



**RESEARCH LETTER**

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**Key Points:**

- Source distribution and seasonal variation of size-aggregated sulfate aerosols collected at Baring Head, New Zealand were investigated
- Coarse aerosol sulfate was mainly from sea salt; sulfate in fine aerosols was mostly secondary sulfate
- Most secondary sulfate was originated from marine DMS emission and should explain the seasonal variations of Southern Ocean CCN

**Supporting Information:**

- Supporting Information S1

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# Investigating Source Contributions of Size-Aggregated Aerosols Collected in Southern Ocean and Baring Head, New Zealand Using Sulfur Isotopes

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**Abstract** Marine sulfate aerosols in the Southern Ocean are critical to the global radiation balance, yet the sources of sulfate and their seasonal variations are unclear. We separately sampled marine and ambient aerosols at Baring Head, New Zealand for 1 year using two collectors and evaluated the sources of sulfate in coarse (1–10 μm) and fine (0.05–1 μm) aerosols using sulfur isotopes ( $\delta^{34}\text{S}$ ). In both collectors, sea-salt sulfate ( $\text{SO}_4^{2-}\text{SS}$ ) mainly existed in coarse aerosols and nonsea-salt sulfate ( $\text{SO}_4^{2-}\text{NSS}$ ) dominated the sulfate in fine aerosols, although some summer  $\text{SO}_4^{2-}\text{NSS}$  appeared in coarse particles due to aerosol coagulation.  $\text{SO}_4^{2-}\text{NSS}$  in the marine aerosols was mainly (88–100%) from marine biogenic dimethylsulfide (DMS) emission, while the  $\text{SO}_4^{2-}\text{NSS}$  in the ambient aerosols was a combination of DMS (73–79%) and  $\text{SO}_2$  emissions from shipping activities (~21–27%). The seasonal variations of  $\text{SO}_4^{2-}\text{NSS}$  concentrations inferred from the  $\delta^{34}\text{S}$  values in both collectors were mainly controlled by the DMS flux.

**Plain Language Summary** Marine sulfate aerosols are critical to the global radiation balance through directly scattering sunlight or forming clouds; however, their feedback effects are poorly quantified because their sources and size distributions are unclear. We investigated the origins and size distributions of sulfate aerosols from the Southern Ocean as well as the ambient environment at Baring Head, New Zealand. We found that the sulfate in coarse (>1 μm) aerosols was dominated by sea-salt sulfate; while the fine aerosol (<1 μm) sulfate, which could act as cloud condensation nuclei, was mostly formed via atmospheric oxidation of sulfur-bearing gases. The origin of the secondary sulfate was then identified using sulfur isotopic analysis: Dimethylsulfide emitted by phytoplankton contributed over 90% of the secondary sulfate on the Southern Ocean; it also contributed ~73–79% of secondary sulfate aerosols in the ambient air at Baring Head, while the remainder was from anthropogenic sulfur emissions. Our work suggest that marine biological activity is an important factor that controls the amount of sulfate aerosols in remote marine atmosphere, which is of great importance to global climate models.

## 1. Introduction

Sulfate is one of the major inorganic components in aerosols and is essential to aerosol nucleation and accumulation processes (Andronache et al., 1997; Kulmala et al., 2000), which greatly affect Earth's radiation budget. However, the impact of sulfate aerosols to the radiation budget is still poorly quantified (IPCC, 2007), partly because the sources and fluxes of sulfate show strong spatial and seasonal variations. In the marine boundary layer, sulfate aerosols consist of primary and secondary sulfate. Primary sulfate, that is, sea-salt sulfate ( $\text{SO}_4^{2-}\text{SS}$ ) is formed via sea spray and air bubble bursting at the ocean surface (Lewis & Schwartz, 2004; O'Dowd et al., 2007); its size distribution and flux are controlled by wind speed, wave height, and other meteorological conditions (Gong, 2003; Lewis & Schwartz, 2004; Van Eijk et al., 2011). Nonsea-salt sulfate ( $\text{SO}_4^{2-}\text{NSS}$ ), also called secondary sulfate, is formed via atmospheric oxidation of S, the sources of which are (1) dimethylsulfide ( $\text{SO}_4^{2-}\text{DMS}$ ) emitted by marine phytoplankton (Barnes et al., 2006); (2) natural terrestrial S emission ( $\text{SO}_4^{2-}\text{nat}$ ), including sulfate from  $\text{SO}_2$  emitted by volcanic and terrestrial biological activities; or (3) anthropogenic S emissions ( $\text{SO}_4^{2-}\text{anth}$ ). In the midlatitudes of the Southern Ocean (~35–45°S),  $\text{SO}_4^{2-}\text{DMS}$  is thought to play a critical role in the cloud physics and climate by controlling the number of cloud condensation nuclei (CCN), resulting in strong reflection of solar radiation in the summer when the DMS flux is high (Ayers & Gras, 1991; Boers et al., 1994; Korhonen et al., 2008; McCoy et al., 2015). However, the sources, size

