Formation of nitrate and non-sea-salt sulfate on coarse particles

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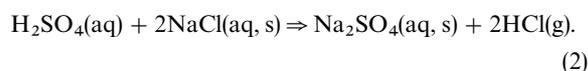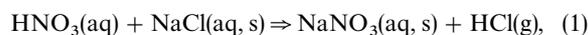
Abstract

The formation of nitrate and sulfate on coarse particles and its relationships with meteorological conditions and relative abundance of sea-salt and soil particles were studied. Size distributions of particulate SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+, K^+, Mg^{2+} and Ca^{2+} were measured using a MOUDI cascade impactor for 11 days in July to December 1997 at a coastal site in Hong Kong. Most of the nitrate and a small fraction of sulfate were distributed in the coarse mode. Since Hong Kong is influenced by both marine and continental aerosols, the distribution of coarse mode nitrate and sulfate depends on the weather conditions. Evidence of nitrate formation on both sea-salt and soil compounds was found in this study. Chloride depletion of sea-salt by both nitrate and sulfate formation was also observed. When Hong Kong was under prevailing easterly wind accompanied with high relative humidity, Na^+ was the dominant cation species and significant chloride depletion (74–88%) from coarse mode sea-salt aerosols was observed. Nitrate accounted for 65% of chloride depletion. During a heavily polluted period when there were high concentrations of both fine (18 μg m^{-3}) and coarse mode (3 μg m^{-3}) sulfate, significant amount of sulfate was associated with sea-salt particles and accounted for 11–29% of the chloride depletion. At least 16% of chloride depletion was not accounted for by nitrate and sulfate alone in this episode. When Hong Kong was influenced by a northeasterly monsoon, Ca^{2+} was the dominant species in the coarse mode. Soil particles compete with sea-salt particles for acidic gases. Chloride depletion was below 50% and most of the nitrate was found to be associated with Ca^{2+} in soil particles. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

The formation of nitrate and sulfate on coarse particles is an important removal path of gaseous pollutants of SO_2 and NO_x and their reaction products in the atmosphere. When secondary nitrate and sulfate are accumulated in the coarse mode, they can be removed more rapidly by dry or wet deposition because of the larger particle size. The composition of primary coarse particles is related to the formation of secondary species in this mode. For example, sea-salt particles are important to the accumulation of nitrate and non-sea-salt (nss) sulfate in the coarse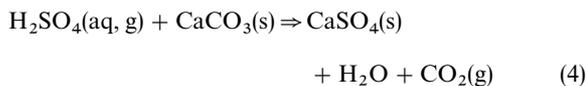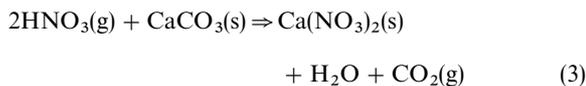 mode. Various research using bulk particle and single particle analyses has concluded that coarse mode nitrate is mainly formed by the reaction of HNO_3 with sea-salt particles, especially when maritime and polluted urban air masses are mixed together. This reaction has been suggested to be the major path for the formation of coarse mode nitrate at many coastal areas. NO_x transforms into gaseous nitrous and nitric acids, which later react with NaCl in sea-salt aerosols to form $NaNO_3$ and HCl in the so called chloride depletion reaction [Reaction (1)] (Savoie and Prospero, 1982; Harrison and Pio, 1983; Wall et al., 1988; Wu and Okada, 1994; Kerminen et al., 1997; Harrison et al., 1994; Pakkanen, 1996):

$$HNO_3(aq) + NaCl(aq, s) \Rightarrow NaNO_3(aq, s) + HCl(g), \quad (1)$$

$$H_2SO_4(aq) + 2NaCl(aq, s) \Rightarrow Na_2SO_4(aq, s) + 2HCl(g). \quad (2)$$

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SO_2 oxidation and to a lesser extent H_2SO_4 vapor condensation on sea-salt aerosols can also lead to chloride depletion [Reaction (2)]. Sievering et al. (1995) found that heterogeneous oxidation of SO_2 by O_3 proceeds rapidly in freshly formed coarse sea-salt aerosol when it contains water, because of the initial alkaline nature of the particles. They found that the conversion is strongly dependent on the amount of sea-salt aerosol water volume. This process has been suggested to be the major path for the formation of coarse mode non-sea-salt sulfate (nss-sulfate) in the marine boundary layer (Sievering et al., 1991, 1995; Chameides and Stelson, 1992). Formation of nss-sulfate by droplet-phase oxidation of SO_2 in cloud was also suggested to be a major mechanism of coarse mode non-sea-salt sulfate (Kerminen and Wexler, 1995). Sea-salt aerosols act as cloud condensation nuclei to form fog or cloud droplets and enhance the sulfate formation by SO_2 oxidation in the droplet phase (McInnes et al., 1994; Kerminen et al., 1997). H_2SO_4 gas can condense on sea-salt particles and react with NaCl to form coarse mode non-sea-salt sulfate. But the contribution to nss-sulfate formation by this reaction is less important because the concentration of gas-phase H_2SO_4 is low in both clean and polluted environments. HNO_3, SO_2 or H_2SO_4 can also react with aqueous carbonates such as dissolved $CaCO_3$ and $MgCO_3$ on soil particles to form coarse mode nitrate and sulfate [Reactions (3) and (4)] (Wolff, 1984; Harrison and Kitto, 1990; Clarke and Karani, 1992; Mamane and Gottlieb, 1992).

$$2HNO_3(g) + CaCO_3(s) \Rightarrow Ca(NO_3)_2(s)$$
$$+ H_2O + CO_2(g) \qquad (3)$$

$$H_2SO_4(aq, g) + CaCO_3(s) \Rightarrow CaSO_4(s)$$
$$+ H_2O + CO_2(g) \qquad (4)$$

Wolff (1984) found that over 70% of nitrate was present in the coarse mode at rural sites in Louisiana, Virginia and South Dakota. The nitrate concentration was well correlated with those of soil elements. Wu and Okada (1994) found that soil associated nitrate was present in a coastal site in Japan and was related to a sandstorm originating from the East Asia deserts. Kerminen et al. (1997) showed that a significant amount of nitrate was associated with both sea-salt and soil particles at a coastal site in southern Finland. Non-sea-salt sulfate formed by the reaction of H_2SO_4 with soil compounds have also been reported (Wall et al., 1988; McInnes et al., 1994; Pakkanen et al., 1996). Using single particle analysis by X-ray spectrometry, Wu and Okada (1994) found that sulfate and nitrate exist on soil particles as a surface layer, suggesting the surface reaction mechanism of these acidic species with soil particles.

