Measurement of Gas and Particle Phase Nitrophenols in the Atmosphere Using High-Volume Filter Sampling

Chemistry 4000 Research Project

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ABSTRACT

Nitrophenols are toxic, semi-volatile organic compounds (SVOC) and a type of secondary organic aerosols (SOA) that have received much interest because of their adverse impacts on the environment and human health. One of the poorly understood aspects of SOA in the atmosphere is the manner in which they are formed from the photo-oxidation of volatile organic compounds (VOCs). Nitrophenols are specifically formed through OH radical initiated photo-oxidation of aromatic VOCs such as benzene and toluene. These compounds are found in both gas and particle phases in the atmosphere due to their semi-volatile nature. To better understand the formation and processing of SOAs, it is important to gain more knowledge about the partitioning of nitrophenols in the atmosphere. In the present research project, high-volume filter sampling was used to collect both gas and particle phase nitrophenols. Quartz fiber filters were used for particle phase collection only and XAD-4 coated quartz fiber filters were used for both gas and particle phase collection. Using this method, the separate gas and particle phase concentrations of a group of five nitrophenols, as well as their partitioning, were measured in the atmosphere. The results of atmospheric nitrophenol concentration measurements were used to observe the correlation between the partitioning of nitrophenols with vapor pressure and temperature. The results were also used to compare the phase distribution of the target nitrophenols obtained from the high-volume filter sampling with those measured using the denuder-filter method. The results from this project indicated that the high-volume filter sampling method has the potential to be used as a sampling technique for the separate collection of both gas and particle phase SVOCs such as nitrophenols. The concentration measurements obtained in this project also indicated that the partitioning of nitrophenols between their gas and particle phases do not necessary depend on their vapor pressure. There is also some indication that the partitioning of nitrophenols may be dependent on the ambient temperature.

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1. INTRODUCTION

A particular class of secondary organic aerosols (SOA) known as nitrophenols is primarily formed in the atmosphere through the OH-radical initiated photo-oxidation of aromatic volatile organic compounds (VOCs), like benzene and toluene (Forstner et al., 1997; Hurley et al., 2001; Hamilton et al., 2005). These VOCs are initially emitted into the atmosphere primarily through anthropogenic processes (Tremp et al., 1993). Moreover, due to their semi-volatile nature, nitrophenols can exist in the atmosphere in both gas and particle phases. In order to better understand the formation and processing of secondary organic matter in the atmosphere, it is necessary to study the partitioning of nitrophenols between their gas and particle phases.

Nitrophenols have received interest from the scientific community because they can have an especially harmful impact on the environment and/or human health, depending on their level of concentration (Morville et al., 2004). While many research groups monitor the concentration levels of nitrophenols in various mediums such as fog (Richartz et al., 1990; Herterich, R, 1991) plant leaves (Natangelo, et al., 1999), rain (Leuenberger et al., 1988; Levsen et al., 1990) and snow (Kawamura and Kaplan 1986; Albert et al., 1989), our knowledge of the partitioning of nitrophenols between their gas and particle phases in the atmosphere is still lacking.

Previous research carried out in Dr. Rudolph's group (Moukhtar et al., 2011) has determined that the concentration levels of methyl nitrophenols in atmospheric particulate matter were much lower than predicted from the measurement of concentration levels obtained in laboratory studies, therefore suggesting that many of these nitrophenols may be present in the gas phase. Busca (2010), as part of her master's thesis, discovered that ambient nitrophenols are dominated by gas phase concentrations, but are still lower than predicted level.

The purpose of this research is to measure the particle to gas phase ratio of nitrophenols in the atmosphere using high-volume filter sampling. The other aim of this research is to observe any possible changes in gas and particle phase distribution of nitrophenols due to meteorological conditions such as seasonal temperature variability. The method that will be applied for sampling and analysis of nitrophenols in both the gas and particle phase has been developed by R. Busca and M. Saccon but was only used to collect a limited number of samples (Busca, 2010; Saccon et al., 2013).

The sampling events that have been performed in this project involved sampling an uncoated quartz filter to collect particle phase on one high-volume sampler and a sorbent impregnated filter (SIF), to collect both particle and gas phases on a parallel sampler at the same time, to determine the separate gas and particle phase concentrations and therefore the partitioning of nitrophenols between the two phases. Since sampling these filters in parallel only yields a first order estimate of gas and particle phase partitioning of nitrophenols, samples were also collected in parallel to a denuder-filter method, which was acquired by C. Facca. The results of this project would provide information about the gas to particle phase partitioning of ambient nitrophenols. They will also provide details about the suitability of using high-volume sampling for analysis of phenols in the atmosphere.

2. THEORY AND BACKGROUND

As will be explained in section 2.1, nitrophenols are semi-volatile compounds due to their intermediate ambient vapor pressures (see table 2.1). It is essential to gain knowledge about their gas-particle phase partitioning since the fate, transport and deposition of semi-volatile species in the atmosphere is strongly dependent upon whether they exist in the gas phase or in the particle phase (Bidleman, 1988). One of the main reasons for the lack of data regarding the atmospheric partitioning of nitrophenols is because of the difficulty to collect the two phases separately. Previous research carried out in Dr. Rudolph's group includes the development of a new method for sampling and analysis of the total amount of gas and particle phase nitrophenols in the atmosphere using high-volume air samplers (Busca R., 2010). To enable the collection of both gas and particle phase nitrophenols, quartz fiber filter are coated with XAD-4^{MT} resin, which is a polystyrene-divinylbenzene copolymer resin (see Figure 2.1). The cleaning, grinding and coating procedure was based on a method developed by Lane (1999) and modified by Busca (2010) and Saccon et al., (2013). XAD-4^{MT} is a type of sorbent that has been used to collect gas phase phenols in air and water (Herterich, 1990; Morville et al., 2004). The gas phase compounds can be collected onto the coated filter by diffusion onto the XAD-4^{MT} resin. High-volume air sampling technique is commonly used to collect particle phase species from ambient air onto a quartz fiber filter, while the gas phase compounds pass through the filter (Katz, R. 1977).

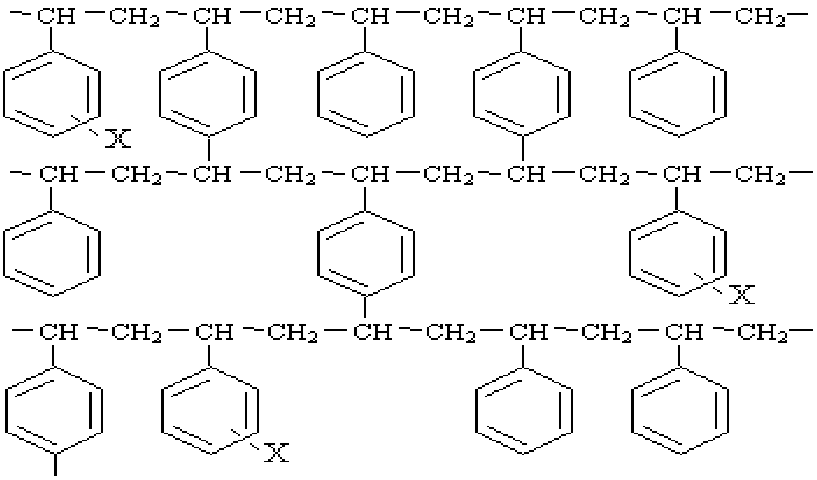


Figure 2.1: Polystyrene-divinylbenzene copolymer resin.

A more ideal method, which enables the separate measurement of gas and particle phase nitrophenols is to use a denuder (Cecinato et al., 2005). A denuder-filter method is a better technique in measuring the separate gas and particle phase concentrations of atmospheric nitrophenols since it reduces some of the sampling artifacts associated with the high-volume filter sampling. However one of the main disadvantages of using a denuder- filter method is that the masses of nitrophenols collected using this method are not sufficient for GC-IRMS analysis. Collecting nitrophenols in amounts suitable for GC-IRMS is important since isotope ratio analysis of nitrophenol is one of the main objectives in Dr. Rudolph's group.

