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Method for the determination of concentration and stable carbon isotope ratios of atmospheric phenols

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Abstract

A method for the determination of the stable carbon isotopic composition of atmospheric nitrophenols in the gas and particulate phases is presented. It has been proposed to use the combination of concentration and isotope ratio measurements of
5 precursor and product to test the applicability of results of laboratory studies to the atmosphere. Nitrophenols are suspected to be secondary products formed specifically from the photooxidation of volatile organic compounds. XAD-4™ resin was used as an adsorbent on quartz filters to sample ambient phenols using conventional high-volume air samplers at York University in Toronto, Canada. Filters were extracted in acetoni-
10 trile, with a HPLC clean-up step and a solid phase extraction step prior to derivatization with BSTFA. Concentration measurements were done with gas chromatography-mass spectrometry and gas chromatography-isotope ratio mass spectrometry was used for isotope ratio analysis.

The technique presented allows for atmospheric compound-specific isotopic composition measurements for five semi-volatile phenols with an estimated accuracy of
15 position measurements for five semi-volatile phenols with an estimated accuracy of
0.3 ‰ to 0.5 ‰ at atmospheric concentrations exceeding $0.1\,ng\,m^{-3}$ while the detection limits for concentration measurements are in the $pg\,m^{-3}$ range. Isotopic fractionation throughout the entire extraction procedure and analysis was proven to be below the precision of the isotope ratio measurements. The method was tested by conducting
20 ambient measurements from September to December 2011.

1 Introduction

Primary emissions of volatile organic compounds (VOC) can undergo photo-oxidation in the atmosphere to produce numerous compounds, including a range of low volatility substances that contribute to atmospheric particulate organic matter (POM). Nitro-
25 phenols are semi-volatile compounds that have been proposed to be formed specifically through the reactions of benzene and alkylbenzenes such as toluene and xylenes

(Atkinson, 2000; Forstner et al., 1997; Hamilton et al., 2005; Jang and Kamens, 2001; Sato et al., 2007). While a range of alkylnitrophenols have been observed in the atmosphere in the particle phase as well as in the gas phase (Cecinato et al., 2005; Morville et al., 2004), the yield of alkylnitrophenols from VOC oxidation and their contribution to secondary organic aerosols (SOA) is highly uncertain. Laboratory studies show a wide range of SOA yields from oxidation of aromatic VOC and the extrapolation from laboratory experiments, which typically are conducted at ppm levels of precursors, adds significant uncertainty in estimates of ambient POM yields (Forstner et al., 1997; Irei, 2008). Moreover, alkylnitrophenols are semi-volatile and it therefore can be expected that they will be found only partly in the airborne particle phase.

It has been proposed that knowing the isotope composition of secondary POM can be used to gain insight into the formation of SOA and differentiate between atmospheric processes such as mixing, dilution and chemical processing (Goldstein and Shaw, 2003; Rudolph, 2007). Specifically, the use of isotope ratios to substantiate the validity of extrapolation of smog chamber studies to atmospheric conditions through the comparison of ambient measurements with smog chamber studies has been suggested (Irei et al., 2011). Stable carbon isotopic compositions of SOA precursors have been previously measured at their emissions sources (Czapiewski et al., 2002; Rudolph et al., 2002; Rudolph, 2007; Smallwood et al., 2002) as well as in ambient air (Goldstein and Shaw, 2003; Kornilova, 2012; Rudolph et al., 2007). Recently, a measurement method for isotope ratios of methylnitrophenols in atmospheric particulate matter (PM) has been established (Moukhtar et al., 2011). In the case of semi-volatile organic compounds (sVOC), this provides merely part of the information needed for comparison with laboratory results since the isotope ratio of sVOC in the gas phase is not necessarily identical to that in the particle phase. However, apart from some laboratory studies of the stable carbon isotope ratios of POM formed by oxidation of toluene (Irei et al., 2011; Irei, 2008) and very few measurements of some nitrophenols in the particle phase published by Moukhtar et al. (2011), no measurement of the carbon isotope ratio of nitrophenols formed by the photooxidation of alkylbenzenes are known to us.

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Moreover, there is strong evidence that the majority of nitrophenols exist in the gas phase (Busca, 2010) and measurements of the isotopic composition of nitrophenols in the gas phase have not been published thus far.

Given that nitrophenols are secondary pollutants, their expected concentrations in the atmosphere are difficult to predict, but from the extrapolation of laboratory studies, are projected to be in the several $ng\,m^{-3}$ range (Hamilton et al., 2005; Irei, 2008). However, they often have been found in very low concentrations in the sub $ng\,m^{-3}$ range in PM (Cecinato et al., 2005; Morville et al., 2004; Moukhtar et al., 2011). This results in certain challenges since measuring the compound specific stable carbon isotope composition, which is typically done by gas chromatography coupled to isotope ratio mass spectrometry (GC-IRMS), requires a mass of carbon per compound that is several orders of magnitude higher than the mass needed for concentration measurements (Rudolph, 2007).

