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Methods for the sampling and analysis of marine aerosols: results from the 2008 GEOTRACES aerosol intercalibration experiment

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Abstract

Atmospheric deposition of trace elements and isotopes (TEI) is an important source of trace metals to the open ocean, impacting TEI budgets and distributions, stimulating oceanic primary productivity, and influencing biological community structure and function. Thus, accurate sampling of aerosol TEIs is a vital component of ongoing GEOTRACES cruises, and standardized aerosol TEI sampling and analysis procedures allow the comparison of data from different sites and investigators. Here, we report the results of an aerosol analysis intercalibration study by seventeen laboratories for select GEOTRACES-relevant aerosol species (Al, Fe, Ti, V, Zn, Pb, Hg, NO_3^-, and SO_4^{2-}) for samples collected in September 2008. The collection equipment and filter substrates are appropriate for the GEOTRACES program, as evidenced by low blanks and detection limits relative to analyte concentrations. Analysis of bulk aerosol sample replicates were in better agreement when the processing protocol was constrained (± 9% RSD or better on replicate analyses by a single lab, $n = 7$) than when it was not (generally 20% RSD or worse among laboratories using different methodologies), suggesting that the observed variability was mainly due to methodological differences rather than sample heterogeneity. Much greater variability was observed for fractional solubility of aerosol trace elements and major anions, due to differing extraction methods. Accuracy is difficult to establish without an SRM representative of aerosols, and we are developing an SRM for this purpose. Based on these findings, we provide recommendations for the GEOTRACES program to establish consistent and reliable procedures for the collection and analysis of aerosol samples.

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Atmospheric deposition is an important source of micro-

and macro-nutrients to the open ocean (Okin et al. 2011) and is a key component of the international GEOTRACES program (GEOTRACES Planning Group 2006). A priority of the GEOTRACES program is to quantify both major and trace elements (e.g., Al, Fe, Ti, V, Zn, Pb, and Hg) and species such as nitrate and sulfate in marine aerosols. Therefore, marine aerosol samples collected during GEOTRACES cruises must follow sampling protocols that permit the collection and analysis of as many elements and compounds as possible, while meeting the constraints associated with basin-wide oceanographic cruises (e.g., space limitations, high-frequency sampling, etc.).

In this study, seventeen laboratories analyzed replicate aerosol samples collected at a single site (Miami, Florida, USA) in September 2008, when Saharan dust is likely to be observed in the southeastern United States after crossing the Atlantic Ocean (Prospero 1999). By selecting these dates and this location, the aerosols collected in Miami could reasonably be expected to have a mixed marine, lithogenic, and anthropogenic composition (Zamora et al. 2011), similar to the mixed aerosol composition expected during basin-wide GEOTRACES cruises.

To develop protocols for more precise and internally consistent aerosol data for GEOTRACES, our specific objectives were to test and intercalibrate high-volume bulk and size-fractionated aerosol sampling equipment during a field experiment, and solicit collaborators from the US and abroad for the purposes of comparing analytical methods. Here, we report the findings of the 2008 GEOTRACES aerosol intercalibration for a selection of major and trace elements and compounds in bulk and size-fractionated aerosols, and recommend protocols for atmospheric sampling and analysis for use on GEOTRACES cruises to the international GEOTRACES community.

Materials and procedures

Aerosol collection equipment

We selected an aerosol sampler that could accommodate an assortment of filter types and configurations to concurrently collect the greatest variety of analytes in a single GEOTRACES deployment event. Aerosols were collected with three unmodified, commercially available Volumetric Flow Controlled (VFC) high volume samplers (Tisch Environmental, TE-5170V-BL, Fig. 1). The VFC sampler collects aerosols by filtering air at a flow rate of ca. 1 m^3 min^{-1} (allowing for greater analyte-to-filter blank ratios) and is sturdy enough for heavy weather and extended (> 1 month) deployments at sea (Baker et al. 2006b). The normal TE-3000 (Tisch Environmental) filter holder is designed to sample with a 20 cm × 25 cm sheet for bulk aerosol studies (actual size: 20.3 cm × 25.4 cm) and the sampler also accepts a Sierra-type (high-volume) slotted cascade impactor (Tisch Environmental TE-235) for particle size distribution studies. The cascade impactor is available with as many as six stages (plus the final backing 20 cm × 25 cm filter). During this study, two samplers were outfitted with the normal filter holder for bulk aerosol collection. The third sampler was outfitted with a five-stage impactor, and the nominal particle size cut-offs were 7.2 µm, 3 µm, 1.5 µm, 0.95 µm, and 0.49 µm

Fig. 1. Three Tisch VFC samplers, as deployed on the rooftop of the Rosenstiel School of Marine and Atmospheric Science building at the University of Miami.

diameter. It is important to note that the cascade impactor was deployed without a backing filter (0-0.49 μm particle size). Initial attempts at deploying the backing filter resulted in vacuum readings that exceeded the capacity of the slack-tube manometers provided by the manufacturer (> 40 inches of water). We have since acquired digital manometers with a range of 0-200 inches of water and recommend that other groups using similar sampling equipment do likewise.

The calibration of each unit was regularly checked using a Variable Orifice Calibrator (Tisch Environmental TE-5028A) and two handheld digital manometers (Dwyer Instruments 475-3-FM) to ensure that flow rates were within the technical specifications provided by Tisch Environmental. Flow conversion tables are provided with each sampler, which relate air filtration rates to the reduced pressure under the filter holder.

Filter materials

The choice of filter type depends on the aerosol loading in the region of study, the desired list of analytes, and the design of the sampling equipment. Typical aerosol TEI concentrations vary temporally and spatially by orders of magnitude across an ocean basin. For example, total aerosol Fe concentrations from samples collected from the North Atlantic and Pacific on the recent CLIVAR/Repeat Hydrography cruises were 1.3-4200 ng m^{-3} and total aerosol Al concentrations were 9-5940 ng m^{-3} (Buck et al. 2010; Buck submitted for publication). The VFC sampler is designed to use only high porosity filters, which must have low TEI concentrations (or be capable of being sufficiently cleaned) and be compatible with a variety of analytical methods.

Whatman 41 (W41) cellulose fiber filters used during the SEAREX (e.g., Uematsu et al. 1983) and AEROCE (e.g., Arimoto et al. 1995) programs are appropriate for applications requiring low trace element background levels (Baker et al. 2006a; Baker et al. 2006b). Observed aerosol particle collection efficiency for W41 filters is high, with efficiencies from 95% for 0.2 μm-diameter particles (Stafford and Ettinger 1972) up to 99% for larger aerosol dust (Savoie 1984). In addition, W41 filters are easily subdivided and distributed to multiple investigators as required by intercalibration studies.

However, W41 filters are not appropriate for studies of every GEOTRACES analyte. Volatile analytes such as Hg, water soluble organic carbon and nitrate require filters where background levels can be eliminated through heating and volatilization. For these other species, we used Whatman quartz microfiber filters (QMA), which can be heated in an oven to drive off volatile species. The particle collection efficiency for QMA filters is similar to that of W41 filters (Pszenny et al. 1993), which simplifies direct comparisons of analytes collected on different filter types.

Filter configuration

The VFC sampler can accept different filter types and configurations, for collecting both bulk aerosol and particle size-fractionated samples. Bulk aerosol material was collected using W41 or QMA 20 cm × 25 cm filters. The sheets are held within a frame that covers a ~1 cm border of the sheet, decreasing the effective sampling area to 18.3 cm × 23.4 cm. Size-fractionated samples were collected using W41 slotted impactor filter sheets installed onto the slotted plates of the impactor. Whereas the principles and details behind cascade impactors are discussed elsewhere (Marple and Willeke 1976; McMurry 2000), a brief description follows. Each filter comes pre-cut with ten open slots that allow for ten subsamples per stage. The slotted filters were staggered so that the W41 substrate strips were directly below the slots of the overlying stage. In contrast to the W41 20 cm × 25 cm sheet, the air does not pass through the impactor filters. Instead, the air is accelerated into the cascade impactor through the slots in the top plate. The coarsest particles (7.2 μm) are impacted on the strips of W41 filter substrate that sit directly under the slots as "stripes" of impacted aerosols, whereas particles smaller than 7.2 μm weave with the air through the open slots cut into W41 filter substrate and accelerate through the slightly smaller slots in the second plate. Particles between 3 and 7.2 μm are impacted on the filter strips of the second stage, whereas particles smaller than 3 μm are carried with the air and accelerated through slightly smaller slots in the third stage plate. Particles between 1.5 and 3 μm are then impacted on the third stage filter strips, and so on. Thus, as the air is pulled through the cascade impactor and accelerated through each slotted plate, particles of successively smaller aerodynamic radius are impacted on the filter strips below each plate. Each stage encounters the same volume of air, no matter how many stages are employed. The nominal particle size cut-offs used for the 2008 experiment were 7.2 μm, 3 μm, 1.5 μm, 0.95 μm, and 0.49 μm, and particles less than 0.49 μm are normally collected on a 20 cm × 25 cm W41backing filter.

