

1 **Stable Carbon Isotope Ratios of Ambient Secondary Organic Aerosols in Toronto**

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1 **Abstract**

2 A method to quantify concentrations and stable carbon isotope ratios of secondary organic
3 aerosols (SOA) has been applied to study atmospheric nitrophenols in Toronto, Canada. The
4 sampling of five nitrophenols, all with substantial secondary formation from the photooxidation
5 of aromatic volatile organic compounds (VOC), in the gas phase and particulate matter (PM)
6 together and PM alone was conducted. Their concentrations in the atmosphere are in the low ng
7 m⁻³ range and consequently, a large volume of air (> 1000 m³) is needed to analyze samples for
8 stable carbon isotope ratios, resulting in sampling periods of typically 24 hours. While this
9 extended sampling period increases the representativeness of average values, it at the same time
10 reduces possibilities to identify meteorological conditions or atmospheric pollution levels
11 determining nitrophenol concentrations and isotope ratios.

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

19 Limited evidence for local production of nitrophenols is observed since sampling was
20 done in the Toronto area, an urban centre with significant anthropogenic emission sources.
21 Strong evidence for significant local formation of nitrophenols is only found for samples
22 collected in summer. On average, the difference in carbon isotope ratios between nitrophenols in
23 the particle phase and in the gas phase is insignificant, but for a limited number of observations

1 in summer, a substantial difference is observed. This indicates that at high OH radical
2 concentrations, photochemical formation or removal of nitrophenols can be faster than exchange
3 between the two phases.

4 The dependence between the concentrations and isotope ratios of the nitrophenols and
5 meteorological conditions as well as pollution levels (NO₂, O₃, SO₂ and CO) demonstrate that
6 the influence of precursor concentrations on nitrophenol concentrations is far more important
7 than the extent of photochemical processing. While it cannot be excluded that primary emissions
8 contribute to the observed levels of nitrophenols, overall the available evidence demonstrates
9 that secondary formation is the dominant source for atmospheric nitrophenols in Toronto.

10 **1. Introduction**

11 Volatile organic compounds (VOC) are emitted into the atmosphere by both anthropogenic
12 and biogenic sources. Once emitted, the VOC undergo both physical and chemical processes,
13 such as dilution and chemical reactions. Reactions in the atmosphere are mainly oxidation
14 reactions with OH, ozone or chlorine radicals. These oxidation reactions produce products which
15 are typically heavier and have lower vapour pressures than the precursor. Many of the products
16 are considered to be semi-volatile organic compounds (SVOC), which have properties that allow
17 them to exist both in the gas phase and in particulate matter (PM), and compose secondary
18 organic aerosols (SOA), making up a substantial portion of aerosols in the troposphere.
19 Nitrophenols, the target compounds of this paper, are SVOC that are produced by processes in
20 the atmosphere from aromatic VOC such as benzene, toluene and m-xylene, according to the
21 reaction scheme in Fig. 1 (Forstner et al., 1997; Atkinson, 2000; Jang and Kamens, 2001;
22 Hamilton et al., 2005; Sato et al., 2007). The nitrophenol formation pathway from toluene and

1 m-xylene is proposed to be similar. Once emitted, the aromatic VOC can undergo
2 photooxidation with the OH radical to produce a (di)methyl hydroxycyclohexadienyl radical,
3 which can then form a (di)methyl phenol (Forstner et al., 1997). These intermediates can then
4 react with OH and NO₂ to produce (di)methyl nitrophenols.

5 4-Nitrophenol has several proposed formation pathways which includes pathways in both
6 the gas phase and the aqueous phase. Atkinson et al. (1992) proposed that benzene undergoes
7 photooxidation to produce a phenoxy radical with subsequent reaction with NO₂. Alternatively,
8 Bolzacchini et al. (2001) suggested the addition of NO₃ to the OH carbon of phenol, followed by
9 the addition of NO₂ to the para carbon and final loss of HNO₃, forming 4-nitrophenol. Irei et al.
10 (2015) found 4-nitrophenol to be a reaction product from the gas phase photooxidation of
11 toluene.

12 It has been proposed that the aqueous phase production of nitrophenols could occur from
13 the reaction of cresols with NO₃ (Herrmann et al., 1995). Aqueous phase formation of 4-
14 nitrophenol has also been proposed by Harrison et al. (2005), suggesting that once phenol is
15 produced from the reaction of benzene and the OH radical, it partitions into the aqueous phase,
16 reacts with NO₃ to form 4-nitrophenol, which then partitions favourably into the gas phase.
17 Based on model calculations, the aqueous formation processes can have a substantial
18 contribution to the total formation rate at high liquid water content, such as in clouds, but at low
19 liquid water contents, this process contributes less than 2 % to nitrophenol formation (Harrison et
20 al., 2005).

21 Nitrophenols have been found in trace amounts as primary emissions, such as gasoline
22 fueled automobile exhaust (Trempe et al., 1993). In a very recent study, Inomata et al. (2015)

1 reported that emission factors for 4-nitrophenol in PM from gasoline fueled engines are below
2 the quantification limits of $6 \times 10^{-3} \mu\text{g km}^{-1}$, whereas for diesel engines emission factors ranged
3 from $0.23 \mu\text{g km}^{-1}$ to $29.5 \mu\text{g km}^{-1}$ for 4-nitrophenol in PM. The reported values for 3-methyl-4-
4 nitrophenol and 2-methyl-4-nitrophenol are in the range of $0.32 \mu\text{g km}^{-1}$ to $11.4 \mu\text{g km}^{-1}$ for
5 diesel engines and were below the quantification limits for gasoline engines. 4-nitrophenol has
6 also been found in the gas phase of diesel engine exhaust at highly variable levels (Inomata et al.,
7 2013) corresponding to emissions factors ranging from effectively zero to hundreds of $\mu\text{g km}^{-1}$.

8 Considering the many possible sources of atmospheric nitrophenols it can be difficult to
9 identify the most important sources using only concentration measurements. Stable carbon
10 isotope ratio measurements have been useful tools in atmospheric chemistry (Gensch et al.,
11 2014). The ratio of the ^{13}C isotope, which has a natural abundance of approximately 1.1 %, and
12 the ^{12}C isotope is compared to a standard, the Vienna-Peedee Belemnite (V-PDB) with a value of
13 0.0112372 (Craig, 1957), as shown in Eq. (1). This relative difference in per mille notation is
14 referred to as the delta value ($\delta^{13}\text{C}$). Stable carbon isotope ratio measurements in combination
15 with concentration measurements have been proposed to be used to gain insight on the formation
16 and processing of secondary organic aerosols in the atmosphere (Goldstein and Shaw, 2003;
17 Rudolph, 2007; Gensch et al., 2014). Although still a developing field, especially in atmospheric
18 chemistry, stable carbon isotope ratio measurements have been used to measure a wide range of
19 compounds to gain information on sources, chemical processes and transport in the atmosphere.
20 Nitrophenols were chosen as the target compounds in this study for three reasons. The first
21 reason is that nitrophenols are formed from one reaction pathway and are specific to the aromatic
22 VOC + OH reaction (Forstner et al., 1997). This is important so that the nitrophenols can be
23 traced back to the precursor, which has a measured and known isotope ratio at the source

1 (Rudolph et al., 2002). Secondly, the target compounds should be ring retaining products so that
2 the possibility of being formed from other precursors decreases compared to ring fragmentation
3 products. Lastly, and most importantly, it has been shown that one of the methyl nitrophenols, 2-
4 methyl-4-nitrophenol, has an isotope ratio that is within ± 1.33 ‰ of the isotope ratio of the sum
5 of all reaction products for the reaction of toluene (between 10 % and 27 % reacted) with the OH
6 radical, allowing for a first order prediction of the dependence between isotope ratios of reaction
7 products and photochemical precursor processing in the atmosphere from mass balance
8 calculations (Irei et al., 2015). Measurements of nitrophenol concentrations and their isotope
9 ratios in a mixed residential and industrial area are reported and discussed in this paper.

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

10 **2. Method**

11 The method used for filter preparation, sample collection, extraction and analysis has been
12 previously described by Saccon et al. (2013), Moukhtar et al. (2011) and Irei et al. (2013).
13 Samples were collected at York University (Fig. 2) in the outskirts of Toronto, Canada using
14 high volume air samplers (Fig. 2). Figure 2 also shows the location of two monitoring stations of
15 the Ontario Ministry of the Environment (OME), which provided measurements of ambient
16 concentrations of NO₂, O₃, CO, SO₂, and PM with a nominal aerodynamic diameter of less than
17 2.5 μm (PM_{2.5}). The sampling period was from March 2009 to August 2012. Prebaked quartz
18 fibre filters were used for PM collection and prebaked quartz fibre filters coated with XAD-4TM
19 resin were used for gas phase + PM collection. The sampling times for XAD-4TM coated filters
20 were typically 24 hours and from one to three days for uncoated filters.

1 Uncoated quartz filters have the possibility of sampling artifacts, including gas phase target
2 compounds. Nitrophenol artifacts could not be ruled out but were found to be limited. The mass
3 of artifacts on a filter is expected to be proportional to sampling time. For the target compounds
4 analyzed, an average percent difference of approximately 6.5 % was observed between three
5 samples collected for one day each and a sample collected continuously for three days. Saccon et
6 al. (2013) showed that partitioning results from denuder sampling, which is designed to limit
7 artifacts from the separation of the gas phase from the PM phase, are consistent with results from
8 conventional filter sampling, such that the majority of nitrophenols are found in the gas phase.
9 From denuder sampling experiments it is estimated that the gas phase component of each of the
10 target compounds, apart from 4-methyl-2-nitrophenol, is about 10 to 30 % higher than what is
11 found from high volume filter samples. This difference is consistent with the sampling efficiency
12 of XAD-4TM coated filters (Saccon et al., 2013).

