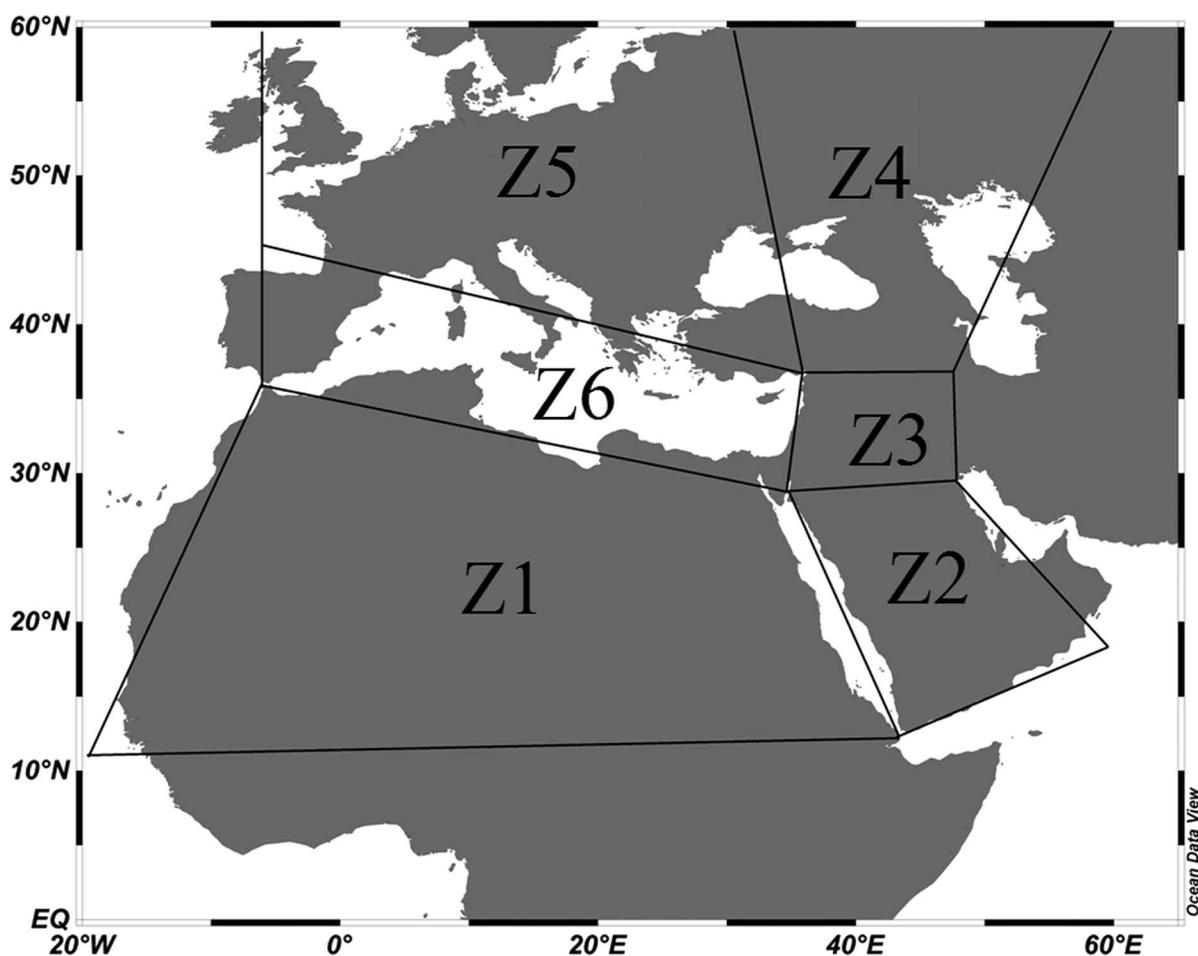


Fig. 1. Five-day air mass back-trajectories for samples collected at Eilat, Israel, were classified based on transport path. Z1–North Africa, Z2–Arabian Peninsula, Z3–Local region, Z4–Eastern Europe, Z5–Western Europe, Z6–Mediterranean Sea. The general aerosol sources were assigned to a sector based on the residence time (>60% of total time) in a particular sector over the last 5 d of transport. This figure and classification method were adapted from Chen et al. (2008).

aerosol sources were assigned to a sector based on the residence time (>60% of total time) in a particular sector over the last 5 d of transport. That classification scheme was used to define samples collected during this study. The majority of samples collected during the filter type comparison originated over the Mediterranean Sea (72%) with the remainder transported from North Africa (8%), the Arabian Peninsula (4%), Eastern Europe (10%), and also sources in the local region (6%). As noted by Chen et al. (2008), Mediterranean air flows may be influenced by European anthropogenic and/or African crustal aerosols before and during their time over the marine environment. Aerosol source region was not correlated with trace element solubility.

Filter blank concentrations

The digested filter blank concentrations (nM) are reported in Table 2. The means $\pm 1\sigma$ are reported for multiple measurements greater than the detection limit. In some cases, only one measurement was greater than the instrument detection limit. The mean blank concentrations were used to calculate blank to sample molar ratios for samples collected on each filter type, also reported in Table 2, and shown as percentages. Digested blanks that were lower than the detection limit are reported as less than or equal to the respective limit and that value was used to calculate the blank to sample ratio. The blank to sample ratios were generally low, often on the order of a few percent. The most notable exception to this pattern was the Cu blanks in the MCE and GN-6 digests, which

Table 2. The blank concentration of each filter type was measured in strong acid digests. This blank was applied to each sample concentration and a mean blank:sample ratio was calculated for all of the samples for each filter type. The ratio of the blank to the minimum sample concentration is reported for each filter type. All concentrations are in nM. Values without an accompanying standard deviation indicate a single blank filter was above the detection limit.

