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Offline thermal-desorption proton-transfer-reaction mass spectrometry to study composition of organic aerosol

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ABSTRACT

We present a novel approach to study the organic composition of aerosol filter samples using thermal-desorption proton-transfer-reaction mass spectrometry (TD-PTR-MS) in the laboratory. The method is tested and validated based on the comparison with in situ TD-PTR-MS measurements. In general, we observe correspondence within the levels of uncertainty between in situ and offline TD-PTR-MS measurements for compounds desorbing at temperatures above 100 °C and for quartz fiber filters that were sampled for more than one day. Positive sampling artifacts (50–80%, with respect to the in situ measurements) from adsorption of semivolatile organic gas phase compounds are apparent on filters sampled for one day. Detailed chemical analysis shows that these positive sampling artifacts are likely caused by primary emissions that have not been strongly oxidized. Negative sampling artifacts (7–35%, with respect to the in situ measurements) are observed for most filters sampled for two and three days, and potentially caused by incomplete desorption of aerosols (in particular, nitrogen-containing organics) from the filters during the offline measurements and chemical reactions on the filters.

1. Introduction

Atmospheric aerosols have been studied intensively because of their impact on climate and their health effects. Organic aerosol (OA) typically accounts for 20–90% of the total aerosol mass (Kanakidou et al., 2005). The chemical composition of organic aerosol is very complex and has not been resolved completely at a molecular level. It has been characterized using a suite of online and in situ instruments in field studies: for example, aerosol mass spectrometer (AMS) (e.g., Jayne et al., 2000), micro-orifice volatilization impactor coupled to a chemical ionization mass spectrometer (MOVI–CIMS) (e.g., Yatavelli & Thornton, 2010), particle-into-liquid sampler (PILS) (e.g., Weber et al., 2001), filter inlet for gases and aerosols (FIGAERO) (Lopez-Hilfiker et al., 2014), in situ thermal-desorption proton-transfer-reaction mass spectrometer (TD-PTR-MS) (e.g., Holzinger et al., 2010a) and thermal desorption aerosol gas chromatograph/mass spectrometer (TAG) (Williams et al., 2006). These in situ methods are powerful tools

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to get information on aerosol composition, but field studies using these instruments are expensive and often can cover only limited time periods.

In order to be able to perform long-term aerosol measurements at low cost, sampling of aerosol on filters with offline analysis in the laboratory is often used (e.g., ten Brink et al., 2004; Subramanian et al., 2004; Viana et al., 2006, 2007). Among the advantages of offline methods are easy implementation of sampling and the possibility to sample a large volume of air, which allows for a low detection limit. Furthermore, filter samples can be stored and measured with offline methods later, whereas online aerosol composition data cannot be obtained or re-measured after a field campaign is over. Among the disadvantages of organic aerosol sampling on filters are complicated sampling artifacts. Two principal types of artifacts have been observed: positive (i.e. the aerosol concentrations determined based on the offline technique are overestimated) and negative (the corresponding concentrations are underestimated).

Positive artifacts can be caused by the adsorption of organic vapors on the filters and are difficult to quantify (Turpin et al., 2000), because they depend on sampling time, location and face velocity (McDow & Hunzicker, 1990; Turpin et al. 1994; Subramanian et al., 2004). Moreover, it was shown that filters manufactured by the same company, but having different lot number, exhibit different organic vapor adsorption capacity (Kirchstetter et al., 2001). Negative artifacts are caused by volatilization of compounds that have been already collected on filters, e.g. relatively light polycyclic aromatic hydrocarbons (PAHs) (Coutant et al., 1988). Additionally, Schauer et al. (2003) showed that chemical reactions on the filters can cause a negative artifact for measurements of particle-bound PAHs in the atmosphere (up to 100% underestimation).

Both negative and positive artifacts are particularly influenced by semivolatile organic compounds (SVOCs), which partition between the gas and the condensed phases. Lipsky and Robinson (2006) showed that the degree of dilution strongly influences the partitioning of SVOCs in diesel exhaust. They discovered that SVOCs tend to be in the gas phase when the exhaust is diluted (causing negative artifacts on filter samples), and the SVOCs tend to be in the condensed phase when exhaust is undiluted (causing positive artifacts). Some attempts have been made to quantify the partitioning of SVOCs, but it is problematic to apply this quantification to real-atmosphere conditions (e.g., Mader & Pankow, 2001).

Attempts to correct for the artifacts using field blanks, backup filters and denuders have been performed. Nevertheless, the filter material itself influences the magnitude of sampling artifacts (Turpin et al., 2000). In general, quartz fiber filters are used for aerosol sampling due to their high temperature resistance. The latter is needed for organic carbon measurements, which require high temperatures for complete desorption. However, high positive artifacts are observed for the quartz filters due to their high specific area and consequently high gas adsorption. As an alternative, the use of Teflon filters is possible with lower specific area. On the other hand, these filters cannot withstand high temperatures needed to desorb most of OA (Turpin et al., 2000). The use of a quartz backup filter along with a quartz front filter is common. However, e.g., Watson et al. (2009) discovered in an extensive study that the use of backup filters (and field blanks) does not fully represent filter sampling artifacts. Viana et al. (2006) showed that the use of a diffusion denuder might reduce organic carbon (OC) mass observed without a denuder by 34%, therefore correcting for positive artifacts. However, they also found that the use of such a denuder does not provide a good comparability between high- and low-volume filter samplers.

While multiple studies have been performed to examine total organic carbon artifacts, there is only a limited number of investigations where artifacts are studied along with the chemical composition of OA. For example, Lambe et al. (2010) performed more detailed studies on the chemical composition of organic aerosols sampled on filters. They compared GC–MS analysis of organic aerosol desorbed from filter samples to in situ TAG measurements for a limited set of compounds (n-alkanes, PAHs, and hopanes). Based on the ambient air measurements they found reasonable agreement for hopanes (r^2=0.55–0.95, slope=1.0–1.7) and PAHs (r^2=0.58–0.97, slope=0.8–1.0). However, for n-alkanes (C27–C32) the agreement was poor: r^2=0.17–0.85, slope=0.4–1.7, and the exact reason for this was not established.

The objectives of this study were (i) to introduce and validate a new offline analytical technique based on quartz fiber filter sampling and subsequent analysis by thermal-desorption proton-transfer-reaction mass-spectrometry (TD-PTR-MS) and (ii) to use this method to investigate some filter sampling artifacts in more detail. We evaluate and characterize the new offline method by comparison with in situ TD-PTR-MS measurements (Holzinger et al., 2010a). The in situ TD-PTR-MS measurements and filter sampling were performed at the same time and location and in both analyses the same instrument (PTR-TOF-MS) was used, facilitating direct comparison of the two datasets.

2. Experimental methods

2.1. Measurement campaign

The measurement campaign for comparison of the in situ TD-PTR-MS, the filter-based TD-PTR-MS (referred to as 'offline' method hereafter) and the Scanning Mobility Particle Sizer (SPMS) methods took place from 8 February 2011 till 7 March 2011 at the Cabauw Experimental Site for Atmospheric Research (CESAR)[1] about 20 km south-west of the city of Utrecht in the Netherlands (51.971°N, 4.927°E). The inlet for the in situ measurements was located at the height of ~5 m above the ground and a high volume filter sampler was located directly on the ground and sampled 2 m above the ground at a distance of ~4 m from the TD-PTR-MS inlet. The inlet of the SMPS was located at 60 m height on the Cabauw tall tower.

[1] http://www.cesar-observatory.nl/