13 Filters, prior to extraction, were stored in a freezer. After being spiked with internal
14 standards, filters were extracted with acetonitrile, underwent an HPLC and solid phase extraction
15 cleanup step and were analyzed. An HP 5890 GC coupled to an HP 5972 MS was used for
16 concentration measurements and an HP 6890 GC coupled to a Micromass Isoprime IRMS was
17 used for isotope ratio measurements. All samples were derivatized with bis(trimethylsilyl)
18 trifluoroacetamide (BSTFA) prior to analysis. A summary of performance characteristics is
19 shown in Table 1. Only samples containing more than 3 ng of carbon for at least one of the target
20 compound per 3 μ L injection were used for quantifying stable carbon isotope ratios.

1 3. Results & Discussion

2 3.1 Overview of Measured Carbon Isotope Ratios

3 An overview of the measured isotope ratios of nitrophenols is given in Table 2. The
4 nitrophenols chosen as the target compounds for this study were 4-nitrophenol, 4-methyl-2-
5 nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol and 2,6-dimethyl-4-nitrophenol.
6 Since only sample extracts with concentrations of at least $1 \text{ ng } \mu\text{L}^{-1}$ of carbon for a target
7 compound were suitable for isotope ratio measurement, only a subset of the samples collected
8 was analyzed for $\delta^{13}\text{C}$ of the target nitrophenols. This reduced the number of samples with low
9 nitrophenol concentrations and therefore could result in subsets of $\delta^{13}\text{C}$ data biased towards
10 samples with higher nitrophenol concentrations. For the most abundant target compounds, 4-
11 nitrophenol and 2-methyl-4-nitrophenol, 85 % and 98 %, respectively, of the 102 samples (47
12 PM and 55 gas + PM) could be analyzed for isotope ratios. For the lower in abundance
13 compounds, 4-methyl-2-nitrophenol, 3-methyl-4-nitrophenol and 2,6-dimethyl-4-nitrophenol,
14 only 17 %, 47 % and 22 %, respectively, of the samples were analyzed for carbon isotope ratios.
15 As can be seen from Fig. 3, the variability of the carbon isotope ratio substantially exceeds any
16 systematic dependence between concentration and $\delta^{13}\text{C}$.

17 The range of $\delta^{13}\text{C}$ values covered by the individual target compounds is between 4 and
18 nearly 9 ‰ and 50 % of the $\delta^{13}\text{C}$ values differ by more than 1 ‰ from the average (Fig. 4). The
19 measurement precision is 0.3 ‰ and the resulting measurement uncertainty for differences
20 between two observations for the same target substance is 0.4 ‰. Differences exceeding 0.7 ‰
21 and 1.1 ‰ exceed the measurement uncertainty within a 90 % and 99 % confidence limit,
22 respectively. Therefore, most of the observed variability of the measurements cannot be
23 explained by measurement uncertainty. The dominant factors creating variability in the isotope

1 ratios of organic compounds in the atmosphere are atmospheric reactions or varying
2 contributions from sources with different isotopic composition (Gensch et al., 2014).

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

1 The overview of the results in Fig. 3 and 4 and Table 2 show that nearly all measured
2 $\delta^{13}\text{C}$ values of the target compounds are significantly depleted relative to the parent material
3 (Table 3). This is fully consistent with a secondary origin of the target compounds. However, 4-
4 nitrophenol and two methyl nitrophenol isomers have been found in exhaust from diesel powered
5 vehicles (Inomata et al., 2013, 2015) and the possibility of contributions from direct emissions
6 has to be considered. The average ratios of 4-nitrophenol over NO_x volume mixing ratios
7 calculated from the results reported by Inomata et al. (2013) range from approximately 5×10^{-5}
8 for the engine with the highest 4-nitrophenol emissions to 7.5×10^{-8} for the engine with the
9 lowest emissions. The average ratio of 4-nitrophenol over NO_x for our measurements is $9.5 \times$
10 10^{-5} on a molar basis with an error of the mean of 0.2×10^{-5} . Although this comparison ignores
11 the existence of NO_2 sources other than diesel engines in the GTA, this is nevertheless a factor of
12 approximately two higher than the upper end of emission ratios for the measurements reported
13 by Inomata et al. (2015). Still, based on the limited number of diesel engines investigated by
14 Inomata et al. (2013), it cannot be ruled out that direct emissions to some extent contributed to
15 the 4-nitrophenol concentrations we observed.

16 4-Nitrophenol has also been found to be a product from toluene photooxidation (Irei et
17 al., 2015), but with a yield that is only about 6 % of the yield for 2-methyl-4-nitrophenol. The
18 carbon isotope ratio of 4-nitrophenol formed by the photooxidation of toluene is, within
19 measurement uncertainty, identical to the carbon isotope ratio of the precursor. Since the
20 measured concentrations of 4-nitrophenol are on average a factor of approximately 2.5 higher
21 than those of the most abundant methyl nitrophenol and the observed 4-nitrophenol carbon
22 isotope ratios are on average 6.6 ± 1.7 ‰ lower than those of the parent material a substantial
23 contribution of toluene oxidation to the observed levels of 4-nitrophenol can be ruled out.

1 For methyl nitrophenols, a measurable contribution from direct emissions is not likely.
2 The emission factors reported by Inomata et al. (2015) for 3-methyl-4-nitrophenol are between a
3 factor of 45 and 500 lower than the average emission factor of 4-nitrophenol reported by Inomata
4 et al. (2013) for the engine with the highest 4-nitrophenol emission factor while on average our
5 measured 3-methyl-4-nitrophenol concentrations are on average only a factor of seven lower
6 than the 4-nitrophenol concentrations. For 2-methyl-4-nitrophenol, the difference is even larger;
7 the emission factors are between a factor of 65 and 625 lower than for 4-nitrophenol while our
8 measured concentrations differ on average by only a factor of 2.5. Moreover, Inomata et al.
9 (2015) did not report the observation of 4-methyl-2-nitrophenol in PM from diesel engine
10 exhaust although their quantification limit for this isomer was nearly identical to that for 2-
11 methyl-4-nitrophenol and 3-methyl-4-nitrophenol.

12 There are no measurements of the carbon isotope ratio of emissions for any of the target
13 compounds, but there have been a substantial number of studies of the carbon isotope ratios of
14 emissions for other VOC (Gensch et al., 2014). The carbon isotope ratios of VOC emitted from
15 incomplete combustion sources are either close to the isotope ratios of the parent material or
16 heavier and all reported traffic or incomplete combustion related VOC emissions are heavier
17 than -29 ‰. The measured $\delta^{13}\text{C}$ values of the target compounds are, with very few exceptions
18 substantially lower than -29 ‰, which is consistent with secondary formation from VOC
19 precursors.

20 It has been postulated that nitrophenols can be formed in clouds via the formation of
21 phenol by the gas phase reaction of benzene with OH radicals and subsequent absorption of
22 phenol into cloud water. Following the formation of nitrophenols in the liquid phase, the
23 nitrophenols can partition into the gas phase (Harrison et al., 2005). Since the phenol formed by

1 reaction of aromatic VOC with OH radicals will be depleted in ^{13}C relative to the parent VOC,
2 such a mechanism would be consistent with the light $\delta^{13}\text{C}$ values observed here. However, the
3 measurements presented here were conducted very close to ground level, at the top of a four
4 floor building. Due to the strong vertical gradients of primary pollutants over regions with strong
5 anthropogenic sources (see for example Glaser et al., 2003) only low level clouds can contribute
6 to the formation of nitrophenols. Harrison et al. (2005) calculated that at a “benchmark” value of
7 a liquid volume fraction of 3×10^{-7} , corresponding to 0.3 g m^{-3} , 58 % of nitrophenol formation is
8 via the liquid phase. This liquid water content is typical for low level clouds such as stratus or
9 cumulus clouds. For North America, the average coverage with low level clouds is
10 approximately 18 % (International Cloud Climatology Project). Our measurements were made at
11 an altitude much lower than the cloud base of even low level clouds. Considering all this, overall
12 a significant contribution of cloud processing to the levels of the target compounds we observed
13 can be ruled out.

14 As predicted by the postulated gas phase formation mechanisms and subsequent reaction
15 with the OH radical, most of the measured $\delta^{13}\text{C}$ values of 4-nitrophenol are larger than -34 ‰
16 (Fig. 4). The lower end of the measured $\delta^{13}\text{C}$ values for 4-nitrophenol is approximately 1 to 2 ‰
17 lower than $\delta^{13}\text{C}$ values predicted from the $\delta^{13}\text{C}$ values of benzene emissions and the KIE for
18 reaction of benzene with the OH radical, however this difference is within the uncertainty of the
19 prediction (Table 3) and the measurement error (Table 1). For two of the reaction products of the
20 photooxidation of toluene, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol, the discrepancy
21 between prediction and the lower end of observations is more pronounced. For both compounds,
22 the lower end of the observations is approximately 2 to 3 ‰ lighter than predicted, a difference
23 that is larger than the uncertainty of the predictions (Table 3). Similarly for 2,6-dimethyl-4-

1 nitrophenol, the 25th percentiles are 2.7 ‰ lower than predicted for the reaction of unprocessed
2 VOC emissions. In total, 19 % of all measurements are below the 99 % confidence limit
3 calculated from the combined uncertainty of measurement and $\delta^{13}\text{C}_i$. However, a substantial part,
4 if not all, of the uncertainty of $\delta^{13}\text{C}_i$ may be systematic. Assuming that the total calculated
5 uncertainty of $\delta^{13}\text{C}_i$ is systematic, 12 % of the observations are below the 2σ uncertainty of $\delta^{13}\text{C}_i$
6 and 5 % below the 3σ limit.