Filter cleaning procedures

In preliminary tests, acid-washing W41 filters decreased background concentrations of elements such as Al and Fe (data not shown). W41 filters were cleaned according to trace element protocols in a HEPA-filtered laminar flow hood, similar to Baker et al. (2006b). Both 20 cm × 25 cm sheets and slotted impactor configurations were arranged in layers, one filter at a time, between polypropylene mesh. The filters and mesh were placed together into a 0.5 M quartz-distilled HCl (q-HCl) acid bath for 24 h at room temperature. Filters were then removed one at a time from the acid bath using acid-washed plastic tweezers, individually rinsed with ultrahigh purity water (UHP; > 18.2 MΩ cm^{-1}, Barnsted E-pure). After rinsing, the filters were placed into a 2 L bath of UHP water to soak for 24 h and then transferred to a fresh 0.5 M q-HCl bath for 24 h. The filters were soaked and rinsed in this way three times, using a fresh acid bath each time. Finally, the filters soaked in sequential (five to six) freshly made UHP water baths for 24 h, until the measured pH of the bath after soaking matched that of freshly dispensed UHP water (pH 5.4-5.6). The filters were then rinsed under flowing UHP water and left to dry for 12 h, and subsequently stored individually in new plastic zipper bags.

Volatile TEIs from QMA filters were driven off in the following way. Fifteen to twenty QMA filters were placed in an aluminum pan on a layer of amber glass vials. The pan was covered with aluminum foil and baked for 10 h at 480°C. The baked filters were handled with tweezers, individually wrapped in similarly prebaked aluminum foil, and stored in new plastic zipper bags. All filter handling was performed in a HEPA-filtered laminar flow hood and away from potential volatile contaminants (e.g., nitric acid).

Sampling location and deployment

The Tisch VFC samplers were deployed on the rooftop of the Rosenstiel School of Marine and Atmospheric Science (RSMAS)-University of Miami building from 11–21 Sep 2008 in a coastal, urban area (Fig. 1). Three samplers were deployed simultaneously: one for bulk major and trace elements (W41 20 cm × 25 cm sheet); one for organics, major anions and Hg (QMA 20 cm × 25 cm sheet); and one for size-fractionated major and trace elements (W41 impactor). The different types of filters were assigned their own dedicated filter assemblies and high-volume sampler, and they were not interchanged.

Prior to deployment, clean 20 cm × 25 cm filters were loaded into their respective filter holders under a HEPA-filtered laminar flow hood. The filter holders were covered (to prevent filter exposure) until secured in the sampler housing. The high-volume cascade impactor was loaded with five impactor stages, loaded upwards from stage 5 (finest particle size) to stage 1 (coarsest size). The entire assembly was placed into a clean polyethylene bag until secured in the sampler housing. The samplers ran continuously for 24 h to simulate sampling intervals at sea, as implemented during previous research cruises (e.g., Baker et al. 2006b; Buck et al. 2010) and subsequent 2010/2011 U.S. GEOTRACES cruises (the sampling time can be adjusted to accommodate greater or lesser dust loading if necessary).

During sample recovery, the filter assemblies were swapped with duplicate assemblies that had been preloaded with new filters. The recovered filter assemblies were covered and bagged for transport to the laminar flow bench. Filter handling was minimized, and clean room gloves (polyethylene, Fisher: 19-181-533, or white nitrile clean room, VWR: 89130-852) were worn when handling was unavoidable. Any necessary manipulation was performed using clean plastic tweezers and limited to the borders of the filter sheets where particles are not deposited.

The filters were not immediately subsampled, but instead were carefully stored to minimize any contamination or loss of dust. Individual 20 cm × 25 cm filters were folded inwards, so the aerosols were protected. The impactor filters were similarly folded, so that the aerosol-laden strips were folded upon themselves. Each W41filter was placed in two clean polyethylene bags, and each QMA filter was folded inside pre-combusted aluminum foil and bagged in a clean polyethylene bag; both filter types were stored frozen at –20°C.

Sample processing

Filter distribution

The W41 and QMA filters were trimmed to remove the unused 1 cm border, then subdivided into 28 pieces (2.5 cm × 5.7 cm), using a zirconium oxide ceramic knife (Kyocera: FK-075 WH-BK) and scissors (Kyocera: CH-350). Participants were provided subsamples with a unique identifying number, weight, date of collection, and filter type. Results were submitted as ng of element/filter piece and then converted to ng of element/volume of filtered air (or nmol of ion/volume of filtered air) using the following equation:

$$Conc.\left(\frac{ng}{m^3}\right) = Conc.\left(\frac{ng}{mass\ of\ filter\ piece\ (g)}\right) \times \frac{mass\ of\ trimmed\ filter\ (g)}{volume\ of\ filtered\ air\ (m^3)} \quad (1)$$

Each set of impactor samples consists of five W41 impactor substrates (one for each stage), and each substrate has ten stripes of impacted aerosols. Nine of the aerosol stripes are impacted on strips on the impactor substrate that are bordered by a pre-cut slot, while a tenth stripe is located between a single slot and the filter border. Whereas we have assumed for this report that each stripe of the impactor substrate represents one-tenth of the aerosol material collected on the entire substrate (Eq. 2), we have recently confirmed that slightly less aerosol material (75 ± 11% for Fe) is collected on the tenth (border) stripe (as suggested by A.R. Baker unpub. data). This results in a slight overestimate (2.5%) of the aerosol concentration for each size-fraction.

$$Conc.\left(\frac{ng}{m^3}\right) = Conc.\left(\frac{ng}{filter\ strip}\right) \times \frac{10\ filter\ strips}{volume\ of\ filtered\ air\ (m^3)} \quad (2)$$

Filter digestions

Participating laboratories were free to digest and analyze the aerosol samples using their preferred methods. Brief summaries of the methods employed, associated references, and standard reference material (SRM) recoveries are listed in Table 1. In general, all laboratory groups measuring total element concentrations used a combination of HNO_3 and HF to digest the aerosol sample. Heat and/or pressure were applied by digesting the samples in specially designed microwaves (Hassan et al. 2007; Hsu et al. 2008; Measures et al. 2010; Trapp et al. 2010; Upadhyay et al. 2009; Xia and Gao 2010), in sealed Teflon jars on hotplates (see method below; Bowie et al. 2010) or in an oven (Gombert et al. 2004). Participants analyzed the aerosol digest solutions using inductively coupled plasma-mass spectrometry (ICP-MS; quadrupole or magnetic sector), inductively coupled plasma-atomic emission spec-

Table 1. W41 aerosol digestion techniques.

Participant/ Group	Digestion reference	Heat/pressure method	Reagents	Detector	SRM	Al	Ti	Fe	V	Zn	Pb
Aguilar-Islas	This study (modified)	Hotplate	HNO_3, HF	ICP-MS (magnetic sector)	NRCC HISS-1	n.r.	n.r.	92%	n.r.	n.r.	n.r.
Bowie,	Bowie et al. 2010	Hotplate	HNO_3, HF	ICP-MS (magnetic sector)	NRCC MESS-3	87%	0%	88%	93%	91%	105%
van der Merwe, Lannuzel				IRMM BCR-414	144%	0%	100%	104%	95%	99%	
Buck, Paytan	Trapp et al. 2010	Microwave	HNO_3, HF, H_2O_2, H_3BO_3	ICP-MS (magnetic sector)	NIST 2709	62%	90%	73%	96%	78%	87%
Vandermark, Church	This study	Hotplate	HNO_3, HF	ICP-MS (quad)	(none)						
Gao	Xia and Gao 2010	Microwave	HNO_3, HF, H_3BO_3	ICP-MS (magnetic sector)	NIST 1648a	107%	n.r.	103%	104%	102%	96%
Hatta, Measures	Measures et al. 2010	Microwave	HNO_3, HF, H_2O_2, H_3BO_3	FIA (Al only)	USGS AGV-2	94%	n.r.	n.r.	n.r.	n.r.	n.r.
Hsu	Hsu et al. 2008	Microwave	HNO_3, HF	ICP-MS (quad)	NIST 1648	101%	101%	100%	107%	95%	109%
Losno	Gombert et al. 2004	Oven	HNO_3, HF	ICP-AES	(none)						
Morton, Landing	This study	Hotplate	HNO_3, HF	ICP-MS (magnetic sector)	USGS RGM-1	107%	99%	87%	88%	n.r.	93%
				NIST 2704	94%	68%	95%	96%	75%	89%	
Mead	Upadhyay et al. 2009	Microwave	HNO_3, HF	ICP-MS (magnetic sector)	NIST 2709	90%	97%	92%	95%	97%	98%
				NIST 1649a	n.c.	n.c.	92%	87%	104%	105%	
Patey, Achterberg	Hassan et al. 2007	Microwave	HNO_3, HF, HCl, $HClO_4$	ICP-MS (quad)	LOESS GeoPT13	98%	92%	92%	85%	88%	97%
				NIST 2704	94%	68%	95%	96%	75%	89%	

n.r.— not reported
n.c.—not certified

trometry (ICP-AES), or flow-injection analysis (FIA for Al). Most participants certified their digestion efficiency and recovery against some type of SRM.

