

The authors would like to thank the three reviewers for their valuable comments. Most of the referee's comments were concerning the proposed reaction mechanisms and uncertainty of the methodology.

Anonymous Referee #2:

Referee Comment: The authors presented results for five nitrophenols from aromatic VOC photooxidation. 4-NP and 2-me-4-NP are abundant and analyzed in most samples. However, the other three nitrophenols, 4-me-2-NP, 3-me-4-NP, and 2,6-dime- 4-NP are not as abundant and only 17%, 47%, and 22% of the overall samples have enough signal to provide results. The authors admitted that this “could result in subsets of $\delta^{13}\text{C}$ data biased towards samples with higher nitrophenol concentrations”. Any idea how large could such bias be? Some discussion could be added. For example, For the three NPs from toluene photooxidation, 2-me-4-NP is more abundant; 3-me-4-NP and 4-me-2-NP are less abundant. But one could imagine the isotope ratios of the three being similar. Comparing the isotope ratio results between the three NPs, the authors may be able to provide some insights about such bias. This actually is discussed later in Section 3.3, but the authors did not effectively link the two parts there.

Reply: The uncertainty of the isotope ratio measurements of the nitrophenols was found to be 0.3 ‰. Results shown in Fig. 3 indicate that there is no systematic dependence between the concentration of a species and its isotope ratio. With the given uncertainty, it cannot be determined if there is a bias resulting from the inability of measuring isotope ratios of samples with low concentrations. This is addressed on page 13 lines 7 to 15. Indeed, the problem of bias due to the limited lower concentration range for isotope ratio measurements is not limited to nitrophenols, but is a general limitation resulting from the current state of isotope ratio measurement techniques for atmospheric VOC. We added a brief explanation to the end of the conclusions.

Referee Comment:

There are a number of places in this paper that the authors compare the differences between observations with measurement uncertainties. For example, comparing the measurements vs. predictions in 3.1, comparing total vs. PM phase in 3.2, comparing isotope ratios of different nitrophenols in 3.3. In many of these comparisons, the differences are not very far from the measurement uncertainties. Given the small number of available samples, it is somehow difficult to draw clear conclusions as the main flaws of this paper, substantially decreasing the potential impact of this work.

Reply: The authors understand that the measurements uncertainty of 0.3 ‰ can sometimes prevent the interpretation of differences observed between certain samples. However, differences

exceeding 0.7 ‰ exceed this uncertainty within a 90 % confidence limit and the spread of the data is in the range of 4 to 8 ‰. A discussion of this was added on page 8, line 17 to 23.

Referee Comment: The authors mentioned in the introduction section that nitrophenols have been found in trace amounts as primary emissions from vehicles. But in the results and discussions, never mentioned that again. If the primary sources of the nitrophenols are important fractions of total nitrophenols in the area of this study, the interference can cause a large impact. The authors at least need to estimate the primary emission of nitrophenols and aromatic VOCs (benzene, toluene, and m-xylene). Then with the known yields of nitrophenols from their photooxidation, estimate the mass of the secondary nitrophenols. Only with such discussion and if the primary source is minor, the results from this paper can be reliably used. Otherwise, the entire conclusion should be doubted.

Reply: Primary emissions of the target compounds from vehicles were indeed mentioned in the introduction section, and were again addressed and discussed in Section 3.4. To demonstrate that the nitrophenols are found to be consistent with the hypothesis of being dominantly formed from secondary processes, this discussion was moved to Section 3.1, specifically, page 10 line 3 to page 11 line 11. The ambient isotope ratio measurements of target nitrophenols indicate that they have a delta value that is significantly more depleted in ^{13}C , compared to the parent VOC. Given this information, primary emissions of the nitrophenols can be ruled out as a significant source. Providing strong evidence that secondary formation is, for the conditions studied here, the dominant source of the target nitrophenols is an important point for this paper. We clarified this in the conclusions (Page 23, lines 8-10).

Referee Comment: From page 15433, line 23 to page 15434, line 11, the authors gave a very detailed introduction of the chemical mechanism of 4-nitrophenol formation from benzene. The authors should also provide the formation mechanisms of the methylnitrophenols and dimethyl-nitrophenols in the similar level of detail, at least the four nitrophenols (4-methyl-2-nitrophenol, 3-methyl-4-nitrophenol, 2-methyl-4-phenol, and 2,6-dimethyl-4-nitrophenol) focused in this study. The authors may want to add a figure or a scheme that shows the general chemical mechanisms leading to the formation of the five nitrophenols from benzene, toluene, and m-xylene. It would be more intuitive than just the text description here.

Reply: A figure showing a schematic of the postulated reaction mechanism was added as Fig. 1.

Referee Comment: Page 15435, line 12. The word “close” is vague. Close by how much?

Reply: A quantitative description of the relation in isotope ratio of 2-methyl-4-nitrophenol with that of the sum of the oxidation products of the photooxidation of toluene was added in 3.3 (page 17, line 1 to page 18, line 18).

Referee Comment: Page 15436, line 1-3. Quartz fibre filters are known to absorb gas-phase organics. How did the author make sure only PM are collected on the uncoated filters? Also, add the collection efficiency of the coated filters (84%) and the reference in the text.

Reply: The sampling of artifacts is indeed a problem for all PM filter sampling. Sampling artifacts were addressed in Saccon et al. (2013) a short summary of this is now added to Section 2, page 7 lines 1 to 12.

Referee Comment: Page 15437, line 12. A equation should be provided with the estimate of isotope ratios of nitrophenol formed in the initial phase of the reaction.

Reply: A description of how to estimate the isotope ratio of the nitrophenols during the initial phase of the reaction was added on page 9, lines 8 to 10. Details can be found in the cited paper by Irei et al. (2015).

Referee Comment: Could 4-nitrophenol also be formed from toluene photooxidation? Irei et al. (2014) seems to observe 4-nitrophenol from toluene photooxidation from the H-abstraction pathway. Thus, this compound can be produced from both benzene and toluene. There is no way to differentiate the source. Then the comparison of the isotope ratios of 4- nitrophenol with only benzene does not seem appropriate. The conclusion drawn from that species is less convincing.

Reply: Irei et al. (2015) has found 4-nitrophenol to be a product of toluene photooxidation, and this now is mentioned in the introduction on page 4, lines 7 to 9. Once ambient isotope ratio results of 4-nitrophenol are presented, the possibility of having toluene as a precursor as the main source of 4-nitrophenol in the atmosphere is proven to be unlikely, which now is discussed on page 10, lines 16 to 23. In addition to the low yields reported by Irei et al, the carbon isotope ratios of 4-nitrophenol derived from toluene oxidation are very different from the isotope ratios expected from reaction of benzene thus carbon isotope ratios are useful to differentiate between different formation mechanisms as explained in the added text.

