Short communication

A survey of $NO_2:SO_2$ emission ratios measured in marine vessel plumes in the Strait of Georgia

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ABSTRACT

We report nocturnal measurements of NO_2 and SO_2 by DOAS within marine vessel plumes that impact an island site close to Vancouver during the summer of 2005. The median NO_2/SO_2 molar ratio from 17 ship plumes (2.86) is marginally higher than the molar NO_x/SO_x emissions ratio for both: marine vessel emissions (2.39–2.66) in a 2005 inventory for the region and, "underway" emissions of major ocean going vessels (2.04–2.12) in a related marine inventory. Due to the limited nature of our survey, we conclude that the difference between observations and inventories is not unreasonable. The generally low NO_2/SO_2 ratios we observe are a direct result of the high sulfur content of marine fuels. Measurement of NO_2/SO_2 ratios is one way to monitor future changes that will occur when new regulations come into force in the Emissions Control Area (ECA) for North American waters, with restrictions on the sulfur content of marine fuel by 2012.

1. Introduction

Marine vessels are among the highest polluting combustion sources in the world on a fuel consumption basis (Corbett and Fischbeck, 1997). In populated coastal regions, these emissions are of concern due to air quality degradation (Lu et al., 2006), the impact on ozone and methane (Dalsøren et al., 2010) and their impact on radiative forcing (Capaldo et al., 1999). Uncontrolled marine vessel emissions have an enhanced impact in coastal cities due to increased shipping activity concurrent with a decrease in other mobile source emissions, that are subject to new emissions control and fuel composition regulations. Marine vessel emissions include NO_x, SO_2, CO_2, CO, VOCs, and particulate matter (PM) (Corbett et al., 1999; Sinha et al., 2003; Lack et al., 2009; Williams et al., 2009). The NO_x emissions are a function of engine type, operation mode and combustion temperature, while SO_2 emissions are determined by fuel sulfur content. The NO_x/SO_2 ratio decreases with the fuel sulfur content (Sinha et al., 2003).

The International Maritime Organization (IMO) has been responsible for a series of regulations governing sulfur content of marine vessel fuels used in global waters since 1987 (Corbett and Fischbeck, 1997) and has overseen the designation of Emission Control Areas (ECA) in sensitive regions, where marine vessels are subject to more stringent emission and fuel standards. In 2010, the IMO officially designated ECA status to the territorial waters of North America (Transport Canada, 2010; EPA, 2010), limiting sulfur content of marine fuels to 1.0% in 2012 and 0.1% in 2015. Further NO_x regulations will also take effect, although the NO_x reductions are predicted to be much less than the SO_2 reductions (Metro Vancouver, 2007). These new regulations will require monitoring to verify effectiveness of the new standards. Monitoring of marine emissions in plumes has been reported by satellite remote sensing (Richter et al., 2004), interception by aircraft (Sinha et al., 2003), interception by ships (Williams et al., 2009; Lack et al., 2009) and passive detection at coastal sites (Lu et al., 2006). Pollutant emissions can be characterized by power, distance or fuel-based emission factors combined with activity data. Fuel-based emission factors can be measured in plumes through simultaneous measurement of the pollutant and carbon-based emissions of CO_2, CO, VOC, etc. (Sinha et al., 2003; Williams et al., 2009), if the fuel carbon content is known. The relative emission rate of pollutants can be determined by the ratio of plume pollutants. In particular, due to future regulations regarding NO_x and SO_2, we focus on the relative emission of NO_x and SO_2 through NO_2/SO_2 ratio measurements in plumes under nocturnal conditions. We report passive detection of marine vessel plumes on Saturna Island in proximity to major shipping activity in the Strait of Georgia. Using Differential Optical Absorption Spectroscopy (DOAS), we measured NO_2, SO_2, and O_3. The NO_2/SO_2 ratios are compared to the NO_x/SO_2 emission

ratios predicted in recent emission inventories in the Lower Fraser Valley (LFV) region.

