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Stable carbon isotope ratios of ambient secondary organic aerosols in Toronto

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Abstract

A method to quantify concentrations and stable carbon isotope ratios of secondary organic aerosols (SOA) has been applied to study atmospheric nitrophenols in Toronto, Canada. The sampling of five nitrophenols, all primarily formed from the photo-oxidation of aromatic volatile organic compounds (VOC), in the gas phase and particulate matter (PM) together and PM alone was conducted. Since all of the target compounds are secondary products, their concentrations in the atmosphere are in the low $ng\,m^{-3}$ range and consequently a large volume of air ($> 1000\,m^3$) is needed to analyze samples for stable carbon isotope ratios, resulting in sampling periods of typically 24 h. While this extended sampling period increases the representativeness of average values, it at the same time reduces possibilities to identify meteorological conditions or atmospheric pollution levels determining nitrophenol concentrations and isotope ratios.

Average measured carbon isotope ratios of the different nitrophenols are between −34 and −33 ‰, which is well within the range predicted by mass balance calculations. However, the observed carbon isotope ratios cover a range of nearly 9 ‰, and approximately 20 % of the isotope ratios of the products have isotope ratios lower than predicted from the kinetic isotope effect of the first step of the reaction mechanism and the isotope ratio of the precursor. This can be explained by isotope fractionation during reaction steps following the initial reaction of the precursor VOCs with the OH radical.

Limited evidence for local production of nitrophenols is observed since sampling was done in the Toronto area, an urban centre with significant anthropogenic emission sources. Strong evidence for significant local formation of nitrophenols is only found for samples collected in summer. On average, the difference in carbon isotope ratios between nitrophenols in the particle phase and in the gas phase is insignificant, but for a limited number of observations in summer, a substantial difference is observed. This indicates that at high OH radical concentrations, photochemical formation or removal of nitrophenols can be faster than exchange between the two phases.

The dependence between the concentrations and isotope ratios of the nitrophenols and meteorological conditions as well as pollution levels (NO_2, O_3, SO_2 and CO) demonstrate that the influence of precursor concentrations on nitrophenol concentrations is far more important than the extent of photochemical processing.

1   Introduction

Volatile organic compounds (VOC) are emitted into the atmosphere by both anthropogenic and biogenic sources. Once emitted, the VOC undergo both physical and chemical processes, such as dilution and chemical reactions. Reactions in the atmosphere are mainly oxidation reactions from OH, ozone or chlorine radicals. These oxidation reactions produce products which are typically heavier and have lower vapor pressures than the reactants. Many of the products are considered to be semi-volatile organic compounds (SVOC), which have properties that allow them to exist both in the gas phase and in particulate matter (PM), and compose secondary organic aerosols (SOA), making up a substantial portion of aerosols in the troposphere. Nitrophenols, the target compounds of this paper, are SVOC that are believed to be dominantly produced by processes in the atmosphere from aromatic VOC such as benzene, toluene and m-xylene (Forstner et al., 1997; Atkinson, 2000; Jang and Kamens, 2001; Hamilton et al., 2005; Sato et al., 2007). The nitrophenol formation pathway from toluene and m-xylene is proposed to be similar, and once emitted, the aromatic VOC can undergo photo-oxidation with the OH radical to produce a (di)methyl hydroxycyclohexadienyl radical, which can then form a (di)methyl phenol (Forstner et al., 1997). These intermediates can then react with OH and NO_2 to produce (di)methyl nitrophenols.

4-nitrophenol, has several proposed formation pathways which includes pathways in both the gas phase and the aqueous phase. Atkinson et al. (1992) proposed that benzene undergoes photo-oxidation to produce a phenoxy radical with subsequent reaction with NO_2. Alternatively, Bolzacchini et al. (2001) suggested the addition of

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NO$_3$ to the OH carbon of phenol, followed by the addition of NO$_2$ to the para carbon and final loss of HNO$_3$, forming 4-nitrophenol.

It has been proposed that the aqueous phase production of nitrophenols could occur from the reaction of cresols with NO$_3$ (Herrmann et al., 1995). Aqueous phase formation of 4-nitrophenol has also been proposed by Harrison et al. (2005), suggesting that once phenol is produced from the reaction of benzene and the OH radical, it partitions into the aqueous phase, reacts with NO$_3$ to form 4-nitrophenol, which then partitions favourably into the gas phase. Based on model calculations the aqueous formation processes can have a substantial contribution to the total formation rate at high liquid water content, such as in clouds, but at low liquid water contents, this process contributes less than 2 % to nitrophenol formation (Hamilton et al., 2005).

Nitrophenols have been found in trace amounts as primary emissions, such as gasoline fueled automobile exhaust (Tremp et al., 1993). In a very recent study, Inomata et al. (2015) reported that emission factors for 4-nitrophenol in PM from gasoline fueled engines were below the quantification limits of 6×10^{-3} µg km^{-1}, whereas for diesel engines, 4-nitrophenol in PM emission factors range from 0.23 to 29.5 µg km^{-1}. The reported values for 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol are in the range of 0.32 to 11.4 µg km^{-1} for diesel engines and were below the quantification limits for gasoline engines. 4-Nitrophenol has also been found in the gas phase of diesel engine exhaust at highly variable levels (Inomata et al., 2013) corresponding to emissions factors ranging from effectively zero to several hundred µg km^{-1}.

Stable carbon isotope ratio measurements have been useful tools in atmospheric chemistry. The ratio of the ^{13}C isotope, which has a natural abundance of approximately 1.1 %, and the ^{12}C isotope is compared to a standard, the Vienna–Peedee Belemnite (V-PDB) with a value of 0.0112372 (Craig, 1957), as shown in Eq. (1). This relative difference in per mille notation is referred to as the delta value (δ^{13}C). Stable carbon isotope ratio measurements in combination with concentration measurements have been proposed to be used to gain insight on the formation and processing of secondary organic aerosols in the atmosphere (Goldstein and Shaw, 2003; Rudolph, 2007;

Gensch et al., 2014). Although still a developing field, especially in atmospheric chemistry, stable carbon isotope ratio measurements have been used to measure a wide range of compounds to gain information on sources, chemical processes and transport in the atmosphere. Nitrophenols were chosen as the target compounds in this study for three reasons. The first reason is that nitrophenols are formed from one reaction pathway and are specific to the aromatic VOC + OH reaction (Forstner et al., 1997). This is important so that the nitrophenols can be traced back to the precursor, which has a known isotope ratio at the source (Rudolph et al., 2002). Secondly, the target compounds should be ring retaining products so that the possibility of being formed from other precursors decreases compared to ring fragmentation products. Lastly, and most importantly, it has been suggested that nitrophenols have an isotope ratio that is close to the isotope ratio of the sum of all reaction products. This allows for a first order prediction of the dependence between isotope ratios of reaction products and photochemical precursor processing in the atmosphere (Irei et al., 2015). Measurements of nitrophenol concentrations and their isotope ratios in a mixed residential and industrial area are reported and discussed in this paper.