Anonymous Referee #3:

Referee Comment: The interpretation of the isotope ratio data is predicated on the concept that nitrophenols present in the atmosphere are formed from one reaction pathway, the gas-phase reaction between benzene (or toluene or xylene) and the OH radical; for example: on page 15433 lines 15-20 it is stated “. . .the aromatic VOC can undergo photo-oxidation with the OH radical. . .”, on page 15435 line 5 it is stated “. . .nitrophenols are formed from one reaction pathway and are specific to the aromatic VOC + OH reaction”; whilst on page 15439, line 10 it is stated that “Formation of nitrophenols from aromatic VOC is the result of a gas phase reaction sequence. . .”. There is a substantial body of previous work that indicates a potential substantial role for a range of aqueous-phase chemistry in the production of nitrophenols from mono-aromatic precursors. This includes the potential that a portion of nitrophenol measured in the gas phase has re-partitioned back into the gas phase following reaction pathways through the aqueous phase, e.g. through a phenol emitted precursor or a phenol intermediate. The authors have briefly highlighted some of this literature in the second and third paragraphs of the Introduction. In the fourth paragraph of the Introduction (starting p15434, line 12) the authors also refer to primary sources of nitrophenol to the atmosphere from traffic exhausts. So why, having referred to these other sources and reaction pathways to nitrophenol formation, do the authors indicate that their measurements can be interpreted in the context of a single gas-phase reaction of aromatic with OH? Indeed there appears to be a direct contradiction in the opening lines of the Introduction between page 15433, lines 15-20 where it is stated that nitrophenols are dominantly produced by gas-phase reaction with OH, and line 24 where it is stated that 4-nitrophenol has several proposed formation pathways in both gas and aqueous phases.

Reply: While there are several different possible sources for atmospheric nitrophenols, the overall evidence points strongly towards secondary production as dominant source (revised discussion...). We eliminated statements that could be interpreted as a priori assumptions about the sources of nitrophenols and added more detailed explanations (introduction page 4 line 12-20, discussion page 11, line 20 to page 12 line 13 and conclusions page 23, lines 10-12) to clarify that this is not an a priori assumption but a conclusion that is evaluated based on the available overall evidence and the measurements presented here.

Referee Comment: Similarly, on page 15441, line 18, it is stated that “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” – this seems to be an assertion, rather than based on direct evidence, for samples collected from the atmosphere (as opposed to a controlled chamber study); the authors themselves cite in the introduction that methyl nitrophenols have been noted to be emitted to the atmosphere from direct emissions from vehicle exhausts. The authors do return to the issue of atmospheric nitrophenols derived from direct emissions rather than via atmospheric oxidation of mono-aromatic VOC, but this is not until the second and third from last paragraphs of the Results and Discussion section, and the direct emissions are largely dismissed as not being important. More clarity on the authors’

interpretation in the context of only a gas-phase OH reaction is needed earlier on in the Introduction and during the Results sections.

Reply: We rearranged the parts of the paper dealing with conclusions about possible sources into one part early in the discussion to avoid confusion between conclusions drawn from the observations and a-priori assumptions and added a discussion of the possible role of all currently known sources of the target compounds (page 10, line 3 to page 12, line 13).

Referee Comment: This reader's attempt to interpret analysis in the context of this sole gas-phase formation pathway was not helped by some unclear phrasing in the description of chemical reactions. As examples. . .(1) on page 15437, lines 13 & 20, and on p15438, line 15, the phrase "initial phase of the reaction" is used. What is meant here by a "phase" (in a kinetic sense) of a reaction? I don't think the authors mean the formation of a transition state in a reaction? The nitrophenol formation pathways are multi-reaction sequences. Perhaps by "phase" the authors mean the first, and/or rate-determining, reaction of a multi-reaction scheme? In each case, the text needs to make clear what chemical reaction is the subject. (2) Likewise, on page 15435, line 12, it is not clear to which reaction the phrase "sum of all reaction products" refers – the generation of a nitrophenol from an aromatic involves more than one reaction. (3) And, again, on page 15435, line 12, I could not work out what actual reaction or reaction(s) are being referred to in the sentence "This allows for a first order prediction of the dependence between isotope ratios of reaction products and photo-chemical precursor processing in the atmosphere". The understanding of the authors' work would benefit from a schematic of the chemical reaction sequence their study provides information on.

Reply: We changed "initial phase of the reaction" to "secondary products formed from unprocessed emissions" to clarify the meaning. The "sum of all reaction products" means exactly what it says, all products of the reaction, which can easily be derived from a mass balance. We added an explanation to clarify this (page 6, lines 3-9). This is based on the cited paper by Irei et al., 2015 A figure with the reaction scheme has been added.

Referee Comment: P15443, lines 18-26: Some analysis of results is undertaken with respect to wind direction during a sample collection, but there is little detail on the stability of a wind direction during a sample collection. There is only the sentence "Only samples with a relatively stable wind direction during sampling were used for the analysis"; what criteria actually defines "relatively stable wind direction" and how many samples were retained and excluded from analysis after application of the sample selection? Is this analysis in fact based on only a minority of samples?

Reply: A clarification of how many samples and what was classified as a "stable wind direction" was added on page 19, lines 16 to 118.

Referee Comment: Technical comments: P15434, 111: The citation to Hamilton et al. 2005 doesn't look like a correct citation here.

Reply: The reference was corrected to Harrison et al., 2005.

Referee Comment: P15442, 123: Better to phrase as “the values actually observed for. . .”

Reply: Done.

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

2 **Saccon, M.¹, Kornilova, A.¹, Huang, L.², Moukhtar, S.¹, Rudolph, J.¹**

3
4 Affiliation:

5 1. Centre for Atmospheric Chemistry

6 York University

7 4700 Keele St.

8 Toronto, ON.

9 M3J 1P3

10
11 2. Climate Research Division

12 Atmospheric Science & Technology Directorate

13 Environment Canada

14 4905 Dufferin St.

