

## *Interactive comment on* "Organic and inorganic decomposition products from the thermal desorption of atmospheric particles" *by* B. J. Williams et al.

## B. J. Williams et al.

brentw@wustl.edu

Received and published: 19 March 2016

\*A revised document (with Track Changes enabled) as well as corrected figures and supplemental figures has been provided to the editor.

## Anonymous Referee #1

1) The presented manuscript by Williams et al. is very interesting and well written. The paper focuses on a new type of data that highlights the analytical challenges associated with quantitative analysis of organic aerosol using thermal desorption AMS techniques on ambient aerosol. In this work, the authors have focused on decompo-

C5761

sition compounds that result from the rapid heating of humidified ambient aerosol in the collection thermal desorption cell used in the TAG instrument. This rapid heating in an inert atmosphere appears to result in both inorganic and organic decomposition fragment ions identified by the AMS. Assuming the ions observed in non-TAG AMS measurements also result from thermal decomposition, the authors compared observations and found agreements. The description of the challenges associated with these measurements is adequately balanced and suggests further work to be done in the future.

Author Response: The authors thank the reviewer for their comments and address further questions below.

2) There are two instrument limitations described in the introduction of the paper (low mass transfer of highly oxygenated OA and  $\sim$ 20% detection) that likely affect the comparison of the TAG measurements to the AMS measurements. However, I did not find them to be discussed in terms of the data comparisons.

Author Response: These are known limitations as discussed in previous work. Here we are proposing that much of this difference between TAG and AMS is now showing up in the TAG decomposition window. This point has been more specifically highlighted at the end of section 2:

"The TDO and TDI components are the focus of this paper."

And in the conclusions:

"Inclusion of these thermally decomposed organic (TDO) and inorganic (TDI) components increases the fraction of aerosol observed by the TAG system."

3) Another minor point of consideration is the use of the term "solvent delay". The time period referred to here is also referred to as "thermal desorption period" by the authors. The latter is more technically correct and avoids misunderstanding. Note, the TAG does not employ a solvent injection, thus the term solvent delay is not at all

correct. Furthermore, the implication that traditional GC measurements with solvent injections also result in similar thermal decomposition products is also incorrect. This is mainly due to the fact that the analytes injected using a solvent carrier are flash vaporized to the head of the analytical column in the absence of inorganic substances that can catalyze decomposition.

Author Response: We thank the reviewer for bringing out a need for clarity regarding this point. The term "solvent delay" is initially referred to here since it is a common term used in GCMS analysis to delay acquisition of data by the MS to protect from solvent detection. The TAG does frequently employ a solvent injection (as in the case of the inorganic calibrations and whenever we inject organic calibration standards, this is performed through solvent/solute injections). Additionally, the TAG previously avoided acquiring data during this period in ambient sampling to avoid volatile components and large signals from aerosol water. We now record during this "solvent delay" period and since it is no longer a delay in the MS detection, we term it "thermal desorption period". It is likely that traditional GC with a glass lined injection port would have less thermal decomposition, but some could still occur, not being detected due to the traditional solvent delay. Additional clarification is offered in the text near the end of section 1:

"Analysis of these decomposition products is the focus of this paper, and instead of applying a traditional "solvent delay time period" we now acquire data in what we interchangeably refer to as the "thermal desorption period", "sample injection period", or "thermal decomposition window" depending on which process we are highlighting."

4) Another very minor point pertaining to terminology on page 13386 should be addressed. Here the authors present a list of the TAG fractions, including non-eluting organics and later non-eluting inorganics. How are non-eluting compounds TAG fractions? Non-eluting compounds are not observed in the TAG instrument because they are irreversibly bound to the analytical column stationary phase, right?

Author Response: That is correct, this fraction is not observed by TAG. It is a known

C5763

missing fraction (the fraction is not known yet, but there is some that does not elute). We have attempted to clarify this point by not referring to these fractions as "TAG fractions", but just as aerosol fractions from the perspective of the TAG system. The NEO and NEI definitions already clearly state these do not elute through the TAG system. Clarification is offered in the text:

Text changed from: "fractions of total fine aerosol as observed by TAG," To: "fractions of total fine aerosol from the perspective of TAG measurements,"

Text changed from: "classified according to TAG fractions" To: "classified according to these fractions"

Interactive comment on Atmos. Meas. Tech. Discuss., 8, 13377, 2015.