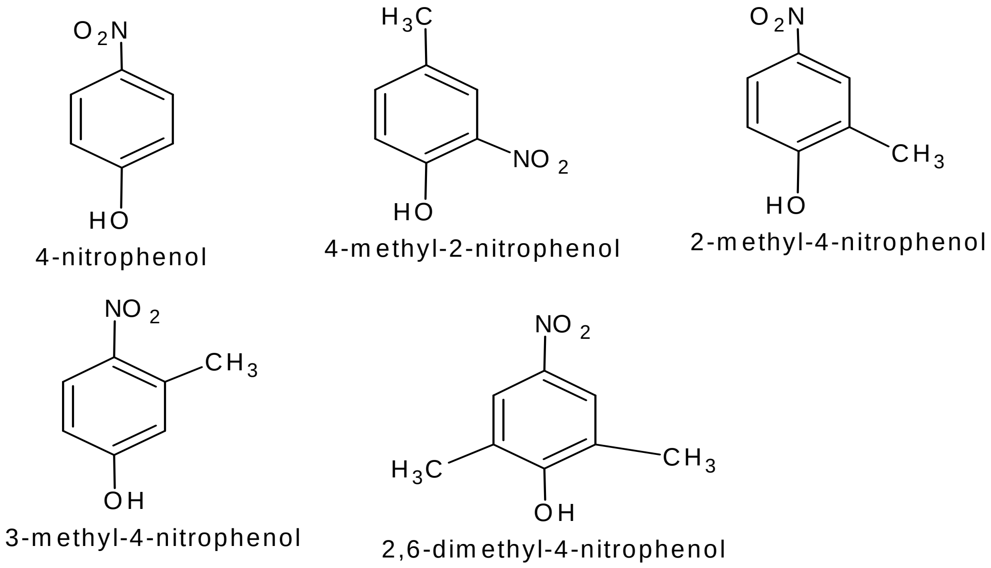
2.1 Gas to Particle Partitioning

The five target nitrophenol compounds chosen to study in this project, chemical structures are shown in Figure 2.2, are classified as semi-volatile compounds based on their ambient vapor pressures. According to a study done by Junge (1977), compounds with vapor pressures less than 10^{-6} Pa are expected to exist in the particle phase; those with vapor pressure higher than 10^{-2} Pa will exist in the gas phase. Compounds that fall within the range of 10^{-2} and 10^{-6} Pa are termed semi-volatile species and can exist in both gas and particle phases. The vapor pressures of the five target nitrophenols, which are listed in Table 2.1, corroborate that these compounds are semi-volatile. From the values shown in Table 2.1, 4-methyl-2-nitrophenol is expected to exist entirely in the gas phase. The other four compounds however fall into the range for semi-volatile species and are expected to be found in both gas and particle phases. It is important to note however that the partitioning of a compound between the gas and particle phase is not only confined to its vapor pressure and may depend on some other factors such as ambient temperature, relative humidity, particle mass concentration and chemical composition (Pankow, 1994; Odume et al., 1996; Forstner et al., 1997).

Table 2.1: *Measured vapor pressure of nitrophenols found in the atmosphere*

Compound	Vapor pressure (Pa)
4-methyl-2-nitrophenol	$1.11x10^{1}$ (at 30 ºC)
4-Nitrophenol	$1.03x10^{-2}$ (at 30 ºC)
3-methyl-4-nitrophenol	$3.13x10^{-3}$ (at 30 ºC)
2-methyl-4-nitrophenol	$8.69x10^{-3}$ (at 30 ºC)
2,6-dimethyl-4-nitrophenol	$6.42x10^{-4}$ (at 30 ºC)

Measurements were made by Dr. X. Gong (private communication)


4-nitrophenol

4-methyl-2-nitrophenol

2-methyl-4-nitrophenol

3-methyl-4-nitrophenol

2,6-dimethyl-4-nitrophenol

Figure 2.2: Chemical structure of the five target nitrophenols.

2.2 Formation Mechanism of Nitrophenols from VOC

Nitrophenols found in the atmosphere are primarily formed through the photo-oxidation of aromatic volatile organic compounds (VOCs), such as toluene, benzene and xylenes. VOCs are emitted into the atmosphere mainly through vehicle exhaust and industrial sources (Tremp et al., 1993). Once emitted, these compounds can undergo reaction with hydroxyl radicals (OH^{*}) and nitrogen dioxide (NO_2) producing various products, including nitrophenols (Forstner et al., 1997, Atkinson et al., 1992). The oxidation of aromatic compounds like benzene and the alkyl-substituted benzenes are initiated by reaction with OH radical, which can either add to the aromatic ring or can proceed by H-atom abstraction from the aromatic ring or from an alkyl substituent. The H-atom abstraction however is a minor reaction pathway since only about 10% of the OH radical initiated reaction results from H-abstraction (Atkinson et al., 1992; Zhao et al., 2005). Therefore a more efficient reaction is achieved by the OH radical addition to aromatic ring in any of the *ortho*-, *meta*-, or *para*- positions. The products formed from the main reaction pathway are hydroxycyclohexadienyl radicals or alkyl-substituted hydroxycyclohexadienyl radicals. The subsequent reaction of these compounds in presence of O_2, NO and NO_2 lead to formation of a wide range of products, including cresols (Atkinson et al., 1992, Forstner et al., 1997). Formation of cresols from toluene favors the *ortho*- and *para*- positions due to the activating nature of the alkyl-substituent on toluene. Methyl nitrophenols can then form when cresols undergo nitration in the atmosphere. The nitration of a cresol favors the *ortho*- and *para*- positions relative to the OH group rather than the methyl group. This is due to the fact that OH group on the cresol is a stronger activating group as it goes through the π-bond interactions, compared to the methyl group, which goes through the □-bond. As a result the main products from this reaction are expected to be 2-methyl-4-nitrophenol, 4 methyl-2-nitrophenol and 3-methyl-4-nitrophenol. The reaction mechanism for the formation of these methyl nitrophenols from the oxidation of toluene was adapted from Forstner and coworkers (1997) and is depicted in Figure 2.3.

According to the formation mechanism adapted from Zhao and coworkers (2005), 2,6-dimethyl-4-nitrophenol is the dominant product to form from oxidation of m-xylene (Figure 2.4). This is because of the addition of the OH radical in a position *ortho*- to both methyl groups, which is the most favorable position due to the ortho-directing effect from both methyl groups on m-xylene. Figure 2.5 shows the formation pathway for 4-nitrophenols from phenol, which also favors the *ortho*- and *para*- positions (Atkinson et al., 1992).

