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Chemical markers for sea salt in IMPROVE aerosol data

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Abstract

The Interagency Monitoring of PROtected Visual Environments (IMPROVE) network monitors chemically speciated fine-particle concentrations at about 170 rural or remote sites in the United States, including several in coastal settings. Sea salt is a major component of marine aerosols, and can have significant optical effects on both global and local scales. Sodium is the most commonly employed chemical marker for sea salt, but the ion is not a target of IMPROVE's routine chromatography and the element is poorly detected by IMPROVE's routine X-ray fluorescence analysis. This paper examines data from six coastal sites where sea salt is abundant, to identify more reliable signatures of fresh sea salt in routine IMPROVE data. The chloride ion measurement, by ion chromatography on a Nylon filter sampling behind a carbonate denuder, appears to represent the total concentration of this reactive species at the selected sites. It is shown to be a good predictor of conserved sea salt markers such as non-crustal strontium, calcium and potassium, as well as the portion of gravimetric mass not explained by terrestrial fractions. These conclusions may not extend to other locations where sea salt is a smaller and more aged fraction of the aerosol mix.

Keywords: Sea salt; IMPROVE network; Chloride; Depletion; Sodium; Accuracy

1. Introduction

Sea salt is a major component of the global aerosol. The submicron fraction is of particular interest for its disproportionate direct and indirect impacts on radiative transfer (O'Dowd et al., 1997; Murphy et al., 1998; Quinn et al., 2002). This relatively benign material has generally received less attention from air pollution researchers, who are traditionally more concerned with health impacts in populated areas.

Ambitious regulatory targets for fine particle concentrations are now starting to raise sea salt's on-shore profile. The Regional Haze Rule, for example, sets an ultimate goal of "reaching natural background conditions" in many national parks and wilderness areas of the United States (USEPA, 1999). Lowenthal and Kumar (2003, 2006) and Tombach and Brewer (2005) have called attention to sea salt as an influence on this "natural background" target at coastal locations. Similarly, the health-based national ambient air quality standard for fine particulate mass ($PM_{2.5}$) is specified in terms of chemically undifferentiated gravimetric mass but rests on risk assessments that exclude the effects of materials from natural sources (USEPA, 2005). In some populated areas (Song et al., 2001; Lee et al., 2002; Maykut et al., 2003; Kim and Hopke, 2004; Zhao and Hopke, 2004;

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Table 1
Mass concentrations ($g\,g^{-1}$) of selected elements in fresh sea salt (Millero, 2004; Table 1) and average continental crust (Mason and Moore, 1982; Table 3.5)

	Na	Cl	S	K	Ca	Fe	Sr
Sea salt	0.308	0.554	0.0258	0.0114	0.0118	–	0.000227
Continental crust	0.028	0.000	0.0003	0.0259	0.0363	0.0500	0.000375

These values are referenced elsewhere in the text as $a_{\text{col,row}}$, for example, $a_{\text{NA,salt}} = 0.308$.

Kim et al., 2004) the annual-average $PM_{2.5}$ attributed to sea salt is of the order $1\,\mu g\,m^{-3}$; this is a small fraction of the $15\,\mu g\,m^{-3}$ national standard, but potentially of significance for binary determinations of whether the standard has been met.

Sea salt is predominantly NaCl (Table 1). With occasional exceptions—Maykut et al. (2003) identified Kraft pulp mills as a possible source of sodium in Seattle—the ocean is thought to be the dominant source of atmospheric sodium and chlorine in coastal areas (Eldering et al., 1991; Sturges and Shaw, 1993). Some of the chlorine in fine-particle NaCl is displaced to the gas phase in atmospheric reactions with nitric and sulfuric acid (McInnes et al., 1994; Newberg et al., 2005):

$$NaCl(p) + HNO_3(g) \rightarrow HCl(g) + NaNO_3(p), \quad (R1)$$

$$2NaCl(p) + H_2SO_4(g + aq) \rightarrow 2HCl(g) + Na_2SO_4(p) \quad (R2)$$

This depletion of particle chlorine makes sodium the preferred particle-phase marker for sea salt. The sum of particle and gas chloride concentrations is unaffected by reactions (R1) and (R2), so total chloride could also be interpreted as a tracer for sea salt's conserved constituents under conditions where HCl deposition losses can be neglected. This option appears to have received little attention, despite a demonstration by Eldering et al. (1991) that total chloride in the Los Angeles basin exhibited good agreement with sodium.

Many haze and source-attribution studies in the United States rely on data from the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network. IMPROVE is a cooperative effort by federal, tribal and state agencies (Joseph et al., 1987; Malm et al., 2004) to characterize and track the chemical composition of haze aerosols at predominantly rural or remote locations (Fig. 1). Twenty-four-hour $PM_{2.5}$ samples are collected every third day, on three different filter media by three independent sampling trains. Sodium and chlorine are among the elements that are measured by X-ray spectrometry on undenuded Teflon filters, as described below. Chloride is also measured independently, by ion chromatography of denuded Nylon filters. Throughout this paper, "chlorine" and "chloride" will refer to the X-ray-spectrometric and ion-chromatographic measurements, respectively.

IMPROVE made a significant change several years ago in the method used for analysis of light elements on the Teflon filters. In samples collected since 1 December 2001, elements from sodium to manganese in atomic number have been determined by tube-generated X-ray fluorescence (XRF). In earlier samples, those elements were determined by proton-induced X-ray emission (PIXE). The XRF analysis yields greatly improved sensitivities for the heavier elements in this range, such as titanium, vanadium and manganese. The unfortunate trade-off is that XRF is unable to quantify sodium reliably (Fig. 2).

It was noted above that total chloride might serve as a satisfactory marker of sea salt. IMPROVE has generally treated the ion chromatographic (IC) determination of chloride as an unexamined adjunct of the nitrate and sulfate measurements. The original motivation for collecting and analyzing samples on Nylon filters was to obtain an accurate fine-particle nitrate measurement, unaffected by NH_4NO_3 volatilization (Appel et al., 1981; White and Macias, 1987). Subsequent scrutiny has verified the success of this effort (Ashbaugh and Eldred, 2004; Yu et al., 2005; Lee and Collett, 2006). The IC sulfate measurement acquired as a by-product has served as a quality check for the elemental sulfur measurement on the Teflon filter. In this role, sulfate has received close scrutiny of its own (Eldred and Cahill, 1997; Malm et al., 2002; White et al., 2005). Although chloride has occasionally been included in multivariate analyzes of IMPROVE data (Lee et al., 2002; Kim et al., 2004, 2005), its measurement appears never to have been experimentally or theoretically characterized.