As Hong Kong is influenced by easterly winds rich in marine aerosols and northerly winds (from China) rich in soil aerosols, the formation of coarse mode nitrate and sulfate will be affected by wind direction and thereby the primary coarse mode compositions. Recent study on receptor modeling of respirable suspended particulates has revealed that chloride depleted sea-salt aerosols and crustal aerosols, in addition to ammonium sulfate, are sources containing sulfate in HK (Lee et al., 1999). In this study, the formation and size distributions of nitrate and nss-sulfate in coarse particles were investigated. Evidence of nitrate and sulfate formation on both sea-salt particles and soil particles has been observed in our study. The partition of nitrate and nss-sulfate in sea-salt and soil particles will be discussed.

2. Experiment

The experiment procedures, similar to those described in Zhuang et al. (1999), are briefly mentioned here. Sampling was performed in the period of July–December 1997, for a total of 11 sets of samples. Sample collection began at 10:00 am and lasted for 24 h. Sampling dates and meteorological conditions are listed in Table 1.

The sampling location was at the Hong Kong University of Science and Technology (HKUST) at Clear Water Bay, which is a sparsely populated area on the eastern coast of the New Territories (Fig. 1). The sampling site was located on the roof of an academic building, which is about 20 m in height above the ground and about 65 m above sea level and about 500 m from the coast. The site was about 500 m from a lightly trafficked road and was 5 km from the closest industrial area. The sampler inlet was about 1.5 m height and distant from any obstacles. The prevailing wind direction is east or southeast. In fall and winter, monsoon from China can occasionally bring in northerly or northeasterly wind.

Ambient aerosols were collected using a Micro-Orifice Uniform Deposit Impactor (MOUDI-100, MSP Corp.). It has 10 size-fractionated stages with nominal cut-size of 18 (inlet), 9.9, 6.2, 3.1, 1.8, 1.0, 0.54, 0.32, 0.177, 0.097, 0.052 μm and an after filter. The flow rate was controlled at 30 l/min (Marple et al., 1991). The substrates used in the MOUDI were Teflon membrane filters 47 mm in diameter and 2 μm pores (Teflo™ R2PJ047, Gelman Sciences). Water soluble inorganic species of SO_4^{2-}, NO_3^-, NH_4^+, Cl^-, Na^+, K^+, Mg^{2+} and Ca^{2+} at each stage were extracted using 10 ml of ultra-pure water (specific resistance $\geqslant 18.1 \, M\Omega - cm$). Chemical analysis of the inorganic species was conducted by ion chromatography (DIONEX 500) with an electrochemical detector (DIONEX ED40). The detection limits are: 0.008 μg m^{-3} for SO_4^{2-}, Cl^- and NH_4^+, 0.005 μg m^{-3} for NO_3^- and Mg^{2+}, 0.014 μg m^{-3} for Na^+, and 0.011 μg m^{-3} for Ca^{2+}.

Table 1
Meteorological conditions and concentrations of major inorganic ions in the coarse mode (1.8 μm < Dp < 18 μm)

Sampling date	T (°C) Min.-Max.	Average	RH (%) Min.-Max.	Average	Prevailing wind direction	[Na$^+$]	[Cl$^-$]	[NO$_3^-$] (μg m^{-3})	[SO$_4^{2-}$]	[Ca^{2+}]	Notes
July 23 1997	27.0–35.5	30.5	52.0–84.0	65.5	360	0.614	0.226	1.597	0.355	0.076	After rain
July 24 1997	26.5–36.0	32.0	52.5–87.0	78.9	220	0.519	0.145	1.505	0.379	0.061	
July 28 1997	28.0–35.5	31.1	53.0–91.0	74.1	200	0.344	0.132	0.738	0.248	0.027	
July 29 1997	27.8–35.5	30.8	58.0–91.0	76.4	120	0.382	0.142	0.749	0.341	0.005	
November 4 1997	18.5–27.0	22.8	33.0–41.0	36.7	10	0.207	0.211	0.659	0.370	0.465	November 4–5 northeasterly monsoon
November 5 1997	18.0–26.0	21.4	28.0–55.0	41.0	10	0.474	0.621	1.281	0.655	0.880	
November 6 1997	19.0–25.5	21.7	48.0–83.0	61.9	70	1.647	1.575	3.214	0.810	0.624	
November 7 1997	20.0–25.0	22.4	48.0–88.0	70.0	60	2.328	2.225	3.263	0.758	0.243	
December 18 1997	20.0–24.0	20.8	74.0–99.0	90.5	60	1.731	0.835	2.728	1.272	0.145	December 18–20: In the morning,
December 19 1997	20.0–26.5	22.0	65.0–97.0	85.1	50	1.218	0.272	2.388	1.082	0.129	
December 20 1997	19.5–21.5	20.6	90.0–100.0	95.9	50	1.497	0.672	1.616	2.973	0.085	API > 100[a]

[a] API: Air pollution index of Hong Kong. API = 100 corresponds to the Hong Kong air quality standard.

3. Results

The size distributions of the inorganic ions were calculated from the size-fractionated concentration of each MOUDI stage. Unless specified otherwise, equivalent ionic concentrations are used in this paper. The impactor data was fitted with lognormal distribution functions using DISTFIT (TSI). SO_4^{2-} and NH_4^+ are mainly distributed in the fine mode with the mode diameter around 0.6 μm. Only a small fraction of sulfate is found in the coarse mode, defined as particles larger than 1.8 μm here. NO_3^-, Na^+, Cl^-, Mg^{2+} and Ca^{2+} are mainly distributed in the coarse mode with the mode diameter around 4 μm. Mode distribution characteristics of SO_4^{2-}, NH_4^+ and NO_3^- at this site have been reported by Zhuang et al. (1999).