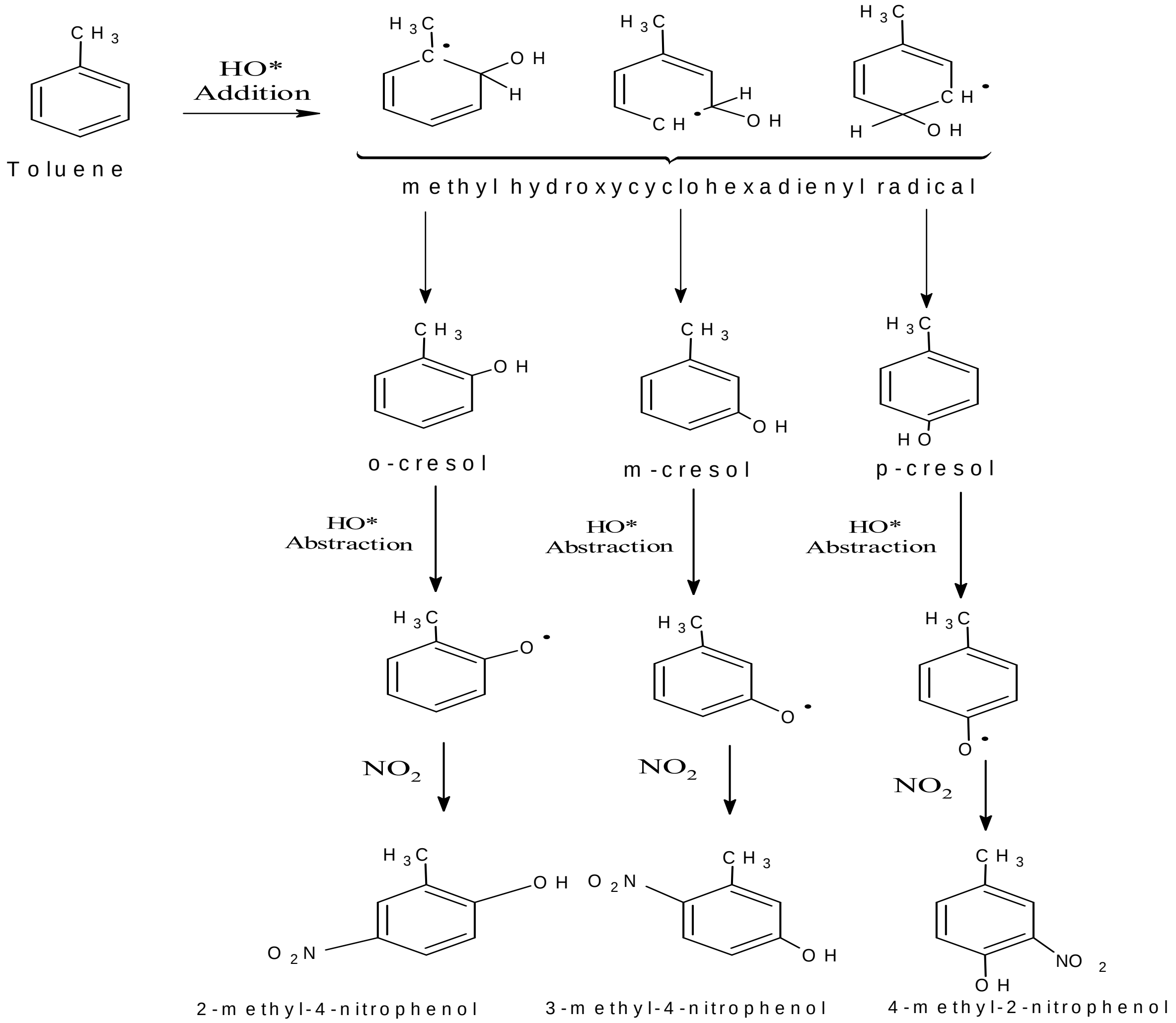


Figure 2.3: Reaction mechanism for formation of methyl nitrophenol from toluene (Forstner et al., 1997).

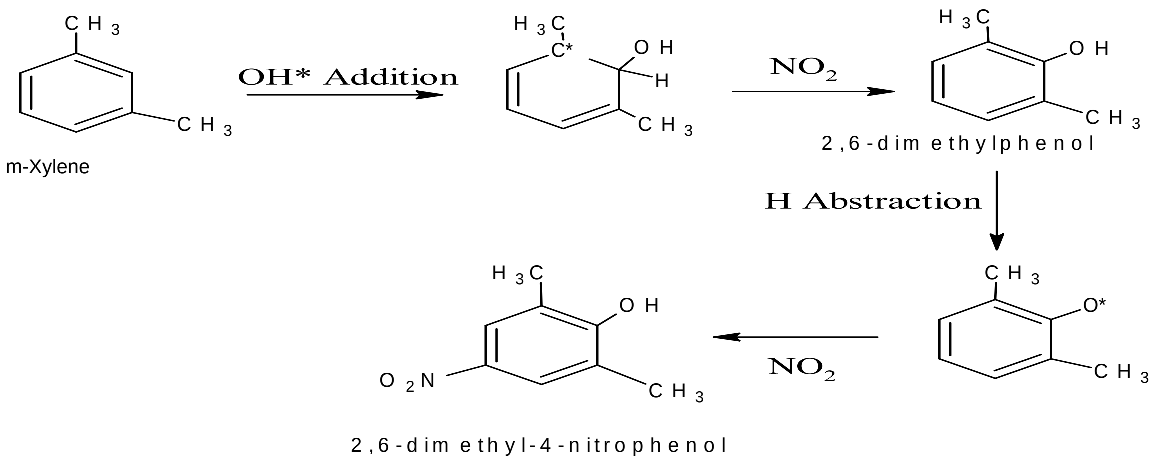


Figure 2.4: Formation mechanism of 2,6-dimethyl-4-nitrophenol from xylene (Zhao et al., 2005)

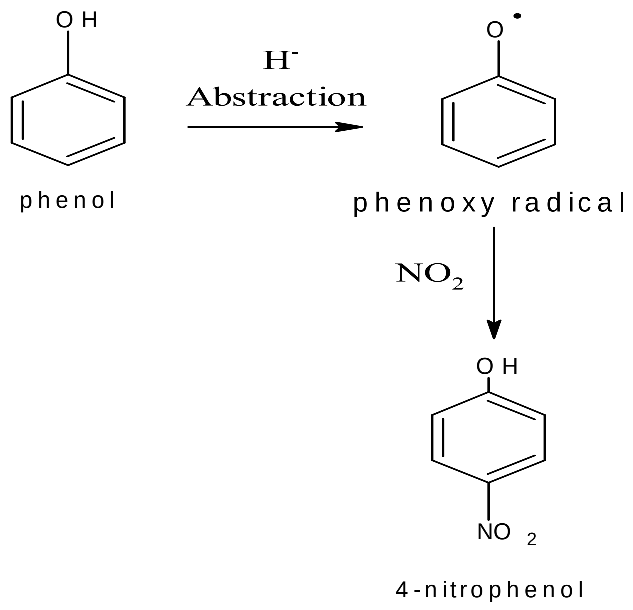


Figure 2.5: Formation mechanism of 4-nitrophenol from phenol (Atkinson et al., 1992).

3. METHODOLOGY

3.1 Filter Preparation

8 x 10 inch quartz fiber filters (Pallflex Membrane Filters – 2500QAT-UP), were used to sample both particle and gas phase nitrophenols found in the atmosphere. Before sampling, the filters were baked at 850 °C in a muffle furnace (Fischer Scientific, Model 550-58) for a period of 24 hours to remove any organic impurities. After baking, filters used for gas phase collection were coated with XAD-4 adsorbent before sampling, while filters used for collecting particle phase species were left untreated.

3.1.1 Coating 8” x 10” Quartz Fiber Filters

The coating procedure for quartz fiber filter with XAD was preformed based on the method developed by Lane (1999) and modified by Busca (2010) and Saccon et al., (2013). To coat 12 quartz fiber filters a slurry consisting of XAD-4 and hexane was prepared by placing 22 g of ground XAD-4 in a 2 L hexane (Saccon et al., 2013). The slurry was then placed in a thin layer chromatography (TLC) chamber. The TLC chamber containing the slurry was placed in a 5510R-DTH Bransonic Ultrasonic Cleaner and sonicated for 30 minutes. Twelve stainless steel meshes (folded in a pocket form) were used to hold one quartz fiber filter each. The filters were then coated by separately immersing each filter ten times in the slurry. Once all the filters had been coated ten times, the slurry was sonicated for another 30 minutes. To ensure an even and uniform coating the filters were immersed ten times each again into the slurry, but in the reverse order. The coated filters were then covered with clean aluminum foil and allowed to dry over night. The following day, each of the filters was rinsed with hexane in order to remove any excess XAD. The coated filters were then stored in a Pyrex glass dish and covered with a Teflon sheet and plastic lid until used for sampling.

3.2 Sampling and Analysis

3.2.1 Sampling Procedure

Two high volume air samplers (TE-6070-BL PM-10 Tisch Environmental, Inc.) were used to collect ambient samples. The samplers were equipped with an adapter containing 40 impactor jets, which collect particles larger than PM-2.5. Each sample was collected for 24 hours at a standard flow rate of 1.13 m^3 min^{-1} corresponding to a total sampled air volume of 1627 m^3. All sampling was conducted on the roof of Petrie Science and Engineering Building at York University. Following sampling filters were stored individually in a sealed mason jars in a freezer at -20 ºC until analysis.

3.2.2 Reagents and Standards

Acetonitrile (Chromasolv® Plus, ≥ 99.9% purity) and Acetonitrile (Pestanal) were purchased from Sigma-Aldrich. Acetone was purchased from Caledon Laboratories. Hexane and the derivatizing agent N,O-bis(trimethylsilyl)trifluroacetamide (BSTFA) were also purchased from Sigma-Aldric. Table 3.1 summarizes the concentration and level of purity for all the standard target nitrophenol compounds and the internal standards. These chemicals were of the highest purity commercially available and were used without any further purification. Primary stock solutions of each of these compounds were prepared by dissolving approximately 10 mg of each compound in 100 mL acetonitrile. A primary stock solution of the three alkanes ($C_{17}H_{36}$, $C_{18}H_{38}$, $C_{19}H_{40}$) was prepared by dissolving approximately 20 mg of each alkane in 100 mL acetonitrile. Secondary solutions containing the 5 target compounds (4-methyl-2-nitrophenol, 4-nitrophenol, 3-methyl-4-nitrophenol, 2-methyl-4-nitrophenol and 2,6-dimethyl-4-nitrophenol), the 3 internal standards (2-methylphenol, 2-methyl-3nitrophenol and 2-methyl-5nitrophenol) as well as the volumetric standards (mixture of the 3 alkanes) were prepared by diluting the primary solutions in acetonitrile for the purpose of obtaining calibration curves.