7 In situations with precursor isotope ratios close to unprocessed emissions, the
8 concentration of secondary compounds will be low. Consequently, it is expected that the lowest
9 nitrophenol carbon isotope ratios will be for samples with low concentrations. In contrast to this
10 expectation there is no systematic dependence between isotope ratios and concentrations (Fig. 3)
11 for the concentration range with measurable carbon isotope ratios. However, since some of the
12 samples collected were too low in the concentration of the target compounds to be analyzed for
13 carbon isotope ratios, it cannot be determined if the lower end of the observed distributions is
14 biased due to limitations of the $\delta^{13}\text{C}$ measurements or represents the true lower limit of the
15 isotope ratios of atmospheric nitrophenols.

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

22

1 **3.2 Comparison of Gas Phase and PM Phase Isotope Ratios**

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

15 For the measurements presented here, the average concentration of nitrophenols in PM is
16 only about 20 % of the average of the total atmospheric nitrophenol concentrations, similar to the
17 findings reported by Saccon et al. (2013). Consequently, on average, the carbon isotope ratio of
18 total atmospheric nitrophenols is dominated by the carbon isotope ratio of gas phase
19 nitrophenols. The frequency distributions (Fig. 4) as well as a comparison of average carbon
20 isotope ratios (Fig. 5) show no systematic difference in the isotope ratios between the two
21 phases. In the case of 4-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol, the
22 differences between averages for PM + gas phase and PM only are less than 0.5 ‰ and for 4-
23 methyl-2-nitrophenol and 2,6-dimethyl-4-nitrophenol the differences are less than 1 ‰. These

1 differences are all within the uncertainties of the averages. The larger errors for 4-methyl-2-
2 nitrophenol and 2,6-dimethyl-4-nitrophenol are due to the smaller number of samples, which is
3 less than 15 for each phase.

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

12 For 2-methyl-4-nitrophenol, the most abundant targeted product from toluene
13 photooxidation, there were eight pairs of samples in which the isotope ratios were quantified in
14 both types of samples; 4-nitrophenol and 3-methyl-4-nitrophenol had six and two sample pairs,
15 respectively. An overview of the differences between total and PM only isotope ratios for
16 samples collected in parallel ($\Delta\delta^{13}\text{C}$) is shown in Fig. 6. On average the difference is 0.3 ‰ with
17 an error of the mean of 0.5 ‰, consistent with the results in Fig. 5. However, the standard
18 deviation for $\Delta\delta^{13}\text{C}$ is 1.8 ‰, outside of the 99 % confidence limit expected from the uncertainty
19 of the measurements. Disequilibrium without significant systematic bias in $\Delta\delta^{13}\text{C}$ indicates that
20 exchange between the two phases is slower than the change of $\delta^{13}\text{C}$ in one of the two phases.
21 Since, apart from exchange with the gas phase, no processes are known that will change the
22 concentration or carbon isotope ratio of nitrophenols in the particle phase, it is likely that the

1 change of $\delta^{13}\text{C}$ in the gas phase due to formation from aromatic VOC or gas phase loss reactions
2 of nitrophenols is creating the disequilibrium in carbon isotope ratio between the two phases.

3 Indeed the variability of $\Delta\delta^{13}\text{C}$ for sample pairs collected in summer is substantially higher
4 than for late fall, when photochemical activity is expected to be lower than in the summer (Table
5 4). Although the number of measurements is small and the averages are identical, the standard
6 deviation of $\Delta\delta^{13}\text{C}$ for summer sample pairs is 3.2 ‰ and well outside of the variability expected
7 from measurement errors. In contrast to this the standard deviation of $\Delta\delta^{13}\text{C}$ for late fall is only
8 0.9 ‰, which is only slightly higher than expected from the uncertainty of the measurements.
9 The variances for the summer and winter data sets are statistically different with a 99.5 %
10 probability (F-test).

11 In addition to a slower photochemical production or destruction of the nitrophenols in late
12 fall a lower variance of $\Delta\delta^{13}\text{C}$ in late fall can also be caused by the temperature dependence of
13 phase partitioning. For the sample pairs collected in summer, PM contributed on average 12 % of
14 the total atmospheric nitrophenol concentration. Therefore, the measured $\Delta\delta^{13}\text{C}$ values are a
15 good approximation for the difference in $\delta^{13}\text{C}$ between nitrophenols in the gas phase and in PM.
16 For the sample pairs collected in late fall, the contributions from PM range from 30 % to
17 approximately 100 % and consequently the difference in $\delta^{13}\text{C}$ between nitrophenols in the gas
18 phase and in PM will be larger than the measured $\Delta\delta^{13}\text{C}$ values. Unfortunately, for the late fall
19 samples, the large contribution of measurement error to the $\Delta\delta^{13}\text{C}$ values, combined with the
20 uncertainty of concentration measurements prevents a meaningful determination of the
21 difference in $\delta^{13}\text{C}$ between nitrophenols in the gas phase and in PM

22

1 3.3 Correlation between Isotope Ratios of Nitrophenols

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

8 Indeed, the average $\delta^{13}\text{C}$ values of the three isomers are very similar (Table 2) and differ
9 from each other only by 0.1 ‰ or less. However, based on the average, differences between
10 isomers in individual samples cannot be ruled out. Figure 7 shows a plot of the carbon isotope
11 ratios of 4-methyl-2-nitrophenol and 3-methyl-4-nitrophenol versus the carbon isotope ratio of 2-
12 methyl-4-nitrophenol for all samples which could be analyzed for the carbon isotope ratio of
13 more than one of the methyl nitrophenols. The data show scatter around the 1:1 line, but most of
14 this scatter can be explained by measurement uncertainty. For approximately 50 % of the data
15 pairs, the difference in isotope ratios between isomers ($\Delta\delta^{13}\text{C}$) is within the uncertainty of the
16 measurements and only for 6 of the 58 data pairs the difference is larger than three times the
17 measurement error. The mean value for $\Delta\delta^{13}\text{C}$ is 0.15 ‰, which is less than the error of the mean
18 (0.18 ‰). The standard deviation for $\Delta\delta^{13}\text{C}$ is 1.3 ‰, which is 0.6 ‰ larger than expected from
19 measurement errors alone. Although these findings cannot completely rule out the existence of
20 differences in KIEs or rate constants for formation or removal processes between methyl
21 nitrophenols, the impact of such differences can only be small and a systematic bias cannot be
22 identified within the uncertainty of the measurements.

1 The standard deviations observed for differences between carbon isotope ratios of
2 nitrophenols which are not isomers are substantially larger than expected from measurement
3 uncertainty and very similar to the standard deviation expected from the variance of $\delta^{13}\text{C}$ within
4 the data sets for the individual nitrophenols (Table 5). However, on average the difference in
5 isotope ratios ($\Delta\delta^{13}\text{C}$) between non-isomeric nitrophenols is only marginally larger than $\Delta\delta^{13}\text{C}$
6 for the methyl nitrophenol isomers (Tables 2 and 5). To some extent this can be explained by the
7 very similar carbon isotope ratios of the different precursor VOC (Table 3). However, from the
8 differences in KIEs for the initial step of the reaction sequence leading to formation of
9 nitrophenols it is expected that isotope ratios of non-isomeric nitrophenols formed from
10 unprocessed emissions will differ by a few per mille (Table 3). Compared to these predicted
11 differences the values actually observed for the average of $\Delta\delta^{13}\text{C}$ are surprisingly small. This
12 may be due to the fact that with increasing extent of atmospheric processing the carbon isotope
13 ratio of the precursor will increase and that this increase will depend on the KIE and the rate
14 constant for the reaction of precursor. Depending on the extent of processing, this will, at least
15 partly, compensate for the larger depletion in ^{13}C for reaction products formed from unprocessed
16 emissions since the more reactive aromatic precursor VOC have lower KIEs. On average the
17 observed $\Delta\delta^{13}\text{C}$ are very small suggesting that on average precursor processing has been
18 substantial, independent of the precursor reactivity.

19 **3.4 Seasonal Variation of the Concentrations and Carbon Isotope Ratios of Nitrophenols**

20
21 Table 6 shows a comparison of 2-methyl-4-nitrophenol and 4-nitrophenol concentrations
22 and carbon isotope ratios for different temperature ranges. The separation into different
23 temperature ranges is based on the average temperatures during sampling. Measurements with
24 average temperatures below 10 °C were made between mid of October and end of January,

1 measurements with average temperatures exceeding 20 °C in June, July and August. Also
2 included are air quality data from two OME monitoring stations in Toronto (Fig. 2). Remarkably,
3 a distinct seasonal difference in isotope ratios is not observed. With the exception of the 4-
4 nitrophenol isotope ratios in PM, the difference in average carbon isotope ratios between
5 measurements made at low and high temperatures is less than 0.5 ‰. For the 4-nitrophenol
6 isotope ratios in PM this difference is 0.9 ‰, but this difference is within the uncertainty of the
7 average values.