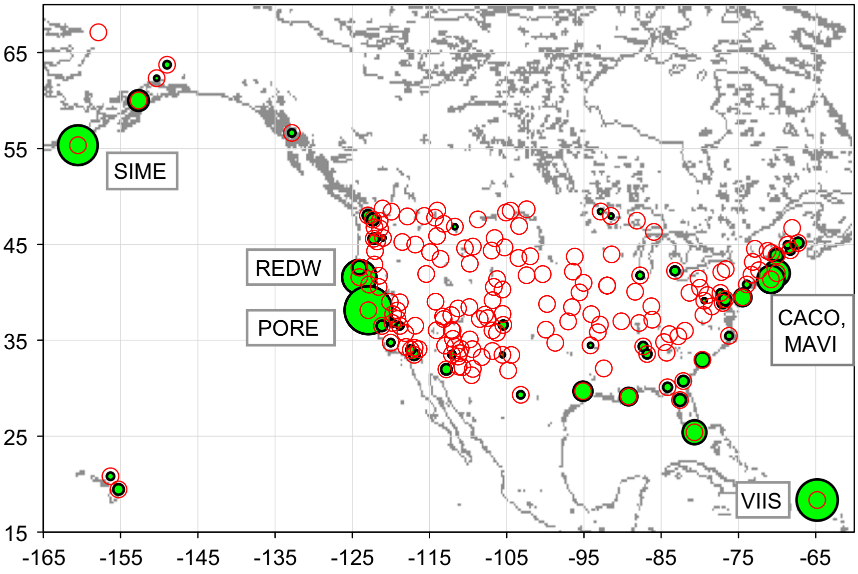

Fig. 1. IMPROVE monitoring sites in 2004. Areas of filled circles are proportional to numbers of "marine days" ($[\mathrm{Cl}^-]/a_{\mathrm{Cl.salt}} \geqslant 1\,\mu\mathrm{g\,m^{-3}}$) during 2004, in which 24 h chloride ion concentrations implied at least $1\,\mu\mathrm{g\,m^{-3}}$ sea salt. Size of open circles corresponds to 10 days (out of 122 total sampling days in 2004). Chloride episodes were most frequent at Point Reyes (PORE, 80 days); Redwood (REDW, 41); Simeonoff (SIME, 55); Cape Cod (CACO, 24); Martha's Vineyard (MAVI, 26) and Virgin Islands (VIIS, 59). Underlying map is from Generic Mapping Tools (2006).

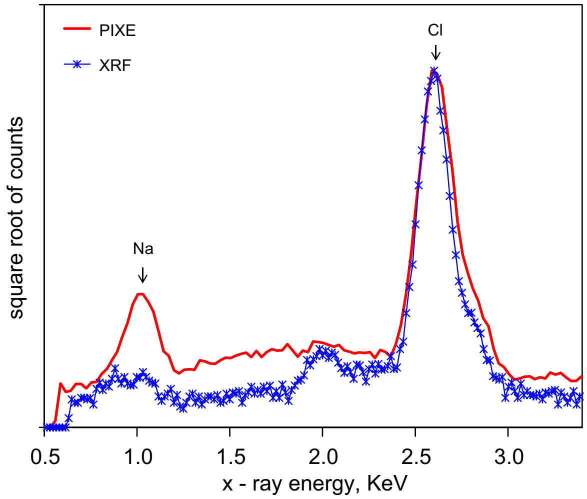

Fig. 2. A portion of the PIXE and XRF spectra for a NaCl calibration standard. Spectra are plotted as the square root of the counts in each energy interval and are normalized to the chlorine peak height. Sodium is poorly detected by XRF.

For chloride to function as a quantitative marker for sea salt, the IMPROVE measurement must include the contribution from any HCl in the gas phase. On the one hand, collection on a Nylon filter is an accepted sampling method for HCl; it is particularly well established at the low-to-moderate concentrations and moderate-to-high relative humidities expected to accompany sea salt (Sturges and Harrison, 1989; Appel et al., 1991; Tsai et al., 2004). On the other hand, IMPROVE's Nylon filter sits behind an annular denuder that might reasonably be expected to remove HCl along with the HNO_3 it is designed to strip out (Tsai et al., 2001; Yu et al., 2005). Actual HCl removal efficiencies in the field are uncertain, however, and have not been measured.

This paper presents evidence that the IMPROVE chloride measurement does represent total chloride at some sites where it does track the conserved constituents of sea salt. Section 2 gives a brief introduction to the IMPROVE measurement suite. Measured chloride (on Nylon) is then shown to exceed measured particle chlorine (on Teflon) at IMPROVE coastal sites, generally by the equivalent of measured particle nitrate. Finally, chloride is shown to exhibit the expected quantitative relationships to various other sea-salt indicators; these include non-crustal potassium, calcium and strontium, and gravimetric mass reduced by measured carbon, sulfur and crustal species. The agreement with expectations supports IMPROVE's measurement accuracy, because sea salt can be viewed as a "standard reference material" that is available *in situ* at coastal environments. The focus throughout is on coastal environments where all species of interest (other than sodium) are at quantifiable levels.

2. Measurements and data

The IMPROVE monitoring program is described by Malm et al. (2004); Fig. 1 shows the spatial coverage of the network in 2004. The program has grown significantly since sampling began in March 1988 (Joseph et al., 1987; Malm et al., 1994), but the basic measurement strategy has remained stable. Data, standard operating procedures and site descriptions are all available in detail at http://vista.cira.colostate.edu/improve/. All ambient concentration data in this paper were downloaded in May 2006 from the public-access server at http://vista.cira.colostate.edu/views/.

This section will describe only the measurements needed in the present analysis. The standard IMPROVE sampling system includes three $PM_{2.5}$ modules and one PM_{10} module. A set of four 24 h filter samples is now collected every third day; before 2000, samples were collected every Wednesday and Saturday. The PM_{10} filter is analyzed only for mass and is not considered here. The modules share a single controller, but are otherwise independent sampling trains, with separate inlets, cyclones, critical orifices and pumps. Flows are passively controlled; AIHL cyclones (John and Reischl, 1980) on each of the $PM_{2.5}$ modules produce fairly sharp particle-size discrimination at an aerodynamic diameter of 2.5 μm for flow rates around the $22.8\,\mathrm{l\,min^{-1}}$ nominal value (Turner et al., 2006).

Module A collects undenuded $PM_{2.5}$ on a 25 mm Teflon filter for weighing and a variety of elemental analyzes. Strontium has been determined since 1992 by energy-dispersive XRF using a Mo-anode tube and Si–Li detector. Elements from sodium to iron in atomic number have been determined since December 2001 by a similar XRF system using a Cu-anode tube. Before December 2001, elements from sodium to manganese were determined by PIXE and iron was determined by XRF with the Mo-anode system. As Fig. 2 shows, the change from PIXE to Cu-anode XRF significantly degraded the sodium measurement.