Table 3.1: *Concentration of primary stock solutions (ng µL^{-1}) made for the target nitrophenol compounds, internal standards and the volumetric standards.*

Compound	Standard Concentration
4-methyl-2-nitrophenol (≥99%, Sigma-Aldrich)	133
4-Nitrophenol (≥99%, Sigma-Aldrich)	100.5
3-methyl-4-nitrophenol (≥98%, Sigma-Aldrich)	103
2-methyl-4-nitrophenol (≥97%, Sigma-Aldrich)	108
2,6-dimethyl-4-nitrophenol (≥98%, Sigma-Aldrich)	101
2-methyl-3-nitrophenol (≥98%, Sigma-Aldrich)	103
2-methyl-5-nitrophenol (≥98%, Sigma-Aldrich)	106
4-methylphenol (≥99%, Sigma-Aldrich)	
2-methylphenol (≥99%, Sigma-Aldrich)	
Heptadecane, C_{17} (≥99%, Sigma-Aldrich)	228
Octadecane, C_{18} (≥99%, Sigma-Aldrich)	213
Nonadecane, C_{19} (≥99%, Sigma-Aldrich)	209

3.2.3 Extraction procedure:

The analytical scheme for filter analysis described here is based on the method developed by Moukhtar et al., 2011 and is organized in four steps such as filter extraction, HPLC sample clean up, solid phase extraction and analysis with GS-MS. A simplified diagram of this procedure is shown in Figure 3.1.

Following sample collection, an 8” x 10” atmospheric filter was cut up into 8 pieces and placed in a 120 mL amber glass jar. One of the pieces was then spiked with 40 µL each of 2-methyl-3-nitrophenol and 2-methyl-5-nitrophenol, which were the internal standards. The filter pieces were then fully immersed in approximately 20 mL of acetonitrile and mixed with a stirring rod. The jar containing the filter pieces was then placed in an ultrasonic bath (Bransonic Ultrasonic Cleaner, model 3310R-DTH) for 15 minutes. After sonication the solution was transferred using a pipette into a syringe equipped with a 0.25 µm-pore-diameter PTFE syringe filter (Chromatographic Specialties, Inc.) and the filtered extract was collected into a 250 mL round-bottom flask. This extraction step was repeated three more times and the filtered extracts were combined together. Using a rotary evaporator at 42-44 ºC the volume of the four extracts in the round-bottom flask was reduced to approximately 1 mL. The concentrated solution was then centrifuged for at least 10 minutes and transferred into a conical vial where its volume was further reduced under a soft stream of ultra-high pure nitrogen (Grade 5.0, > 99 %, Linde) and mechanical stirring to approximately 220 µL.

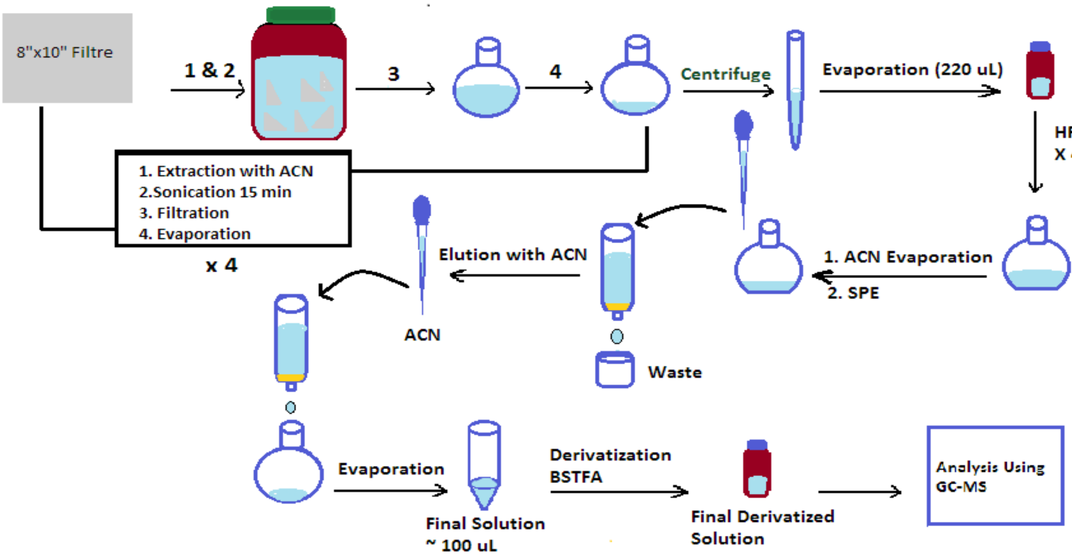


Figure 3.1: Schematic of the extraction procedure carried out for filter analysis.

3.2.4 Sample Clean up by HPLC

The concentrated 220 µL solution was transferred into a HPLC vial and injected into HPLC (Hewlett Packard 1050) as a purification procedure. The empty round-bottom flask was then rinsed twice with approximately 3 mL of acetonitrile, the solvent partially evaporated, and transferred into a conical vial. The remaining solutions from the three rinses were combined and further evaporated under a soft stream of nitrogen until the volume of the final solution was reduced to 220 µL. This solution was also injected and separated by HPLC.

The separation was performed using a Hewlett Packard 1050 HPLC instrument with a Supelco Supelcosil LC-18 column (5 µm particle size, L 25 cm, I.D. 4.6 mm), a 200 µL injection loop and a Variable Wavelength Detector. The wavelength was set to 320 nm and a solvent flow rate of 1.00 mL min^{-1} was used. A linear solvent gradient system was used, which was set up to start with 100 % Milli-Q water (water was deionized using a Milli-Q Gradient A10 Millipore system) and end after 30 minutes with 100% of acetonitrile. The eluent fraction at a time frame of 10 to 17 minutes was collected, which is the time that the target compounds and the internal standards were expected to elute according to the standards that were run before.

3.2.5 Solid Phase Extraction

The eluent collected from the HPLC contains approximately equal amount of water and acetonitrile. The volume of the collected solution was reduced using a rotary evaporator at room temperature, until half of the solution had evaporated. This step was done to remove acetonitrile from the sample.

In order to separate nitrophenols from water, the concentrated solution was acidified with 3 μL of dilute H_3PO_4 (pH ~ 1.8) and subjected to a solid phase extraction (SPE) using a 3 cc 60 mg Waters Oasis® HLB cartridge.

Prior to use of the SPE cartridge, it was first conditioned with 1 mL of acetonitrile followed by 1 mL of Milli-Q water. Once all of the Milli-Q water was eluted, the acidified solution was pipetted into the cartridge, to elute into waste. To rinse the empty flask, 3 mL of Milli-Q water was added and this solution was passed through the cartridge as well. Once all of the water solution has been completely eluted from the cartridge, the phenols were recovered from the SPE cartridge by filling the cartridge with acetonitrile and collecting it into a clean flank. The cartridge was refilled with acetonitrile and collected two more times. The eluted solution was then evaporated to approximately 1 mL using a rotary evaporator at 42-44 ºC, and transferred into a conical vial. The empty flask was rinsed twice using approximately 3 mL of acetonitrile, evaporating it and collecting it into the same conical vial as the first evaporation. The volume of the combined solution was further reduced to approximately 100 μL, using a soft stream of nitrogen.

3.2.6 Sample Analysis with GC-MS

To the 100 μL solution obtained after SPE, 20 μL of volumetric standard containing the 3 alkanes $C_{17}H_{36}$, $C_{18}H_{38}$ and $C_{19}H_{40}$ (~ 200 ng/ μL) was added. Half of this solution was saved in a glass vial for later use if needed and the other half was derivatized with 10 μL BSTFA and mixed for 5 minutes. The derivatization reaction of 3-methyl-4-nitrophenol with BSTFA is shown in Figure 3.2. The derivatized solution was then transferred into a glass vial. 1 μL this derivatized solution was then injected splitless into the GC-MS (Hewlett Packard 5890 Series II GC with Hewlett Packard 5972 Series Mass Selective Detector). Ultra high pure Helium (5.0 Grade, > 99 %, Linde) was used as a carrier gas at 2 mL min^{-1}. Chromatographic column was a DB-5MS column (60 m x 0.25 mm i.d. x 1 μm film thickness). This column was renewed once during this project and the compounds' retention times were shifted accordingly, as shown in Table 3.2.

