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

M. Saccon et al.

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Following the referees' comments we will add some more information and clarifications. Referee 1: Reply to comment 1: The potential impact of breakthrough on the measured stable carbon isotope ratio is discussed in the paper based on measurement of isotope ratios on filters collected in series and it has been shown that fractionation is small compared to measurement errors. Nevertheless, we will add more information and discussion about tests we conducted to determine sampling efficiency of XAD coated filters and gas-particle distribution of nitrophenols: “The vast majority of nitrophenols in ambient air have been found to be present in the gas phase (Fig. 1 and 2). This

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was determined by sampling with denuder filter-pack combinations and filter-packs as well as a high-volume quartz filter and XAD-coated filters in parallel. On average, 60 % to 90 % of nitrophenols were found to be in the gas phase. The fraction found on the second XAD-coated filter in the filter pack study is consistent with approximately 15 % breakthrough of gas phase nitrophenols through XAD coated filters. Several tests were conducted to determine the efficiency of the XAD coated filters. Two filters were sampled in series on high volume air samplers, with a stainless steel mesh (5 mm x 5 mm grid size, wire thickness about 0.8 mm) in between, at a flow rate of 0.65 or 1.13 m³ min⁻¹. Filters were also sampled in series on low volume air samplers at a standard flow rate of 16.7 L min⁻¹. Results are summarized in Fig. 4. The percentage of phenols on the second XAD coated filter relative to the first filter decreased from, on average, 36 % to around 15 % as a result of the coating method modifications. Breakthrough for low volume air samplers was on average less than 10 %, somewhat lower than for high volume samples. This may be due to the lower linear face velocity of 16 cm s⁻¹ versus 41 cm s⁻¹ for standard high volume air sampling. However, when sampling on high volume air samplers at different flow rates, there was no significant change of sampling efficiency (Fig. 4). A low volume air sampler was used to monitor the efficiency of the XAD-coated filters with a commercially available filter holder that allowed for the sampling of three 47 mm filters in series. A quartz filter was placed first to remove PM, followed by two XAD-coated filters which collected the gas phase and blow-off. Approximately 10 % of the total mass collected was found to be on the second XAD-coated filter (Fig. 5). This is less than what was observed using the high-volume air samplers. The increased breakthrough observed for the high-volume air samplers was thought to be attributed to incomplete sealing of the first filter resulting from the stainless steel mesh used to separate the two high volume filters when running breakthrough tests.” We will also add a short comment in the conclusions: “The sampling efficiency of XADTM coated filters could be improved by modification of existing coating methods to approximately 80 % to 90 % for total atmospheric nitrophenols. Although tests demonstrated that the breakthrough has no detectable impact on the isotope ratio

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measurements, this adds uncertainty to concentration measurements since. If deemed necessary using two filters in series allows a total sampling efficiency better than 95 %. “ Recovery and factors influencing recovery have been presented in detail in the cited paper by Moukthar et al., which describes the methodology for filter extraction. We do not think it is necessary to repeat these previously published findings, but will point out the similarity in our recoveries to those reported in Moukthar et al. “The recoveries of the two internal standards was used for diagnostic testing of the GC-MS and to monitor possible isotopic fractionation using GC-IRMS. Concentrations were calculated using the ratios of the target compound and internal standard peak areas and calibration factors. Blank filters spiked with target compounds and internal standards showed similar recoveries to the internal standards (Table 3). The ratio of the recoveries for the two internal standards was 0.95 with an error of the mean of 0.02. These results are very similar to recoveries reported and discussed in detail by Moukthar et al. (2011) for quartz fiber filters using a nearly identical extraction and extract processing method.” The referee also mentions the potential problem of losses due to the stainless steel mesh separating the two filters when using a high-volume sampler to collect two filters in series. The mesh had a grid size of 5 mm x 5 mm and a wired thickness of 0.8 mm. At the flow rates used for sampling only a very small fraction of molecules will, due to diffusion limitations, get into contact with the stainless steel surface. We will add information about the dimension of the mesh. Reply to comment 2: We will add more information about the separation: “Chromatographic separation of the target compounds was verified by analysing ambient samples in scanning mode of the GC-MS system. Figure 3 shows a typical GC-MS chromatogram that was run in scanning mode. Complete resolution of each of the target compounds and internal standards is observed, apart from 4-nitrophenol and 2-methyl-3-nitrophenol and in some cases a small shoulder for the 5-methyl-3-nitrophenol peak. This was confirmed through analysis of the mass spectra. Incomplete resolution of 4-nitrophenol and 2-methyl-3-nitrophenol was not an issue for concentration measurements since selective ion monitoring was used and different characteristic peaks were targeted for each of