Module B collects $PM_{2.5}$ on a Nylon filter behind an annular denuder coated with Na_2CO_3 and glycerol. This filter is analyzed by IC for the anions chloride, nitrate and sulfate; ammonium and other cations are not routinely measured. Filters are not washed before sampling; their initial composition is accounted for by subtracting the median of all field blanks collected throughout the network during the month in which the sample was collected. Fig. 3 shows time series of raw sample and field blank loadings for chloride. The filter supplier, filter size, IC laboratory, IC eluent and denuder coating procedure have all undergone changes during the course of the program and the effects of some of these are evident in the raw data.

Module C collects undenuded $PM_{2.5}$ on a 25 mm quartz-fiber filter for thermal fractionation of organic and elemental carbon with an optical correction for pyrolysis (Chow et al., 1993). Only the total carbon value, which is insensitive to methodological details (Chow et al., 2001), will be used here.

All valid samples for which the relevant concentrations are above minimum detectable levels are considered in our analyzes. Data selection is applied only to monitoring sites, emphasizing those with longer records and more frequent marine episodes. Fig. 1 highlights the six locations with most frequently elevated chloride ion concentrations in 2004. Of these, only Point Reyes National Seashore (installed March 1988) and Redwood National Park (March 1988) collected extended series of complete data before the change from PIXE to XRF in December 2001. Virgin Islands National Park has collected module A data since October 1990, but module B began operation there only in March 1998 and has yielded reliable data only since June 2003 (White, 2006). The three remaining sites were all installed more recently: Cape Cod (April 2001), Simeonoff National Wildlife Refuge (December 2001) and Martha's Vineyard (February 2003).

While IMPROVE's basic measurement strategy has remained stable over the years, changes and adjustments have been made to individual measurements. Some of these had effects that can be seen in Fig. 4, which compares time series of three candidate markers for sea salt at Point Reyes. Small effects from methods changes can be obscured in raw concentration series by over-riding variations in atmosphere dispersion and ventilation. Sodium, chlorine and chloride ion are accordingly normalized in Fig. 4 by a fourth, wholly independent, sea-salt estimator derived from gravimetric mass. The December 2001 transition from PIXE to XRF

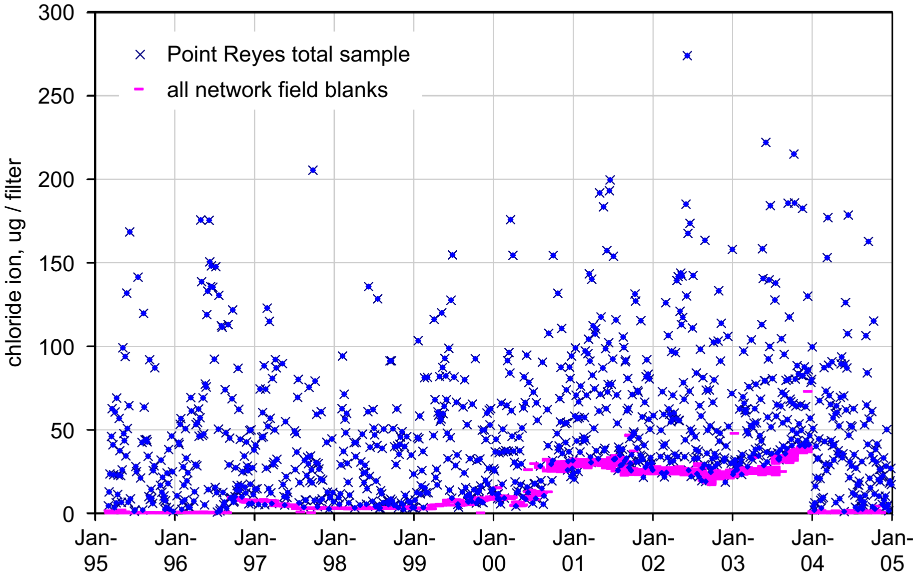

Fig. 3. Example of chloride ion data before correction for blank. All chloride data presented elsewhere in this paper have been blank-corrected by subtracting the monthly median of all network field blanks. Nylon blank levels increased in summer 2000 with the transition from 25 to 37 mm filters to reduce clogging. Blank values returned to minimal levels with a switch to a new supplier at the beginning of 2004.

effectively eliminated sodium (top) as a useful marker, as Fig. 2 foreshadowed. Conversely, chloride ion (bottom) has more closely tracked other sea salt markers since 2000, when larger Nylon filters and improved flow recording were introduced. Equally notable in the chloride ion series is the absence of any evident impact from the January 2004 introduction of cleaner Nylon filters, which validates the accounting done for the contribution of the blank.

The denominator in Fig. 4 is obtained by subtracting from measured gravimetric mass FM the estimated contributions of major chemical fractions from terrestrial sources. The contribution of fine soil dust and other crustal material to total mass is estimated as $(1/a_{\mathrm{Fe,crust}})[\mathrm{Fe}]$, from the measured iron concentration and the Table 1 value for the average iron content of the continental crust. The mass of carbonaceous material is estimated as 1.8[C], based on the range of recommendations by Turpin and Lim (2001) and El-Zanan et al. (2005). The remainder of the measured mass is modeled as a mixture of ammonium sulfate and sea salt:

$$\mathrm{FM} - 1.8[\mathrm{C}] - \frac{1}{a_{\mathrm{Fe,crust}}}[\mathrm{Fe}] \cong \frac{132}{96}[\mathrm{SO}_4^=]_{\mathrm{nss}} + M_{\mathrm{ss}}. \tag{1}$$

Eq. (1) contains two unmeasured quantities, non-sea-salt sulfate $[\mathrm{SO}_4^=]_{\mathrm{nss}}$ and sea salt mass M_{ss}, but these are independently constrained by the measured sulfate concentration:

$$[\mathrm{SO}_4^=] = [\mathrm{SO}_4^=]_{\mathrm{nss}} + a_{\mathrm{SO_4,salt}} \times M_{\mathrm{ss}}. \tag{2}$$

Eliminating $[\mathrm{SO}_4^=]_{\mathrm{nss}}$ between Eqs. (1) and (2) yields an estimate for sea salt mass that involves no sea-salt markers:

$$M_{\mathrm{ss}} \cong \frac{(\mathrm{FM} - (132/96)[\mathrm{SO}_4^=] - 1.8[\mathrm{C}] - (1/a_{\mathrm{Fe,crust}})[\mathrm{Fe}])}{1 - (132/96)a_{\mathrm{SO_4,salt}}}. \tag{3}$$

The quantity on the right side of Eq. (3) will be referred to here as *reduced mass* (RM).