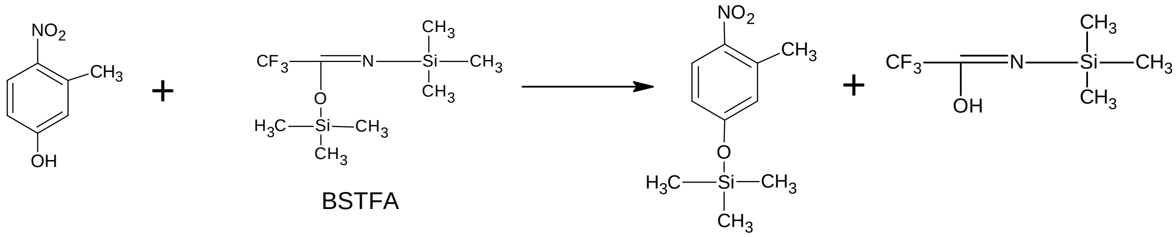


Figure 3.2: Derivatization reaction of 3-methyl-4-nitrophenol with BSTFA.

The GC temperature program that was used for sample and calibration analysis was set up to start at a temperature of 100 ºC. This temperature was initially held for 10 minutes following the splitless injection, then programmed to raise at 1ºC min^{-1} to 200 ºC, held at 200 ºC for a minute, then programmed to 280 ºC at 10 ºC min^{-1}and the final temperature, 280 ºC, was held for 6 minutes.

The MS detection system was operated at selective ion mode and samples were run twice to test for reproducibility. The target nitrophenol compounds in ambient samples were identified in accordance to their standard solutions by using their GC retention time and mass to charge ratios, m/z, shown in Table 3.2. The ambient masses for the target compounds were then obtained by using the response factors from the calibration curves and the sum of the peak areas for the same m/z used in the calibration (this calculations are shown in section 3.4.1).

***Table 3.2:** Approximate retention time of the target nitrophenol compounds, internal standards and volumetric standards along with their m/z.*

Compound	**GC-MS column (Sep-Oct) (min)**	**GC-MS column (Oct-April) (min)**	**m/z**
4-me-2-NP	57.27	73.75	225, 210, 165
4-NP	58.29	74.87	211, 196, 150
3-me-4-NP	64.10	80.98	225, 210, 165
2-me-4-NP	68.56	85.78	225, 210, 165
2,6-dime-4-NP	82.05	100.11	225, 210, 165
2-me-3-NP (IS)	58.56	75.15	225, 208, 165
2-me-5-NP (IS)	60.06	76.86	225, 210, 165
$C_{17}H_{36}$	77.72	97.40	85
$C_{18}H_{38}$	87.96	108.21	85
$C_{19}H_{40}$	97.75	115.45	85

3.3 Method Validation Tests

3.3.1 Blank Test:

Blank tests were performed on clean XAD coated filters. These filters were treated in the same way as the ambient filter samples. In other words they were extracted and analyzed in the same manner as described for the ambient samples (see sections 3.2.3 to 3.2.6). The blank tests were conducted to check for the presence of target nitrophenol compounds or any contamination that could exist on the clean XAD coated filters, at the same retention time as the target compound, which may interfere with the actual ambient concentrations.

3.3.2 Breakthrough Test

A total of three tests were conducted at different times using a high-volume air sampler at a standard flow rate of 1.13 m^3 min^{-1}, where two XAD coated filters were stacked in series and separated by a stainless steel mesh in between them. Sampling was conducted for a period of approximately 24 hours for all the three tests and the filters were extracted and analyzed as it is described in sections 3.2.3 to 3.2.6.

3.3.3 Parallel Filter Sampling Test

Two XAD coated filters were sampled in parallel using two high-volume air sampling units at a standard flow rate of 1.13 m^3 min^{-1} for approximately 24 hours. The two filters were then extracted and analyzed in the same manner described in sections 3.2.3 to 3.2.6. This test was conducted to determine the reproducibility of sampling two individual filters in parallel using two different high-volume sampling units. The reproducibility of the parallel sample collection can be checked by the closeness of the concentrations of each target compounds obtained from the two filters.

3.4 Ambient Nitrophenol Measurements

3.4.1 Sampling XAD and Quartz Fiber Filters in Parallel

XAD-coated quartz fiber filter was sampled in parallel to an uncoated quartz fiber filter using two separate high-volume sampling units at the standard flow rate of 1.13 m^3 min^{-1} for a period of 24 hours. Each filter was then stored, extracted and analyzed as described in sections 3.2.3 to 3.2.6. Sampling coated and uncoated filters in parallel was conducted to measure the separate gas to particle phase concentrations and the gas-particle partitioning of the target nitrophenols in the atmosphere.

To calculate the ambient mass of target nitrophenols on both coated and uncoated filters, the relative response (C_{rel}) for the target compounds with respect to each internal standard (2-me-3-NP and 2-me-5-NP) was measured first using known concentration mixtures of the internal standards and the target nitrophenol compounds. The relative response was calculated by:

$$C_{rel} = (PA_X / m_X) / (PA_{IS} / m_{IS}) \qquad (1)$$

Where, C_{rel} is the relative response of the GC-MS to the internal standard and the target compound, PA_X is the peak area of the target compound, m_X is the derivatized mass of target compound, PA_{IS} is the peak area of the internal standard and m_{IS} is the derivatized mass of the internal standard. This calculation was done for all target nitrophenols. For all measurements it was assumed that all factors such as the recovery, GC sensitivity and final sample volume, affect the peak area of both the internal standard and the target compounds in the same way. The precision of the method, expressed as the relative standard deviation of the target compounds' relative response factors was found to lie in the 5-10 % range.

The masses of the target nitrophenols are then calculated with respect to each internal standard, which were spiked onto the filters prior to extraction. Equation (2) was used to calculate the mass for the target nitrophenols.

$$m_{NP} = [(PA_{NP} * m_{IS}) / (C_{rel} * PA_{IS})] * (MW_{NP} / MW_{NPder}) \qquad (2)$$

Where, m_{NP} is mass of the target nitrophenol, PA_{NP} peak area of the target nitrophenol, PA_{IS} is the peak area of the spiked internal standard, m_{IS} is the mass of the internal standard spiked, MW_{NP} is the molecular weight of the target compound, and MW_{NPder} is the derivatized molecular weight of the target nitrophenol.

The Ambient concentration, for the target nitrophenols with respect to each internal standard was then calculated using equation (3).

$$C = (m_{NP} - \text{Blank}) / V_{air} \qquad (3)$$

Where, C is the ambient concentration of target compound, Blank is the filter blank value and V_{air} is the volume of total air sampled. The average concentrations obtained from the two internal standards were then used as the concentrations of the ambient target nitrophenols.

To monitor the overall extraction procedure and the GC performance, the recoveries of the two internal standards (2-me-3-NP and 2-me-5-NP), which were spiked onto the filters prior to extraction, were always measured. The thought behind this was that if the difference between the recoveries of these internal standards were consistent (lie in the 10-20% range), it would indicate that the recovery of the ambient target nitrophenols would behave the same way. To calculate the recoveries for the internal standards, the final volume of the filter extract, (V_f), was calculated first. (V_f) was determined using the volumetric standards (3 alkanes) mixture that was spiked into the final extract prior to injection into the GC, see equation (4).

$$V_f = (C_i \times V_i) / C_f \qquad (4)$$

Where, V_f is the final volume of the extract, C_i is the concentration of volumetric standards spiked, V_i is the volume of the 3 alkanes spiked into the final extract and C_f is the concentration of each alkane obtained from their peak areas over responses. V_f, for all three alkanes was calculated in this manner and the average of the three V_f was used as the final filter extract volume.

The recovery of the two internal standards (IS) was calculated in few steps. First, using equation (5) the theoretical mass of each of the spiked IS was calculated, then equation (6) was used to calculate the actual mass of each IS after the extraction procedures and finally equation (7) was used to calculate the percentage recovery yield for each IS.

$$m_{theor.} = C_{i\ (spiked)} \times V_{i\ (spiked)} \qquad (5)$$

Where m_{theor} is the theoretical mass, $C_{i\ (spiked)}$ is the initial concentration of the IS spiked, and $V_{i\ (spiked)}$ is the volume of the IS spiked on the filter.

$$m_{actual} = (C_{GC} \times V_f \times MW_{IS}) / MW_{IS\ der} \qquad (6)$$

Where m_{actual} is the actual mass of the IS recovered after extraction, C_{GC} is the derivatized IS concentration obtained from GC-MS (peak area / response), V_f is the volume of the final filter extract, MW_{IS} is the molecular weight of the IS and $MW_{IS\ der}$ is the derivatized molecular weight of the internal standard.

$$\%\ Recovery = (m_{actual} / m_{theor.}) * 100\% \qquad (7)$$

3.4.2 High-Volume Filter Sampling Method in Parallel to Denuder-Filter Method

Atmospheric samples, using XAD coated filter in one high-volume sampler and uncoated quartz filter on another sampler, were conducted in parallel to a denuder-filter method (acquired by C. Facca). The samples were collected at a flow rate of 1.13 $m^3\ min^{-1}$ on both high-volume samplers and at a flow rate of 0.0167 $m^3\ min^{-1}$ on the denuder-filter method for a period of approximately 24 hours.