$$\delta^{13}C = \frac{(^{13}C/^{12}C)_{\text{sample}} - (^{13}C/^{12}C)_{\text{V-PDB}}}{(^{13}C/^{12}C)_{\text{V-PDB}}} \times 1000\,‰ \tag{1}$$

2 Method

The method used for filter preparation, sample collection, extraction and analysis have been previously described by Saccon et al. (2013) which was based on methods developed by Moukhtar et al. (2011) and Irei et al. (2013). Samples were collected at York University (Fig. 1) in the outskirts of Toronto, Canada using high volume air samplers. Figure 1 also shows the location of two monitoring stations of the Ontario Ministry of the Environment (OME), which provided measurements of ambient concentrations of NO_2, O_3, CO, SO_2, and PM with a nominal aerodynamic diameter of less than 2.5 µm

(PM$_{2.5}$). The sampling period was from March 2009 to August 2012. Prebaked quartz fibre filters were used for PM collection and prebaked quartz fibre filters coated with XAD-4™ resin were used for gas phase + PM collection. The sampling times for XAD-4™ coated filters were typically 24 h and from one to three days for uncoated filters.

Filters, prior to extraction, were stored in a freezer. After being spiked with internal standards, filters were extracted with acetonitrile, underwent an HPLC and solid phase extraction cleanup step and were analyzed. An HP 5890 GC coupled to an HP 5972 MS was used for concentration measurements and an HP 6890 GC coupled to a Micromass Isoprime IRMS was used for isotope ratio measurements. All samples were derivatized with BSTFA prior to analysis. A summary of performance characteristics is shown in Table 1. Only samples containing more than 3 ng of carbon for a target compound per 3 μL injection were used for quantifying stable carbon isotope ratios.

3   Results and discussion

3.1   Overview of measured carbon isotope ratios

An overview of the measured isotope ratios of nitrophenols is given in Table 2. The nitrophenols chosen as the target compounds for this study were 4-nitrophenol, derived from benzene, 4-methyl-2-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol, derived from toluene and 2,6-dimethyl-4-nitrophenol, derived from m-xylene. Since only sample extracts with concentrations of at least 1 ng μL^{-1} of carbon for a target compound were suitable for isotope ratio measurement, only a subset of the samples collected could be analyzed for δ^{13}C of the target nitrophenols. This reduced the number of samples with low nitrophenol concentrations and therefore could result in subsets of δ^{13}C data biased towards samples with higher nitrophenol concentrations. For the most abundant target compounds, 4-nitrophenol and 2-methyl-4-nitrophenol, 85 and 98 %, respectively, of the 102 samples (47 PM and 55 gas + PM) could be analyzed for isotope ratios. For the lower in abundance compounds, 4-methyl-

2-nitrophenol, 3-methyl-4-nitrophenol and 2,6-dimethyl-4-nitrophenol, only 17, 47 and 22 %, respectively, of the samples were analyzed for carbon isotope ratios. As can be seen from Fig. 2, the variability of the carbon isotope ratio substantially exceeds any systematic dependence between concentration and δ^{13}C.

Irei et al. (2015) report that the main factor determining the carbon isotope ratio of the particle phase products of toluene oxidation is the kinetic isotope effect (KIE) for the reaction of toluene with the OH radical and the carbon isotope ratio of the reacting toluene. The KIEs for the reactions of benzene, toluene and m-xylene with the OH radical have been measured in the laboratory (Anderson et al., 2004) and the carbon isotope ratio of their emissions in the Greater Toronto Area (GTA) have been determined by Rudolph et al. (2002). Using these values, which are summarized in Table 3, the carbon isotope ratios of nitrophenols formed in the initial phase of the reaction can be estimated (Table 3). It should be noted that the δ^{13}C values for the methyl nitrophenols formed by the gas phase photo-oxidation of toluene in laboratory experiments are in many cases between 1 and 4 ‰ lighter than predicted by a model based on reaction mechanisms proposed in literature (Irei et al., 2015) and the assumption that the isotope fractionation between precursor and product is completely determined by the initial reaction step. Since these laboratory data exhibit substantial scatter, this possible additional fractionation was not considered in the calculation of the carbon isotope ratios for the initial phase of the reaction. It is assumed that benzene and m-xylene reactions follow the same principle as postulated by Irei et al. (2015) for toluene reactions. As the reaction progresses, the products will be enriched in ^{13}C due to the reaction of the parent VOC as well as that of the reaction product with the OH radical in the gas phase. Although the KIEs for reactions of nitrophenols have not been measured, they most likely will be normal KIEs, similar to all KIEs measured for reactions of light aromatic VOC in the gas phase (Anderson et al., 2004).

As predicted by the postulated formation mechanisms and subsequent reaction with the OH radical, most of the measured δ^{13}C values of 4-nitrophenol are larger than −34 ‰ (Fig. 3). The lower end of the measured δ^{13}C values for 4-nitrophenol is approx-

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imately 1 to 2 ‰ lower than δ^{13}C values predicted from the δ^{13}C values of benzene emissions and the KIE for reaction of benzene with the OH radical, however this difference is within the uncertainty of the prediction (Table 3) and the measurement error (Fig. 3). For two of the reaction products of the photo-oxidation of toluene, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol, the discrepancy between prediction and the lower end of observations is more pronounced. For both compounds, the lower end of the observations is approximately 2 to 3 ‰ lighter than predicted, a difference that is larger than the uncertainty of the predictions (Table 3). Similarly for 2,6-dimethyl-4-nitrophenol the 25th percentiles are 2.7 ‰ lower than predicted for the initial phase of the VOC precursor reaction. In total, 19 % of all measurements are below the 99 % confidence limit calculated from the combined uncertainty of measurement and δ^{13}C$_i$. However, a substantial part, if not all, of the uncertainty of δ^{13}C$_i$ will be systematic. Assuming that the total calculated uncertainty of δ^{13}C$_i$ is systematic, 12 % of the observations are below the 2σ uncertainty of δ^{13}C$_i$ and 5 % below the 3σ limit.

In the initial phase of the reaction, the concentration of secondary compounds will be low. Consequently it is expected that the lowest nitrophenol carbon isotope ratios will be for samples with low concentrations. Although there is no systematic dependence between isotope ratios and concentrations (Fig. 2) it therefore cannot be determined if the lower end of the observed distributions is biased due to limitations of the δ^{13}C measurements or represents the true lower limit of the isotope ratios of atmospheric nitrophenols.

In spite of the various uncertainties in the comparison between the predicted and observed lower end of frequency distributions for the isotope ratios, the observations are consistent with the laboratory studies of Irei et al. (2015) which show that the formation of methyl nitrophenols by photo-oxidation of toluene in the atmosphere results in a carbon isotope fractionation between precursor and reaction product that is slightly larger than the KIE for the reaction of aromatic VOC with the OH radical.