Nitrate compounds are not subtracted out in Eq. (3), and so contribute to reduced mass. They are left in because *secondary* sea-salt nitrate—$\mathrm{NaNO_3}$ produced by reaction (R1)—can account for a significant fraction of total particle nitrate near the coast. It is therefore difficult to estimate and remove the contribution of terrestrial $\mathrm{NH_4NO_3}$ without introducing a specific marker for sea salt, thereby destroying the independence of reduced mass as an indicator. Some fraction of the $\mathrm{NH_4NO_3}$ sampled on Teflon volatilizes before weighing in any case, eliminating the need for its numerical subtraction.

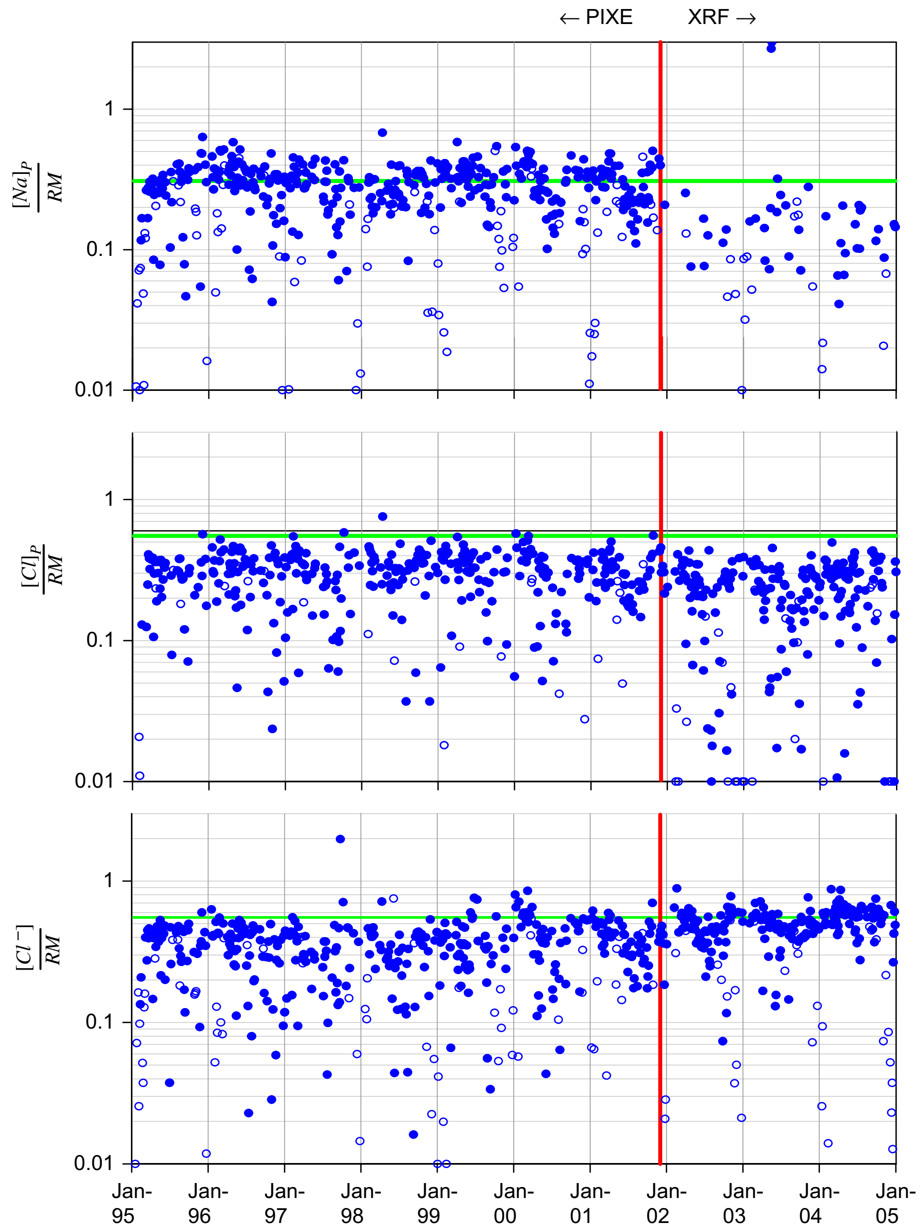

Fig. 4. Non-soil particle sodium, particle chlorine and total chloride at Point Reyes as fractions of reduced mass $\mathrm{RM} = (\mathrm{FM} - (132/96)[\mathrm{SO}_4^=] - 1.8[\mathrm{C}] - (1/a_{\mathrm{Fe,crust}})[\mathrm{Fe}])/(1 - (132/96)a_{\mathrm{SO_4,salt}})$ for all complete observations with $\mathrm{RM} \geqslant 1\,\mu\mathrm{g\,m}^{-3}$. Open symbols identify observations with particle nitrate concentrations exceeding $1\,\mu\mathrm{g\,m}^{-3}$ and heavy horizontal lines indicate sodium and chloride fractions in fresh sea salt.

Eq. (3) treats sulfate differently because terrestrial ammonium salts account for nearly all secondary sulfate and are stable on the Teflon filter.

Fig. 4 indicates that reduced mass, itself an estimator for sea salt, now tracks chloride as well as it once tracked sodium. Particle chlorine concentrations, on the other hand, have always been low relative to these other indicators. Section 3 shows this deficit to be a function of particle nitrate concentrations.

3. Chloride replacement

The fresh sea salt left by evaporating seawater is a well-defined mineral whose major species are present in fixed proportions (Millero, 2004). Fig. 5