| Filter type <i>n</i> = # of blanks | PC 4 | PCTE 5 | MCE 3 | GN-6 3 | HPWP 7 | PTFE 5 |
|---------------------------------------|------------------|-------------------|------------------|-------------------|------------------|-------------------|
| Al Digest Blank | 565 \pm 540 | 422 \pm 345 | 3540 \pm 70.4 | 2690 \pm 1420 | 330 \pm 160 | 1120 \pm 754 |
| Blank/Min. Sample % | 3.3% | 2.5% | 8.2% | 16.3% | 1.0% | 3.0% |
| Mean Blank/Sample % | 1.2% \pm 0.7% | 1.0% \pm 0.7% | 2.9% \pm 2.2% | 4.9% \pm 3.4% | 0.3% \pm 0.1% | 1.3% \pm 0.7% |
| P Digest Blank | \leq 94.6 | \leq 70.4 | \leq 110 | \leq 110 | 672 \pm 94.5 | 959 \pm 180 |
| Blank/Min. Sample % | 9.9% | 6.6% | 18.7% | 21.7% | 29.9% | 17.6% |
| Mean Blank/Sample % | 2.7% \pm 2.1% | 1.4% \pm 1.1% | 2.8% \pm 2.8% | 2.6% \pm 2.6% | 7.7% \pm 7.0% | 9.7% \pm 4.1% |
| Ti Digest Blank | 32.2 \pm 34.3 | 19.7 \pm 5.3 | 132 \pm 24.5 | 19.5 | 24.7 \pm 32.6 | 54.9 \pm 39.3 |
| Blank/Min. Sample % | 2.9% | 2.6% | 16.4% | 3.3% | 1.9% | 2.9% |
| Mean Blank/Sample % | 1.2% \pm 0.6% | 1.0% \pm 0.7% | 5.4% \pm 4.4% | 0.9% \pm 0.7% | 0.6% \pm 0.3% | 0.04% \pm 0.01% |
| V Digest Blank | \leq 3.24 | \leq 2.65 | \leq 2.65 | \leq 2.65 | 3.87 | \leq 1.92 |
| Blank/Min. Sample % | 10.3% | 9.2% | 18.4% | 20.2% | 9.9% | 3.8% |
| Mean Blank/Sample % | 4.6% \pm 2.7% | 3.5% \pm 2.5% | 3.3% \pm 2.7% | 3.0% \pm 2.0% | 2.9% \pm 1.5% | 13.0% \pm 0.3% |
| Mn Digest Blank | \leq 3.42 | \leq 2.68 | \leq 2.68 | \leq 2.68 | 6.63 \pm 5.52 | 3.46 \pm 0.30 |
| Blank/Min. Sample % | 2.4% | 2.0% | 3.6% | 5.0% | 4.4% | 0.9% |
| Mean Blank/Sample % | 1.4% \pm 0.7% | 0.9% \pm 0.6% | 0.7% \pm 0.5% | 0.8% \pm 0.5% | 1.4% \pm 0.7% | 0.5% \pm 0.2% |
| Fe Digest Blank | 41.8 \pm 37.9 | 63.0 \pm 48.8 | 79.0 \pm 24.2 | 102 \pm 51.9 | 73.9 \pm 77.1 | 85.1 \pm 58.3 |
| Blank/Min. Sample % | 0.7% | 0.6% | 1.1% | 1.5% | 0.4% | 0.5% |
| Mean Blank/Sample % | 0.3% \pm 0.2% | 0.2% \pm 0.2% | 0.4% \pm 0.3% | 0.5% \pm 0.3% | 0.1% \pm 0.1% | 0.3% \pm 0.1% |
| Ni Digest Blank | 4.82 \pm 0.12 | \leq 3.97 | \leq 3.97 | \leq 3.97 | 8.0 \pm 10.7 | 2.53 \pm 0.42 |
| Blank/Min. Sample % | 24.5% | 21.8% | 40.5% | 34.2% | 11.6% | 5.2% |
| Mean Blank/Sample % | 12.1% \pm 6.2% | 9.9% \pm 6.5% | 8.8% \pm 6.1% | 7.2% \pm 4.0% | 3.9% \pm 1.8% | 3.2% \pm 1.1% |
| Cu Digest Blank | 4.40 \pm 2.06 | 4.55 \pm 3.20 | 39.7 \pm 3.0 | 41.7 \pm 3.1 | 2.99 | 2.49 \pm 0.61 |
| Blank/Min. Sample % | 18.3% | 16.3% | 40.0% | 79.7% | 40.7% | 3.4% |
| Mean Blank/Sample % | 9.0% \pm 4.4% | 7.6% \pm 4.1% | 24.3% \pm 7.7% | 40.1% \pm 20.4% | 11.0% \pm 4.7% | 2.2% \pm 0.8% |
| Zn Digest Blank | 58.4 \pm 58.9 | 18.5 \pm 5.4 | \leq 5.05 | \leq 5.05 | 23.4 \pm 22.5 | 45.5 \pm 28.0 |
| Blank/Min. Sample % | 18.1% | 26.1% | 15.7% | 14.1% | 23.9% | 9.6% |
| Mean Blank/Sample % | 16.7% \pm 8.4% | 20.0% \pm 12.7% | 3.1% \pm 2.2% | 2.4% \pm 1.5% | 6.2% \pm 3.5% | 6.2% \pm 1.9% |
| Pb Digest Blank | \leq 0.49 | \leq 0.61 | \leq 0.61 | \leq 0.61 | \leq 2.11 | \leq 2.11 |
| Blank/Min. Sample % | 13.0% | 13.9% | 14.2% | 17.4% | 53.2% | 25.5% |
| Mean Blank/Sample % | 2.7% \pm 1.9% | 3.4% \pm 3.0% | 3.1% \pm 1.9% | 2.7% \pm 1.8% | 10.5% \pm 9.7% | 4.2% \pm 2.1% |

had mean ratios of 24% and 40%, respectively. Table 2 also includes ratios of the measured blank to minimum sample for each element and filter pair.

Filter type

Figs. 2-4 and 5-14 show boxplots of the soluble major anionic species and trace elements, as well as the results of the statistical tests for each of the sampling periods. When the null hypothesis was rejected, all of the samples from each treatment group (filter type) were subsequently compared with one another through multiple comparison testing. Following the presentation style of Helsel and Hirsch (2002), cases wherein the treatment groups were not found to significantly differ are denoted by shared letters positioned beneath the boxplots.

Filter type was a source of significant differences for each of the major anions and 58% of the sampling periods. Sulfate was found to be affected most often with three of the four sampling periods showing differences. Oxalate and nitrate were significantly different in half of the sampling periods. Filter type also introduced significant differences in trace element solubility observations 60% of the time and for all elements but one. Only Ni solubility was found to be uninfluenced by filter type. The results of the multiple comparison testing are discussed below.

Discussion

Extraction method

Aerosol measurements have the greatest value to the larger oceanographic community when they are easily compared with other observations. Comparability is especially important given the recent recognition of the significant role source material plays in aerosol solubility (e.g., Journet et al. 2008; Schroth et al. 2009; Sholkovitz et al. 2009; Aguilar-Islas et al. 2010; Paris et al. 2011). Standardizing methodology is vital to reducing the variability in solubility estimates, and using a common extraction solvent is the logical first step in achieving that goal. Ultrapure deionized water is the ideal solvent because of its analytical versatility as well as its ubiquitous availability in laboratories and at sea. Other solvents have been used to mimic specific environmental conditions or meet certain analytical criteria. These extraction strategies have scientific merit and should be continued in conjunction with UHP extractions to, not only recognize that the former may be desirable in some situations, e.g., seawater extractions to quantify the effects of varying concentrations of Fe binding ligands, but that the latter provides data that is intercomparable and valuable to the broader community.

Filter type

The observed concentrations of soluble anions were influenced by filter type. Sulfate concentrations were significantly different during sampling periods A, B, and C (Fig. 2). HPWP samples were found to most often differ during the first sampling period and were only in agreement with the PCTE samples. The HPWP samples were generally higher than those col-

lected on the other substrates. This trend continued during the second sampling period when the HPWP samples differed significantly from the other three treatment groups and were again somewhat higher in concentration. During period C, PC samples were found to differ from GF/F, Quartz, and PTFE. Each of these showed higher concentrations of sulfate than the PC samples. None of the filter types were significantly different during period D, however PC concentrations were again lower and HPWP higher.

Oxalate observations also tended to be higher in samples collected on HPWP filters, although not significantly so during period A (Fig. 3). During period B, PC and HPWP samples differed from PCTE and GN-6 samples. The four filter types deployed during period C did not significantly differ but the quartz samples' values spanned a wider range than the other treatment groups. The treatment groups of period D were significantly different as a whole but the PC and GN-6 and the HPWP and PTFE treatment groups agreed with one another, respectively. The latter pair had higher concentrations.

Nitrate concentrations from the first two sampling periods were not significantly different and the trend of higher concentrations from HPWP samples was not observed (Fig. 4). The data were significantly different in periods C and D. The former showed lower concentrations in PC samples, which differed from the other three treatment groups. The latter also found lower concentrations in the PC samples. It has been argued that polycarbonate filters are the preferable substrate for collecting aerosol nitrate samples, as opposed to filters made of quartz or PTFE, because there is less uncertainty introduced by evaporation and adsorption. However, this effect is confounded by the particle mass of the sample and meteorological conditions (Chen et al. 2007 and references therein). We could not quantify the impact of these effects, and therefore, are unable to dismiss them as possible sources of the observed differences.