15 Toronto, ON.

16 M3H 5T4

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 primarily formed from the photo-oxidation of aromatic volatile
5 organic compounds (VOC), in the gas phase and particulate matter (PM) together and PM alone
6 was conducted. Since all of the target compounds are secondary products, their concentrations in
7 the atmosphere are in the low ng m^{-3} range and consequently, a large volume of air ($> 1000 \text{ m}^3$)
8 is needed to analyze samples for stable carbon isotope ratios, resulting in sampling periods of
9 typically 24 hours. While this extended sampling period increases the representativeness of
10 average values, it at the same time reduces possibilities to identify meteorological conditions or
11 atmospheric pollution levels 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 from OH, ozone or chlorine radicals. These oxidation reactions produce products which
15 are typically heavier and have lower vapor pressures than the precursorreactant. Many of the
16 products are considered to be semi-volatile organic compounds (SVOC), which have properties
17 that allow them to exist both in the gas phase and in particulate matter (PM), and compose
18 secondary organic aerosols (SOA), making up a substantial portion of aerosols in the
19 troposphere. Nitrophenols, the target compounds of this paper, are SVOC that are believed to be
20 dominantly produced by processes in the atmosphere from aromatic VOC such as benzene,
21 toluene and m-xylene, according to the reaction scheme in Fig. 1 (Forstner et al., 1997;
22 Atkinson, 2000; Jang and Kamens, 2001; Hamilton et al., 2005; Sato et al., 2007). The

1 | nitrophenol formation pathway from toluene and m-xylene is proposed to be similar. ~~Once~~, and
2 | ~~once~~-emitted, the aromatic VOC can undergo photo-oxidation with the OH radical to produce a
3 | (di)methyl hydroxycyclohexadienyl radical, which can then form a (di)methyl phenol (Forstner
4 | et al., 1997). These intermediates can then react with OH and NO₂ to produce (di)methyl
5 | nitrophenols.

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

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

1 Nitrophenols have been found in trace amounts as primary emissions, such as gasoline
2 fueled automobile exhaust (Trempe et al., 1993). In a very recent study, Inomata et al. (2015)
3 reported that emission factors for 4-nitrophenol in PM from gasoline fueled engines were below
4 the quantification limits of $6 \times 10^{-3} \mu\text{g km}^{-1}$, whereas for diesel engines, ~~4-nitrophenol in PM~~
5 emission factors range from $0.23 \mu\text{g km}^{-1}$ to $29.5 \mu\text{g km}^{-1}$ for 4-nitrophenol in PM. The reported
6 values for 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol are in the range of $0.32 \mu\text{g km}^{-1}$ to
7 $11.4 \mu\text{g km}^{-1}$ for diesel engines and were below the quantification limits for gasoline engines. 4-
8 Nitrophenol has also been found in the gas phase of diesel engine exhaust at highly variable
9 levels (Inomata et al., 2013) corresponding to emissions factors ranging from effectively zero to
10 several hundred $\mu\text{g km}^{-1}$.

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

1 reason is that nitrophenols are formed from one reaction pathway and are specific to the aromatic
2 VOC + OH reaction (Forstner et al., 1997). This is important so that the nitrophenols can be
3 traced back to the precursor, which has a measured and known isotope ratio at the source
4 (Rudolph et al., 2002). Secondly, the target compounds should be ring retaining products so that
5 the possibility of being formed from other precursors decreases compared to ring fragmentation
6 products. Lastly, and most importantly, it has been shown that one of the methyl nitrophenols, 2-
7 methyl-4-nitrophenol, has an isotope ratio that is within ± 1.33 ‰ of the isotope ratio of the sum
8 of all reaction products for the reaction of toluene (between 10 % and 27 % reacted) with the OH
9 radical, allowing suggested that nitrophenols have an isotope ratio that is close to the isotope ratio
10 of the sum of all reaction products. This allows for a first order prediction of the dependence
11 between isotope ratios of reaction products and photochemical precursor processing in the
12 atmosphere (Irei et al., 2015). Measurements of nitrophenol concentrations and their isotope
13 ratios in a mixed residential and industrial area are reported and discussed in this paper.

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

14 2. Method

15 The method used for filter preparation, sample collection, extraction and analysis have
16 been previously described by Saccon et al. (2013), ~~which was based on methods developed by~~
17 Moukhtar et al. (2011) and Irei et al. (2013). Samples were collected at York University (Fig. 42)
18 in the outskirts of Toronto, Canada using high volume air samplers (Fig. 24). Figure 42 also
19 shows the location of two monitoring stations of the Ontario Ministry of the Environment
20 (OME), which provided measurements of ambient concentrations of NO₂, O₃, CO, SO₂, and PM
21 with a nominal aerodynamic diameter of less than 2.5 μm (PM_{2.5}). The sampling period was

1 from March 2009 to August 2012. Prebaked quartz fibre filters were used for PM collection and
2 prebaked quartz fibre filters coated with XAD-4TM resin were used for gas phase + PM
3 collection. The sampling times for XAD-4TM coated filters were typically 24 hours and from
4 one to three days for uncoated filters. Uncoated quartz filters have the possibility of sampling
5 artifacts, including gas phase target compounds. Nitrophenol artifacts could not be ruled out but
6 were found to be limited. The mass of artifacts on a filter is expected to be proportional to
7 sampling time. For the target compounds analyzed, an average percent difference of
8 approximately 6.5 % was observed between three samples collected for one day each and a
9 sample collected continuously for three days. Saccon et al. (2013) showed that partitioning
10 results from denuder sampling, which is designed to limit artifacts from the separation of the gas
11 phase from the PM phase, are consistent with results from conventional filter sampling, such that
12 the majority of nitrophenols are found in the gas phase. From denuder sampling experiments it is
13 estimated that the gas phase component of each of the target compounds, apart from 4-methyl-2-
14 nitrophenol, is about 10 to 30 % higher than what is found from high volume filter samples. This
15 difference is consistent with the sampling efficiency of XAD-4TM coated filters (Saccon et al.,
16 2013).

17 Filters, prior to extraction, were stored in a freezer. After being spiked with internal
18 standards, filters were extracted with acetonitrile, underwent an HPLC and solid phase extraction
19 cleanup step and were analyzed. An HP 5890 GC coupled to an HP 5972 MS was used for
20 concentration measurements and an HP 6890 GC coupled to a Micromass Isoprime IRMS was
21 used for isotope ratio measurements. All samples were derivatized with BSTFA prior to analysis.
22 A summary of performance characteristics is shown in Table 1. Only samples containing more

1 than 3 ng of carbon for a target compound per 3 μL injection were used for quantifying stable
2 carbon isotope ratios.