Moukhtar et al. (2011) have previously developed a method for the sampling and analysis of the isotope ratio of nitrophenols in PM but also reported that isotope ratios of nitrophenols could only be determined for a very small subset of the samples due to the low concentration in most of the PM samples collected. Since, as mentioned above, a significant part of the total atmospheric nitrophenol concentration is expected to be in the gas phase, measuring the isotope ratio of the sum of gas phase and particle phase nitrophenols would not only reduce uncertainties in the interpretation of measured isotope ratios resulting from distribution between the two phases, but also avoid the problem of acquiring sufficient mass for isotope ratio analysis.

High volume air sampling is an established method for collecting atmospheric trace components in PM from large volumes of air. This sampling method allows having a large sampling volume and flow rate, which is important when analyzing compounds at low concentrations, such as the nitrophenols. However, quartz fiber filters will sample only PM efficiently. There are several applications that use sorbent impregnated filters to collect volatile or semi-volatile compounds from large volumes of air. XAD-4™ resin has been previously used as an adsorbent when sampling several

atmosphericsemi-volatile substances on low volume filters and denuders (Galarneau et al., 2006; Gundel and Lane, 1999). A method was developed using XAD-4™ coated high-volume filters for sampling for compound-specific concentration and isotope ratio measurements of nitrophenols in both gas phase and PM. A detailed description, several method validation tests as well as examples for ambient measurements are reported and discussed.

2 Materials and method

2.1 Preparation of adsorbent and coating of filters

For isotope ratio analysis high volume quartz fiber filters (20.32 cm × 25.4 cm Pallflex® Tissuquartz™ filters – 2500 QAT – PallGelman Sciences) were used, however some tests were conducted using low-volume sampling with 47 mm diameter round filters of the same material. Prior to coating, the quartz fiber filters were baked at 1123 K for 24 h to remove organic contaminants. The filters were then covered with Teflon sheets and stored in Pyrex containers. Filters were coated according to the procedure described by Gundel and Herring (1998) and Galarneau et al. (2006) with some modifications. XAD-4™, 20–60 mesh (Sigma Aldrich), was cleaned by sonication for 30 min successively in methanol, dichloromethane and hexane. The slurry was then filtered and dried. The XAD was ground for either 17 h or 34 h at 400 rpm in a Retsch planetary ball mill.

Filters were coated by immersing them in an XAD-hexane slurry with a concentration of approximately either 6.5 or 10.5 g XAD L^{-1}. Before use, the slurry was sonicated for 30 min. Twelve filters, each in a stainless steel mesh holder, were immersed in the slurry 10 times. Following sonication of the slurry for 30 min, the filters were again immersed in the slurry in opposite order 10 times and were then left to dry overnight. To remove excess particles from the filters, the filters were immersed in hexane 10 times, dried, and stored in a Pyrex container until sampling.

2.2 Sampling

Samples were collected between September and December 2011 with high volume air samplers (Tisch TE-6001 40 CFM PM-10 retrofitted with a $PM_{2.5}$ micron head) on the roof of the Petrie Science and Engineering building at York University, which is a sub-
5 urban mixed industrial and residential area in the outskirts of metropolitan Toronto, Canada. The sampling flow rate was varied between 0.65 and 1.13 m^3 min^{-1} and the sampling time was 24 h. The air samplers were calibrated using a TE-5028A calibrator (Tisch Environmental Inc.). Uncertainty of the flow rate, including drift between calibra-tions was typically around 5 %. Following sampling, filters were stored in sealed glass
10 jars in a freezer at 253 K.

2.3 Filter extraction

The filter extraction procedure is similar to that described by Moukhtar et al. (2011). Filters were spiked with approximately 4 µg each of three internal standards, 2-methylphenol, 2-methyl-3-nitrophenol and 2-methyl-5-nitrophenol. The concentrations
15 of 2-methylphenol, 2-methyl-3-nitrophenol and 2-methyl-5-nitrophenol in extracts of high volume filter samples without adding internal standards were consistently be-low the detection limit. For extraction, filters were immersed in acetonitrile (pesticide residue analysis grade from Sigma Aldrich) in amber glass jars and sonicated for 15 min. This was followed by filtration with a syringe equipped with a 0.2 µm PTFE
20 Chromspec filter and the sonication and filtration procedures were repeated three ad-ditional times. All extracts were collected in a round bottom flask and the volume was reduced by rotary evaporation. The sample extract was further blown down to a final volume of approximately 200 µL in a 5 mL conical vial.

HPLC separation was used to reduce interference from the complex matrix of the
25 sample. The HPLC (HP 1050) was equipped with a Supelco Supelcosil™ LC-18 col-umn with dimensions 25 cm × 4.6 mm and 5 µm packing size; the detector used was a variable wavelength detector (VWD) set to 320 nm. Solvent flow rate was constant

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at 1 mL min⁻¹, and the solvent gradient began with 100 % deionized Milli-Q water and linearly decreased to 45 % water and 55 % acetonitrile at 10 min. At 15 min, the mobile phase was 15 % water and 85 % acetonitrile and at 30 min the gradient ended with 100 % acetonitrile. The effluent fraction in the retention time window between 600 s and 1020 s, which contained the nitrophenols, was collected and was subsequently evaporated at room temperature to remove acetonitrile. It was then acidified to pH 2 with phosphoric acid and passed through a Waters Oasis HLB 3 cc solid phase extraction (SPE) cartridge. Prior to use SPE cartridges were conditioned with 1 mL of acetonitrile, followed by 1 mL of Milli-Q water. The target compounds were recovered with approximately 10 mL of acetonitrile.

