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Atmospheric Measurement Techniques Discussions

Method for determination of stable carbon isotope ratio of methylnitrophenols in atmospheric PM

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Abstract

A technique for the measurement of the stable isotope ratio of methylnitrophenols in atmospheric particulate matter (PM) is presented. It has been found in numerous laboratory studies that these compounds are photooxidation products of toluene in PM. Atmospheric samples from rural and suburban areas were collected for evaluation of the procedure. PM was collected on quartz fibre filters using dichotomous high volume air samplers for PM 2.5. Methylnitrophenols were extracted from the filters using acetonitrile. The sample was then purified using a combination of high-performance liquid chromatography (HPLC) and solid phase extraction (SPE). The final solution was then divided into two aliquots. To one aliquot, a derivatising agent, Bis(trimethylsilyl)trifluoroacetamide (BSTFA), was added to the solution for Gas Chromatography/Mass Spectroscopy (GC/MS) analysis. The second half of the sample was stored at low temperature. When GC/MS analysis showed high enough concentrations the remaining sample was derivatized with BSTFA and analysed for stable isotope ratio using a Gas Chromatography/Isotope Ratio Mass Spectrometry (GC-IRMS).

In all atmospheric PM samples analysed, 2-methyl-4-nitrophenol was found to be the most abundant methylnitrophenol. Nevertheless, due to low pollution levels occurring in the rural area, no samples had concentrations high enough to perform stable carbon isotope composition measurements of the methylnitrophenols. Samples collected in the suburban area could be analysed for carbon stable isotope ratio using GC-IRMS.

The procedure described in this paper provides a very sensitive and selective method for the analysis of methylnitrophenols in atmospheric PM at concentrations as low as 1 pg m^{-3}. For accurate (within ±0.5‰) stable isotope ratio analysis significantly higher concentrations in the range of 100 pg m^{-3} or more are required.

1 Introduction

Particulate matter (PM) pollution has recently received much interest because of its significant impact on human health as well as climate change and local visibility (Thurston et al., 1994; Ramanathan et al., 2001; Anderson et al., 2003). Despite the well-known importance of PM, the mechanisms and processes which determine the atmospheric levels of PM are not well understood. Especially the origin of the organic fraction of atmospheric PM particulate organic matter (POM), which contributes typically in the range of 30–50 % to atmospheric PM (Blanchard et al., 2002), is only poorly understood. A significant source of secondary PM is the atmospheric degradation of man-made volatile organic compounds (VOCs) such as benzene, toluene and other alkyl-benzenes, as well as heavier alkenes and a variety of compounds emitted from vegetation, such as terpenes. There are numerous uncertainties in quantitative understanding of the formation rate and efficiency of atmospheric POM (Pandis et al., 1992; Turpin et al., 2000; Tsigaridis et al., 2003). One of the main sources of uncertainty is the extrapolation of laboratory experiments, which are typically conducted at high pollutant concentrations, to ambient conditions. Simulating ambient conditions is very difficult due to the complex chemical reactions and physical processes that occur in the real atmosphere as well as the technical difficulties resulting from conducting laboratory studies at low pollutant concentrations. The novel aspect of this project is the inclusion of stable carbon isotope composition measurements. It has been suggested that a combination of isotope ratio and concentration measurements of precursors and products can help to improve our understanding of the relation between laboratory studies (Irei et al., 2006; Irei, 2008) and ambient observations.

In this study, we focused on the measurement of methylnitrophenol concentrations and stable isotope ratios in ambient PM. Phenols and related substances are of interest not only due to their toxicity, but also due to the fact that they can be formed in the atmosphere from VOCs in the gas phase. There have been a substantial number of studies examining the yield of methylnitrophenols in POM resulting from toluene

degradation in smog chambers (Forstner et al., 1997; Jang et al., 2001; Hamilton et al., 2005). Methylnitrophenols have also been measured in atmospheric PM.

The method developed in this study was used to analyze samples from rural and suburban areas. The samples were collected during the Border Air Quality Study (BAQS) campaign which took place in June and July 2007 in Southern Ontario (Canada), close to the US border. Samples were also collected in a suburban, mixed residential and industrial area (York University, Toronto, Canada).

2 Materials and method

2.1 Sampling

PM (diameter <2.5 µm) was collected on 8x10 inch quartz fiber filters (Pallflex membrane filters – 2500QAT – PallGelman Sciences) using high volume air samplers (TE-6070-BL PM2.5 Tisch Environmental, Inc.) equipped with PM 2.5 heads. The average flow rate was 1.13 $m^3\,min^{-1}$. Filter collection took place during the BAQS campaign in June and July 2007. Each sample was collected for an average of three days on two different sites: Ridgetown and Harrow (Ontario, Canada).

Ridgetown (42°36′ N, 81°53′ W, elevation 212 m) is a small city with a total population of about 3400 people. It is located away from industrial centres (London and Windsor, ON), about six km south of McDonald-Cartier Freeway, and seven km north of Lake Erie; surrounded mainly by agricultural fields and local roads. The sampling site was set up on the Ridgetown campus of Guelph University. There were no large point sources of the major trace gases, industrial complexes, or neighboring cities with high population, thus this site was considered as a rural site.

Harrow (42°02′ N, 82°55′ W, elevation 191 m), a town of around 3000 people was chosen to be representative for a semi-rural area due to its closeness (approximately 40 km) to two major cities (Windsor and Detroit) with a total population close to a million people. The sampling site was located in an open field surrounded by farm land and local roads.

Some samples were also collected in 2007 and 2008 on the roof of a parking garage at York University in Toronto, Canada. York University is located in a mixed industrial -residential area at the northern edge of Toronto (2.6 million inhabitants) about 15 km from the downtown business area and Lake Ontario. North of York University is the regional municipality of York (≈1 million inhabitants). A map indicating the sampling locations is shown in Fig. 1.

Following sampling, filters were stored at 253 K in glass jars. Prior to sampling, new filters were baked under synthetic air at 1073 K for 48 h in a large chamber muffle furnace (Fisher Scientific Model 550-58, Napanee, Ontario, Canada) to remove organic contaminants.