3.2 Comparison of gas phase and PM phase isotope ratios

Perraud et al. (2011) have suggested that there is a non-equilibrium in the partitioning of SVOC between the particle phase and the gas phase, and that contrary to widely used equilibrium models, SVOC, such as organic nitrates, can adsorb onto existing particles and, before partitioning back into the gas phase, are buried irreversibly into the particle. While fractionation due to the partitioning between different phases is usually small (Kaye, 1992) and within the uncertainty of the measurement, changes in carbon isotope ratio of SVOC in the atmosphere will result in a difference in carbon isotope ratio between the two phases if partitioning into the particle phase is irreversible. Formation of nitrophenols from aromatic VOC is the result of a gas phase reaction sequence and the only known reactions of nitrophenols are in the gas phase with the OH radical (Grosjean, 1991; Bejan et al., 2007) and no solid or aqueous phase loss processes are known, apart from possible oligomerization. Consequently, irreversible partitioning into particles should result in differences in carbon isotope ratios between the gas phase and particle phase for nitrophenols.

For the measurements presented here, the average concentration of nitrophenols in PM is only about 20 % of the average of the total atmospheric nitrophenol concentrations, similar to the findings reported by Saccon et al. (2013). Consequently, on average, the carbon isotope ratio of total atmospheric nitrophenols is dominated by the carbon isotope ratio of gas phase nitrophenols. The frequency distributions (Fig. 3) as well as a comparison of average carbon isotope ratios (Fig. 4) show no systematic difference in the isotope ratios between the two phases. In the case of 4-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol, the differences between averages for PM + gas phase and PM only are less than 0.5‰ and for 4-methyl-2-nitrophenol and 2,6-dimethyl-4-nitrophenol the differences are less than 1‰. These differences are all within the uncertainties of the averages. The larger errors for 4-methyl-2-nitrophenol and 2,6-dimethyl-4-nitrophenol are due to the smaller number of samples, which is less than 15 for each phase.

The distributions, as well as the average values, are based on a set of samples which only contained a limited subset of simultaneous measurements of the isotope ratios of total nitrophenols and particle phase nitrophenols. Therefore, the finding of very small differences in carbon isotope ratios between nitrophenols in PM and total nitrophenols only rules out a significant systematic enrichment in one of the two phases, but not the existence of a disequilibrium for different atmospheric conditions. More insight into a possible disequilibrium between the two phases can be gained from the small subset of simultaneously collected PM and PM + gas phase samples.

For 2-methyl-4-nitrophenol, the most abundant targeted product from toluene photo-oxidation, there were eight pairs of samples in which the isotope ratios were quantified in both types of samples; 4-nitrophenol and 3-methyl-4-nitrophenol had six and two sample pairs, respectively. An overview of the differences between total and PM only isotope ratios for samples collected in parallel ($\Delta\delta^{13}C$) is shown in Fig. 5. On average the difference is 0.3‰ with an error of the mean of 0.5‰, consistent with the results in Fig. 4. However, the standard deviation for $\Delta\delta^{13}C$ is 1.8‰, nearly three times higher and outside of the 99% confidence limit expected from the uncertainty of the measurements. Disequilibrium without significant systematic bias in $\Delta\delta^{13}C$ indicates that exchange between the two phases is slower than the change of $\delta^{13}C$ in one of the two phases. Since, apart from exchange with the gas phase, no processes are known that will change the concentration or carbon isotope ratio of nitrophenols in the particle phase, it is likely that the change of $\delta^{13}C$ in the gas phase due to formation from aromatic VOC or gas phase loss reactions of nitrophenols is creating the disequilibrium in carbon isotope ratio between the two phases.

Indeed the variability of $\Delta\delta^{13}C$ for sample pairs collected in summer is substantially higher than for late fall, when photochemical activity is expected to be lower than in the summer (Table 4). Although the number of measurements is small and the averages are identical, the standard deviation of $\Delta\delta^{13}C$ for summer sample pairs is 3.2‰ and well outside of the variability expected from measurement errors. In contrast to this the

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standard deviation of $\Delta\delta^{13}$C for late fall is only 0.9‰, which is only slightly higher than expected from the uncertainty of the measurements.

For the sample pairs collected in summer, PM contributed on average 12 % of the total atmospheric nitrophenol concentration. Therefore, the measured $\Delta\delta^{13}$C values are a good approximation for the difference in δ^{13}C between nitrophenols in the gas phase and in PM. For the sample pairs collected in late fall, the contributions from PM range from 30 % to approximately 100 % and consequently the difference in δ^{13}C between nitrophenols in the gas phase and in PM will be larger than the measured $\Delta\delta^{13}$C values. Unfortunately, for the late fall samples, the large contribution of measurement error to the $\Delta\delta^{13}$C values, combined with the uncertainty of concentration measurements prevents a meaningful determination of the true difference in δ^{13}C between nitrophenols in the gas phase and in PM. Including experimental uncertainty, the upper limit for the uncertainty of the gas-particle phase difference in δ^{13}C is approximately 2‰. This is lower than the variability observed for summer sample pairs and supports the hypothesis that disequilibrium between gas and particle phase is the result of changes in δ^{13}C of gas phase nitrophenols due to photo-chemical formation or loss reactions.

3.3 Correlation between isotope ratios of nitrophenols

The three methyl nitrophenol isomers we studied are formed from the same precursor following the same initial reaction step, the addition of an OH radical to the aromatic ring of toluene. Consequently it is expected that the freshly formed isomers will have similar carbon isotope ratios. Later differentiation in δ^{13}C could result from differences in carbon isotope effects for the reaction sequences following the initial reaction. Similarly, different KIEs for the loss reactions of the different isomers could cause differences in δ^{13}C between isomers.

Indeed, the average δ^{13}C values of the three isomers are very similar (Table 2) and differ from each other only by 0.1‰ or less. However, based on the average, differences between isomers in individual samples cannot be ruled out. Figure 6 shows a plot of

the carbon isotope ratios of 4-methyl-2-nitrophenol and 3-methyl-4-nitrophenol vs. the carbon isotope ratio of 2-methyl-4-nitrophenol for all samples which could be analyzed for the carbon isotope ratio of more than one of the methyl nitrophenols. The data show scatter around the 1 : 1 line, but most of this scatter can be explained by measurement uncertainty. For approximately 50 % of the data pairs, the difference in isotope ratios between isomers ($\Delta\delta^{13}$C) is within the uncertainty of the measurements and only for 6 of the 58 data pairs, the difference is larger than three times the measurement error. The mean value for $\Delta\delta^{13}$C is 0.15 ‰, which is less than the error of the mean (0.18 ‰). The standard deviation for $\Delta\delta^{13}$C is 1.3 ‰, which is 0.6 ‰ larger than expected from measurement errors alone. Although these findings cannot completely rule out the existence of differences in KIEs or rate constants for formation or removal processes between methyl nitrophenols, the impact of such differences can only be small.

