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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Seasonal variation of secondary organic aerosol in Nam Co, Central Tibetan Plateau" *by* R.-Q. Shen et al.

Anonymous Referee #2

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The manuscript presents new measurements of SOA tracers in the Central Tibetan Plateau and discusses seasonal variations in the absolute and relative contributions of biogenic and SOA tracers, particularly in the context of air mass origins. The manuscript requires major revisions prior to reconsideration for publication, namely in the broader discussion of potential local influences on SOA formation, the stability of the utilized tracers during transport, and the specificity and representativeness of a single toluene-SOA tracer to represent all of anthropogenic SOA. Analytically, differences between the methods utilized here and prior studies (e.g. Kleindienst et al. 2007) introduce complications and biases to the use of the SOA-tracer based source apportionment method. These biases, as well as others in quantification stemming from the use of surrogate quantification standards and an extraction protocol giving

65% recovery at times, need to be discussed and quantitatively assessed in order to develop realistic estimates of the errors in absolute quantification of SOA tracers. Specific comments are provided here:

1. The title should be revised – "tracers" should be added after "secondary organic aerosol" in order to clarify that a select sub-set of SOA tracers were measured, and SOA in its entirety is not discussed. Also suggest removing "Nam Co" from the title to make it more concise.

2. The authors attribute SOA to long-range transport, but to not address the potential for SOA to form from local VOC precursors or combustion activities. The potential for release of biogenic VOC from nearby vegetation and NOx from local combustion sources (e.g. dung or biomass burning) must be addressed (Duo et al. 2015; Xiao et al. 2015).

3. Related, to what extent are the measured SOA tracers stable over the distance and time suggested for long-range transport? Prior studies have demonstrated extensive processing of organic aerosols in the region (Meng et al. 2013) as well as the loss of molecular tracers for organic aerosol during long-range transport (Stone et al. 2007).

4. Section 2.2: Specify what type of ionization was used by the mass spectrometer

5. Kleindienst et al. (2007) utilized chemical ionization, a soft ionization technique, to identify SOA tracers using molecular ions and high-m/z ratios, and analyzed SOA chamber samples in parallel to ambient samples to ensure consistency in mass fragmentation and gas chromatography (GC) retention times. Evidence in the form of retention data, observed MS fragments, and relative ratios of MS fragments are needed as evidence for the correct identification of the SOA tracer compounds. This information should be added as supplemental information.

6. SOA tracers were quantified using surrogate standards, because analytical standards are not commercially-available for most of these compounds. The use of a sur-

rogate standard introduces bias to the measurement, because it does not accurately represent the ionization and mass fragmentation of the target analyte. Moreover, the comparison of response factors of the five surrogate standards (1-8 on page 7147) is irrelevant, because the issue is about the agreement of the response factors of the SOA tracers with the surrogates, not between the surrogates and each other. Consequently, the reported absolute concentrations of SOA tracers, are thus subject to large uncertainties, particularly when the structural match between the surrogate standard and analyte is poor (Stone et al. 2012). The manuscript should clearly state that presence and significance of this uncertainty and discuss the potential bias it may introduce to the results.

7. Major issues arise when deviating from the quantification method of Kleindienst et al. (2007) for SOA tracers and using the SOA-tracer method for source apportionment. Namely, the f-SOC values (page 7154 line 15) were developed using the 5-ion quantification approach with a single-point calibration with ketopinic acid as the quantification standard and chemical ionization in the MS source. In this work, the authors have changed the MS detection method, internal standard, and surrogate standards, such that the f-SOC values cannot be directly applied. A large degree of bias is expectedly introduced, but is not quantifiable. The authors need to be realistic about the magnitude of error that this could introduce, which is likely on the order of 5-10 times different, rather than 23%.

8. Revision with respect to uncertainty in SOA tracer measuremetns is needed in section 3.2, page 7155 line 3.

9. Clarify the "paired duplicate samples" described in section 2.3 line 16. Are these duplicate samples of ambient aerosol that were collected in parallel? Or were these extracts that were split and analyzed twice?

10. Were the absolute concentrations of SOA tracers corrected for the less than optimal recoveries reported in section 2.3? Or is this another source of error in the ambient

measurements?

11. The sentence on page 7149 (lines 9-10) should be moved to follow the description of the model.

12. The authors should work towards developing a deeper discussion of the monoterpene SOA tracers using knowledge of first and multi-generation oxidation products of monoterpenes (Glasius et al. 2000; Jaoui et al. 2005; Szmigielski et al. 2007) and reaction pathways (Eddingsaas et al. 2012) as has been done for isoprene.

13. The conclusion that biogenic SOC "dominated over anthropogenic SOC" is not robust, in part because only a single organic molecule is being used as a tracer of anthropogenic VOC – DHOPA. The specificity of DHOPA to anthropogenic sources is not fully established (Kleindienst et al. 2004). For example, biomass burning is a major source of toluene in many parts of the world (Lewis et al. 2013). Hence, DHOPA may be an indicator of the processing of biomass burning emissions, and not a measure of urban pollutants from solvent and fossil fuel use. The limitations of using a single, and potentially non-specific tracer for anthropogenic SOA must be discussed and the conclusions restated.

14. Clarification needed on page 7154 line 11-12 – What specifically has been done to show that the SOA tracer approach provides "reasonable results"?

15. Page 7142 line 18: replace "emission and tracers partitioning." With "emission and gas-particle partitioning."

16. Page 7142, line 28: revise to "to estimate secondary. . ."

17. Page 7155, line 17 "not measure OC"

18. Table 1 – improve the "Month column" The six numbers are not easily interpreted. Suggest writing out the month and year, e.g. July 2012

19. Figure 2 – suggest replacing numerical dates on the x-axis with "July 2012" to

improve readability..

20. Table 1 – Indicate that temp and RH are monthly averages.

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