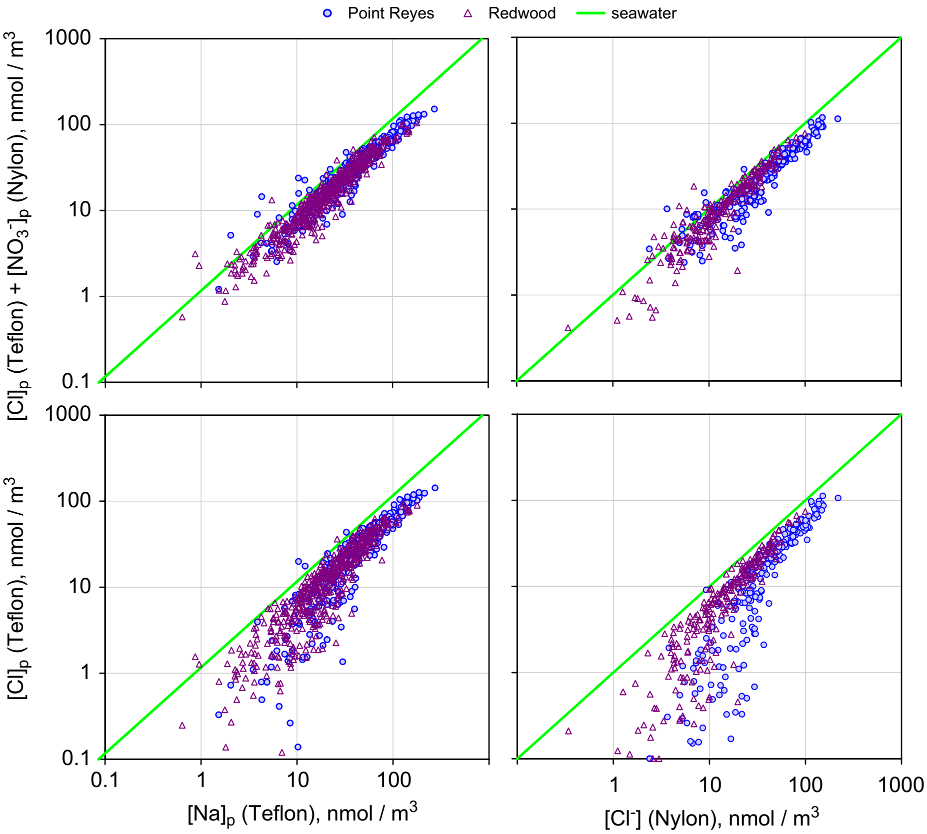

Fig. 5. The sum of particle chlorine and particle nitrate (top), or particle chlorine alone (bottom), in relation to particle sodium during 1 January 1995–30 November 2001 (left) or total chloride ion during 1 December 2001–31 December 2004 (right). All observations with particle nitrate concentrations below $1\,\mu g\,m^{-3}$ are shown.

shows the molar proportions of Na and Cl in this mineral as sloping lines. Through reactions such as (R1) and (R2), airborne sea salt particles lose chlorine relative to other constituents. This depletion is evident in the bottom plots. The top plots show the molar deficit in particle chlorine to be offset by particle nitrate, as Eldering et al. (1991) found was the case in southern California. This result suggests that replacement by nitrate accounts for much of the observed chloride loss. Replacement by sulfate may be of comparable or greater importance, but is harder to distinguish against the higher background of sulfate's ammonium salts.

Fig. 5 excludes observations at nitrate concentrations above $1\,\mu g\,m^{-3}$ because these can be dominated by ammonium nitrate of non-marine origin. The impact of non-marine sources can be detected in Fig. 4, where they contribute only to the denominator RM of the plotted ratios. Most low values of $[Na]_p$/RM (especially before December 2001) and $\lfloor Cl^- \rfloor$/RM (especially after 2000) are plotted with the open symbols that indicate $\lfloor NO_3^- \rfloor > 1\,\mu g\,m^{-3}$. Such nitrate excursions occur primarily in the winter months, when this site receives outflows from the inland San Joaquin Valley (MacDonald et al., 2006). Ammonium nitrate concentrations in this agricultural valley can reach tens of $\mu g\,m^{-3}$ (Watson and Chow, 2002).

The replacement of chloride by nitrate or sulfate obviously alters sea salt's properties. One change is that sea salt gains mass with age, because the nitrate and sulfate ions are heavier than their chloride equivalents. The mass increment can be calculated as follows. Consider a unit mass of sea salt, and let a fraction f_N of the chloride be replaced by nitrate. The chloride mass $f_N a_{Cl,salt}$ is then replaced by a nitrate mass $(MW_{NO_3}/MW_{Cl}) f_N a_{Cl,salt}$, for a net change of $((MW_{NO_3} - MW_{Cl})/MW_{Cl}) f_N a_{Cl,salt} = 0.41 f_N$. Sulfate replacement yields an increment about half this size, $((MW_{SO_4} - 2MW_{Cl})/2MW_{Cl})$

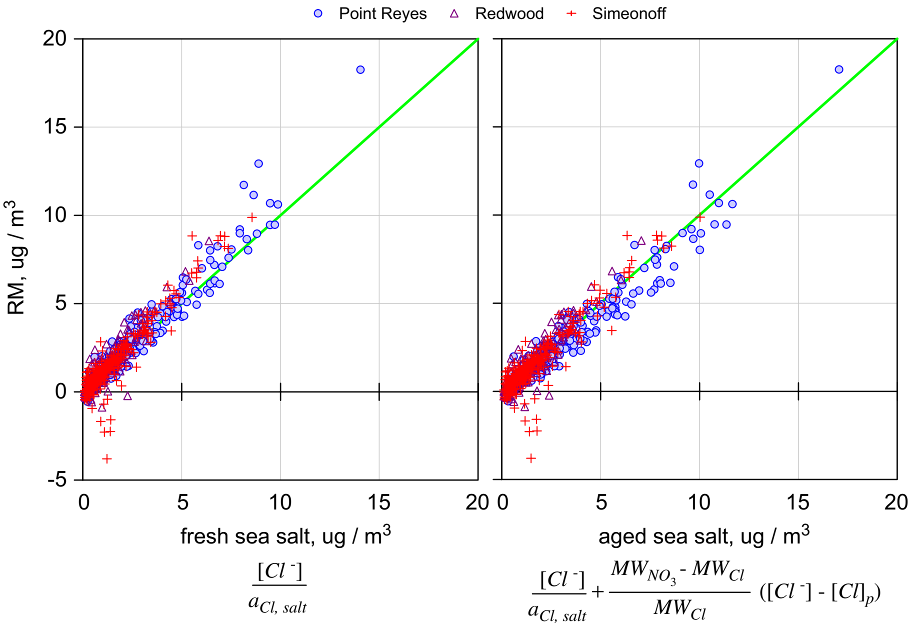

Fig. 6. Observed reduced mass $\mathrm{RM} = (\mathrm{FM} - (132/96)[\mathrm{SO}_4^=] - 1.8[\mathrm{C}] - (1/a_{\mathrm{Fe,crust}})[\mathrm{Fe}])/(1 - (132/96)a_{\mathrm{SO_4,salt}})$ compared with two estimates of sea salt mass, from $[\mathrm{Cl}^-]$ (on Nylon) alone or $[\mathrm{Cl}^-]$ and $[\mathrm{Cl}^-]_p$ (on Teflon) together. All complete 1 December 2001–31 December 2004 observations with detected particle chlorine, and particle nitrate concentrations below $1\,\mu\mathrm{g\,m}^{-3}$.

$f_S a_{\mathrm{Cl,salt}} = 0.20 f_S$. The total fraction of chloride replaced can be estimated from IMPROVE data as $f_N + f_S = ([\mathrm{Cl}^-] - [\mathrm{Cl}]_p)/[\mathrm{Cl}^-]$, and the combined relative increase in sea salt mass is then somewhere between 20% and 41% of the fraction of chloride replaced.

Fig. 6 suggests that the moderate mass gain from anion replacement is detectable in IMPROVE data. Interpreting chloride as a tracer for fresh sea salt yields a slight under-prediction of reduced mass (left). This bias disappears when mass gained with aging is taken into account (right). The calculation here attributes all chloride replacement to nitrate, overestimating the mass gain to the degree that sulfate also contributes. Table 2 provides a more quantitative indication of mass gains from anion replacement.