While other digestion methods have been published and referenced in Table 1, we evaluated several methods at Florida State University (FSU) for simplicity, minimal use of reagents, and ability to completely digest the W41 filter (e.g., Baker et al. 2006a; Sedwick et al. 2007; Trapp et al. 2010). Ultimately, we adopted a digestion method combining HNO_3 and HF, heat, and pressure. Briefly, a W41 filter/aerosol sample was digested and dried-down three times in a 15-mL flat-bottom/round-interior Teflon jar (Savillex: 200-015-20 and 600-033-01); first with HNO_3, next with HNO_3 and HF, and finally with HNO_3 only (all acids were Fisher Optima grade). All filter digestions were performed under a continuous flow of HEPA-filtered air within a Class-1000 clean room (Geochemistry clean lab, National High Magnetic Field Laboratory, Tallahassee, Florida, USA). The masses of the filter and final solution were recorded to the nearest milligram for calculation of the dust concentrations.

Soluble extractions

Participating laboratories used a variety of methods to extract soluble analytes from the W41 and QMA filters (Table 2). These methods are distinguished by the leaching solution, time of exposure, and contact technique (flow-through versus batch leach). Most participants used a simple UHP water extraction, but some also extracted soluble analytes using solutions of formate, ammonium acetate, sodium bicarbonate, or desferrioxamine B (DFB). Aerosol-soluble element concentrations were analyzed using quadrupole or magnetic sector ICP-MS, ICP-AES, and ferrozine/ultraviolet-visible spectrophotometry (Viollier et al. 2000). Concentrations of SO_4^{2-} and NO_3^- (or NO_3^- + NO_2^-) were determined by colorimetry or ion chromatography (Table 2).

Mercury

Total aerosol mercury was analyzed on QMA filters by two laboratories using dual amalgamation cold vapor atomic fluorescence spectrometry (Balcom et al. 2008; Lamborg et al. 1995). Mercury was extracted from the filter pieces using either a mixture of 1.6 M HNO_3 and BrCl (Lamborg et al. 1995) or 4 M HNO_3 and BrCl where the BrCl was added 1 h before analysis (Balcom et al. 2008). Aliquots of this solution were analyzed using purge-and-trap preconcentration of the Hg, first by reaction with hydroxylamine hydrochloride to quench reactive intermediates, then mixed with $SnCl_2$ to reduce Hg(II) to Hg°, followed by sparging and amalgamation onto gold-coated sand. The amalgamated Hg was released from the sand trap by heating and detected by cold vapor atomic fluorescence spectrometry.

Assessment

Table 2. W41 and QMA aerosol soluble extraction techniques.

Participant/ Group	Extraction reference	Solution	Contact method	Extraction	Exposure Time (h)	Backing filter	Anion detector	TM detector
Aguilar-Islas	Aguilar-Islas et al. 2010	UHP water, DFB	Flow-through	Vacuum filtration	instant	0.4 µm PC	n/a	ICP-MS (magnetic sector)
Baker, Chance	Baker et al. 2007	Ammonium acetate, pH 4.7	Submersion	Shaker	1-2	0.2 µm PES	n/a	ICP-AES/ICP-MS (quad)
Buck, Paytan	Chen et al. 2006	UHP water	Submersion	Sonication	0.5	0.4 µm PC	Ion chromatography	ICP-MS (magnetic sector)
Hastings	Yeatman et al. 2001	UHP water	Submersion	Sonication	1		Colorimetry	n/a
Hsu	Hsu et al. 2010	UHP water	Submersion	Shaker	1	0.4 µm Nuclepore	Ion chromatography	ICP-MS (quad)
Johansen	Johansen et al. 2000	Formate, pH 4.2	Submersion	Shaker	instant	0.2 µm syringe	n/a	UV-Vis ferrozine Viollier et al. 2000
Losno		UHP water	Submersion	Vacuum filtration	instant	0.2 µm PC	n/a	ICP-AES
Morton, Landing	Buck et al. 2006	UHP water	Flow-through	Vacuum filtration	instant	0.025 µm GN6	Ion chromatography	ICP-MS (quad)
Zamora	Baker et al. 2003, Aminot and Andrieux 1996	$NaHCO_3$, pH 8.6	Submersion	Shaker	24	0.2 µm PES	Colorimetry Zhang et al. 1997	n/a

Abbreviations: UHP, ultrahigh purity; DFB, desferrioxamine B; PC, polycarbonate; PES, polyethersulfone; GN6, mixed cellulose ester (Pall)

Blanks and detection limits

Preliminary blank comparisons between washed and unwashed W41 filters before the 2008 experiment indicated that acid-washing greatly decreased the background levels of some TEIs. However, in subsequent tests conducted during this exercise, background TEI concentrations in unwashed filters generally agreed with those reported by other groups (e.g., Upadhyay et al. 2009) and were as low as or lower than concentrations found in washed filters for Al, Ti, V, and Zn (Table 3). In addition, filter blank replicate precision for Al, Ti, Fe, V, Zn, and Pb was better in unwashed filters than in washed filters, resulting in lower detection limits in unwashed filters. Higher blanks and detection limits in washed filters may have resulted from the necessarily greater handling of filters during the washing process. While there may be some variation in analyte concentrations among filter batches, careful handling of unwashed filters may be sufficient to yield blanks and detection limits that are low enough for open-ocean aerosol studies. Following the previously published recommendations for acid-washing W41 filters, all of the tests conducted in this exercise used acid-washed W41 filters, and Table 4 shows blanks for acid-washed impactor filters.

A typical volume of air collected during a 24-h deployment (ca. 1400 m^3) is used to calculate filter blanks for aerosol samples, to compare them to the aerosol TEI concentrations on a "per cubic meter of air" basis. In general, all filter blank concentrations and detection limits (3*s* of filter blanks; Table 3) are well below aerosol concentrations reported for the Pacific and Atlantic oceans. As stated above, marine aerosols are often collected over 24-h sampling periods (e.g., Baker et al. 2006b; Buck et al. 2010; Trapp et al. 2010; Zamora et al. 2011), but if the concentration of a specific TEI is expected to approach the detection limit, then the sampling time can be increased accordingly.

Bulk aerosol: total concentrations

Bulk aerosol TEI concentrations were determined from total digestions of W41 filter pieces, according to the methods in Table 1. The resulting trends in TEI concentrations across the 11 sampling days were similar for all groups (Fig. 2), and no single group consistently reported the highest or lowest value. From these results, several conclusions can be drawn about filter types, minimum digestion conditions and sample variability.

Filter type

The similar trends in day-to-day variability observed for the different TEIs (Fig. 2) reflect natural variations in aerosol loading for each sampling period, indicating that W41 filters are an appropriate substrate for operationally-defined aerosol trace element sample collection. Quartz-fiber filters were not specially cleaned and handled for trace element analysis like the W41 filters, as background concentrations of many TEIs within the QMA filter material were expected to be 50-100 times higher than in marine aerosols (Upadhyay et al. 2009). One participant performed a total digest of the QMA filters to gauge their suitability for trace metal analysis. In general, the

Table 3. Comparison of unwashed versus washed W41 filters: blanks and detection limits (FSU reporting).