3 3. Results & Discussion

4 3.1 Overview of Measured Carbon Isotope Ratios

5 An overview of the measured isotope ratios of nitrophenols is given in Table 2. The
6 nitrophenols chosen as the target compounds for this study were 4-nitrophenol, ~~derived from~~
7 ~~benzene~~, 4-methyl-2-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol, ~~derived~~
8 ~~from toluene~~ and 2,6-dimethyl-4-nitrophenol, ~~derived from m-xylene~~. Since only sample extracts
9 with concentrations of at least 1 ng μL^{-1} of carbon for a target compound were suitable for
10 isotope ratio measurement, only a subset of the samples collected could be analyzed for $\delta^{13}\text{C}$ of
11 the target nitrophenols. This reduced the number of samples with low nitrophenol concentrations
12 and therefore could result in subsets of $\delta^{13}\text{C}$ data biased towards samples with higher nitrophenol
13 concentrations. For the most abundant target compounds, 4-nitrophenol and 2-methyl-4-
14 nitrophenol, 85 % and 98 %, respectively, of the 102 samples (47 PM and 55 gas + PM) could be
15 analyzed for isotope ratios. For the lower in abundance compounds, 4-methyl-2-nitrophenol, 3-
16 methyl-4-nitrophenol and 2,6-dimethyl-4-nitrophenol, only 17 %, 47 % and 22 %, respectively,
17 of the samples were analyzed for carbon isotope ratios. As can be seen from Fig. 23, the
18 variability of the carbon isotope ratio substantially exceeds any systematic dependence between
19 concentration and $\delta^{13}\text{C}$.

20 The range of $\delta^{13}\text{C}$ values covered by the individual target compounds is between 4 and
21 nearly 9 ‰ and 50 % of the $\delta^{13}\text{C}$ values differ by more than 1 ‰ from the average (Fig. 4). The
22 measurement precision is 0.3 ‰ and the resulting measurement uncertainty for differences

1 between two observations for the same target substance is 0.4 ‰. Differences exceeding 0.7 ‰
2 and 1.1 ‰ exceed the measurement uncertainty within a 90 % and 99 % confidence limit,
3 respectively. Therefore, most of the observed variability of the measurements cannot be
4 explained by measurement uncertainty. The dominant factors creating variability in the isotope
5 ratios of organic compounds in the atmosphere are atmospheric reactions or varying
6 contributions from sources with different isotopic composition (Gensch et al., 2014).

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

1 for toluene reactions. As the reaction progresses, the products will be enriched in ^{13}C due to the
2 reaction of the parent VOC as well as that of the reaction product with the OH radical in the gas
3 phase. Although the KIEs for reactions of nitrophenols have not been measured, they most likely
4 will be normal KIEs, similar to all KIEs measured for reactions of light aromatic VOC in the gas
5 phase (Anderson et al., 2004).

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

21 4-Nitrophenol has also been found to be a product from toluene photooxidation (Irei et
22 al., 2015), but with a yield that is only about 6 % of the yield for 2-methyl-4-nitrophenol. The
23 carbon isotope ratio of 4-nitrophenol formed by the photooxidation of toluene is, within

1 measurement uncertainty, identical to the carbon isotope ratio of the precursor. Since the
2 measured concentrations of 4-nitrophenol are on average a factor of approximately 2.5 higher
3 than those of the most abundant methyl nitrophenol and the observed 4-nitrophenol carbon
4 isotope ratios are on average 6.6 ± 1.7 ‰ lower than those of the parent material a substantial
5 contribution of toluene oxidation to the observed levels of 4-nitrophenol can be ruled out.

6 For methyl nitrophenols, a measurable contribution from direct emissions is not likely.
7 The emission factors reported by Inomata et al. (2015) for 3-methyl-4-nitrophenol are between a
8 factor of 45 and 500 lower than the average emission factor of 4-nitrophenol reported by Inomata
9 et al. (2013) for the engine with the highest 4-nitrophenol emission factor while on average our
10 measured 3-methyl-4-nitrophenol concentrations are on average only a factor of seven lower
11 than the 4-nitrophenol concentrations. For 2-methyl-4-nitrophenol, the difference is even larger;
12 the emission factors are between a factor of 65 and 625 lower than for 4-nitrophenol while our
13 measured concentrations differ on average by only a factor of 2.5. Moreover, Inomata et al.
14 (2015) did not report the observation of 4-methyl-2-nitrophenol in PM from diesel engine
15 exhaust although their quantification limit for this isomer was nearly identical to that for 2-
16 methyl-4-nitrophenol and 3-methyl-4-nitrophenol.

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

1 substantially lower than -29 ‰, which is consistent with secondary formation from VOC
2 precursors.

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

20 As predicted by the postulated formation mechanisms and subsequent reaction with the OH
21 radical, most of the measured $\delta^{13}\text{C}$ values of 4-nitrophenol are larger than -34 ‰ (Fig. 34). The
22 lower end of the measured $\delta^{13}\text{C}$ values for 4-nitrophenol is approximately 1 ‰ to 2 ‰ lower
23 than $\delta^{13}\text{C}$ values predicted from the $\delta^{13}\text{C}$ values of benzene emissions and the KIE for reaction of

1 benzene with the OH radical, however this difference is within the uncertainty of the prediction
2 (Table 3) and the measurement error (Fig. 34). For two of the reaction products of the photo-
3 oxidation of toluene, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol, the discrepancy
4 between prediction and the lower end of observations is more pronounced. For both compounds,
5 the lower end of the observations is approximately 2 ‰ to 3 ‰ lighter than predicted, a
6 difference that is larger than the uncertainty of the predictions (Table 3). Similarly for 2,6-
7 dimethyl-4-nitrophenol the 25th percentiles are 2.7 ‰ lower than predicted for the initial phase of
8 the VOC precursor reaction. In total, 19 % of all measurements are below the 99 % confidence
9 limit calculated from the combined uncertainty of measurement and $\delta^{13}\text{C}_i$. However, a
10 substantial part, if not all, of the uncertainty of $\delta^{13}\text{C}_i$ will be systematic. Assuming that the total
11 calculated uncertainty of $\delta^{13}\text{C}_i$ is systematic, 12 % of the observations are below the 2σ
12 uncertainty of $\delta^{13}\text{C}_i$ and 5 % below the ~~2 σ~~ 3 σ limit.

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

22 ~~In the initial phase of the reaction, the concentration of secondary compounds will be low.~~
23 ~~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 $\delta^{13}\text{C}$ 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

1 partitioning into particles should result in differences in carbon isotope ratios between the gas
2 phase and particle phase for nitrophenols.

3 For the measurements presented here, the average concentration of nitrophenols in PM is
4 only about 20 % of the average of the total atmospheric nitrophenol concentrations, similar to the
5 findings reported by Saccon et al. (2013). Consequently, on average, the carbon isotope ratio of
6 total atmospheric nitrophenols is dominated by the carbon isotope ratio of gas phase
7 nitrophenols. The frequency distributions (Fig. 34) as well as a comparison of average carbon
8 isotope ratios (Fig. 45) show no systematic difference in the isotope ratios between the two
9 phases. In the case of 4-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol, the
10 differences between averages for PM + gas phase and PM only are less than 0.5 ‰ and for 4-
11 methyl-2-nitrophenol and 2,6-dimethyl-4-nitrophenol the differences are less than 1 ‰. These
12 differences are all within the uncertainties of the averages. The larger errors for 4-methyl-2-
13 nitrophenol and 2,6-dimethyl-4-nitrophenol are due to the smaller number of samples, which is
14 less than 15 for each phase.