The mass concentrations of the major inorganic species in the coarse mode and meteorological conditions are listed in Table 1. Coarse mode nitrate and sulfate concentrations were in the range of 0.66–3.26 μg m^{-3} and 0.25–2.97 μg m^{-3}, respectively. On average, nitrate and sulfate accounted for about 22 and 13% (neq%) of the total concentrations of measured ions in the coarse mode, respectively. As shown in Table 2, the equivalent ratios of $[NO_3^-]/[Na^+]$ and $[SO_4^{2-}]/[Na^+]$ are higher than those of original sea water. Hence, additional nitrate and sulfate are present in the coarse mode particles.

As there is no known major emission source for coarse mode nitrate, the coarse mode nitrate is assumed to be from the reaction of HNO_3 or NO_x with coarse particles. Coarse mode sulfate, albeit at lower concentrations than nitrate, can be attributed to a few sources. There is a natural amount of sulfate in sea water (sea-salt sulfate) and there are nss-sulfate from condensation of H_2SO_4 and reaction of SO_2 and emission of other sulfates such as gypsum (Fitzgerald, 1991). nss-sulfate contributes mostly over 50% of the total coarse mode sulfate in our study, ranging from 21 to 87%.

Na^+ and nss-Ca^{2+} were used as tracers of sea-salt and soil components for comparing the relative abundance of sea-salt and soil particles in the coarse mode. Na^+ is assumed to be mainly from seasalt aerosols. Based on the species concentrations and the weather conditions listed in Tables 1 and 2, the 11 sampling days can be classified into 2 categories when Na^+ or Ca^{2+} dominates the cation concentrations.

When Hong Kong was under the prevailing easterly wind with high relative humidity, $[Ca^{2+}]/[Na^+]$ equivalent ratios are smaller than 0.13 (July 23, 24, 28, 29, and December 18–20, 1997; see Table 2). nss-Ca^{2+} concentration is less than 0.08 μg m^{-3} and only accounts for about 5% (neq%) of Na^+ concentration (> 0.34 μg m^{-3}). Na^+ is the dominant cation (in equivalent) in the coarse mode in this period. We will refer this as the Na^+ dominant period in the following discussions.
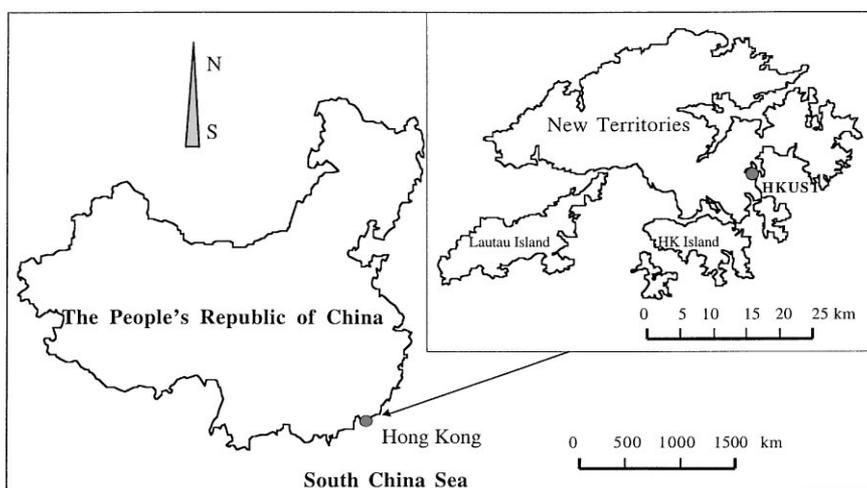
Fig. 1. Sampling location in Hong Kong.

Table 2
Chloride depletion and equivalent ratios of measured Na^+, Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-} in the coarse particles

Date	$\dfrac{[Ca^{2+}]}{[Na^+]}$	$\dfrac{[Cl^-]}{[Na^+]}$	$\dfrac{[NO_3^-]}{[Na^+]}$	$\dfrac{[SO_4^{2-}]}{[Na^+]}$	Cl-dep (%)	$\dfrac{[ex\text{-}SO_4^{2-}]^a}{[NO_3^-]}$	$\dfrac{[nss\text{-}Ca^{2+}]}{[NO_3^-]}$	$\dfrac{[NO_3^-]}{[Cl\text{-dep}]}$	$r_0^{\,b}$	$r_2^{\,b}$
July 23	0.134	0.239	0.964	0.277	79.6	0.080	0.093	1.30	0.83	0.78
July 24	0.134	0.181	1.074	0.350	84.6	0.184	0.084	1.08	0.80	0.69
July 28	0.089	0.248	0.794	0.344	78.9	0.250	0.057	0.86	0.96	0.81
July 29	BDL	0.241	0.726	0.428	79.5	0.228	BDL[c]	0.78	1.04	0.88
November 4	2.581	0.661	1.182	0.857	43.7	0.290	2.153	2.30	0.54	0.46
November 5	2.129	0.849	1.002	0.661	27.7	0.288	2.076	3.08	0.54	0.47
November 6	0.434	0.620	0.723	0.235	47.2	0.090	0.550	1.31	0.75	0.71
November 7	0.120	0.620	0.520	0.156	47.2	BDL	0.153	0.94	0.88	0.88
December 18	0.096	0.313	0.584	0.352	73.4	0.228	0.089	0.68	1.12	0.97
December 19	0.122	0.145	0.727	0.425	87.7	0.163	0.107	0.71	1.15	1.01
December 20	0.065	0.291	0.400	0.951	75.2	0.649	0.053	0.45	1.45	1.05
Sea water	0.044	1.174	N/A	0.123	—	—	—	—	0.85	—

[a] Ex-SO_4^{2-}: Excess sulfate, non-sea-salt sulfate that not associated with NH_4^+.
[b] $r_0 = [Na^+]/([Cl^-] + [NO_3^-])$ the ratio of measured Na^+ concentration to the total measured concentration of NO_3^- and Cl^-. r_2 is r evaluated at $[NH_4^+]/[SO_4^{2-}] = 2$.
[c] BDL: Below detection limit.

When Hong Kong was under a northeasterly monsoon with low relative humidity (November 4–7), $[Ca^{2+}]/[Na^+]$ ratios are higher and reach 2.6 and 2.1 in November 4 and 5, respectively. Ca^{2+} is the dominant cation (in equivalent) in the coarse mode, with concentration ranging from 0.47 to 0.88 μg m^{-3}. On November 6, the northeasterly monsoon starts to weaken and the easterly wind resumed. On November 7, the $[Ca^{2+}]/[Na^+]$ ratio decreases back to 0.12, a typical ratio found in the Na^+ dominant period.