Element	Average (ng cm^{-2})		Average* (ng m^{-3})		Detection Limit† (ng m^{-3})		RSMAS 2008 (ng m^{-3})	
	Unwashed	Washed	Unwashed	Washed	Unwashed	Washed	Minimum	Maximum
Al	9.59	20.71	2.84	6.12	1.36	7.94	16.4	268.7
Ti	1.62	4.15	0.48	1.23	0.09	0.98	3.0	26.5
Fe	18.87	4.15	5.58	1.23	0.62	0.46	38.6	192.1
V	0.013	0.014	0.004	0.004	0.007	0.002	2.18	5.85
Zn	0.78	1.04	0.23	0.31	0.10	0.35	4.0	134.8
Pb	0.054	0.032	0.016	0.010	0.015	0.016	0.21	2.18

*Filter blanks in units of "ng m^{-3}" were calculated assuming a typical 24-h filtered air volume of 1400 m^3 and are shown for comparison with bulk aerosol concentrations from the 2008 RSMAS intercalibration.
†Detection limit reported as 3*s* of the blanks (n = 5 for unwashed filters, n = 8 for washed filters).

Table 4. Size-fractionated W41 blanks and detection limits (all groups reporting).

	Size-fractionated (W41 slotted impactor)		
Element	Average (ng cm^{-2})	Average* (ng m^{-3})	Detection Limit (3*s*) (ng m^{-3})
Al	7.57	0.660	1.242
Ti	1.71	0.149	0.385
Fe	8.36	0.729	1.928
V	0.056	0.005	0.009
Zn	1.878	0.164	0.280
Pb	0.554	0.048	0.368

*Filter blanks in units of "ng m^{-3}" were calculated assuming a typical 24-h filtered air volume of 1400 m^3 and are shown for comparison against observed aerosol concentrations.

Al and Fe concentrations within the QMA filter material overwhelmed any contribution from the aerosol material. Therefore, QMA filters are not recommended for major and trace element studies of marine aerosols (except as required by certain analytes such as Hg, organic compounds, and nitrate).

Minimum digestion conditions

While digestion methods varied (Table 1), most laboratories used a mixture of HNO_3 and HF, along with heat and/or pressure. The influence of HF and pressure were tested separately by one laboratory using two digestion protocols: (a) HNO_3 acid only, with heat (140°C) and pressure (6 bar); and (b) HNO_3 and HF, with heat (140°C) but in an open digestion vessel (no pressure). Neither method efficiently recovered Ti, found in the refractory minerals titanite ($CaTiSiO_5$) and rutile (TiO_2) (Castillo et al. 2008; Moreno et al. 2006; Yarincik et al. 2000). Most Ti concentrations from digestions of the 2008 RSMAS aerosol samples using HNO_3, heat, and pressure (without HF) were below detection limit, and results from digestions using HNO_3, HF, and heat (without pressure) were the lowest of all reported values for all days but one (Fig. 2). Concentrations of Al, Fe, V, and Zn by these alternative methods were within the range of concentrations determined using digestion methods that included HNO_3, HF, heat, and pressure (Table 1). It appears that near-complete recoveries of many TEIs can be obtained using a digestion method that includes a combination of HNO_3 and heat with either HF or pressure. However, as observed in the case of Ti, the use of HNO_3, HF, heat, and pressure are recommended to avoid risk of incomplete recoveries of more refractory elements.

Sample variability

Table 5 summarizes the range of precisions determined through replicate analyses within a laboratory and among all labs. Variability in TEI concentrations may result from several factors, including analytical uncertainty and sample heterogeneity. Table 5 shows the relative standard deviation (RSD), determined from all reported values, except those omitted as outliers among all values for a single day as determined by the Grubbs outlier test (P = 0.05). Ultimately, only five outliers were omitted: three values (out of 103) for total Al concentrations, one value (out of 113) for total Fe concentrations, and one value (out of 94) for total Zn concentrations. Analyses of replicate filter subsamples by a single laboratory were treated as individual values when calculating the RSD of all values. It is important to note that all but two groups reported filter subsample masses, which were used to correct for differences in filter subsample size. Those groups that did not report filter masses were assigned an average value of 1/28th of the total (filter pieces averaged 0.1232 g ± 4.6% RSD). Relative precision for duplicate samples (n = 2) is reported as relative percent difference (RPD) and was calculated by the following formula:

$$\textit{Relative percent difference } (RPD) = \frac{x - \bar{x}}{\bar{x}} \times 100\% \qquad (3)$$

Overall, single-laboratory precision (n = 2) was better than precision among laboratories, suggesting that variations in the actual digestion procedure and analysis of the samples contribute significantly to differences in values. However, a single laboratory reporting 0.1% RPD for a pair of replicates from one day would also report 9.8% RPD for a pair of replicates from another day at similar concentrations (Zn; 15 Sep 08 versus 12 Sep 08), which suggests at least some heterogeneity of aerosol distribution over a filter.

One might predict that TEIs associated with coarser (lithogenic) particles, such as Al and Fe, would demonstrate greater

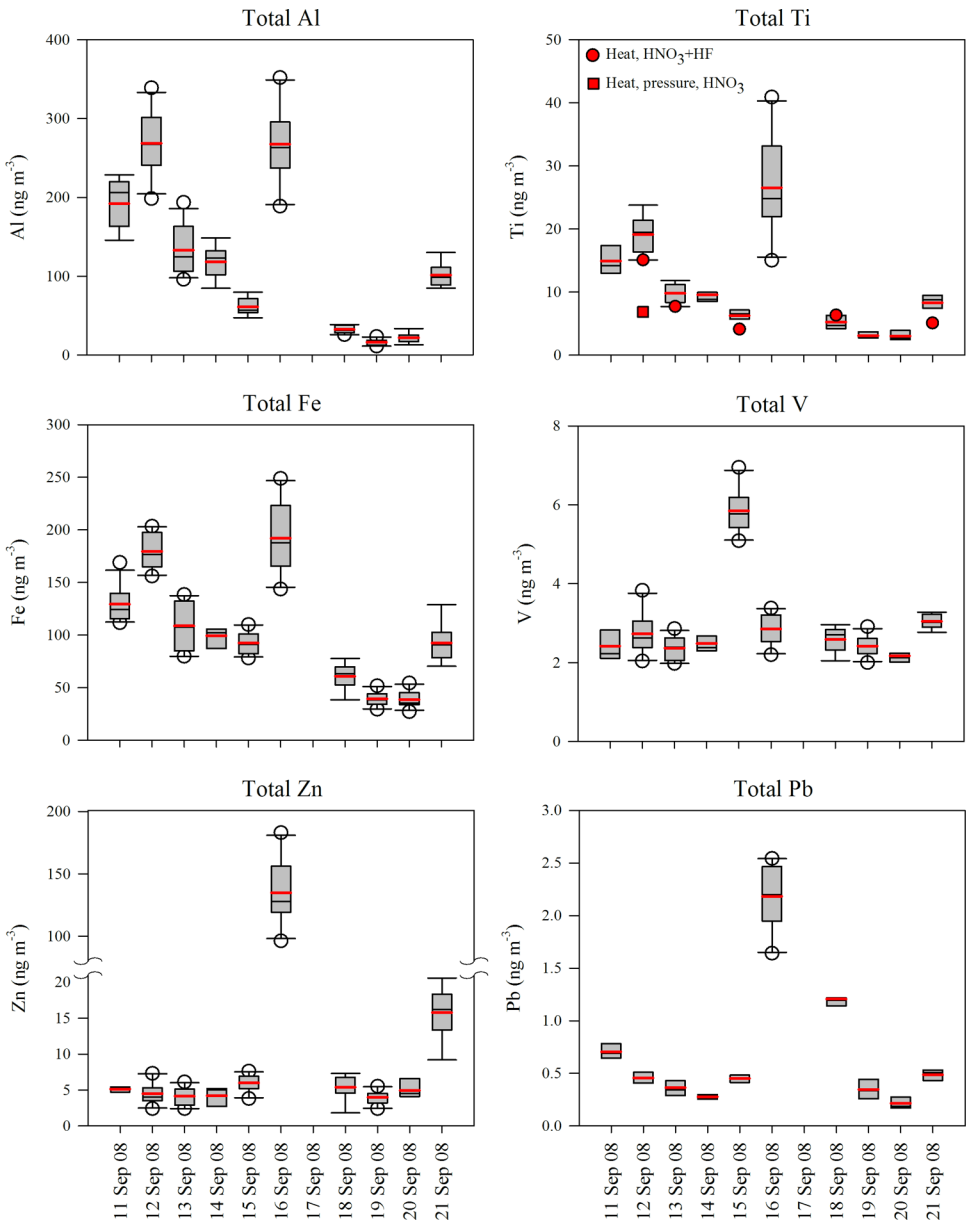

Fig. 2. Box-and-whisker plots of total aerosol concentrations (W41 filters) of Al, Ti, Fe, V, Zn and Pb, from 11–21 Sep 08. Filled boxes show the 25th to 75th percentiles, whereas whiskers show the 10th to 90th percentiles (when $n \geq 9$). Open circles represent values outside the 10th to 90th percentiles. Inside each box, the black line shows the median and the red line shows the mean. (Ti only) Red-filled circles represent heated, unpressurized HNO_3 + HF digestions (included in averages); red-filled squares represent heated, pressurized HNO_3 only digestions (not included in averages).

heterogeneity in the distribution over a filter than those TEIs associated with finer (anthropogenic) particles, such as V. However, the RPD values for most elements were similar, regardless of their association with coarse or fine fraction particles. Furthermore, a large RSD among laboratories for a given day (e.g., 20.2% RSD for V: 12 Sep 08) was not necessarily accompanied by a similarly large variability reported by a single laboratory (e.g., 0.7% RPD for V: 12 Sep 08), which would indicate heterogeneous aerosol distribution on the filter.