2.2 Reagents and standards

Standard and stock solutions of 2-methyl-4-nitrophenol (97 %, CAS: 99-53-6, Sigma-Aldrich), 4-methyl-2-nitrophenol (98 %, CAS: 119-33-1, Sigma-Aldrich), 2-methyl-5-nitrophenol (97 %, CAS: 5428-54-6, Sigma-Aldrich), 2-methyl-3-nitrophenol (98 %, CAS: 5460-31-1, Sigma-Aldrich) and heptadecane (99 %, CAS: 629-78-7 Sigma-Aldrich) were prepared by diluting approximately 10 mg of each pure compound in 100 ml of acetonitrile (CHROMASOLV® Plus, for HPLC, ≥99.9 %) in 120 ml brown glass vials. These stock solutions were prepared monthly. Solutions with lower concentrations (between 0.8 and 30 ng μl^{-1}) were prepared by diluting the stock solutions in acetonitrile. The chemicals as well as the derivatisation agent BSTFA (CAS:25561-30-2, Regis technology) were of the highest purity commercially available and were used without further purification.

2.3 Extraction procedure

The extraction method was based on the one devised by Rudolph and Stupak (2002), but in order to be applicable to stable isotope ratio analysis of nitrophenols at extremely low trace levels several changes were made. Following sample collection two Internal

Standards (IS), were spiked on the filter. The filter was then cut in several pieces and introduced into a glass jar. The filter pieces were fully immersed in acetonitrile (approximately 20 ml) and the jar was placed in an ultrasonic bath (Bransonic Ultrasonic Cleaner, Model SS10R-DTH) for 15 min. The liquid phase was removed using a Pasteur pipette and loaded into a syringe equipped with a 45 µm-pore-diameter PTFE Chromspec filter. This procedure was repeated three times.

The combined liquid phases of approximately 50 ml were evaporated to a volume of a few milliliters under vacuum at a temperature of 315 K using a rotary evaporator. The volume of the solution was then further reduced under a stream of pure nitrogen and mechanical stirring to 200–300 µl. The concentrated solution was injected into a HPLC (Hewlett Packard 1050) and separated on a Supelco Supelcosil LC-18 column (5 µm particles size, L 25 cm, I.D. 4.6 mm). A Variable Wavelength Detector (VWD) wavelength was set to 320 nm to monitor the elution of nitrophenols. Solvent flow rate was 1 ml min^{-1}. A linear solvent gradient was used, starting with 100 % water (deionized milli Q-water, 18 Ω) and ending after 30 min with 100 % of acetonitrile.

The eluent fraction containing the target compounds and IS was collected during a specified time window into a glass flask. The volume of the collected solution (several millilitres containing approximately equal amounts of acetonitrile and water) was reduced by half using a rotator evaporator. During volume reduction temperature of the solution was kept between 278 and 283 K. The remaining solution was acidified with H_3PO_4 so that the final pH was around 2. This solution was then subjected to solid phase extraction (SPE) using Waters Oasis HLB cartridges. Prior to their use, the SPE cartridges were conditioned by rinsing with 1 ml of methanol followed by 1 ml of milli-Q water. The acidified solution was then passed through the cartridge. A few millilitres of milli-Q water were dispensed into the flask, acidified with H_3PO_4 to a pH of 2 and also passed through the cartridge. For recovery of the methylnitrophenols, the SPE cartridge was extracted with approximately 10 ml of acetonitrile. The eluent was collected in a flask and evaporated using a rotary evaporator until the solution was approximately 1 ml. The solution was then transferred into a conic vial and reduced under a flow of

nitrogen and mechanical stirring to a final volume of approximately 100 µl. The flask was rinsed several times with acetonitrile which was then added to the conic vial before the final volume reduction step.

20 µl of an Internal Standard for Recovery Control (ISRC) was added to the final solution. Half of the solution was saved in a glass vial and stored at 253K for stable isotope ratio analysis. The other half of the solution was derivatized by adding 10 µl of BSTFA (Fig. 2). 1 µl of this final derivatized solution was injected splitless into a GC-MS (HP 5890 Series II GC, equipped with an HP 5972 Series MS detector) equipped with DB-5MS column (60 m × 0.25 mm i.d. × 1 µm film thickness).

The initial temperature of the GC column was held at 373 K for 10 min then programmed to 453 K at 10 K min^{-1}, to 493 K at 1 K min^{-1} and to 553 K at 4 K min^{-1}. The final temperature, 553 K, was held for 6 min. Helium was used as carrier gas at a flow rate of 2 ml min^{-1}.

Typically each sample was analyzed three times using selective ion monitoring (SIM), using three characteristic *m*/*z* values as well as one run in scanning mode. Methylnitrophenol concentrations were determined from the SIM chromatograms.

When SIM chromatograms showed methylnitrophenols concentrations greater than 1 ng µl^{-1} and total ion current chromatograms from the scanning mode runs showed no overlapping for the target compounds, the remaining fraction of the samples were analyzed for stable carbon isotope ratios. In this case, the stored solution was concentrated to a few microliters, derivatized using BSTFA and analyzed with an online GC/IRMS (Finnigan, MAT 252) instrument at the Environment Canada (Toronto, Canada). The GC (Varian 3600) was equipped with a DB-5MS column (60 m × 0.25 mm i.d. × 1 µm film thickness). The temperature program was similar to the one used for the GC-MS measurements. The column was connected to a combustion interface that converts the organic components in the column effluent to carbon dioxide and water. The design of the interface was very similar to that described by Matthew and Hayes (1978) and was modified (Irei, 2008) for methylnitrophenol analysis. After removal of water by a Nafion permeation dryer, about 0.5 ml min^{-1} of the carrier gas was transferred via an

open split and a fused silica restriction capillary to the ion source of the isotope ratio mass spectrometer. For calibration of the isotope ratio measurements a reference gas containing carbon dioxide with a known $^{13}C/^{12}C$ ratio (traceable to V-PDB) was added via an open split for 20s at different times during the analysis.

