THE EFFECT OF SEA SALT ON AEROSOL CONCENTRATION AND COMPOSITION: A CASE STUDY IN THE LOWER FRASER VALLEY

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1. INTRODUCTION

In the marine boundary layer and coastal regions, sea salt aerosols regulate the atmospheric cycle of other biogenic or anthropogenic species such as sulfate, nitrate, mercury and ozone. In addition, sea salt aerosols affect visibility and alter cloud properties. Therefore, adequate representation of sea salt aerosols in air quality models is crucial for coastal regions. Recently, USEPA has developed a sea salt module as an integral part of the Models-3/CMAQ system (USEPA, 2006).

The purpose of this study is to investigate the effect of sea salt on atmospheric aerosol concentrations and compositions. The Pacific 2001 period, from August 9 to August 21, 2001, in the Lower Fraser Valley (LFV) was simulated using CMAQ 4.5.1. Specifically the model simulations are to address two questions: (1) Does CMAQ with the sea salt module perform well when compared to observational sea salt data? and (2) Does the CMAQ sea salt module affect the performance of other aerosol components of CMAQ? If so, will those effects be more pronounced along the coastal region, or, under certain atmospheric conditios, more pronounced further inland? Some preliminary results are presented in this paper.

2. MODELING SYSTEM AND MODEL SET UP

The Pacific 2001 period, from August 9 to August 21, 2001, in the Lower Fraser Valley region, including the Strait of Georgia, British Columbia, Canada, was simulated using CMAQ 4.5.1 with the sea salt module enabled (hereafter simply referred to as 'with sea salt'). For comparison, another simulation was also conducted with identical conditions but without the sea salt module (hereafter referred to as 'without sea salt'). A nested modeling domain was used in this study. The outer domain consists of a 33 × 55 grid with 12 km resolution, and the inner domain consists of a 45 × 42 grid with 4 km resolution, as shown in Figure 1. There are 15 vertical layers and the full-layer heights above the ground for layers 1 to 6 are approximately 40, 130, 230, 380, 600 and 1000 m, respectively. The emissions used in this study were (1) 2000 inventory for the Greater Vancouver Regional Districts (GVRD) and the Fraser Valley Regional Districts (FVRD), (2)1995 Canadian emissions in the domain except for GVRD and FVRD, and (3) 1999 US emissions in the domain, all three projected to 2001, except for 2001 US mobile emissions (Smyth et al., 2006).

The OCEANfile, which was used to generate sea salt emissions in CMAQ, was created employing land use data in the MM5 output. The sea salt emissions from the ocean were calculated in CMAQ as a function of wind speed and relative humidity (USEPA, 2006). Before they are internally mixed with other aerosol species, sea salt emissions are speciated into Na^+, Cl^-, and SO_4^{2-} with factors of 0.3856, 0.5389, and 0.0755, respectively based on sea salt dry mass. These three species are distributed by size to the accumulation (J) and coarse (K) modes (USEPA, 2006), i.e., ANAJ, ANAK, ACLJ, ACLK, ASO4J, and ASO4K. It is noted that all these species, except for ASO4J, are solely from sea salt.

Measurements of chloride (Cl^-) and sodium (Na^+) concentrations were available during the simulation period at three monitoring sites. At Langley Ecole Lochiel (LEL), Slocan Park (SP), and Sumas Eagle Ridge (SER), Cl^- and Na^+ in $PM_{2.5}$ were measured using 4-hour averages

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during the day and an 8-hour average overnight, i.e. 6:00-10:00, 10:00-14:00, 14:00-18:00, 18:00-22:00, and 22:00-6:00 in PDT. In addition, at LEL and SP, Cl^- and Na^+ in all 12 size bins were also reported as twice daily ten-hour averages, i.e. 09:00-19:00 and 21:00-07:00 in PDT. The simulation results were averaged in the same manner as mentioned above. The mass concentration measurements of of $PM_{2.5}$ were available at LEL, SP, T12, T20, and T31 while its major inorganic aerosol components, including sulfate (ASO4), ammonium (ANH4), and nitrate (ANO3), were available at LEL and SP. The processed measurements at these five sites by Smyth et al. (2006) were used in this study.

The simulated total PM is a summation of all aerosol species in Aitken (I), J, and K modes in CMAQ, except for water. The simulated $PM_{2.5}$ concentration without water was calculated in CMAQ following the scheme of Jiang et al (2006).

