Author Comments
April 26, 2011

Much appreciation for the very generous and helpful *comments from Anonymous Referee #1*. Please see our replies below.

The paper is clearly written and complete, and minor revisions are recommended. One area requiring additional analysis is that only diel average values and uncertainties are generally presented, due to incomplete episodic data. It would be helpful if the authors could directly compare the variability and uncertainties in the SO2 and SO4 budgets for those times and sources/sinks where daily or hourly terms can be estimated. Even if incomplete, this would help put the uncertainties in perspective, and would help address how synoptic variability affects the relative importance of the sources and sinks presented.

We agree that a time-series of sources and sinks for SO_4^2 and SO_2 would be of additional value. However, in order to make our budget estimates, steady state was assumed on a ~monthly timescale and on a regional spatial scale. This allowed us to constrain the most uncertain terms, such as in-cloud oxidation of SO_2 to SO_4^2 and wet deposition of SO_4^2. On shorter timescales (e.g. daily), the stead state assumption is less likely to hold; advection, which we estimated to be insignificant on a long/larger scale, may become more important also. Thus we think such time-series budget calculations are not practical.

We could compute hourly or daily rates such as OH oxidation and entrainment with more certainty, and would be glad to provide those estimates to specific readers of interest on an individual basis rather than adding a section to this already length paper.

Specific comments:
page 2882, line 10: "Because the aircraft usually took off from Arica in the early morning, reached 80~85°W at around sunrise, and returned to shore in the afternoon, spatial and temporal biases are inherent." It may be helpful to discuss how these biases affect Figure 3 and other results.

The aircraft typically reached the westernmost location (80~85°W) by sunrise; before 0900 and after 1500, the aircraft was closer to the coast. As a result, aircraft measurements near the westernmost location represent values around sunrise only, whereas mean values at 75°W, for examples, are from the outbound (pre-dawn) and return flights (later morning to afternoon). Photochemistry during this period would most likely have reduced DMS and increased SO_2 concentration, etc. To minimize bias, we relied on shipboard measurements for diel cycles instead of aircraft observations, except for SO_2, which was only quantified on the aircraft. We also included only measurements west of 78°W for SO_2 in Fig. 13 to reduce the effect of longitudinal gradient.

page 2885, line 25: if the O3/SO2 increase after sunset is due to boundary layer recouping, what is the most likely source of the higher concentrations in the descending air? a) between LCL and top of the MBL b) cloud level c) free troposphere, entrained into MBL d) all of the above, to varying degrees
This will necessitate a more sophisticated calculation than Lilly (1968), but the available C-130 vertical profiles should support it. If quantified through observations, this would be an important finding in itself, and may have implications for other findings. How would you tell which layer was the source for SO2? For O3? Are they the same? Look at relative rates, and use the time series of observations to address the variability.

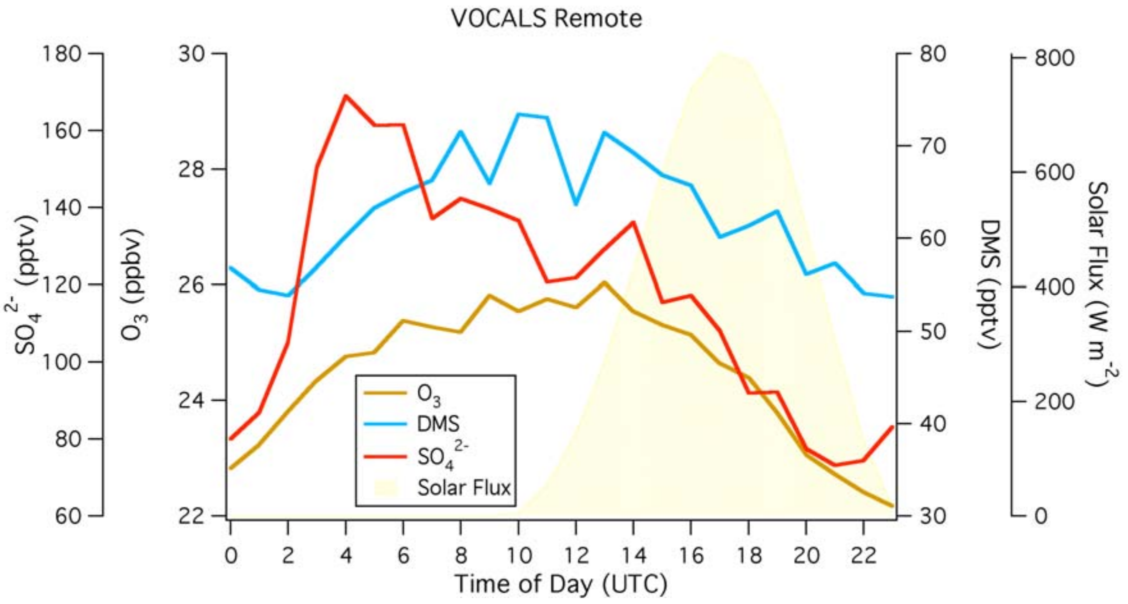
For O_3, the source of high concentration should be strictly the free troposphere, consistent with the observation from Allen et al. (2011) that elevated O_3 is almost always associated with low specific humidity and vice versa. Even during the decoupled afternoon, O_3 concentrations from aircraft profiles appear to be largely constant below the inversion.

For SO_4^{2-} (assuming that was what the reviewer meant, instead of SO_2), the source of high concentration is unlikely to be the free troposphere. At an entrainment velocity of 4~6 mm/sec, the free tropospheric (FT) SO_4^{2-} concentration would need to be 2~3 ppbv to cause the observed nighttime increase in SO_4^{2-} concentration, while aircraft measurements show typical FT SO_4^{2-} concentrations of 40~50 pptv. The region between the top of well-mixed layer and the cloud bottom also does not show high SO_4^{2-} concentration, judging from aircraft profiles during the decoupled afternoon. That leaves the cloud level to be the most logical source of high SO_4^{2-} concentration. The amount of SO_2 expected to be oxidized in cloud is qualitatively consistent with the amount SO_4^{2-} required to explain the observed nighttime increase in SO_4^{2-} concentration accounting for boundary layer decoupling/coupling. Moreover, measured bulk cloud water SO_4^{2-} concentration is on average about twice the MBL concentration.

The plot attached shows the average diel profiles for DMS, O_3, and SO_4^{2-} in the VOCALS remote region. The nighttime build up in DMS is due to continuous sea-to-air flux and no oxidative loss. While increases in both O_3 and SO_4^{2-} suggest higher concentrations above, their sources and the physical mechanisms involved are quite different, as implied by their distinct diel profiles. For O_3, the increase over the first four hours after sunset is about 2%/hr. Over the same time span, the increase in SO_4^{2-} is about four times faster. O_3 and DMS both decrease after sunrise due to photochemical reactions, whereas SO_4^{2-} decreases much sooner, probably as a result of wet removal by drizzle.

Minor comments:
page 2884, line 25: "The optical rain [gauge] detected"
page 2885, line 19: SI units: 11 knots = 5.66 m/s

Thank you for pointing out these errors.


VOCALS Remote
SO$_4^{2-}$ (pptv)
180
160
140
120
100
80
60
O$_3$ (ppbv)
30
28
26
24
22
DMS (pptv)
80
70
60
50
40
30
Solar Flux (W m^{-2})
800
600
400
200
0
0
2
4
6
8
10
12
14
16
18
20
22
Time of Day (UTC)
O$_3$
DMS
SO$_4^{2-}$
Solar Flux