Atmospheric
Measurement
Techniques
Open Access
Discussions

Interactive comment on "Method for the determination of concentration and stable carbon isotope ratios of atmospheric phenols" by M. Saccon et al.

Anonymous Referee #1

Received and published: 22 July 2013

This manuscript presents a new method to determine the concentrations and stable carbon isotope ratios for atmospheric nitrophenols in both the gas and particulate phases. The method is an interesting and ambitious step forward, and the manuscript is well written. However, I have several major comments that should be addressed before the paper is ready for publication and this method is ready for further use.

Major comments: 1) The collection and recovery is referred to as "efficient" in the manuscript, but in fact the recovery of phenols for blank filters spiked with standards shown in Table 3 are relatively poor, as evidenced by the internal standards which "each consistently had recoveries from 50% to70%". Furthermore, the collection effi-

ciency tests for the filters as shown in Figure 2 demonstrate that even in the best case there was breakthrough of around 15% collected on the backup filter. The sampling system and the stainless steel mesh used in between the XAD coated filters likely also collected some of the targeted semi-volatile phenols, but this was not addressed at all in the manuscript. The relative amount of nitrophenols expected in the gas and particle phases were also not addressed, but presumably the particle phase is collected efficiently while the gas phase collection efficiency is lower and is solely responsible for the observed breakthrough. It is possible (perhaps even likely) that the gas and particle phase nitrophenols have different d13C, thus the fraction of gas phase collection and the gas/particle partitioning in the atmosphere could easily have an impact on the measured d13C using the proposed method. More careful evaluation is required regarding potential gas phase losses in the sampling system, and the importance of gas/particle partitioning on the collection efficiency and resulting d13C measurements.

2) Perhaps the most critical issue in measuring compound specific d13C is achieving clean chromatographic separation of the target compounds such that there is no contamination of the d13C from other C containing chemicals. Particularly in a complex mixture of semivolatile organics from the gas and particle phases in the atmosphere, this is an extreme analytical challenge. Complete separation of nitrophenols from the complex mixture of atmospheric organics must be clearly demonstrated, with proof that no other C containing chemicals are co-eluting with the target compounds. Without this demonstration of clean separation, it is hard to accept that the measured d13C in the atmospheric samples is indicative of only the targeted compounds.

3) It is not clear from the manuscript specifically what can be learned from observing the isotopic ratios of the nitrophenols. At the end of the "Ambient measurements" section the authors write that their observations "support the hypothesis that these compounds are indeed formed through secondary processes and are not primary emissions". Is there any doubt in the literature that these compounds are secondary and produced in the atmosphere? That information can be gleaned from the concentra-

tion measurements alone. What is the added value of the d13C measurements which make the method worthwhile and deserving of further application? Addressing this question in the context of the reported d13C accuracy and detection limits would be a worthwhile addition to this methods paper.