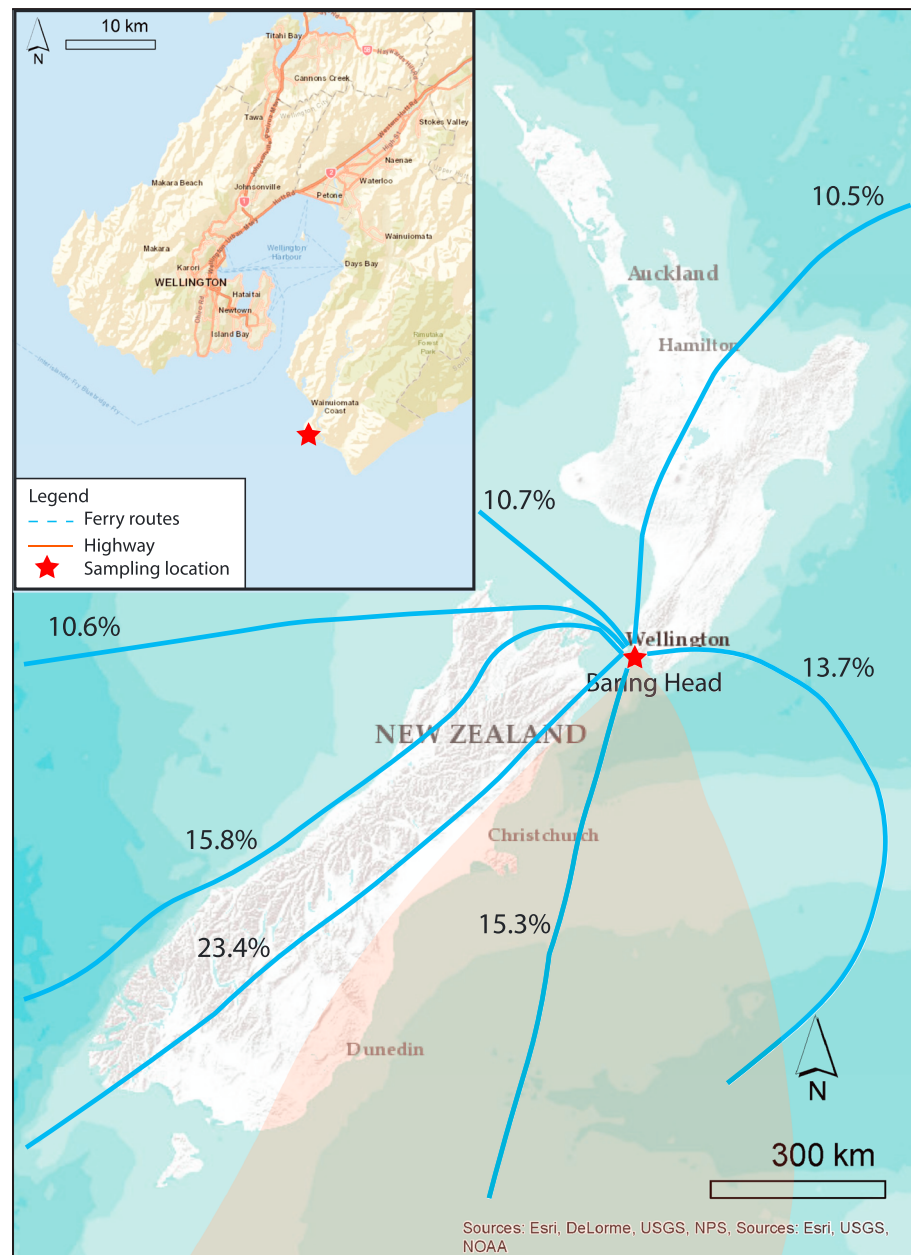
distributions, and seasonal variations of the Southern Ocean sulfate are not well understood, which limits our ability to predict its response to the changing climate.

Previous studies have investigated the sources and size distributions of marine sulfate aerosols in several locations (Calhoun & Bates, 1989; Calhoun et al., 1991; Faloon, 2009; Ghahremaninezhad et al., 2016; Norman et al., 1999; Novák et al., 2001; Rempillo et al., 2011; Seguin et al., 2011); however, several questions remain unanswered. First, substantial amounts of  $\text{SO}_4^{2-}\text{N}_{\text{SS}}$  had been observed in the coarse aerosols (0.9–16  $\mu\text{m}$ ) sampled at Baring Head originating from the biologically productive subtropical frontal region of the Chatham Rise (Sievering et al., 2004), suggesting  $\text{SO}_4^{2-}\text{N}_{\text{SS}}$  was mainly formed on coarse sea-salt particles. This is in contrast with observations in the Northern Hemisphere (Ghahremaninezhad et al., 2016; Norman et al., 1999; Rempillo et al., 2011; Seguin et al., 2011) and modeling results (Alexander et al., 2005), all of which suggested  $\text{SO}_4^{2-}\text{N}_{\text{SS}}$  should mainly distributed in the fine particles (<0.95  $\mu\text{m}$ ). Second, the contribution of anthropogenic emission to the Southern Ocean sulfate is uncertain. Capaldo et al. (1999) suggested that international shipping emission, which is the main anthropogenic sulfur source in midlatitude Southern Ocean (~40°S), contributes to ~5% to 20% of total sulfate, while McCoy et al. (2015) showed a higher anthropogenic contribution of 20%–35% at 40°S. Third, the observed seasonal variations of Southern Ocean sulfate (e.g., McCoy et al., 2015; Udisti et al., 2012) were unexplained and difficult to predict because the variation of each sulfate source was unknown.

Geochemical and sulfur isotopic analyses are useful tools in determining the sources of sulfate. Cation and anion analyses are useful in partitioning between  $\text{SO}_4^{2-}\text{SS}$  and  $\text{SO}_4^{2-}\text{N}_{\text{SS}}$ , and changes in the sulfur isotopic composition ( $\delta^{34}\text{S}$ ) can help in differentiating  $\text{SO}_4^{2-}$  sources:  $\delta^{34}\text{S}$  of  $\text{SO}_4^{2-}\text{SS}$  ( $\delta^{34}\text{S}_{\text{SS}}$ ) is a constant +21‰ (Rees et al., 1978),  $\delta^{34}\text{S}$  values of DMS range between +15‰ and +19‰ (Amrani et al., 2013; Krouse & Grinenko, 1991; Oduro et al., 2012), while most anthropogenic and terrestrial sulfates display much lower  $\delta^{34}\text{S}$  values between –5‰ and +10‰ (Calhoun et al., 1991; Krouse & Grinenko, 1991; McArdle et al., 1998; Sakai et al., 1982; Zhu et al., 2016). In this work, a full-year sampling campaign was conducted to collect size-segregated aerosols derived from the marine sector (subtropical frontal region and the Southern Ocean) and all sectors (ambient environment) at Baring Head, New Zealand (41.4°S, 174.9°E, Figure 1). Geochemical and sulfur isotopic analyses were used to investigate S sources and their seasonal variations.