2. Experimental

The site details, measurements of NO_2, SO_2 and O_3 by DOAS, and meteorological observations have been described in detail elsewhere (Wojtal et al., 2011; McLaren et al., 2010). Instrumentation was located at the eastern tip of Saturna Island. The LFV region is impacted by anthropogenic sources from the cities of Vancouver, Victoria, Bellingham and Seattle. Marine vessels arriving and departing from ports in Vancouver pass around the tip of Saturna Island at a distance of 2–3 km, on their way to and from the Pacific Ocean. The DOAS system was used for nocturnal measurements (6 pm–8 am PDT) during the period July 24-Aug 09, 2005. For two days, Environment Canada's instrumented mobile vehicle (CRUISER) was located at East Point within 100 m of the DOAS telescope. CRUISER houses high-sensitivity gas and particle analyzers including a SO_2 monitor (Thermo Scientific 43TLE), and a chemiluminescence NO detector (Thermo Scientific 42C) retrofit with a NO_2 photolytic converter (Droplet Measurement Technologies BLC 24). CRUISER operated on diesel generator while at East Point, which self-contaminates the on-board measurements at times. Using measurements of NO and black carbon, the CRUISER data was filtered, removing periods of contamination. A contamination free period of 5 h on the night of Aug 6/7 (9:30 pm–2:30 am) was used to intercompare the DOAS and CRUISER measurements of NO_2 and SO_2. The CRUISER/DOAS mixing ratio comparisons were $103 \pm 21\%$ (95% CI, $R^2 = 0.87$) for NO_2 and $121 \pm 29\%$ (95% CI, $R^2 = 0.83$) for SO_2, indicating reasonable agreement between the two methods. From this, we estimate a standard uncertainty in our measured NO_2/SO_2 ratios of $\pm 13\%$ with a 95% uncertainty interval of $\pm 31\%$.

3. Results and discussion

3.1. Study wide observations of NO_2 and SO_2

The temporal behavior of NO_2 and SO_2 throughout the study was shown elsewhere (Wojtal et al., 2011). A linear regression of all NO_2 and SO_2 measurements (Fig. 1) has a slope of 2.87 ± 0.07. The figure also includes lines indicating molar emission ratios of NO_x and SO_2 taken from inventories in the region. The 2005 annual emissions inventory for the LFV (Metro Vancouver, 2007) indicated that marine emissions of NO_x and SO_2 were 7334 tonnes (NO_2 equivalent) and 3829 tonnes respectively ($NO_2/SO_2 = 2.66$ mol mol^{-1}) in the Canadian domain; and 8375 and 4867 tonnes respectively ($NO_2/SO_2 = 2.39$ mol mol^{-1}) in the total domain (Canadian + USA LFV). Of relevance to marine vessel plumes are "underway" emissions for major ocean going vessels. A detailed marine emissions inventory for 2005/06 (Chamber of Shipping, 2007) indicated that "underway" (full cruise or sea speed) NO_2/SO_2 molar emissions ratio was 2.04 for ocean going vessels in LFV waters and 2.12 for those in BC waters, both relevant to our observations. Marine sources are responsible for a substantial 14% and 47% of the total anthropogenic NO_x and SO_2 emissions respectively in the LFV (Metro Vancouver, 2007), with these emissions spatially concentrated in the western side of the domain that includes the Strait of Georgia. The total anthropogenic emissions from non-marine sources in the LFV is 52,591 and 5435 tonnes ($NO_2/SO_2 = 13.5$ mol mol^{-1}), a ratio much higher than those for marine sources. The closeness of the observed regression ratio (2.87) to the marine inventory NO_x/SO_2 ratio (2.39–2.66) supports a general conclusion that the Saturna Island site is heavily impacted by marine vessel emissions of NO_x and SO_2.
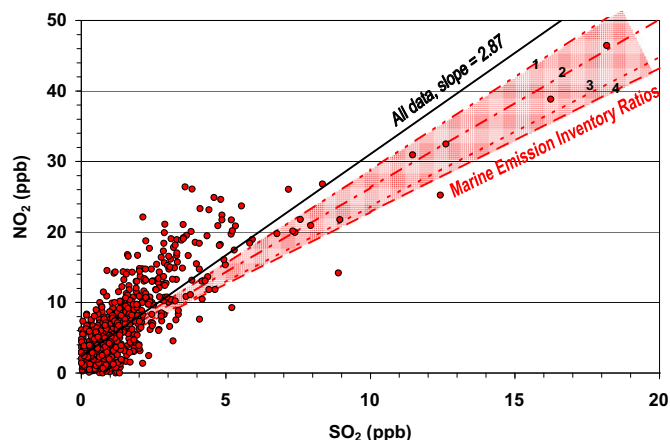

Fig. 1. Observations of NO_2 and SO_2 at Saturna island. Linear regression: $NO_2 = 2.87(\pm 0.07) \times SO_2 + 2.37(\pm 0.17)$ $R^2 = 0.68$. 2005 Emissions inventory molar NO_2/SO_2 ratios for marine vessels in: 1. Canadian LFV − 2.64, 2. Total LFV -2.39, and ocean going vessel underway emission ratios for: 3. British Columbia - 2.12, 4. LFV − 2.04.