The columns headed "m_g/seawater" compare observed ratios of various constituents at the six sites identified in Fig. 1. Results are presented as the geometric means (m_g) of the ratios measured in individual 24 h samples, normalized by reference ratios expected in fresh sea salt.

The first three rows of Table 2 support our interpretation of IMPROVE's chloride ion measurement as a quantitative indicator of sea salt mass. The geometric means of $\mathrm{RM}/[\mathrm{Cl}^-]$ in the first row are all above the mass/chloride ratio $1/a_{\mathrm{Cl,salt}}$ in fresh sea salt. Aggregated over all six sites, the observed value is 13% higher than the reference. The second and third rows of Table 2 account for chloride replacement explicitly, adjusting reduced mass as indicated for its effects.

The quantity $\mathrm{RM}(-\mathrm{NO}_3)$ is an estimate for fresh sea salt based on the assumption that nitrate accounts for all chloride replacement. The adjustment $-((\mathrm{MW}_{\mathrm{NO}_3} - \mathrm{MW}_{\mathrm{Cl}})/\mathrm{MW}_{\mathrm{Cl}})([\mathrm{Cl}^-] - [\mathrm{Cl}]_p)$ accounts for the net change in the weight of the anion. The resulting ratios $\mathrm{RM}(-\mathrm{NO}_3)/[\mathrm{Cl}^-]$ in the second row fall on both sides of the seawater reference, with an overall mean that is only 5% low.

$\mathrm{RM}(-\mathrm{SO}_4)$ is the analogous estimate on the assumption that sulfate accounts for all chloride replacement. Since RM is defined to exclude all secondary sulfate, the adjustment in this case involves only the addition of lost chloride. The generally high values $\mathrm{RM}(-\mathrm{SO}_4)/[\mathrm{Cl}^-]$ in the third row suggest that nitrate is the more important replacement ion. The geometric standard deviations are smaller, but this may be only a numerical artifact of the adjustment. If chloride is depleted by a constant fraction $f = ([\mathrm{Cl}^-] - [\mathrm{Cl}]_p)/[\mathrm{Cl}^-]$, for example, then $\mathrm{RM}(-\mathrm{SO}_4)/[\mathrm{Cl}^-] = \mathrm{RM}/[\mathrm{Cl}^-] + f$

Table 2
Observed aerosol composition relative to fresh sea salt

Ratio	Modules involved	m_g/seawater						Ln s_g						"Marine" sample count						Notes
		PORE	REDW	SIME	CACO	MAVI	VIIS	PORE	REDW	SIME	CACO	MAVI	VIIS	PORE	REDW	SIME	CACO	MAVI	VIIS	
RM/Cl^-	A,B,C/B	1.06	1.17	1.12	1.11	1.19	1.31	0.19	0.23	0.17	0.25	0.22	0.31	182	91	126	49	35	64	a,e
RM($-NO_3$)/Cl^-	A,B,C/A,B	0.83	1.01	0.99	0.92	0.96	1.17	0.28	0.28	0.23	0.33	0.24	0.41	181	91	126	49	33	64	a,e
RM($-SO_4$)/Cl^-	A,B,C/A,B	1.36	1.39	1.29	1.36	1.43	1.47	0.17	0.20	0.13	0.21	0.20	0.24	181	91	126	49	33	64	a,e
$Sr_{n\text{-}c}$/Cl^-	A/B	1.08	1.23	0.97	1.20	1.18	1.17	0.27	0.33	0.31	0.39	0.37	0.47	205	102	143	56	46	44	a,b,h
$K_{n\text{-}c}$/Cl^-	A/B	0.96	1.23	0.96	1.31	1.17	1.20	0.26	0.33	0.23	0.27	0.23	0.35	128	44	122	27	15	38	a,c,f,h
$Ca_{n\text{-}c}$/Cl^-	A/B	0.99	1.18	0.99	1.18	1.24	1.08	0.24	0.40	0.20	0.27	0.29	0.37	190	98	138	53	43	35	a,d,h
$Ca_{n\text{-}c}$/$Sr_{n\text{-}c}$	A/A	0.92	1.00	1.03	0.96	1.07	0.93	0.21	0.30	0.31	0.26	0.25	0.22	190	97	137	53	42	35	a,b,c,h
All valid samples														337	345	372	353	217	174	

The quantities considered include reduced mass, $\mathrm{RM} = (\mathrm{FM} - (132/96)\left[\mathrm{SO}_4^{=}\right] - 1.8[\mathrm{C}] - (1/a_{\mathrm{Fe,crust}})[\mathrm{Fe}])/(1 - (132/96)a_{\mathrm{SO_4,salt}})$; reduced mass adjusted for chloride displacement by nitrate, $\mathrm{RM}(-\mathrm{NO}_3) = \mathrm{RM} - ((\mathrm{MW}_{\mathrm{NO}_3} - \mathrm{MW}_{\mathrm{Cl}})/\mathrm{MW}_{\mathrm{Cl}})([\mathrm{Cl}^-] - [\mathrm{Cl}]_p)$; reduced mass adjusted for chloride displacement by sulfate, $\mathrm{RM}(-\mathrm{SO}_4) = \mathrm{RM} + [\mathrm{Cl}^-] - [\mathrm{Cl}]_p$ and the non-crustal concentrations of Sr, K and Ca, $\mathrm{X}_{\text{n-c}} = [\mathrm{X}] - (a_{\mathrm{X,crust}}/a_{\mathrm{Fe,crust}})[\mathrm{Fe}]$. Three statistics are shown for each ratio: the geometric mean m_g, normalized to the ratio in reference seawater (Millero, 2004); the natural logarithm of the geometric standard deviation s_g and the number of identifiably "marine" samples. Samples are considered "marine" if they meet the criteria indicated in the notes column, and all 1 December 2001–31 December 2004 samples meeting these criteria are included. The Martha's Vineyard sampler was installed in February 2003 and data from module B at Virgin Islands are considered valid only since June 2003, yielding smaller sample populations at these sites.

Notes: (a) $[\mathrm{Cl}^-]/a_{\mathrm{Cl,salt}} \geqslant 1\,\mu\mathrm{g\,m^{-3}}$; (b) $[\mathrm{Sr}]/[\mathrm{Fe}] \geqslant 1.5(a_{\mathrm{Sr,crust}}/a_{\mathrm{Fe,crust}})$; (c) $[\mathrm{K}]/[\mathrm{Fe}] \geqslant 1.5(a_{\mathrm{K,crust}}/a_{\mathrm{Fe,crust}})$; (d) $[\mathrm{Ca}]/[\mathrm{Fe}] \geqslant 1.5(a_{\mathrm{Ca,crust}}/a_{\mathrm{Fe,crust}})$; (e) $\mathrm{RM} \geqslant 1\,\mu\mathrm{g\,m^{-3}}$; (f) $1.8[\mathrm{C}] < 1\,\mu\mathrm{g\,m^{-3}}$ and (h) "July 4" excluded.

necessarily has less relative variability than RM/$[\mathrm{Cl}^-]$ does.