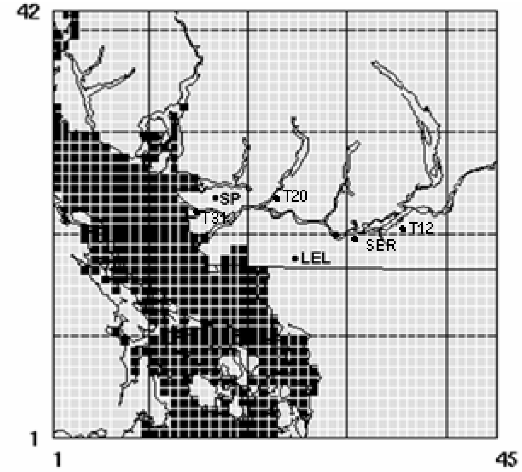

Figure 1. The inner simulation domain with measurement sites, black grids representing the open sea water area in the OCEANfile.

3. RESULTS AND DISCUSSION

3.1 Sea Salt Emission

Hourly sea salt emissions were obtained from the diagnostic sea salt emission file in CMAQ output. Figure 2a shows the time-averaged total sea salt (TSS) emissions during the simulation period. As shown in the figure, the emissions are stronger in the centers of the northern and southern ends of the Strait of Georgia. Figure 2b depicts emissions at 7:00 am August 10, 2001 (PDT) when high sea salt emissions of 7-8 kg/hour/grid were predicted.

The sea salt mass is a summation of six species, i.e. ANAJ, ACLJ, ASO4J, ANAK, ACLK, and ASO4K. Note that ASO4J here is only from sea salt. The emitted amounts of total sea salt and all six species exhibited diurnal variations with the maximum occurring mostly at early morning hours (not shown here). More than 90% of the sea salt mass was in the coarse mode ANAK and ACLK. The mass of ANAJ, ACLJ, ASO4J, and ASO4K accounted for 0.4%, 0.6%, 0.08%, and 7.5% in sea salt mass, respectively.

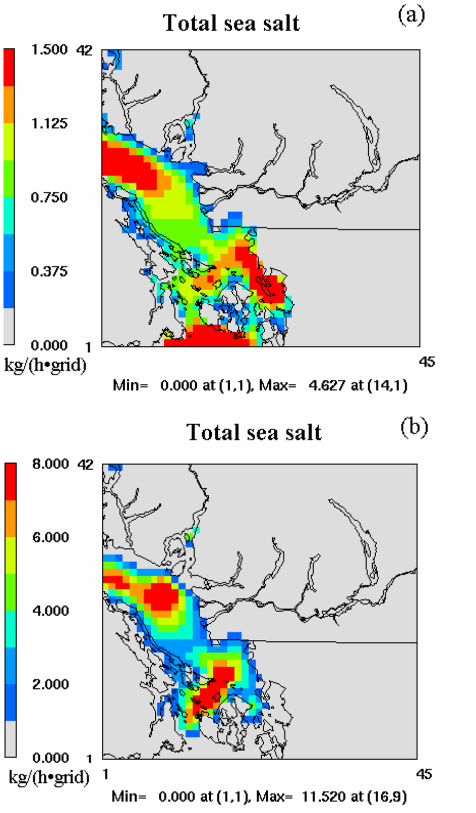

Figure 2. (a) Time-averaged TSS emissions during the simulation period, (b) TSS emissions at 7:00am August 10, 2001 (PDT).

3.2 Spatial Distribution of Sea Salt

The average sea salt concentration over the Strait of Georgia during the simulation period was 1.0 μg/m^3. Figure 3 shows the distribution of sea salt represented by the concentration isosurface of 0.2 μg/m^3, which is 20% of the base value of 1.0 μg/m^3, under strong vertical mixing (Fig 3a), and strong advection conditions (Fig 3b), respectively. Sea salt aerosol can be transported up to 950 m vertically (Fig 3a), i.e. within the sixth model layer at 7:00 am August 16 (PDT), and transported horizontally beyond the southern and eastern boundaries of the domain (Fig 3b) at 4:00 am August 17 (PDT). Figure 4 shows the isosurface of