## 2. Method

The aerosol sampling campaign spanned from 30 June 2015 to 11 August 2016 and sampled both marine and ambient air. Two high-volume samplers equipped with Cascade Impactors were set up on a 15 m tower at Baring Head, New Zealand (Figure 1), where the metrological conditions were measured, to collect coarse (1–10  $\mu\text{m}$ ) and fine aerosols (0.05–1.0  $\mu\text{m}$ ) at a flow rate of ~1  $\text{m}^3/\text{min}$ . Cellulose filters were used to minimize ion contamination (especially  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ ), which were tested using eight blanks and resulted in  $[\text{Na}^+] < 0.6\%$  of average  $[\text{Na}^+]$  in the field samples (e.g., <0.05  $\text{nmol}/\text{m}^3$ ). One of the collectors (marine collector, set on top of the tower) was configured to sample oceanic air masses by only collecting when the average southerly (onshore) wind speed was above 5 m/s for at least 30 min. Filters on this collector were replaced after 100 to 150 hr of collection to acquire enough sample (every 2 to 6 weeks). The ambient collector sampled air mass regardless of the wind direction, and filters were replaced every 7 days (154 hr). Previous studies (Dorling et al., 1992; Steinkamp et al., 2017) confirmed the origins of the collected aerosols using cluster analysis (Figure 1) showing aerosols in the marine collector originated from the oceanic sector of the subtropical front/Chatham Rise (red shaded area), while the aerosols in the ambient collector were from both the ocean and the New Zealand mainland (blue lines). Meantime, a wave buoy off the coast was used to measure the wave peak height. The filters were carefully sealed and shipped to Purdue Stable Isotope Laboratory, where standard methods were used to analyze cations (inductively coupled plasma optical emission spectrometry, ICP-OES), anions (Ion Chromatography), and sulfur isotopic compositions of sulfate (isotope-ratio mass spectrometry, see supporting information for detailed description of analytical methods and data). The concentrations of  $\text{SO}_4^{2-}\text{SS}$  were calculated using the seawater  $[\text{SO}_4^{2-}\text{Na}^+]$  molar ratio (0.058) and the measured Na concentrations:  $[\text{SO}_4^{2-}\text{SS}] = 0.058 * [\text{Na}^+]$  (Keene et al., 2007). The residual sulfate was considered  $\text{SO}_4^{2-}\text{N}_{\text{SS}}$ . This assumes sodium is a conservative element, seawater is its sole source, and it is insensitive to chemical or biological loss (Keene et al., 1986).

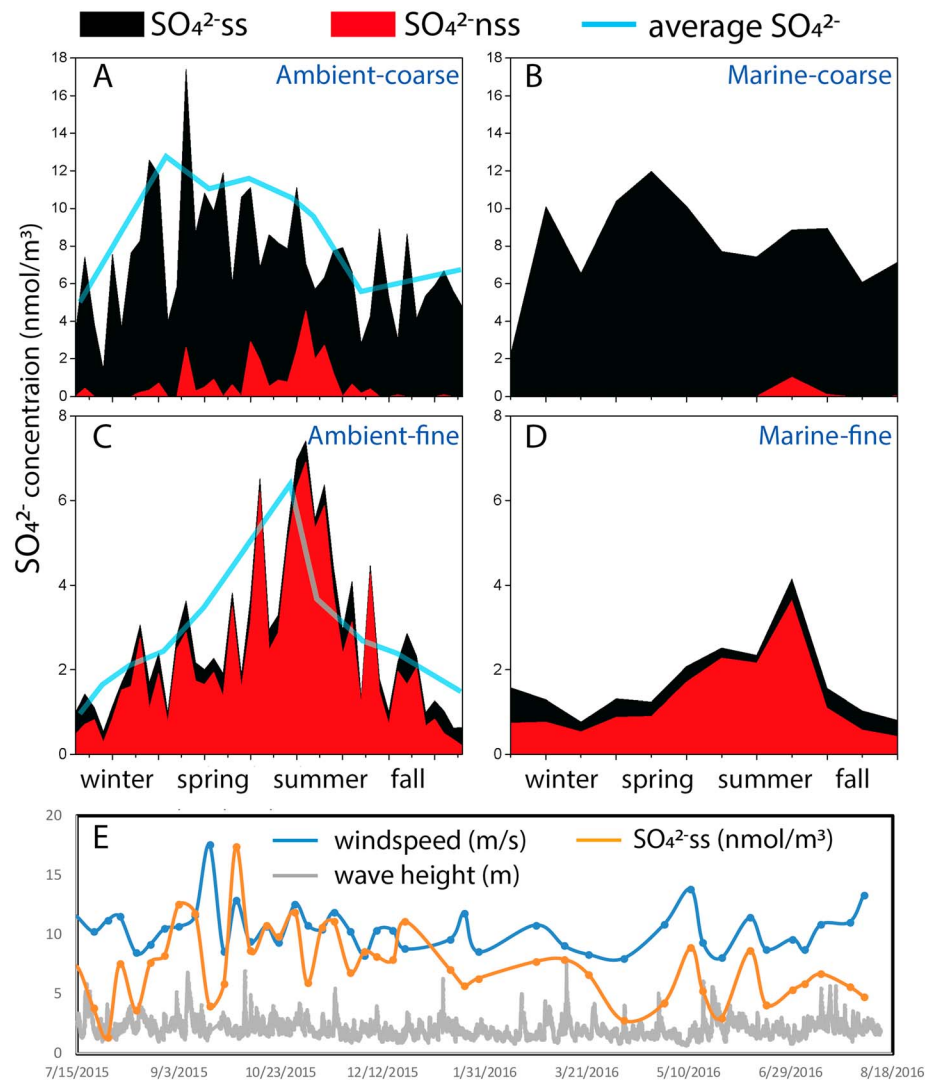


**Figure 1.** Sampling location and result of air parcel 4-day back trajectory of air mass arriving at Baring Head. Blue lines and the numbers above indicate the mean path and percentage of air mass from each cluster; red shaded area indicates the envelope of all trajectories during southerly wind, modified from Steinkamp et al. (2017).

### 3. Results and Discussions

#### 3.1. Distribution of Sea-Salt and Nonsea-Salt Sulfate in Coarse and Fine Aerosols

Sulfate in coarse aerosols was mainly  $\text{SO}_4^{2-}_{\text{SS}}$ , and  $\text{SO}_4^{2-}_{\text{NSS}}$  was found primarily in the fine aerosol fraction, which was in contrast with a previous study at Baring Head (Sievering et al., 2004). Coarse aerosol sulfate concentrations in the two collectors were similar ( $8.8 \pm 1.9 \text{ nmol/m}^3$  in marine collector and  $8.1 \pm 3.8 \text{ nmol/m}^3$  in ambient collector), which is remarkably close to a previous study at Baring Head that averaged  $8.3 \text{ nmol/m}^3$  (Sievering et al., 2004).  $\text{SO}_4^{2-}_{\text{SS}}$  accounted for  $88 \pm 5\%$  of the coarse aerosol sulfate (Figures 2a and 2b), but the contribution of  $\text{SO}_4^{2-}_{\text{NSS}}$  in the coarse mode slightly increased during the summer (discussed below). In contrast, fine particle sulfate concentrations were lower, (averaging  $1.7 \text{ nmol/m}^3$  in marine collector and



**Figure 2.** (a–d)  $\text{SO}_4^{2-}$ - $\text{SS}$  (black) and  $\text{SO}_4^{2-}$ - $\text{NSS}$  (red) concentrations in coarse and fine aerosols from ambient and marine collectors; blue lines in Figures 2a and 2c are averaged (to fit the marine collector sampling window) total sulfate concentrations. (e) Wind speed, wave height, and coarse  $\text{SO}_4^{2-}$ - $\text{SS}$  concentrations in ambient collector.

