Attribution of Atmospheric Sulfur Dioxide over the English Channel to Dimethylsulfide and Changing Ship Emissions

Mingxi Yang[1*], Thomas G. Bell[1*], Frances E. Hopkins[1], Timothy J. Smyth[1]

[1] Plymouth Marine Laboratory, Prospect Place, Plymouth, UK PL1 3DH.

Correspondence to: M. Yang (miya@pml.ac.uk) and T. Bell (tbe@pml.ac.uk)

Abstract. Atmospheric sulfur dioxide (SO_2) was measured continuously from the Penlee Point Atmospheric Observatory (PPAO) near Plymouth, United Kingdom between May 2014 and November 2015. This coastal site is exposed to marine air across a wide wind sector. The predominant southwesterly winds carry relatively clean background Atlantic air. In contrast, air from the southeast is heavily influenced by exhaust plumes from ships in the English Channel as well as near the Plymouth Sound. New International Maritime Organization (IMO) regulation came in to force in January 2015 to reduce the maximum allowed sulfur content in ships' fuel tenfold in Sulfur Emission Control Areas such as the English Channel. Our observations suggest a three-fold reduction in ship-emitted SO_2 from 2014 to 2015. Apparent fuel sulfur content calculated from coincidental SO_2 and carbon dioxide (CO_2) peaks from local ship plumes show a high level of compliance to the IMO regulation (>95%) in both years (~70% of ships in 2014 were already emitting at levels below the 2015 cap). Dimethylsulfide (DMS) is an important source of atmospheric SO_2 even in this semi-polluted region. The relative contribution of DMS oxidation to the SO_2 burden over the English Channel increased from ~1/3 in 2014 to ~1/2 in 2015 due to the reduction in ship sulfur emissions. Our diel analysis suggests that SO_2 is removed from the marine atmospheric boundary layer in about half a day, with dry deposition to the ocean accounting for a quarter of the total loss.

1 Introduction

The trace gas sulfur dioxide (SO_2) is important for atmospheric chemistry (Charlson and Rodhe, 1982) as a principal air pollutant (e.g. contributor to acid rain). Atmospheric oxidation of SO_2 leads to sulfate aerosols, which influence the Earth's radiative balance directly by scattering incoming radiation and indirectly by affecting cloud formation (Charlson et al. 1987). Important natural sources of SO_2 include the atmospheric oxidation of dimethylsulfide (DMS, which is formed by marine biota) and volcanic eruptions. Anthropogenic fossil fuel combustion also produces SO_2. SO_2 is removed from the lower atmosphere by dry deposition and oxidation in both the gas phase and the aqueous phase. The relatively slow gas phase oxidation of SO_2 leads to sulfuric acid vapor, which usually condenses upon pre-existing aerosols but can nucleate to form new particles under specific

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conditions (e.g. Clarke et al. 1998). The much faster aqueous phase oxidation of SO_2 takes place primarily in cloud water (e.g. Hegg 1985; Yang et al. 2011b) and leads to particulate sulfate, which is removed from the atmosphere mainly by wet deposition.

SO_2 production from DMS occurs principally via daytime oxidation by the hydroxyl radical (OH). From observations in the Equatorial Pacific, Bandy et al. (1996) and Chen et al. (2000) reported a clear increase in SO_2 mixing ratio and coincidental decrease in DMS during the day. This anti-correlation confirmed that DMS oxidation by OH is an important source of SO_2 over the remote ocean. Yang et al (2011b) showed that DMS remains the predominant sulfur precursor in the marine atmospheric boundary layer of the relatively unpolluted Southeast Pacific.

In the last few decades, SO_2 emissions from terrestrial combustion sources such as power plants and ground transportation have been subject to strict regulation (e.g. UK Clean Air Acts). These forms of legislation have significantly reduced the atmospheric sulfur burden over land in North America and Europe (e.g. Lynch et al. 2000; Malm et al, 2002; Vestreng et al, 2007). Unlike terrestrial SO_2 emissions, ship emissions were for a long period excluded from international environmental agreements. This allowed ships to burn low-grade fuels with high sulfur content (i.e. heavy fuel oils), which resulted in large SO_2 emissions from ship engine exhausts (hereafter ship emissions). In addition to SO_2, ship exhausts also contain carbon dioxide (CO_2), nitrogen oxides, carbon monoxide, heavy metals, organic toxins, and particulates such as black carbon (e.g. Agrawal et al 2008). Closer to the coast and near shipping lanes, ship emissions can be an important contributor to the atmospheric sulfur budget (Capaldo et al. 1999; Dalsoren et al, 2009). Eyring et al. (2005a) estimated that global, transport-related emissions of SO_2 from ships in the year 2000 were approximately 3-fold greater than from road traffic and aviation combined. Air quality models predict that aerosols resulting from ship emissions contribute to tens of thousands of cases of premature mortality near coastlines (Corbett et al., 2007). Impacts may be further exacerbated as the global population expands and shipping-based trade increases (Eyring et al., 2005b).

In January 2015, new air quality regulations from the International Maritime Organisation (IMO), an agency of the United Nations, came into force. These regulations aim to reduce sulfur emissions in Sulfur Emission Control Areas (SECAs) by decreasing the maximum allowed sulfur content in ship fuel from 1% (regulation since 2010) to 0.1% by mass. The English Channel and the surrounding European coastal waters are within a SECA. The IMO further intends to reduce the ship's fuel sulfur content in the open ocean from the current cap of 3.5% to 0.35% by 2020. As an alternative to burning lower sulfur fuel, these regulations also allow ships to use scrubber technology to reduce SO_2 emissions. Winebrake et al. (2009) estimated that such reduced emissions would approximately halve the premature mortality rate in coastal regions. A decrease in anthropogenic sulfur emission is also expected to make DMS a relatively more important sulfur source in regions such as the North Atlantic.

There have been few direct measurements of ship emissions that are relevant for a regional scale. Kattner et al. (2015) reported large reductions of SO_2 in ship plumes from 2014 to 2015 near the mouth of the Hamburg harbor on the river Elbe, which is about 100 km away from the North Sea. Using the SO_2:CO_2 ratio in ship plumes, they found a high compliance rate of ~95% after the stricter regulation in January 2015. Based on SO_2 and CO_2 measurements from the Saint Petersburg Dam, which spans the Gulf of Finland and separates the Neva Bay from the rest of the Baltic Sea, Beecken et al (2015) found a compliance rate of 90-97% in 2011 and 2012. They observed a bimodal distribution in the ship's fuel sulfur content, with the lower mode centering around ~0.2% by mass and the higher mode centering around ~0.9%. Compliance checks are mainly limited to manual checking of fuel logs and fuel quality certificates when ships are in port.