3.2. Marine vessel plumes

Major ocean going vessels (bulk vessels, container ships, military ships, tankers, etc.) passing Saturna Island were frequently visible during the study, as were their plumes that impacted the site on occasion. In particular, when winds were from the SSW, plumes from ships traveling along a line south of the site impacted the site for a period of 30–60 min during the ships passage down the Strait. These impact periods were most commonly experienced in early evening. As there are few other major SO_2 emitters close to Saturna Island, the plumes were easy to identify. Frequently, several major vessels were observed in the channel at the same time. For this reason, the plumes were not attributed to individual ships; our intent here is to look at a survey of many ships in the region.

In order to characterize the NO_2/SO_2 ratio from these sources, 17 plume events were identified, typically with maximum $NO_2 > 10$ ppb. The timing and conditions associated with each plume are given in Table 1. For comparison, the NO_2/SO_2 ratios were determined using two related methods, illustrated in Fig. 2. In the first method, the NO_2/SO_2 ratio is calculated via the integrated excess pollutants (ΔX) during the plume event, with suitable background subtraction (Fig. 2A):

$$\frac{NO_2}{SO_2} = \frac{\int \Delta NO_2 dt}{\int \Delta SO_2 dt} \tag{1}$$

A baseline is manually identified for each event; the standard uncertainties in the ratios (Table 1) were calculated through propagation of uncertainties in the plume and baseline points resulting from the DOAS retrieval. The second method involves a two-sided linear least squares regression of NO_2 to SO_2 using all points within the plume event including suitable baseline points (Fig. 2B). This second method is similar to that used for the determination of emission factors in ship plume events (Williams et al., 2009). The two methods are conceptually identical, retrieving the molar ratio of NO_2 to SO_2 above a background level of NO_2 and SO_2 during each plume event. The first method is more subjective as baseline points must be identified on each side of the event, whereas the second method intrinsically accounts for the relative baselines through statistical regression including an intercept. As Table 1 shows, the separate means and medians of NO_2/SO_2 ratios for all 17 plumes are not statistically different using the two

Table 1
Observations of trace gases (ppb) and molar NO_2/SO_2 ratios (ppb ppb^{-1}) in ship plumes.

#	Date/Time	WD (deg)	WS (km/h)	Max NO_2	Max SO_2	Avg O_3	Integrated NO_2/SO_2	Regression NO_2/SO_2	N	R^2
1	Jul 24 − 21:09	205	5	46.5	18.2	12.8	2.72 ± 0.15	2.26 ± 0.16	16	0.88
2	Jul 25 − 21:29	170	7	26.8	12.4	20.9	2.69 ± 0.43	2.20 ± 0.33	6	0.85
3	Jul 28 − 21:49	205	23	10.5	3.4	68.5	2.22 ± 0.65	2.44 ± 0.60	6	0.68
4	Jul 29 − 02:08	220	17	13.0	1.9	61.9	5.59 ± 3.47	6.06 ± 0.53	9	0.90
5	Jul 29 − 04:32	225	16	11.6	2.5	58.4	4.18 ± 1.01	4.68 ± 0.58	12	0.77
6	Jul 29 − 05:37	220	17	17.0	3.3	37.5	4.52 ± 0.93	4.77 ± 0.83	5	0.85
7	Jul 29 − 21:12	205	13	26.0	7.2	26.1	2.96 ± 0.52	2.75 ± 0.33	7	0.87
8	Jul 29 − 23:17	220	18	14.3	2.7	26.4	3.49 ± 1.30	3.71 ± 0.58	6	0.84
9	Jul 30 − 00:30	210	26	9.6	1.6	22.9	2.68 ± 2.84	3.20 ± 0.27	5	0.96
10	Jul 30 − 01:54	220	23	13.4	4.2	24.7	2.13 ± 0.51	2.64 ± 0.54	6	0.76
11	Jul 30 − 22:12	220	19	13.1	4.3	17.2	2.42 ± 0.96	2.44 ± 0.42	7	0.77
12	Jul 31 − 01:25	220	19	17.4	8.9	21.2	2.42 ± 0.39	1.42 ± 0.36	9	0.54
13	Jul 31 − 02:28	220	20	13.7	2.9	20.0	3.53 ± 1.37	3.78 ± 0.82	5	0.78
14	Jul 31 − 03:04	210	19	11.1	3.8	19.2	0.77 ± 0.36	1.59 ± 0.53	6	0.55
15	Jul 31 − 04:55	230	19	10.7	2.9	20.7	2.64 ± 1.08	2.96 ± 0.35	10	0.82
16	Aug 1 − 23:59	220	12	14.9	3.5	41.6	5.64 ± 1.84	4.39 ± 0.36	11	0.89
17	Aug 9 − 05:24	220	15	13.0	2.5	23.9	3.24 ± 1.72	4.70 ± 0.40	10	0.90
Mean ± confidence interval (95%)							3.14 ± 0.63	3.29 ± 0.66		
Medians							2.72	2.96		
Combined Mean ± confidence interval (95%)							3.22 ± 0.43			
Combined Median							2.86			