Because ambient concentrations of HNO_3, SO_2 and H_2SO_4 were not measured, the contributions of HNO_3

and H_2SO_4 to the size distribution of the ionic species cannot be quantitatively determined. Nevertheless, we can study the trends of the formation of nitrate and nss-sulfate on sea-salt and soil particles. In the Na^+ dominant period, coarse mode nitrate accounts for the major fraction of chloride depletion. nss-sulfate accounts for 10–30% of the chloride depletion in 5 of the 7 days samples collected in the Na^+ dominant period, including a heavy pollution episode (December 18–20) when the local Air Pollution Index (API) was above the air quality objective of 100. In the Ca^{2+} dominant days, nitrate has higher equivalent concentrations than Na^+ in the coarse

mode. Nitrate was found to be associated with soil particles.

4. Discussions

4.1. Nitrate and sulfate formation on sea-salt particles

4.1.1. Chloride depletion

Chloride depletion is resulted when the acidic species, mainly nitrate, sulfate and some organic acids, react with NaCl in sea-salt particles and replace Cl^- in the form of HCl gas. The extent of chloride depletion is important in estimating the amount of nitrate and sulfate formed on sea-salt particles. Since the original chloride concentration $[Cl]_{original}$ is 1.174 times that of the Na^+ concentration in sea-salt, the percentage of chloride depletion can be calculated as

$$Cl\text{-dep}(\%) = ([Cl^-]_{original} - [Cl^-])/[Cl^-]_{original} \times 100\%$$

$$= (1.174[Na^+] - [Cl^-])/1.174[Na^+] \times 100\%.$$

In the above equation, sea-salt Na^+ concentration is assumed to be the measured $[Na^+]$. As shown in Table 2, $[Cl^-]/[Na^+]$ ratios are consistently smaller than 1.174 for all the samples. The percentage of chloride depletion percentage ranges from 28 to 88% during the sampling period.

4.1.1.1. The effect of relative humidity and relative abundance of Ca^{2+} and Na^+ on the extent of chloride depletion.
High percentage of chloride depletion (73–88%) was found in the Na^+ dominant period (July 23–29, December 18–20). Low $[Ca^{2+}]/[Na^+]$ ratios (< 0.14) and high relative humidity (52–100%) were observed in these days. The lowest total depletion (28–47%) was found when Hong Kong was under the influence of a northeasterly monsoon, resulting in high Ca^{2+} concentrations such as in November 4 and 5. The relative humidity was mostly lower than 50% in these two days. It is clear that there are two factors affecting the extent of chloride depletion: one is the relative humidity and the other is the competition of Ca^{2+} with Na^+ for the acidic gases.

In our study, nitrate formation contributes to the major fraction of chloride depletion. Ten Brink (1998) found that significant nitrate can only be formed when sea-salt aerosols become droplets. Aqueous-phase reactions will be promoted when sea-salt particles are deliquesced at higher RH. Cloud processing has also been suggested to be the main process for sulfate formation in sea-salt aerosols (Kerminen et al., 1998). Similar to the formation of fine mode nss-sulfate, significant amount of sulfate can be accumulated through droplet phase SO_2 oxidation in sea-salt aerosols. Sea-salt particles can be activated to fog or cloud droplets at supersaturation conditions. High

humidity provides favorable conditions for SO_2 oxidation in both aerosol and droplet reactions.

Higher percentage of chloride depletion was found when the relative humidity was sometimes above the deliquescence relative humidity of NaCl (76% at 25°C). The highest relative humidity in July 23–29 and December 18–20 ranges from 85 to 100% (See Table 1). Fog and low clouds, promoting the chloride depletion of sea-salt aerosols, occasionally appeared. Almost $3\ \mu g\ m^{-3}$ coarse mode nss-sulfate was observed on December 20, when the average RH was 95%. In the days when relative humidity was mostly lower than 50% during the sampling period, sea-salt particles were dry and cloud process was unlikely the major process to form nitrate and sulfate to deplete chloride. The chloride depletion was reduced because the reaction was limited to the surface of the particles with very slow reaction rate.

The competition of Ca^{2+} with Na^+ for the acidic gases will be discussed later.

4.1.1.2. The effect of particle size on the extent of chloride depletion.
The extent of chloride depletion was found to decrease with increasing particle size in the coarse mode. It decreases from 98% to 10% as particle size increases from 1.8 μm to 18 μm. July 23–29 and December 18–20 were humid with daily average relative humidity above 65%. Chloride depletion is 88–100% at 1.8 μm but drops to 21–80% at larger sizes (Fig. 2 (a) and (c)) in these days. Even in drier days such as November 4 and 5, chloride depletion still reaches 57–68% at 1.8 μm but decreases to around 10–35% for particles larger than 10 μm (Fig. 2 (b)). Similar size dependence was also observed by others. For example, Pakkanen (1996) reported a reduction of chloride depletion of 90–100% at particle size of 1–2 μm to less than 40% at particle size of 8–15 μm for sea-salt particles in Finland.

It has been suggested that the surface reaction mechanism is the principal explanation for higher depletion of smaller particles (Pakkanen, 1996; McInnes et al., 1994). The major acidic gaseous species such as HNO_3 reacts on the sea-salt particle surface in a condensation reaction, whose dynamics favors smaller particles because of their much larger surface area distribution and longer atmospheric residence time.