Global and regional ship emission estimates have typically been scaled from inventories for individual vessels in combination with information about ship traffic (e.g. Endresen et al. 2003; Collins et al. 2008; Matthias et al. 2010; Whall et al. 2010; Aulinger et al. 2015; Jalkanen et al. 2016). Accurate assessment of the success of IMO regulations requires long-term, continuous observations at strategic locations. Here we present 1.5 years of continuous atmospheric SO_2 measurements from the Penlee Point Atmospheric Observatory (PPAO) in the English Channel, one of the busiest shipping lanes in the world. The PPAO measurements date back to seven months before recent IMO sulfur regulations came into force, providing a reference point for future changes in emissions. The unique location of PPAO (Figure 1; http://www.westernchannelobservatory.org.uk/penlee/) allows us to partition the atmospheric SO_2 budget to natural (mostly dimethylsulfide) and anthropogenic (mostly ship emission) sources.

2 Experimental

The Penlee Point Atmospheric Observatory (PPAO) is located on the western side of the mouth of the Plymouth Sound (Figure 1). See Yang et al (2016) for detailed site description. About 11 m above mean sea level and ~30 m away from the high water mark, the site is exposed to air that has travelled over water across a wide wind sector (from northeast to southwest). Near-continuous measurements of SO_2, CO_2, ozone (O_3), methane (CH_4), as well as standard meteorological parameters have been made at the PPAO since May 2014.

SO_2 mixing ratio was measured every 10 seconds by a Trace Level-Enhanced Pulsed Fluorescence SO_2 analyzer (Thermo Scientific, Model 43i). The instrument noise level is about 0.06 parts per billion (ppb) at a one-minute averaging interval and 0.025 ppb at a five-minute averaging interval. O_3 mixing ratio was measured every 10 seconds by a dual-beam, UV absorption Ozone monitor (2B Technologies, Inc. Model 205), which has a noise level of about 2.2 ppb at a one-minute averaging interval and 1.0 ppb at a five-minute averaging interval. The SO_2 and O_3 sensors shared the same air inlet, which consisted of a ~4 m long 0.64 cm outer diameter PFA (perfluoroalkoxy) tubing that extended just outside the air vent of the building (~2 m above ground; ~13 m above mean sea level). A 5 micron diameter Teflon filter was installed upstream of the instruments to reduce particulates in sampled air. The O_3 instrument sampled through an additional 5 micron particle filter.

These filters were replaced approximately every 2-4 weeks. Blank measurements of SO_2 and O_3 were made simultaneously by directing sample air through the existing particle filters, ~8 m of 0.64 cm outer diameter copper tubing (which efficiently removed SO_2), and an O_3 scrubber. Linearly interpolated blanks are subtracted from the raw data. We checked the calibration of the SO_2 instrument twice a year with a SO_2 gas standard diluted in nitrogen (100 ppb, BOC). The measured SO_2 mixing ratio was within a few percent of the gas standard. An O_3 calibration device was unavailable during the duration of these measurements. However, an intercomparison with a recently-calibrated 2B O_3 Monitor showed that the accuracy of the O_3 measurement at PPAO was within ±5%.

CO_2 mixing ratio was measured by a Picarro cavity-ringdown analyzer (G2311-f) every 0.1 second (See Yang et al. 2016 for details). Ambient air was drawn from a mast on the rooftop of the observatory (nominally at ~18 m above mean sea level) through a ~18 m long 0.95 cm outer diameter perfluoroalkoxy (PFA) tubing at about 15–30 L min^{-1} by a dry vacuum pump. The Picarro analyzer subsampled from this main flow via a ~2 m long 0.64 cm outer diameter Teflon PFA tubing and a high throughput dryer (Nafion PD-200T-24M) at a flow rate of ~5 L min^{-1}. The total delay time from the inlet tip to the analyzer was 1.9–3.3 seconds. The instrument calibration was checked with a CO_2 gas standard (BOC) and the accuracy was within 0.5%. The instrument noise for one minute-averaged CO_2 is less than 0.05 ppm.

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SO_2, O_3, and meteorological parameters data were logged and timestamped by the same PC. Given the short inlet tubing length and the specified flow rates, the calculated delay time for these gases from the inlet tip to the sensors was less than four seconds. CO_2 data were logged on a separate computer (Picarro internal PC). Both PCs were synchronized to network UTC clocks once a week. The time difference between the SO_2/O_3/meteorology measurements and the CO_2 measurements was less than a minute. We note that the gas inlets for both the SO_2 and the CO_2 instruments (~13 and 18 m above mean sea level) were within the surface layer of the marine atmosphere; they should be sampling the same airmass (and the same ship plume) under typical meteorological conditions. Dispersion modeling from von Glasow et al (2003) predicts that just 10 seconds after emission, a ship plume will have already expanded vertically to a height of 20 m from the surface.

3 Results

Figure 1 shows the frequency distribution of winds from 2014 to 2015 (wind distributions were nearly identical for these two years). Winds came predominantly from west/southwest at moderate-to-high speeds, which were typically associated with low pressure systems in the North Atlantic and generally carried low mixing ratios of SO_2 and CO_2 (Yang et al. 2016). The wind sector between 110 and 250° is unobstructed by land. The Rame Head peninsula sits ~1.5 km west of PPAO, beyond which lie ~40 km of coastal seas, the county of Cornwall (width of ~30 km), and the North Atlantic Ocean. The north/northeast sector is more influenced by emissions from terrestrial anthropogenic sources, while winds from 50–110° face the eastern side of the

Plymouth Sound, which is busy with ship traffic. The southeasterly sector is likely affected by emissions from local ships as well as distant pollution from the English Channel and continental Europe. According to the Devonport Naval Base Ship Movement Report, the total number of ships in the Plymouth Sound varies from about 4000 per month in winter to 6000 per month in summer. The volume of ship traffic in the English Channel is about 15000 per month (Maritime and Coastguard Agency, 2007).

Atmospheric SO_2 and humidity varied significantly at PPAO depending on wind direction (Figure 2). Increased relative humidity clearly indicates the marine-influenced wind sector from northeast to west/southwest. SO_2 mixing ratios were higher and more variable when the air mass had travelled from the southeast than when it had come from the southwest. This elevated SO_2 signal was more pronounced in 2014 (averaged between May and December) than in 2015 (averaged between January and November). The lowest SO_2 mixing ratios were observed in the western wind sector in both years. In the Appendix, we show episodes of large SO_2 plumes from the Icelandic volcano Bardarbunga as observed at PPAO. These volcanic events do not affect our analysis of SO_2 in the marine atmosphere since winds were from the northwest.