4. RESULTS AND DISCUSSION

4.1 Summary of the Blank Tests

The results of the blank XAD coated filter analysis explained in section 3.3.1 are presented in Table 4.1 below. These results present some variability between the masses of the blanks that were conducted on December 12th and April 8th, but they are generally comparable to the average blank values obtained by Busca (2010). But the blank masses from the test obtained on February 26th are much higher than the other two tests as well as the blank masses obtained by Busca. This irregularity might be due to some systematic uncertainties and contamination associated with this particular test. In all three cases, however, a significantly higher mass was observed for 4-nitrophenol, which may be due to some contamination. Other group members in our laboratory also observed high blank value for this compound. This indicates that further investigation is required to determine a potential source of contamination. Table 4.2 presents detection limits (DLs). The upper DL values include the outlier (blank mass from Feb. 26th). While the other DL values calculated for each compound are based on only two blank tests and do not include the outlier. Although the reliability of this DL value is limited since it is based on only two data points, its similarity to the DL obtained by Busca (2010) for all compounds, except for 4-nitrophenol, can be used to justify this as a reasonable estimate of DLs.

Table 4.1: *Mass (ng) of three blank XAD coated filters conducted at different times in comparison to the average blank values obtained by Busca (2010).*

	Mass of Blank (ng)			
Compounds	**Dec. 12th 2012**	**Feb. 26th 2013**	**Apr. 08th 2013**	**Busca (2010)**
4-me-2-NP	2.1	87	5.2	4.5
4-NP	107	269	185	7.0
3-me-4-NP	2.4	102	4.8	3.9
2-me-4-NP	3.5	77	2.4	2.5
2,6-dime-4-NP	0.9	45	0.8	2.4

Table 4.2: *XAD coated filter detection limits (DL) in comparison to the average DL measured by Busca (2010). The calculations of DL as atmospheric concentrations are presented for a typical volume of air, 1627 m^3.*

	Detection Limits (ng m^{-3})		
Compounds	**Upper DL***	**DL****	**Busca (2010)**
4-me-2-NP	0.11	0.006	0.003
4-NP	0.26	0.191	0.005
3-me-4-NP	0.13	0.005	0.002
2-me-4-NP	0.10	0.003	0.002
2,6-dime-4-NP	0.06	0.001	0.001

* This DL calculation includes the outlier (Feb. 26th blank mass)

** This DL calculation is based on blank values from Dec.12th and Apr. 8th, it does not include the outlier (blank value from Feb. 26th).

4.2 Breakthrough Test for XAD Coated Quartz Filters

Busca (2010) in her master's thesis pointed out that the sampling efficiency of XAD coated filters in collecting ambient nitrophenols were low. Some method modifications were then made, by increasing the concentration of XAD on the coated filters (Saccon et. al. 2013). As a result some breakthrough tests were performed to check the sampling efficiency of these filters. The result of the breakthrough tests, which was explained in section 3.3.2, are summarized in Table 4.3. The average percentage of each compound collected on the top XAD coated filter, from the three tests are presented in Table 4.4.

Table 4.3: *Concentration of target nitrophenol compounds on the Top and Bottom XAD coated filters (ng m^{-3}) as well as the percentages captured on the Top XAD coated Filter.*

	Test 1			**Test 2**			**Test 3**		
	Aug. 8/12 - Aug 9/12 Sample Volume 1503 m^3			Sep. 12/12 – Sep. 13/12 Sample Volume 1672 m^3			Sep. 13/12 – Sep. 14/12 Sample Volume 1667 m^3		
Compounds	**Top**	**Bottom**	**% Top**	**Top**	**Bottom**	**% Top**	**Top**	**Bottom**	**% Top**
4-me-2-NP	0.81	0.07	91	0.93	0.20	79	0.30	0.07	77
4-NP	6.02	0.17	97	5.86	0.12	98	1.81	0.14	92
3-me-4-NP	0.32	0.05	84	0.34	0.01	98	0.15	0.01	91
2-me-4-NP	0.98	0.08	92	1.21	0.06	95	0.67	0.08	88
2,6-dime-4-NP	0.33	0.03	90	0.78	0.03	96	0.59	0.01	98

Table 4.4: *Average percentages of target compounds captured on the Top XAD coated filters from the 3 breakthrough tests.*

Compounds	**Average**	**STDEV**	**Error of mean**
4-me-2-NP	82	7.7	4.5
4-NP	96	3	1.7
3-me-4-NP	91	6.9	4
2-me-4-NP	92	3.4	2
2,6-dime-4-NP	95	4.5	2.6

The result from this test indicates a very high sampling efficiency for the XAD coated filters. As it was expected, higher concentrations of the target nitrophenols were collected on the top filter on all three tests, which were conducted on three separate days. As shown in Table 4.3, in all three cases a slightly higher breakthrough into the bottom XAD coated filter was observed for 4-methyl-2-nitrophenol. This result however is consistent with the high vapor pressure (11 Pa at 30ºC) associated with this compound. Also, based on previous studies done by Busca (2010) and Saccon, et. al. (2013) a general breakthrough of about 20% is expected for this compound.

4.3 Parallel Filter Test

The other method validation test that was performed in this project was to check for the similarity in concentrations of two filters sampled in parallel. This test was explained in section 3.3.3 and the results are presented in Figure 4.1.

The results presented in Figure 4.1, show that contrary to what was expected, the concentrations of the target compounds between the two XAD coated filters are not very similar. However it must be pointed out that the result shown in Figure 4.1 is based on a single test. Nevertheless the ratio of the concentration obtained from sampler A to sampler B is on average 0.64 ± 0.07 for all compounds and the concentrations using sampler B are constantly higher than those from sampler A (see Figure 4.1). Moreover, the recoveries of the internal standards for both measurements were within the expected range. This may indicate that the discrepancy in concentration between the two filters may be due to the uncertainty associated with the volume from the air sampler B, which is biased into the same direction for all compounds. The volume of sampler B is suspected since the flow rate on this sampler was always calibrated indirectly. The results may also be impacted by systematic errors and/or the existence of possible contaminations that may have interfered with the results. However, although there may have been differences in the concentrations obtained from the two filters, the limited number of the tests conducted renders it difficult to make a conclusion about the similarity of concentrations obtained from the two filters sampled in parallel. Conducting more tests in the future would certainly help provide more details and possibly explain this discrepancy in concentration values between the two filters.