Through testing different target compounds, IS, ISRC, varying HPLC collection windows as well as changing the GC column type, a procedure suitable for isotope ratio analysis was developed. The specifics of the procedures are summarized in Table 1. 2-Methyl-4-nitrophenol and 4-methyl-2-nitrophenol have been chosen as target compounds as they were the most abundant nitrophenols measured in atmospheric PM samples.

IS, 2-methyl-5-nitrophenol and 2-methyl-3-nitrophenol, were selected for their structural similarities with the target compounds and their comparable behaviour during extraction. Moreover, in measurements without adding these IS none of these compounds have been detected in atmospheric PM samples collected at York University.

3 Calibration and method validation

3.1 GC-MS system

Calibrations of the GC-MS system were performed at eight concentration levels ranging from 0.8 to 30 ng µl^{-1} with three repeat measurements for each level (Fig. 3). The average relative standard deviation of repeat measurements was less than 5 %.

The extraction procedure was applied to three blank quartz filters and to one field blank filter. The field blank filter was transported to the BAQS field site and handled in the same way as the other filters but no PM were collected on this filter. Target compounds as well as IS were never detected in these blank filters. Quantitative detection limits for methylnitrophenols were calculated using baseline noise from chromatograms of blank filter extracts. Using SIM mode the average detection limit was 5 pg µl^{-1}. For an average of three days of sampling with a flow rate of 1.13 m^3 min^{-1}, a volume of 100

µl for the processed filter extract, and a recovery of 40 % for the extraction procedure (see below) this corresponds to detection limits of approximately 0.3 pg m^{-3} of air.

Recovery of the method was tested by spiking 1 or 4 µg of each target compound and IS on a quartz filter before extraction. Two different types of tests were performed, in one set methylnitrophenols were spiked on clean, pre-baked filters and in another set on filters on which PM2.5 had been collected for 3 days.

The recovery for each IS was consistently between 35 and 50 % of whichever the mass spiked on the filter was (Table 2). Using the average recovery for these two IS, the target compound masses were calculated and compared to the spiked mass. As can be seen from Table 2, with very few exceptions the recovery relative to the IS was quantitative within 10 %. For 4-methyl-2-nitrophenol, the average IS corrected recovery was 92 ± 9 %. Although this average value is only slightly below 100 % and within the estimated range of uncertainty for recovery, this has been taken into account when calculating its mass for ambient samples. No correction was made for 4-methyl-2-nitrophenol since any correction would have been well below the reproducibility of the measurements.

In order to determine the recovery for individual steps of the procedure, different methylnitrophenols were added at several stages of the sample preparation procedure. 2-methyl-3-nitrophenol was spiked on the clean filter before extraction. 3-methyl-2-nitrophenol was added to the solution before HPLC separation and 4-methyl-2-nitrophenol was added to the solution collected from the HPLC. 2-methyl-5-nitrophenol was spiked to the solution just before the solid phase extraction and 2-methyl-4-nitrophenol was spiked before the final volume reduction step. The results of this test are presented in Table 3.

3.2 GC-IRMS measurements

Stable carbon isotope ratios are generally measured and calculated in the form of relative differences between the sample and a reference standard ($\delta^{13}C$). Changes in

isotopic composition are usually small; they typically are given in permil (1).

$$\delta^{13}C(‰) = (C_{13}/C_{12} - {}^{ref}C_{13}/{}^{ref}C_{12})/({}^{ref}C_{13}/{}^{ref}C_{12}) \times 1000 \quad (1)$$

Here C_{13} and C_{12} denote the abundance of different isotopes in the studied compound, and ^{ref}C is the reference standard which is traceable to Peedee belemnite.

To determine the carbon stable isotope ratio of methylnitrophenols analyzed with GC-IRMS, Masses 44 ($^{12}C^{16}O_2$), 45 ($^{13}C^{16}O_2$ and $^{12}C^{17}O^{16}O$) and 46 ($^{12}C^{18}O^{16}O$) were monitored and stored for subsequent evaluation of the chromatograms. The areas of the chromatographic peaks for masses 44, 45 and 46 were determined manually. The $^{13}C/^{12}C$ ratio was calculated from the mass 45/44 ratio after applying a small correction for the ^{17}O contribution to the mass 45 following the procedure suggested by Craig (1957).

The correction procedure has been slightly modified to avoid biased correction due to the contribution of NO_2 to *m*/*z* 46. An additional correction was applied to correct for the change in stable carbon isotope ratio resulting from the derivatisation. Since the reaction between BSTFA and methylnitrophenol occurs by breaking the O-H bond in methylnitrophenol, isotopic carbon fractionation due to the reaction will be negligible. However, the addition of three carbon atoms to the methylnitrophenols induces a change in the isotopic composition which has to be corrected using mass balance.

$$\delta^{13}C_{free} = \frac{\#C_{deriv}}{\#C_{free}} \times \delta^{13}C_{deriv} - \frac{\#C_{TMS}}{\#C_{free}} \times \delta^{13}C_{TMS} \quad (2)$$

$\#C_{deriv}$, $\#C_{free}$ and $\#C_{TMS}$ are the number of carbon atoms in the derivative, free methylnitrophenol and the trimethylsillyl (TMS) group, respectively. $\delta^{13}C_{deriv}$ and $\delta^{13}C_{TMS}$ are the stable carbon isotope ratio of derivatized methylnitrophenol and the TMS group. $\delta^{13}C_{free}$, represents the stable carbon isotope ratio of underivatized methylnitrophenols.