2.7  $\text{nmol/m}^3$  in ambient collector), and  $\text{SO}_4^{2-}$ - $\text{SS}$  accounted for only  $\sim 16 \pm 1\%$  of total sulfate, the remaining  $84 \pm 1\%$  was  $\text{SO}_4^{2-}$ - $\text{NSS}$ . This general  $\text{SO}_4^{2-}$ - $\text{SS}$  distribution pattern was similar to the distribution previously observed at Baring Head by Sievering et al. (2004), but in that study only 53% of coarse aerosol sulfate was attributed to  $\text{SO}_4^{2-}$ - $\text{SS}$  compared to this study's 88%. They also suggested coarse aerosol sulfate accounted for 81% of total  $\text{SO}_4^{2-}$ - $\text{NSS}$ , while our results showed a much lower contribution of  $\sim 24$ –36%.

The discrepancy in  $\text{SO}_4^{2-}$ - $\text{NSS}$  distribution could be attributed to either (1) differences in sampling conditions or (2) differences in  $\text{SO}_4^{2-}$ - $\text{SS}$  estimation. Sievering et al. (2004) suggested that under clear-sky conditions, pH buffering by excess calcium provided from coccolithophores fragments could enhance the effectiveness of ozone-mediated oxidation in sea-salt aerosol droplets, leading to greater coarse mode  $\text{SO}_4^{2-}$ - $\text{NSS}$ . In this work, aerosols from both clear and cloudy conditions were sampled; therefore, this mechanism was likely less important and results in lower coarse mode  $\text{SO}_4^{2-}$ - $\text{NSS}$ . Alternatively, the discrepancy may be due to our use of aerosol  $[\text{Na}^+]$  to estimate  $\text{SO}_4^{2-}$ - $\text{SS}$  rather than  $[\text{Mg}^{2+}]$  used by Sievering et al. (2004). Sodium is the most widely used conservative tracer of sea salt (Lin et al., 2017; Norman et al., 1999; Udisti et al., 2016) because (1) it has a high concentration in the seawater, (2) nonmarine sodium inputs are trivial in most places (McInnes et al., 1994), and (3) it is insensitive to secondary alterations. Sievering et al. (2004) used  $[\text{Mg}^{2+}]$  to calculate

$\text{SO}_4^{2-}$ <sub>SS</sub> fraction because of abnormally high  $[\text{Na}^+\text{Cl}^-]$  and  $[\text{Na}^+\text{Mg}^{2+}]$  ratios in their aerosols that they attributed to either contamination by filter blanks or possible contributions of sodium in soil. Likewise,  $[\text{Mg}^{2+}]$  has been used to estimate  $\text{SO}_4^{2-}$ <sub>SS</sub> in aerosols collected at Cape Grim, Tasmania, and La Jolla, California because sodium from either filter blanks or soil was believed to be significant (Cainey et al., 1999; Hill-Falkenthal et al., 2012; Priyadarshi et al., 2012). The cellulose filters used in this study had a very low  $\text{Na}^+$  blank relative to typical glass fiber filters (Dams et al., 1972), and Southern Ocean derived air masses should have minimal terrestrial influence at Baring Head. Further, the coarse aerosol  $[\text{Mg}^{2+}\text{Na}^+]$  in both of our collectors averaged at  $0.111 \pm 0.005$ , much higher than the 0.05 ratio determined by Sievering et al. (2004) and very close to the seawater ratio of 0.11 (Keene et al., 2007), indicating minimal contribution of sodium from either soil or filter blank. Furthermore, the low  $[\text{Mg}^{2+}\text{Na}^+]$  ratio observed by Sievering et al. (2004) may be a consequence of biased  $[\text{Mg}^{2+}]$  measurements. A recent study has observed that sea-spray  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  form complexes with lipids, fatty acids, and saccharides (Jayarathne et al., 2016) during sea-salt aerosol formation, potentially biasing  $[\text{Mg}^{2+}]$  analyzed by ion chromatography (Sievering et al., 2004). Using ICP-OES to analyze  $[\text{Mg}^{2+}]$  does not require it to be in ionic form, so could be a more accurate measure of  $[\text{Mg}^{2+}\text{Na}^+]$  in the sea-salt aerosols given the possibility of complexation and provides confidence in the accuracy of the  $\text{SO}_4^{2-}$ <sub>SS</sub> presented here.

