

Posting type Informational
Subject Negative chloride concentrations at salt-poor sites
Module/Species B/ Cl^-
Sites entire network
Period 2000 – 2003
Submitter W.H. White, whwhite@ucdavis.edu

Supporting information

Fine-particle chloride reacts with other aerosol species, both in ambient air and after collection on the Nylon filter of module B for ion chromatography (Cl^-) or the PTFE filter of module A for X-ray fluorescence (Cl). At coastal sites exposed to marine aerosol, the B-module chloride ion measurement has been identified as a useful indicator of fresh sea salt (White, 2008). Chloride is a less reliable tracer farther inland, where it can be replaced by nitrate and other ions in atmospherically aged sea salt; chloride concentrations at sites in the continental interior are generally low. Starting in 2000, and extending through 2003, many samples at interior sites reported strictly negative chloride concentrations. These negative concentrations are evident in the figure below, which contrasts an inland National Park's historical series with one from a National Seashore.

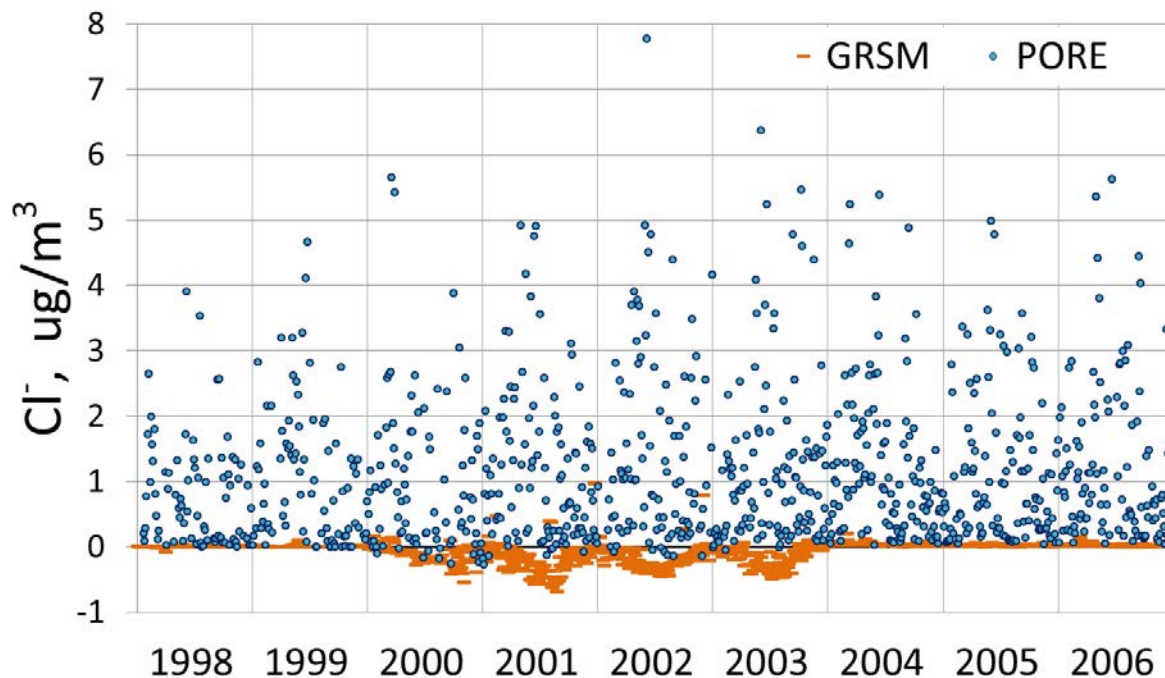
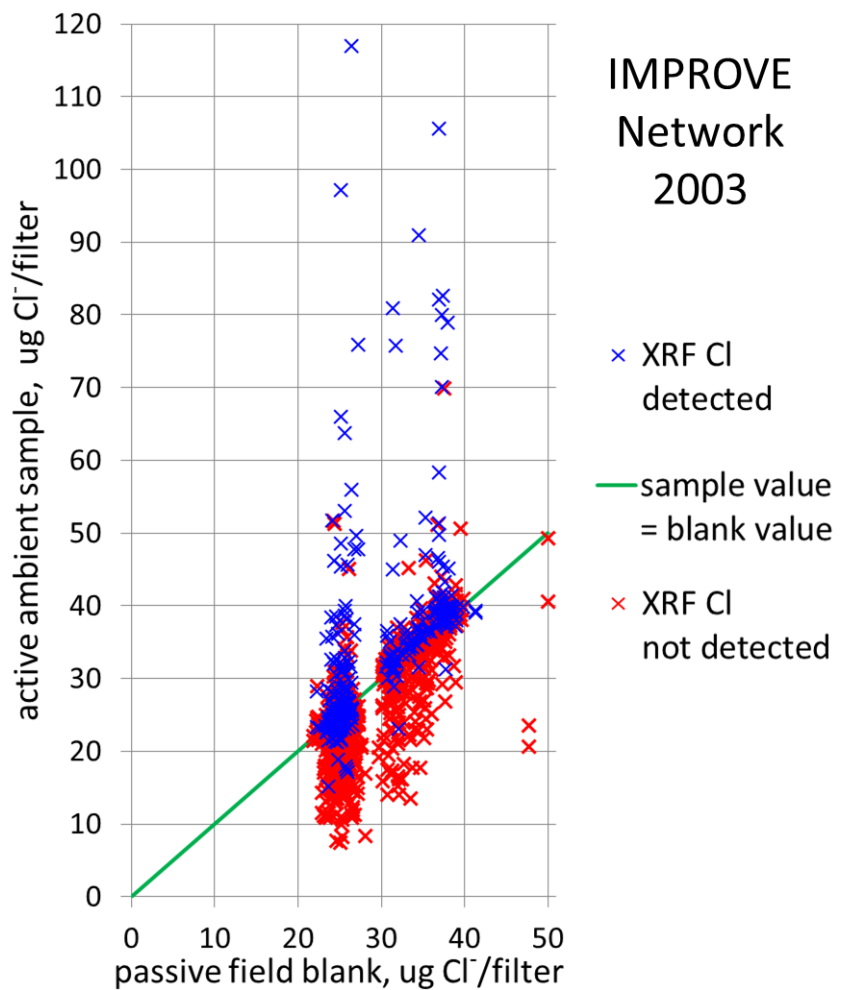