In order to determine the carbon isotope ratio of the TMS group solutions with high concentrations of methylnitrophenols (between 15 and 35 ng μl^{-1}) were prepared from

pure methylnitrophenols. The stable carbon isotope ratios of the bulk methylnitrophenols were determined by off-line combustion of pure substances and subsequent dual-inlet analysis of the carbon isotope ratio of the formed CO_2. In total twelve standard solutions were analysed by GC-IRMS. For each compound, $\delta^{13}C_{TMS}$ was calculated using mass balance (Eq. 2) and the $\delta^{13}C_{free}$ value from the off-line measurements. The stable isotope ratio of the derivative compounds $\delta^{13}C_{deriv}$ as well as the stable isotope ratio calculated for the derivatisation agent $\delta^{13}C_{TMS}$ are summarized in Table 4 for each standard solution. Since there is no significant difference between $\delta^{13}C_{TMS}$ values derived from different methylnitrophenols, an overall average of -45.31 ± 0.07‰ (standard deviation of 0.51‰) was used in the following calculations to determine the free nitrophenol isotope ratios using mass balance (Eq. 2).

To check GC-IRMS stability and to verify absence of isotope fractionation during GC-IRMS analysis, low concentration standards (from 1 to 20 ng µl^{-1}) were injected into the instrument before and after samples analysis. The average relative standard deviation of repeat isotopic ratios measurements was less than 0.2‰. The observed difference between the measured and the reference $\delta^{13}C$ values (offset) was nearly always less than ±0.5‰, even for concentrations as low as 1 ng µl^{-1} (Fig. 4).

To evaluate possible isotopic fractionation that may occur during extraction, one microgram of each target compound was spiked on two blank filters. These filters were then extracted following the normal procedure and the carbon isotopic composition of these extracted methylnitrophenols was measured and compared with offline analysis (Table 5). No detectable isotopic fractionation occurred during the extraction and clean-up procedure as the online measurements of extracted compounds are similar to the offline values within better than 0.5‰.

4 Results of ambient measurements

4.1 Concentration of methylnitrophenols in atmospheric PM

The results of the analysis of filters collected during the BAQS campaign are summarized in Table 6 and the results for filters collected at York University in Table 7. For all samples from BAQS, methylnitrophenol concentrations were very low and could only be determined reliably using selective ion chromatograms. The average recovery calculated for both IS in these extractions was 46 ± 5 %.

The average concentrations were 11.5 ± 2.8 pg m^{-3} and 4.7 ± 1.4 pg m^{-3} for 2-methyl-4-nitrophenol and 4-methyl-2-nitrophenol, respectively, in PM collected at Ridgetown. In PM collected at Harrow, the concentrations were on average very similar, 14.8 ± 3.7 pg m^{-3} and 6.0 ± 1.8 pg m^{-3} for 2-methyl-4-nitrophenol and 4-methyl-2-nitrophenol, respectively. The concentrations of 2-methyl-4-nitrophenol at York University were on average 144 ± 60 pg m^{-3}, approximately an order of magnitude higher than at Harrow and Ridgetown. This is consistent with the expectation of higher levels of pollutants at York University due to its location at the edge of a city of several million inhabitants.

4.2 Stable isotope ratios measurements

For five of the samples collected at York University stable carbon isotope ratio measurements for the most abundant target compound, 2-methyl-4-nitrophenol, was possible (Table 8). For these samples, no overlapping between 2-methyl-4-nitrophenol and other compounds occurred and the extract concentration was sufficient for accurate GC-IRMS measurements.

Two measurements were performed for each sample. Stable carbon isotope ratios of these repeat measurements agree within 0.1‰. The isotope ratios range from −31.6‰ to −32.9‰. Based on the tests performed the accuracy of the measurements is estimated to be 0.5‰.

5 Discussion

Depending on sampling duration PM from around 1000 m^3 to 5000 m^3 of air is collected on the quartz fibre filters. The concentrations of PM with a diameter of less than 2.5 µm generally ranges from several µg m^{-3} in remote rural areas to 100 µg m^{-3} or more for heavily polluted urban and industrialized locations. Consequently the mass of PM accumulated on the filter is in the range of several 10 mg and some 100 mg. The mass of methylnitrophenols in the samples is in the range of 10 ng to 500 ng, for truly remote regions most likely less. Based on the detection limit of 5 pg μl^{-1} analyses of methylnitrophenols in extract volumes of a few millilitres should be possible. However, such a sample will also contain a wide range of different organic and inorganic substances at a total concentration in the range of some ten µg μl^{-1} or more. Such a large excess of a complex and variable matrix makes reliable detection of trace components without further sample clean-up extremely difficult, if not impossible. While in the case of concentration measurement conventional GC-MS detection to some extent may help to reduce interference problems, this option does not exist for GC-IRMS where all peak overlaps will result in biased isotope ratios. The use of HPLC as sample clean-up procedure allows to greatly reduce overlap probability; it is worthwhile to remember that it allows for easy tuning of the clean-up procedure for different sets of target compounds. The risk of interfering overlap in the final GC-IRMS measurements depends on the quality of the HPLC separation as well as on the width of the collection windows and therefore is strongly dependent on the number of target compounds. Based on the finding that some of the methylnitrophenols are not present at concentrations exceeding the detection limit, the duration for collection of the HPLC eluent was reduced in order to reduce the solvent volume for further processing and to minimize the possibility of interferences for the GC analysis.

One disadvantage of the sample purification by HPLC is that the composition of the solvent in which the target substances are dissolved after the separation is determined by the conditions of the HPLC separation and not its suitability for GC-analysis. The

methylnitrophenols are eluted in an acetonitrile-water mixture with a high water content, which is unsuitable for carrying out a derivatisation with BSTFA and analysis by GC-MS.

Changing the solvent composition is the main purpose of the SPE step in the method. In order to achieve a high efficiency for the solid phase extraction (Table 3), the organic solvent content of the solution is reduced and the pH is adjusted to a value (pH 2), which efficiently suppresses the dissociation of the phenols. Recovery of the methylnitrophenols can be achieved with a variety of solvents. Acetonitrile was chosen for its suitability as a solvent for the derivatisation procedure and its high volatility, which facilitates volume reduction by evaporation as well as splitless GC-injection.