The standard deviation observed for differences between carbon isotope ratios of nitrophenols which are not isomers are substantially larger than expected from measurement uncertainty and very similar to the standard deviation expected from the variance of δ^{13}C within the data sets for the individual nitrophenols (Table 5). However, on average the difference in isotope ratios ($\Delta\delta^{13}$C) between non-isomeric nitrophenols are only marginally larger than $\Delta\delta^{13}$C for the methyl nitrophenol isomers (Tables 2 and 5). To some extent this can be explained by the very similar carbon isotope ratios of the different precursor VOC (Table 3). However, from the differences in KIEs for the initial step of the reaction sequence leading to formation of nitrophenols it is expected that isotope ratios of non-isomeric nitrophenols during the initial phase of their formation will differ by a few per mille (Table 3). Compared to these predicted differences the actually observed values for the average of $\Delta\delta^{13}$C are surprisingly small. This may be due to the fact that with increasing extent of atmospheric processing the carbon isotope ratio of the precursor will increase and that this increase will depend on the KIE and the rate constant for the reaction of precursor. Depending on the extent of processing, this will, at least partly, compensate for the larger depletion in ^{13}C during the initial phase of the reaction. Since on average the observed $\Delta\delta^{13}$C are very small, this suggests that

on average precursor processing has been substantial, independent of the precursor reactivity.

3.4 Seasonal variation of the concentrations and carbon isotope ratios of nitrophenols

Table 6 shows a comparison of 2-methyl-4-nitrophenol and 4-nitrophenol concentrations and carbon isotope ratios for different temperature ranges. The separation into different temperature ranges is based on the average temperatures during sampling. Measurements with average temperatures below 10 °C were made between mid of October and end of January, measurements with average temperatures exceeding 20 °C in June, July and August. Also included are air quality data from two OME monitoring stations in Toronto (Fig. 1). Remarkably, a distinct seasonal difference in isotope ratios is not observed. With the exception of the 4-nitrophenol isotope ratios in PM, the difference in average carbon isotope ratios between measurements made at low and high temperatures is less than 0.5‰. For the 4-nitrophenol isotope ratios in PM this difference is 0.9‰, but this difference is within the uncertainty of the average values.

This is in contrast to the expectation that, due to higher photochemical activity in summer, samples collected in summer should be subject to more processing and therefore be, compared to less processed samples, enriched in ^{13}C. A more detailed look at the dependence between temperature, wind direction and carbon isotope ratio can provide a possible explanation for this unexpected finding. Figure 7 shows the frequency of observations of δ^{13}C values for methyl nitrophenols and 4-nitrophenol binned into intervals of 2‰ and separated by wind direction and average temperature during sampling. The selection of the wind directions, north and southwest, was based on the number of available measurements and the difference in nearby major sources of nitrophenol precursors. Only samples with a relatively stable wind direction during sampling were used for this analysis. Three major highways and their intersections are located within 15 km or less southwest of the sampling locations whereas there is only one major highway directly north of York University (Fig. 1).

For medium (10 to 20 °C) and low (< 10 °C) temperatures, the number of methyl nitrophenol data points in each $\delta^{13}C$ bin is identical, while for high average temperatures the number of observations peak in the center bin (−34 to −32 ‰). Therefore, the absence of a difference in the seasonal averages of the methyl nitrophenol carbon isotope ratio is not due to the absence of a seasonal impact on processing, but the coincidence that for summer, seventeen out of twenty nine $\delta^{13}C$ measurements are close to the average of all observations.

Nevertheless, it is somewhat surprising that only three of the fifteen observations in the −34 to −32 ‰ bin were at high average temperatures since this bin represents the largest extent of methyl nitrophenol precursor processing. The most likely reason is a more pronounced influence of local scale processing on the methyl nitrophenol concentration and therefore also its carbon isotope ratio in summer compared to fall and winter.

Although the lower number of data points available for 4-nitrophenol results in higher statistical uncertainty of the distribution, Fig. 7 shows some substantial differences between the carbon isotope ratios of methyl nitrophenols and 4-nitrophenol. For 4-nitrophenol only 13 % of all data points are in the −34 to −32 ‰ range and more than 50 % of the $\delta^{13}C$ values measured at high average temperatures are below −34 ‰. This can be explained by the different reactivity of the precursors. The rate constant for the reaction of benzene with the OH radical is only one fourth of that for the reaction of toluene (Table 3) and therefore photochemical processing will result in a lower enrichment of ^{13}C in the products from reactions of benzene compared to products derived from toluene.

The preference of low and medium enrichment of nitrophenols in ^{13}C during summer is independent of wind direction. Compared to northerly wind directions, the larger number of observations under southwesterly airflow reflects the larger percentage of observations with southwesterly wind in summer (eighteen of twenty nine) and not a wind direction dependence of methyl nitrophenol carbon isotope ratios. Since it is expected that the different wind directions result in different pollution levels, this is consis-

tent with the finding that there is no systematic dependence between the concentration of methyl nitrophenols and carbon isotope ratio (Fig. 1). Similarly, the carbon isotope ratios of the methyl nitrophenols and 4-nitrophenol show no correlation with CO, NO_2, O_3 or oxidant ($O_3 + NO_2$) concentrations (R^2 is consistently below 0.1).

Although the nitrophenols exhibit only small seasonal changes in carbon isotope ratios, there are substantial differences in concentrations. For 2-methyl-4-nitrophenol and 4-nitrophenol the difference in concentrations in PM between summer and winter is a factor of 6.5 and 3.5, respectively. Most of these differences can be explained by a temperature dependence of the distribution between gas phase and PM. For average temperatures exceeding 20 °C, slightly less than 10 % of the total concentration is found in PM. For average temperatures below 10 °C the fraction in PM increases to approximately 40 %.

There are some differences in PM + gas concentrations between the two different temperature ranges. The average 2-methyl-4-nitrophenol concentration in PM + gas is at low temperatures on average approximately 60 % higher than at high temperatures. An increase in photochemical processing of the precursors can be ruled out as explanation for the higher methyl nitrophenol concentrations at low temperatures. It is unlikely that photochemical processing is faster in winter and fall than in summer and the methyl nitrophenol isotope ratios show, on average, no indication for enhanced processing at low temperatures. The most likely explanation is higher precursor concentrations in fall and winter. The concentration of 2-methyl-4-nitrophenol in PM + gas is correlated ($R^2 = 0.64$) with the NO_2 concentration (Fig. 8a). Therefore it is expected that on average, higher NO_2 concentrations in fall and winter will result in higher 2-methyl-4-nitrophenol levels. The larger NO_2 concentrations in fall and winter may be attributed to the decreased boundary layer height coupled with increased pollution rates, but the higher photolysis rate of NO_2 in summer may also contribute to the difference in NO_2 concentrations between seasons.

Both toluene and NO_2 are required for the formation of methyl nitrophenols in the atmosphere and it is expected that the concentration of toluene also will influence the

formation rate of methyl nitrophenols. However, the correlation of the NO_2 concentration with other indicators of atmospheric pollution such as CO ($R^2 = 0.33$) and SO_2 ($R^2 = 0.41$) prevents separating between the influence of NO_2 and other precursors.