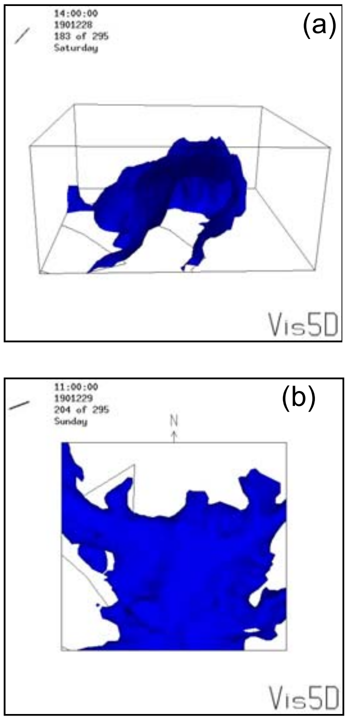

Figure 3. The distribution of sea salt aerosol, represented by the concentration isosurface of 0.2 µg/m^3 under (a) strong vertical mixing conditions, and (b) strong horizontal advection conditions. The vertical extension of the display box is approximately 1600 m.

0.2 µg/m^3 for time-averaged sea salt concentrations, when wind direction was southwest (hereafter referred to as on-shore winds). There were 166 hours of on-shore winds during the simulation period. Considering time-averaged values with on-shore winds, the sea salt aerosol concentration decreased by approximately 80% over areas 20 km inland from those over coastal areas and at heights of 450 m (i.e. within the fifth model layer) from those at the surface.

3.3 Effect of Sea Salt Module on Modeled PM$_{2.5}$ and Total PM

The relative change of concentrations, i.e. ($C_{\text{with seasalt}} - C_{\text{without seasalt}}$)/ $C_{\text{without seasalt}}$ *100%, was calculated to analyze the effect of sea salt on mass concentrations of PM$_{2.5}$ and total PM. Here, $C_{\text{with seasalt}}$ is the concentration of PM$_{2.5}$ or total PM with sea salt, and $C_{\text{without seasalt}}$ is the concentration of PM$_{2.5}$ or total PM without sea salt. Figure 5a shows the time-averaged relative change of PM$_{2.5}$ with on-shore winds. Compared to the simulation result without sea salt, the time-averaged PM$_{2.5}$ concentration increased by less than 1.7% over the Strait and the surrounding areas due to sea salt addition, and decreased further inland likely due to chemical reactions associated with sea salt. The detailed chemistry in both gaseous and aerosol phases is under investigation and will be reported in another paper.

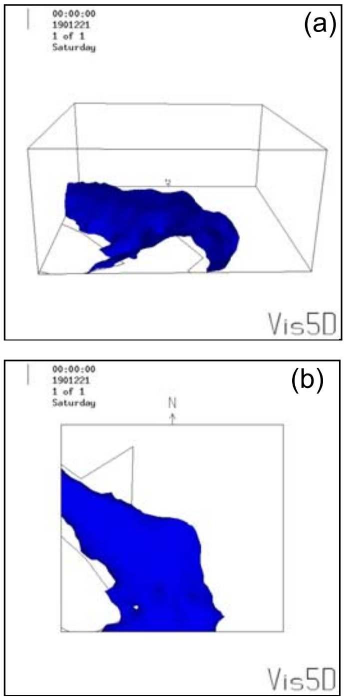

Figure 4. Time-averaged distribution of sea salt aerosol with on-shore winds, represented by the isosurface of 0.2 µg/m^3 of time-averaged concentrations, in (a) vertical and (b) horizontal directions. The vertical extension of the display box is approximately 1600 m.

Figure 5b shows the relative change at 1:00 am August 17, 2001 (PDT), when high values of relative change were predicted over the Strait and the coastal regions. The relative change of PM$_{2.5}$ shown in Figure 5b exhibits a similar pattern as in Figure 5a. While PM$_{2.5}$ increased over the Strait and the surrounding areas, the concentrations decreased in some inland grid by as much as 6%.

Figure 6a shows the time-averaged relative change of total PM with on-shore winds. The concentration of total PM increased at nearly all grids. The time-averaged total PM increased mostly by 8-10% over the Strait and the concentration increased less in the costal regions and further inland. The relatively large increase in total PM was mainly due to the addition of ANAK and ACLK, which accounted for >90% of sea salt mass. In contrast, relatively smaller changes were observed in PM$_{2.5}$, since sea salt components in J mode, i.e. ANAJ, ACLJ, and ASO4J, accounted for <2% of sea salt mass.