8 This is in contrast to the expectation that, due to higher photochemical activity in
9 summer, samples collected in summer should be subject to more processing and therefore be,
10 compared to less processed samples, enriched in ^{13}C . A more detailed look at the dependence
11 between temperature, wind direction and carbon isotope ratio can provide a possible explanation
12 for this unexpected finding. Figure 8 shows the frequency of observations of $\delta^{13}\text{C}$ values for
13 methyl nitrophenols and 4-nitrophenol binned into intervals of 2 ‰ and separated by wind
14 direction and average temperature during sampling. The selection of the wind directions, north
15 and southwest, was based on the number of available measurements and the difference in nearby
16 major sources of nitrophenol precursors. Only samples with a wind direction that was stable
17 (with 45 °) during sampling were used for this analysis. The total number of samples fitting this
18 criterion was 64, out of a total of 102. Three major highways and their intersections are located
19 within 15 km or less southwest of the sampling locations whereas there is only one major
20 highway directly north of York University (Fig. 2).

21 For medium (10 °C to 20 °C) and low (<10 °C) temperatures, the number of methyl
22 nitrophenol data points in each $\delta^{13}\text{C}$ bin is identical, while for high average temperatures the
23 number of observations peak in the center bin (-34 ‰ to -32 ‰). Therefore, the absence of a

1 difference in the seasonal averages of the methyl nitrophenol carbon isotope ratio is not due to
2 the absence of a seasonal impact on processing, but the coincidence that for summer seventeen
3 out of twenty nine $\delta^{13}\text{C}$ measurements are close to the average of all observations.

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

9 Although the lower number of data points available for 4-nitrophenol results in higher
10 statistical uncertainty of the distribution, Fig. 8 shows some substantial differences between the
11 carbon isotope ratios of methyl nitrophenols and 4-nitrophenol. For 4-nitrophenol only 13 % of
12 all data points are in the -34 ‰ to -32 ‰ range and more than 50 % of the $\delta^{13}\text{C}$ values measured
13 at high average temperatures are below -34 ‰. This can be explained by the different reactivity
14 of the precursors. The rate constant for the reaction of benzene with the OH radical is only one
15 fourth of that for the reaction of toluene (Table 3) and therefore photochemical processing results
16 in lower enrichment of ^{13}C in the products from reactions of benzene compared to products
17 derived from toluene.

18 The preference of low and medium enrichment of nitrophenols in ^{13}C during summer is
19 independent of wind direction. Compared to northerly wind directions, the larger number of
20 observations under southwesterly airflow reflects the larger percentage of observations with
21 southwesterly wind in summer (eighteen of twenty nine) and not a wind direction dependence of
22 methyl nitrophenol carbon isotope ratios. Since it is expected that the different wind directions
23 result in different pollution levels, this is consistent with the finding that there is no systematic

1 dependence between the concentration of methyl nitrophenols and carbon isotope ratio (Fig. 2).
2 Similarly, the carbon isotope ratios of the methyl nitrophenols and 4-nitrophenol show no
3 correlation with CO, NO₂, O₃ or oxidant (O₃ + NO₂) concentrations (R^2 is consistently below
4 0.1).

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

12 There are some differences in PM + gas concentrations between the two different
13 temperature ranges. The average 2-methyl-4-nitrophenol concentration in PM + gas is at low
14 temperatures on average approximately 60 % higher than at high temperatures. An increase in
15 photochemical processing of the precursors can be ruled out as explanation for the higher methyl
16 nitrophenol concentrations at low temperatures. It is unlikely that photochemical processing is
17 faster in winter and fall than in summer and the methyl nitrophenol isotope ratios show, on
18 average, no indication for enhanced processing at low temperatures. The most likely explanation
19 is higher precursor concentrations in fall and winter. The concentration of 2-methyl-4-
20 nitrophenol in PM + gas is correlated ($R^2 = 0.64$) with the NO₂ concentration (Fig. 9a).
21 Therefore it is expected that on average, higher NO₂ concentrations in fall and winter will result
22 in higher 2-methyl-4-nitrophenol levels. The larger NO₂ concentrations in fall and winter may be
23 attributed to the decreased boundary layer height coupled with increased pollution rates, but the

1 higher photolysis rate of NO₂ in summer may also contribute to the difference in NO₂
2 concentrations between seasons.

3 Both toluene and NO₂ are required for the formation of methyl nitrophenols in the
4 atmosphere and it is expected that the concentration of toluene also will influence the formation
5 rate of methyl nitrophenols. However, there is a weak correlation of the NO₂ concentration with
6 other indicators of atmospheric pollution such as CO ($R^2 = 0.33$) and SO₂ ($R^2 = 0.41$), which
7 prevents separating between the influence of NO₂ and other precursors and it is therefore not
8 possible to distinguish between the impact of different pollutants on methyl nitrophenol
9 concentrations.

10 In contrast to 2-methyl-4-nitrophenol, the correlation between the concentrations of 4-
11 nitrophenol and NO₂ is only weak (Fig. 9b). This indicates that, consistent with the low reactivity
12 of 4-nitrophenol and its benzene precursor, the processes determining the concentration of 4-
13 nitrophenol are occurring at a time scale that is different from the processes determining the NO₂
14 concentrations.

15 Atmospheric nitrophenols are produced by photochemical oxidation of aromatic VOC in
16 the presence of NO_x. Since atmospheric oxidants (O₃ and NO₂) are also formed from
17 photooxidation of VOC, we expect correlation between oxidant and nitrophenol concentrations.
18 Indeed, there is a strong correlation ($R^2 = 0.60$) between the concentration of oxidants and 4-
19 nitrophenol (Fig. 10a). Surprisingly, the correlation between 2-methyl-4-nitrophenol and oxidant
20 concentrations is only weak (Fig. 10b). This most likely reflects the different reactivity of the
21 precursors (Table 3) and indicates that the timescale for processes determining oxidant levels is
22 similar to the timescale determining formation of 4-nitrophenol, but different from that for 2-
23 methyl-4-nitrophenol formation.

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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 $\delta^{13}\text{C}$ values range from -37 ‰ to -28 ‰. The substantial variability of the nitrophenol carbon isotope ratios can 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 combination of carbon isotope ratio and concentration measurements provide strong evidence that, for the conditions studied here, secondary processes in the atmosphere are the dominant source for the target compounds.

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

1 supported by the difference between summer and winter carbon isotope frequency distributions
2 of methyl nitrophenols.

3 There is no significant correlation between the carbon isotope ratio of nitrophenols and
4 their concentration. This demonstrates that, for the conditions studied here, atmospheric mixing
5 is the dominant process in determining the concentrations of nitrophenols. Indeed, for some
6 nitrophenols strong correlations between their concentrations and the concentration of precursors
7 or indicators of pollution are found. In principle in aged air masses with no impact from nearby
8 sources nitrophenol carbon isotope ratios substantially heavier than the carbon isotope ratios of
9 the precursors can be expected, which was not observed. It cannot be excluded that the lack of
10 observations of such low nitrophenol isotope ratios is due to the limited ability to measure
11 carbon isotope ratios in samples with very low nitrophenol concentrations. However, the
12 percentage of samples for which none of the nitrophenols could be analyzed for carbon isotope
13 ratios is small and it can therefore be concluded that for the conditions studied here such
14 conditions will be the exception.

15 The concentration of 4-nitrophenol is strongly correlated with the oxidant ($O_3 + NO_2$)
16 levels whereas there is no significant correlation between the concentration of other nitrophenols
17 and oxidant concentration. It can be concluded that the processes determining oxidant
18 concentrations are occurring on timescales that are better represented by the processes resulting
19 in formation of 4-nitrophenols than those for formation of alkyl nitrophenols. Most likely these
20 differences in timescales are determined by the reactivity of the aromatic precursors of the
21 different nitrophenols.

22 The importance of precursor reactivity on the carbon isotope ratios of nitrophenols is
23 supported by the comparison of carbon isotope ratios of different methyl nitrophenol isomers.

1 Overall, these differences in carbon isotope ratios for different isomers are small compared to the
2 overall variability of the carbon isotope ratios of individual isomers of methyl nitrophenols.

3 Combining measurement of the atmospheric concentrations of secondary organic
4 compounds with measurement of their carbon isotope ratios provides detailed insight into the
5 processes and the timescales at which the formation occurs. However, currently this insight is
6 limited to qualitative or semi-quantitative conclusions since the current quantitative
7 understanding of the dependence between the carbon isotope ratio of secondary organic
8 compounds and photochemical aging is limited. Another current limitation of the use of isotope
9 ratios is resulting from the required minimum concentrations for meaningful isotope ratio
10 measurements, which limits the possibility to study the relationship between isotope ratio and
11 concentration under conditions of very low processing or at very low pollutant levels/
12

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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 TM 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 $\delta^{13}\text{C}$ measurements	0.3 ‰
Overall uncertainty of $\delta^{13}\text{C}$ measurements	0.5 ‰

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

Target Compound	Abbreviation	Carbon Isotope Ratio (‰)						
		Average	Error of the Mean	Median	Max	Min	25 th Percentile	75 th 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

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

	k_{OH}^a ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$)	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.

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

	$\Delta\delta^{13}\text{C}$ (‰) ^a	Temperature (K)	[O ₃] (nmol mol ⁻¹)	[NO ₂] (nmol mol ⁻¹)	[PM 2.5] ^b ($\mu\text{g m}^{-3}$)
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 ($\Delta\delta^{13}\text{C}$) between different nitrophenols analyzed in the same sample

	n ^a	$\Delta\delta^{13}\text{C}$ (‰) ^b	Observed SD (‰) ^c	Expected SD (‰) ^d
4-NP & me-NP ^e	101	-0.34	1.8	2.2
2,6-dime-4-NP & 4-NP	17	-0.24	2.5	2.4
2,6-dime-4-NP & 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.