3.1 Ship Plumes and SO_2 Frequency Distributions

Figure 3 shows a ship plume-influenced time series during a period of southeasterly winds. Sharp spikes in SO_2 coincided with spikes in CO_2 (e.g. at about 12:00 and 15:40 UTC), which lasted for just a few minutes and likely corresponded to local (within a few km) ship emissions. O_3 was significantly depleted in these plumes because of its reaction with nitrogen oxides (NOx) emitted from ships. A lower, broader hump in SO_2 can also be observed between about 18:30 to 20:00 UTC. This was likely due to more distant ship emissions that have been diluted and mixed in the atmosphere. A concurrent increase in CO_2 was not obvious during these 1.5 hours. Given the high background mixing ratio of CO_2 (~400 ppm), ship plumes result in much smaller (additional) signal:background ratios for CO_2 than for SO_2. As a result, CO_2 emitted from point sources tends to quickly become indistinguishable from the background with increasing distance (i.e. greater air dilution/dispersion). In Section 4.2, we use the ratio between the SO_2 and CO_2 peaks to estimate the ship's apparent fuel sulfur content.

Figure 4 shows the histograms of SO_2 mixing ratios (from 5-minute averages) in 2014 and 2015. We have separated the data into two wind sectors, southeast (80-170°) and southwest (210-250°). The southeast sector encompasses the English Channel while avoiding most of the UK landmass. The southwest sector, with largely an unobstructed oceanic fetch of thousands of kilometers, bypasses the northwestern coast of France as well as the busiest part of the shipping lanes (see ship's Automatic Identification System maps from Jalkanen et al. 2016). On average, winds came from our SW sector 7.5 days a month, and came from the SE sector 2.1 days a month. The SO_2 distributions shifted towards lower mixing ratios in 2015 compared to 2014, especially for the southeast wind sector. For example, SO_2 mixing ratios from the southeast exceeded 0.5 ppb ~1% of the time in 2015 (compared to ~11% in 2014).

3.2 Diel Variability in SO_2

We compute the mean diel cycles of SO_2 mixing ratio in the southeast and the southwest sectors for both 2014 (May to December) and 2015 (January to November), which are shown in Figure 5. The long averaging periods help to reduce measurement noise and also allow variability caused by horizontal transport to largely cancel. SO_2 from the southwest shows a very tight diel cycle and low variability (relative standard errors less than 10%). SO_2 mixing ratio was the lowest near sunrise, increased throughout the day, and decreased after sunset. This diel cycle suggests that SO_2 from the southwest came primarily from the photooxidation of biologically-derived DMS. Differences in the mean SO_2 diel cycles in 2014 and 2015 for the southwest sector are largely due to the different months used in the averaging. Considering only the months of May to November, mean SO_2 mixing ratios in this wind sector for the two years differ by only ~0.01 ppb (see Section 4.1).

SO_2 from the southeast was about three times higher and also more variable than from the southwest in 2014. Peaks in SO_2 were observed in the morning, mid-afternoon, and early evening. These timings are consistent with the schedule of channel-crossing ferries, which enter the Plymouth Sound at least once a day from approximately due south. In 2015, SO_2 from the southeast was about two times higher than from the southwest and variability in SO_2 mixing ratio was reduced. In both years, SO_2 from the southeast shows an underlying diel trend (i.e. increasing during the day and decreasing at night) that suggests contributions from DMS oxidation. This implies that SO_2 from the southeast is made up of at least two major components: ship emissions and DMS oxidation.

3.3 SO_2 from DMS Oxidation

The SO_2 diel cycle from the southwest wind sector (Figure 5) is consistent with daytime SO_2 production from DMS oxidation by the OH radical (e.g. Bandy et al. 1996; Yang et al. 2009). DMS was measured using a high resolution proton-transfer-reaction mass spectrometer (Ionicon, Austria) from the rooftop of the PML building in Plymouth (~6 km north/northeast of PPAO) in 2012 (Yang et al. 2013) and in 2015. Recently-calibrated transmission efficiencies from the manufacturer and kinetic reaction rates from Zhao and Zhang (2004) were used to derive the DMS mixing ratio (uncertainty ≤40%). DMS levels in marine air from the southwest and southeast were comparable during the 2015 measurement period (21 April to 15 May). The mean DMS diel cycle from the marine sector (Figure 6) clearly shows an anti-correlation with shortwave irradiance, implying daytime oxidation by OH (mostly to SO_2). The diel amplitude in DMS mixing ratio was ~0.09 ppb. A day/night difference in atmospheric DMS was also observed from the PML rooftop in June 2012 from marine air (Yang et al. 2013).

The conversion efficiency from DMS to SO_2 due to OH oxidation is about 70-90% (Davis et al., 1999; Chen et al., 2000; Shon et al., 2001). At a conversion efficiency of 80%, 0.09 ppb of oxidized DMS would lead to about 0.07 ppb of SO_2 produced during the day. In comparison, over the 1.5 years of observations at PPAO the mean amplitude of the SO_2 diel cycle from the southwest was ~0.06 ppb. This comparison is qualitative because DMS was only measured during the spring/summer periods and at a different location. Nevertheless, it appears that within the measurement uncertainties DMS oxidation can account for the vast majority of the observed SO_2 diel cycle from the southwest wind sector.

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3.4 Removal of SO_2 from the Marine Atmosphere

SO_2 is mainly removed from the marine boundary layer via aqueous oxidation (e.g. cloud processing), deposition to the ocean, and possibly dilution by the free tropospheric air. We can approximate the total loss of SO_2 from the nighttime change in the averaged SO_2 mixing ratio (daytime SO_2 oxidation is very slow). This calculation assumes no temporal trend in any nocturnal ship emissions (on a diel timescale) and a constant marine boundary layer height. In a polluted marine environment, a small amount of SO_2 could be formed at night via DMS oxidation by the nitrate radical (NO_3; Yvon et al. 1996), a process we neglect here. A linear fit to the nighttime decrease of SO_2 from the southwest in 2014 (Figure 5A) yields a total loss rate of about 0.2 ppb per day. The average SO_2 mixing ratio was about 0.1 ppb in the evening hours, which implies a SO_2 residence time of approximately 0.5 d. In 2015, the total loss rate was about 0.1 ppb per day, which also implies a SO_2 residence time of ~0.5 d. This residence time is in close agreement with previous estimates in the marine atmosphere (e.g. Cuong et al. 1975; Yang et al 2011b).