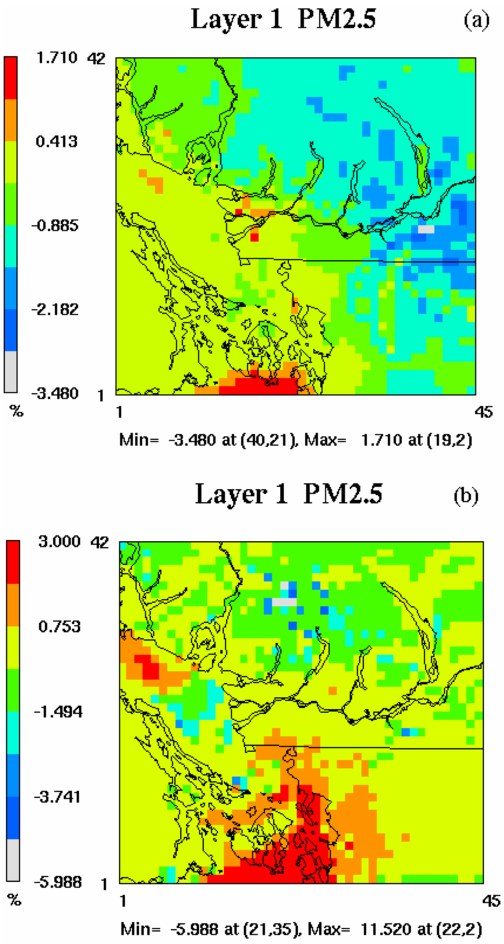

Figure 5. (a)Time-averaged relative change of $PM_{2.5}$ with on-shore winds, and (b) relative change at 1:00 am August 17, 2001 (PDT) in the surface layer (0-40m).

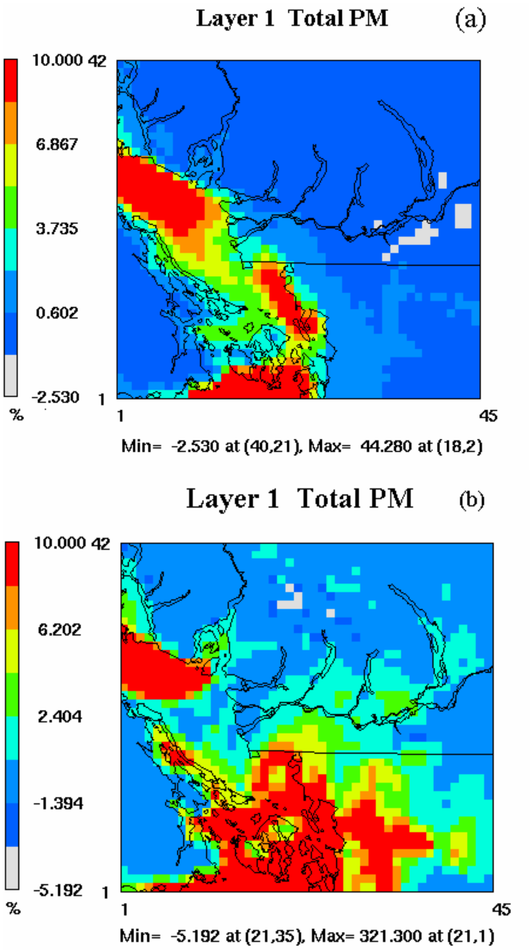

Figure 6. (a) Time-averaged relative change of total PM with on-shore winds, and (b) relative change of total PM at 1:00 am August 17 (PDT), in the surface layer (0-40m).

Figure 6b shows the relative change in total PM at 1:00 am August 17, 2001 (PDT), when high values of relative change were predicted over the Strait and surrounding areas. The overall spatial pattern is similar to that in Figure 6a. However, the area with relatively higher increases, at the southern end of the Strait, was larger.

3.4 Model Performance Evaluation

3.4.1 Sea salt concentrations

Figure 7 shows the model-measurement comparison of Cl^- and Na^+ at SP. It shows similar time variation patterns most of the time between modeled and observed Cl^- and Na^+ in total PM. However, the model was not able to reproduce the peak concentrations for Cl^- and Na^+ in both $PM_{2.5}$ and total PM, especially for Na^+. Table 1 lists the measured and modeled means, correlation coefficient (r), mean bias (MB), normalized mean bias (NMB), mean error (ME), and normalized mean error (NME) at LEL, SP, and SER. Except for 4-hour Cl^- in $PM_{2.5}$ at LEL, the modeled means were lower than measured means for Cl^- and Na^+ (especially for Na^+), indicating model under-prediction. The r values are in the range of 0.19-0.73, except for 12-hour Na^+ in total PM at LEL and SP as well as 4-hour Na^+ in $PM_{2.5}$ at SER (<0.1), indicating a positive but generally low to moderate correlation. The mostly negative values of MB and NMB also indicate model under-prediction. The NME values are greater than 50% for all the compared quantities. We suspect that the model under-prediction is primarily due to the omission of fine and ultra-fine surf zone sea salt emissions in the current CMAQ. However, the observed data also need to be analyzed further considering possible measurement uncertainties.