This volume was reduced to approximately 0.5 mL on a rotary evaporator and was further evaporated at room temperature in a 5 mL conical vial to approximately 50 µL under a flow of nitrogen gas at approximately 200 mL min⁻¹. 20 µL of a volumetric standard containing heptadecane, octadecane and nonadecane was added to the sample, which was then divided in two approximately equal portions; one for concentration measurements and one for isotopic composition analysis.

2.4 Analysis

Prior to injection, samples were derivatized with derivatization grade bis(trimethylsilyl) trifluoroacetamide (BSTFA) from Sigma Aldrich (99.6 % purity). The mixture was stirred for 5 min at room temperature before transfer to autosampler vials for GC-MS or GC-IRMS analysis. For concentration measurements, 1 µL of the sample was injected into an HP 5890 Series II GC with an HP 5972 Series MS detector. Helium was used as a carrier gas and was kept at a constant flow rate of 2 mL min⁻¹. A SLB-5 ms column (60 m × 0.25 mm i.d. × 0.5 µm film thickness) was used. The injection port temperature was 538 K and the samples were injected splitless with a duration of the splitless mode of 60 s. The initial temperature of the oven was 373 K, which was held for 10 min. The temperature was ramped at 1 K min⁻¹ until 473 K, held for 1 min and ramped at

$10 \, \text{K min}^{-1}$ until reaching 553 K and held for 6 min. Each sample was typically analyzed twice using selective ion monitoring (SIM). The m/z monitored for standards and target compounds is listed in Table 1. The GC-MS was calibrated monthly by injecting 1 µL standards containing all target compounds and internal standards, ranging in concentration from 1 to 15 ng µL^{-1}. Each calibration mixture was run in random order, twice.

Samples that contained nitrophenols with concentrations greater than 1 ng µL^{-1} were analyzed with GC-IRMS. This setup (Fig. 1) included an electronically controlled heart split valve in the GC oven that directed the column effluent to the FID when the GC column's background was eluting or to the combustion furnace when target compounds were eluting to minimize contamination of the IRMS. For isotopic composition measurements, 3 µL of the derivatized sample was injected onto a SLB-5ms (60 m × 0.25 mm i.d. × 0.5 µm film thickness) column which had a helium carrier gas flow rate of 1 mL min^{-1}. The initial temperature of the oven was 373 K and held for 10 min. It was then ramped at $0.5 \, \text{K min}^{-1}$ until 423 K, then ramped at $5 \, \text{K min}^{-1}$ until 473 K and held for 1 min. It was finally ramped at $10 \, \text{K min}^{-1}$ until reaching the final temperature of 553 K and was held for 6 min. A calibration curve of the GC-IRMS was made in a similar way to GC-MS calibration, only injecting 3 µL of standards to increase the mass of carbon and therefore the signal.

The GC-combustion furnace interface was similar to that described by Matthews and Hayes (1978) with some modifications as described by Irei (2008). The temperature of the furnace was held at 1223 K and was used to combust eluting compounds to carbon dioxide and water. Water was removed by passing through a Nafion permeation dryer and the sample then proceeded to the IRMS for analysis. For calibration of the isotope ratio measurements, a carbon dioxide reference gas was injected several times directly for 30 s periods into the IRMS during the GC runs. The carbon isotope ratio of this carbon dioxide is traceable to the internationally accepted Vienna-Pee Dee Belemnite reference (Huang et al., 2012).

Masses 44, 45 and 46 were monitored by the IRMS for the analysis of $^{12}\text{C}^{16}\text{O}_2$ and its isotopologues. All peaks were evaluated based on peak boundaries that have

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been determined using measurements of standard mixtures. Allison's algorithm (1995), which is similar to the one used by Craig (1957), has been applied to correct the ^{17}O interferences in mass 45. NO_2, which also contributes to mass 46 and the addition of the trimethylsilyl (TMS) contribution from derivatization with BSTFA using Eq. (1) were also corrected by following a procedure described by Irei (2008). To correct for the change in carbon isotope ratio due to introducing a TMS group, compounds with known isotope ratios were derivatized and analyzed. The isotope ratio of underivatized phenols was calculated from the isotope ratios of the derivative and the TMS group using mass balance as follows:

$$\delta^{13}C_{free} = \frac{\#C_{deriv}}{\#C_{free}} \times \delta^{13}C_{deriv} - \frac{\#C_{TMS}}{\#C_{free}} \times \delta^{13}C_{TMS} \tag{1}$$

3   Results and discussion

3.1   Method validation

GC-MS calibration measurements generally had a better than 5 % relative standard deviation for repeat runs. The uncertainty of the slope of calibration curves for GC-MS measurements was, with very few exceptions, less than 5 %. For GC-IRMS measurements, the uncertainty of the calibration was typically between 5 % and 10 %. The regression coefficient (R^2) of the calibration curves was greater than 0.98 (Table 2). Peak areas for repeat measurements of extracts of ambient filters using GC-IRMS had relative standard deviations of approximately 5 %.