The remaining rows of Table 2 examine three trace metals conserved in the particle phase under atmospheric reactions. Their observed proportions further support the suitability of chloride ion as a tracer for sea salt, as discussed in Section 4.

4. Conserved trace metals

Potassium, calcium and strontium are present at comparable concentrations in continental crust and sea salt (Table 1). Aluminum, silicon and iron are crustal elements that are much less abundant in sea salt, and each has been successfully used to estimate the contributions of soil dust to ambient particulate matter (Miller et al., 1972; Lewis et al., 1988; Lowenthal and Kumar, 2006). Of these potential soil markers, iron is the best-measured by IMPROVE. It is used here as the basis for estimating ambient concentrations attributable to crustal material: $[\mathrm{X}]_{\mathrm{crustal}} = (a_{\mathrm{X,crust}}/a_{\mathrm{Fe,crust}})[\mathrm{Fe}]$. Although iron also has industrial (Moreno et al., 2004) and vehicular (Harrison et al., 2003) sources, these can reasonably be neglected at remote IMPROVE sites.

Figs. 7 and 8 plot estimated concentrations of non-crustal potassium, calcium and strontium against measured concentrations of chloride ion. Departures from the proportions found in seawater are associated with wood smoke and fireworks.

The contribution of wood smoke to potassium can be seen in the difference between the paired plots in Fig. 7. The potassium outlier in the top plot is from a sample at Point Reyes on 12 October 2004, when the total carbon concentration ($13.2\,\mu\mathrm{g\,m^{-3}}$) was the highest ever measured there. This observation can be attributed with confidence to a specific wildfire in Rumsey Canyon, <100 km from the sampler (Schmaltz, 2004; Rubenstein et al., 2004). Smoke's impacts are rarely so well-documented. Vegetative burning is known to be a significant potassium source, however, and samples richer in carbon can be expected to include more vegetative smoke (Tanner et al., 2001; Hays et al., 2005). The bottom plot excludes samples with more than $1\,\mu\mathrm{g\,m^{-3}}$ of estimated carbonaceous mass, eliminating about one-third of the observations. The carbon-poor samples exhibit proportions of non-crustal potassium and chloride that approximate those in seawater.

Fig. 8 presents observations of non-crustal calcium and strontium at all carbon concentrations.

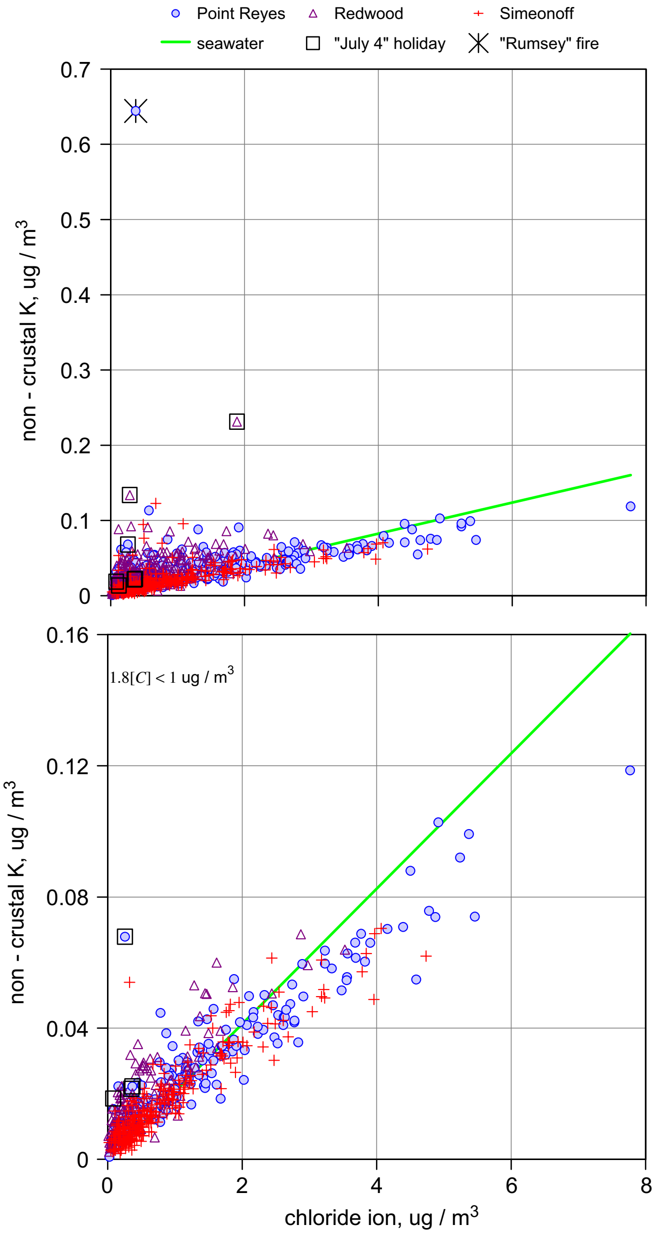

Fig. 7. Non-crustal potassium relative to chloride ion. Crustal contributions $K_{\mathrm{crustal}} = (a_{\mathrm{K,crust}}/a_{\mathrm{Fe,crust}})[\mathrm{Fe}]$ are estimated from iron concentrations and the crustal composition in Table 1. Top: all complete 1 December 2001–31 December 2004 observations for which total measured potassium is at least 50% above the crustal estimate. Bottom: the subset of these observations for which estimated carbonaceous mass is less than 1 μg m^{-3}.

Except for the direct impact of the Rumsey fire at Point Reyes on 12 October 2004, the contributions of smoke appear to have been negligible.