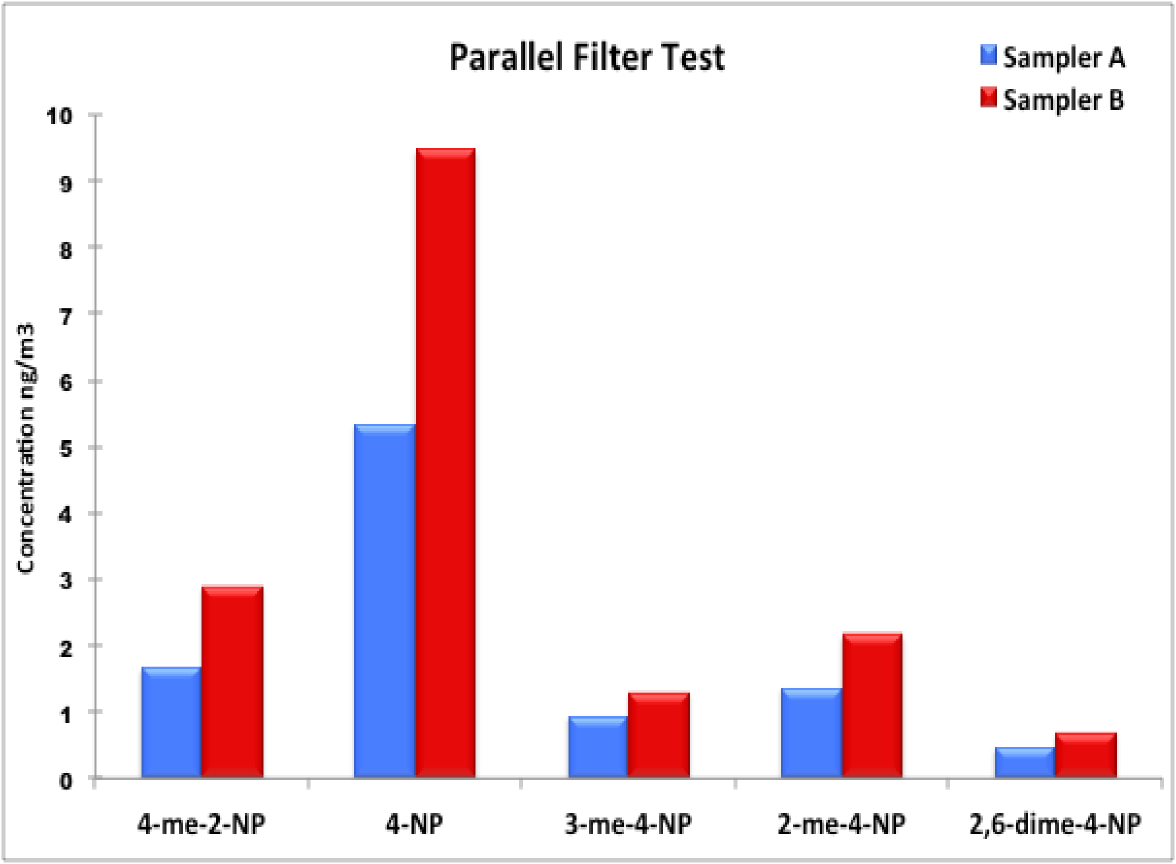


Figure 4.1: Comparison of target nitrophenol compounds' concentrations on two XAD coated filters sampled in parallel using two separate high-volume sampling units.

4.4 Concentrations and Partitioning Measurements of Nitrophenols in the Ambient Air

A total of ten parallel ambient samples (explained in section 3.4.1) were collected in this project and the results are presented in Table 4.5 below. Using these results, the average ambient concentrations of each target compounds in both gas and particle phases are calculated and summarized in Table 4.6. The average particle phase to total ratios of the nitrophenol compounds were also calculated from the individual parallel measurements shown in Table 4.5. The average particle to total ratios of each compound are grouped by vapor pressure, in decreasing order and are presented in Table 4.8. A plot depicting the correlation of particle/total ratios of nitrophenols with vapor pressure is presented in Figure 4.2.

Table 4.5: *Ambient concentration measurements (ng/m^3) of ten XAD coated and uncoated quartz filters and the percentage of each nitrophenol in particle phase, particle phase/Total= ((concentration on quartz filter / concentration on XAD coated filter) x 100%).*

	Test 1			**Test 2**		
	Oct. 11/12 - Oc. 12/12			Nov. 06/12 - Nov. 07/12		
Compounds	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particle/ Total) %**	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particle /Total) %**
4-me-2-NP	1.59	< DL	NA	0.21	< DL	NA
4-NP	1.65	0.48	29.1	1.26	0.50	39.9
3-me-4-NP	0.12	0.05	40.5	0.15	0.10	66.7
2-me-4-NP	0.36	0.10	26.5	0.31	0.13	41.0
2,6-dime-4-NP	0.13	0.01	4.6	0.15	0.01	9.3

	Test 3			**Test 4**		
	Nov. 14/12 - Nov. 15/12			Nov. 21/12 -Nov. 22/12		
Compounds	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particl e/Total) %**	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particle /Total) %**
4-me-2-NP	0.15	<DL	NA	<DL	<DL	NA
4-NP	1.68	0.31	18.2	3.58	0.86	24.1
3-me-4-NP	0.16	0.10	59.2	0.29	0.14	48.1
2-me-4-NP	0.36	0.14	38.4	1.08	0.16	14.4
2,6-dime-4-NP	0.21	0.01	6.2	0.26	0.02	6.1

	Test 5			**Test 6**		
	Nov. 27/12 - Nov. 28/12			Dec. 13/12 - Dec. 14/12		
Compounds	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particle/ Total) %**	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particle /Total) %**
4-me-2-NP	0.14	<DL	NA	1.86	<DL	NA
4-NP	2.15	1.71	79.6	2.60	0.92	35.3
3-me-4-NP	0.17	0.17	98.8	0.34	0.15	44.1
2-me-4-NP	0.26	0.17	64.6	0.62	0.16	26.1
2,6-dime-4-NP	0.10	0.02	22.5	0.29	0.02	6.9

Table 4.5: *Continued*

	Test 7			**Test 8**		
	Feb. 06/13 - Feb. 07/13			Feb. 12/13 - Feb. 13/13		
Compounds	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particle/ Total) %**	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particle /Total) %**
4-me-2-NP	3.16	<DL	NA	2.51	<DL	NA
4-NP	3.52	2.10	59.6	3.29	1.46	44.2
3-me-4-NP	0.75	0.76	100.7	0.43	0.29	68.8
2-me-4-NP	1.50	1.09	72.5	0.80	0.33	41.4
2,6-dime-4-NP	0.43	0.13	30.8	0.19	0.03	15.2

	Test 9			**Test 10**		
	Feb. 13/13 - Feb. 14/13			Feb. 28/13 - Feb. 29/13		
Compounds	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particle/ Total) %**	**XAD Coated Filter (ng/m^3)**	**Uncoated Filter (ng/m^3)**	**(Particle /Total) %**
4-me-2-NP	1.68	< DL	NA	1.05	< DL	NA
4-NP	8.41	2.40	28.5	2.53	1.35	53.5
3-me-4-NP	1.39	0.57	40.8	0.28	0.14	51.1
2-me-4-NP	2.20	0.75	34.2	0.77	0.25	31.7
2,6-dime-4-NP	0.77	0.07	8.5	0.32	0.02	6.9

Table 4.6: *Average of ambient concentration (ng/m^3) of gas and particle phase nitrophenol compounds obtained from the ten measurements shown in Table 4.5. The errors represent the stdev.*

Compounds	**Average gas phase (ng/m^3)**	**Average particle phase (ng/m^3)**
4-me-2-NP	1.49 ± 1.05	NA*
4-NP	1.86 ± 1.59	1.34 ± 0.71
3-me-4-NP	0.20 ± 0.19	0.28 ± 0.23
2-me-4-NP	0.50 ± 0.41	0.36 ± 0.33
2,6-dime-4-NP	0.25 ± 0.18	0.04 ± 0.04

* The concentration of this compound was always less than DL on the quartz filters as shown in Table 4.5.

The results shown in Table 4.5, presents that in all the samples collected in this project, 4-methyl-2-nitrophenol was always found on the XAD coated filters but not on the uncoated filters. This result is in agreement with what was expected, since this compound has one of the highest vapor pressures. The measurements reported by Cecinato (2005), shown in Table 4.7, also reported finding a high concentration of this compound in the gas phase. In this project on average a higher concentration of 3-methy-4-nitrophenol was found in the particle phase, which was expected based on its low vapor pressure. High concentration of this compound in the particle phase is also consistent with those from Cecinato (2005), who reported finding this compound mainly in the particle phase. However, as shown in Table 4.7, Cecinato (2005) also reported higher concentration of 4-nitrophenol and 2,6-dimethyl-4-nitrophenol on the particle phase, which was not observed in the present project. In the current study, on average both of these nitrophenol compounds were mainly found on the gas phase. Nevertheless, finding 2,6-dimethyl-4-nitrophenol predominantly in the gas phase was not expected since it has the lowest vapor pressure.

Although the ambient partitioning of some of target nitrophenols measured in this project were similar to those found by Cecinato (2005), the concentrations measured in this project however are much lower. One possible explanation for the higher concentration of these compounds reported by Cecinato is that the air of downtown Rome is more polluted than the air samples collected at York University in Toronto.