Fig. 3 shows the typical size distributions of the coarse mode ions observed in the Na^+ dominant days. The MMAD of nitrate is slightly smaller than Na^+ (Fig. 3 (b) and (c)), which can be attributed to the surface reaction of HNO_3 with NaCl on sea-salt particles (Savoie and Prospero, 1982; Harrison and Pio, 1983; Wall et al., 1988; John et al., 1990; Ottley and Harrison, 1992). Chloride depletion was almost complete (> 80%) at high relative humidities. On July 23, the relative humidity was sometimes over 80% and above the relative humidity of deliquescence of NaCl (Table 1). Most of the NaCl in
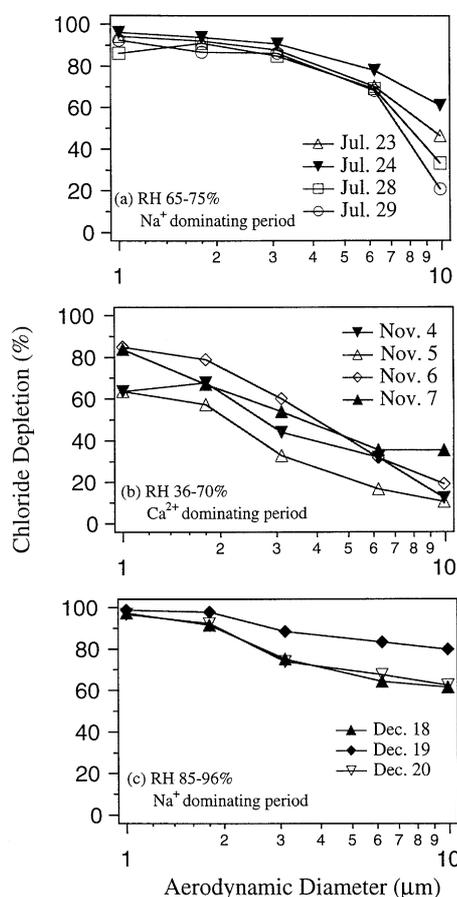
Fig. 2. Chloride depletion at different particle sizes.

Fig. 3. Typical size distributions of major coarse mode ions in the Na$^+$ dominant days.

sea-salt particles has been transformed to NaNO$_3$ because nss-sulfate concentration is only about 15% of nitrate concentration in the coarse mode (Table 2). Since the reaction has proceeded almost to completion, the size distributions of NO$_3^-$ and Na$^+$ almost overlap each other (Fig. 3 (a)). Similar distributions were observed on July 24, 28 and 29, when the relative humidity was high and Na$^+$ concentration was relatively low (between 0.3 and 0.6 μg m^{-3}) but still significantly higher than that of Ca^{2+} (Table 1).

Besides surface reaction, in-cloud processes to form nss-sulfate and possibly nitrate on sea-salt particles can also explain the observed size dependence of extent of chloride depletion (Kerminen et al., 1998). Although the amount of products of droplet-phase reactions may not be size dependent, smaller sea-salt particles would result in a larger fraction of chloride loss when water evaporates from cloud droplets. The shorter time scale of sulfate formation by O$_3$ or H$_2$O$_2$ in cloud droplets of smaller particles also contributes to the observed trend of chloride depletion.
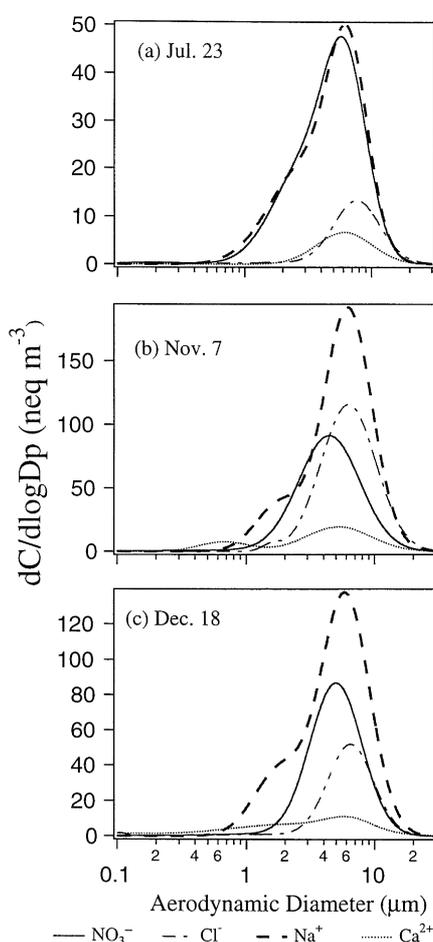
4.2. Partition of nitrate and sulfate associated with NaCl

4.2.1. Contribution of nitrate to chloride depletion

A simple way to evaluate the contributions of nitrate and sulfate is to compare the equivalent concentrations of excess sulfate to nitrate ([ex-SO$_4^{2-}$]/[NO$_3^-$]). Excess sulfate is the amount of nss-sulfate not associated with NH$_4^+$ on the coarse particles and may cause chloride depletion. The nitrate concentration is usually larger than the excess sulfate concentration. As listed in Table 2, the equivalent ratio of excess sulfate to nitrate ranges from 0.08 to 0.29, except on December 20 when the ratio is 0.65. Based on the [NO$_3^-$]/[Cl-dep] ratio, coarse mode nitrate can account for over 68% of the chloride depletion if we assume that all the coarse nitrate is formed on sea-salt particles. Again, December 20 is an exception when nitrate can only account for 45% of the chloride depletion. Sulfate has significant contributions to chloride depletion on this day.

4.2.2. Contribution of non-sea-salt sulfate to chloride depletion

A value r_0, defined as the ratio of the measured Na^+ concentration to the estimated original Cl^- concentration in sea-salt ($[Na^+]/([Cl^-] + [NO_3^-])$), was used to estimate the contribution of sulfate to chloride depletion (Pakkanen, 1996). r_0 of unreacted original sea water is 0.85. The original concentration of Cl^- in sea-salt particles is estimated to be the sum of measured chloride and nitrate concentrations, assuming that chloride depletion results primarily from nitrate formation processes so that the amount of measured nitrate is equal to the amount of lost chloride.

Deviations of r_0 from 0.85 provide information as to what other processes may interfere with the chloride depletion reaction by nitrate formation. The calculated value of r_0 can be affected by a few factors: (1) A *smaller value* would be resulted if the amount of nitrate causing chloride depletion was overestimated, i.e., the measured nitrate concentration was not totally from nitrate formed in sea-salt but was also from other sources such as those associated with Ca^{2+} in soil particles. (2a) A *larger value* would be resulted if the extent of chloride depletion was underestimated by using the measured nitrate concentration, i.e., the measured nitrate concentration cannot account for all the chloride depleted. In this case, some of the chloride depletion can be attributed to sulfate or organic ion formation in sea-salt particles. (2b) A *larger value* would also be resulted if the sodium concentration was overestimated when there were other sources of Na^+ besides sea-salt at this site.