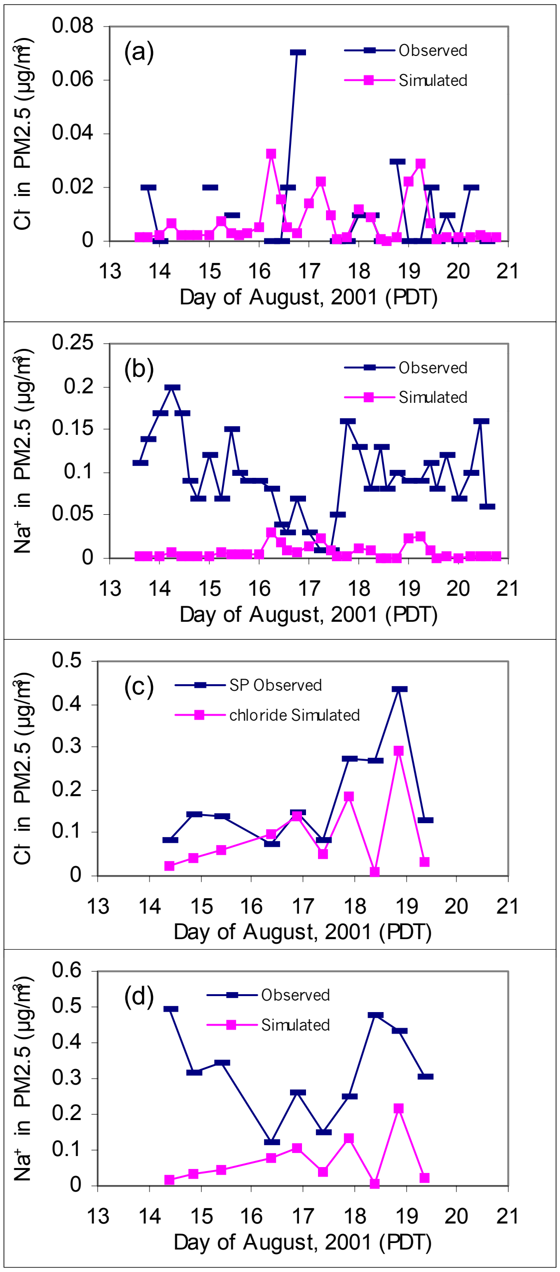

Figure 7.Comparison of simulations with observations at SP: (a) 4-hour Cl$^-$ in PM$_{2.5}$, (b) 4-hour Na$^+$ in PM$_{2.5}$, (c) 12-hour Cl$^-$ in total PM, and (d) 12-hour Na$^+$ in total PM.

3.4.2 PM$_{2.5}$ and its major inorganic species

Table 2 lists the performance statistics for concentrations of PM$_{2.5}$ and its major inorganic species, with and without sea salt, all sites combined. The concentrations of ASO4, ANH4, ANO3 and PM$_{2.5}$ were overestimated across the domain, which is similar to results shown in Smyth et al. (2006). For all four statistics used here, i.e. MB, NMB, ME, and NME, the lower the absolute value, the better the model performance. Compared to the simulation results without sea salt, all four statistics decreased slightly for concentrations of ASO4, ANH4, ANO3 and PM$_{2.5}$, after sea salt addition. Overall, it appeared that the addition of sea salt in the current CMAQ version improved the model performance slightly in the Lower Fraser Valley. However, the improvements were small and may not be significant. Nevertheless, the changes that result from enabling the sea salt module are in the right direction. The addition of fine and ultra-fine sea salt emissions from surf zone might result in more Na$^+$ and Cl$^-$ available in the model for chemical reactions, which could further improve model performance.

4. SUMMARY AND CONCLUSION

In the Lower Fraser Valley, the emissions of sea salt exhibited diurnal variations with higher values during early morning hours. The sea salt emissions were stronger in the centers of the northern and southern ends of the Strait of Georgia. On average with on-shore winds, the sea salt aerosol concentration decreased by approximately 80% over areas 20 km inland from those over coastal areas and at heights of 450 m (i.e. within the fifth model layer) from those at the surface.