We compute the dry deposition flux of SO_2 to the surface ocean as $-V_d * [SO_2]$, where $[SO_2]$ is the atmospheric SO_2 concentration and V_d is the deposition velocity of SO_2. Upon contact with seawater, SO_2 rapidly dissociates to form HSO_3^- and then sulfite (Eigen et al. 1964). The effective solubility of SO_2 in seawater (pH ~8) due to this chemical enhancement is very large (dimensionless water:air solubility of about $5e^8$), which means that air-sea SO_2 exchange should be gas phase controlled. Oxidation to sulfate permanently removes sulfite from the surface ocean with a time scale of minutes to hours (Schwartz 1992). The combination of a low aqueous S(IV) concentration (e.g. Campanella et al. 1995; Hayes et al. 2006) and a high effective solubility results in a near zero interfacial SO_2 concentration that is in equilibrium with seawater (e.g. Liss and Slater, 1974). We compute the deposition velocity of SO_2 using the COARE gas transfer model (Fairall et al. 2011), which utilizes the airside diffusivity of SO_2 from Johnson (2010) and the measured wind speed at PPAO. Diel cycles in SO_2 deposition flux (Figure 7) resemble the mirror image of SO_2 mixing ratio. For the southwest wind sector, the average SO_2 deposition flux was about -1 to -2 μmole m^{-2} d^{-1}.

For the southeast sector, deposition flux averaged about -3 μmole m^{-2} d^{-1} in 2014 and -1 μmole m^{-2} d^{-1} in 2015. Interestingly, while SO_2 mixing ratio from the southeast was still higher than from the southwest in 2015, deposition fluxes between the two wind sectors were comparable. This is because wind speeds were typically lower from the southeast. Overall, dry deposition removes SO_2 from a well-mixed, 1 km deep marine atmospheric boundary layer with a timescale of ~2 days at PPAO. It accounted for approximately a quarter of the total SO_2 losses, similar to previous findings (e.g. Yang et al. 2011b).

4 Discussion

4.1 Long Term Changes in SO_2 and Ship Emissions

We evaluate the long-term trends in SO_2 from different wind sectors in order to understand seasonal variability and assess any changes due to ship emissions. SO_2 mixing ratios from the southeast and the southwest are averaged into monthly intervals (Figure 8). Mean SO_2 from the southwest in the summer months were comparable between 2014 and 2015. In contrast, SO_2 from the southeast was significantly lower in summer 2015 than in summer 2014. For both wind sectors, lower SO_2 mixing ratios were observed in winter/early spring compared to summer/early autumn. The seasonal cycle in SO_2 from the southwest is consistent with the variability in surface seawater DMS concentration previously measured at the nearby L4 mooring station (~6 nM in summer and ~1 nM in winter; Archer et al. 2009). Using those seawater DMS concentrations, local wind speeds and temperatures, and the DMS air-sea transfer velocity from Yang et al. (2011a), we predict DMS fluxes on the order of ~10 and 3 μmole m^{-2} d^{-1} for the summer and winter, respectively. These fluxes would be sufficient to account for the observed SO_2 burden from the southwest (~0.10 ppb in summer and ~0.02 ppb in winter) assuming a SO_2 residence time of 0.5 day in a 1 km deep marine boundary layer (~8 and ~2 μmole m^{-2} d^{-1} of sulfur required). In addition to lower seawater DMS concentrations in winter, less incoming irradiance and shorter daylight hours in those months will also reduce the photochemical production of SO_2 from atmospheric DMS. Overall, we see that the seasonal cycle of SO_2 in air from the southwest can largely be explained by natural variability.

The difference in SO_2 mixing ratio between the southeast and southwest sectors (ΔSO_2) is shown in Figure 9. There is a fair amount of scatter in ΔSO_2, which is partly because SO_2 measurements from the two wind sectors were not concurrent (i.e. winds could not be blowing from the southeast and southwest at any single moment). Nevertheless, mean (±standard error) ΔSO_2 decreased from ~0.15 (±0.03) ppb in 2014 to ~0.05 (±0.01) ppb in 2015, with a sharp drop off coincident with the 1st January 2015 mandate for ship sulfur emission reduction.

We attribute ΔSO_2 to ship sulfur emissions based on the following assumptions: I) SO_2 from the southwest is from DMS oxidation only; II) SO_2 from the southeast is affected by both DMS oxidation and ship emissions; III) DMS oxidation contributes equally to the SO_2 burden in both the southeast and southwest wind sectors. Data from the southwest sector will almost certainly include some ship contributions but the tightly constrained diel cycle in SO_2 suggests this influence is fairly small. Automatic Identification System maps (http://www.marinetraffic.com/) indicate lower ship density and greater distances between the shipping lanes and PPAO (i.e. lower SO_2 emissions, increased plume dilution and greater SO_2 removal) in the southwest sector than in the southeast sector. This information corroborates the idea that ship emissions from the southwest only have a minor effect on our observations.

Entrainment from the free troposphere could bring anthropogenic SO_2 into the marine boundary layer (e.g. Simpson et al. 2014), which is not accounted for here. We further assume negligible influence of terrestrial SO_2 emissions (e.g. from Continental Europe) in the southeast sector because of atmospheric dilution and rapid removal of SO_2 from the lower atmosphere (residence time ~0.5 d, see Section 3.4). The English Channel near Plymouth has a width of approximately 200 km. At a speed of 5 m s^{-1}, southeasterly winds blow over the channel in approximately half a day, comparable to the removal time.

4.2 Local Ship Plumes and Fuel sulfur content

The SO_2 signals from the southeast include local ship emissions (e.g. from ships entering/exiting the Plymouth Sound) as well as more distant emissions from the English Channel. Local emissions usually appear as sharp spikes, while more distant emissions tend to have plumes that are broader and less intense due to atmospheric dilution. We use concurrent peaks in SO_2 and CO_2 to estimate the ships' apparent fuel sulfur content (FSC). The FSC calculation assumes that all of the carbon and sulfur in fuel are released into the atmosphere during combustion. We use the word 'apparent' here because our calculation reflects the downstream emissions rather than the actual fuel composition. Ships that 'scrub' sulfur from stack emissions will have apparent FSC values that are lower than the actual fuel sulfur content. To minimize the uncertainty in our estimate, we focus on well-resolved plumes from nearby ships only.