Several 20.32 cm × 25.4 cm and 47 mm baked quartz fiber filters were analyzed for blank values. Filters used for blank value determination were stored in the same manner as filters used for sampling. Filters were not spiked with internal standards but were extracted according to the described extraction procedure. Blank values and detection limits for each of the compounds for both filter sizes are presented in Table 3.

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The internal standards used were 2-methyl-3-nitrophenol and 2-methyl-5-nitrophenol and each consistently had recoveries from 50 % to 70 %. The average of the recoveries of the two internal standards was used to determine the recoveries of the target compounds. Blank filters spiked with target compounds and internal standards showed similar recoveries (Table 3). The cresols, 2-methylphenol and 4-methylphenol had, on average, low and highly variable recoveries, perhaps due to the high vapor pressure which can result in losses during the volume reduction steps.

3.2 Sampling efficiency of XAD-coated filters

Tests conducted by Busca (2010) showed that filters coated following exactly the procedure described by Gundel and Herring (1998) and Galarneau et al. (2006) had a collection efficiency of, on average, around 60 %, with significant variability between individual phenols (Fig. 2). Modifications to the method (Table 4) were made to improve nitrophenol collection efficiency. To increase the mass and surface area of XAD on filters, XAD was ground for a longer time period to decrease average particle size and the XAD concentration of the slurry used in the coating process was also increased.

Several tests were conducted to determine the efficiency of the XAD coated filters. To do so, two filters were sampled in series on high volume air samplers, with a stainless steel mesh in between, at a flow rate of 0.65 or 1.13 m^3 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. 2. 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. 2).

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3.3 Isotope ratio measurements

The carbon isotope ratio of the TMS group was derived from analysis of standards of phenols with known isotope ratios by using carbon isotope mass balance, Eq. (1) (Fig. 3). Averaging over the different compounds, the delta value of the TMS group was found to be −48 ± 0.1 ‰.

The result of GC-IRMS isotope ratio measurements for varying masses of phenols injected showed that isotopic composition could be measured accurately within approximately 0.2 ‰ for compounds that had 5 ng or more per 3 µL injection (Fig. 4). At lower concentrations, the isotopic composition of each compound showed larger variations. Although there is an indication that for samples containing less than 3.4 ng of phenols the measured isotope ratios were on average lower than the offline value. This difference is statistically insignificant due to the higher variability of measurements in this mass range. Nevertheless, for injected samples containing more than 1.7 ng of phenols the difference between offline and online values never exceeded 0.6 ‰.

The measured isotope ratio for standards spiked on filters or injected directly into the GC-IRMS were identical within the uncertainty of measurement (Table 5). Offline and online measurements agreed within the uncertainty of the GC-IRMS measurements. Furthermore, the isotopic composition of internal standards that were spiked on the filter prior to filter extraction was very similar to offline determined values (Table 6) and the very small differences did not exceed the reproducibility of the measurements.

For 11 filter pairs collected in series, the extract of the second filter had sufficiently high concentrations (0.2–7 ng µL^{-1}) to allow isotope ratio measurements for 4-nitrophenol and 2-methyl-4-nitrophenol. The lower end of the concentrations is below the range for which the GC-IRMS isotope ratio measurement results agree with the offline data within 0.2 ‰ (Fig. 4) and therefore the analysis of the second filters may have higher uncertainty and possibly be biased. Nevertheless, the average difference and standard deviation of the differences in the delta values for 4-nitrophenol and 2-methyl-4-nitrophenol between the first and second filter was only 0.59 ± 0.28 ‰ and

0.27 ± 0.16 ‰, respectively. Using an average breakthrough of around 20 %, the maximum bias of isotope ratios for phenols collected on the first filter can be estimated using a simple isotope mass balance to 0.2 ‰ for 4-nitrophenol and 0.1 ‰ for 2-methyl-4-nitrophenol. The reproducibility of isotope ratio measurements was derived from repeat measurement of samples and standards as well as four repeat measurements of two filter extracts. The standard deviations were consistently in the range of 0.2–0.3 ‰ (Table 7).

Although the final volume of the extract as well as the recovery somewhat varies, it is possible to estimate the atmospheric phenol concentrations which will give meaningful isotope ratio measurements from typical sample volumes and average recoveries and final extract volumes. Based on an average recovery of 60 %, a volume of the final extract (including volumetric standard and derivatization reagent) of less than 100 μL, a sample air volume of $1627\,m^3$ (24 h of high volume sampling) and an 80 % sampling efficiency, it is estimated that isotope ratio measurements can be conducted with a precision of 0.3 ‰ or better for phenols with atmospheric concentrations exceeding $0.1\,ng\,m^{-3}$, which is comparable to the lowest concentration of 2-methyl-4-nitrophenol that was successfully analyzed for these measurements.