As shown in Fig. 4 (a), r_0 is close to 0.85 on July 23, 24 and November 7. Chloride depletion was mostly due to nitrate formation in these days. Although the combined effects of the above 3 possibilities might also result in $r_0 = 0.85$, it is unlikely to be the case because both nss-sulfate and nss-Ca^{2+} concentrations were low in these days. Hence, NO_3^- formation can account for the chloride depletion in these days. Higher values of r_0 are found in July 28, 29 and December 18–20, when there was insufficient nitrate to account for all the chloride depletion. December 18–20 was a heavy pollution period that had the highest sulfate concentration in the coarse mode. The nitrate concentration on December 20 can account for at most 45% of the chloride depletion (Table 2). This suggests that the existence of a significant amount of sulfate or other anions causing additional chloride depletion.

Since non-sea-salt sulfate can also be attributed to soil compounds like $CaSO_4$ (Wu and Okada, 1994; De Bock et al., 1994) and those associated with NH_4^+ on coarse mode particles, the amount of sulfate as a result of chloride depletion in sea-salt particles can be estimated by Eq. (1a):

$$[nss\text{-}SO_4^{2-}]_{sea} = [nss\text{-}SO_4^{2-}] - [nss\text{-}SO_4^{2-}]_{Ca}$$
$$- [nss\text{-}SO_4^{2-}]_{NH}$$
$$= [ex\text{-}SO_4^{2-}] - [nss\text{-}SO_4^{2-}]_{Ca}, \qquad (1a)$$
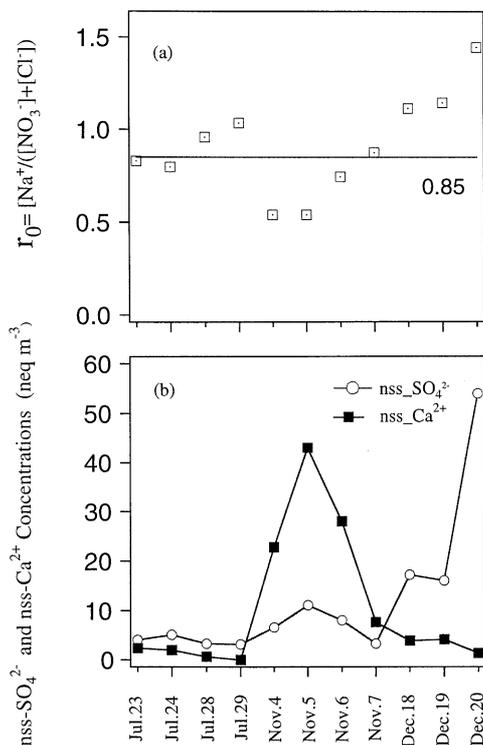

Fig. 4. (a) $r_0 = [Na^+]/([NO_3^-] + [Cl^-])$ during the sampling period. r_1 and r_2 are defined as $[Na^+]/([Cl^-] + [NO_3^-] + [ex\text{-}SO_4^{2-}])$ at $[NH_4^+]/[SO_4^{2-}]$ ratios of 1 and 2, respectively; (b) non-sea-salt SO_4^{2-} and non-sea-salt Ca^{2+} Concentrations during the sampling period.

where: $[nss\text{-}SO_4^{2-}]_{sea}$ is the concentration of non-sea-salt sulfate as a result of chloride depletion reaction of sea-salt particles, $[nss\text{-}SO_4^{2-}]_{Ca}$ is the concentration of non-sea-salt sulfate associated with soil compounds, $[nss\text{-}SO_4^{2-}]_{NH}$ is the concentration of non-sea-salt sulfate associated with NH_4^+ on coarse particles, and $[ex\text{-}SO_4^{2-}]$ is the concentration of excess sulfate, i.e., non-sea-salt sulfate that not associated with NH_4^+.

Because nss-Ca^{2+} concentrations are much lower than the sulfate concentrations (Fig. 4 (b)), the fraction of sulfate associated with soil compounds is insignificant in December 18–20. $[nss\text{-}SO_4^{2-}]_{sea} \approx [ex\text{-}SO_4^{2-}]$ in these days. The amount of chloride depleted can be approximated as $[NO_3^-] + [ex\text{-}SO_4^{2-}]$. However, the amount of sulfate associated with ammonium will depend on aerosol acidity. The molar ratio of $[NH_4^+]/[SO_4^{2-}]$ in the fine mode is about 1 during these 3 days but the ratio in the coarse mode may be different.

To account for the deviation of r_0 from 0.85, modified r values of r_0 are used. Taking consideration that both nitrate and sulfate can participate in the chloride loss reaction, r_1 and r_2 are defined as $[Na^+]/([Cl^-] + [NO_3^-] + [ex\text{-}SO_4^{2-}])$ at $[NH_4^+]/[SO_4^{2-}]$ molar ratios of
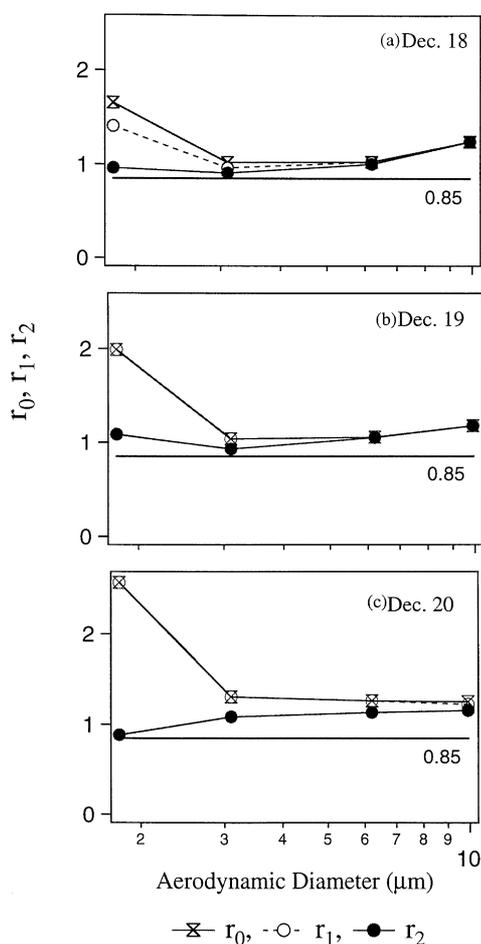
Fig. 5. Modified r value by reaction of excess sulfate with NaCl in December 18–20.

