Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2019-275-AC1, 2019

Atmospheric Measurement Techniques Discussions

Interactive comment on "Chemical discrimination of the particulate and gas phases of miniCAST exhausts using a two-filter collection method" *by* Linh Dan Ngo et al.

Linh Dan Ngo et al.

yvain.carpentier@univ-lille.fr

Received and published: 31 October 2019

Specific comments

1) It is well established that quartz fiber filters (such as the front filter used to collect particles) adsorb organic vapors quite well. Was anything done in this study to evaluate the effect of this on the results and data interpretation? If not, then I suggest some vapors of standard PAHs with a range of volatilities be sampled and analyzed using this system. Alternatively, if others have conducted such studies then the authors could review the results of that work and discuss its consequences for the sampling and measurement approach employed here.

Authors' response to specific comment 1):

We thank the reviewer for his/her suggestion of discussing the consequences of the adsorption of organic vapors onto the filters in our two-filter sampling system and measurement approach. We will make sure that this possibility is acknowledged and briefly explain why we are confident that this phenomenon does not affect our results in a revised version of our manuscript. Please find our detailed response below.

The reviewer is right that the adsorption of gaseous hydrocarbons onto filters was investigated in numerous works. Specific studies assessing the ability of various filters to sorb gaseous organic species have even been carried out [e.g. 1-5]. They show that filters can collect organic vapors in addition to particulate matter. The efficiency of the adsorption of such vapors depends on a number of factors, including sampling duration and gas flow through the filter. In our study we used two filters placed in series in the exhaust line of a miniCAST, i.e. a bare quartz fiber filter (front filter) followed by a second black-carbon-covered quartz fiber filter (back filter). By doing so, we observed after a short sampling time (20 min) a clear partitioning where the particulate matter is essentially found on the first filter, while organic vapors (i.e. polycyclic aromatic hydrocarbons (PAHs) of different masses) are found condensed either onto both filters or just onto the back filter depending upon the masses of the PAHs.

Prior to sampling, spectra of neat quartz fiber filters (QFFs) have been recorded for both L2MS and SIMS measurements. The thermal treatment applied to the back filter proved to be very efficient at limiting the adsorption of aromatic species as evidenced when comparing the mass spectra of the quartz fiber filters before and after exposure to the exhaust. Moreover, the masses retained from our front and back filters to perform statistical analyses do not include specific masses associated with the substrate. Therefore, none of our deduction from statistical analysis is impacted by the possible condensation of organic vapors.

During our experiment, adsorption of organic vapors on the filters could affect the

chemical characterization of the particulate matter if we were using an analytical technique probing the bulk of the sample, i.e. from the sample surface all the way down to the filter. For instance, it is true that the adsorption of gaseous organic compounds onto filters is a potential source of errors in measurement when determining the mass of collected particles and the concentration of certain species/organic carbon (OC) in the particulate phase with a thermo-optical method [3-5]. However, in this work, we use instead two-step laser mass spectrometry (L2MS). L2MS is a surface characterization technique; since the laser penetration depth at λ_d=532 nm is only a few nm (orders of magnitude smaller than the average particle size in the studied regimes) only species present on the surface of the particulate matter are desorbed and analyzed. Therefore, if organic vapors are adsorbed onto the filter, they should not induce any measurement artifact when analyzing the particulate matter. This does not mean that organic vapor did not condense onto the particulate matter. We acknowledge and mention in the main text of our article that particulate matter likely consists of an adsorbed layer of organics onto an elemental carbon core. However, our experiment has not been designed to identify for certain whether heavy PAHs (>4 rings) are part of the particulate matter (chemisorbed or physisorbed) or "free" in the gas phase, insofar as they are both concomitantly present in the exhaust line and that we cannot avoid the fact that heavy PAHs may condense along with/onto the particulate matter when the latter is trapped by the first filter.

References:

1. Chase R., Duszkiewicz G., Richer, J., Lewis D., Maricq M., and Xu N., "PM Measurement Artifact: Organic Vapor Deposition on Different Filter Media," SAE Technical Paper, 2004, 2004-01-0967, 1-11.

2. Cotham W. E., and Bidlemant T. F., "Laboratory Investigations of the Partitioning of Organochlorine Compounds between the Gas Phase and Atmospheric Aerosols on Glass Fiber Filters", Environ. Sci. Technol., 1992, 26, 469-478.

3. Hartt K. M., and Pankow J. F., "High-Volume Air Sampler for Particle and Gas Sampling. 2. Use of Backup Filters To Correct for the Adsorption of Gas-Phase Polycyclic Aromatic Hydrocarbons to the Front Filter", Environ. Sci. Technol., 1994, 28, 655-661.

4. James J. Schauer, Michael J. Kleeman, Glen R. Cass, and Bernd R. T. Simoneit, "Measurement of Emissions from Air Pollution Sources. 2. C1 through C30 Organic Compounds from Medium Duty Diesel Trucks", Environ. Sci. Technol., 1999, 33 (10), 1578- 1587.

5. Mader B. T., and Pankow J. F., "Gas/Solid Partitioning of Semivolatile Organic Compounds (SOCs) to Air Filters. 3. An Analysis of Gas Adsorption Artifacts in Measurements of Atmospheric SOCs and Organic Carbon (OC) When Using Teflon Membrane Filters and Quartz Fiber Filters", Environ. Sci. Technol., 2001, 35(17), 3422-3432.

2) I found the Results and Discussion section rather challenging to read, due primarily to the somewhat monotonous style in which each observation was described in detail and then a possible explanation was provided. This made it difficult for me to differentiate important observations from minor ones. Although this made for a very thorough presentation, I'm not sure that readers will get the important take-away messages until they read the Conclusions (which may be all they choose to fully read). I suggest that the authors make a greater effort to emphasize the major points in each section of the manuscript, and perhaps eliminate some of the discussion that is mostly just minor observations with speculative explanations.

Authors' response to specific comment 2):

We will follow the reviewer's comment and improve the Results and Discussion section of our article in a revised version where we will outline the most important observations for each paragraph and remove extended descriptions/discussions about less important points that currently disrupt the thread.

Technical comment

1) Line 46: It seems unlikely that reviews published in 2011 and 2014 cover advances made over the last decade. Sentence should be reworded.

Authors' response to technical comment 1):

The sentence on line 46 will be reworded in our revised version. We will additionally replace "decade" by "decades" and add a more recent reference.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2019-275, 2019.