Filter type also contributed to differences in trace element solubility in nearly all cases. Nickel was the only element for which no significant differences were found (Fig. 5). However, due to the balanced design requirement of the Friedman test, period D only included two observations from each treatment group. Conversely, Cu solubility had significant differences in each of the four sampling periods (Fig. 6). During period A, the data followed a bimodal pattern with the MCE and GN-6 samples in agreement and the PCTE and HPWP agreeing with one another. The latter pair had higher median solubilities. The GN-6 samples from period B were significantly different than the other three treatment groups. The GN-6 medians were the highest but also included statistical outliers on the high and low ends, indicating significant spread in the data that was not observed in the other treatment groups. Samples from period C were also significantly different but, as explained above, these filter types were extracted using different methods by necessity; therefore the observed differences cannot be solely attributed to filter type. In period D, the PC and HPWP samples were found to

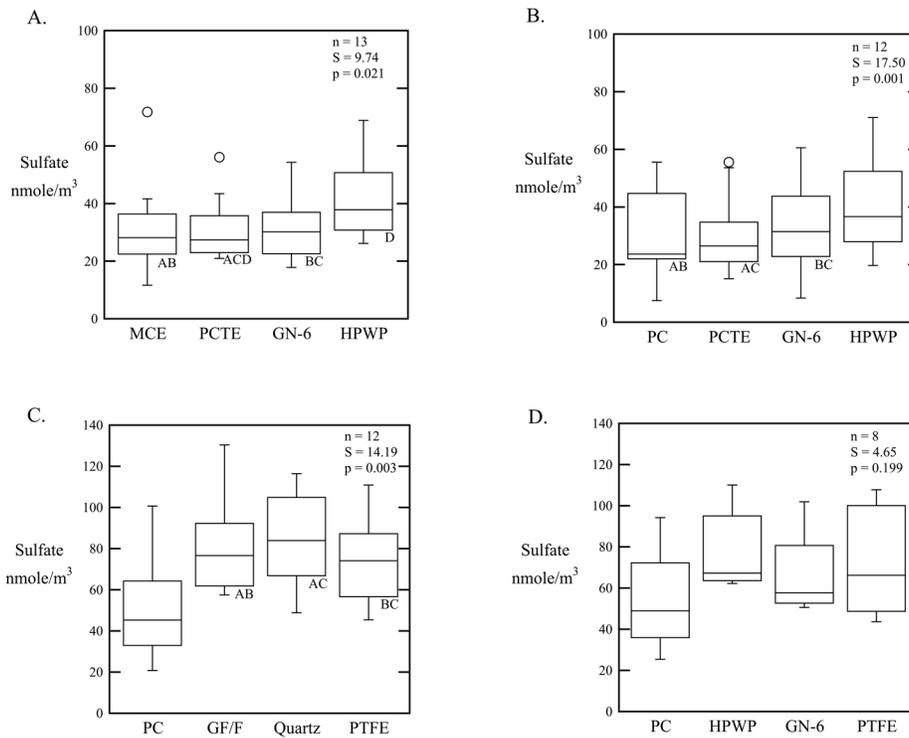


Fig. 2. Boxplots of the soluble aerosol sulfate concentrations for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

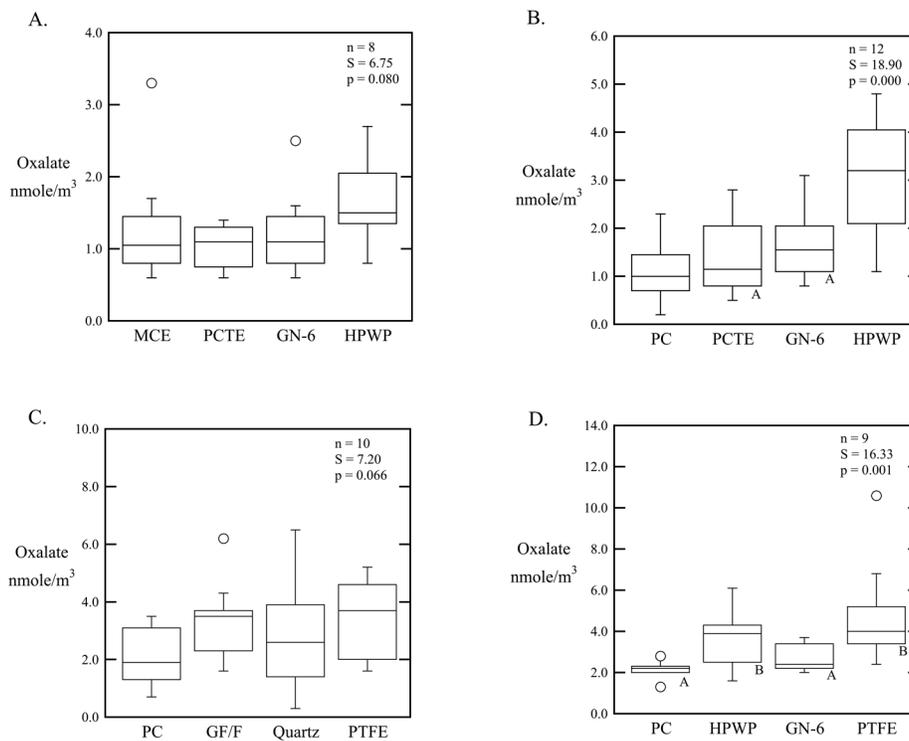


Fig. 3. Boxplots of the soluble aerosol oxalate concentrations for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

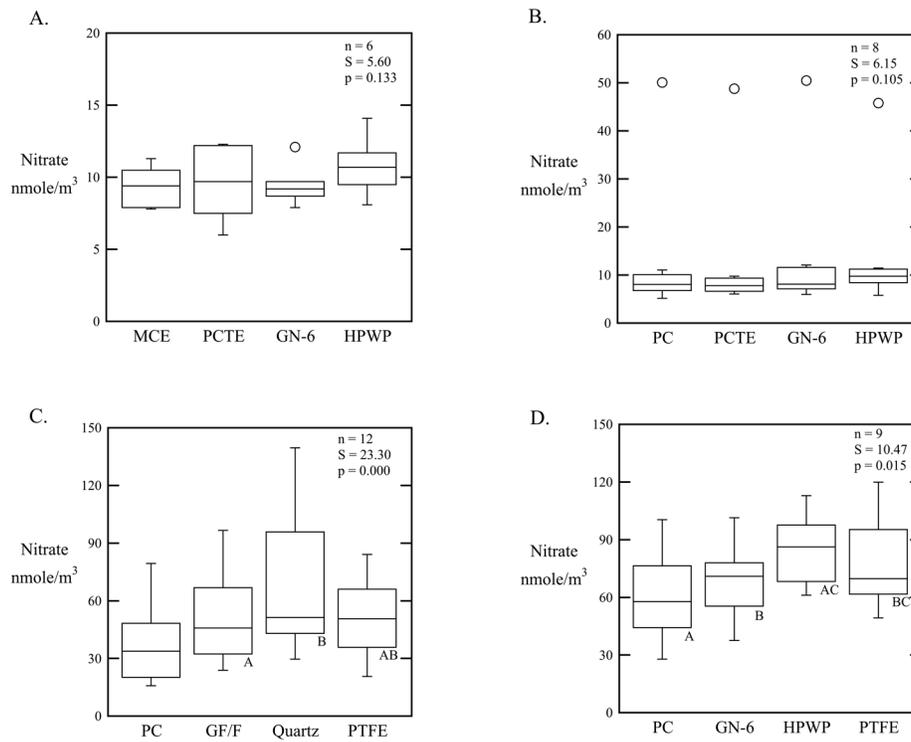


Fig. 4. Boxplots of the soluble aerosol nitrate concentrations for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