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

1 For 2-methyl-4-nitrophenol, the most abundant targeted product from toluene photo-
2 oxidation, there were eight pairs of samples in which the isotope ratios were quantified in both
3 types of samples; 4-nitrophenol and 3-methyl-4-nitrophenol had six and two sample pairs,
4 respectively. An overview of the differences between total and PM only isotope ratios for
5 samples collected in parallel ($\Delta\delta^{13}\text{C}$) is shown in Fig. 56. On average the difference is 0.3 ‰
6 with an error of the mean of 0.5 ‰, consistent with the results in Fig. 45. However, the standard
7 deviation for $\Delta\delta^{13}\text{C}$ is 1.8 ‰, ~~nearly three times higher and~~ outside of the 99 % confidence limit
8 expected from the uncertainty of the measurements. Disequilibrium without significant
9 systematic bias in $\Delta\delta^{13}\text{C}$ indicates that exchange between the two phases is slower than the
10 change of $\delta^{13}\text{C}$ in one of the two phases. Since, apart from exchange with the gas phase, no
11 processes are known that will change the concentration or carbon isotope ratio of nitrophenols in
12 the particle phase, it is likely that the change of $\delta^{13}\text{C}$ in the gas phase due to formation from
13 aromatic VOC or gas phase loss reactions of nitrophenols is creating the disequilibrium in carbon
14 isotope ratio between the two phases.

15 Indeed the variability of $\Delta\delta^{13}\text{C}$ for sample pairs collected in summer is substantially higher
16 than for late fall, when photochemical activity is expected to be lower than in the summer (Table
17 4). Although the number of measurements is small and the averages are identical, the standard
18 deviation of $\Delta\delta^{13}\text{C}$ for summer sample pairs is 3.2 ‰ and well outside of the variability expected
19 from measurement errors. In contrast to this the standard deviation of $\Delta\delta^{13}\text{C}$ for late fall is only
20 0.9 ‰, which is only slightly higher than expected from the uncertainty of the measurements.
21 The variances for the summer and winter data sets are statistically different with a 99.5 %
22 probability (F-test).

1 In addition to a slower photochemical production or destruction of the nitrophenols in late
2 fall a lower variance of $\Delta\delta^{13}\text{C}$ in late fall can also be caused by the temperature dependence of
3 phase partitioning. For the sample pairs collected in summer, PM contributed on average 12 % of
4 the total atmospheric nitrophenol concentration. Therefore, the measured $\Delta\delta^{13}\text{C}$ values are a
5 good approximation for the difference in $\delta^{13}\text{C}$ between nitrophenols in the gas phase and in PM.
6 For the sample pairs collected in late fall, the contributions from PM range from 30 % to
7 approximately 100 % and consequently the difference in $\delta^{13}\text{C}$ between nitrophenols in the gas
8 phase and in PM will be larger than the measured $\Delta\delta^{13}\text{C}$ values. Unfortunately, for the late fall
9 samples, the large contribution of measurement error to the $\Delta\delta^{13}\text{C}$ values, combined with the
10 uncertainty of concentration measurements prevents a meaningful determination of the true
11 difference in $\delta^{13}\text{C}$ between nitrophenols in the gas phase and in PM. ~~Including experimental~~
12 ~~uncertainty, the upper limit for the uncertainty of the gas particle phase difference in $\delta^{13}\text{C}$ is~~
13 ~~approximately 2 %.~~ This is lower than the variability observed for summer sample pairs and
14 ~~supports the hypothesis that disequilibrium between gas and particle phase is the result of~~
15 ~~changes in $\delta^{13}\text{C}$ of gas phase nitrophenols due to photo-chemical formation or loss reactions.~~

16 **3.3 Correlation between Isotope Ratios of Nitrophenols**

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

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

16 The standard deviation observed for differences between carbon isotope ratios of
17 nitrophenols which are not isomers are substantially larger than expected from measurement
18 uncertainty and very similar to the standard deviation expected from the variance of $\delta^{13}\text{C}$ within
19 the data sets for the individual nitrophenols (Table 5). However, on average the difference in
20 isotope ratios ($\Delta\delta^{13}\text{C}$) between non-isomeric nitrophenols are only marginally larger than $\Delta\delta^{13}\text{C}$
21 for the methyl nitrophenol isomers (Tables 2 and 5). To some extent this can be explained by the
22 very similar carbon isotope ratios of the different precursor VOC (Table 3). However, from the
23 differences in KIEs for the initial step of the reaction sequence leading to formation of

1 nitrophenols it is expected that isotope ratios of non-isomeric nitrophenols during the initial
2 phase of their formation will differ by a few per mille (Table 3). Compared to these predicted
3 differences the actually observed values for the average of $\Delta\delta^{13}\text{C}$ are surprisingly small. This
4 may be due to the fact that with increasing extent of atmospheric processing the carbon isotope
5 ratio of the precursor will increase and that this increase will depend on the KIE and the rate
6 constant for the reaction of precursor. Depending on the extent of processing, this will, at least
7 partly, compensate for the larger depletion in ^{13}C for reaction products formed from unprocessed
8 emissions since the more reactive aromatic precursor VOC have lower KIEs during the initial
9 phase of the reaction. Since on average the observed $\Delta\delta^{13}\text{C}$ are very small, suggesting, this
10 suggests that on average precursor processing has been substantial, independent of the precursor
11 reactivity.

12 **3.4 Seasonal Variation of the Concentrations and Carbon Isotope Ratios of Nitrophenols**

13
14 Table 6 shows a comparison of 2-methyl-4-nitrophenol and 4-nitrophenol concentrations
15 and carbon isotope ratios for different temperature ranges. The separation into different
16 temperature ranges is based on the average temperatures during sampling. Measurements with
17 average temperatures below 10 °C were made between mid of October and end of January,
18 measurements with average temperatures exceeding 20 °C in June, July and August. Also
19 included are air quality data from two OME monitoring stations in Toronto (Fig. 42).
20 Remarkably, a distinct seasonal difference in isotope ratios is not observed. With the exception
21 of the 4-nitrophenol isotope ratios in PM, the difference in average carbon isotope ratios between
22 measurements made at low and high temperatures is less than 0.5 ‰. For the 4-nitrophenol
23 isotope ratios in PM this difference is 0.9 ‰, but this difference is within the uncertainty of the
24 average values.

