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Comment

Interactive comment on “Investigating the sources and atmospheric processing of fine particles from Asia and the Northwestern United States measured during INTExB” by R. E. Peltier et al.

R. E. Peltier et al.

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We thank the reviewer for helpful comments in order to improve this manuscript. The reviewer's comments, and our responses, are listed below. We have attempted correct some of the formatting errors with the Cosis reviewer document to the best of our ability.

1) Much of the insoluble OC might be smaller than 0.1 μm – ; by <0.1 μm do you mean OC mixed with other components (e.g. sulphate, water soluble OC)? For example, could particles composed of insoluble OC mixed with sulphate that are combined larger than 0.1 μm but the insoluble OC component alone is <0.1 μm be detected? Is the threshold you have evaluated set by the activation point in the PILS, and were your tests done on pure WSOC, mixed or both?

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The PILS operates by dissolving particles in an ultra purified stream of deionized water. Thus, it does not matter if sampled aerosol is externally or internally mixed – the soluble portion of the aerosol will dissolve. The PILS also activates and then collects all particles greater than $\sim 10\text{nm}$. In the case of mixed insoluble OC-sulfate particle of (for example) 150 nm diameter, the entire particle will be collected by the PILS and the sulfate fraction is analyzed by ion chromatography. If the remaining insoluble fraction is greater than $\sim 0.1\mu\text{m}$, it will be delivered to the Sievers TOC analyzer, but not detected due to oxidation inefficiency of the analyzer itself. If the remaining insoluble OC fraction is less than $\sim 0.1\mu\text{m}$, it will be detected by the analyzer. However, small particles contribute very little mass in ambient conditions and, if detected, would be unlikely to substantially alter our results. While “water-soluble organic carbon” is operationally defined, we have published a number of studies describing the technique, including calibrations and field measurements (several of which are referenced in this manuscript).

Section 3.1

2) Is sufficient dissolution time such that all species that are even slightly soluble will be completely measured? For example, could some species of OC or some calcium compounds not be fully dissolved in the time allotted in the PILS?

The ionic compounds that we measure are typically highly soluble and present in the ambient atmosphere as salts (e.g. ammonium sulfate, sodium chloride, potassium nitrate). Thus, we believe that the residence time in the PILS transport water (at least 30 seconds) represents adequate dissolution time to measure these species. Water soluble organic carbon is somewhat more complicated as it is likely comprised of many compounds, each with a unique solubility in water. While WSOC dissolution time (approximately 10-15 seconds) prior to analysis is somewhat smaller than PILS-IC, we maintain that this measurement is operationally defined. To our knowledge, the online PILS-TOC system has not been tested for sensitivity to ambient aerosol dissolution time.

3) Your mean Asian sulphate seems lower than that discussed by van Donkelaar et al. (this issue). In particular, their (Fig 6) presentation of the C130 PILS data looks a little different than what I would estimate by combining your Figures 2b and 2d. Are they consistent?

We are unable to find the reference (van Donkelaar, et al) the reviewer is discussing.

4) North American nitrate is 7x's higher than Asian nitrate, but there are 10x's more Asian samples than nitrate samples. Is the NA nitrate just an anomaly?

The reviewer points out that North American nitrate is ~7 times higher than Asian nitrate, despite having significantly more 'Asia' measurements. The reviewer estimates this by comparing the mean concentration (NA = 0.07 ug/sm³, Asian = 0.01ug/sm³). This is probably an over interpretation because we have noted the observed concentrations are log-normally distributed. A better comparison figure would be the median (or geometric mean), as this indicates the typical concentrations were statistically identical.

5) Page 17440, lines 25-26 - The low correlation of sulphate and WSOC suggests different sources and atmospheric processing. I can imagine that varying amounts of SO₂ conversion could drive such a poor correlation. This would be one form of atmospheric processing, but I find it interesting that later on in discussing the North American aerosol you invoke atmospheric processing to explain your WSOC observations. So why does it occur over North America, but not over the North Pacific? In section 3.4, you refer to the short time constant for SOA formation. Is this the explanation?

The comparatively short time constant for SOA formation (~1 day, de Gouw et al, 2007) and sulfur oxidation (varies, but typically 3-4 days, Brock, et al, 2004 & 2007) is responsible for this lack of correlation. In the case of Asian pollution, we believe that SOA formation occurred relatively rapidly (e.g. within a day). Cloud scavenging and wet deposition then removed the newly-formed SOA (along with any primary aerosols).