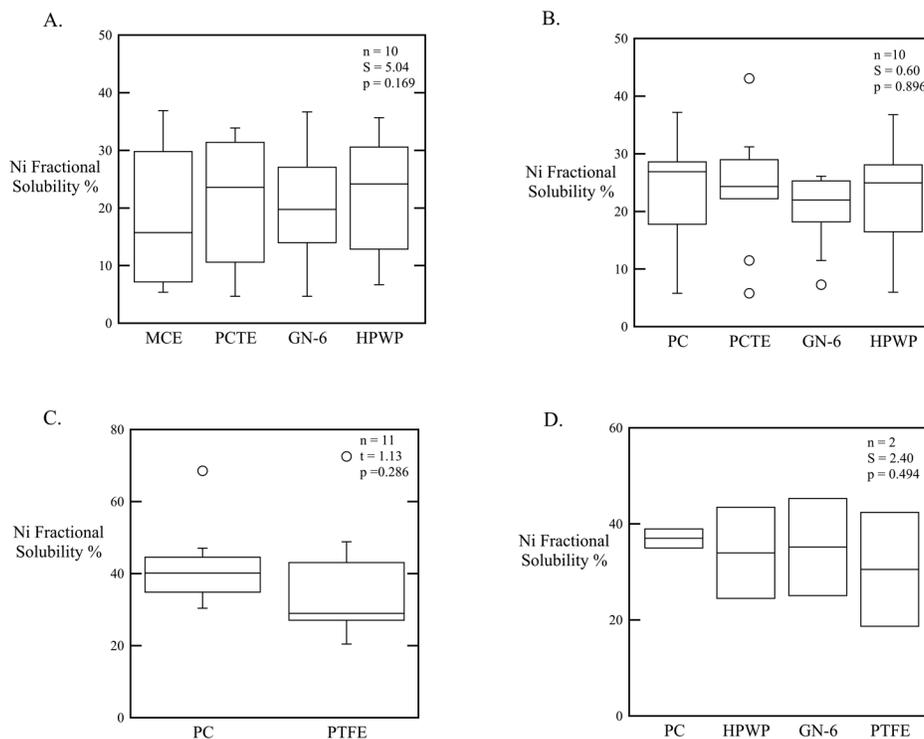


Fig. 5. Boxplots of the aerosol Ni fractional solubilities for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

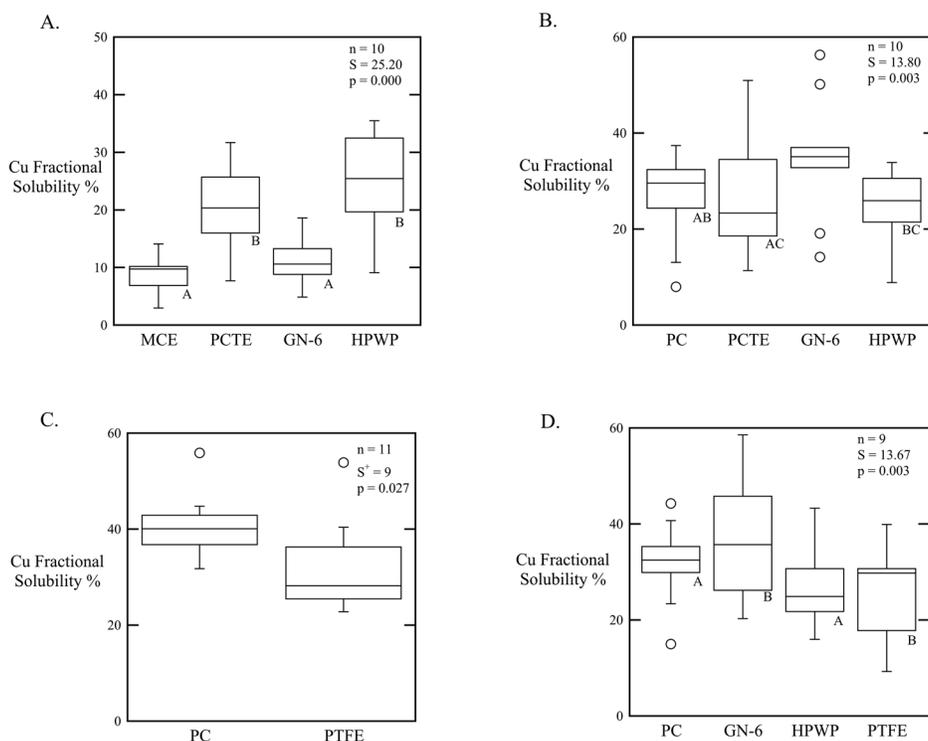


Fig. 6. Boxplots of the aerosol Cu fractional solubilities for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

agree while GN-6 and PTFE agreed. As in period B, the GN-6 samples encompassed a wider range of solubility values than the other concurrently collected treatment groups.

The solubility of four of the trace elements of interest, Ti, V, Fe, and Zn, were found to differ significantly during two of the four sampling periods. Titanium (Fig. 7) and Fe (Fig. 8) were both significantly different during periods B and D. In both cases, the variability in observations was less than a few percent. During period B, the Ti observations were highest for GN-6 samples, which agreed with the PC samples. The treatment groups were again in agreement during period D and the GN-6 samples had the highest median. For Fe, period B's HPWP samples had the lowest solubility and were only found to agree with the PCTE samples. During period D, the Fe solubility observations followed the same pattern as Ti with the PC and GN-6 samples being greater than the HPWP and PTFE samples. The fractional solubilities of V (Fig. 9) and Zn (Fig. 10) were impacted by filter type during periods C and D. This result is most apparent in the widely different results for Zn solubility measurements on PC and PTFE filters with solubility approximately three times greater on PC samples. Again, the differing extraction methods may have contributed to the observed differences. These filter types are included in period D and whereas the differences in the data were not as great, they remain significantly different. The remaining

trace elements, Al (Fig. 11), P (Fig. 12), Mn (Fig. 13), and Pb (Fig. 14), showed significant differences most of the time. Period C's PC and PTFE samples were the only examples found to be similar for Al, P, and Mn. Lead solubility, on the other hand, was significantly different during period C but not so during period B.

All filter types had low blank-to-sample ratios with few exceptions. Nickel, Cu, and Zn were more prone to high blank concentrations. Without analytical motivation to choose one filter over the others, operational factors may be considered. One drawback of PC and PCTE filters is that they are prone to absorbing a static electrical charge making these filters difficult to handle. The more substantial HPWP, GN-6, and MCE filter are considerably easier to handle, a characteristic that is potentially valuable in the field, but these carbon-based filters may introduce complications if used to collect samples of organic aerosols.

Comments and recommendations

It is necessary for the marine aerosol community to produce data that are both consistent and accurate to "establish the range of fractional solubility of key atmospheric components and the process that underlie that variability" (SCOR Working Group 2006). The work presented here demonstrates that the choice of filter substrate can have significant impact on trace element solu-

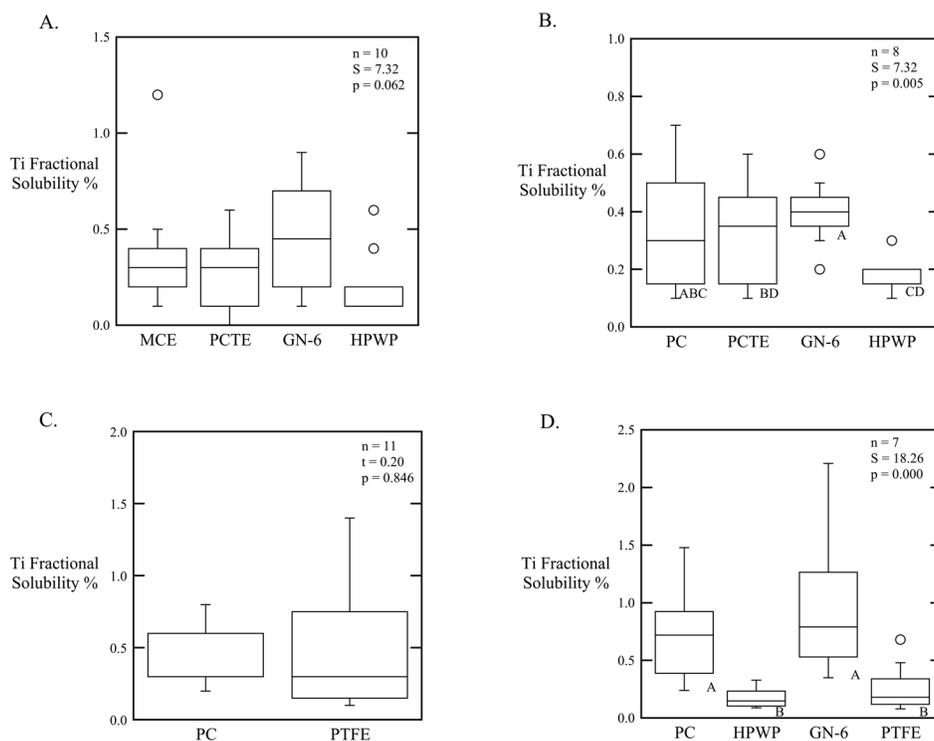


Fig. 7. Boxplots of the aerosol Ti fractional solubilities for each of the four sampling periods. The results of the Friedman and paired t tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