PM Samples	<10°C	>20°C
	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}] (µg m ⁻³) ^b	6 (6)	12 (13)
Average [SO ₂] (µmol mol ⁻¹) ^b	1.4	1.0
Average [CO] (µmol mol ⁻¹) ^b	0.18	0.21
δ ¹³ C _{2-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
δ ¹³ C _{4-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}] (µg m ⁻³) ^b	8 (9)	12 (13)
Average [SO ₂] (µmol mol ⁻¹) ^b	2.0	1.3
Average [CO] (µmol mol ⁻¹) ^b	0.21	0.21
δ ¹³ C _{2-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
δ ¹³ C _{4-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 Captions

Figure 1. Reaction scheme of proposed mechanism of the gas phase formation pathway of the target compounds from aromatic VOC. Here, the R represents either a hydrogen atom or a methyl group (adapted from Forstner et al., 1997).

Figure 2. 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 3. Plot of isotope ratio values as a function of concentration for 4-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol.

Figure 4. 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 from the reaction of unprocessed precursor emissions, which is calculated from 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).

Figure 5. 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 6. 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 7. Plot of isotope ratios for 4-methyl-2-nitrophenol and 3-methyl-4-nitrophenol (y-axis) against 2-methyl-4-nitrophenol isotope ratios for filter samples.

Figure 8: 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 based on HYSPLIT (Hybrid Single

Particle Lagrangian Integrated Trajectory Model by Air Resources Laboratory, NOAA) trajectory analysis.

Figure 9. Plot of gas + PM sample concentrations of 2-methyl-4-nitrophenol (a) and 4-nitrophenol (b) versus 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 10. Plot of gas + PM sample concentrations of 2-methyl-4-nitrophenol (a) and 4-nitrophenol (b) versus oxidant ($\text{O}_3 + \text{NO}_2$) 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.