methods, hence we also present combined mean and median results. The molar NO_2/SO_2 ratios fall in the range of 1.5−5.6 (5th−95th percentiles) for the 17 plume events.

A brief discussion of the assumptions made is warranted before we compare the observed NO_2/SO_2 ratios with inventory NO_x/SO_2
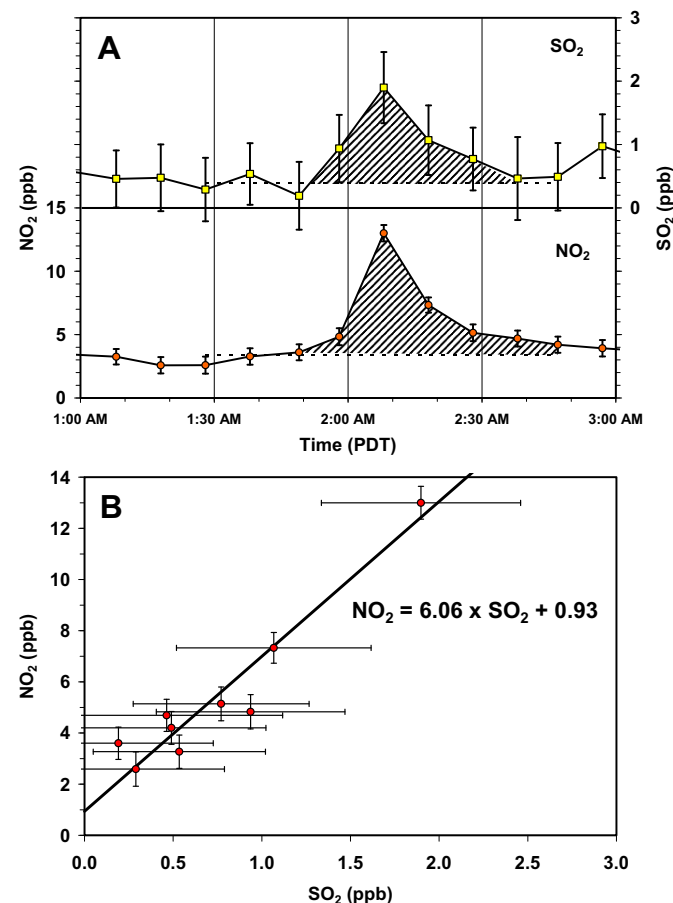

Fig. 2. Marine vessel plume # 4 showing the (A) integrated method and (B) linear regression method for determination of NO_2/SO_2 ratios.