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As the air mass was transported, SO₂ conversion continued to take place, resulting in depleted organic aerosol, and enhanced sulfate aerosol, as observed in our data. It is unlikely that the process is so simple, since clouds have also been shown to enhance SOA formation (e.g. Sorooshian, et al, JGR 2006 and ES&T 2007). In the case of North American pollution, the role of clouds was likely different in that it actually enhanced SOA formation, resulting in increased WSOC concentration, but that precipitation loss was minimal. In Asian air masses, cloud processing may have initially been responsible for enhanced SOA formation near Asia (or less than ~1 day downwind). But precipitation preferentially depleted the SOA itself and possibly the SOA precursors. SO₂ was not depleted to the same extent by the precipitation and could go on to form secondary aerosol (sulfate) which resulted in the observed ratios.

Section 3.2

6) When you refer to Asian air masses in terms of vertical profile data, is the air mass of Asian origin all the way from the surface to 6 km? That is, when you bin data in altitude blocks is each bin categorized by a trajectory?

The bin refers to the altitude in which the air mass was sampled by the C130 aircraft. The origin of each measurement is determined from flexpart. So the process involved segregating the measurements by origin of CO (based on flexpart), then for each group of data binning it by altitude and creating the alt profile.

Section 3.2.1

7) Lines 11-13, page 17442 – ; clarify ‘lost in transport’; – ; the reduction in OC was 10-20 times versus the reduction in CO of about 3 in CO. So do you mean that deposition (dry and wet) contributed significantly as well as dilution during transport?

Yes, we are saying that the decreases in observed concentration of aged Asia air masses are largely due to deposition (wet or dry) during transport. This is a ‘back

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of the envelope' calculation that compares CO, a relatively inert tracer of urban pollution, measured directly above Asia (during TRACE-P) with transported Asian CO observed near North American. If we assume CO emission rate in 2006 was approximately similar to the emission rate in Spring 2001, we can get a rough estimate of dilution by measuring CO after it had been transported across the Pacific Ocean. From this, we estimate that dilution accounts for $\sim 3\times$ decrease in concentration. Assuming dilution acts the same on aerosol as it does CO, this can not account for the 10-20 times lower concentration of organic aerosol during INTEx-B, compared to that measured during TRACE-P. In other words, if dilution were the only removal mechanism, we would expect to also see a ~ 3 times decrease in WSOC during INTEx-B.

8) Can the references to observations near the Asian continent be presumed to be representative of air precursor to that impacting western North America?

This is often true, but certainly not always. Depending on meteorology, western North American can be affected by air masses from all directions. In this analysis, we have used the Flexpart (and to a lesser extent, HYSPLIT) dispersion model which tells us when air is mainly from Asia, or elsewhere, using tracers. In fact, of all of the C130 observations, just $\sim 48\%$ of air masses were mainly from Asia, $\sim 12\%$ were from North America, and the remaining $\sim 40\%$ where a combination of NA and Asian, and other continent air masses.

Section 3.3

9) How much “less statistical significance”?

This is an ambiguous phrase, which we will change to ‘... not statistically significant.’

10) You separate your sample points into 30-60 s intervals based on FlexPart analyses. How are the points distributed with respect to flights? If some flights are represented by more points than others then are your results improperly weighted towards those flights?

Spatial and temporal distribution was investigated for this analysis, but not included in the manuscript. 'Asian' interceptions were widespread, and occurred on nearly every research flight and in most regions sampled. 'North American' interceptions were somewhat sporadic, and with the exception of one flight (15 May 06), took place over the continental United States. We include the number of measurements within each altitude bin to provide insight into the quality of the calculation.

Section 3.5.1

11) P 17446, lines 26-29 – ; it is not unusual to find water vapour correlated with pollution, such as particles and CO (e.g. Kleinman et al., JGR, 1996). Combustion is a source of water vapour. Whether RH correlates or not depends on how the temperature in the air mass is changing as it is transported (cooling or warming). The increased correlation downwind of cloud is interesting, but it may be only marginal as there are only about 3 points out of about 25 in the fresh case that prevent a much higher correlation.

The reviewer points out that a correlation between water vapor and pollution is not entirely surprising. Though combustion is a source of water vapor and pollution, the relationship is probably more likely because both can act as quasi-tracers for surface emissions. Recent studies have shown that relative humidity may play some role in SOA formation (Lim et al., 2005; Matsunaga et al., 2005; Altieri et al., 2006; Carlton et al., 2006, referenced in this manuscript). Because of the nature of the sampling platform (which rapidly changes altitude, transverses clouds, etc), we believe a comparison with water vapor to be more appropriate. A relationship between water vapor and WSOC is clear in the 'cloud enhanced' observations (Fig 6), though the reviewer correctly points out that our lack of high correlation in the 'Fresh Central Valley' observation is driven by just a few data points. Though this is true, each data point has been thorough checked and we find no reason to discount these as outliers. We do mention that cloud processing may also have affected Central Valley WSOC since clouds were observed in the region. The visual evidence for cloud process in the Central Valley is

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not as strong.