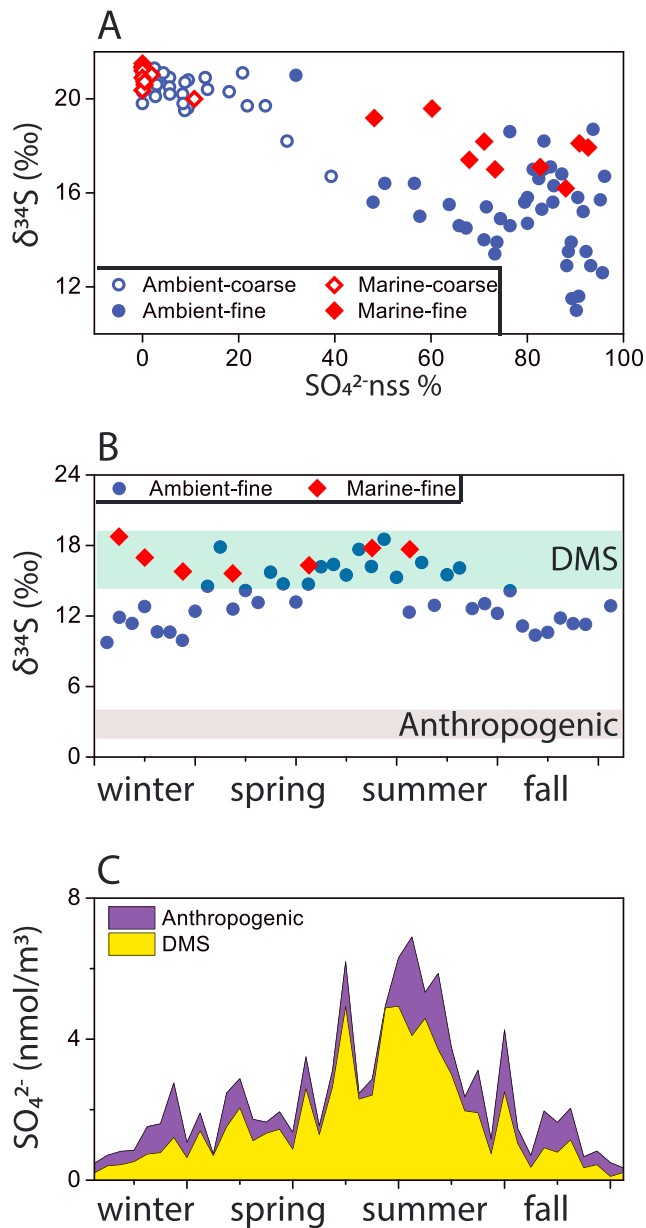
The size distribution patterns of  $\text{SO}_4^{2-}$ <sub>SS</sub> and  $\text{SO}_4^{2-}$ <sub>NSS</sub> agrees with other field observations and atmospheric modeling results, indicating  $\text{SO}_4^{2-}$ <sub>NSS</sub> is the main sulfur source in CCN. Observations in the North Atlantic, Arctic, and Pacific Ocean have suggested similar distribution patterns, of which >90% of  $\text{SO}_4^{2-}$ <sub>SS</sub> was distributed in coarse aerosols and > 60% of  $\text{SO}_4^{2-}$ <sub>NSS</sub> was in fine aerosols (Ghahremaninezhad et al., 2016; Murphy et al., 1998; Norman et al., 1999; Rempillo et al., 2011; Seguin et al., 2011). Therefore, we suggest in the Southern Ocean  $\text{SO}_4^{2-}$ <sub>NSS</sub> was also the main sulfate source of CCN, since CCN are usually <0.2  $\mu\text{m}$  (Hudson & Noble, 2006). Additionally, we noticed coarse aerosol  $\text{SO}_4^{2-}$ <sub>NSS</sub> was observed when the total  $\text{SO}_4^{2-}$ <sub>NSS</sub> concentrations ( $\text{SO}_4^{2-}$ <sub>NSS-coarse</sub> +  $\text{SO}_4^{2-}$ <sub>NSS-fine</sub>) exceeded 2.0 nmol/m<sup>3</sup>. This indicates higher  $\text{SO}_4^{2-}$ <sub>NSS</sub> concentrations helped coagulation forms larger  $\text{SO}_4^{2-}$ <sub>NSS</sub> particles. Further experiments and field sample analysis should take place to quantify the relationship between  $\text{SO}_4^{2-}$ <sub>NSS</sub> concentration and their size distribution.

The variations in  $\text{SO}_4^{2-}$ <sub>SS</sub> concentrations were attributed to variations in wind speed and wave heights at Baring Head. Early studies have suggested that the mass concentration of sea-salt aerosols is positively correlated to wind speed (O'Dowd et al., 1997; O'Dowd & Smith, 1993); however, recent studies had suggested other physical conditions, such as whitecap coverage and wave peak height on the coast are also important (Clarke et al., 2006; Lewis & Schwartz, 2004; Mårtensson et al., 2003; O'Dowd et al., 2007). Our observed  $\text{SO}_4^{2-}$ <sub>SS</sub> concentrations only showed a weak correlation with the average wind speed ( $P > 0.05$ ,  $R^2 = 0.03$ , Figure 2e) similar to other field studies (Ghahremaninezhad et al., 2016; Jaeglé et al., 2011; Lewis & Schwartz, 2004; Rempillo et al., 2011; Seguin et al., 2011). In contrast, maximums in wave peak heights usually corresponded to high  $\text{SO}_4^{2-}$ <sub>SS</sub> concentrations at Baring Head (Figure 2e), supporting the hypothesis that breaking waves increase sea-salt aerosol formation near the coast (Jensen et al., 1997; Monahan et al., 1986; Van Eijk et al., 2011). Therefore, we suggest that wave height was more important than wind speed, under low median wind speeds ( $9.9 \pm 3.9$  m/s), in generating sea-salt aerosols at Baring Head during the study period.

### 3.2. Sources and Seasonal Variations of $\text{SO}_4^{2-}$ <sub>NSS</sub> in the Marine Collector

The sulfur isotopic compositions of sulfate also indicated a mixture of  $\text{SO}_4^{2-}$ <sub>SS</sub> and  $\text{SO}_4^{2-}$ <sub>NSS</sub>. The  $\delta^{34}\text{S}$  values of total sulfate ( $\text{SO}_4^{2-}$ <sub>SS</sub> +  $\text{SO}_4^{2-}$ <sub>NSS</sub>) were interpreted using a two-end-member isotope mixing model (Figure 3a):  $\text{SO}_4^{2-}$ <sub>SS</sub> with  $\delta^{34}\text{S}$  value that is the same (+21‰) as seawater (Rees et al., 1978) and  $\text{SO}_4^{2-}$ <sub>NSS</sub> with lower  $\delta^{34}\text{S}$  value(s). Most coarse aerosol sulfate had  $\delta^{34}\text{S}$  values near the seawater end-member, indicating the coarse aerosol sulfate was predominately composed of  $\text{SO}_4^{2-}$ <sub>SS</sub>, which supports our  $\text{SO}_4^{2-}$ <sub>SS</sub> estimates using  $[\text{Na}^+]$ . In contrast, the fine aerosol had lower  $\delta^{34}\text{S}$  values (+11‰ to +21‰), suggesting a higher proportion of  $\text{SO}_4^{2-}$ <sub>NSS</sub> relative to the coarse aerosols.