1 and 2, respectively. Less sulfate will be associated with ammonium and hence more excess sulfate can be attributed to the chloride depletion when $[NH_4^+]/[SO_4^{2-}] = 2$ is assumed.

Fig. 5 shows the modified r values at different particle size in December 18–20, when the sulfate concentrations were the highest in both fine (17.5–18.0 μg m^{-3}) and coarse mode (1.1–3.0 μg m^{-3}). r_2 is closer to 0.85 than r_0 and r_1, especially for particles smaller than 6 μm. So part of the nss-sulfate contributes to chloride depletion in these 3 days when there was high sulfate concentration and high relative humidity (85–96%). Using the ratio of $[NH_4^+]/[SO_4^{2-}] = 1$ cannot account for the excess chloride depletion in addition to that due to nitrate. The values of r_1 are virtually identical to r_0 in December 19 and 20 because there is little excess sulfate (i.e. [nss-SO$_4^{2-}$] ≈ [NH$_4^+$]) if $[NH_4^+]/[SO_4^{2-}] = 1$ is assumed (Fig. 5 (b) and (c)). However, r_2 is much closer to 0.85. The assumption of ammonium to sulfate ratio of 2 gives the

maximum amount of excess sulfate available to account for chloride depletion. However, some of the r_2 values are still higher than 0.85, especially in diameter of 6–10 μm. Based on Table 2, 16–25% of chloride depletion has not been accounted for by nitrate and sulfate in this period.

The additional chloride depletion which cannot be compensated by nitrate and nss-sulfate may be attributed to the existence of organic ions such as methanesulfonate (MSA$^-$) and oxalate, etc., which were not measured in this study. Oxalate and some of the acids have greater potential to deplete additional chloride (12–22%) when the sea-salt aerosols are transported to urban area because of their anthropogenic sources (Kerminen et al., 1998). It may be a plausible explanation for the additional chloride depletion in the heavy pollution episode. Sources of Na$^+$ other than sea-salt, possibly from soil or other anthropogenic sources, may be derived from other sources in the larger particles at this site (Milford and Davidson, 1985). However, this factor alone cannot account for the 16–20% additional chloride depletion observed.

A similar modification was also applied to data in July 28 and 29, when the r_0 values were also larger than 0.85. After modification of r_0, assuming excess sulfate are formed by H$_2$SO$_4$ with sea-salt particles, the chloride depletion is well accounted for by both nitrate and sulfate formation in these 2 days. The average value of r_2 reaches to 0.81 and 0.88 (Table 2), which are close to 0.85 (r_1 equals r_0 in these two days since no excess sulfate was present using $[NH_4^+]/[SO_4^{2-}] = 1$).

In conclusion, both nitrate and sulfate can deplete chloride from sea-salt aerosols in Hong Kong. Although nitrate was the major contributor to chloride depletion, significant chloride depletion due to sulfate was found in the days when the $[ex-SO_4^{2-}]/[NO_3^-]$ ratio was larger than 0.2 during the Na$^+$ dominant periods. About 28–90% of nss-sulfate is estimated to be excess sulfate, contributing to 11–29% of chloride depletion in these days. The highest contribution of 29% was found on December 20, when the concentration of sulfate was highest among all the samples. Although higher ratios of $[ex-SO_4^{2-}]/[NO_3^-]$ were also found in November 4–7, ex-SO$_4^{2-}$ in these days may be partially derived from the original soil contents because of the high concentrations of nss-Ca^{2+} during the monsoon period.

4.3. Formation of nitrate on soil particles

Although most of the coarse mode nitrate and sulfate is found to be associated with sea-salt particles in the Na$^+$ dominant period at this site, nitrate associated with soil compounds during the northeasterly monsoon episode (Ca^{2+} dominant period) cannot be ignored. As shown in Fig. 4 (a), lower values of r_0 are observed in November 4–6, when nss-Ca^{2+} concentrations are highest. It indicates an overestimation of nitrate associated
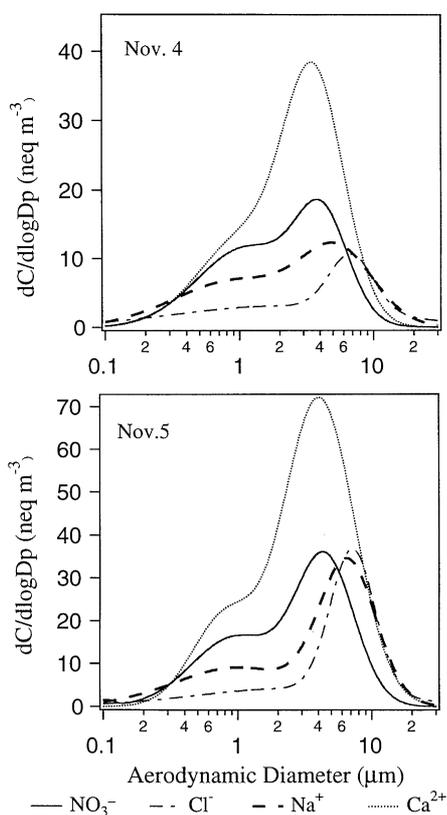
Fig. 6. Size distributions of major species in the coarse mode in November 4 and 5 (Ca^{2+} dominant days).

with sea-salt particles. Part of the nitrate was associated with soil compounds during the Ca^{2+} dominant period. On November 4 and 5, nss-Ca^{2+} concentrations were 0.5 and 0.9 $\mu g\,m^{-3}$, respectively. The equivalent ratio of $[Ca^{2+}]/[Na^+]$ was over 2, much higher than other days, since Hong Kong was under the influence of a northeasterly monsoon (Table 2). The relative humidity was lower than 41% and the highest wind speed was over 30 $km\,h^{-1}$ during the sampling period. The increase of $[Ca^{2+}]$ in the coarse mode was due to strong wind in these days. Ca^{2+} may be from the local dusts that are blown up by the strong wind near the site. But it is most likely from the soil particles brought by the northerly wind from China. The wind passes through South China and northern New Territories in HK, where a lot of undeveloped areas still exist. The MMAD of Ca^{2+} in these days are around 3–4 μm (Fig. 6), which is smaller than 5–6 μm found in other days (Fig. 3). Smaller particles may be transported to this site.