However, statistically significant variability is poorly established when only duplicate (n = 2) samples are compared. To better assess sample homogeneity, a single participant analyzed seven replicates from a single day (21 Sep 08) for total element concentrations (Table 6). Replicate precision was 4.8-8.3% RSD for all elements, suggesting that sample heterogeneity does not contribute more than 4.8-8.3% of the variability for this day, depending on the TEI. Precision among laboratories was worse than single-laboratory precision for all elements but V. When agreement among laboratories is poorer than expected based on single-laboratory precision, sample heterogeneity is likely not the cause of the observed variation, and the remaining variability likely results from differences in analytical and

Table 5. Range of precision for W41 total aerosol concentrations within laboratories and among laboratories, all days (11–21 Sep 08).

Element	Single-laboratory precision (n = 2; relative % difference)	Precision among laboratories (n = 4–13; % RSD)
Al	0.0–20.2%	14.2–28.4%
Ti	0.3–20.0%	10.4–37.3%
Fe	0.0–20.1%	9.3–21.2%
V	0.0–21.2%	5.9–20.2%
Zn	0.1–21.2%	18.6–39.4%
Pb	0.6–21.2%	6.5–33.4%

Single laboratory precision is described by the analytical uncertainty on replicate determinations by individual laboratories, expressed as RPD on mean of replicate determination, where RPD = $(x - \bar{x})/\bar{x} \times 100\%$. Precision among laboratories is described by the overall analytical uncertainty expressed as %RSD on mean of all determinations made by participating laboratories.

Table 6. Range of precision (as % RSD) within a single laboratory and among multiple laboratories; only for samples from 21 Sep 08.

Element	Single laboratory precision (n = 7)	Precision among laboratories (n = 5–9)
Al	5.2%	14.2%
Ti	5.7%	11.2%
Fe	5.3%	19.5%
V	8.3%	5.9%
Zn	7.4%	22.2%
Pb	4.9%	11.5%

methodological practice among labs, such as variable digestion recoveries (e.g., Fe) or contamination (e.g., Zn).

Bulk aerosol solubility

The soluble concentrations of bulk aerosol TEIs were determined on W41 subsamples using a wider variety of methods than the total aerosol analyses (summarized in Table 2). It is likely that the variety of soluble extraction methods coupled with relatively low TEI concentrations resulted in the high variability observed in reported soluble values (Fig. 3, Table 7). For some elements, the differences are dramatic, where extractions using ammonium acetate recovered ~36% to 98% of total Pb as soluble Pb, ten times as much as other extraction methods (~1% to 11%). For other elements, such as V, different extraction methods all appear to recover similar fractions. On the other hand, the cause of variability is more difficult to assign for soluble Ti recoveries, where one group using submersion extraction with UHP water reported ~50-100 times higher soluble Ti fractions than another group using a similar method, despite both groups reporting reasonable analytical figures of merit (e.g., appropriate detection limits, certification against reference materials, etc.). Only a few laboratories reported occasional replicate (n = 2) values, but single-laboratory precision was much better (lower %RPD) than precision among laboratories (higher %RSD), reinforcing the conclusion that variability among methods at the different laboratories was a significant contributor to the poor precision for soluble aerosol Ti.

A previous investigation into the influence of differing aerosol solubility methods has shown that the nature of the aerosol material (e.g., mineral dust versus anthropogenic aerosols) has a greater effect on aerosol Fe solubility than differences in the extraction technique (Aguilar-Islas et al. 2010). In the 2008 RSMAS intercalibration project, participants extracted aerosol-soluble TEIs using a variety of methods on subsamples taken from the same aerosol filters; therefore, differences in aerosol composition should not be a factor.

Previous work has shown that extractions using UHP water recover significantly more aerosol-soluble TEIs than extractions using seawater (Buck et al. 2010; Buck et al. 2006; Chen et al. 2006). Conversely, Aguilar-Islas et al. (2010) reported higher aerosol Fe solubility in seawater versus UHP water due to the presence of Fe-binding ligands in seawater. No differences in aerosol-soluble Fe concentrations or percent Fe solubilities were observed in the 2008 RSMAS samples among flow-through leaches using UHP water (Buck et al. 2006), filtered seawater, and UHP water + 2 nM desferrioxamine B (DFB), a strong Fe chelator. However, when the UHP water + DFB leach exposure times were increased to 60 min, the aerosol-soluble Fe concentrations increased 6-fold or more, from 0.33 ng m^{-3} to 2.0 ng m^{-3} (0.3% to 1.7% Fe solubility; 11 Sep 08) and from 0.55 ng m^{-3} to 4.5 ng m^{-3} (0.6% to 4.8% Fe solubility; 15 Sep 08). A similar test comparing exposure times with UHP water or seawater was not conducted in this intercalibration. In a comparison of all extraction solutions, concentrations of aerosol-soluble Fe decreased according to this sequence of extraction solutions: ammonium acetate (pH 4.7) > formate (pH 4.2) > seawater (pH 8) = UHP water + DFB (pH 8) = UHP water (pH ~5.5).

Differences in apparent aerosol TEI solubility caused by the use of different extraction solutions were likely to be large enough to mask differences in extraction times and backing filter pore size, where larger pore sizes could allow undissolved particles to pass into solution and be misinterpreted as soluble. Aerosol-soluble V concentrations were similar regardless of the extraction method, but extractions using ammonium acetate (red-filled circles, Fig. 3) recovered much greater fractions of aerosol-soluble Al and Pb than extractions using UHP water. While each of these extraction methods may be well-justified within the context of a single study, the use of different methods makes precision among laboratories impossible to assess. Therefore, we recommend extraction of replicate subsamples using a simple flow-through UHP water leach (e.g., Buck et al. 2006), to compare results across different studies and among laboratory groups.