The  $\delta^{34}\text{S}$  values of  $\text{SO}_4^{2-}$ <sub>NSS</sub> ( $\delta^{34}\text{S}_{\text{NSS}}$ ) can give insight into the origin of  $\text{SO}_4^{2-}$ <sub>NSS</sub> sources. The  $\delta^{34}\text{S}_{\text{NSS}}$  values were calculated using  $\delta^{34}\text{S}_{\text{NSS}} = (\delta^{34}\text{S}_{\text{bulk}} - (1 - \text{SO}_4^{2-}\text{NSS}\%) * +21\text{‰}) / \text{SO}_4^{2-}\text{NSS}\%$ , where  $\text{SO}_4^{2-}\text{NSS}\%$  is the fraction of  $\text{SO}_4^{2-}$ <sub>NSS</sub> (using  $[\text{Na}^+]$ ), the +21‰ is the  $\delta^{34}\text{S}$  value of seawater sulfate, and  $\delta^{34}\text{S}_{\text{bulk}}$  is the  $\delta^{34}\text{S}$  value of the total aerosol sulfate. The calculated  $\delta^{34}\text{S}_{\text{NSS}}$  values ranged from +6‰ to +19‰ (Figure 3).  $\delta^{34}\text{S}_{\text{NSS}}$  values in the marine collector range from +15‰ to +19‰ (Figure 3b), which is the same range previously observed



**Figure 3.** (a)  $\delta^{34}\text{S}$  distribution of all samples, showing a mixing of  $\text{SO}_4^{2-}\text{NSS}$  and  $\text{SO}_4^{2-}\text{DMS}$ ; (b) the  $\delta^{34}\text{S}_{\text{NSS}}$  values of ambient and marine fine sulfate; horizontal bars indicate the  $\delta^{34}\text{S}$  values of each end-member; and (c) estimated anthropogenic and DMS contribution to  $\text{SO}_4^{2-}\text{NSS}$  in ambient fine sulfate.

in  $\delta^{34}\text{S}_{\text{DMS}}$  (Krouse & Grinenko, 1991; Patris et al., 2002; Sanusi et al., 2006; Wadleigh, 2004). This indicates that  $\text{SO}_4^{2-}\text{DMS}$  was the dominant source of  $\text{SO}_4^{2-}\text{NSS}$  in the marine collector. The ambient aerosol  $\delta^{34}\text{S}_{\text{NSS}}$  values were as low as +6‰, which cannot be explained by oxidation of DMS, and points to nonmarine sulfur sources. The main anthropogenic S sources in the region are international and local shipping activity (Capaldo et al., 1999; McCoy et al., 2015) and the  $\delta^{34}\text{S}$  value of sulfur derived from ships has been estimated to be +3‰ (Patris et al., 2000; Rempillo et al., 2011). Likewise, the  $\delta^{34}\text{S}$  values of sulfate derived from terrestrial sulfur sources near Baring Head also have been estimated to be +3‰ (discussed below). Thus, the range of Baring Head  $\text{SO}_4^{2-}\text{NSS}$  values is interpreted as a second mixture of  $\text{SO}_4^{2-}\text{DMS}$  (Calhoun et al., 1991; Krouse & Grinenko, 1991; Patris et al., 2002; Sanusi et al., 2006) and  $\text{SO}_4^{2-}\text{anth}$  whose fractions ( $f_{\text{DMS}}$ ,  $f_{\text{anth}}$ ) can be quantified using a simple two end-member isotope mixing model:  $\delta^{34}\text{S}_{\text{NSS}} = f_{\text{DMS}} \cdot \delta^{34}\text{S}_{\text{DMS}} + f_{\text{anth}} \cdot \delta^{34}\text{S}_{\text{anth}}$ . Using this mixing model, we can first estimate the  $f_{\text{DMS}}$  and  $f_{\text{anth}}$  (given in %) in the marine collector.

The high  $\delta^{34}\text{S}_{\text{NSS}}$  values (Figure 2b) of marine  $\text{SO}_4^{2-}\text{NSS}$  indicate that it was primarily (88–100%)  $\text{SO}_4^{2-}\text{DMS}$  and only 0–12% was  $\text{SO}_4^{2-}\text{anth}$ . To estimate the upper limit of  $f_{\text{anth}}$ , we assume a constant  $\delta^{34}\text{S}_{\text{DMS}}$  end-member of +19‰ (Wadleigh, 2004), and the  $\delta^{34}\text{S}_{\text{anth}}$  end-member was from ship emissions with  $\delta^{34}\text{S} = +3$ ‰. The variation of  $\delta^{34}\text{S}_{\text{NSS}}$  can be solely attributed to changing in  $f_{\text{anth}}$ , and the calculated upper limit of  $f_{\text{anth}}$  is ~12%. This  $\text{SO}_4^{2-}\text{anth}$  contribution to  $\text{SO}_4^{2-}\text{NSS}$  is much lower than the 20–35% estimated by McCoy et al. (2015) but in agreement with the 5–20% estimated by Capaldo et al. (1999). However, this calculation assumed the  $\delta^{34}\text{S}_{\text{DMS}}$  was a constant +19‰ and ignored the observed +15‰ to +19‰ range in other studies (Krouse & Grinenko, 1991; Patris et al., 2002; Sanusi et al., 2006; Wadleigh, 2004). This 4‰ variation in  $\delta^{34}\text{S}_{\text{DMS}}$  values is thought to be caused by a combination of (1) variation of isotopic fractionation during  $\text{SO}_2$  oxidized to sulfate ( $\delta^{34}\text{S}_{\text{sulfate}} - \delta^{34}\text{S}_{\text{SO}_2}$ , Harris et al., 2012, 2013) and (2) the  $\delta^{34}\text{S}$  of DMS gas could slightly vary (Amrani et al., 2013). If we consider the  $\delta^{34}\text{S}_{\text{DMS}}$  variation, then the contribution of anthropogenic S in marine aerosols could be as low as zero at Baring Head. This 0–12% anthropogenic S contribution to the  $\text{SO}_4^{2-}\text{NSS}$  budget is significantly lower than the estimates of 30–70% in the Northern Atlantic Ocean and other Pacific Ocean sites (Capaldo et al., 1999; Patris et al., 2000; Yang et al., 2017). We suggest that this lower anthropogenic sulfate fraction in  $\text{SO}_4^{2-}\text{NSS}$  at Baring Head is due to significantly lower sulfur emission in the Southern Hemisphere (IEA, 2014), fewer shipping routes in the Southern Hemisphere, thus minimal influence of ship sulfur emissions

(Paxian et al., 2010), and poor interhemispheric mixing of sulfate that minimizes the influence of the Northern Hemisphere sulfur emissions at Baring Head (Capaldo et al., 1999).