Fig. 6 shows the size distributions of NO_3^-, Cl^-, Na^+ and Ca^{2+} on November 4 and 5. Contrary to observations on other days, concentration of nitrate was slightly higher than sodium. The percentage of chloride depletion was only 28–47%, indicating that a smaller fraction of

sea-salt particles reacted to form nitrate. In addition, the nitrate distribution is similar to that of Ca^{2+}, which is in contrast with what we have found for the other days as shown in Fig. 2, where the nitrate distribution is similar to the Na^+ distribution. A significant portion of the nitrate is believed to be associated with soil particles. Although the excess sulfate concentration is available, the amount of sulfate formed on soil particles cannot be calculated because the partition of excess sulfate on soil and sea-salt particles is unknown.

Nevertheless, the extent of nitrate associated with Ca^{2+} can be investigated. The amount of nitrate associated with soil particles ($[NO_3^-]_{soil}$) can be estimated by subtracting the amount of nitrate associated with sea-salt particles ($[NO_3^-]_{sea-salt}$) from the total nitrate concentration ($[NO_3^-]$) (Eq. (2a)). Assuming that chloride depletion is caused by both nitrate and excess sulfate, the amount of nitrate associated with sea-salt equals the amount of chloride depleted minus the amount of sulfate formed on sea-salt particles. Therefore, the maximum and minimum amounts of nitrate formed on soil particles can be estimated simply by assuming that ex-SO_4^{2-} is wholly associated with sea-salt particles as Na_2SO_4 (Eq. (3a)) and wholly associated with soil particles as $CaSO_4$ (Eq. (4a)), respectively:

$$[NO_3^-]_{soil} = [NO_3^-] - [NO_3^-]_{sea-salt}, \qquad (2a)$$

$$[NO_3^-]_{soil,max} = [NO_3^-] - (1.174[Na^+]$$
$$- [Cl^-] - [ex\text{-}SO_4^{2-}]), \qquad (3a)$$

$$[NO_3^-]_{soil,min} = [NO_3^-] - (1.174[Na^+] - [Cl^-]), \quad (4a)$$

where $[NO_3^-]_{soil}$ is the concentration of nitrate associated with soil particles, $[NO_3^-]_{sea-salt}$ is the concentration of nitrate associated with sea-salt particles, $[NO_3^-]_{soil,max}$ is the maximum concentration of nitrate associated with soil particles and $[NO_3^-]_{soil,min}$ is the minimum concentration of nitrate associated with soil particles.

The nitrate concentrations and the percentages of total coarse mode nitrate associated with soil compounds on November 4–6 are listed in Table 3. It shows that under the influence of a strong northeasterly monsoon on November 4 and 5, between 57–68% ($[NO_3^-]_{soil,min}$) and 86–96% ($[NO_3^-]_{soil,max}$) of coarse mode nitrate is associated with soil particles, depending on the partition of excess sulfate between sea-salt and soil particles.

The partition of nitrate in soil particles decreases rapidly when the monsoon weakens and the prevailing easterly wind from the ocean accompanied by a high concentration of Na^+ resumes on November 6. The ratio of $[Ca^{2+}]/[Na^+]$ decreases from above 2 to 0.4 despite a high Ca^{2+} concentration of 0.56 $\mu g\,m^{-3}$ (Table 2). The fraction of nitrate associated with soil compounds also decreases to 23–32%. Even though a large fraction of the nitrate is found to be associated with soil particles during

Table 3
Fraction of nitrate formed on soil particles in the coarse mode during the monsoon episode in November 4–6

	November 4	November 5	November 6
$[NO_3^-]_{soil.min}/[NO_3^-{}_{coarse}]$ (%)	56.6	67.6	23.4
$[NO_3^-]_{soil.max}/[NO_3^-{}_{coarse}]$ (%)	85.6	96.3	32.4
$[Ca^{2+}]/[Na^+]$ ratio	2.58	2.13	0.43

the monsoon episode, the nitrate concentration is only 0.66 and 1.28 $\mu g\ m^{-3}$ on November 4 and 5. It increases rapidly to 3.2 $\mu g\ m^{-3}$ the next day when Hong Kong was under prevailing easterly wind and most of the nitrate was associated with sea-salt aerosols again. This is because nitrate formation in deliquescent sea-salt aerosols at high RH is more efficient than that in soil particles at low RH.

5. Conclusions

The size distributions of ambient aerosols at this site are the results of mixture of aerosols from marine and continental sources. In most days, sea-salt particles dominate the coarse mode with prevailing easterly wind from the ocean. Soil particles dominate the coarse mode when there is a northeasterly monsoon episode with strong winds.

Coarse mode nitrate and non-sea-salt sulfate were consistently observed in the samples. On average, they altogether accounted for more than 35% (neq%) of the total coarse mode ions concentration. Chloride depletion in conjunction with nitrate and sulfate formation in sea-salt particles was found in all samples. On a daily average, 27–88% of chloride was depleted from sea-salt particles, with larger depletion in the days with prevailing easterly wind and higher humidity. The extent of chloride depletion in the coarse mode decreases with increasing particle size. Chloride depletion at 1.8 μm reached about 90–100% in the Na^+ dominant period (at RH = 65–96%) and about 65–85% during the northeasterly monsoon episode. In the episode, RH was low (< 50%) and $[Ca^{2+}]$ was higher than $[Na^+]$. The lower chloride depletion observed is the result of competition of acidic gases between Ca^{2+} and Na^+ and the reduced formation of sulfate and nitrate on dry sea-salt particles.

In most days with the prevailing easterly wind in HK, $[Na^+]$ was much higher than $[Ca^{2+}]$. Nitrate dominates in chloride depletion of sea-salt aerosols. However, in heavily polluted days with total sulfate concentration as high as 20 $\mu g\ m^{-3}$ (1.1–3.0 $\mu g\ m^{-3}$ in coarse mode), sulfate can contribute up to 29% of chloride depletion. This large amount of sulfate is likely to be caused by cloud processing since this occurs in a period with the 24 h

average RH larger than 95%. However, at least 16% of chloride depletion cannot be accounted for by nitrate and nss-sulfate alone. It may be due to the formation of organic ions in sea-salt particles. During the northeasterly monsoon episode, up to 96% of coarse mode nitrate was associated with soil particles in this period. The fraction decreased to 23–32% when the monsoon ceased and the wind direction changed to easterly.

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