Simple dispersion modeling predicts that local ship plumes have a typical duration of a few minutes. For example, von Glasow et al (2003) estimated the horizontal dispersion of a ship plume as:

$$H = H_0 \bullet (t/t_0)^{0.75} \qquad (1)$$

H_0 and H are the horizontal extents of a plume at the initial time t_0 (1 second) and the time of interest t. The initial plume extent (H_0) is assumed to be 10 m. We estimate the horizontal dispersion of plumes emitted from an upwind distance of 2 km (e.g. half away across Plymouth Sound) and 100 km (e.g. half away across the English Channel). At a speed of 8 m s^{-1}, wind travels 2 km and 100 km in ~4 and 200 minutes, respectively. Applying these timescales to Eq. 1 yields horizontal plume extents of 600 m and 11000 m. For a ship 2 km away that is traversing perpendicular to the mean wind at a speed of 4 m s^{-1}, its emission should be observable at PPAO for 2.5 minutes. A ship 100 km away would have a plume that is theoretically observable for nearly an hour. These timescales are roughly consistent with our time series observations (e.g. Figure 3). Ships that do not travel perpendicular to the wind will have plumes that are observable for longer periods. Faster wind speeds or ship speeds shorten the duration of plume detection, and vice versa.

The following steps were used to separate local ship emissions from the background or more distant emissions based on 1 minute average gas mixing ratios. All data processing was done with Igor Pro (WaveMetrics).

1) Apply 2 hour running-median smoothing to the SO_2 time series
2) Identify 'no plume' times as when the 1 minute average SO_2 was within 0.1 ppb (i.e. < twice the instrument noise) of the smoothed SO_2
3) Subtract the linear interpolation of the 'no plume' SO_2 time series from the 1 minute average SO_2 time series to derive the SO_2 deviations from the background (SO_2')
4) Apply the 'FindPeak' function to SO_2' to identify the time, height, leading edge, and trailing edge of a peak within non-overlapping 10-minute windows. A minimum peak height of 0.2 ppb (i.e. > three times the instrument noise) was required for positive peak identification
5) Integrate SO_2' between the leading edge and the trailing edge to yield the SO_2 plume peak area

The 10-minute window in step 4 was chosen to minimize the occurrence of multiple plumes within a single window but also allow for identifications of plumes persisting for several minutes. A total of 816 distinct SO_2 plumes were identified from May 2014 to November 2015 from the marine wind sector. The mean SO_2 plume height (1 minute average) was 1.35 ppb in 2014 and 0.48 ppb in 2015, with a typical plume duration of ~3 minutes.

CO_2 plumes from local ship emissions were identified in an analogous fashion based on an analysis of the 1 minute average CO_2 time series (i.e. independent of the SO_2 analysis). The 'no plume' CO_2 threshold (Step 2 above) was set to be 0.2 ppm, and the minimum peak height required for positive peak identification (Step 4) was set to be 1.0 ppm. Based on these schemes, a total number of 1242 separate CO_2 plumes were identified from May 2014 to November 2015, with a mean plume height of 2.6 ppm.

Apparent fuel sulfur content (FSC) is computed from coincidental SO_2 and CO_2 plume heights as well as plume areas (N = 245) following Kattner et al. (2015). To account for clock drift between the PCs that recorded the SO_2 and CO_2 data, we allowed the times of the SO_2 and CO_2 peaks to differ by up to one minute. The results of these calculations for the marine wind sector are shown in Figure 10. Gaps in observations were largely due to the CO_2 analyzer malfunctioning or winds out of sector. The peak area and peak height methods yielded similar results. FSC from peak area appears to be slightly more variable, possibly due to a greater sensitivity toward the definition of plume baseline. Based on peak height, in 2014 the mean (± standard error) FSC was 0.17 (±0.03) %, with ~99% of the plumes below the IMO threshold of 1% FSC. About 70% of the plumes were already below 0.1% FSC in 2014. In 2015, mean FSC decreased to 0.047 (±0.003) %, with ~99% of the plumes below the new

IMO threshold of 0.1%. FSC estimated from the peak area method shows slightly lower levels of compliance (~95% for both years). The reduction in mean FSC from 2014 to 2015 is proportionally comparable to the decrease in ΔSO_2 computed in Section 4.1.

Our FSC estimates illustrate a fairly similar decreasing trend to that observed near the Hamburg harbor (Kattner et al., 2015). The mean FSC value at PPAO is approximately half of what was estimated by Kattner et al. (2015) for the year 2014 and is comparable to their estimate for 2015. However, our observations are different in several aspects. The vast majority of the ships entering/leaving Plymouth Sound are naval, commercial ferries, and private vessels according to the Devonport Naval Base Ship Movement Report. The number of large container ships entering the Plymouth Sound is proportionally much lower than near Hamburg. Because the distances between ships and PPAO were not fixed (as opposed to spatially restricted sampling locations in Kattner et al. 2015 and Beecken et al. 2015), plumes observed at our site were usually more dilute and variable in duration. This variability made plume identification more challenging. We expect the bulk of the uncertainty in FSC to be due to instrument noise in SO_2, which should be within 20% for plumes in 2015 and better in 2014. Total uncertainty in FSC may be higher though due to inexact plume baseline quantification, uncertainty in the threshold required for SO_2 spike detection, and the small but variable time lag between the SO_2 and CO_2 measurements. A higher SO_2 spike threshold could bias our FSC estimates towards plumes with greater sulfur content, while a lower threshold would be too close to the noise level of the measurement. Long-term records of another tracer (e.g. nitrogen oxides or black carbon) would allow for a more independent identification of ship plumes for the calculation of FSC. Finally, we reiterate that our FSC estimates are for well-resolved peaks from local ship plumes, which do not necessarily reflect ship emissions from the main shipping lanes of the English Channel.

4.3 Top-down Estimates of SO_2 Emissions from the English Channel

We use ΔSO_2 with local ship emissions excluded (Figure 9) to estimate distant anthropogenic SO_2 emissions (e.g. from the English Channel). Without local spikes (i.e. the 'no plume' SO_2 time series in Section 4.2), the computed mean SO_2 mixing ratio from the southwest is only slightly lower, as might be expected due to the relatively low ship density in that direction; in contrast, mean SO_2 mixing ratio from the southeast is lowered by ~0.04 ppb in 2014 and ~0.01 ppb in 2015. Approximately a quarter of the SO_2 attributed to ship emissions in Section 4.1 (ΔSO_2) was due to local ship plumes. ΔSO_2 excluding local ship emissions was ~0.11 (±0.03) ppb in 2014 and ~0.04 (±0.01) ppb in 2015. The largest differences in ΔSO_2 with and without nearby plumes occurred in the summer for both years, when the ship traffic was the heaviest.