3.4 Ambient measurements

Results for filters sampled using high volume air samplers at York University from September to December 2011, are presented in Figs. 5 and 6. Only isotope ratios for those compounds that had more than 5 ng per 3 μL injection and had no overlap in the chromatogram are included. For 4-methyl-2-nitrophenol and 3-methyl-4-nitrophenol, only 2 and 3 samples, respectively, out of 12 filters, had enough mass for isotope ratio measurements.

Toluene, thought to be the precursor for the methyl nitrophenols, was found to have an average ambient isotope ratio of −24.8 ‰ in Toronto (Kornilova, 2012), with toluene source signatures being approximately −28 to −27 ‰ (Rudolph et al., 2002). The average isotopic composition of the nitrophenols measured in this study is approximately

4–5 ‰ lighter than that of the precursors. These ambient results are consistent with predictions from laboratory studies (Irei, 2008; Irei et al., 2011) in which the isotope ratio of toluene, as well as that of the sum of all products was monitored over the course of the photooxidation reaction. Similar measurements were made at York University by Moukhtar et al. (2011) for nitrophenols in ambient particulate matter. Although the limited number of these measurements was very small, the observed delta values of 2-methyl-4-nitrophenol were within a range from −32.9 to −31.6 ‰ for 5 samples and are comparable to this study. The difference in isotope ratio between precursor and product, along with evidence from laboratory studies, supports the hypothesis that these compounds are indeed formed through secondary processes and are not primary emissions.

4 Summary and conclusions

A method has been developed to determine compound specific carbon isotope ratios of atmospheric phenols in the gas phase and PM. Quartz fiber high volume filters coated by a procedure derived from methodology used to coat low volume filters have been found to be efficient for the collection of nitrophenols in PM and in the gas phase together. The developed sampling, extraction and extract processing procedure creates no detectable bias of the carbon isotope ratio. For atmospheric concentrations exceeding $0.1\,\mathrm{ng\,m^{-3}}$ the estimated accuracy is better than 0.3 ‰.

It has also been validated that concentrations in the range of $\mathrm{pg\,m^{-3}}$ can be detected for concentration measurements. Nevertheless, for most atmospheric conditions, low volume filter sampling will be sufficient and only for extremely low atmospheric phenol levels should high volume filter sampling be necessary for concentration measurements. However, with the exception of extremely high levels of atmospheric phenols, low volume filter sampling would not allow to collect sufficient phenol masses for accurate isotope ratio measurements.

The newly developed methodology has been successfully applied to conduct atmospheric measurements at a suburban location in a major metropolitan area (northern edge of Toronto, Canada). For the most abundant nitrophenols (4-nitrophenol and 2-methyl-4-nitrophenol) accurate isotope ratio measurements were possible for 21 out of 22 collected filter samples. Ambient results suggest that the phenols analyzed are dominantly formed from secondary processes. For several of the studied phenols the observed atmospheric variability of carbon isotope ratios is more than an order of magnitude larger than the precision of the measurement. The sampling and sample processing method presented can potentially be applied to other atmospheric sVOC and SOA to obtain samples that can by analyzed by GC-IRMS.

In several samples the mass of certain nitrophenols collected was not sufficient for accurate carbon isotope ratio analysis. In principle, it should be possible to reduce the current limit of approximately $0.1\,\mathrm{ng\,m^{-3}}$ by increasing the volume of air sampled, using injections larger than $3\,\mu\mathrm{L}$ for GC-IRMS analysis or further reducing the final volume of the extract. However, tests to determine sampling efficiency, recovery and possible bias for such modified procedures have not yet been conducted.

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Table 1. Description of standards used; all standards were 97 to 99.8 % purity and were purchased from Sigma Aldrich or Supelco.

Standard	Abbreviation	Retention time window (min)	m/z monitored in SIM
2-methylphenol[a]	2-me-ph	15–55	210, 165
4-methylphenol	4-me-ph	15–55	210, 165
4-methyl-2-nitrophenol	4-me-2-NP	55–80	225, 210, 165
4-nitrophenol	4-NP	55–80	211, 196, 150
2-methyl-3-nitrophenol[a]	2-me-3-NP	55–80	225, 208, 165
2-methyl-5-nitrophenol[a]	2-me-5-NP	55–80	225, 210, 165
3-methyl-4-nitrophenol	3-me-4-NP	55–80	225, 210, 165
2-methyl-4-nitrophenol	2-me-4-NP	55–80	225, 210, 165
2,6-dimethyl-4-nitrophenol	2,6-dime-4-NP	80–125	239, 224
heptadecane[b]	C17	80–125	85
octadecane[b]	C18	80–125	85
nonadecane[b]	C19	80–125	85

Nitrophenols listed are target compounds, with exceptions: [a] used as internal standards; [b] used as volumetric standards

Table 2. Slope, error of the slope and regression data from typical GC-MS and GC-IRMS calibration curves of target compounds, internal standards and volumetric standards. Units of slope and error of slope are counts ng^{-1} µL.