1 This is in contrast to the expectation that, due to higher photochemical activity in
2 summer, samples collected in summer should be subject to more processing and therefore be,
3 compared to less processed samples, enriched in ^{13}C . A more detailed look at the dependence
4 between temperature, wind direction and carbon isotope ratio can provide a possible explanation
5 for this unexpected finding. Figure ~~7-8~~ shows the frequency of observations of $\delta^{13}\text{C}$ values for
6 methyl nitrophenols and 4-nitrophenol binned into intervals of 2 ‰ and separated by wind
7 direction and average temperature during sampling. The selection of the wind directions, north
8 and southwest, was based on the number of available measurements and the difference in nearby
9 major sources of nitrophenol precursors. Only samples with a ~~relatively stable~~ wind direction
10 that was stable (with 45 °) during sampling were used for this analysis. Three major highways
11 and their intersections are located within 15 km or less southwest of the sampling locations
12 whereas there is only one major highway directly north of York University (Fig. ~~42~~).

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

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

1 Although the lower number of data points available for 4-nitrophenol results in higher
2 | statistical uncertainty of the distribution, Fig. 7-8 shows some substantial differences between the
3 | carbon isotope ratios of methyl nitrophenols and 4-nitrophenol. For 4-nitrophenol only 13 % of
4 | all data points are in the -34 ‰ to -32 ‰ range and more than 50 % of the $\delta^{13}\text{C}$ values measured
5 | at high average temperatures are below -34 ‰. This can be explained by the different reactivity
6 | of the precursors. The rate constant for the reaction of benzene with the OH radical is only one
7 | fourth of that for the reaction of toluene (Table 3) and therefore photochemical processing ~~will~~
8 | results in a lower enrichment of ^{13}C in the products from reactions of benzene compared to
9 | products derived from toluene.

10 The preference of low and medium enrichment of nitrophenols in ^{13}C during summer is
11 | independent of wind direction. Compared to northerly wind directions, the larger number of
12 | observations under southwesterly airflow reflects the larger percentage of observations with
13 | southwesterly wind in summer (eighteen of twenty nine) and not a wind direction dependence of
14 | methyl nitrophenol carbon isotope ratios. Since it is expected that the different wind directions
15 | result in different pollution levels, this is consistent with the finding that there is no systematic
16 | dependence between the concentration of methyl nitrophenols and carbon isotope ratio (Fig. 42).
17 | Similarly, the carbon isotope ratios of the methyl nitrophenols and 4-nitrophenol show no
18 | correlation with CO, NO₂, O₃ or oxidant (O₃ + NO₂) concentrations (R^2 is consistently below
19 | 0.1).

20 Although the nitrophenols exhibit only small seasonal changes in carbon isotope ratios,
21 | there are substantial differences in concentrations. For 2-methyl-4-nitrophenol and 4-nitrophenol
22 | the difference in concentrations in PM between summer and winter is a factor of 6.5 and 3.5,
23 | respectively. Most of these differences can be explained by a temperature dependence of the

1 distribution between gas phase and PM. For average temperatures exceeding 20 °C, slightly less
2 than 10 % of the total concentration is found in PM. For average temperatures below 10 °C the
3 fraction in PM increases to approximately 40 %.

4 There are some differences in PM + gas concentrations between the two different
5 temperature ranges. The average 2-methyl-4-nitrophenol concentration in PM + gas is at low
6 temperatures on average approximately 60 % higher than at high temperatures. An increase in
7 photochemical processing of the precursors can be ruled out as explanation for the higher methyl
8 nitrophenol concentrations at low temperatures. It is unlikely that photochemical processing is
9 faster in winter and fall than in summer and the methyl nitrophenol isotope ratios show, on
10 average, no indication for enhanced processing at low temperatures. The most likely explanation
11 is higher precursor concentrations in fall and winter. The concentration of 2-methyl-4-
12 nitrophenol in PM + gas is correlated ($R^2 = 0.64$) with the NO_2 concentration (Fig. [8a9a](#)).
13 Therefore it is expected that on average, higher NO_2 concentrations in fall and winter will result
14 in higher 2-methyl-4-nitrophenol levels. The larger NO_2 concentrations in fall and winter may be
15 attributed to the decreased boundary layer height coupled with increased pollution rates, but the
16 higher photolysis rate of NO_2 in summer may also contribute to the difference in NO_2
17 concentrations between seasons.

18 Both toluene and NO_2 are required for the formation of methyl nitrophenols in the
19 atmosphere and it is expected that the concentration of toluene also will influence the formation
20 rate of methyl nitrophenols. However, ~~there is a weak correlation~~ the correlation of the NO_2
21 concentration with other indicators of atmospheric pollution such as CO ($R^2 = 0.33$) and SO_2 (R^2
22 = 0.41), which prevents separating between the influence of NO_2 and other precursors and it is

1 therefore not possible to distinguish between the impact of different pollutants on methyl
2 nitrophenol concentrations.

3 In contrast to 2-methyl-4-nitrophenol, the correlation between the concentrations of 4-
4 nitrophenol and NO₂ is only weak (Fig. ~~8b9b~~). This indicates that, consistent with the low
5 reactivity of 4-nitrophenol and its ~~of the~~ benzene precursor, the processes determining the
6 concentration of 4-nitrophenol are occurring at a time scale that is different from the processes
7 determining the NO₂ concentrations.

8 ~~Correlation between NO₂ and 4-nitrophenol or alkyl nitrophenols may also be due to~~
9 ~~direct emissions since 4-nitrophenol and two methyl nitrophenol isomers have been found in~~
10 ~~exhaust from diesel powered vehicles (Inomata et al., 2013, 2015) which are also substantial~~
11 ~~sources for nitrogen oxides. The average ratios of 4-nitrophenol over NO_x volume mixing ratios~~
12 ~~calculated from the results reported by Inomata et al. (2013) range from approximately 5×10^{-5}~~
13 ~~for the engine with the highest 4-nitrophenol emissions to 7.5×10^{-8} for the engine with the~~
14 ~~lowest emissions. The average ratio of 4-nitrophenol over NO_x for our measurements is $9.5 \times$~~
15 ~~10^{-5} on a molar basis with an error of the mean of 0.2×10^{-5} . Although this comparison ignores~~
16 ~~the existence of NO₂ sources other than diesel engines in the GTA, this is approximately a factor~~
17 ~~of two higher than the upper end of emission ratios for the measurements reported by Inomata et~~
18 ~~al. (2015). Nevertheless, based on the limited number of diesel engines investigated by Inomata~~
19 ~~et al. (2013), it cannot be ruled out that direct emissions contribute to the 4-nitrophenol~~
20 ~~concentrations we observed.~~

21 ~~For methyl nitrophenols a significant contribution from direct emissions is less likely.~~
22 ~~The emission factors reported by Inomata et al. (2015) for 3-methyl-4-nitrophenol are between a~~
23 ~~factor of 45 and 500 lower than the average emission factor of 4-nitrophenol reported by Inomata~~

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

9
10 Atmospheric nitrophenols are produced by photochemical oxidation of aromatic VOC in
11 the presence of NO_x. Since atmospheric oxidants (O₃ and NO₂) are also formed from photo-
12 oxidation of VOC, we expect correlation between oxidant and nitrophenol concentrations.
13 Indeed, there is a strong correlation ($R^2 = 0.60$) between the concentration of oxidants and 4-
14 nitrophenol (Fig. [9a10a](#)). Surprisingly, the correlation between 2-methyl-4-nitrophenol and
15 oxidant concentrations is only weak (Fig. [9b10b](#)). This most likely reflects the different
16 reactivity of the precursors (Table 3) and indicates that the timescale for processes determining
17 oxidant levels is similar to the timescale determining formation of 4-nitrophenol, but different
18 from that for 2-methyl-4-nitrophenol formation.