We make an order of magnitude estimate for the ship emissions in the English Channel required to sustain the observed SO_2 mixing ratios. This calculation assumes a SO_2 residence time of 0.5 d in a well-mixed, 1 km deep marine atmospheric boundary layer. For this scenario it would take ~9 μmole m^{-2} d^{-1} of SO_2 from ships to account for a ΔSO_2 of 0.11 ppb, and ~3 μmole m^{-2} d^{-1} of SO_2 emission from ships to account for a ΔSO_2 of 0.04 ppb. Simplistic extrapolation of these fluxes to the area of the English Channel (about 75000 km^2) yields a total ship SO_2 emission of ~16 Gg per year in 2014 and ~5 Gg per year in 2015. Compared to previous inventory-based SO_2 emission estimates for the English Channel, our 2014 value is about 40% of that reported by Jalkanen et al. (2016) for 2011, and about a quarter of the Ship Emissions Inventory found in the UK Department for Environment Food and Rural Affairs (DEFRA) report (Whall et al. 2010).

Our SO_2 emission estimate is low in part because we have purposely excluded local ship plumes. Also, ΔSO_2 could be a slight underestimate of ship emissions due to the assumption of zero ship influence in the southwest wind sector. More accurate constraints of sulfur emissions from the English Channel from point measurements such as at PPAO probably requires modeling of air trajectory/dispersion, detailed information about ship traffic, and knowledge of the SO_2 source area (i.e. the concentration footprint; Wilson and Swaters, 1991; Schmid 1994). A more complete description of the sulfur budget in this environment would also require sulfate concentration measurements in aerosols as well as in precipitation droplets.

5 Conclusions

In this paper, we analyzed 1.5 years of continuous atmospheric SO_2 measurements by the coast of the English Channel. SO_2 mixing ratio in southwesterly winds was generally low and showed a diel cycle that is largely consistent with DMS oxidation. In contrast, SO_2 mixing ratio in southeasterly winds was elevated and more variable due to additional contribution from ships. This ship contribution was reduced by approximately three-fold from 2014 to 2015 in response to the International Maritime Organization regulation on sulfur emissions in European coastal waters. Apparent fuel sulfur content calculated from coincidental SO_2 and CO_2 peaks from local ship plumes suggest a high level of compliance (>95%) in both years. About 70% of ships were already emitting SO_2 at levels below the 2015 cap in 2014. As ship sulfur emissions reduce, DMS becomes relatively more important to the atmospheric SO_2 burden, accounting for about half of the atmospheric SO_2 over the English Channel in 2015. Our data show that the residence time of SO_2 in the marine atmosphere is approximately 0.5 d, with dry deposition explaining about a quarter of the total SO_2 sink.

Appendix: SO_2 from Volcanic Eruption

The Icelandic volcano Bardarbunga was active for the spring and summer months of 2014. Under favorable meteorological conditions, SO_2 emitted from the volcano was transported in the upper atmosphere from Iceland to the UK, where it was entrained into the atmospheric boundary layer. SO_2 from volcanic eruption, with surface mixing ratios up to 30 ppb, was clearly detected at PPAO between 21 and 24 September 2014 (Figure A1). These SO_2 plumes were observed all over the UK (http://uk-air.defra.gov.uk) and were also apparent from space (e.g. O_3 Monitoring Instrument, http://sacs.aeronomie.be/nrt/). Winds were generally from the northwest during these days of relatively high atmospheric pressure. Elevated O_3 mixing ratios and reduced humidity generally coincided with the high SO_2 mixing ratios in these plumes, qualitatively consistent with entrainment from the troposphere. These volcanic plumes of SO_2 were outside of our southeast and southwest marine wind sectors.

Acknowledgement

Trinity House (http://www.trinityhouse.co.uk/) owns the Penlee site and has kindly agreed to lease the building to PML so that the instruments can be protected from the elements. We are able to access the site thanks to the cooperation of Mount Edgcumbe Estate (http://www.mountedgcumbe.gov.uk/). Thanks to S. Atkinson and M. Sillett (Plymouth University) for routine maintenance of site, S. Ussher (Plymouth University), P. Agnew, N. Savage, and L. Neal (UK Met Office) for valuable scientific discussions, R. Pascal and M. Yelland (National Oceanography Centre, Southampton) for letting us deploy the Picarro instrument, and B. Carlton (Plymouth Marine Laboratory) for setting up data communication. We also thank the reviewers for their constructive comments and suggestions. T. Bell and M. Yang dedicate this publication to the late Roland von Glasow, who was a source of great inspiration and support to us both.

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Figures

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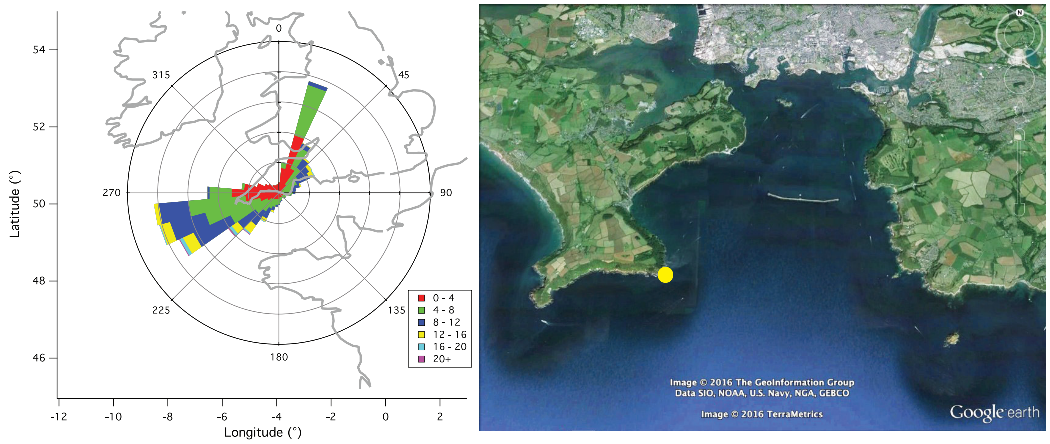

Figure 1. Wind rose at Penlee Point Atmospheric Observatory from 2014 to 2015 overlaid on a map of the British Isles (left), and a map showing the observatory (yellow circle) on the west side of the 4-km wide Plymouth Sound (right). The English Channel lies between the UK and the north of France. Colors on the spokes correspond to wind speeds in units of m s^{-1} and concentric circles indicate frequency of occurrence in 2.5% intervals (outer circle = 12.5%). Winds predominantly came from the west/southwest at speeds of 4-12 m s^{-1}.