The presented method includes several separation steps combined with volume reduction. Although the loss of sample for each individual step is generally only around 20 % or less, the combination of a series of sample processing steps results in a relatively low overall recovery (Tables 2 and 3). Nevertheless, the estimated relative accuracy of the measurements is around 20 %. This is due to the chemical similarity between target compounds and IS, which results in recovery ratios close to unity (Table 2). The choice of IS depends on the absence of significant levels of the IS in the PM sample. This was verified by analysis of samples using different IS. However, for atmospheric PM analysis it has to be considered that the composition of samples can be highly variable with location and time and therefore the choice of the optimum IS may vary with sampling location.

One of the main advantages of the somewhat elaborate sample clean-up steps is that the detection limit is primarily determined by the baseline noise of the gas chromatographic measurement. Combined with the possibility to process large samples, this results in detection limits significantly lower than those of previously published methods (Morville et al., 2004; Cecinato et al., 2005). The detection limit for this method is 0.3 pg m^{-3} for 2-methyl-4-nitrophenol and 4-methyl-2-nitrophenol. This low detection limit allows measurements in suburban and rural areas where the methylnitrophenols concentrations are substantially lower than in urban areas. Moreover, the developed

method is easily adaptable to the analysis of a wide range of related compounds, especially other phenolic compounds, in atmospheric PM.

The method presented here is the first one to allow compound specific stable carbon isotopic measurements of secondary POM at very low concentrations. In fact, the carbon isotope ratio of compounds with concentrations lower than 1 ng m^{-3} could be analysed with GC-IRMS with an estimated accuracy of 0.5‰ and a reproducibility of 0.1‰. One of the main limitations of the method is the necessity to collect samples for few days to collect sufficient methylnitrophenol mass on the filter. This reduces the possibilities to determine short-term variability of concentration and also increases the risk of sampling bias. However, this problem is somewhat specific for areas with very low nitrophenol concentration. The concentration data in Tables 6 and 7 show that for the two BAQS sampling sites (Harrow and Ridgewood) as well as York University PM collected was very low in methylnitrophenols. For areas with higher pollution levels it is expected that sampling duration can be reduced substantially.

The final goal of measurements of isotope ratios of secondary POM is to better understand precursor processing in the atmosphere and add new constraints for extrapolation of laboratory experiments to atmospheric conditions. The data set presented here is very limited and it would be premature to generalize the findings. Moreover, due to the restriction of isotope ratio measurements to samples with methylnitrophenol concentrations at the upper end of observed ambient levels our findings do not necessarily apply to samples at the lower end of the concentration range.

Nevertheless, our results allow some important progress in understanding the origin of atmospheric methylnitrophenols in PM, with the caveat that they may not be representative for the atmosphere in general. First of all, the isotope ratio of 2-methyl-4-nitrophenol in samples collected at York University is in the relatively narrow range of −31.6‰ to −32.9‰ with an average of −32.0‰ ± 0.2‰ (standard deviation 0.5‰). This is significantly lighter than the toluene stable isotope ratio measured close to important sources (Rudolph et al., 2002). It should be noted that most of the results presented by Rudolph et al. were from measurements in Toronto and its vicinity. Therefore the

reported values, which range from −28.4 ± 2.9 to −27.1 ± 0.7‰ provide a solid basis for comparison and we can conclude that in this case secondary POM is approximately 4–5‰ lighter than the precursor. This is consistent with the known kinetic isotope effect for the reaction of toluene with OH of (5.95 ± 0.28‰) (Anderson et al., 2004) and it therefore is expected that the products of toluene oxidation in the initial phase of the reaction will be significantly lighter than the parent compound. Indeed, Irei et al. (2006) observed that secondary POM formed by the OH-radical initiated oxidation of toluene in a flow reactor is on average 5.6‰ lighter under conditions where less than 30 % of toluene has reacted (Fig. 5). Furthermore, Irei (2008) reports measurements of the isotope ratios of 2-methyl-4-nitrophenol formed by the oxidation of toluene in a smog chamber and in a flow reactor. The observed isotope ratio was on average (4 ± 1)‰ lighter than the reactant, in very good agreement with our ambient observations. This strongly suggests that 2-methyl-4-nitrophenol found in atmospheric PM is indeed the product of the atmospheric oxidation of toluene and that the 2-methyl-4-nitrophenol formation mechanisms for laboratory conditions and the atmosphere are identical. Based on theoretical considerations as well as results from laboratory studies it is expected that the stable isotope ratio of the products of toluene oxidation depends on the extent of precursor processing (Fig. 5). Within the uncertainty and scatter of the measurements the ambient data agree very well with the laboratory studies for less than 50 % of toluene processing. This is consistent with the average atmospheric lifetime of toluene (approximately 2 days) and a sampling location in a suburban area of a major city.

It should be noted that the extremely low concentrations of 2-methyl-4-nitrophenol in atmospheric PM suggest that the methylnitrophenol yield under atmospheric conditions is substantially lower than in laboratory studies (Irei, 2008). This may be explained by differences in gas-particle distributions resulting from the lower PM load in the atmosphere or an unrealistically high methylnitrophenol yield in laboratory studies due to the very high NO_x concentrations used in the laboratory studies (Irei, 2008).

For semi-volatile compounds sampling on high-volume filters carries the risk of losses during sampling due to volatilisation of semi-volatile compounds from collected

particles, which would result in measurements underestimating atmospheric concentrations. In contrast to this, adsorption of gas-phase methylnitrophenols on quartz fibres potentially results in an overestimation of particle-phase concentrations. It is difficult to estimate the extent of such bias therefore it is not possible to provide an estimate uncertainty arising from these effects for concentration measurements. However, it is unlikely that isotope ratio measurements will be significantly biased by volatilisation or adsorption. Phase transitions such as evaporation typically cause only very small isotope effects. For example Irei et al. (2006) found a difference of (0.33 ± 0.02‰) between gas and liquid phase during partial evaporation of toluene. It therefore is very likely that for isotope ratio measurements bias from changes in distribution between particle-phase and gas-phase during sampling will be below the estimated overall uncertainty of the isotope ratio measurements of 0.5‰.