In contrast to 2-methyl-4-nitrophenol, the correlation between the concentrations of 4-nitrophenol and NO_2 is only weak (Fig. 8b). This indicates that, consistent with the low reactivity of the benzene precursor, the processes determining the concentration of 4-nitrophenol are occurring at a time scale that is different from the processes determining the NO_2 concentrations.

Correlation between NO_2 and 4-nitrophenol or alkyl nitrophenols may also be due to direct emissions since 4-nitrophenol and two methyl nitrophenol isomers have been found in exhaust from diesel powered vehicles (Inomata et al., 2013, 2015) which are also substantial sources for nitrogen oxides. The average ratios of 4-nitrophenol over NO_x volume mixing ratios calculated from the results reported by Inomata et al. (2013) range from approximately 5×10^{-5} for the engine with the highest 4-nitrophenol emissions to 7.5×10^{-8} for the engine with the lowest emissions. The average ratio of 4-nitrophenol over NO_x for our measurements is 9.5×10^{-5} on a molar basis with an error of the mean of 0.2×10^{-5}. Although this comparison ignores the existence of NO_2 sources other than diesel engines in the GTA, this is approximately a factor of two higher than the upper end of emission ratios for the measurements reported by Inomata et al. (2015). Nevertheless, based on the limited number of diesel engines investigated by Inomata et al. (2013), it cannot be ruled out that direct emissions contribute to the 4-nitrophenol concentrations we observed.

For methyl nitrophenols a significant contribution from direct emissions is less likely. The emission factors reported by Inomata et al. (2015) for 3-methyl-4-nitrophenol are between a factor of 45 and 500 lower than the average emission factor of 4-nitrophenol reported by Inomata et al. (2013) for the engine with the highest 4-nitrophenol emission factor while our measured 3-methyl-4-nitrophenol concentrations are on average only a factor of seven lower than the 4-nitrophenol concentrations. For 2-methyl-4-nitrophenol, the difference is even larger; the emission factors are between a factor

of 65 and 625 lower than for 4-nitrophenol while our measured concentrations differ on average by only a factor of 2.5. Moreover, Inomata et al. (2015) did not report the observation of 4-methyl-2-nitrophenol in PM from diesel engine exhaust although their quantification limit for this isomer was nearly identical to that for 2-methyl-4-nitrophenol

5 and 3-methyl-4-nitrophenol.

Atmospheric nitrophenols are produced by photochemical oxidation of aromatic VOC in the presence of NO_x. Since atmospheric oxidants (O_3 and NO_2) are also formed from photo-oxidation of VOC, we expect correlation between oxidant and nitrophenol concentrations. Indeed, there is a correlation ($R^2 = 0.60$) between the concentration of

10 oxidants and 4-nitrophenol (Fig. 9a). Surprisingly, the correlation between 2-methyl-4-nitrophenol and oxidant concentrations is only weak (Fig. 9b). This most likely reflects the different reactivity of the precursors (Table 3) and indicates that the timescale for processes determining oxidant levels is similar to the timescale determining formation of 4-nitrophenol, but different from that for 2-methyl-4-nitrophenol formation.

15 **4 Conclusions**

In this study, concentration and stable carbon isotope ratio measurements of nitrophenols in Toronto were taken. On average, the ^{13}C depletion relative to the carbon isotope ratios of the precursors is approximately 6 ‰, and the observed δ^{13}C values range from −37 to −28 ‰. The substantial variability of the nitrophenol carbon isotope ratios can

20 be explained by a varying degree of photochemical processing. Consequently, changes in the carbon isotope ratio of atmospheric nitrophenols are indicators for differences in photochemical processing, although currently no simple quantitative relation between nitrophenol isotope ratio and photochemical age has been established.

The lower end of measured ambient isotope ratios that is about 2 to 3 ‰ lower than

25 predictions based on the KIE for the reaction of the precursor with OH-radicals. This is consistent with results of the laboratory studies of Irei et al. (2015) and therefore provides additional evidence for a predominantly photochemical origin of the nitrophenols.

On average, the difference in carbon isotope ratios of nitrophenols between the gas phase and the particle phase is very small. This suggests that, on average, there is equilibrium between nitrophenols in the gas phase and in the particle phase, but there are several observations of a significant difference in nitrophenol carbon isotope ratios

5   between gas and particle phase. Since this is only observed in summer, it can be concluded that in these cases photochemical production or removal of nitrophenols is faster than their exchange between the two phases. The assumption of significant local photochemical processing of nitrophenols in summer is also supported by the difference between summer and winter carbon isotope frequency distributions of methyl

10   nitrophenols.

There is no significant correlation between the carbon isotope ratio of nitrophenols and their concentration. This demonstrates that, for the conditions studied here, atmospheric mixing is the dominant process in determining the concentrations of nitrophenols. Indeed, for some nitrophenols strong correlations between their concentrations

15   and the concentration of precursors or indicators of pollution are found.

The concentration of 4-nitrophenol is strongly correlated with the oxidant ($O_3 + NO_2$) levels whereas the correlation between the concentration of alkyl nitrophenols and oxidant concentration is weak. It can be concluded that the processes determining oxidant concentrations are occurring on timescales that are better represented by the

20   processes resulting in formation of 4-nitrophenols than those for formation of alkyl nitrophenols. Most likely these differences in timescales are determined by the reactivity of the aromatic precursors of the different nitrophenols.

The importance of precursor reactivity on the carbon isotope ratios of nitrophenols is supported by the comparison of carbon isotope ratios of different methyl nitrophenol isomers. Overall, these differences in carbon isotope ratios for different isomers

25   are small compared to the overall variability of the carbon isotope ratios of individual isomers of methyl nitrophenols.

Combining measurement of the atmospheric concentrations of secondary organic compounds with measurement of their carbon isotope ratios provides detailed insight

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into the processes and the timescales at which the formation occurs. However, currently this insight is limited to qualitative or semi-quantitative conclusions since the current quantitative understanding of the dependence between the carbon isotope ratio of secondary organic compounds and photochemical aging is limited.

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Table 1. Summary of performance characteristics of the sampling, extraction and analysis method of nitrophenols in PM and in the gas phase + PM (Saccon et al., 2013).

XAD-4™ collection efficiency	84 %
Detection limit	0.002 ng m^{-3}
GC-MS calibration R^2	0.99
GC-IRMS calibration R^2	0.99
Precision of δ^{13}C measurements	0.3 ‰
Overall uncertainty of δ^{13}C measurements	0.5 ‰

Table 2. Summary of ambient isotope ratio measurements of nitrophenols.