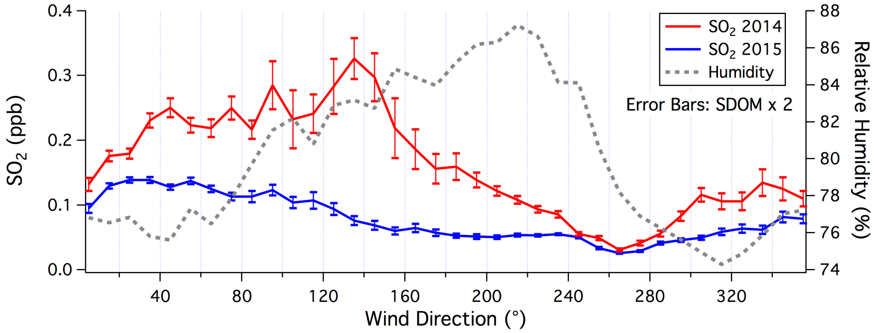

Figure 2. Averaged SO_2 mixing ratio and relative humidity vs wind direction for year 2014 and 2015. Error bars on SO_2 indicate two standard errors. Elevated humidity marks the marine-influenced wind sector to be between about 60 and 260°. Higher and more variable SO_2 mixing ratios were observed from the southeast direction, particularly in 2014. Icelandic volcano plumes (e.g. Figure A1) were excluded from averaging.

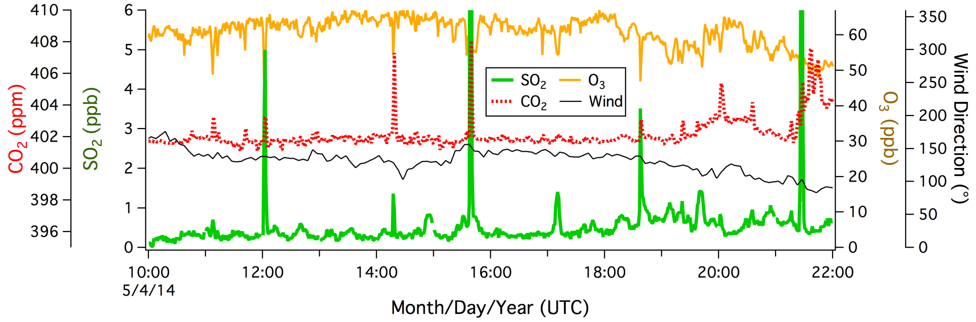

Figure 3. Example of local ship plumes on a day of southeasterly winds. Sharp peaks in SO_2 and CO_2 generally coincided with sudden depletions in O_3. (1-minute average).

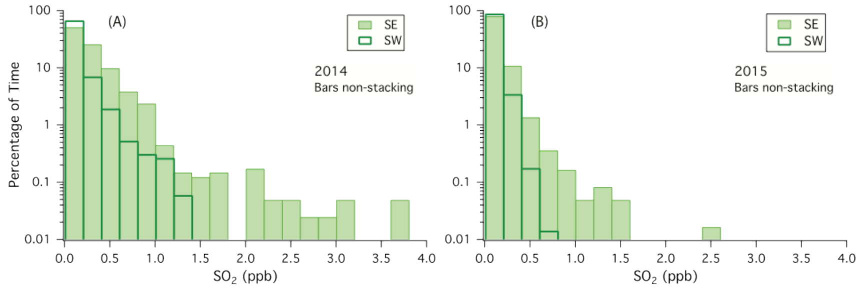

Figure 4. Histogram distributions of SO_2 mixing ratios in 2014 (A) and 2015 (B) from the southeast and southwest wind sectors (5-minute average). Distributions are normalized to the total number of observations from the respective wind sectors.

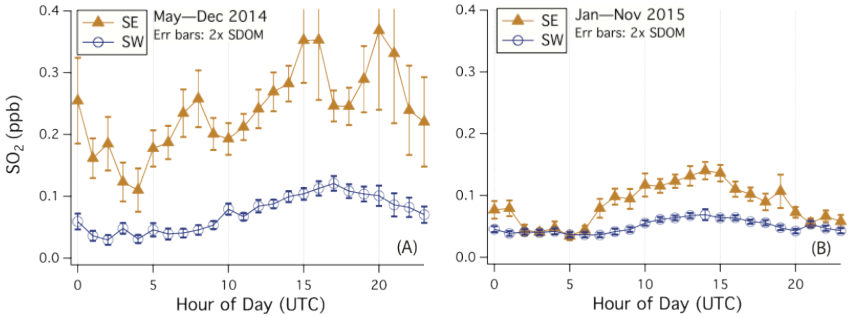

Figure 5. Average diel cycles of SO_2 mixing ratio, separated into the southeast and southwest wind sectors for 2014 (A) and 2015 (B). SO_2 in the southwest sector showed diel variability that is largely consistent with DMS oxidation. SO_2 in the southeast sector was significantly lower and less variable in 2015 than in 2014.

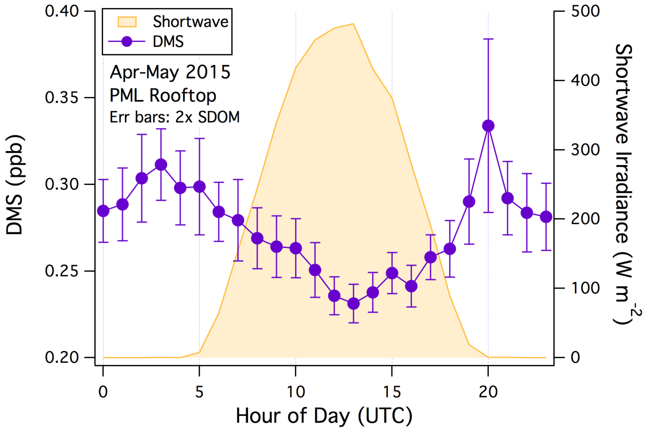

Figure 6. Average diel variability in DMS mixing ratio and shortwave irradiance, measured from the PML rooftop between April and May 2015 (wind from the marine sector). Error bars indicate two standard errors.