Soluble anions: filter loading precision

Prior to the 2008 RSMAS intercalibration project, aerosol

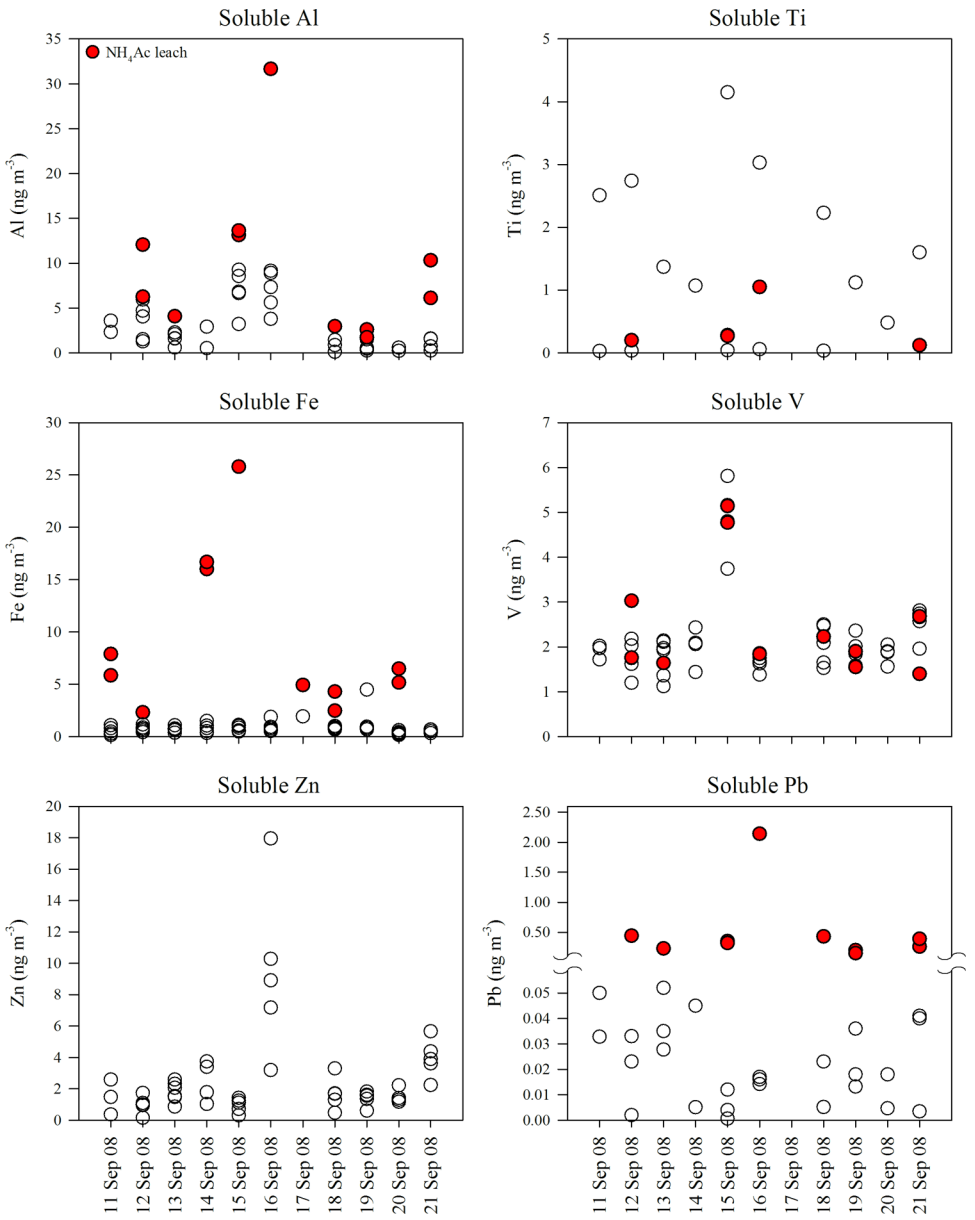

Fig. 3. Soluble aerosol concentrations (W41 filters) of Al, Ti, Fe, V, Zn, and Pb, from 11–21 Sep 08. Open circle symbols represent individual replicates, and red-filled symbols represent extractions using ammonium acetate.

homogeneity was tested by a single lab using a single aerosol sample collected at FSU. Thirteen subsample pieces were tested for UHP water soluble NO_3^- and SO_4^{2-} concentrations collected on a W41 20 cm × 25 cm filter. Nitrate concentrations varied by 4.8% RSD, while SO_4^{2-} concentrations varied by 11.2% RSD. This relative variability is expected in the "best case scenario," with a single laboratory processing and analyzing all samples for major anion concentrations. We take these variabilities to represent primarily subsample heterogeneity because the analytical precision is typically 2% to 3% RSD. No analogous test was conducted for QMA filters, based on previously reported similarities for soluble NO_3^- and SO_4^{2-} between W41 and QMA filters (Pszenny et al. 1993).

Soluble anions: single-laboratory precision and precision among laboratories

Concentrations of soluble major anions (NO_3^- and SO_4^{2-}) were measured after extraction using UHP water (pH ~5.5) or $NaHCO_3$ (pH 8.6) from W41 and QMA filters (Table 2). Reported W41 blank concentrations for nitrate ranged from "below detection limit" (no measureable peak above ion chromatography baseline) to 0.05 nmol cm^{-2} (0.02 nmol m^{-3} assuming a typical filtered air volume of 1400 m^3), but one participant reported that filter blanks provided with the aerosol samples yielded unusually high NO_3^- concentrations

Table 7. Range of precision for W41 aerosol-soluble concentrations within laboratories and among laboratories, all days (11–21 Sep 08).

Element	Single laboratory precision (n = 2; relative percent difference)	Precision among laboratories (n = 2–11; % RSD)
Al	0.6–31.7%	21.3–115.8%
Ti	1.7–2.1%	97.0–167.3%
Fe*	1.0–36.1%	17.6–105.9%
V	0.5–31.2%	8.4–29.5%
Zn	1.9–21.9%	31.3–75.5%
Pb*	0.7–45.2%	10.3–101.4%

When n = 2, precision is reported as "relative percent difference" = $(x - \bar{x})/\bar{x} \times 100\%$.

*"Precision among laboratories" excludes results from ammonium acetate extractions, which were 10-50 times greater than other values reported by other participants.

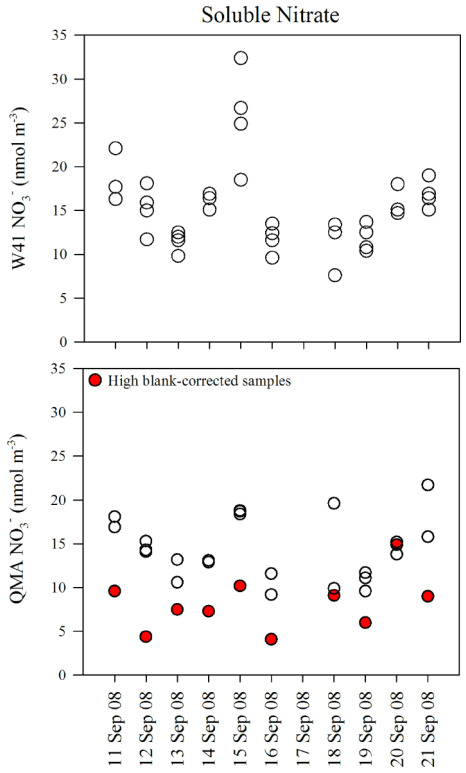

Fig. 4. Soluble nitrate concentrations from W41 (upper panel) and QMA (lower panel) filter from 11–21 Sep 08. Red-filled symbols (lower panel) represent samples extracted from QMA filters with high blank corrections.

that resulted in significant blank corrections. A similar problem was discovered for the QMA filter blanks, where one participant reported blanks "below detection limit" (no measureable peak above ion chromatography baseline) but two other participants reported highly variable nitrate blanks in the range of 0.2-40 nmol cm^{-2} (0.04-12 nmol m^{-3}). Because some groups reported replicate filter blank concentrations that were at or near their detection limits, the contaminated nitrate filter blanks appear to result from differences in sample handling or analysis by individual laboratories.

High QMA filter blanks for 1 group (red-filled circles, Fig. 4) resulted in lower QMA NO_3^- concentrations than those of the other groups. W41 NO_3^- concentrations ranged from 7.6-32.4 nmol m^{-3} (Fig. 4) and were not similarly affected by higher-than-average blanks. The single-laboratory precision for W41 analyses (1.5-3.5% RPD, with a high value of 13.7% on 19 Sep 08) was similar to that determined during the preliminary filter loading test (4.8% RSD). The QMA aerosol-soluble NO_3^- concentrations (4.1-21.7 nmol m^{-3}) and single-laboratory precision (1.1-3.2% RPD) were similar to W41 values. Precision among laboratories for W41 NO_3^- concentrations ranged from 5.7-27.9% RSD and was similar to inter-laboratory variabilities observed for bulk element concentrations. The range in precision among laboratories for QMA NO_3^- concentrations was greater (5.3-46.0% RSD) than for W41 NO_3^- concentrations (5.7-27.9% RSD). When the large blank subtraction results are omitted, the precision among laboratories ranges from 0.6-15.6% RPD (except for 32.9% RPD on 18 Sep 08). The higher observed soluble NO_3^- concentrations from W41 filters relative to QMA filters (Fig. 5) are consistent with previous findings that W41 filters can adsorb gaseous nitric acid while quartz fiber filters can lose HNO_3 due to evaporation at temperatures greater than 20°C (Schaap et al. 2004).

No participants experienced problems with high SO_4^{2-} blanks: all blank values for both QMA and W41 filters were reported as "no measureable peak," "below detection limit," or 0.007 nmol cm^{-2} (~0.002 nmol m^{-3}; W41 only). Sulfate concentrations on W41 filters (Fig. 6) were 9.7-23.8 nmol m^{-3} with single-laboratory precision (2.7-5.6% RPD) better than that of the FSU filter loading test (11.2% RSD) for samples from all days but one (19 Sep 08; 19.0% RPD). Precision among laboratories ranged from 7.0-20.0% RSD. One participant reported SO_4^{2-} concentrations for QMA filters, which agree with the W41 concentrations (Fig. 7). Both filter types seem acceptable for aerosol sulfate studies (Fig. 7), in agreement with a previous report (Pszenny et al. 1993).