12) Line 1, page 17447 – ; section 3.5.3.

Section 3.5.2

This is a copy-edit issue, which will be checked after submission of manuscript.

13) Page 17449, lines 18-19 – ; It would be helpful to this discussion to include Henry's Law values for the SVOCs at one temperature.

We will include a selection of Henry's Law Constants for the variables used in this analysis.

14) Page 17449, lines 22-23 – ; did you include BDL values of WSOC in the analysis? And if you did, why should this significantly reduce the regression? If the variability of WSOC on the scale below detection limit is important to this analysis, then how significant is it overall (it does not correlate with CO)?

We did not include BDL values in the regression analysis, though we did include them (as $1/2$ LOD) in the statistical analysis described in Table 1, as well as the altitude profiles in Figure 2.

15) Tables 1 and 3 – ; Nitrate is only about 2% of the sulphate in the Aisan data, but you find significant correlations of WSOC with organic nitrates in the gas phase and your particles appear to be acidic. Can you measure any organic nitrates with your PILS or could there be a significant missing nitrate component?

We employ a series of denuders upstream of each PILS to remove any confounding gases that may be dissolved in the PILS effluent. This is discussed in detail in the methods section (Section 2). As for particle phase organic nitrates, we were able to detect the nitrate and WSOC fractions if the particle was soluble in water. We are unable to explicitly detect 'organic nitrate' aerosol from others (e.g. pure organic carbon), but can measure only the bulk chemical composition.

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16) What about an oceanic component to the WSOC. The aerosol is spending a several days over the North Pacific, and your profile of Asian WSOC shows it virtually all below 3 km. Phinney et al. (Deep Sea Research, 2006) measured an average OC of 0.3 $\mu\text{g m}^{-3}$ over the North Pacific Ocean in the summer-time. They also measured an average MSA of 0.16 $\mu\text{g m}^{-3}$. These values represent a significant fraction of your total WSOC. Did you measure MSA explicitly or would it be part of WSOC?

Most organics from oceanic sources are considered to be insoluble and thus not detected by the PILS-TOC method. However, particle aging could oxidize this to a soluble form, especially if transport times were long and there was adequate photo oxidation.

The altitude bins illustrated in Figure 2 (and others) is the altitude of the C130 aircraft. In most cases, 'Asian' air intercepted over the Pacific Ocean had actually descended from higher altitudes after transport. The Phinney et al measurements were made aboard a research vessel using an Aerosol Mass Spectrometer, several meters above sea surface. This elevation is within the relatively stable marine boundary layer, and likely uncoupled with the free tropospheric air sampled by the C130.

17) Page 17452, lines 17-25 – ; I see little in this analysis, other than that the observations were made generally downwind of a cloudy region, to suggest that the generally higher WSOC/sulfate ratios were the result of cloud processing. Please explain why it could not be preferential removal of sulphate by the cloud? How much SOA would have to have been produced to give the result, and is it consistent with the mechanisms that the authors refer to?

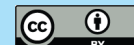
The particles are likely internally mixed and so preferential loss of sulfate over WSOC seems unlikely. It is possible that particles composed of higher sulfate fractions are more readily activated and lost if the cloud was precipitating, but these were not precipitating clouds. We measured air that had recently detrained from the cloud but did

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not contain cloud drops.

While the observation that the 'cloud-processed' interception was in the vicinity of a cloud (as determined by physically observing nearby clouds aboard the C130, as well as archived satellite data), by itself, it is not enough to offer a convincing argument for cloud-processed SOA. Thus, we performed regression analyses on two different sampling periods, each having similar source regions (Central Valley region, Figure 6). For the samples hypothesized as cloud-processed (and thus enhanced with SOA), biogenic and oxygenated VOCs played a larger and more compelling role in determining WSOC variability compared to the 'fresh central valley' period where there was apparently less cloud influence (and also a greater dependence for WSOC variability on anthropogenic VOCs such as MEK and pentane).

Conclusions

18) Page 17453, lines 20-22 – ; I thought that this hypothesis was previously presented by Brock et al. [2004]?

This mechanism was proposed by Brock, et al in a numerical study (coupled with some field measurements) off the West Coast of the United States. We should have included the following in the conclusion:

“Consistent with the mechanism proposed by {Brock et al, 2004}, we propose this was likely caused by precipitation loss of aerosol prior to observation, followed by preferential replenishment of sulfate aerosol as the air mass was transported across the Pacific.”

19) The final statement referring to cloud processing is important, but the authors have not made a sufficient case that their “enhancement” of WSOC was not really a reduction in sulphate.

We believe we have made a reasonable case for this mechanism (see comment # 17).

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