Compound	GC-MS			GC-IRMS		
	Slope	Error of slope	R^2	Slope	Error of slope	R^2
2-me-ph	6.96E5	1.4E4	1			–
4-me-ph	1.06E6	4.0E4	1			–
4-me-2-NP	3.19E5	2.1E4	0.99	9.10E5	4.3E4	1
4-NP	4.61E5	1.6E4	0.99	8.88E5	5.0E4	0.99
2-me-3-NP	1.95E5	0.6E4	1	1.20E6	7.7E4	1
2-me-5-NP	3.78E5	1.5E4	0.99	1.63E6	8.4E4	0.99
3-me-4-NP	2.82E5	1.2E4	0.99	1.48E6	6.7E4	1
2-me-4-NP	3.46E5	1.3E4	0.98	1.66E6	7.1E4	0.99
2,6-dime-4-NP	2.97E5	1.3E4	0.98	2.14E6	1.0E5	0.99
C17	1.52E5	0.5E4	1	3.40E6	2.2E5	0.98
C18	1.50E5	0.4E4	1	4.73E6	3.0E5	0.99
C19	1.47E5	0.4E4	1	5.15E6	3.3E5	0.99

Table 3. Averages and standard deviations for phenols from XAD-4™ blank filter extractions. The calculation of blanks and detection limits as atmospheric concentrations are based on $1627\,m^3$ for high-volume air sampling, and $26\,m^3$ for low-volume air sampling. Recoveries shown are for blank filters spiked with approximately $4\,\mu g$ of each compound.

| Compound | Blank | | Detection limit | | | Recoveries (%) |
	Average mass of blank (ng)	Standard deviation of blank (ng)	Mass (ng)	High volume air sampler $(ng\,m^{-3})$	Low volume air sampler $(ng\,m^{-3})$	
2-me-ph	3.3	2.5	7.5	0.002	0.1	13 ± 8
4-me-ph	7.1	3.4	10	0.002	0.1	64 ± 53
4-me-2-NP	4.5	5.2	16	0.003	0.2	63 ± 26
4-NP	7.0	7.3	22	0.005	0.3	70 ± 3
2-me-3-NP	2.3	1.7	5.1	0.001	0.1	59 ± 11
2-me-5-NP	0.48	0.36	1.1	0.0002	0.01	61 ± 12
3-me-4-NP	3.9	3.9	12	0.002	0.2	63 ± 19
2-me-4-NP	2.5	2.7	8.1	0.002	0.1	71 ± 6
2,6-dime-4-NP	2.4	2.0	6.0	0.001	0.1	90 ± 12

Table 4. Average standard deviations for phenols from repeat runs of calibration standards and ambient samples.

Compound	σ_{avg} (‰)
4-me-2-NP	0.31
4-NP	0.27
2-me-3-NP	0.27
2-me-5-NP	0.19
3-me-4-NP	0.30
2-me-4-NP	0.26
2,6-dime-4-NP	0.31

Table 5. Summary of modifications of the filter coating procedure.

	Gundel and Herring (1998) and Galarneau et al. (2006)	This work
Grinding time	17 h	34 h
XAD slurry concentration	$6.5\,g\,L^{-1}$	$10.5\,g\,L^{-1}$
Average XAD mass on $20.32\,cm \times 25.4\,cm$ quartz filter	$0.09 \pm 0.04\,g$	$0.63 \pm 0.1\,g$

Table 6. Accuracy of GC-IRMS; online values are averaged over 10 points for each compound ± the error of the mean. Values are for injected masses between 2 ng and 55 ng.

Compound	Offline value (‰)	Online value (calibration standard) (‰)	Online value (spiked filter) (‰)
4-me-2-NP	−26.9[a]	−27.0 ± 0.3	–
4-NP	−28.9	−28.9 ± 0.3	−28.5 ± 0.4
2-me-3-NP	−26.7[a]	−26.7 ± 0.2	−26.8 ± 0.4
2-me-5-NP	−27.2[a]	−27.3 ± 0.2	−27.3 ± 0.3
3-me-4-NP	−25.7[b]	−25.6 ± 0.1	−25.5 ± 0.2
2-me-4-NP	−27.4[a]	−27.5 ± 0.3	−27.5 ± 0.1
2,6-dime-4-NP	−29.0[b]	−29.0 ± 0.2	–

[a] measured by Moukhtar et al. (2011);
[b] measured by Irei (2008)

Table 7. Average online delta values of ambient filters spiked with internal standards prior to extraction, ± the standard deviation based on 23 measurements.