6 Conclusions

The developed method for compound specific analysis of methylnitrophenols in atmospheric PM allows measurements with an accuracy of 0.5‰ for concentrations in the range of a few 100 pg m^{-3}. This is sufficient for studies of the methylnitrophenol isomer most abundant in atmospheric PM in a suburban region, but not over rural and semi-rural regions. Processing filter extracts by a combination of several volume reduction and an HPLC sample clean-up step with GC-IRMS measurements allows essentially an overlap free GC separation, a condition for unbiased compound specific isotope ratio measurement. While the method was only tested for analysis of methylnitrophenols, the flexibility of HPLC separations combined with the wide range of compounds that can be analysed by GC makes it a method that can readily be adapted to many semi volatile components of atmospheric POM.

One of the by-products is the possibility to measure methylnitrophenol concentrations in atmospheric PM at the lowest pg m^{-3} range. In contrast to the isotope

ratio measurements, the developed methodology most likely will be sufficient for concentration measurements over rural and remote locations.

The carbon isotope ratio of 2-methyl-4-nitrophenol is approximately 5‰ lower than that of the precursor, consistent with laboratory studies of the products of toluene oxidation as well as mass balance based predictions. This strongly suggests that the most abundant atmospheric methylnitrophenol, 2-methyl-4-nitrophenol, indeed is primarily due to atmospheric oxidation of toluene and that the formation mechanism in the atmosphere is identical to the laboratory, although the yields substantially differ. Due to the limited number of isotope ratio measurements results it is uncertain to which extent these findings can be generalized, but the results presented here demonstrate the value of isotope ratio measurements for understanding the origin and formation processes of organic atmospheric pollutants.

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Table 1. Target compounds, IS, ISRC, HPLC collection windows and GC column used for methylnitrophenol analysis.

Target compounds	4-methyl-2-nitrophenol 2-methyl-4-nitrophenol
IS	2-methyl-3-nitrophenol 2-methyl-5-nitrophenol
ISRC	Heptadecane
HPLC collection window	From 12 to 15.5 min.
GC column	DB-5MS (60 m × 0.25 mm i.d. × 1 µm film thickness)

Table 2. Recovery for IS and recovery relative to IS for target compounds spiked on clean filters and on filters containing atmospheric PM.

	Clean filter	Clean filter	Clean filter	Ambient filter[a]	Ambient filter[b]		
Mass spiked (µg)	4	4	1	4	4	Average	Stdev
IS Recovery (%)						Recovery	(%)
2-methyl-3-nitrophenol	43 ± 4	40 ± 4	39 ± 3	37 ± 3	42 ± 4	ratio (%)	
2-methyl-5-nitrophenol	45 ± 4	39 ± 5	41 ± 3	44 ± 3	48 ± 5		
Recovery relative to IS (%)							
4-methyl-2-nitrophenol	77 ± 11	91 ± 10	100 ± 9	86 ± 9	93 ± 9	92	9
2-methyl-4-nitrophenol	100 ± 8	101 ± 8	108 ± 6	125 ± 7	87 ± 7	97	9

[a] Samples collected at York University from 03/08/07 to 06/08/07.
[b] Samples collected at York University from 25/09 to 28/09/07.

Table 3. Recoveries of methylnitrophenols spiked at different stages of the sample preparation procedure.

Compound spiked	Extraction Steps at which standard was added	Recovery for individual step (%)
2-methyl-3-nitrophenol	Filter extraction	78
3-methyl-2-nitrophenol	HPLC separation	78
4-methyl-2-nitrophenol	Volume reduction of HPLC eluent	86
2-methyl-5-nitrophenol	SPE	87
2-methyl-4-nitrophenol	Final volume reduction	100
Combined recovery	All steps combined	46

Table 4. Stable isotope composition of derivatised target compounds and internal standard and stable isotopic composition of the derivatisation agent $\delta^{13}C_{TMS}$ calculated using mass balance equation (Eq. 2).

Mass inj. (ng)		≈ 13	≈ 13	≈ 13	≈ 13	≈ 13	≈ 4	≈ 13	≈ 13	≈ 13	≈ 20	≈ 35	≈ 35	Avrg (‰)	Stdev (‰)
4Me2ntrphen	$\delta^{13}C_{deriv}$	−32.59	−32.31	−32.445	−32.51	−32.07	−32.54	−32.31	−32.60	−32.28	−32.28	−32.45	−32.29	−32.38	0.16
	$\delta^{13}C_{TMS}$	−45.86	−44.94	−45.37	−45.59	−44.12	−45.68	−44.92	−45.87	−44.81	−44.81	−45.40	−44.86	−45.17	0.54
2Me3ntrphen	$\delta^{13}C_{deriv}$	−32.38	−32.03	−32.35	−32.23	−32.36	−32.39	−32.11	−32.76	−32.14	−32.14	−32.22	−32.26	−32.29	0.19
	$\delta^{13}C_{TMS}$	−45.73	−44.57	−45.63	−45.22	−45.66	−45.75	−44.81	−45.99	−44.91	−44.91	−45.18	−45.33	−45.33	0.43
2Me5ntrphen	$\delta^{13}C_{deriv}$	−32.64	−32.35	−32.74	−32.30	−32.48	−32.80	−32.40	−32.63	−32.74	−32.74	−32.53	−32.53	−32.57	0.17
	$\delta^{13}C_{TMS}$	−45.32	−44.37	−45.64	−44.20	−44.78	−45.87	−44.51	−45.31	−45.65	−45.65	−44.94	−44.95	−45.10	0.56
2Me4ntrphen	$\delta^{13}C_{deriv}$	−33.37	−33.11	−32.84	−32.79	−32.95	−33.15	−32.83	−32.88	−32.89	−32.89	−32.86	−32.94	−32.96	0.17
	$\delta^{13}C_{TMS}$	−45.28	−45.43	−45.51	−45.35	−45.88	−46.54	−45.49	−45.66	−45.70	−45.70	−45.57	−45.85	−45.66	0.33

Table 5. Results of GC-IRMS analysis of 1 µg of compounds with known isotope ratios (from off-line analysis of bulk material) spiked on two blank filters (test 1 and test 2). For comparison the off-line values are also presented.