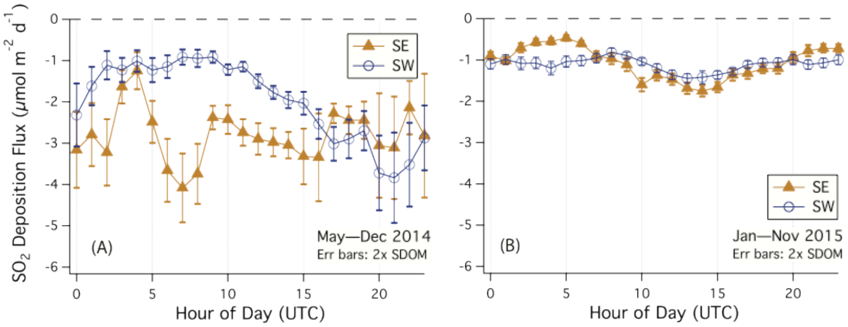

Figure 7. Mean diel cycles in the wind speed-dependent SO_2 deposition flux, separated into the southeast and southwest wind sectors for year 2014 (A) and 2015 (B). Error bars indicate two standard errors. SO_2 deposition flux was significantly greater in the southeast sector than in the southwest sector in 2014.

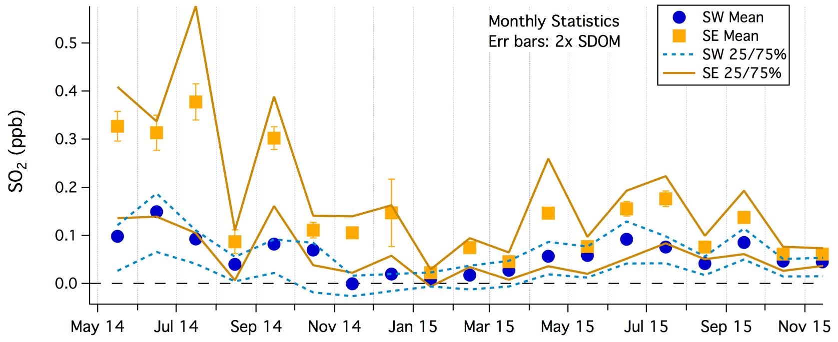

Figure 8. Monthly means and 25th/75th percentiles of SO_2 mixing ratio from southeast and southwest wind sectors. SO_2 from the southwest shows a clear seasonal cycle, with higher values in summer/early autumn, and lower values in winter/early spring. A similar underlying seasonal variability is also apparent in SO_2 from the southeast sector.

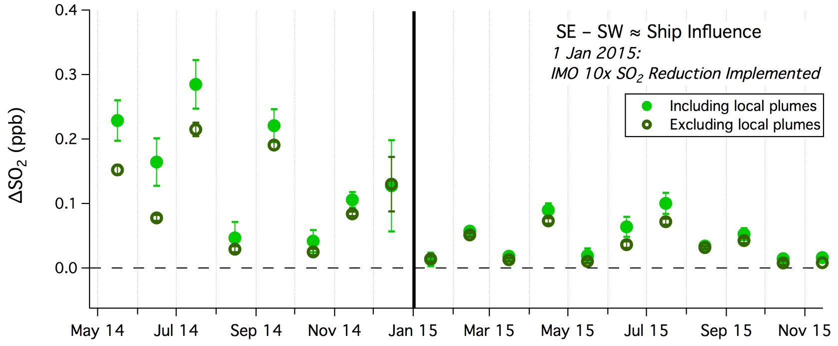

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Figure 9. The difference between monthly averaged SO_2 mixing ratios from the southeast and southwest (ΔSO_2), which we consider to approximately represent ship emissions. ΔSO_2 including and excluding local ship plumes are shown. Error bars are propagated from 2 times the standard errors from each wind sector. Solid vertical line indicates the 1st Jan 2015 mandate for reduction in ship SO_2 emissions.

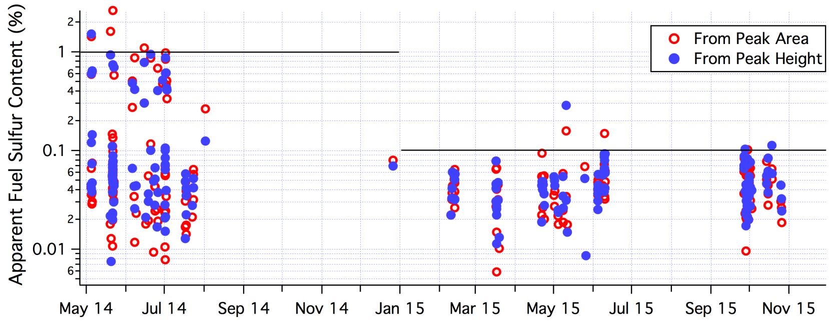

Figure 10. Apparent fuel sulfur content (FSC) estimated from peak areas as well as peak heights of coincidental SO_2 and CO_2 plumes (1-minute averaged data).. Solid horizontal lines indicate IMO fuel sulfur emissioncontent limits in European watersSECA regions: 1% SFC in 2014, 0.1% SFC in 2015.

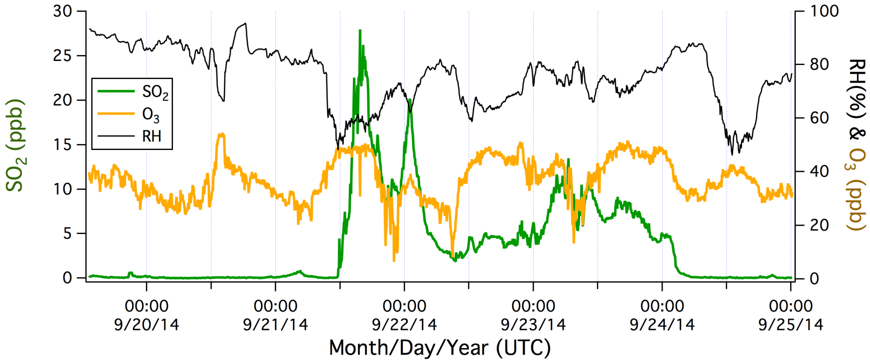

Figure A1. Very high SO_2 mixing ratios were observed in Icelandic volcano plumes. Elevated SO_2 sometimes coincided with increased O_3 and reduced relative humidity (RH), consistent with entrainment from the free troposphere.