The observed seasonal variation of  $\text{SO}_4^{2-}\text{NSS}$  in the marine collector (Figure 2d), which was primarily from DMS emissions, must be controlled by seasonal changes in the DMS flux. Baring Head's average summer  $\text{SO}_4^{2-}\text{DMS}$  concentration was ~2.7 nmol/m<sup>3</sup>, while winter concentrations averaged at 0.6 nmol/m<sup>3</sup> (Figure 2d), similar to the  $\text{SO}_4^{2-}\text{DMS}$  concentrations observed in Arctic, Southern Pacific, and Northern Atlantic Ocean (Allen et al., 1997; Ghahremaninezhad et al., 2016; Huang et al., 2017; Quinn et al., 2009; Rempillo et al., 2011; Seguin et al., 2011). The observed average summer  $\text{SO}_4^{2-}\text{DMS}$  concentration was ~4.5 times higher than the winter  $\text{SO}_4^{2-}\text{DMS}$ , which agrees with the recent observation of dissolved sea-water DMS concentration by Lana et al. (2011) who showed at least a fourfold higher concentration of dissolved

DMS in the austral summer compared to winter. In addition, Law et al. (2017) discussed evidence suggesting this seasonal variation presented by Lana et al. (2011) also occurred in the waters offshore of New Zealand. Therefore, since  $\text{SO}_4^{2-}\text{-DMS}$  was the main source of fine sulfate particles, the seasonal variation of  $\text{SO}_4^{2-}\text{-DMS}$  could explain the 300% increase of CCN in the summer observed by Ayers and Gras (1991).

### 3.3. Sources and Seasonal Variations of $\text{SO}_4^{2-}\text{-NSS}$ in the Ambient Collector

The ambient aerosol  $\delta^{34}\text{S}_{\text{NSS}}$  values were lower than the marine aerosol  $\delta^{34}\text{S}_{\text{NSS}}$  and displayed a distinct seasonal trend, indicating changing contribution of anthropogenic sulfur over the year (Figure 3b). The ambient aerosol  $\delta^{34}\text{S}_{\text{NSS}}$  values (+6‰ to +18‰) were close to those of marine aerosols during the summer, suggesting the  $\text{SO}_4^{2-}\text{-NSS}$  was also dominated by DMS during the summer months. In contrast, the  $\delta^{34}\text{S}_{\text{NSS}}$  values in the winter were significantly lower (Figure 3b) than in the marine aerosols, suggesting  $\text{SO}_4^{2-}\text{-nat}$  and/or  $\text{SO}_4^{2-}\text{-anth}$  input (e.g., Calhoun et al., 1991; Ghahremaninezhad et al., 2016; Patris et al., 2000; Rempillo et al., 2011). Potential terrestrial sulfur sources include terrestrial biogenic emissions, volcanic emissions, and anthropogenic emissions. Terrestrial biogenic sulfur should be a minor contributor because the estimated biogenic sulfur flux ( $<1 \times 10^5$  mol/day) in New Zealand (Bates et al., 1992) is small compared to  $1 \times 10^6$  mol/day anthropogenic emission from Wellington, which is adjacent to the Baring Head site (Ministry of the Environment, 2004). The volcanic activity should also be minor at Baring Head since the nearest volcano and geothermally active regions with  $\text{H}_2\text{S}$  emission are  $\sim 300$  km away, and there was no significant volcanic activity during our sampling period (GeoNet volcanic emission database). Therefore,  $\text{SO}_4^{2-}\text{-nat}$  is likely small, and  $\text{SO}_4^{2-}\text{-anth}$  was likely the main nonmarine sulfur sources of  $\text{SO}_4^{2-}\text{-NSS}$  in the ambient collector. Eighty-two percent of anthropogenic sulfur emissions in the Wellington region were from commercial shipping (Ministry of the Environment, 2004) that uses low-grade fuel oil. Early study showed that the  $\delta^{34}\text{S}$  values of fuel oil center around 5‰ (Nielsen, 1974); recent measurements of ship emissions also have  $\delta^{34}\text{S}$  value of  $+3\text{‰} \pm 3\text{‰}$  (Patris et al., 2000; Rempillo et al., 2011). Other anthropogenic sources, such as coal burning and industrial fossil fuel combustions, also showed  $\delta^{34}\text{S}$  values of  $+3\text{‰} \pm 3\text{‰}$  (e.g., Górká et al., 2017; Proemse & Mayer, 2012). Rainwater sulfate collected at Gracefield, a semi-industrial district  $\sim 25$  km inland from Baring Head and Wellington, had  $\delta^{34}\text{S}$  values of  $\sim +3 \pm 5\text{‰}$  (Mizutani & Rafter, 1969), which was consistent with the end-members. Thus, the ambient aerosol  $\delta^{34}\text{S}_{\text{anth}}$  end-member was estimated to be  $\sim +3\text{‰}$  and the  $\delta^{34}\text{S}_{\text{NSS}}$  in the ambient collector can be again interpreted as a mixing between  $\text{SO}_4^{2-}\text{-anth}$  and  $\text{SO}_4^{2-}\text{-DMS}$  using same isotope mixing model (above).

The  $f_{\text{anth}}$  values varied within and by season:  $\sim 40\text{--}60\%$  in the winter,  $\sim 20\text{--}40\%$  in the spring and fall, and  $0\text{--}20\%$  in the summer. The  $\text{SO}_4^{2-}\text{-anth}$  concentrations ( $f_{\text{anth}} * [\text{SO}_4^{2-}\text{-NSS}]$ ) range from 0 to  $2.5 \text{ nmol/m}^3$ , with an annual average of  $0.6 \text{ nmol/m}^3$ , accounted for 27% of total  $\text{SO}_4^{2-}\text{-NSS}$ . Then, assuming the  $\text{SO}_4^{2-}\text{-NSS}$  in the marine collector was purely derived from DMS, the  $\delta^{34}\text{S}_{\text{NSS}}$  in the marine collector can be used as the  $\delta^{34}\text{S}_{\text{DMS}}$  in the equation. Under this situation, the  $f_{\text{anth}}$  values were  $\sim 40\text{--}50\%$  in the winter,  $\sim 5\text{--}20\%$  in the spring and fall, and  $0\text{--}15\%$  in the summer (Figure 3c). The annual average  $f_{\text{anth}}$  was 21%. Therefore, we suggest the  $\text{SO}_4^{2-}\text{-anth}$  accounted for 21–27% of total  $\text{SO}_4^{2-}\text{-NSS}$  at Baring Head. Davy (2007) and Davy et al. (2008, 2012) had also observed similar  $\text{SO}_4^{2-}\text{-NSS}$  concentrations and seasonal variations at Lower Hutt, a coastal town  $\sim 20$  km from Baring Head, but the contribution of  $\text{SO}_4^{2-}\text{-DMS}$  was unexamined. We suggest their  $\text{SO}_4^{2-}\text{-NSS}$  sources were similar to our results:  $\text{SO}_4^{2-}\text{-DMS}$  contributed  $>70\%$  of total  $\text{SO}_4^{2-}\text{-NSS}$ , and  $\text{SO}_4^{2-}\text{-anth}$  accounted for the rest.