The simulation results showed that the addition of sea salt leads to a higher relative change in total PM concentrations than in PM$_{2.5}$. However, the impact mechanism is different. Total PM concentrations increased at nearly all grids mainly due to the addition of coarse mode sea salt, i.e. ANAK and ACLK, which accounted for more than 90% of the sea salt mass. For PM$_{2.5}$, the concentration increased slightly over the Strait of Georgia and surrounding areas, and decreased further inland. The effects were primarily through chemical reactions associated with sea salt, which demands further investigation.

The model largely captured the time variations of Cl$^-$ and Na$^+$ in PM, but under predicted. Our results suggest the need to consider fine and ultra-fine sea salt emissions from the surf zone. Furthermore, our statistical analysis suggested that the addition of the sea salt module slightly improved the performance of the current version of CMAQ when it was used to simulate the Pacific 2001 period in the Lower Fraser Valley.

Table 1. Model performance statistics for aerosol Cl^- and Na^+

Site	Species	No	Measured mean ($\mu g/m^3$)	Modeled mean ($\mu g/m^3$)	r	MB ($\mu g/m^3$)	NMB (%)	ME ($\mu g/m^3$)	NME (%)
LEL	4-hour Cl^- in $PM_{2.5}$	8	7.5×10^{-3}	7.7×10^{-3}	0.53	<0.001	2.9	0.010	135.3
	4-hour Na^+ in $PM_{2.5}$	28	6.0×10^{-2}	3.5×10^{-5}	0.20	-0.046	-82.6	0.049	89.3
	12-hour Cl^- in total PM	12	1.8×10^{-1}	1.0×10^{-1}	0.29	-0.080	-44.1	0.122	67.8
	12-hour Na^+ in total PM	12	2.3×10^{-1}	7.0×10^{-2}	0.02	-0.155	-67.4	0.179	77.8
SP	4-hour Cl^- in $PM_{2.5}$	22	1.1×10^{-2}	7.1×10^{-3}	0.26	-0.004	-35.2	0.014	126.6
	4-hour Na^+ in $PM_{2.5}$	36	9.0×10^{-2}	4.0×10^{-5}	0.36	-0.089	-92.5	0.089	93.3
	12-hour Cl^- in total PM	10	1.8×10^{-1}	9.0×10^{-2}	0.73	-0.085	-47.7	0.089	50.4
	12-hour Na^+ in total PM	10	3.2×10^{-1}	7.0×10^{-2}	0.07	-0.246	-77.9	0.246	77.9
SER	4-hour Cl^- in $PM_{2.5}$	13	7.7×10^{-3}	5.6×10^{-3}	0.19	-0.002	-27.3	0.010	124.9
	4-hour Na^+ in $PM_{2.5}$	22	5.8×10^{-2}	4.2×10^{-3}	0.09	-0.054	-92.7	0.054	92.7

Table 2. Model performance statistics for concentrations of $PM_{2.5}$ and its components, with (w) and without (w/o) sea salt

Species		No	Measured mean ($\mu g/m^3$)	Modeled mean ($\mu g/m^3$)	MB ($\mu g/m^3$)	NMB (%)	ME ($\mu g/m^3$)	NME (%)
$PM_{2.5}$	w/o	1122	12.03	19.76	7.72	64.2	12.42	103.2
	w			19.68	7.65	63.6	12.37	102.8
ASO_4	w/o	389	1.01	2.80	1.79	177.5	1.83	181.0
	w			2.79	1.78	176.9	1.82	180.5
ANH_4	w/o	65	0.52	2.51	1.99	383.3	2.00	385.7
	w			2.50	1.98	382.6	2.00	385.1
ANO_3	w/o	389	0.30	6.46	6.16	2087.4	6.20	2099.4
	w			6.42	6.12	2074.1	6.16	2086.9

5. REFERENCES

Jiang, W., Smyth, S., Giroux, E., Roth, H., and Yin, D.,2006: Differences between CMAQ fine mode particle and $PM_{2.5}$ concentrations and their impact on model performance evaluation in the Lower Fraser Valley. *Atmospheric Environment,* **40**, 4973-4985.

Smyth, S., Jiang, W., Yin, D., Roth, H., Giroux, E., 2006: Evaluation of CMAQ O_3 and $PM_{2.5}$ performance using Pacific 2001 measurement data. *Atmospheric Environment,* **40**, 2735-2749.

USEPA, 2006. New features of the 2005 release. http://www. cmascenter.org/help/ model_docs/cmaq/4.5.1/Science_Updates.pdf.

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