	Mass spiked on a blank filter		Test 1		Test 2	
Compounds	µg	Offline $\delta^{13}C$ (‰)	Online $\delta^{13}C^{*}$ (‰)	Offset (‰)	Online $\delta^{13}C^{*}$ (‰)	Offset (‰)
IS						
2-me-3-nitrophenol	1	−26.662	−26.953	−0.294	−27.068	−0.407
2-me-5-nitrophenol	1	−27.204	−27.324	−0.120	−27.004	0.200
Target Compounds						
2-me-4-nitrophenol	1	−27.406	−27.797	−0.390	−27.633	−0.227
4-me-2-nitrophenol	1	−26.903	−26.659	0.244	−26.652	0.252
ISRC						
C17	4	−28.063	−28.572	−0.508	−28.390	−0.327

* This value is an average of three repetitive measurements with a relative standard deviation lower than 5 %.

Table 6. Mass (ng) of 2-methyl-4-nitrophenol and 4-methyl-2-nitrophenol in 1 µl of the final solution from extraction of filters collected at Harrow and Ridgetown during BAQS and the corresponding concentrations in the atmosphere.

	Mass (ng) in 1 µl injected in the GC-MS		Concentration (pg m^{-3}) in atmospheric PM		
	2-me-4-nitrophenol	4-me-2-nitrophenol	2-me-4-nitrophenol	4-me-2-nitrophenol	Recovery (%)
Harrow					
From 19/06 to 22/06/07	0.30 ± 0.06	0.10 ± 0.03	13.0 ± 3.2	6.0 ± 1.8	46 ± 5
From 22/06 to 25/06/07	0.20 ± 0.04	0.05 ± 0.01	18.0 ± 4.5	4.0 ± 1.2	35 ± 4
From 25/06 to 28/06/07	0.20 ± 0.04	0.07 ± 0.02	11.0 ± 2.8	4.0 ± 1.2	37 ± 4
From 28/06 to 05/07/07	0.20 ± 0.04	0.07 ± 0.02	14.0 ± 3.5	4.0 ± 1.2	40 ± 4
From 05/07 to 09/07/07	0.50 ± 0.10	0.17 ± 0.04	13.0 ± 3.2	5.0 ± 1.5	46 ± 5
From 09/07 to 10/07/07	0.30 ± 0.06	0.10 ± 0.03	23.0 ± 5.7	13.0 ± 3.9	35 ± 4
Ridgetown					
From 20/06 to 23/06/07	4.30 ± 0.66	0.80 ± 0.20	11.0 ± 2.2	2.0 ± 0.6	51 ± 5
From 23/06 to 26/06/07	0.80 ± 0.16	0.30 ± 0.08	9.0 ± 2.2	4.0 ± 1.2	43 ± 4
From 26/06 to 29/06/07	0.60 ± 0.13	0.30 ± 0.08	6.0 ± 1.5	3.0 ± 0.9	52 ± 5
From 29/06 to 02/07/07	0.60 ± 0.13	0.20 ± 0.05	19.0 ± 4.8	7.0 ± 2.1	58 ± 6
From 02/07 to 05/07/07	1.30 ± 0.26	0.50 ± 0.12	13.0 ± 3.2	5.0 ± 1.5	56 ± 6
From 05/07 to 08/07/07	0.60 ± 0.13	0.40 ± 0.10	11.0 ± 2.7	7.0 ± 2.1	44 ± 4
From 08/07 to 10/07/07	0.50 ± 0.10	0.40 ± 0.10	14.0 ± 3.5	11.0 ± 3.3	50 ± 5

Table 7. Mass (ng) of 2-methyl-4-nitrophenol in 1 µL of the final solution from extraction of filters collected at York University and the corresponding concentrations in the atmosphere.

	Mass (ng) in 1 µL injected in the GC-MS	Concentration (pg m^{-3}) in atmospheric PM	
York University	2-me-4-nitrophenol	2-me-4-nitrophenol	Recovery (%)
2007			
From 28/09 to 01/10	5.2 ± 1.0	60 ± 12	44 ± 4
From 04/10 to 07/10	7.4 ± 1.3	140 ± 23	37 ± 3
From 10/10 to 13/10	11.5 ± 2.3	110 ± 20	43 ± 4
2008			
From 04/07 to 07/07	5.2 ± 1.0	220 ± 46	45 ± 4
From 08/07 to 11/07	13.8 ± 2.8	225 ± 48	45 ± 4
From 11/07 to 14/07	5.3 ± 1.0	100 ± 22	48 ± 5
From 15/07 to 17/07	3.7 ± 0.8	202 ± 40	21 ± 2
From 18/07 to 21/07	15.4 ± 3.1	100 ± 22	48 ± 5
From 25/07 to 28/07	3.9 ± 0.9	90 ± 18	42 ± 4
From 25/08 to 28/08	6.0 ± 1.2	190 ± 38	36 ± 3

Table 8. Stable isotope ratio (‰) of 2-methyl-4-nitrophenol in samples collected at York University.

	2-methyl-4-nitrophenol stable isotope ratio (‰)*		
York University	1st measurement	2nd measurement	Average
2007			
From 28/09 to 01/10	−32.9 ± 0.50	−32.9 ± 0.50	−32.9 ± 0.50
From 04/10 to 07/10	−31.7 ± 0.50	−31.8 ± 0.50	−31.8 ± 0.50
2008			
From 04/07 to 07/07	−31.6 ± 0.50	−31.6 ± 0.50	−31.6 ± 0.50
From 18/07 to 21/07	−31.8 ± 0.50	−31.8 ± 0.50	−31.8 ± 0.50
From 25/08 to 28/08	NA	−32.1 ± 0.50	−32.1 ± 0.50

* The uncertainties given are estimated uncertainties for the complete analytical procedure and not the GC-IRMS measurements.