ratios. First, we assume that all NO_x in the ship plumes is quantitatively converted to NO_2 after emission. Our justification is that despite NO_x emissions being dominated by NO (>90%), reaction of NO with O_3 to produce NO_2 is a fast reaction with rate constant of 1.80×10^{-14} cm^3 molec^{-1} s^{-1} (Atkinson et al., 2004). At background levels of O_3 in the MBL (30 ppb), the lifetime of NO due to this reaction is 76 s at 298 K. NO is quantitatively (>99%) converted to NO_2 in 4−6 min at this rate, provided that O_3 remains in excess and photolysis of NO_2 is absent. For all 17 plumes, the O_3 measured by DOAS during the plume events (Table 1) was in the 10−70 ppb range, indicating that O_3 remained in excess within the diluted plumes. The closest approach of vessels to the site is ∼2 km directly east indicating a minimum transport time of 6 min at a wind speed of 20 km h^{-1}. We estimate a plume transport time of 10−30 min with winds from the SSW. We also assume that losses of NO_2 and SO_2 in the plumes during the transit time to the site is small, justified as follows. Since the plumes were detected either at twilight or in the dark, losses of NO_2 due to photolysis are negligible, as are losses of SO_2 due to reaction with OH. Other potential losses of NO_2 include conversion to NO_3, N_2O_5 and subsequently HNO_3 at night (McLaren et al., 2010), as well as heterogeneous conversion of NO_2 to HONO on the aqueous surface of the ocean (Wojtal et al., 2011). Using a NO_x lifetime of 3.7 h measured in ship plumes (Beirle et al., 2004) and 10−30 min transport time, there is potential loss of 4−13% NO_2. The potential for these processes to bias the NO_2/SO_2 ratios would be negated by heterogeneous loss of SO_2 to form particle sulfate with equivalent lifetimes. Thus, we estimate the maximum error in our measured NO_2/SO_2 ratios due to such loss processes is <10%.

A pooling of observations (Table 1) from both measurement methods indicates that the 95% confidence interval of the mean NO_2/SO_2 ratio for these 17 plume events is 3.22 ± 0.43 ppb ppb^{-1}. To avoid bias by a few high ratio observations, the median molar NO_2/SO_2 ratio of 2.86 is preferred for comparison to the inventories. The 2005 inventory discussed previously indicated a molar NO_x/SO_2 emissions ratio of 2.39−2.66 for all marine emissions and an underway emissions ratio of 2.04−2.12 for ocean going vessels. The median observed NO_2/SO_2 ratio is 35−40% higher than the underway inventory value, the most suitable comparison. This could indicate that the inventory is too low in NO_x or too high in SO_2 emissions. However, it is also valid to point out that our survey includes just 17 marine vessel plumes, which may not be comprehensive enough to make definitive

conclusions concerning the annual emissions inventory methodologies. In particular, we note a high variability in the molar NO_2/SO_2 ratios (1.5–5.6), which can arise from different engine types, engine speeds, engine loads and fuel composition. The variability in reported fuel sulfur content alone (Chamber of Shipping, 2007), could account for the majority of the variability in NO_2/SO_2 ratios. Thus, we conclude that the 35–40% difference in the observation and inventory ratios is not unreasonable. We cannot make conclusions regarding the absolute magnitude of the inventory emissions. The relatively low NO_2/SO_2 ratios in both observations and inventories are a direct result of the high sulfur content of marine fuel used in the region. A 2005 survey of marine fuels in the LFV, central in the marine inventory methodology, found that the average sulfur content of heavy fuel oils (bunker fuel), distillate fuel oils and marine gas oils were 2.55%, 0.59% and 0.60% respectively, with the heavy fuel oil accounting for 85% of the volume of fuel used in the inventory region (Chamber of Shipping, 2007).

4. Conclusions

Nocturnal measurements in the MBL on Saturna Island indicated that NO_2 was correlated with SO_2 with a molar slope of 2.87 ± 0.07, just 20% higher than the 2005 emissions inventory ratio for marine vessels operating in the Lower Fraser Valley domain. Our survey of marine vessel plumes indicated a median molar NO_2/SO_2 ratio of 2.86, about 35–40% higher than indicated in the emissions inventory for underway emissions of major ocean going vessels. Due to the limited number of plumes, we conclude the differences are not unreasonable. It is expected that SO_2 emissions will be reduced more than NO_x emissions, and that the NO_2/SO_2 ratios will increase significantly in future years due to incoming ECA regulations. These changes could be monitored using the techniques identified in this study, or through measurement of emission factors and fuel sulfur content with the addition of CO_2 and CO detectors at the site. Future studies aimed at verifying these trends are recommended.

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