Internal standard	Offline value (‰)	Online value (‰)
2-me-3-NP	−26.7	−26.6 ± 0.2
2-me-5-NP	−27.2	−27.2 ± 0.2

Carrier Gas
Inlet

H$_2$

Heart
Split Valve

FID

Air

N$_2$

SLB-5ms
Column

Make-
up He

0.52mm x 13 cm

Pigtail
0.20mm x 200 cm

He/O$_2$ supply

0.32mm x 16 cm

Nafion
Tubing

Valco
Valve

0.15mm x 200

45 cm
Furnace

0.3mm x 25 cm

SS T Piece

SS T Piece

0.32mm x 26 cm

0.18mm x 100 cm

IRMS

Swagelok
On/Off Valve
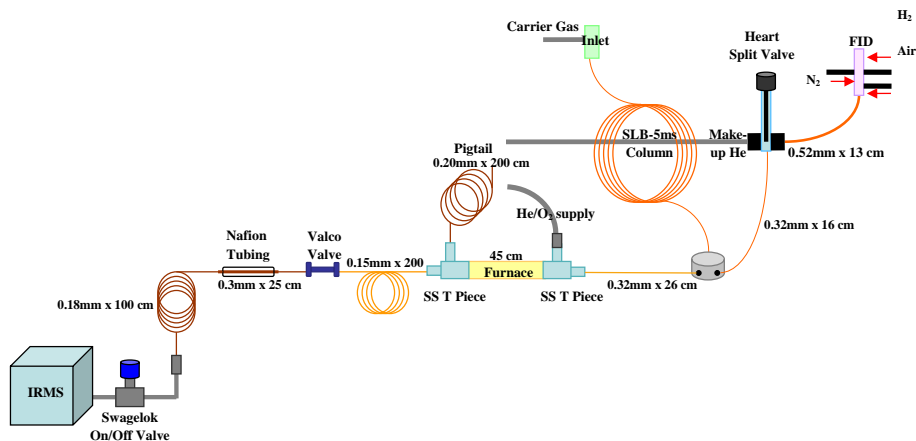
Fig. 1. Schematic of GC-IRMS setup.
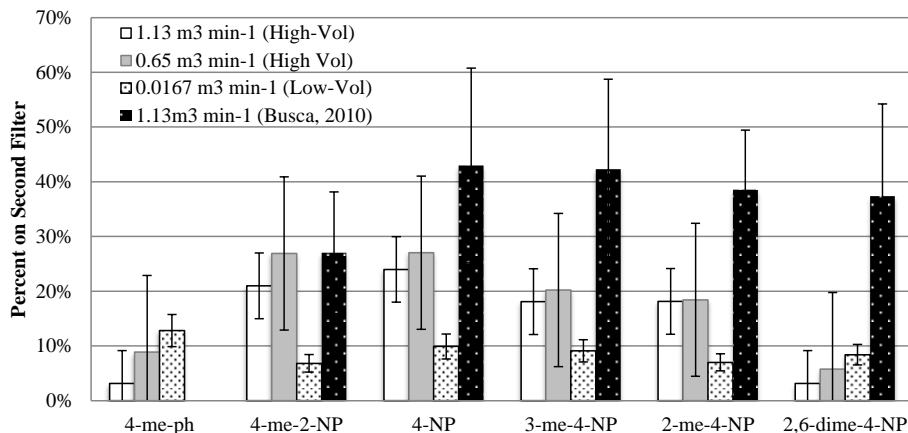
Fig. 2. Efficiency of XAD coated filters; filters were sampled in series with a stainless steel mesh placed in between. Error bars represent the error of the mean. The results from Busca (2010) were obtained using filters coated by the method of Gundel and Herring (1998) and Galarneau et al. (2006). The other results are from this work using a modified coating procedure (Table 4).
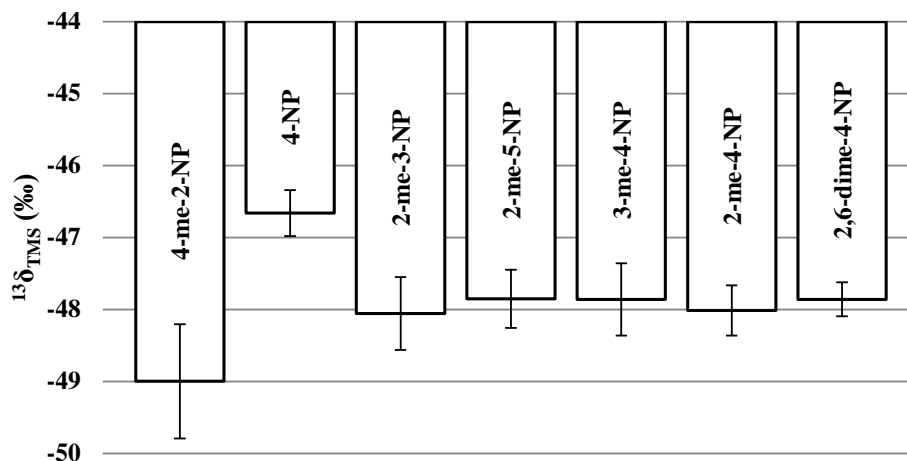
Fig. 3. Isotopic composition of TMS group found by injecting various derivatized compounds. The error bars represent the standard deviations based on an average of 5 measurements for each phenol.

