

Interactive comment on “Particle characterization at the Cape Verde atmospheric observatory during the 2007 RHaMBLe intensive” by K. Müller et al.

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Comment by A. Pszenny and W. Keene

Müller et al. report that our measurements of total particulate bromine (BrT) by neutron activation analysis (NAA) during the spring 2007 campaign at Cape Verde are about a factor of four greater than their measurements of PM₁₀ bromide (Br[−]) by ion chromatographic (IC) analysis of filter extracts. They speculate that the higher concentrations of BrT may reflect contributions from non-ionic bromine species and note that the NAA and IC methods have not been compared previously. In fact, Barrie et al. [1994] analyzed splits of samples collected during the 1992 Polar Sunrise Experiment at Alert in the Canadian high Arctic by both NAA and IC. Although Barrie et al. [1994] did not discuss results of the comparison, according to Sander et al. [2003]: “These paired

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data indicated that most particulate bromine during the experiment was in the form of soluble bromide.”

Two other data sets available in the supplement to the Sander et al. [2003] review offer additional evidence that Br⁻ is the dominant form of particulate bromine in the marine boundary layer. Size-resolved aerosols were sampled with two different cascade impactor types at Samoa in the tropical South Pacific during January and February 1981. Samples from one impactor type were analyzed for trace elements by NAA [Arimoto et al., 1987; sam-81-dry-sierra data set] and from the other type for ionic constituents by IC [Pszenny, 1987; sam-81-dry-anders data set]. The respective size distributions of BrT and Br⁻ are summarized in Figure 1. The distributions are quite similar despite the additional differences that the two impactors used different substrate materials and that the sampling intervals were not exactly coincident. A quantitative comparison of the size distributions is difficult because the cut diameters of the two impactor types differ. However, the medians of the sums over all stages of BrT and Br⁻ agreed within 25% and were not statistically different (Wilcoxon-Mann-Whitney rank test, $n = m = 4$, $p = 0.29$).

In addition, and as noted above, Müller et al. employed a PM₁₀ inlet on their aerosol sampling system at Cape Verde whereas we sampled aerosol in bulk. The data reported by Müller et al. therefore represent lower limits for particulate Br⁻ over the full ambient size distributions, which may account for some of the difference between our respective measurements.

Based on the above, we believe that the presence of non-ionic forms of particulate bromine was not the primary explanation for the factor of four higher concentrations of BrT in bulk aerosol measured by us relative to Br⁻ measured in PM₁₀ aerosol by Müller et al.

Müller et al. also note that large depletions relative to sea salt similar to those they observed were reported by Ayers et al. [1999] from Cape Grim, Tasmania during summer

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and by Gabriel et al. [2002] over the Indian Ocean during the INDOEX campaign. We suggest that comparisons with three other cascade impactor data sets from the tropical North Atlantic would be pertinent in this regard. Data sets for a coastal site on Tenerife, Canary Islands [R. Arimoto, unpublished; ten94 data set] and for a mid-Atlantic meridional transect cruise [Baboukas et al., 2000; atl96b data set] were included in the Sander et al. [2003] supplement. A third data set reported by Keene et al. [2009] is from a meridional transect cruise that passed close to Cape Verde. Median bromine depletions based on these latter data sets are smaller than those reported by Müller et al. We also suggest that Müller et al. indicate in the revised manuscript which species they used as a seawater reference and cite the reference seawater composition on which their calculated enrichments and depletions were based.

A third possible explanation for the factor of four difference between our BrT and Müller et al.'s Br⁻ data is analytical bias. Our samples were analyzed by NAA at the same reactor facility and using procedures very similar to those employed by Arimoto et al. [1987 and several other publications]. The principal difference was the method used to correct for spatial and temporal variations in neutron flux during irradiation of individual samples. Arimoto et al. [1987] used external flux monitors made of aluminum foil whereas we used internal flux monitors consisting of spikes of known amounts of indium. We also irradiated standards (n = 12) made by spotting known amounts of a NIST-traceable mixed element solution onto blank filters that had also been spiked with indium. All filters used for standards and blanks were from the same lot as those used for collecting actual samples. Measured recoveries for Br and several other elements were statistically indistinguishable from 100%.

Finally, we note that Müller et al. also report large particulate chloride depletions relative to sea salt compared to other published values. For example, particulate Cl⁻ depletions summed over all size fractions sampled in the southeastern North Atlantic by Keene et al. [2009] range from 4% to 11% (n=9) whereas those reported by Müller et al. for supermicrometer size fractions, with which most Cl⁻ in marine air is associ-

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ated, ranged from 31% to 38%. Chloride depletions for supermicrometer size fractions, or those summed over all size fractions, that exceed 30% are more typical of highly polluted coastal regions where acid-displacement reactions, primarily by HNO₃, lead to greater dechlorination of marine aerosols than is usually observed over the open ocean [e.g., Graedel and Keene, 1995; Keene et al., 2004; 2007]. We encourage the authors to interpret the large Cl⁻ depletions of supermicrometer size fractions that they report for Cape Verde in the context of measurements by other investigators.

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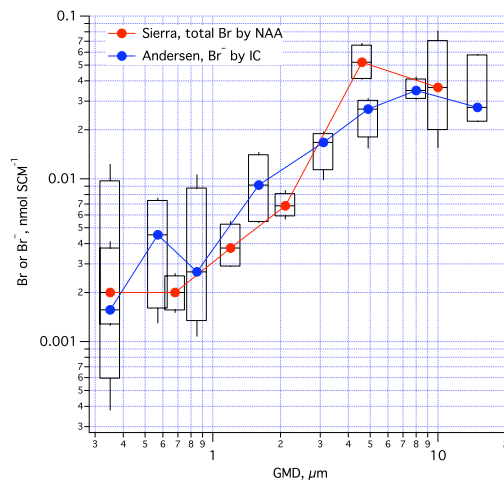
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Figure 1. Box plots of particle size distributions of BrT and Br⁻ for separate sets of cascade impactor samples collected at the NOAA/ESRL/GMD observatory at Cape Matatula, Tutuila Island, American Samoa during January–February 1981. Symbols depict medians (central lines), quartiles (box tops and bottoms), and deciles (whisker ends). Colored lines connect median values for size fractions sampled by each impactor type.

Fig. 1.

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