Mercury

Sample heterogeneity and methodology differences for aerosol Hg collected on QMA filters was assessed by comparing results from two different laboratory groups (Fig. 8). The lowest aerosol Hg concentrations (~110 pg subsample^{-1}; 14 Sep 08) were well above the detection limit (10 fmol; Lamborg et al. 2012). The internal laboratory variabilities for Hg were comparable to other elements (1.2%-23.4% RSD, n = 4; 0.8-14.1% RPD, n = 2, for all days except 21 Sep 08 with 45.6% RPD), suggesting that Hg was as uniformly distributed on the QMA filter as the other species analyzed. Both groups reported similar trends across the sampling period (Fig. 8), but in 60% of the samples there appeared to be a systematic offset that was greater than the combined laboratory uncertainties.

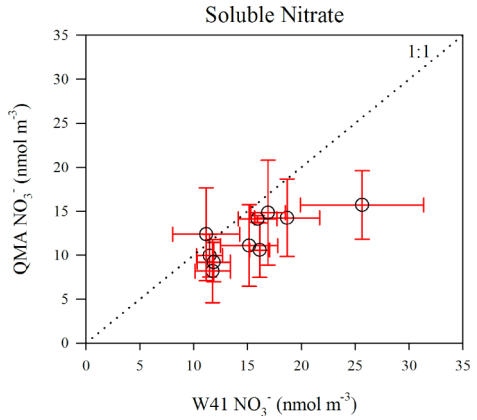

Fig. 5. Relationship between soluble nitrate concentrations from W41 and QMA filters, analyzed on all days by all submitting groups. Symbols represent the average of these concentrations, and red error bars reflect ± 1*s* for results from each filter type. Dotted line shows the 1:1 relationship.

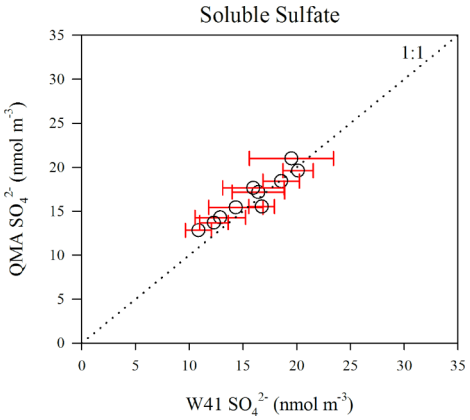

Fig. 7. Relationship between soluble sulfate concentrations from W41 and QMA filters, analyzed on all days by all submitting groups. Symbols represent the average of these concentrations, and red error bars reflect ± 1*s* for results from W41 filters (only 1 group reported SO_4^{2-} results from QMA filters). Dotted line shows the 1:1 relationship.

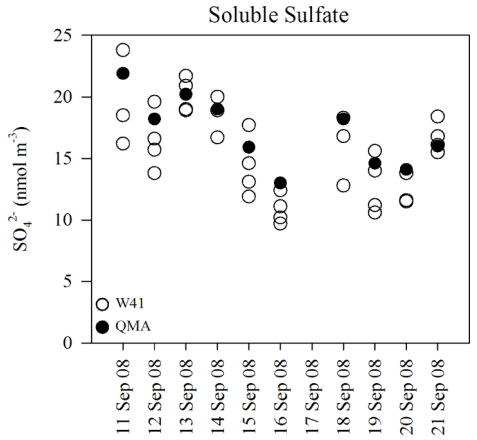

Fig. 6. Soluble sulfate concentrations from 11–21 Sep 08. Open circle symbols represent samples extracted from W41 filters, and filled circle symbols represent samples extracted from QMA filters (one laboratory reporting).

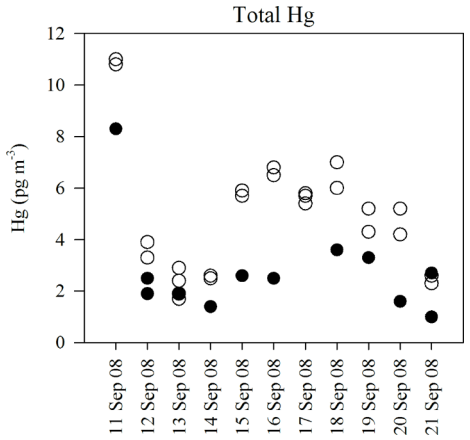

Fig. 8. Total Hg concentrations from 11–21 Sep 08. Similar (filled or open) circles represent replicates from the same laboratory.

While both groups used similar extraction and analytical methods, two differences in the digestion procedure were readily apparent. The group that reported higher concentrations digested using 10% HNO_3 and added the oxidizing agent BrCl directly to the filter (digestion procedure A), while the group reporting lower Hg concentrations used 25% HNO_3 and added the BrCl to an aliquot of the extract one hour prior to analysis (digestion procedure B). To determine if the offsets in the results from the two different laboratories were due to differences in extraction procedures, both laboratories used both extraction procedures to process and analyze filter subsamples of the 17 Sep 08 sample. Mercury concentrations in replicate samples analyzed using digestion procedure A were 4.27 ± 0.27 pg m^{-3} and 5.26 ± 1.87 pg m^{-3}, for laboratory groups 1 and 2, respectively, while concentrations in samples analyzed using digestion procedure B were 5.83 ± 0.72 pg m^{-3} (laboratory group 1) and 6.42 ± 0.20 pg m^{-3} (laboratory group 2). The results between laboratories compared well with each other, demonstrating that the two digestion techniques were not statistically different and all results were statistically identical to the initial analysis (5.64 ± 0.17 pg m^{-3}). The subsequent analyses show that differences observed in the initial comparison were not related to differences in extraction techniques, but were likely due to day-to-day instrumental variability rather than a true difference in the results between the two laboratories. The sharing of authentic aerosol samples between laboratory groups proved invaluable in resolving this discrepancy and emphasizes the importance of ongoing intercalibration among laboratories and validation against actual aerosol samples or realistic reference materials.