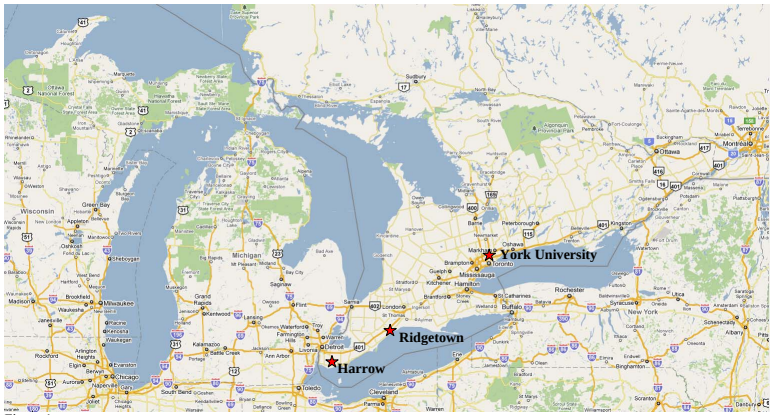

Fig. 1. Location of sampling sites in Ontario, Canada.

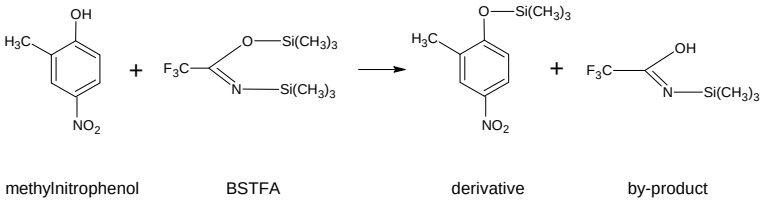

Fig. 2. Example for methylnitrophenol derivatisation using BSTFA.

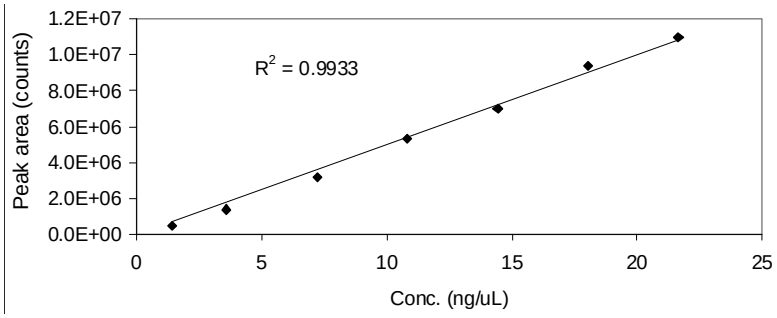

Fig. 3. Example of GC-MS calibration for 2-methy-4-nitrophenol.

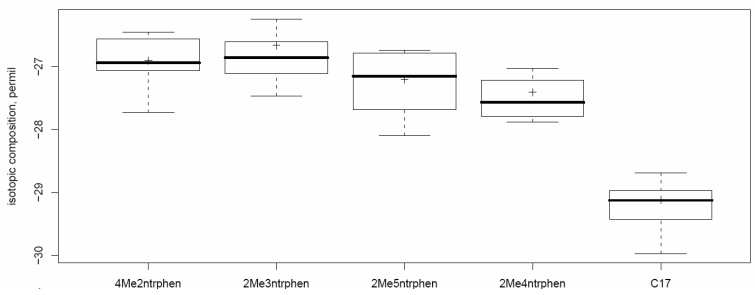

Fig. 4. Comparison of online and offline isotope ratio measurements for methylnitrophenols. (+) represents the offline value and the box plot GC-IRMS measurements of solutions containing between 1 and 20 ng μl^{-1}. The heavy lines give the median values, the boxes indicate the 25 and 75 percentile range and the upper and lower ends of the vertical bars the extreme values of the measurements.

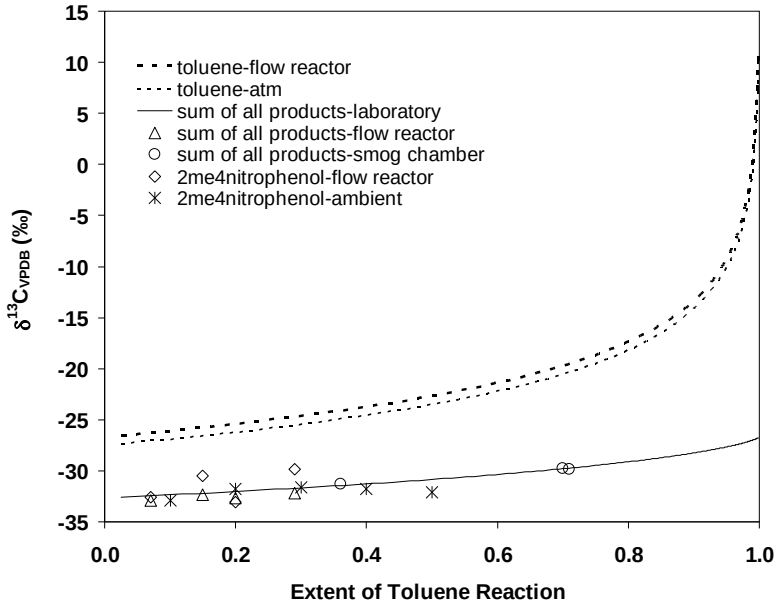

Fig. 5. Stable isotope ratio of toluene and its products as function of precursor processing. The broken lines are calculations based on the initial isotope ratio of toluene. The solid line is the isotope ratio of POM formed by the oxidation of toluene calculated from mass balance under the assumption that there is no fractionation between the phases. Individual data points represent measurements. The flow reactor and smog chamber data are taken from Irei et al. (2006) and Irei (2008). It should be noted that the position of the ambient 2-methyl-4-nitrophenol data along the x-axis does not indicate the extent of toluene processing. Spreading out the data is done for the purpose of indicating the extent of variability as well as to show that these data are consistent with laboratory observations up to approximately 40 % of toluene processing.