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the two compounds. A complete separation of the two compounds was achieved for GC-IRMS measurements by changing the temperature program at the expense of increased duration of the runs (see inlay of Figure 2). It should be noted that the small shoulder sometimes observed for the 5-methyl-3-nitrophenol peak, one of the internal standards, had no detectable impact on the measured isotope ratio as demonstrated by the consistently good agreement between on-line and off-line measurements.” Reply to comment 3: We can only partly agree. First of all, this is a methodology paper and a detailed discussion of ambient observations would be out of place and create a paper of excessive length. We have mentioned the potential value of isotope ratio measurements for atmospheric organic compounds in the introduction and provided some references. The referee mentions “Is there any doubt in the literature that these compounds are secondary and produced in the atmosphere?” We agree that secondary production is one of the identified sources for atmospheric nitrophenols. However, we are not aware of sufficiently detailed published studies that would allow excluding the existence of other sources and indeed there is literature which mentions other possible sources for nitrophenols. We will add those in the introduction: “Methyl nitrophenols have also been reported to be primary emissions in one study (Trempe et al., 1993) and 4-nitrophenol was found to be emitted in vehicle exhaust in small quantities (Nojima et al., 1983).”

Referee 2 provided only one comment about potential impact of contamination and recoveries from the HPLC and SPE sample clean-up steps. Reply: The blanks and recoveries we report are for the entire procedure, completely identical to that used for sample extractions and include both the HPLC and SPE steps. We will make sure that a revised manuscript clearly explains this. References Nojima, K., Kawaguchi, A., Ohya, T., Kanno, S., Hirobe, M.: Studies on photochemical reaction of air pollutants. Identification of nitrophenols in suspended particulates, Chem. Pharm. Bull. 31, 1047-1051, 1983. Trempe, J., Mattrel, P., Fingler, S., Giger, W.: Phenols and nitrophenols as tropospheric pollutants: emissions from automobile exhausts and phase transfer in the atmosphere, Water Air Soil Poll., 68, 113-123, 1993.

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Interactive comment on Atmos. Meas. Tech. Discuss., 6, 4705, 2013.

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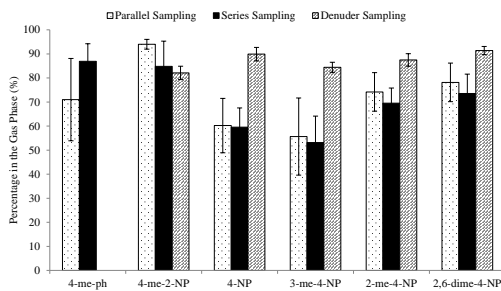
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Fig. 1. Partitioning of nitrophenols determined from sampling in parallel and in series using high volume air samplers and denuders.

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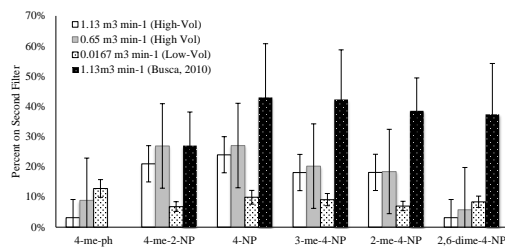


Fig. 2. Efficiency of XAD coated filters; filters were sampled in series with a stainless steel mesh placed in between. Error bars represent the error of the mean. The results from Busca (2010) were obtained

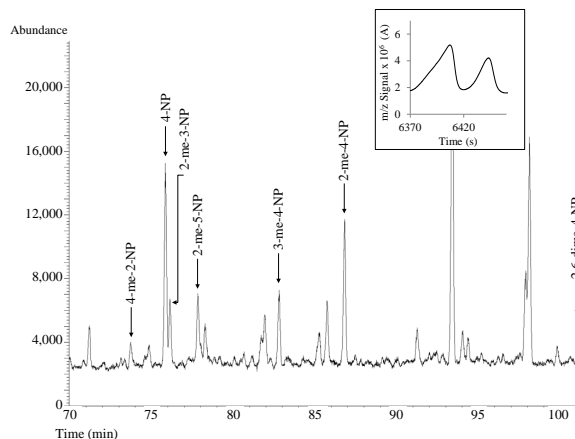


Fig. 3. Fraction of a GC-MS scanning chromatogram of an ambient XAD filter sample. A GC-IRMS chromatogram of the resolved 4-NP and 2-me-3-NP peaks of an ambient filter is shown in the upper right corner.