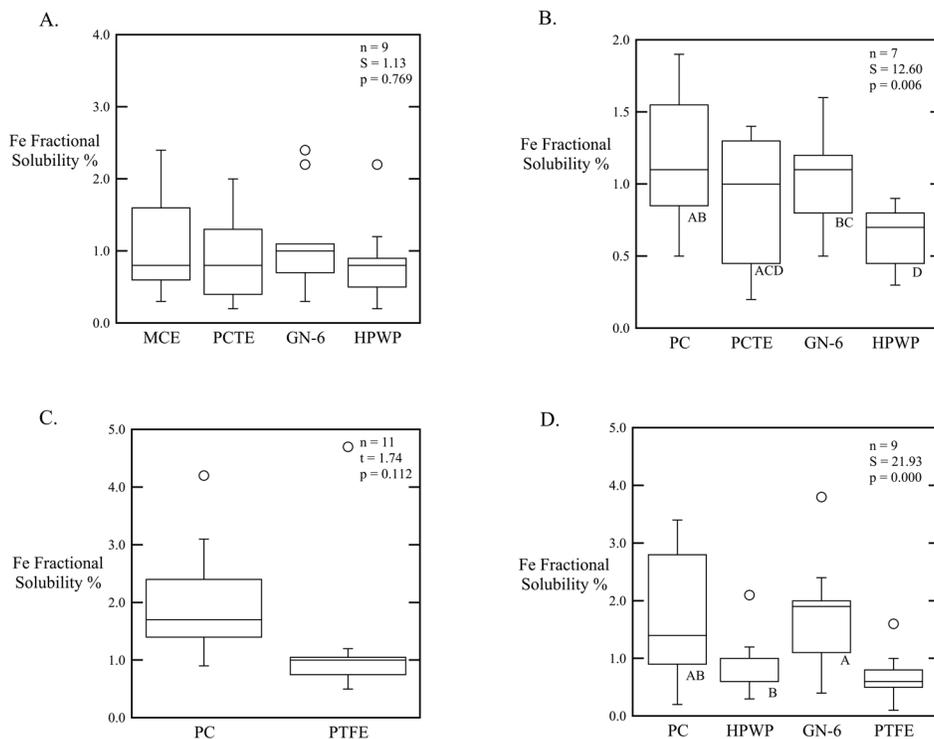


Fig. 8. Boxplots of the aerosol Fe fractional solubilities for each of the four sampling periods. The results of the Friedman and paired t tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

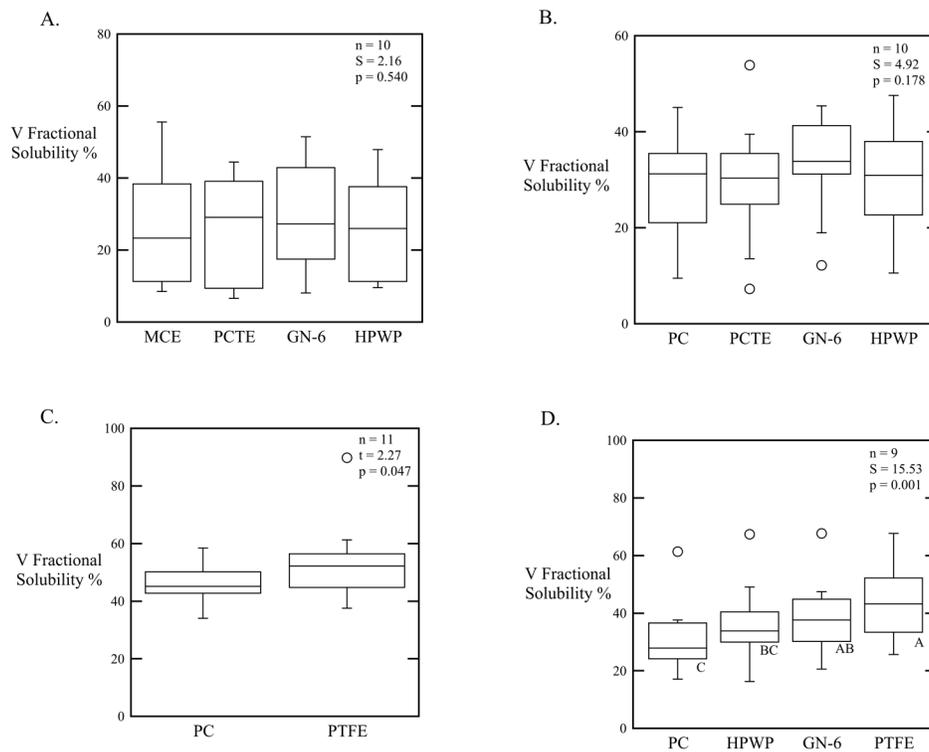


Fig. 9. Boxplots of the aerosol V fractional solubilities for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

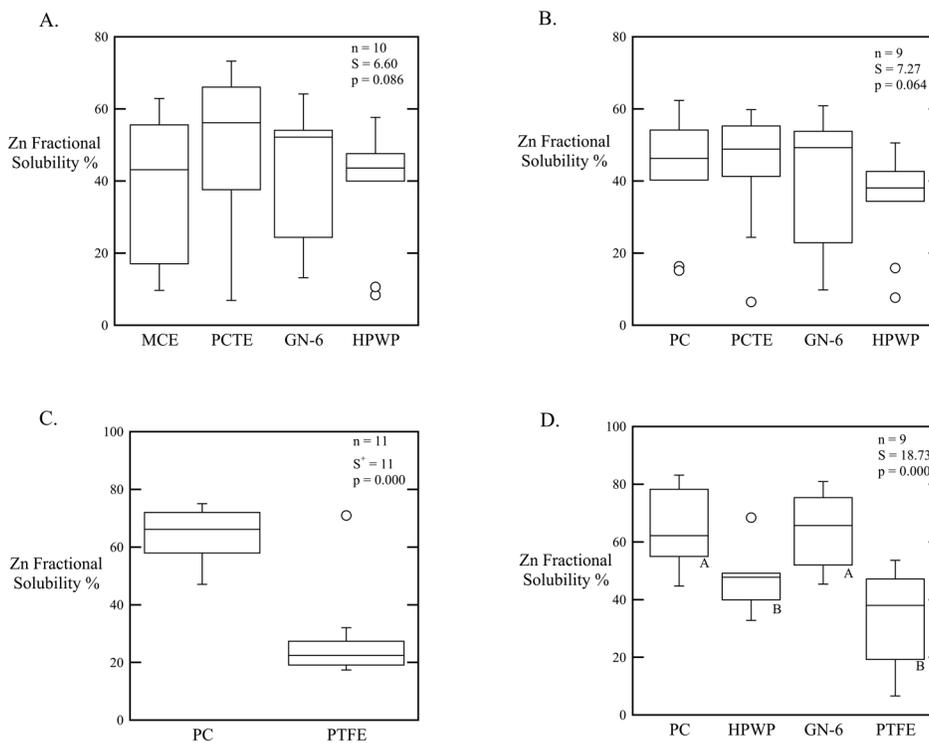


Fig. 10. Boxplots of the aerosol Zn fractional solubilities for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