Additional outliers for potassium and strontium are evident in both figures. These are associated with the principal occasion for fireworks in the United States, the 4 July celebration of national independence. Although 4 July is always a federal holiday, the date does not always coincide with either an IMPROVE sampling day or community pyrotechnic displays. IMPROVE collects a midnight–midnight sample every third day, and the major displays are usually scheduled for weekend nights. The samples highlighted as “July 4” in the figures are 7 July 2002

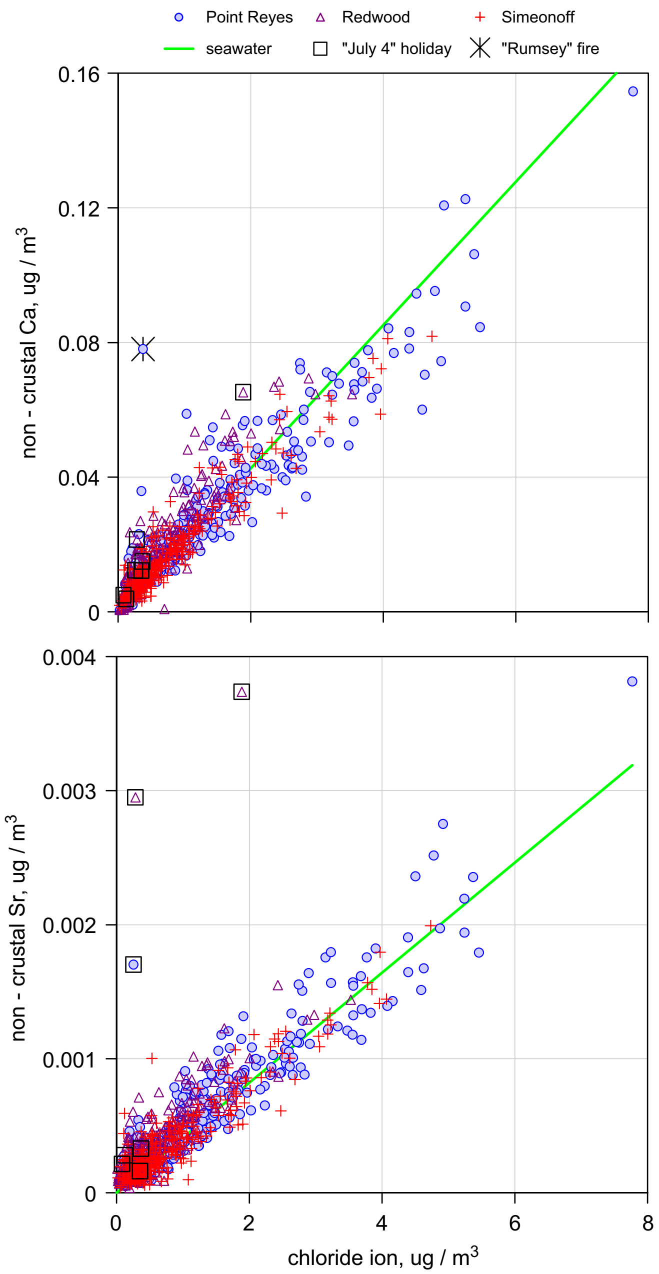

Fig. 8. Non-crustal strontium and calcium relative to chloride ion. Crustal contributions $X_{crustal} = (a_{X,crust}/a_{Fe,crust})[Fe]$ are estimated from iron concentrations and the crustal composition in Table 1. All complete 1 December 2001–31 December 2004 observations are shown for which measured concentrations are at least 50% above their crustal expectations.

(Sunday), 5 July 2003 (Saturday) and 5 July 2004 (Monday). Potassium, calcium and strontium all appear in the compounds used as oxidants and colorants for fireworks (Shimizu, 1981), and potassium and strontium residues have previously been reported in ambient air (Alpert and Hopke, 1981; Kulshrestha et al., 2004).

Rows 4–7 of Table 2 summarize the proportions of K, Ca, Sr and Cl^- observed at the six identified sites in Fig. 1. The observed proportions at each site are close to those in seawater, supporting chloride's use as a tracer for the conserved species in sea salt. The agreement is best at Point Reyes and Simeonoff, which together account for about 60% of the identifiably "marine" observations. The overall geometric mean metal/chloride ratio, aggregated over all three metals in all identifiably marine samples at all six sites, is only 7% above the seawater value.

5. Summary discussion

This paper presents a case for considering the chloride concentration reported by IMPROVE to be a quantitative indicator of fine-particle sea salt concentrations at coastal sites. Our evidence is empirical and somewhat circumstantial. The IMPROVE program determines chloride by ion chromatography of a Nylon-filter sample collected behind a carbonate denuder and $PM_{2.5}$ cyclone. The performance of this system for sulfate and nitrate has received considerable scrutiny, but the chloride measurement has received much less attention. In particular, the denuder efficiency, filter retention and analytical recovery for HCl have yet to be characterized in the laboratory.

If the denuder ahead of the Nylon filter should be found ineffective in removing HCl, then measured chloride would represent total (gas and particle) chloride. In this case, IMPROVE chloride can serve as a sea salt tracer wherever losses of HCl to surface deposition can be neglected. If the denuder is instead shown to remove HCl effectively, as intended, then the agreement of measured chloride with other sea salt markers indicates that marine aerosols at the six sites studied here are largely unreacted. The observed deficit of chlorine on the undenuded Teflon filter then represents a sampling artifact, one likely to affect the mass and sulfur data also reported from that filter. Denuder performance is beyond the reach of our data analyzes and will have to be determined experimentally.

Our characterization of the chloride measurement rests on multiple demonstrations that observed relationships satisfy geochemical expectations. Measured chloride is generally consistent with the portion of gravimetric mass not explained by terrestrial fractions (Figs. 4 and 6; Table 2). The measured difference between particle chlorine on the Teflon filter and chloride ion on the Nylon filter is generally consistent with measured particle nitrate and gravimetric mass (Figs. 5 and 6; Table 2). Measured chloride is generally consistent with the excesses of measured potassium, calcium and strontium over estimated contributions from crustal materials (Figs. 7 and 8; Table 2). The various comparisons involve parallel samples collected on three different filter media (Teflon, Nylon, Quartz) and subjected to five independent analyzes (weighing, ion chromatography, thermal fractionation, Cu-anode and Mo-anode XRF).

The persuasive force of these demonstrations is strengthened by the quantitative and *a priori* character of the relationships. In each case, agreement is defined in terms of the known composition of seawater, not some empirical regression line or multivariate factor. Compositional uncertainties, such as the C/mass fraction of carbonaceous particulate matter or the K/Fe ratio of soil dust, enter only the non-marine terms of our calculations. Their impact on comparisons between marine species is thus indirect, and should diminish as sea salt concentrations increase.

Realistic "reference aerosols" are difficult to generate and present to samplers in the field. Once chloride is accepted as a quantitative tracer, sea salt can be exploited as a "standard reference material" that is available *in situ* at coastal sites. The mean ratios in Table 2 then provide calibration checks for the overall system of sampling and analysis. This is not the place to go into detail, but the mean ratios are consistent with IMPROVE's stated accuracy objectives (IMPROVE, 2002) when account is taken of statistical sampling uncertainties at sites with few identifiably marine episodes.

The standard deviations in Table 2 are affected by real variations (e.g. in the elemental content of crustal dusts) as well as measurement errors. They are calculated differently from the collocated precisions for IMPROVE measurements reported by Hyslop and White (2007), and describe a different population of observations with generally higher concentrations of marine species. With all these *caveats* regarding interpretation, the standard deviations of the various tracer ratios are comparable with the measurement uncertainty estimates derived by propagating the precisions of Hyslop and White.

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