Figure 1. Chloride ion concentrations reported at Great Smoky Mountains National Park (GRSM) and Point Reyes National Seashore (PORE).

The consistently negative chloride values reported in 2000 – 2003 were associated with excessive chloride backgrounds that were present in the 37 mm Nylon filters used during that period. The diameter of the B-module filter was increased from 25 mm to 37 mm in 2000 to address clogging that had biased sample recovery rates in 1998 and 1999 (White et al., 2005, Figure 5), and the larger filters yielded larger blank values. Acceptance testing showed reasonably consistent blank levels within a Nylon lot, so a standard blank subtraction was expected to account satisfactorily for the background. Experience showed (Figure 2) instead that variable amounts of its initial background were lost from the active filter during sampling, with the result that unsampled field blanks were unrepresentative of the contamination remaining on sampled filters. Subtracting a blank's contamination from a filter purged by sampling chloride-poor air then yielded a negative net loading. This problem was eliminated by switching to a supplier (Pall-Gelman) of Nylon filters with much lower backgrounds for 2004 and subsequent sample years.

Figure 2. Chloride ion loadings on all valid Nylon sample filters (n = 1454) from 2003 that were accompanied by field blanks (n = 734). These sample filters represent 7.3% of all valid Nylon samples collected that year. A field blank sits in the sampling plenum from one Tuesday to the next, with no air drawn through it; during this week, 24-h active samples are drawn through two other filters on Thursday and Sunday. About 80% of the associated A-module samples on PTFE filters showed no detectable elemental chlorine under XRF analysis: the chloride values corresponding to these samples are plotted in red. The bimodal distribution of blank values reflects two different filter lots.



The apparent seasonality of negative chloride concentrations at GRSM (Figure 1) and other inland sites deserve note. Observed chloride losses during 2000 – 2003 were generally greatest during summer and fall, when atmospheric conditions are most favorable for the production of secondary acidic aerosol species. In the collection of sample and blank pairings from 2003 that was examined in Figure 2, the lowest chloride loadings were consistently found at high sulfate loadings. Figure 3 suggests some antagonism between these ions in individual samples at loadings above 50 ug SO₄⁼/filter, representing ambient sulfate ion concentrations above 1.5 ug/m³. It is unclear whether the implications of this observation extend beyond the chloride background in Nylon filters to a potential interference in the measurement of fine-particle chloride in air.

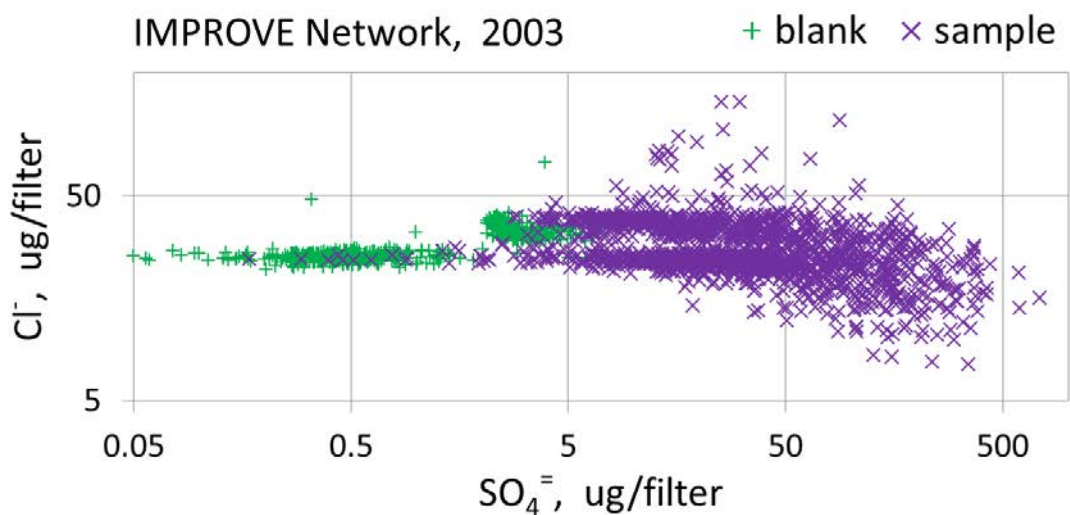


Figure 3. Chloride and sulfate ion loadings on all Nylon sample filters from 2003 that were accompanied by field blanks. Blank and sample data are as described in the Figure 2 caption. The distinctions between blanks from different filter lots, noted in the Figure 2 caption, are evident here in the sulfate as well as chloride backgrounds.

References:

W.H. White, L.L. Ashbaugh, N.P. Hyslop and C.E. McDade (2005) Estimating measurement uncertainty in an ambient sulfate trend. *Atmospheric Environment* 39, 6857-6867.

W.H. White (2008) Chemical markers for sea salt in IMPROVE aerosol data. *Atmospheric Environment* 42, 261-274.