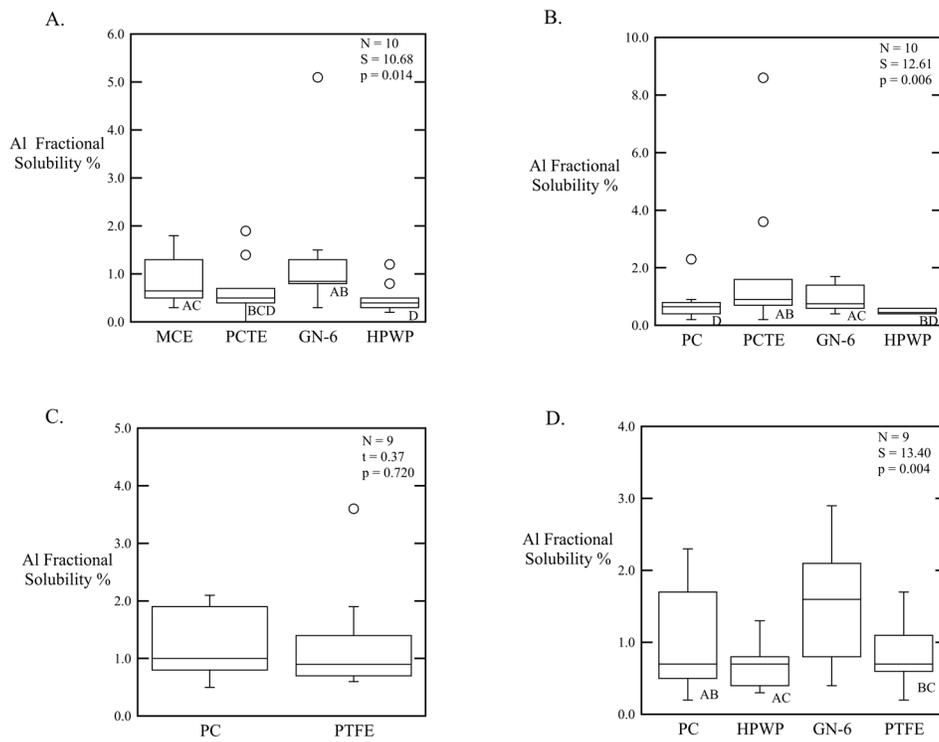


Fig. 11. Boxplots of the aerosol AI fractional solubilities for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

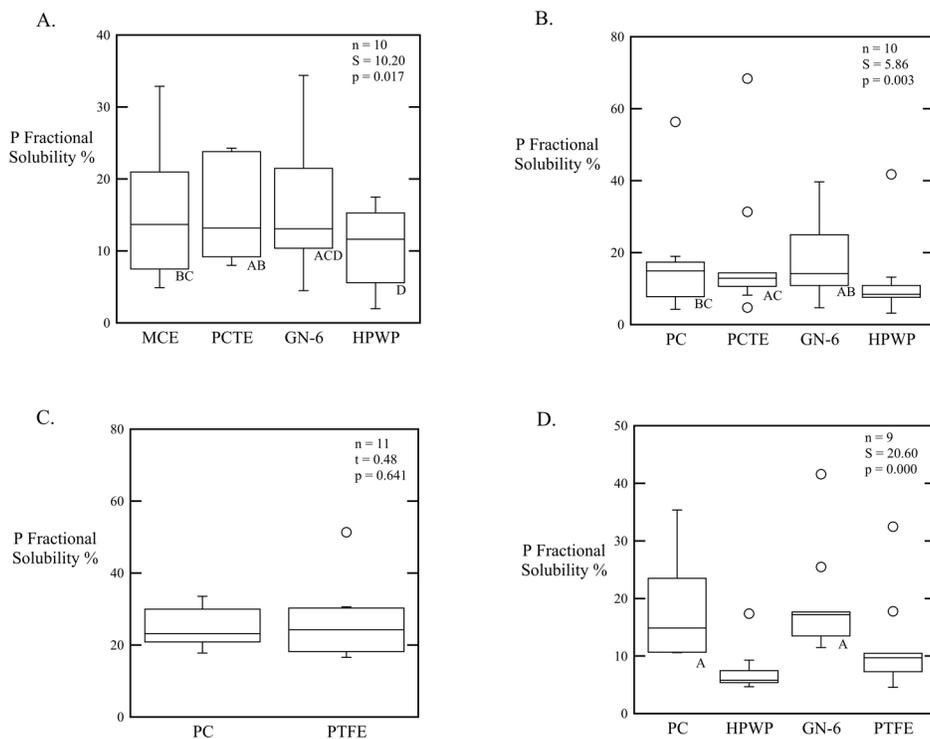


Fig. 12. Boxplots of the aerosol P fractional solubilities for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

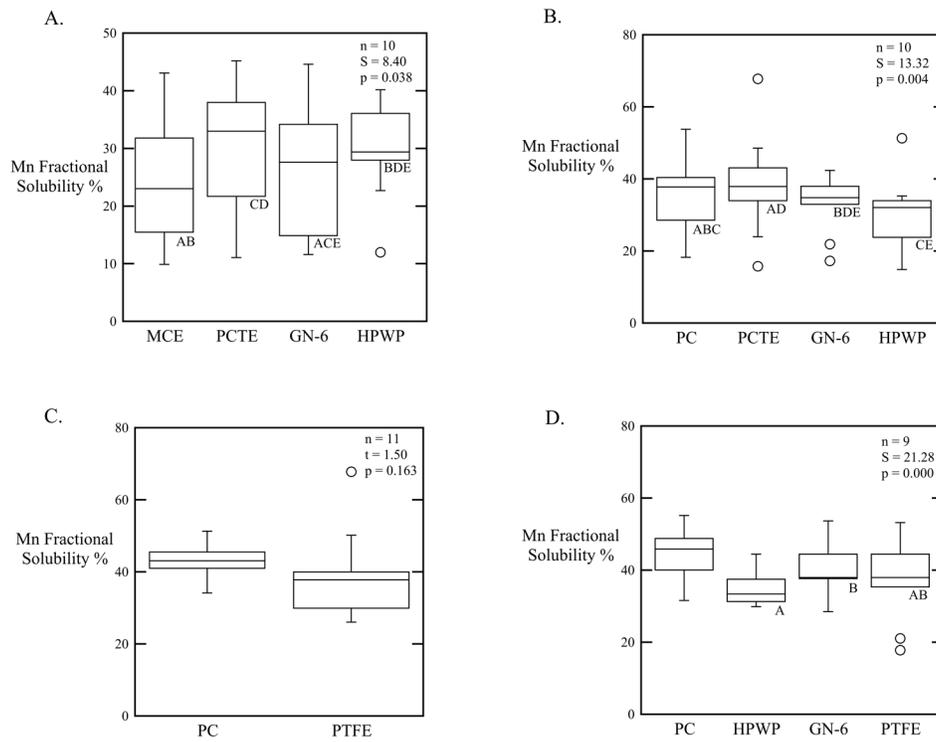


Fig. 13. Boxplots of the aerosol Mn fractional solubilities for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