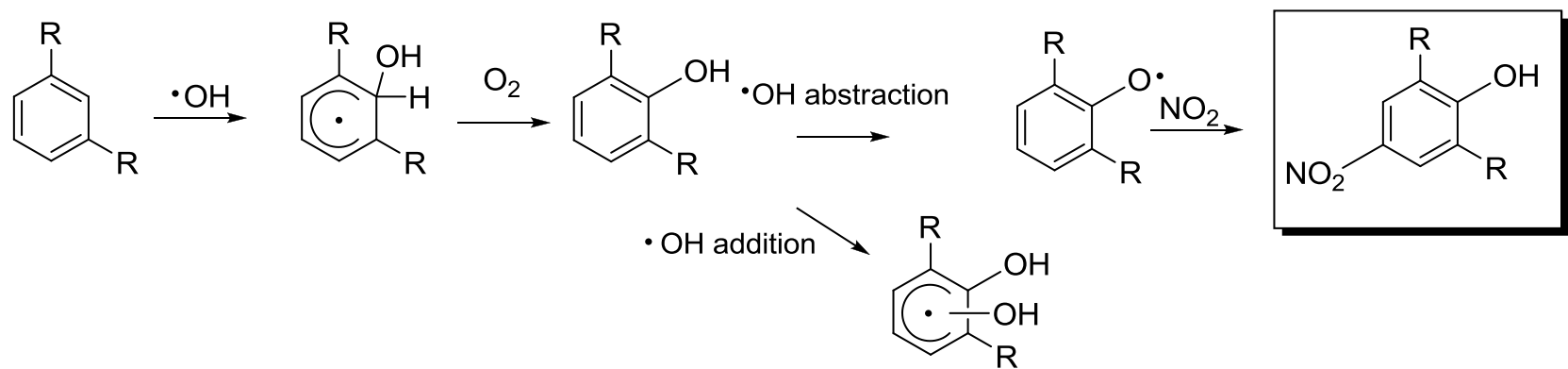


Fig. 1

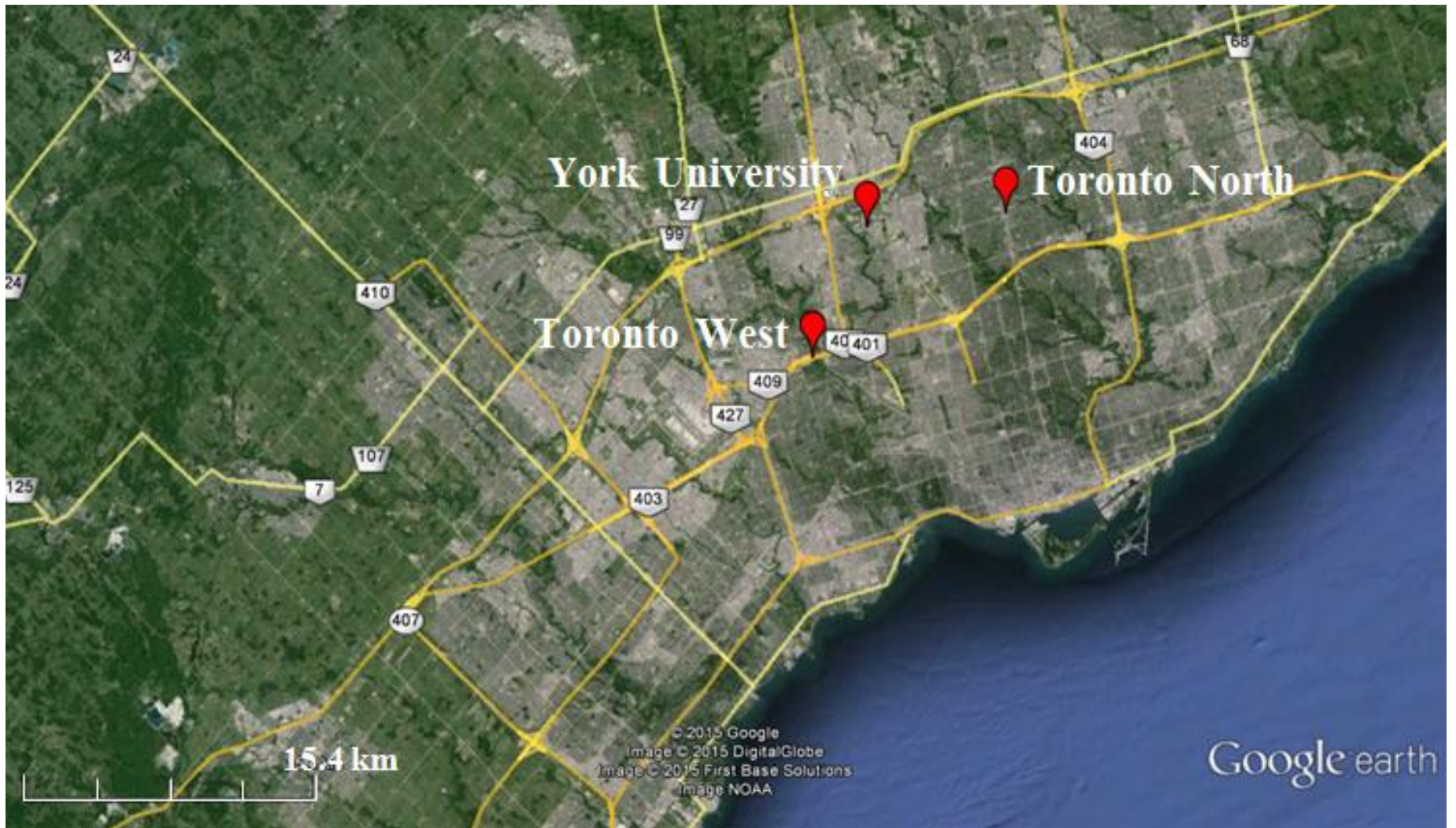


Fig. 2

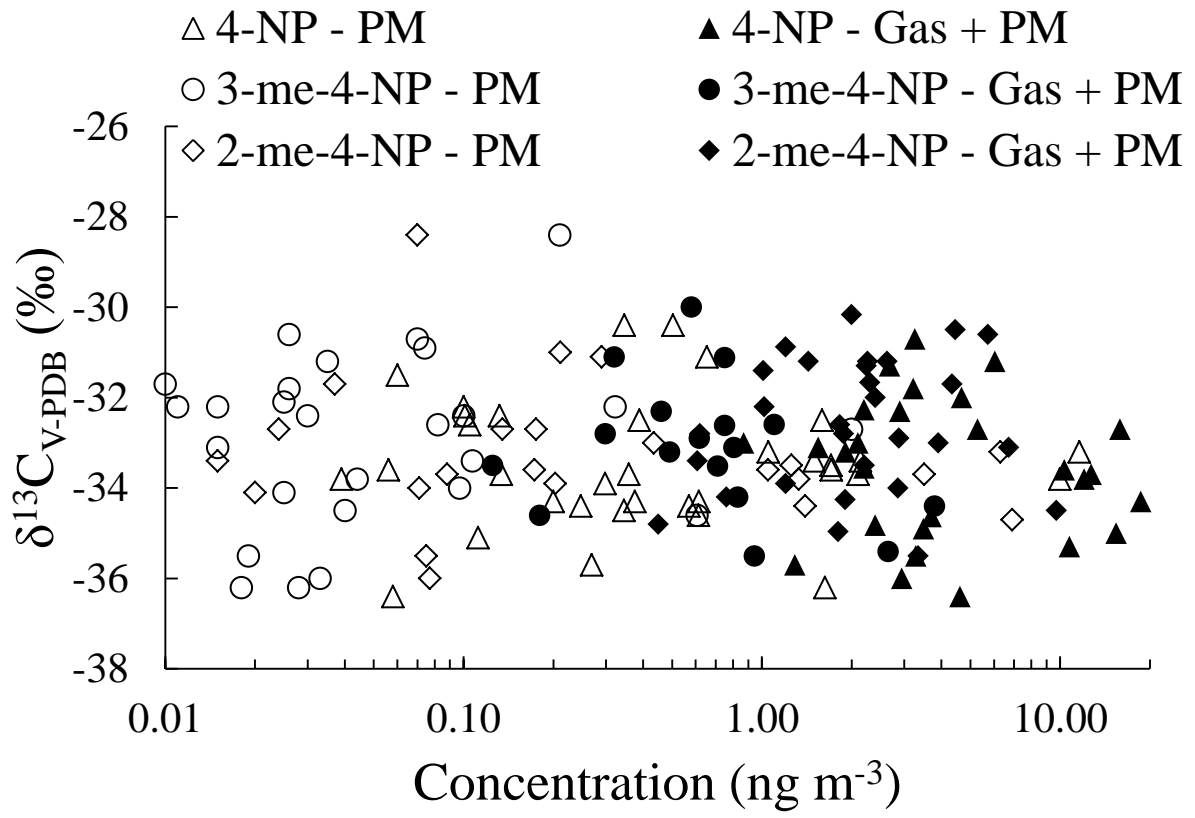


Fig. 3

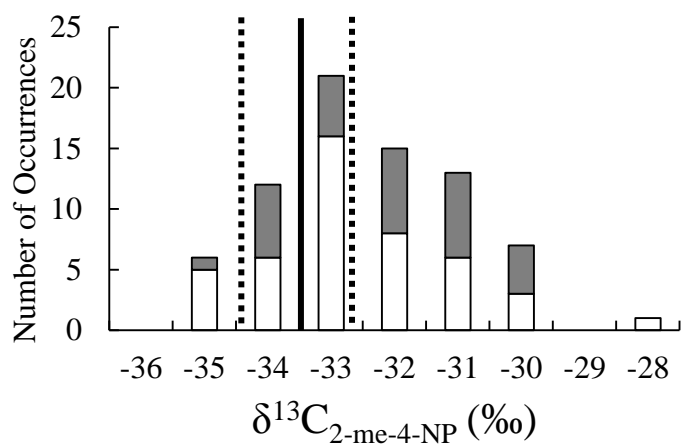
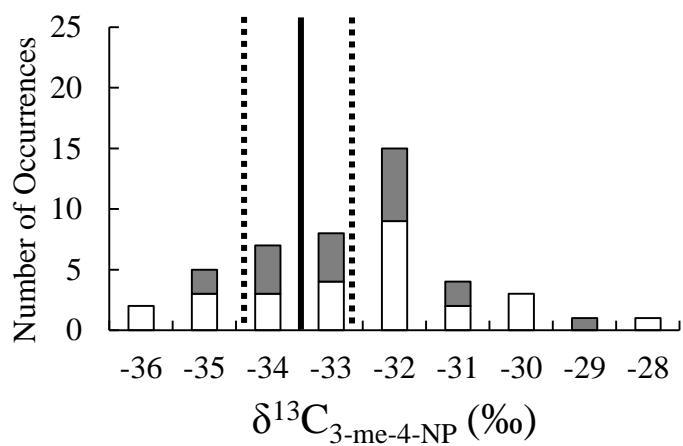
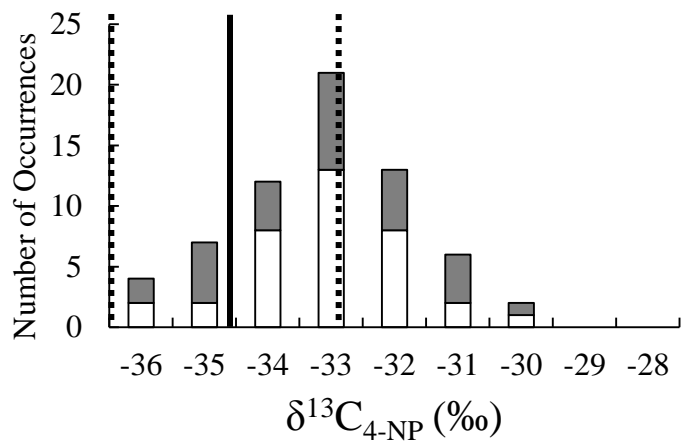