Target Compound	Abbreviation	Carbon Isotope Ratio (‰)						
		Average	Error of the Mean	Median	Max	Min	25th Percentile	75th Percentile
4-nitrophenol	4-NP	−33.5	0.2	−33.6	−30.4	−36.4	−34.5	−32.4
4-methyl-2-nitrophenol	4-me-2-NP	−33.0	0.3	−33.3	−30.7	−34.7	−33.7	−32.5
3-methyl-4-nitrophenol	3-me-4-NP	−33.1	0.3	−32.9	−28.4	−36.2	−34.2	−32.2
2-methyl-4-nitrophenol	2-me-4-NP	−33.0	0.2	−33.1	−28.4	−36.0	−34.0	−31.7
2,6-dimethyl-4-nitrophenol	2,6-dime-4-NP	−33.6	0.4	−33.6	−29.4	−37.0	−34.9	−32.2

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Table 3. Rate constants (k_{OH}), carbon KIE and isotope ratio of emissions ($\delta^{13}C_0$) for reactions of aromatic hydrocarbons with OH radicals. Also given are carbon isotope ratios of reaction products in the initial phase of the reaction of the precursor VOC ($\delta^{13}C_i$).

	k_{OH}^a (cm^3 molec^{-1} s^{-1})	KIE^b (‰)	$\delta^{13}C_0^c$ (‰)	$\delta^{13}C_i^d$ (‰)
Benzene	1.39×10^{-12}	7.83 ± 0.42	-26.9 ± 1.7	-34.7 ± 1.8
Toluene	5.63×10^{-12}	5.95 ± 0.28	-27.6 ± 0.9	-33.5 ± 0.9
m-Xylene	2.31×10^{-11}	4.83 ± 0.05	-27.4 ± 0.5	-32.2 ± 0.5

[a] Calvert et al. (2002).
[b] Anderson et al. (2004).
[c] Rudolph et al. (2002).
[d] The uncertainty of $\delta^{13}C_i$ is calculated from the uncertainties of the emission and of the KIE for reaction with OH radicals.

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Table 4. Overview of the difference in delta values for sample pairs ($\Delta\delta^{13}$C) and environmental conditions for the summer and late fall measurements shown in Fig. 4.

	$\Delta\delta^{13}$C (‰)[a]	Temperature (K)	$[O_3]$ (nmol mol^{-1})	$[NO_2]$ (nmol mol^{-1})	$[PM_{2.5}]$[b] (µg m^{-3})
Late Fall	0.3 ± 0.9 (11)	275	13	23	11
Summer	0.3 ± 3.2 (5)	298	44	10	17

[a] Average and standard deviation, number of data points is given in parenthesis.
[b] Particulate matter < 2.5 µm.

Table 5. Overview of difference in carbon isotope ratios ($\Delta\delta^{13}C$) between different nitrophenols analyzed in the same sample.

	n^a	$\Delta\delta^{13}C$ (‰)^b	Observed SD (‰)^c	Expected SD (‰)^d
4-NP and me-NP[e]	101	−0.34	1.8	2.2
2,6-dime-4-NP and 4-NP	17	−0.24	2.5	2.4
2,6-dime-4-NP and me-NP[e]	42	−0.26	2.0	2.5

[a] Number of measurement pairs.
[b] Average.
[c] Standard deviation determined from measurements pairs.
[d] Standard deviation expected from variability of individual nitrophenols.
[e] All three methyl nitrophenol isomers studied.

Table 6. Average of measured 2-methyl-4-nitrophenol concentrations and carbon isotope ratios for different daily average temperatures. For comparison air quality data from two monitoring sites of OME are also shown.

	< 10 °C	> 20 °C
PM Samples	17[a]	10[a]
Average $[O_3]$ $(nmol\,mol^{-1})$[b]	12 (15)	29 (33)
Average $[NO_2]$ $(nmol\,mol^{-1})$[b]	23 (18)	17 (15)
Average $[PM_{2.5}]$ $(\mu g\,m^{-3})$[b]	6 (6)	12 (13)
Average $[SO_2]$ $(\mu mol\,mol^{-1})$[b]	1.4	1.0
Average $[CO]$ $(\mu mol\,mol^{-1})$[b]	0.18	0.21
$\delta^{13}C_{2\text{-me-4-NP}}$ (‰)[c]	−32.1 ± 0.4	−32.5 ± 0.3
[2-me-4-NP] $(ng\,m^{-3})$[c]	1.3 ± 0.6	0.2 ± 0.1
$\delta^{13}C_{4\text{-NP}}$ (‰)[d]	−33.7 ± 0.5	−32.8 ± 0.8
[4-NP] $(ng\,m^{-3})$[d]	2.5 ± 1.2	0.7 ± 0.3
Gas + PM Samples	10[a]	10[a]
Average $[O_3]$ $(nmol\,mol^{-1})$[b]	9 (12)	34 (39)
Average $[NO_2]$ $(nmol\,mol^{-1})$[b]	25 (22)	14 (10)
Average $[PM_{2.5}]$ $(\mu g\,m^{-3})$[b]	8 (9)	12 (13)
Average $[SO_2]$ $(\mu mol\,mol^{-1})$[b]	2.0	1.3
Average $[CO]$ $(\mu mol\,mol^{-1})$[b]	0.21	0.21
$\delta^{13}C_{2\text{-me-4-NP}}$ (‰)[c]	−32.3 ± 0.5	−32.8 ± 0.5
[2-me-4-NP] $(ng\,m^{-3})$[c]	3.6 ± 0.9	2.2 ± 0.3
$\delta^{13}C_{4\text{-NP}}$ (‰)[d]	−33.9 ± 0.6	−33.6 ± 0.4
[4-NP] $(ng\,m^{-3})$[d]	5.7 ± 1.7	8.9 ± 2.3

[a] Number of measurements of 2-me-4-NP in each category.
[b] Pollution data acquired from Ontario Ministry of the Environment: Historical Pollutant Data, Toronto West Site and values are averaged over the sampling time. Data from the Toronto North Site are listed in brackets, when available.
[c] Average ± error of the mean.
[d] 4-NP data were not available for all samples with 2-me-4-NP measurements, the 4-NP averages are based on a total of 17 PM and 18 gas + PM samples.

