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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Constraining the concentration of the hydroxyl radical in a stratocumulus-topped marine boundary layer from sea-to-air eddy covariance flux measurements of dimethylsulfide" *by* M. Yang et al.

I. Faloona

icfaloona@ucdavis.edu

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In this work the authors use measurements of DMS and its surface flux over a broad subtropical region and a 5 week interval to infer the average OH-equivalent DMS oxidant level in the stratocumulus topped marine boundary layer. The exact correspondence of their estimates to the expected OH in the specific geographical location and season remains somewhat dubious, and in my opinion hinders the ultimate strength of

the work.

Some general comments I would consider in revising the manuscript follow.

The work involves heavy averaging in space and time to derive vertical profiles and steady-state, diel DMS behavior over an area of $\sim$600,000 km2. The overbar in Equation (3) does not represent only a time-average, as the authors state, but a wide spatial average as well. The idea of such an average of the Eulerian derivative in Eq. (3) might be made more clear if a map of the "VOCALS region" and the locations of sampling were presented to the reader. For example, the authors decide to neglect mean advection in the budget because this wide area, long-term average DMS gradient is found to be perpendicular to the mean wind. But it's the gradient just upwind of the "VOCALS region" that might systematically present a contribution to the average DMS budget, and it is likely that such a strong, persistent gradient does indeed exist in the nearshore environment. A question like this that naturally arises in the reader's mind may be more tractable if a map of the region were made available with all the data collection points contained therein.

On p. 16275 (l. 23-25) the authors state that "With an average inversion height of 1.3 km in the VOCALS region, this [DMS] vertical gradient increased signifcantly with boundary layer depth." I do not see any physical reason why the DMS vertical gradient should be directly proportional to MBL depth. In fact, taking the vertical derivative of the decoupling relationship that the authors use indicates that the very opposite is true: viz., the vertical gradient of concentration, C(z), is inversely proportional to MBL depth, zi.

(Equation 1: Scalar Vertical Gradient)

Wood & Bretherton (2004) do in fact find that the magnitude of the lapse rate decreases with increasing zi (and that the decoupling parameter increases along with zi, a fact ignored in the present work.)

One particular concern in reading this was the circumvention of the strong diurnal modulation of the inversion height unique to these stratocumulus topped MBLs. The reason is that the shortwave heating of cloud top acts to stabilize the MBL and dramatically reduces TKE to drive entrainment (and promotes 'decoupling'). On the other hand, longwave cooling at cloud top during the night feeds the energetics of entrainment. That is why the DYCOMS-II results (Faloona et al, 2005) show we of about 1 mm/s for the daytime flight, and $\sim$ 6 mm/s for the night flights.

This effect can be clearly seen in Figure (6): the MBL top descends under subsidence during the day (because the entrainment is much weaker) and rises again after sunset (because of the additional source of TKE from cloud-top radiative cooling.) A rough estimate of the MBL growth after sunset (Fig. 6) shows that it rises about 200 m in about 6-7 hours - approximately 8 mm/s. This MBL growth rate is the net, in excess of subsidence, which is most likely of the same order. Likewise, the depression during the day appears at a similar rate ($\sim$200m/8hr). Thus, when estimating a mean, long-term entrainment by looking at an average nighttime budget, the large variability needs to be considered. In other words, it is highly unlikely that you would obtain an entrainment estimate from data throughout the night that would match the average over the entire diurnal cycle.

As for the comparison of the authors' OH estimate to the expected abundance, the use of OH observations from rural northeast Germany (Holland et al., 1998; Hofzumahaus et al., 1998) seems distinctly misguided (p. 16280). The referenced OH studies took place in mildly polluted continental regions where NOx levels were most likely much higher than in the MBL of the Humboldt Current upwelling system. And if the NOx levels were low (<25 pptv) during VOCALS as expected, then the steady state OH should be more proportional to the square root of the O3 photolysis frequency, rather than linearly dependent as the authors claim. The reason it was linear in the Holland et al. (1998) study was because of the moderately polluted NO_x levels. Intermediate relationships between J_O3 and OH are discussed in Berresheim et al. (2003). But this issue really

begs the nagging question of how much NOx was in the VOCALS region during these measurements. There is, in fact, no effort made to establish the photochemical setting of this experiment whatsoever, thus the 'accuracy' of the technique in estimating OH remains by and large unsubstantiated. Are there no CO, O3, or NOx observations from this experiment that could be used to slightly constrain the photochemical conditions? The works of Tan et al. (2001) and Olson et al. (2001) show that the sources and sinks of OH in the region are fairly simple.

Furthermore, the widespread climatologies of OH published by Davis et al. (2001) are not very representative of the stratocumulus topped MBLs which, judging from their high albedos, most likely reduce the surface actinic fluxes substantially (e.g., Mauldin et al., 2001; Lefer et al., 2003). The airborne data from all the NASA GTE programs are archived and available and would most likely yield specific HOx observations of much greater geographical and/or seasonal relevance to the VOCALS study.

Finally, the authors need to reconsider the meaning of 'zonal averages' used throughout. Typically I have found that a zonal average applies to variables that are averaged along lines of constant latitude and thus lose their dependence on longitude (e.g., Fig. 5).

Specific References:

Berresheim H, Plass-Dulmer C, Elste T, Mihalopoulos N, Rohrer F, OH in the coastal boundary layer of Crete during MINOS: Measurements and relationship with ozone photolysis, Atmospheric Chemistry And Physics, 3, 639-649, 2003.

Lefer BL, Shetter RE, Hall SR, Crawford JH, Olson JR , Impact of clouds and aerosols on photolysis frequencies and photochemistry during TRACE-P: 1. Analysis using radiative transfer and photochemical box models, Journal Of Geophysical Research-Atmospheres, 108 (D21), Article Number: 8821, 2003.

Olson JR, Crawford JH, Davis DD, Chen G, Avery MA, Barrick JDW, Sachse GW,

Vay SA, Sandholm ST, Tan D, Brune WH, Faloona IC, Heikes BG, Shetter RE, Lefer BL, Singh HB, Talbot RW, Blake DR, Seasonal differences in the photochemistry of the South Pacific: A comparison of observations and model results from PEM-Tropics A and B, Journal Of Geophysical Research-Atmospheres, 106 (D23), 32749-32766, 2001.

Tan, D., I. Faloona, J.B. Simpas, W. H. Brune, et al., OH and HO2 in the tropical pacific: Results from PEM-Tropics B, J. Geophys. Res., 106 (D23), 32,667-32,681, 2001.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 16267, 2009.

$$\frac{C(z)}{C(0)} = 1 - \alpha\left(\frac{z}{z_i}\right)$$

$$\Rightarrow \frac{\partial C}{\partial z} = -\frac{\alpha}{z_i}C(0)$$

Fig. 1. Equation 1: Scalar Vertical Gradient