The anthropogenic sulfate contributions at Baring Head were significantly lower than the Northern Hemisphere marine boundary layer. The 21–27% anthropogenic contribution was much lower than most studies in the Northern Hemisphere coastal areas where 30% to  $>90\%$   $\text{SO}_4^{2-}\text{-NSS}$  was anthropogenic (Ghahremaninezhad et al., 2016; Seguin et al., 2011; Xu & Gao, 2015) but only slightly higher than remote Midway Island (20%) in the northern Pacific Ocean (Savoie & Prospero, 1989). Local sulfur emission at Midway Island is minor (IEA, 2014), thus  $\text{SO}_4^{2-}\text{-anth}$  should represent the sulfate background in the Northern Hemisphere. In contrast, Baring Head is  $\sim 20$  km from Wellington that has significant  $\text{SO}_2$  emission, and our data suggest this is the major, if not sole,  $\text{SO}_4^{2-}\text{-anth}$  source at Baring Head. This means the background  $\text{SO}_4^{2-}\text{-anth}$  level near the Southern Ocean must be very low, in agreement with our observation from the marine collector and the modeled results in Capaldo et al. (1999). Future atmospheric modeling work incorporated with sulfur isotopic module could potentially distinguish the Southern Hemisphere background  $\text{SO}_4^{2-}\text{-anth}$  from  $\text{SO}_4^{2-}\text{-anth}$  emissions from Wellington.

$\text{SO}_4^{2-}$ <sub>DMS</sub> collected in the ambient aerosols showed similar seasonal trend as the marine collector, while the anthropogenic sulfate displayed little seasonal variation (Figure 3c). Sulfate source apportionment determined using sulfur isotopes allows us to examine the seasonal variations of both DMS and anthropogenic-derived sulfate. Similar to the  $\text{SO}_4^{2-}$  from the marine collector, the ambient  $\text{SO}_4^{2-}$ <sub>DMS</sub> shows lower flux in the winter and higher flux in the summer but with a more significant variation (0.5 to 4 nmol/m<sup>3</sup>) throughout the year. This is because the samples were collected weekly, so they would better capture the variation of DMS oxidation at a finer time scale. If we average the  $\text{SO}_4^{2-}$ <sub>NSS</sub> concentration in the ambient collector to the same sampling window as the marine collector, a similar seasonal trend was observed. Meantime, the anthropogenic flux ranged from near zero to ~2.5 nmol/m<sup>3</sup>, with little variation throughout the year and no clear seasonal trend. Overall, because of the low contribution of  $\text{SO}_4^{2-}$ <sub>anth</sub>, the seasonal variation of sulfate concentration at Baring Head is mainly controlled by the variation of  $\text{SO}_4^{2-}$ <sub>DMS</sub>.

However, uncertainties exist in our source appointment because (1) the sampling intervals were ~1 month for the marine collector and 1 week for the ambient collector, thus the marine collector could not record the accurate  $\delta^{34}\text{S}_{\text{DMS}}$  end-member; (2) the atmospheric chemistry of sulfate formation in the urban areas and the open ocean was different because of the differences in  $\text{NO}_x$ , volatile organic carbon, and  $\text{O}_3$  concentrations, hence the isotopic fractionation between  $\text{SO}_2$  and sulfate may be different (Harris et al., 2012); and (3) the  $\delta^{34}\text{S}$  of anthropogenic sulfate could display a wider range (Calhoun et al., 1991; Norman et al., 1999; Wadleigh, 2004). Nevertheless, these uncertainties would not significantly impact our calculation.

#### 4. Conclusion

We investigated the source distribution and seasonal variations of size-aggregated sulfate aerosols on a coastal site at Baring Head, New Zealand from marine and ambient collectors. We suggested that using total  $[\text{Na}^+]$  or  $[\text{Mg}^{2+}]$  instead of purely ionic  $[\text{Mg}^{2+}]$  to estimate the sea-salt sulfate concentration could exclude the error caused by high Na in filter blanks and Mg complexes in sea-salt aerosols. In our samples, coarse aerosol sulfate was dominated by  $\text{SO}_4^{2-}$ <sub>SS</sub>, the variation of which was mainly determined by a combination of wind speed and wave height; fine aerosol sulfate was dominated by  $\text{SO}_4^{2-}$ <sub>NSS</sub>. Therefore, the sulfate in the oceanic CCN was mainly controlled by  $\text{SO}_4^{2-}$ <sub>NSS</sub>.

$\delta^{34}\text{S}_{\text{NSS}}$  in both collectors provided a direct observation of the relative importance of  $\text{SO}_4^{2-}$ <sub>DMS</sub> and  $\text{SO}_4^{2-}$ <sub>anth</sub> in the midlatitude Southern Ocean. The  $\text{SO}_4^{2-}$ <sub>NSS</sub> in marine collector was primarily (88–100%) of DMS origin. The concentrations of  $\text{SO}_4^{2-}$ <sub>DMS</sub> showed significant seasonal variation, which allow us to attribute the observed high summer CCN level in the Southern Ocean troposphere to the elevated DMS emission. The ambient  $\text{SO}_4^{2-}$ <sub>NSS</sub> displayed a lower and wider range of  $\delta^{34}\text{S}$  values, indicating a mixture between  $\text{SO}_4^{2-}$ <sub>DMS</sub> and  $\text{SO}_4^{2-}$ <sub>anth</sub> with the average anthropogenic contribution range between 21 and 27%. Our observations suggested a much lower  $\text{SO}_4^{2-}$ <sub>anth</sub> background in the Southern Hemisphere than in the Northern Hemisphere.

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