Figure 1. Map showing the sampling site (York University) as well as the Ontario Ministry of Environment (OME) sites (Toronto West and Toronto North) that collected pollutant data. The map was produced using Google Earth, ©2015 Google, ©2015 DigitalGlobe, ©2015 First Base Solutions and NOAA (August 2009).
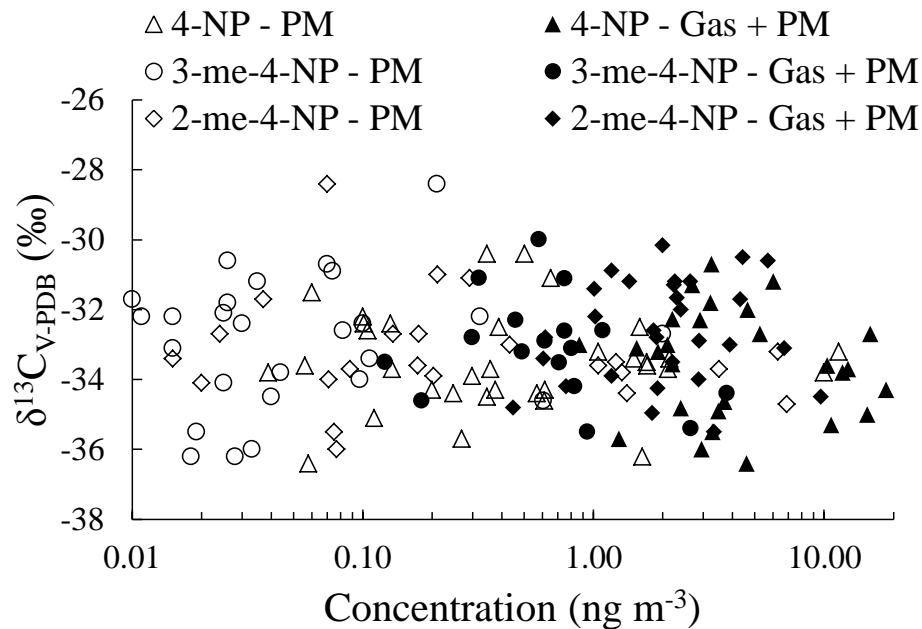
Figure 2. Plot of isotope ratio values as a function of concentration for 4-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol.

Figure 3. Frequency distribution of ambient stable carbon isotope ratios of 4-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol for samples collected in PM alone (white) and in the gas phase and PM together (grey). The solid vertical line in each of the graphs represents the delta value of the nitrophenol formed in the initial phase of the reaction based on the carbon isotope ratio of precursor emissions and the KIE for reaction of the precursor with the OH radical and the dashed vertical lines represent the uncertainty (Table 3).

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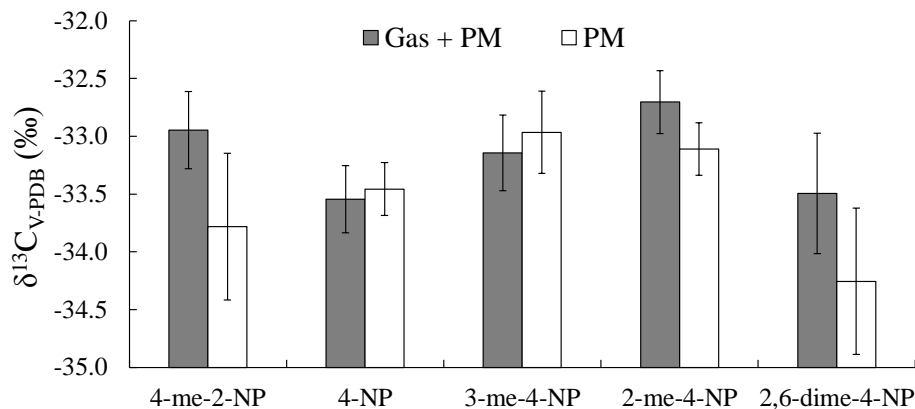
Figure 4. Comparison of average isotope ratios of nitrophenols found in PM alone and in the gas phase + PM. The error bars represent the error of the mean.
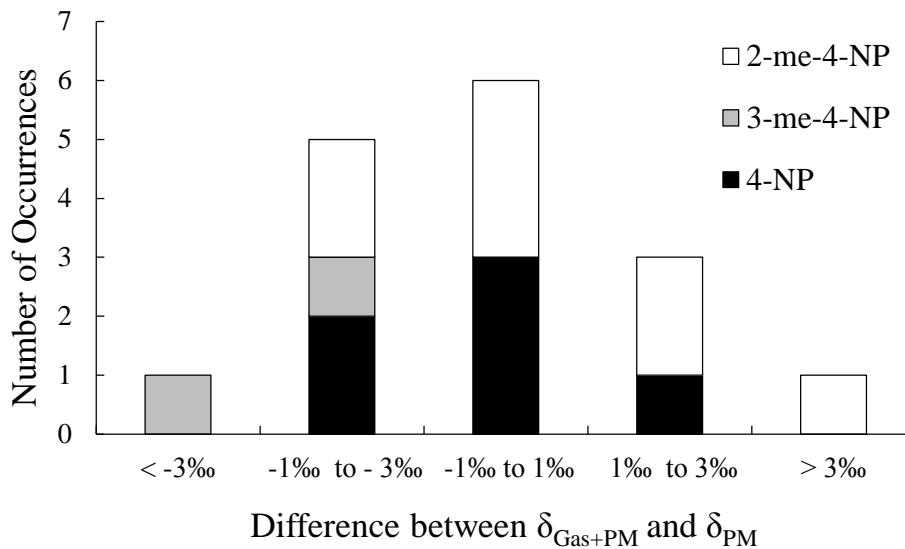
Figure 5. Frequency distribution for the difference in the stable carbon isotope ratio of target nitrophenols in the gas phase + PM and in PM for samples collected in parallel.
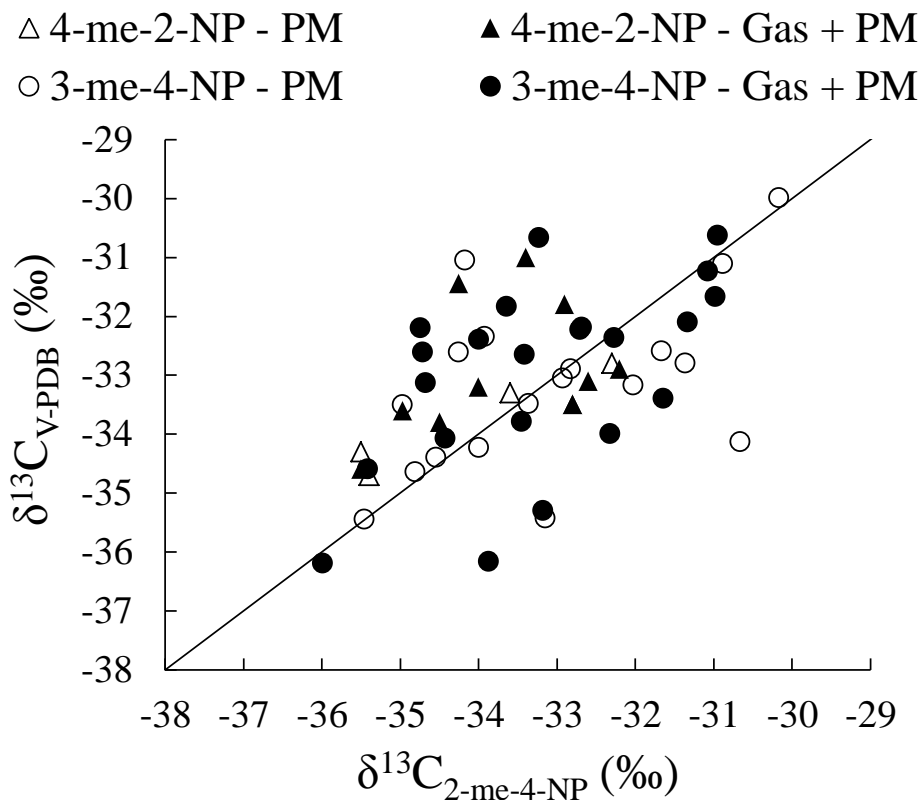
Figure 6. Plot of isotope ratios for 4-methyl-2-nitrophenol and 3-methyl-4-nitrophenol (y axis) against 2-methyl-4-nitrophenol.