Fig. 4

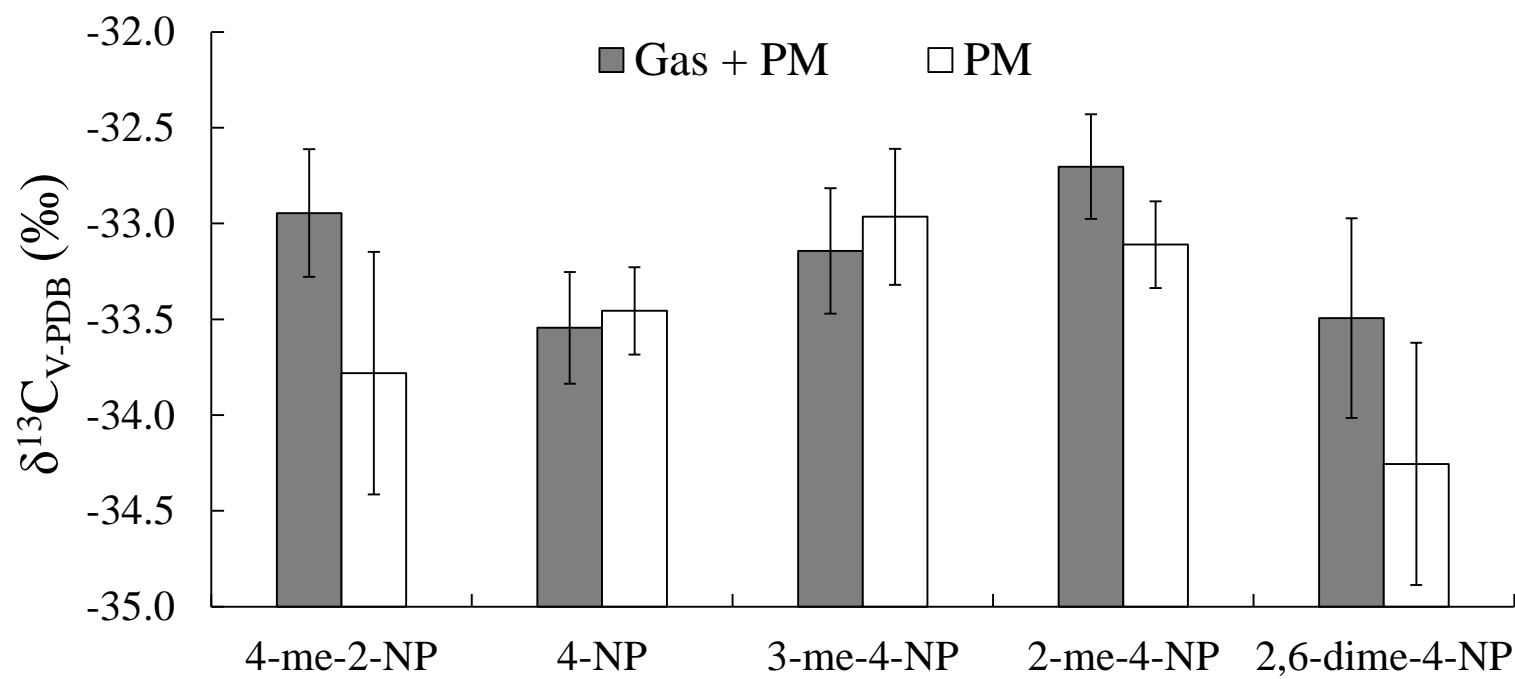


Fig. 5

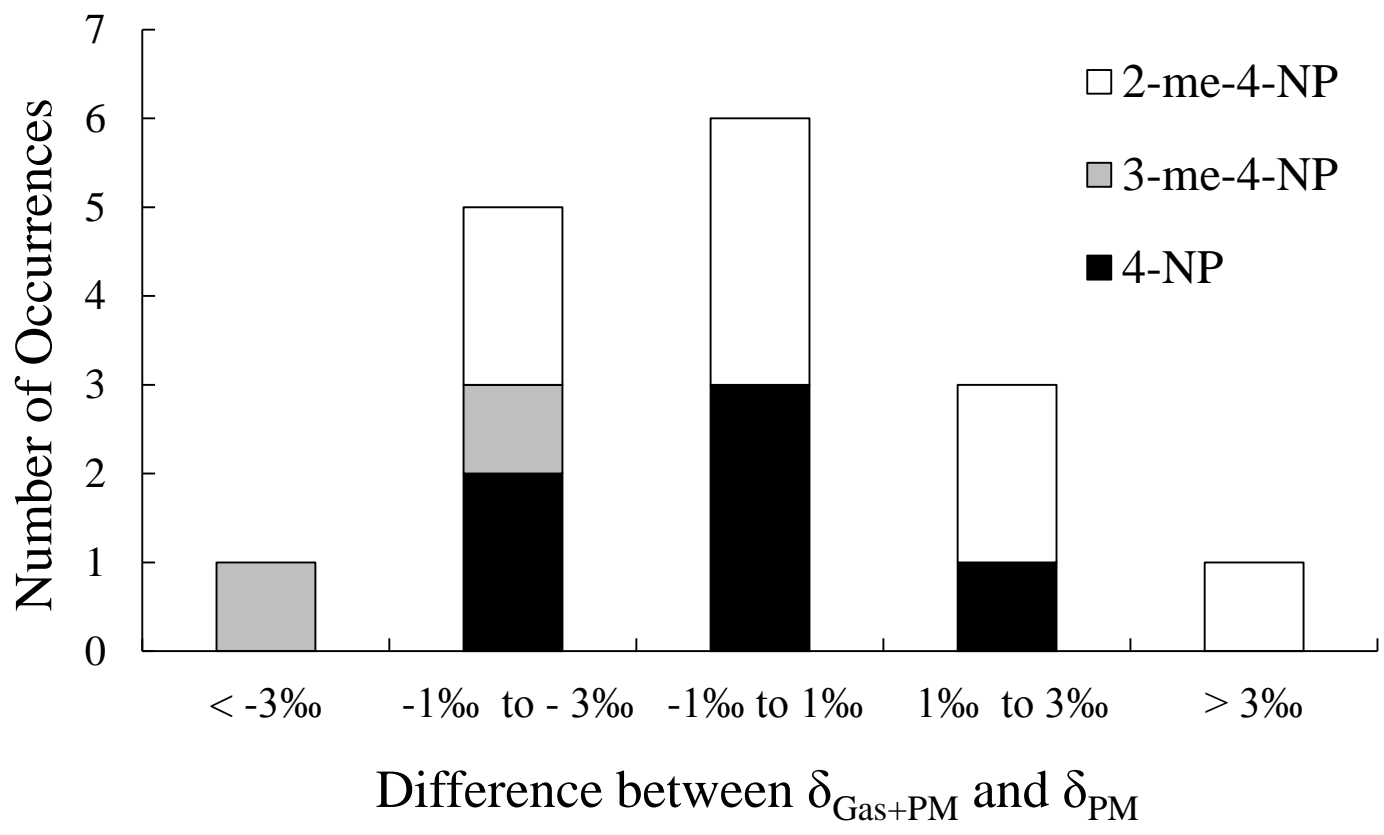


Fig. 6

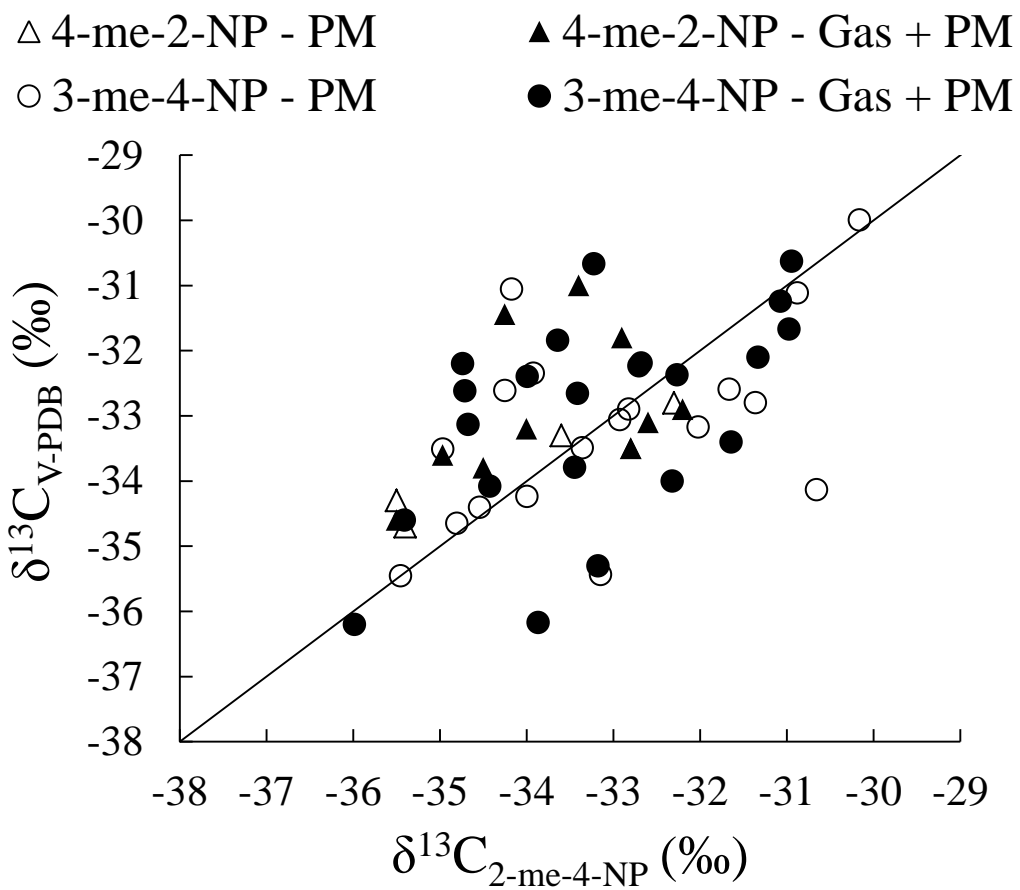


Fig. 7

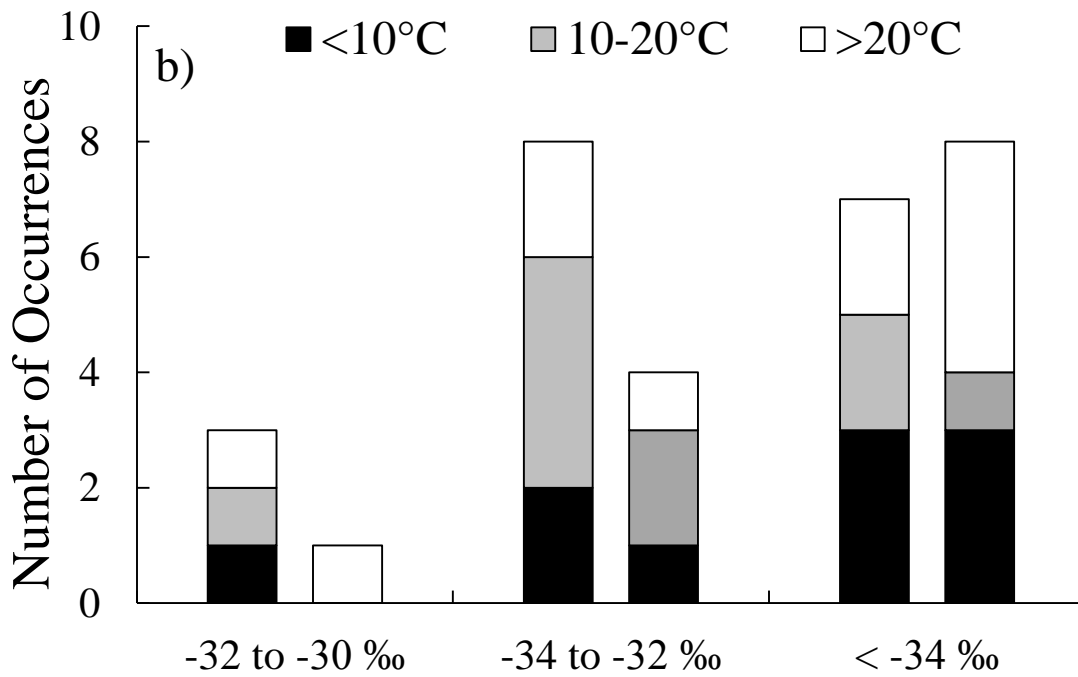
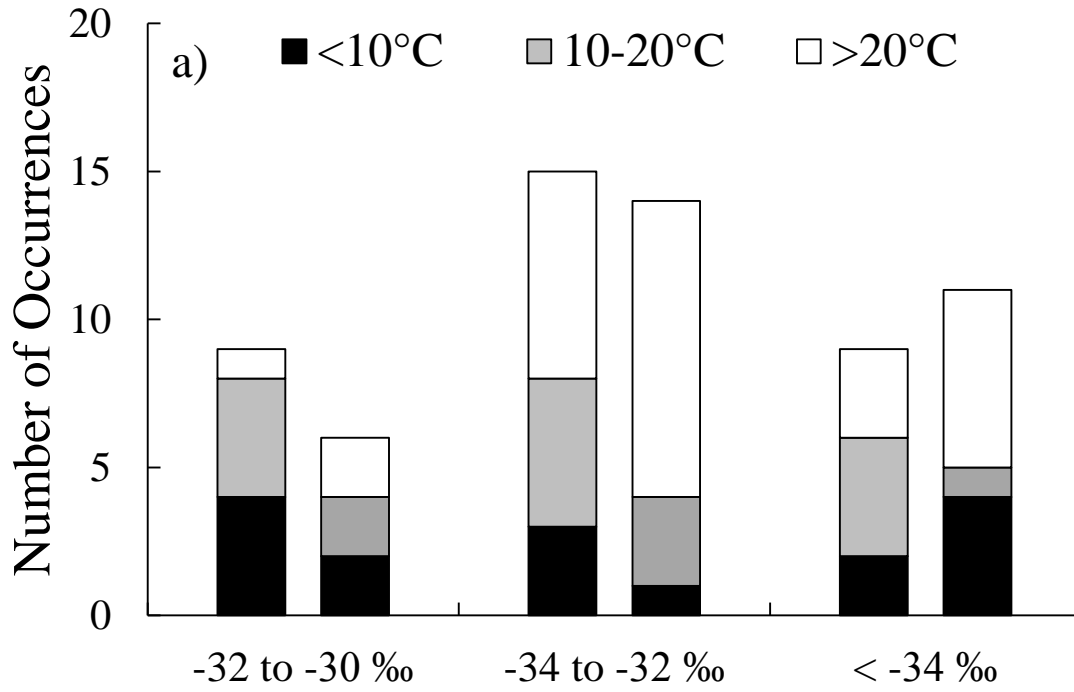