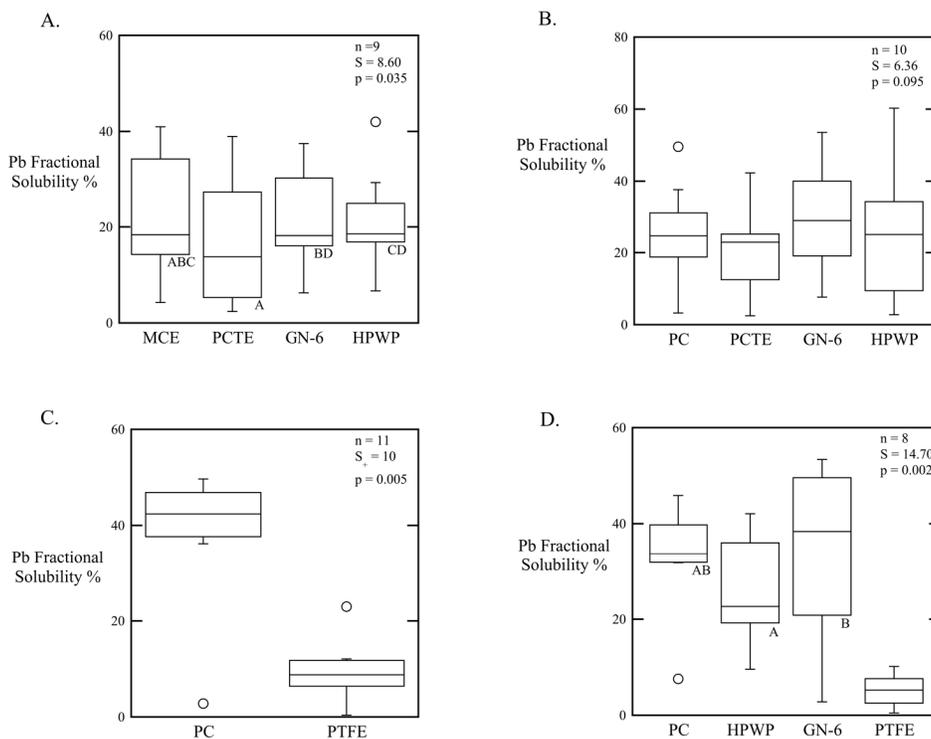


Fig. 14. Boxplots of the aerosol Pb fractional solubilities for each of the four sampling periods. The results of the Friedman and paired *t* tests are shown. Filter types that are not significantly different are identified by shared letter codes that are found beneath the individual boxplots. (A) Period A: 12 Mar–10 May 2009, (B) Period B: 14 May–25 Jun 2009, (C) Period C: 28 Jun–23 Aug 2009, (D) Period D: 27 Aug–6 Dec 2009.

bility observations. Multiple filter types continue to be used by the community hampering intercomparison. Likewise, there is currently no consensus as to the most appropriate extraction solvent. Ultrapure deionized water was chosen for this study because this solvent is commonly available to the general community and offers analytical flexibility. Other solvents have scientific value and should continue to be used; however, aerosol solubility studies should include a common method to produce data sets that are intercomparable.

The design of this study was limited to four filters per sampling period due to limitations in the sampling system. The use of additional 47 mm filter heads (Measures et al. 2010) or larger filters would alleviate this limitation (Morton et al. in press). As this study shows, statistical tests are available that allow for the comparison of multiple independent groups of data. Experiments should be designed to include as many replicates as the sampling system allows, thereby maximizing the power of the statistical tests. Inclusion of additional replicates would also allow for observation of the variability derived from the extraction procedure as well as natural variability related to nonhomogenous distribution of the aerosols on the filters.

References

- Aguilar-Islas, A. M., J. Wu, R. Rember, A. Johansen, and L. M. Shank. 2010. Dissolution of aerosol-derived iron in seawater: Leach solution chemistry, aerosol type, and colloidal iron fraction. *Mar. Chem.* 120:25-33 [doi:10.1016/j.marchem.2009.01.011].
- Baker, A. R., and P. L. Croot. 2010. Atmospheric and marine controls on aerosol iron solubility in seawater. *Mar. Chem.* 120:4-13 [doi:10.1016/j.marchem.2008.09.003].
- Bergametti, G., E. Remoudaki, R. Losno, E. Steiner, B. Chatenet, and P. Buatmenard. 1992. Source, transport and deposition of atmospheric phosphorus over the Northwestern Mediterranean. *J. Atmos. Chem.* 14:501-513 [doi:10.1007/BF00115254].
- Boyd, P. W., and others. 2000. A mesoscale phytoplankton bloom in the polar southern ocean stimulated by iron fertilization. *Nature* 407:695-702 [doi:10.1038/35037500].
- Buck, C., W. Landing, J. Resing, and G. Lebon. 2006. Aerosol iron and aluminum solubility in the northwest Pacific Ocean: Results from the 2002 IOC cruise. *Geochem. Geophys. Geosyst.* 7:4 [doi:10.1029/2005GC000977].
- , W. Landing, J. Resing, and C. Measures. 2010. The solubility and deposition of aerosol Fe and other trace elements in the North Atlantic Ocean: Observations from the A16N CLIVAR/CO2 repeat hydrography section. *Mar. Chem.* 120:57-70 [doi:10.1016/j.marchem.2008.08.003].
- Capone, D.G., and E. J. Carpenter. 1982. Nitrogen fixation in the marine environment. *Science* 217:1140-1142 [doi:10.1126/science.217.4565.1140].
- Chen, Y., and R. L. Siefert. 2004. Seasonal and spatial distributions and dry deposition fluxes of atmospheric total and labile iron over the tropical and subtropical North Atlantic Ocean. *J. Geophys. Res.* 109 [doi:10.1029/2003JD003958].
- , J. Street, and A. Paytan. 2006. Comparison between pure-water- and seawater-soluble nutrient concentrations of aerosols from the Gulf of Aqaba. *Mar. Chem.* 101:141-152 [doi:10.1016/j.marchem.2006.02.002].
- , S. Mills, J. Street, D. Golan, A. Post, M. Jacobson, and A. Paytan. 2007. Estimates of atmospheric dry deposition and associated input of nutrients to Gulf of Aqaba seawater. *J. Geophys. Res.* 112 [doi:10.1029/2006JD007858].
- , A. Paytan, Z. Chase, C. Measures, A. J. Beck, S. A. Sanudo-Wilhelmy, and A. F. Post. 2008. Sources and fluxes of atmospheric trace elements to the Gulf of Aqaba, Red Sea. *J. Geophys. Res.* 113 [doi:10.1029/2007JD009110].
- Coale, K. H., and others. 1996. A massive phytoplankton bloom induced by ecosystem-scale iron fertilization experiment in the equatorial Pacific Ocean. *Nature* 383:495-501 [doi:10.1038/383495a0].
- Draxler, R. R., and G. D. Rolph. 2003. HYSPLIT (Hybrid Single-Particle Lagrangian Integrated Trajectory) Model. NOAA Air Resour. Lab. <<http://www.arl.noaa.gov/ready/hysplit4.html>>.
- Duce, R. A., and N. W. Tindale. 1991. Atmospheric transport of iron and its deposition in the ocean. *Limnol. Oceanogr.* 36(8):1715-1726 [doi:10.4319/lo.1991.36.8.1715].
- , and others. 2008. Impacts of anthropogenic atmospheric nitrogen on the open ocean. *Science* 320:893-897 [doi:10.1126/science.1150369].
- Falkowski, P. G., R. T. Barber, and V. Smetacek. 1998. Biogeochemical controls and feedbacks on ocean primary production. *Science* 281:200-206 [doi:10.1126/science.281.5374.200].
- Helsel, D. R., and R. M. Hirsch. 2002. Statistical methods in water resources. *In* Techniques of water-resources investigations of the United States Geological Survey, hydrologic analysis and interpretation. United States Geological Survey. <<http://water.usgs.gov/pubs/twri/twri4a3/>>
- Herut, B., M. D. Krom, G. Pan, and R. Mortimer. 1999. Atmospheric input of nitrogen and phosphorus to the Southeast Mediterranean: Sources, fluxes, and possible impact. *Limnol. Oceanogr.* 44:1683-1692 [doi:10.4319/lo.1999.44.7.1683].
- , M. Nimmo, A. Medway, R. Chester, and M. D. Krom. 2001. Dry atmospheric inputs of trace metals at the Mediterranean coast of Israel (SE Mediterranean): sources and fluxes. *Atmos. Environ.* 35:803-813 [doi:10.1016/S1352-2310(00)00216-8].
- Hsu, S.-C., and others. 2010. Sources, solubility, and dry deposition of aerosol trace elements over the East China Sea. *Mar. Chem.* 120:116-127 [doi:10.1016/j.marchem.2008.10.003].
- Huang, H.-L., and S. Yang. 2006. Filtration characteristics of polysulfone membrane filters. *Aerosol Sci.* 37:1198-1208 [doi:10.1016/j.jaerosci.2005.11.010].
- Jickells, T. D., and others. 2005. Global iron connections