19 20 **4. Conclusions**

21 In this study, concentration and stable carbon isotope ratio measurements of nitrophenols
22 in Toronto were taken. On average, the ¹³C depletion relative to the carbon isotope ratios of the
23 precursors is approximately 6 ‰, and the observed δ¹³C values range from -37 ‰ to -28 ‰. The

1 substantial variability of the nitrophenol carbon isotope ratios can be explained by a varying
2 degree of photochemical processing. Consequently, changes in the carbon isotope ratio of
3 atmospheric nitrophenols are indicators for differences in photochemical processing, although
4 currently no simple quantitative relation between nitrophenol isotope ratio and photochemical
5 age has been established. The combination of carbon isotope ratio and concentration
6 measurements provide strong evidence that, for the conditions studied here, secondary processes
7 in the atmosphere are the dominant source for the target compounds.
8

9 The lower end of measured ambient isotope ratios that is about 2 ‰ to 3 ‰ lower than
10 predictions based on the KIE for the reaction of the precursor with OH-radicals. This is
11 consistent with results of the laboratory studies of Irei et al. (2015) and therefore provides
12 additional evidence for a predominantly photochemical origin of the nitrophenols.

13 On average, the difference in carbon isotope ratios of nitrophenols between the gas phase
14 and the particle phase is very small. This suggests that, on average, there is equilibrium between
15 nitrophenols in the gas phase and in the particle phase, but there are several observations of a
16 significant difference in nitrophenol carbon isotope ratios between gas and particle phase. Since
17 this is only observed in summer, it can be concluded that in these cases photochemical
18 production or removal of nitrophenols is faster than their exchange between the two phases. The
19 assumption of significant local photochemical processing of nitrophenols in summer is also
20 supported by the difference between summer and winter carbon isotope frequency distributions
21 of methyl nitrophenols.

22 There is no significant correlation between the carbon isotope ratio of nitrophenols and
23 their concentration. This demonstrates that, for the conditions studied here, atmospheric mixing

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

11
12 The concentration of 4-nitrophenol is strongly correlated with the oxidant ($O_3 + NO_2$)
13 levels whereas there is no significant correlation between the concentration of alkyl
14 nitrophenols and oxidant concentration ~~is weak~~. It can be concluded that the processes
15 determining oxidant concentrations are occurring on timescales that are better represented by the
16 processes resulting in formation of 4-nitrophenols than those for formation of alkyl nitrophenols.
17 Most likely these differences in timescales are determined by the reactivity of the aromatic
18 precursors of the different nitrophenols.

19 The importance of precursor reactivity on the carbon isotope ratios of nitrophenols is
20 supported by the comparison of carbon isotope ratios of different methyl nitrophenol isomers.
21 Overall, these differences in carbon isotope ratios for different isomers are small compared to the
22 overall variability of the carbon isotope ratios of individual isomers of methyl nitrophenols.

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

11 **Acknowledgments**

12
13 The authors would like to acknowledge Darrell Ernst and Wendy Zhang at Environment Canada
14 for technical support in isotope ratio measurements. This research was supported financially by
15 the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Canadian
16 Foundation for Climate and Atmospheric Sciences (CFCAS).

17 **References**

- 18 Anderson, R.S., Iannone, R., Thompson, A. E., Rudolph, J., Huang, L.: Carbon kinetic isotope
19 effects in the gas-phase reactions of aromatic hydrocarbons with the OH radical at 296 ± 4 K,
20 *Geophys. Res. Lett.*, 31, L15108, doi:10.1029/2004GL020089, 2004.
- 21 Atkinson, R.: Atmospheric chemistry of VOCs and NO_x, *Atmos. Environ.* 34, 2063-2101, 2000.
- 22 Atkinson, R., Aschmann, S.M., Arey, J.: Reactions of OH and NO₃ radicals with phenol, cresols,
23 and 2-nitrophenol at 296 ± 2 K, *Environ. Sci. & Technol.*, 26, 1397-1403, 1992.
- 24 Bejan, I., Barnes, I., Olariu, R., Zhou, S., Wiesen, P., Benter, T.: Investigations on the gas-phase
25 photolysis and OH radical kinetics of methyl-2-nitrophenols, *Phys. Chem. Chem. Phys.*, 9, 5686-
26 5692, 2007.