Fig. 8

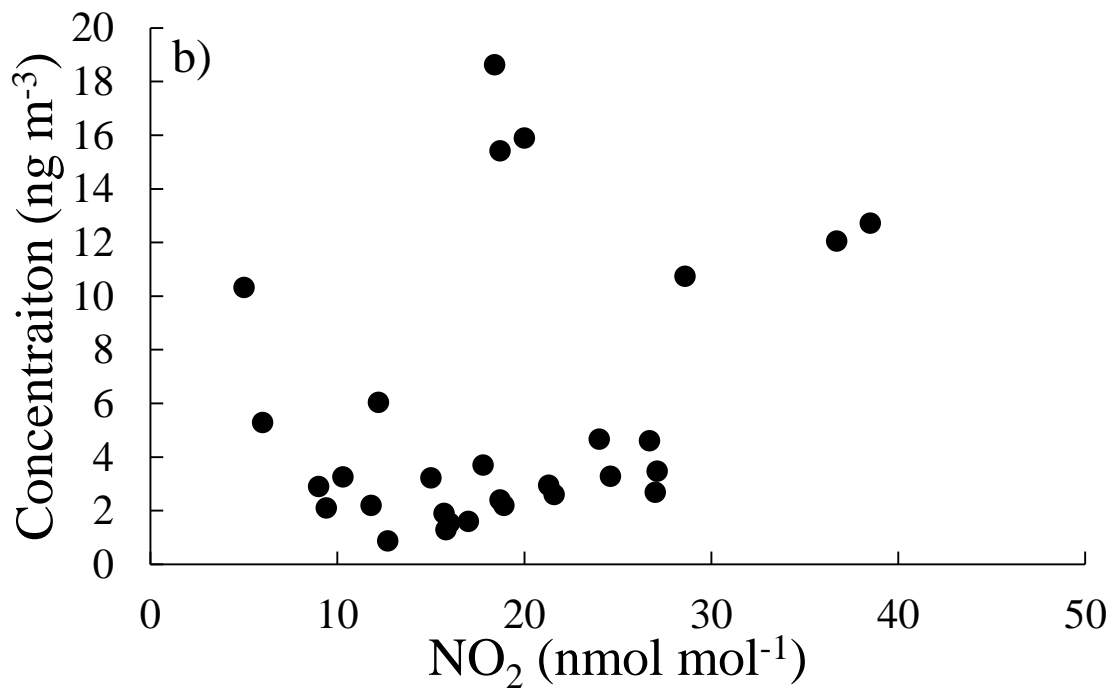
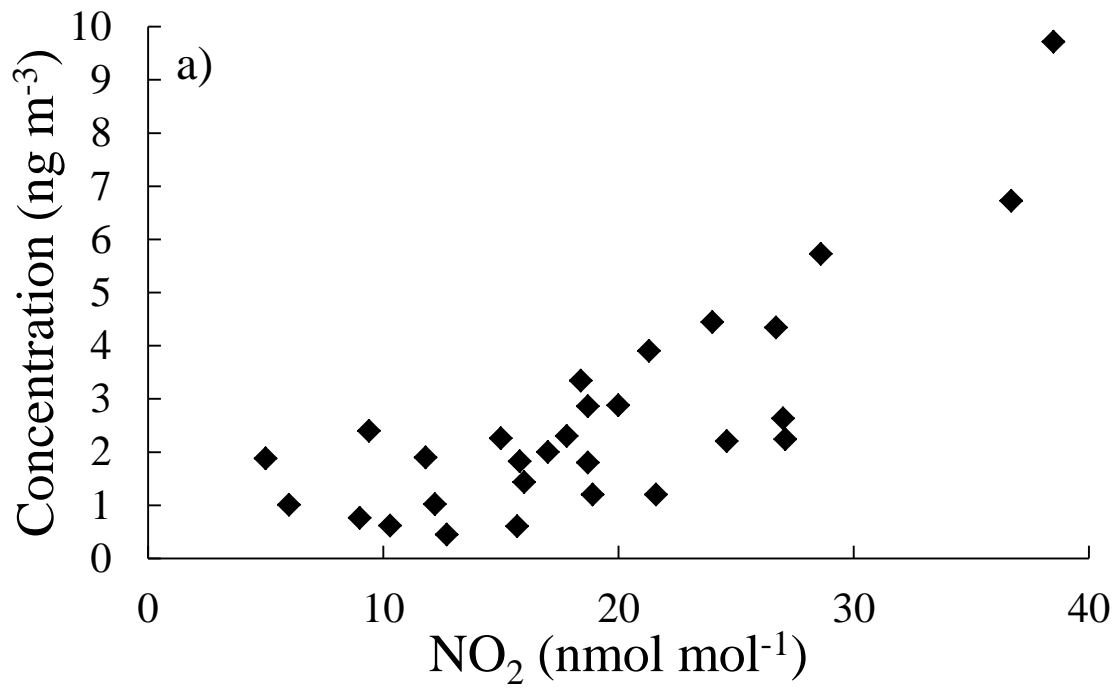


Fig. 9

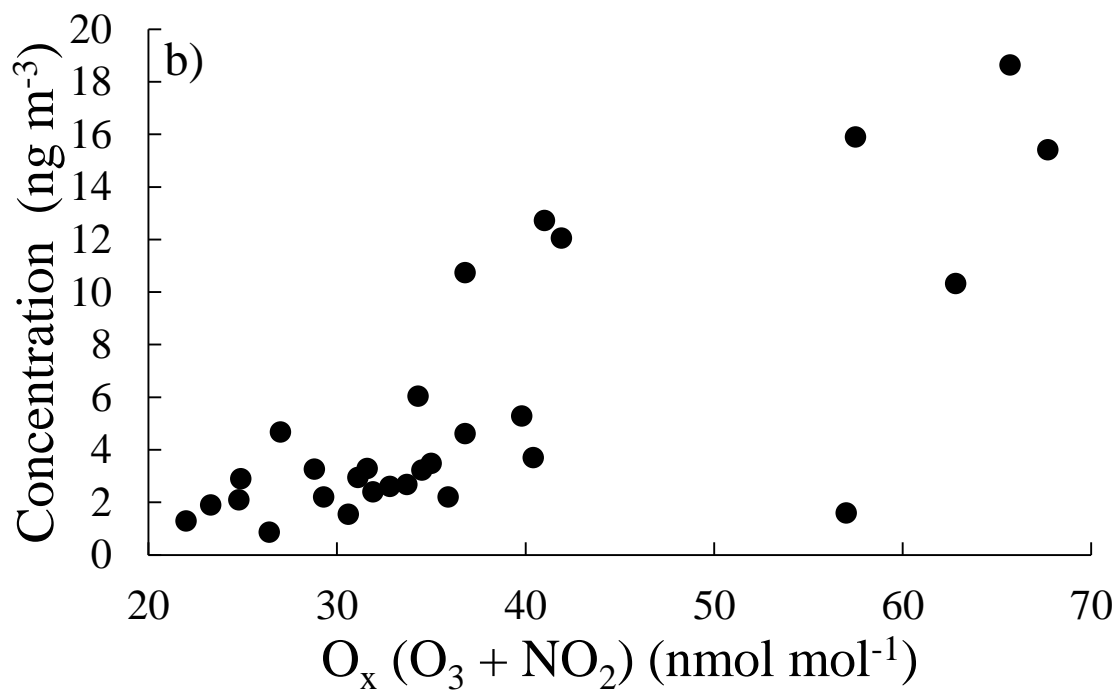
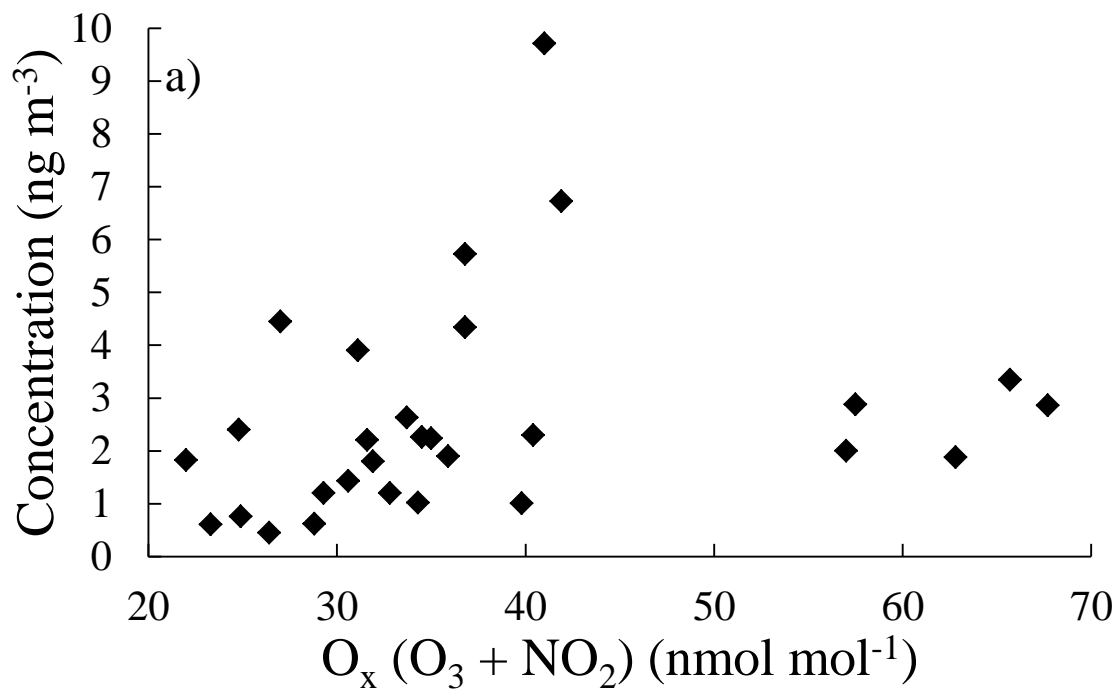


Fig. 10