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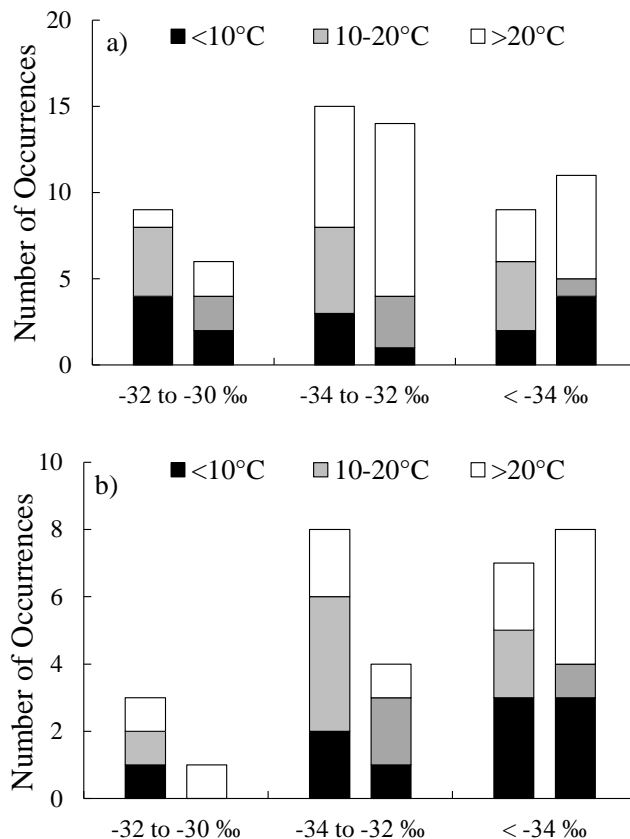
Figure 7. Gas + PM samples for the three methyl nitrophenols **(a)** and 4-nitrophenol **(b)** were binned according to isotope ratio and separated by the given temperature ranges. The left column in each bin has winds originating from the North and the right column in each bin has winds originating from the South–West. Wind direction was taken from HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model) by Air Resources Laboratory (NOAA).
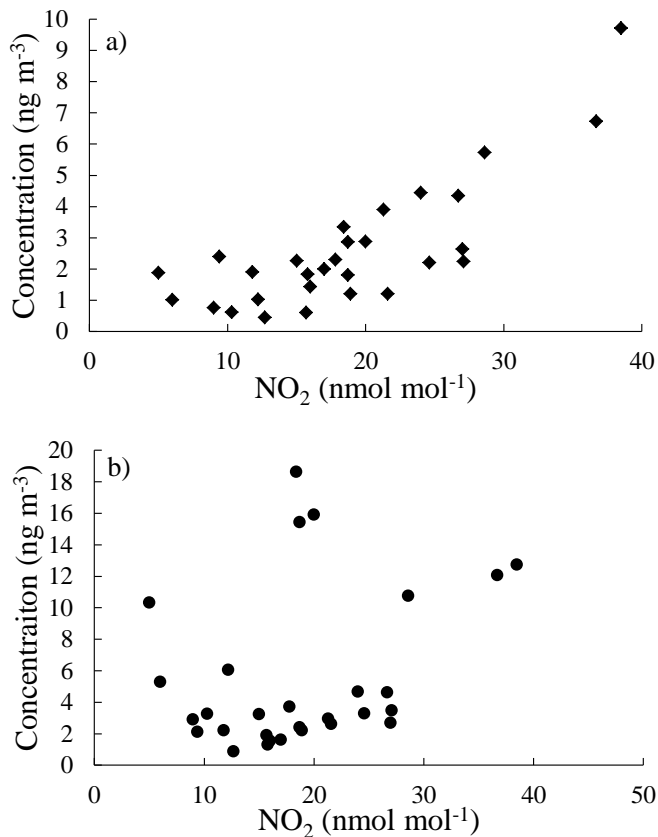
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Figure 8. Plot of gas + PM sample concentrations of 2-methyl-4-nitrophenol **(a)** and 4-nitrophenol **(b)** vs. NO_2 mixing ratios, which is hourly data averaged over the sampling time for each filter sample from Ontario Ministry of the Environment: Historical Pollutant Data, Toronto West Site.
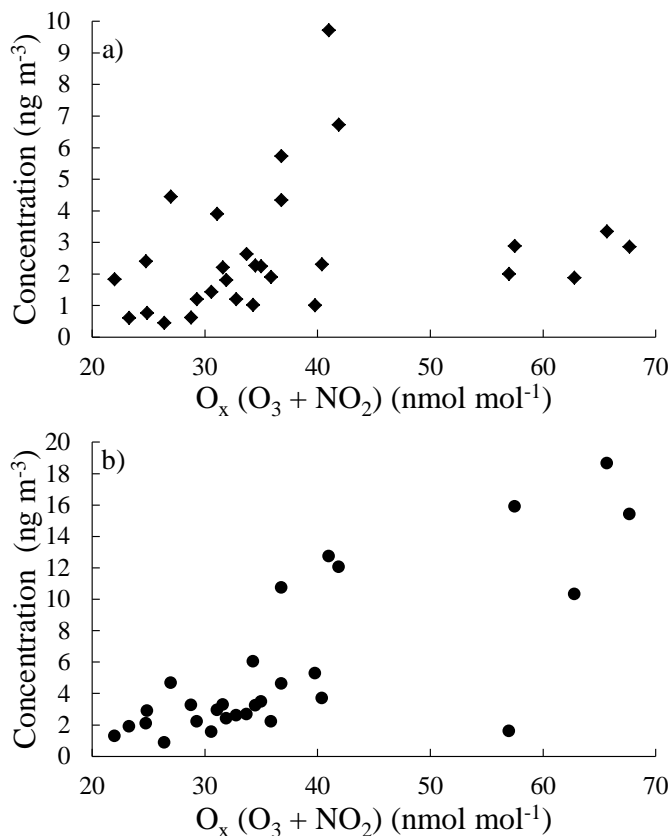
Figure 9. Plot of gas + PM sample concentrations of 2-methyl-4-nitrophenol **(a)** and 4-nitrophenol **(b)** vs. oxidant ($O_3 + NO_2$) mixing ratios, which is hourly data averaged over the sampling time for each filter sample from Ontario Ministry of the Environment: Historical Pollutant Data, Toronto West Site.

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