- 1 Bolzacchini, E., Bruschi, M., Hjorth, J., Meinardi, S., Orlandi, M., Rindone, B., Rosenbohm, E.:
2 Gas-phase reaction of phenol with NO₃, *Environ. Sci & Technol.*, 35, 1791-1797, 2001.
- 3 Calvert, J.G., Atkinson, R., Becker, K.H., Kamens, R.M., Seinfeld, J.H., Wallington, T.J.,
4 Yarwood, G.: *The mechanisms of atmospheric oxidation of aromatic hydrocarbons*, Oxford
5 University Press, New York, United States of America, 2002.
- 6 Craig, H.: Isotopic standards for carbon and oxygen and correction factors for mass-
7 spectrometric analysis of carbon dioxide, *Geochem. Cosmo. Acta*, 12, 133-149, 1957.
- 8 Forstner, H., Flagan, R. & Seinfeld, J.: Secondary organic aerosol from the photooxidation of
9 aromatic hydrocarbons: molecular composition, *Environ. Sci. & Technol.*, 31, 1345-1358, 1997.
- 10 Gensch, I., Kiendler-Scharr, A., and Rudolph, J.: Isotope ratio studies of atmospheric organic
11 compounds: principles, methods, applications and potential, *Int. J. Mass Spectrom.*, 365– 366,
12 206–221, 2014.
- 13 Goldstein, A. and Shaw, S.: Isotopes of volatile organic compounds: An emerging approach for
14 studying atmospheric budgets and chemistry, *Chem. Rev.*, 103, 5025-5048, 2003.
- 15 Google Earth Pro, Version 7.1.2.2041, August 23, 2009, 43°46'25.13"N, 79°30'22.00"W,
16 elevation 0 m, eye altitude 17.86 km. Toronto, Canada, Map Data: Google, Digital Globe, First
17 Base Solutions, NOAA, Accessed: February 13th 2015, 2015.
- 18 Grosjean, D.: Atmospheric fate of toxic aromatic compounds, *Sci. Total Environ.*, 100, 367-414,
19 1991.
- 20 Hamilton, J., Webb, P., Lewis, A., Reviejo, M.: Quantifying small molecules in secondary
21 organic aerosol formed during the photo-oxidation of toluene with hydroxyl radicals, *Atmos.*
22 *Environ.*, 39, 7263-7275, 2005.
- 23 Harrison, M.A.J., Heal, M.R. and Cape, J.N.: Evaluation of the pathways of tropospheric
24 nitrophenol formation from benzene and phenol using a multiphase model, *Atmos. Chem. Phys.*,
25 5, 1679-1695, 2005.
- 26 Herrmann, H., Exner, M., Jacobi, H-W., Raabe, G., Reese, A., Zellner, R.: Laboratory studies of
27 atmospheric aqueous-phase free-radical chemistry: kinetic and spectroscopic studies of reactions
28 of NO₃ and SO₄⁻ radicals with aromatic compounds, *Faraday Discuss.*, 100, 129-153, 1995.
- 29 Inomata, S., Tanimoto, H., Fujitani, Y., Sekimoto, K., Sato, K., Fushimi, A., Yamada, H., Hori,
30 S., Kumazawa, Y., Shimono, A., Hikida, T.: On-line measurements of gaseous nitro-organic
31 compounds in diesel vehicle exhaust by proton-transfer-reaction mass spectrometry, *Atmos.*
32 *Environ.*, 73, 195-203, 2013.

- 1 Inomata, S., Fushimi, A., Sato, K., Fujitani, Y., Yamada, H.: 4-nitrophenol, 1-nitropyrene, and 9-
2 nitroanthracene emissions in exhaust particles from diesel vehicles with different exhaust gas
3 treatments, *Atmos. Environ.*, 110, 93-102, 2015.
- 4 Irei, S., Rudolph, J., Huang, L.: Compound-specific stable carbon isotope ratios of phenols and
5 nitrophenols derivatized with N,O-bis(trimethylsilyl)trifluoroacetamide, *Anal. Chim. Acta*, 786,
6 95-102, 2013.
- 7 Irei, S., Rudolph, J., Huang, L., Auld, J., Collin, F., Hastie, D.: Laboratory studies of carbon
8 kinetic isotope effects on the production mechanism of particulate phenolic compounds formed
9 by toluene photooxidation: a tool to constrain reaction pathways, *J. Phys. Chem.*, 119, 5-13,
10 2015.
- 11 Jang, M. and Kamens, R.: Characterization of secondary aerosol from the photooxidation of
12 toluene in the presence of NO_x and 1-Propene, *Environ. Sci. Technol.*, 35, 3626-3639, 2001.
- 13 Kaye, J.A.: Isotope effects in gas-phase chemical reactions and photodissociation processes:
14 Overview, in: Kaye, J.A.: Isotope effects in gas-phase chemistry, American Chemical Society,
15 United States of America, 1-14, 1992.
- 16 Moukhtar, S., Saccon, M., Kornilova, A., Irei, S., Huang, L., Rudolph, J.: Method for
17 determination of stable carbon isotope ratio of methylnitrophenols in atmospheric particulate
18 matter, *Atmos. Meas. Tech.*, 4, 2453-2464, 2011.
- 19 Nojima, K., Kawaguchi, A., Ohya, T., Kanno, S., Hirobe, M.: Studies on photochemical reaction
20 of air pollutants. X.: Identification of nitrophenols in suspended particulates, *Chem. Pharm. Bull.*
21 31, 1047-1051, 1983.
- 22 Perraud, V., Bruns, E.A., Ezell, M.J., Johnson, S.N., Yu, Y., Alexander, M.L., Zelenyuk, A.,
23 Imre, D., Chang, W.L., Dabdub, D., Pankow, J.F., Finlayson-Pitts, B.J.: Nonequilibrium
24 atmospheric secondary organic aerosol formation and growth, *P. Natl. Acad. Sci. USA.*, 109,
25 2836-2841, 2011.
- 26 Rudolph, J.: Gas chromatography-isotope ratio mass spectrometry, in: Koppmann, R.: Volatile
27 organic compounds in the atmosphere, Blackwell Publishing Ltd., United Kingdom, 388-466,
28 2007.
- 29 Rudolph, J., Czuba, E., Norman, A.L., Huang, L., Ernst, D.: Stable carbon isotope composition of
30 nonmethane hydrocarbons in emissions from transportation related sources and atmospheric
31 observations in an urban atmosphere, *Atmos. Environ.*, 36, 1173-1181, 2002.
- 32 Saccon, M., Busca, R., Facca, C., Huang, L., Irei, S., Kornilova, A., Lane, D., Rudolph, J.:
33 Method for the determination of concentration and stable carbon isotope ratios of atmospheric
34 phenols, *Atmos. Meas. Tech.*, 6, 2965-2974, 2013.
- 35 Sato, K., Hatakeyama, S., Imamura, T.: Secondary organic aerosol formation during the
36 photooxidation of toluene: NO_x dependence of chemical composition, *J. Phys. Chem. A*, 111,
37 9796-9808, 2007.

1 Tremp, J., Mattrel, P., Fingler, S., Giger, W.: Phenols and nitrophenols as tropospheric
2 pollutants: emissions from automobile exhausts and phase transfer in the atmosphere, Water Air
3 Soil Poll, 68, 113-123, 1993.

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

1 Table 1. Summary of performance characteristics of the sampling, extraction and analysis
2 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 ‰

3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22

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 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 formed by the reaction of the unprocessed emissions of in the initial phase of the reaction of the 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. 45.

	$\Delta\delta^{13}\text{C}$ (‰) ^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
<hr/>		
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 42](#). 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 23](#). Plot of isotope ratio values as a function of concentration for 4-nitrophenol, 3-methyl-4-nitrophenol and 2-methyl-4-nitrophenol.

[Figure 34](#). 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).

[Figure 45](#). 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 56](#). 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 67](#). Plot of isotope ratios for 4-methyl-2-nitrophenol and 3-methyl-4-nitrophenol (y-axis) against 2-methyl-4-nitrophenol for filter samples.

[Figure 7:8](#). 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 ~~was found by looking~~ HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model) by Air Resources Laboratory (NOAA) trajectory analysis.

| Figure [89](#). 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 [910](#). 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.