- between desert dust, ocean biogeochemistry, and climate. *Science* 308:67-71 [doi:10.1126/science.1105959].
- Journet, E., K. V. Desboeufs, S. Caquineau, and J. -L. Colin. 2008. Mineralogy as a critical factor of dust iron solubility. *Geophys. Res. Lett.* 35, L07805 [doi:http://dx.doi.org/10.1029/2007GL031589]
- Karthikeyan, S., U. M. Joshi, and R. Balasubramanian. 2006. Microwave assisted sample preparation for determining water-soluble fraction of trace elements in urban airborne particulate matter: Evaluation of bioavailability. *Anal. Chim. Acta.* 576:23-30 [doi:10.1016/j.aca.2006.05.051].
- Krishnamurthy, A., J. K. Moore, C. Luo, and C. S. Zender. 2007. The effects of atmospheric inorganic nitrogen deposition on ocean biogeochemistry. *J. Geophys. Res.* 112 [doi:10.1029/2006JG000334].
- Mackey, K. R. M., R. G. Labiosa, M. Calhoun, J. H. Street, A. F. Post, and A. Paytan. 2007. Phosphorus availability, phytoplankton community dynamics, and taxon-specific phosphorus status in the Gulf of Aqaba, Red Sea. *Limnol. Oceanogr.* 52:873-885 [doi:10.4319/lo.2007.52.2.0873].
- Mahowald, N., and others. 2005. Atmospheric global dust cycle and iron inputs to the ocean. *Global Biogeochem. Cycles.* 19 [doi:10.1029/2004GB002402].
- , and others. 2008. Atmospheric iron deposition: global distribution, variability, and human perturbations. *Annu. Rev. Mar. Sci.* 1:245-278 [doi:10.1146/annurev.marine.010908.163727].
- Martin, J. H., R. M. Gordon, and S. E. Fitzwater. 1990. Iron in Antarctic waters. *Nature* 345:156-158 [doi:10.1038/345156a0].
- Measures, C. I., T. Sato, S. Vink, S. Howell, and Y. H. Li. 2010. The fractional solubility of aluminum from mineral aerosols collected in Hawaii and implications for atmospheric deposition of biogeochemically important trace elements. *Mar. Chem.* 120:144-153 [doi:10.1016/j.marchem.2009.01.014].
- Miller, J. N., and J. C. Miller. 2000. *Statistics and chemometrics for analytical chemistry*, 4th ed. Pearson.
- Mills, M. M., C. Ridame, M. Davey, J. La Roche, and R. J. Geider. 2004. Iron and phosphorus co-limit nitrogen fixation in the eastern tropical North Atlantic. *Nature* 429:292-294 [doi:10.1038/nature02550].
- Morel, F. M. M., and N. M. Price. 2003. The biogeochemical cycles of trace metals in the oceans. *Science* 300:944-947 [doi:10.1126/science.1083545].
- Morton, P. M., and others. In press. Results from the 2008 GEOTRACES aerosol intercalibration study. *Limnol. Oceanogr. Methods.*
- Olgun, N., and others. 2011. Surface ocean iron fertilization: The role of airborne volcanic ash from subduction zone and hot spot volcanoes and related iron fluxes into the Pacific Ocean. *Global Biogeochem. Cycles* 25 [doi:10.1029/2009GB003761].
- Paris, R., K. V. Desboeufs, and E. Journet. 2011. Variability in dust iron solubility in atmospheric waters: Investigation of the role of oxalate organic complexation. *Atmos. Env.* 45:6510-6517 [doi:10.1016/j.atmosenv.2011.08.068].
- Paytan, A., and others. 2009. Toxicity of atmospheric aerosols on marine phytoplankton. *PNAS* 106:4601-4605 [doi:10.1073/pnas.0811486106].
- Pekney, N. J., and C. I. Davidson. 2005. Determination of trace elements in ambient aerosol samples. *Anal. Chim. Acta* 540:269-277 [doi:10.1016/j.aca.2005.03.065].
- Prospero, J. M., and others. 1996. Atmospheric deposition of nutrients to the North Atlantic Basin. *Biogeochemistry* 35(10):27-73 [doi:10.1007/BF02179824].
- Rolph, G. D. 2003. Real-time Environmental Applications and Display sYstem (READY). NOAA Air Resour. Lab. <<http://www.arl.noaa.gov/ready/hysplit4.html>>.
- Schroth, A. W., J. Crusius, E. R. Sholkovitz, and B. C. Bostick. 2009. Iron solubility driven by speciation in dust sources to the ocean. *Nat. Geoscience.* 2:337-340 [doi:10.1038/ngeo501].
- SCOR Working Group. 2006. GEOTRACES: an international study of the marine biogeochemical cycles of trace elements and their isotopes science plan. ISSN 1932-7951.
- Sedwick, P., E. Sholkovitz, and T. Church. 2007. Impact of anthropogenic combustion emissions on the fractional solubility of aerosol iron: Evidence from the Sargasso Sea. *Geochim. Geophys. Geosyst.* 8:10 [doi:10.1029/2007GC001586].
- Shelley, R. U., and others. 2012. Controls on dissolved cobalt in surface waters of the Sargasso Sea: Comparisons with iron and aluminum. *Global Biogeochem. Cycles* 26 [doi:10.1029/2011GB004155].
- Sholkovitz, E. R., P. N. Sedwick, and T. M. Church. 2009. Influence of anthropogenic combustion emissions on the atmospheric deposition of soluble aerosol iron to the oceans: Empirical estimates for island sites in the North Atlantic Ocean. *Geochim. Cosmochim. Acta* 73:3981-4003 [doi:10.1016/j.gca.2009.04.029].
- , P. N. Sedwick, and T. M. Church. 2010. On the fractional solubility of copper in marine aerosols: Toxicity of aeolian copper revisited. *Geophys. Res. Lett.* 37 [doi:10.1029/2010GL044817].
- , P. N. Sedwick, T. M. Church, A. R. Baker, and C. F. Powell. 2012. Fractional solubility of aerosol iron: synthesis of a global-scale data set. *Geochim. Cosmochim. Acta* 89:173-189 [doi:10.1016/j.gca.2012.04.022].
- Sohm, J. A., E. A. Webb, and D. G. Capone. 2011. Emerging patterns of marine nitrogen fixation. *Nat. Rev. Microbiol.* 9(7):499-508 [doi:10.1038/nrmicro2594].
- Upadhyay, N., B. Majestic, P. Prapaipong, and P. Herckes. 2009. Evaluation of polyurethane foam, polypropylene, quartz fiber, and cellulose substrates for multi-element analysis of atmospheric particulate matter by ICP-MS. *Anal. Bioanal. Chem.* 394:255-266 [doi:10.1007/s00216-009-2671-6].
- Wagener, T., C. Guieu, R. Losno, S. Bonnet, and N. Mahowald. 2008. Revisiting atmospheric dust export to the Southern

Hemisphere ocean: Biogeochemical implications. *Global Biogeochem. Cycles* 22 [doi:10.1029/2007GB002984].

Yeatman, S. G., L. J. Spokes, P. F. Dennis, and T. D. Jickells. 2001. Can the study of nitrogen isotopic composition in size-segregated aerosol nitrate and ammonium be used to investigate atmospheric processing mechanisms? *Atmos.*

Environ. 35:1337-1345 [doi:10.1016/S1352-2310(00)00457-X].

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