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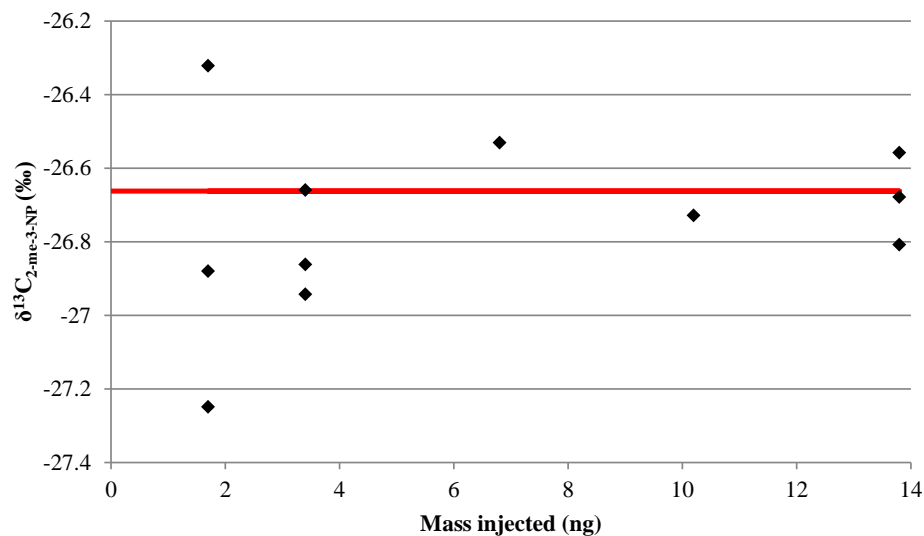
Fig. 4. Changes in the delta value of 2-me-3-NP as a function of mass injected; the red line indicates the offline value of 2-me-3-NP (-26.7‰). Average delta values and standard deviations for data points at 1.7 ng, 3.4 ng and 13.7 ng, are -26.8 ± 0.5‰, -26.8 ± 0.1‰ and -26.7 ± 0.1‰, respectively.
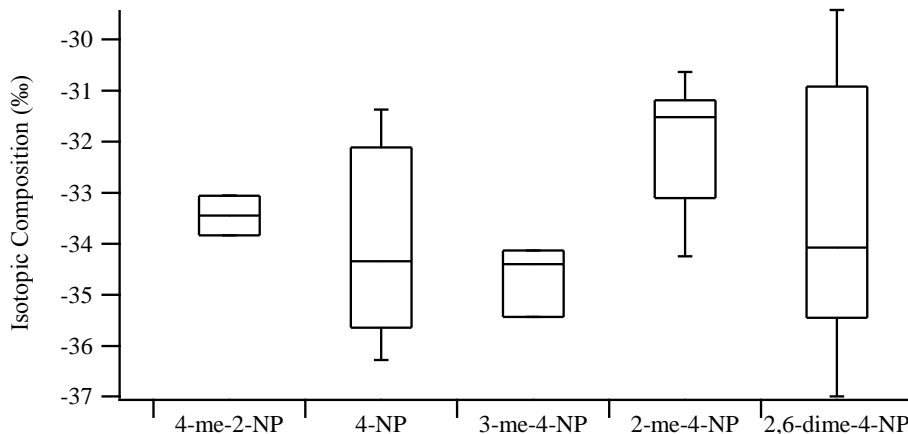
Fig. 5. Box and whisker plot of isotopic composition for the target compounds in ambient air. Error bars represent 90th and 10th percentiles while the upper and lower ends of the box represent the upper (75th) and lower (25th) percentiles; the median is the horizontal line.
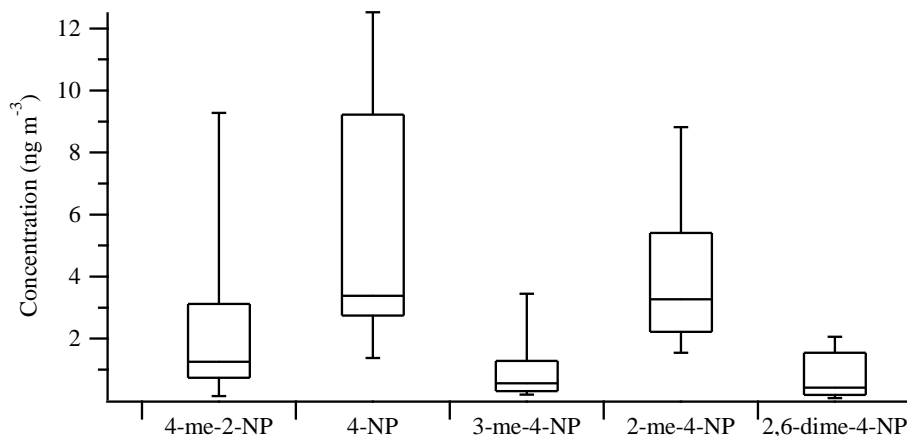
Fig. 6. Box and whisker plot of concentrations for each of the target compounds in ambient air for all samples. Error bars represent 90th and 10th percentiles while the upper and lower ends of the box represent the upper (75th) and lower (25th) percentiles; the median is the horizontal line.