Size-fractionated results

Particle size distribution studies can reveal details about the

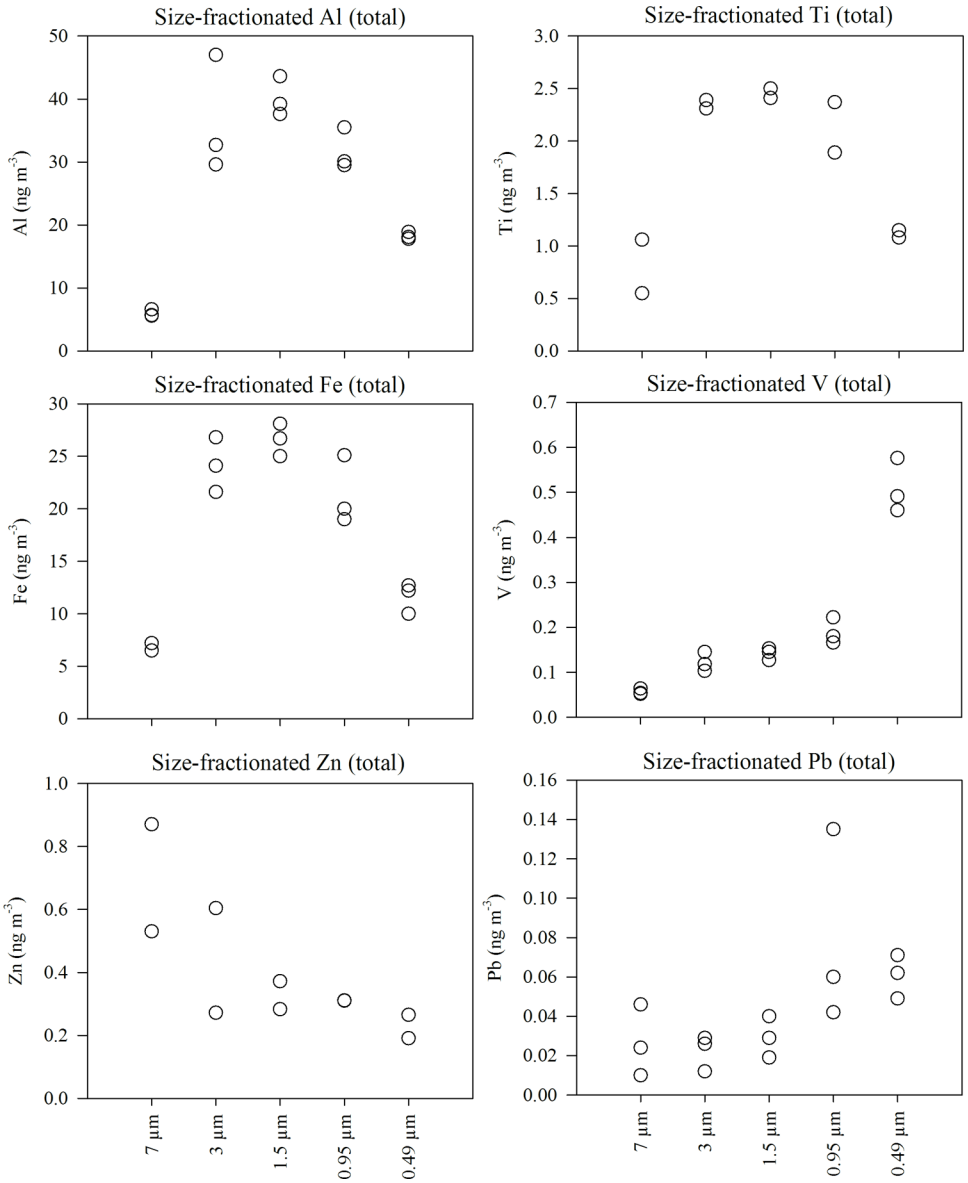

Fig. 9. Size-fractionated (total) aerosol concentrations (W41 impactor filters) of Al, Ti, Fe, V, Zn, and Pb, from 13–14 Sep 08. Open circle symbols represent individual replicates.

composition and chemistry of the bulk aerosol, as aerosol components (crustal or anthropogenic) fractionate differently depending on their composition: crustal aerosols are coarser (4-10 μm; Reid et al. 2003) while anthropogenic aerosols (smoke, pollution, etc.) are finer (< 0.5 μm; Jang et al. 2007). Three laboratories analyzed impactor (size-fractionated) aerosol samples collected on 13 Sep 08 for TEI concentrations (Fig. 9), to compare the sum of the five size fractions with bulk aerosol concentrations. The precision of the TEI concentrations from all 3 groups was similar to the precision of inter-laboratory measurements for bulk TEI concentrations (Fig. 9; Al: 2% to 29% RSD; Ti: 2% to 32% RPD; Fe: 6% to 20% RSD; V: 6% to 20% RSD; Zn: 5% to 33% RPD; Pb: 14% to 72% RSD). The single laboratory precision of TEI concentrations was not evaluated because no participant analyzed replicate samples.

The sum of the TEI concentrations from each of the five size-fractions (0.49 μm to > 7.2 μm) should be equal to the bulk aerosol TEI concentrations since these samples were collected simultaneously. For the crustal elements (Al, Ti, and Fe), the bulk aerosol TEI total concentrations and the sums of the individual size-fractions agree within 83% to 99% (Table 8). However, for pollution-related elements with fine aerosol particles (V, Zn, and Pb), the bulk aerosol concentrations exceed the size-fraction sums. The difference in anthropogenic element concentrations between size-fractionated sums and bulk aerosol concentrations likely results from the lack of a backing filter as a final impactor stage, which would have collected the 0-0.49 μm size-fraction where a significant amount of the

Table 8. Sum of size-fractions (n = 2–3) versus bulk aerosol concentrations (13 Sep 08).

Element	Size-fraction sum (ng m^{-3})	Bulk aerosol (ng m^{-3})	Difference (ng m^{-3})	% of Total Bulk Aerosol
Al	132.5 ± 7.2	133.5 ± 35.9	1.0 ± 36.7	99%
Ti	8.9 ± 0.5	10.5 ± 1.2	1.6 ± 1.3	85%
Fe	90.5 ± 2.7	108.4 ± 22.1	17.9 ± 22.3	83%
V	1.02 ± 0.06	2.40 ± 0.32	1.38 ± 0.32	43%
Zn	2.00 ± 0.59	4.47 ± 1.12	2.47 ± 1.26	45%
Pb	0.217 ± 0.042	0.339 ± 0.076	0.122 ± 0.087	64%

anthropogenic particles are expected to be found. In contrast, only a small amount of crustal-type elements are expected to exist in the < 0.49 µm fraction, and the agreement between size-fraction sums and bulk aerosol for Al and Ti support this conclusion. Therefore, it is highly recommended that a final backing filter be included when using similar cascade impactors for size-fractionated aerosol sampling.

Discussion

The results of the 2008 GEOTRACES aerosol intercalibration study suggest that the sampling equipment, filter substrates, and filter handling (and subsampling) procedures are appropriate for collecting, storing, and subsampling bulk and size-fractionated aerosols for a large international program. Results of bulk replicate aerosol analysis by multiple laboratories agree within 20% or better in most cases. This variation was decreased by the use of a single method for aerosol bulk analysis. For example, replicate sample variability was reduced to 9% RSD or better when replicates (n = 7) were analyzed by a single laboratory using only one protocol. This degree of precision among laboratories reflects all sources of variance, including digestion efficiency and analytical precision and accuracy. Whereas most laboratories compared their digestions and analyses against one or more SRMs, accuracy and precision among laboratories remains a concern for some elements. This concern is further complicated by the fact that commercially available SRMs are not representative of natural bulk aerosol material. For example, the average precision among laboratories for total Ti concentrations in the 2008 RSMAS aerosol samples was 20% RSD (10.4-37.3% RSD; Table 5), but SRM recoveries were highly variable (Table 1). Furthermore, most SRMs are certified for TEIs at masses of at least 250 mg (equivalent to 400,000 ng m^{-3} in aerosols, assuming a dust content of 8% Al and a filtered air volume of 1400 m^3), but actual aerosol dust concentrations might only reach an Al concentration of 6000 ng m^{-3} during a "dust" event (e.g., Buck et al. 2006). Therefore, most laboratories only analyzed a fraction of the certified SRM mass (5-50 mg versus 250 mg). Clearly, an SRM is needed that mimics naturally occurring aerosols, is relatively inexpensive (for use on a regular basis), is homogeneous at low masses, and is suitable for the analysis of crustal, marine, and anthropogenic-type elements. We are currently assessing Arizona Test Dust (0-3 µm; Powder Technology) for use as a consensus reference material. At the time of writing, four participants have submitted results that suggest the material is sufficiently homogeneous (better than 10% RSD) at subsample masses of 10-20 mg. However, there are some significant differences among laboratories for some elements, and additional testing is clearly required before this material is suitable for distribution as a reference material.

Currently, there is no clear consensus on the appropriate method to evaluate the aerosol solubility of Fe and other TEIs, largely because we do not have a good understanding of the biogeochemical significance of the fractions released by the different extraction methods (Baker and Croot 2010). Extraction methods are typically selected based on ease of use (UHP water leaches) or a group's perception of how best to define "solubility" in the context of their research questions. These differing methods make comparisons among studies difficult, and the literature, in general, reflects a large variety of solubility estimates that are all context-specific. Therefore, we suggest that the marine aerosol community select a common extraction method that is always applied to a replicate filter or filter subsample. We believe a simple flow-through UHP water leach in addition to context-specific extraction methods would allow investigators to answer their specific questions on aerosol-soluble TEIs while also producing results that can be directly compared with those from other studies.

Comments and recommendations

The intercalibration of aerosol sample analyses is an ongoing process, and should not be limited to a single event. The following laboratory procedures, applied in a consistent manner, are recommended in order for the marine aerosol community to produce readily comparable and more reliable results. While total aerosol TEI concentrations determined using digestion methods that omitted HF or heat and pressure were generally comparable with the other reported values, the concentrations were consistently in the lower range of values, and we recommend that bulk aerosol digestions include HNO_3, HF, heat, and pressure (especially for refractory-type TEIs such as Ti). Laboratories should test their digestion methods against a common dust reference material (such as Arizona Test Dust) to evaluate the minimum requirements for complete digestions and to improve accuracy and precision among laboratories. Solubility investigations should include a

common (and preferably relatively simple) extraction method such as rapid flow-through exposure to UHP water in addition to any context-specific methods to produce data sets that are intercomparable. Participants within GEOTRACES are required to regularly intercalibrate to produce data-sets that are both accurate and precise (GEOTRACES Science Plan 2006), and this work reflects the efforts of an international group of aerosol scientists to achieve these goals.

Acknowledgments

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