Table 4.7: *Average ambient concentration (ng/m^3) of gas and particle phase, and particle/total ratios of nitrophenol compounds measured by Cecinato (2005) in comparison to particle/total ratios measured in this project*

	Cecinato (2005)			**Current project**
Compounds	Gas phase	Particle phase	Particle/Total	Particle/Total
4-me-2-NP	6.9 ± 1.6	2.9 ± 0.8	30 %	NA*
4-NP	3.9 ± 1.7	17.8 ± 5.6	82 %	39 %
3-me-4-NP	2.2 ± 1.2	7.8 ± 2.6	78%	62 %
2-me-4-NP	**	**	**	41 %
2,6-dime-4-NP	2.0 ± 1.0	5.9 ± 2.9	75%	12 %

* 4-me-2-NP concentration on the uncoated filter was always less than detection limit.
** This compound was not searched for in Cencinato's work

The results from the ten parallel measurements also show that a significant amount of 2-methyl-4-nitrophenol was always collected on both coated and uncoated filters compared to its other two isomers, namely 3-methyl-4-nitrophenol and 4-methyl-2-nitrophenol. This finding is in agreement with what was expected from the proposed reaction pathway explained in section 2.2, where this compound was expected to be the more dominant isomer from the oxidation and subsequent nitration of toluene.

The atmospheric concentration of the target nitrophenol compounds summarized in Table 4.5, shows that higher concentrations of all target compounds were collected on the XAD coated filters as opposed to the uncoated filters. The difference between the coated and uncoated filters, which gives a first order estimate of gas phase nitrophenols, indicates higher concentration of the target nitrophenol compounds in the gas phase (see Table 4.6). This result is analogous to the parallel tests that were conducted by Busca (2010) for the same compounds. An increase in particle phase concentration was expected as a result of decrease in vapor pressure for these semi-volatile compounds as explained in section 2.1. However as seen in Figure 4.2 and the particle/total ratios shown in Table 4.8, not all target nitrophenols partition between their gas and particle phases according to their respective vapor pressures. Except for 4-methyl-2-nitrophenol with the highest vapor pressure (11 Pa at 30 ºC) that was mainly found in the gas phase, the other target nitrophenol compounds studied in this project did not show the expected increase in the particle phase as a result of decrease in the vapor pressure (see Figure 4.2). Nevertheless the experimental results from the ten parallel measurements are more or less the same, which means that the sampling method is reproducible. This therefore indicate that there must be some other factors other than the vapor pressure that affect the partitioning of nitrophenols between the two phases in the atmosphere. Although the nature of gas-particle partitioning of the nitrophenols studied for in this project remains unclear, the results obtained indicate that, for almost all compounds, higher concentrations are generally present in the gas phase. This does nevertheless support previous observations that the partitioning of nitrophenols favors the gas phase.

Table 4.8: *Average of the ten parallel tests shown in Table 4.5 to present the particle to total ratios of each nitrophenol compound along with their vapor pressures in decreasing order.*

Compounds	**Vapor Pressure (Pa)**	**Average (Particle /Total) %**	**STDEV %**
4-me-2-NP	1.11×10^{1} (at 30 ºC)	NA*	NA
4-NP	1.03×10^{-2} (at 30 ºC)	41	19
2-me-4-NP	8.69×10^{-3} (at 30 ºC)	39	18
3-me-4-NP	3.13×10^{-3} (at 30 ºC)	62	22
2,6-dime-4-NP	6.42×10^{-4} (at 30 ºC)	12	9

*No ratio is shown for this compound since its concentration on the quartz filter was always less than DL.

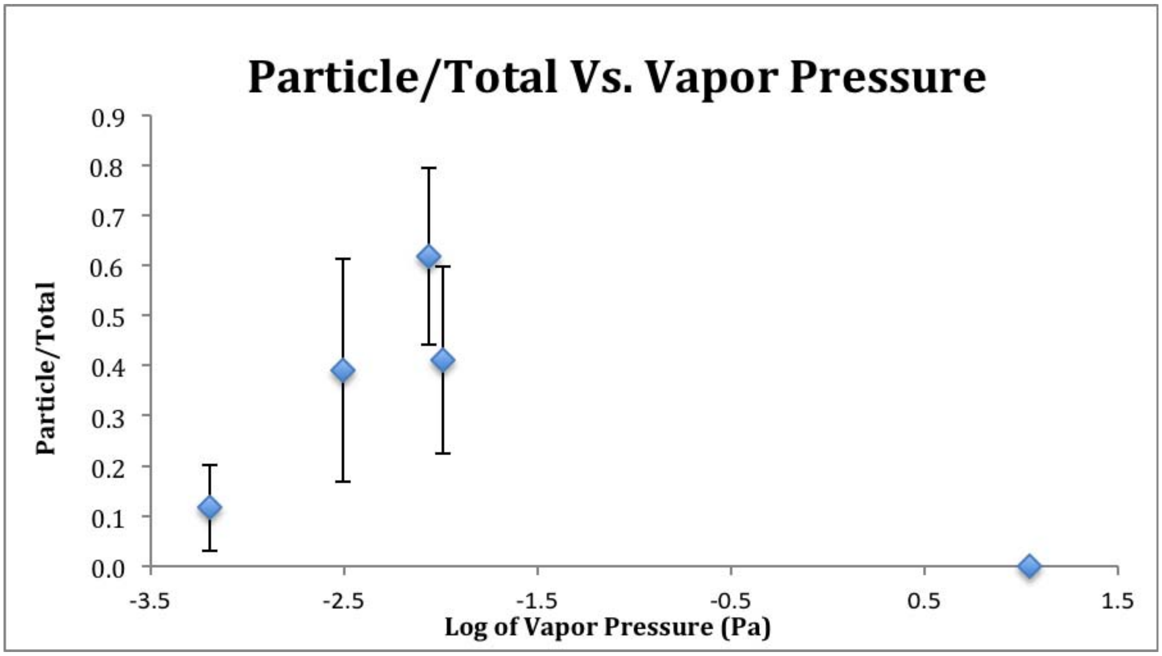


Figure 4.2: Illustrates the overall dependence of target nitrophenol partitioning with vapor pressure (Table 4.8). The average particle to total ratios of each nitrophenol compound from the ten parallel measurements shown in Table 4.5 are plotted against the log of vapor pressures. The error bars represent the standard deviations.

4.5 Comparison of Nitrophenols Phase Distributions between High-Volume Filter sampling and Denuder Sampling Methods

A total of four ambient samples were collected simultaneously using the respective high-volume and low volume sampling methods. The thought behind this test was to compare the partitioning of target nitrophenols between the gas and particle phases using two distinct methods. The results of this test are presented in Figure 4.5

As seen in Figure 4.5, the results from both methods indicate that higher percentages of target nitrophenol compounds appear to be present in the gas phase. This result further supports previous findings that the partitioning of nitrophenols favors the gas phase. Figure 4.5 also show that the gas phase percentages of the target nitrophenols from the low volume sampling method are more or less within the standard deviation of the high-volume sampling method. However, overall the gas phase concentration obtained from the denuder-filter method (low-volume) seems to be higher for some compounds compared to those found using the high-volume sampling method. The discrepancy observed between the two methods related to the partitioning of the nitrophenols could perhaps be attributed to the different sampling efficiency of the two methods. As discussed in section 4.3, a possible reason for lower concentration of gas phase nitrophenol compounds using high-volume sampling method could be due to the uncertainty in the volume of sampler B, which may have biased the ambient concentrations obtained using this method. For example, given that quartz filters were always sampled on air sampler B, the bias associated with the volume of this sampler may have resulted in an increase in the mass of particulate matter on the quartz filters. This might explain the comparatively lower concentration of gas phase nitrophenol compounds obtained from the high-volume sampling method. Moreover, sampling artifacts such as “blow-on” might also be a possible explanation for the relatively lower gas phase concentration of nitrophenols obtained from the high-volume sampling method compared to those from the denuder method. “Blow-on” or positive artifacts result in an overestimation of the particle phase semi-volatile compounds, since some gas phase semi-volatile compounds can be adsorbed onto the surface of the particle phase species that are initially trapped on the quartz filters. Consequently this can result in relatively lower concentrations of gas phase nitrophenols in the case of high-volume sampling method.

That said, the lower gas phase concentrations in the case of the high-volume filtering method might not be due to the sampling efficiency of the XAD coated filter. In fact, the breakthrough tests presented in section 4.2 showed that sampling efficiency of XAD coated filters were consistently in the range of 90%; this high percentage all but eliminates the sampling efficiency of XAD coated filters as a major source of error for the lower gas phase concentration in the case of the high-volume sampling method. Nevertheless the discrepancy in the gas phase concentration between the two methods might be due to some systematic error and/or a possible contamination that may have interfered with the results in both methods. Moreover, it is important to emphasize that the results presented here are based on a limited number of tests and further analysis may improve our understanding of the partitioning of these nitrophenols in the atmosphere.

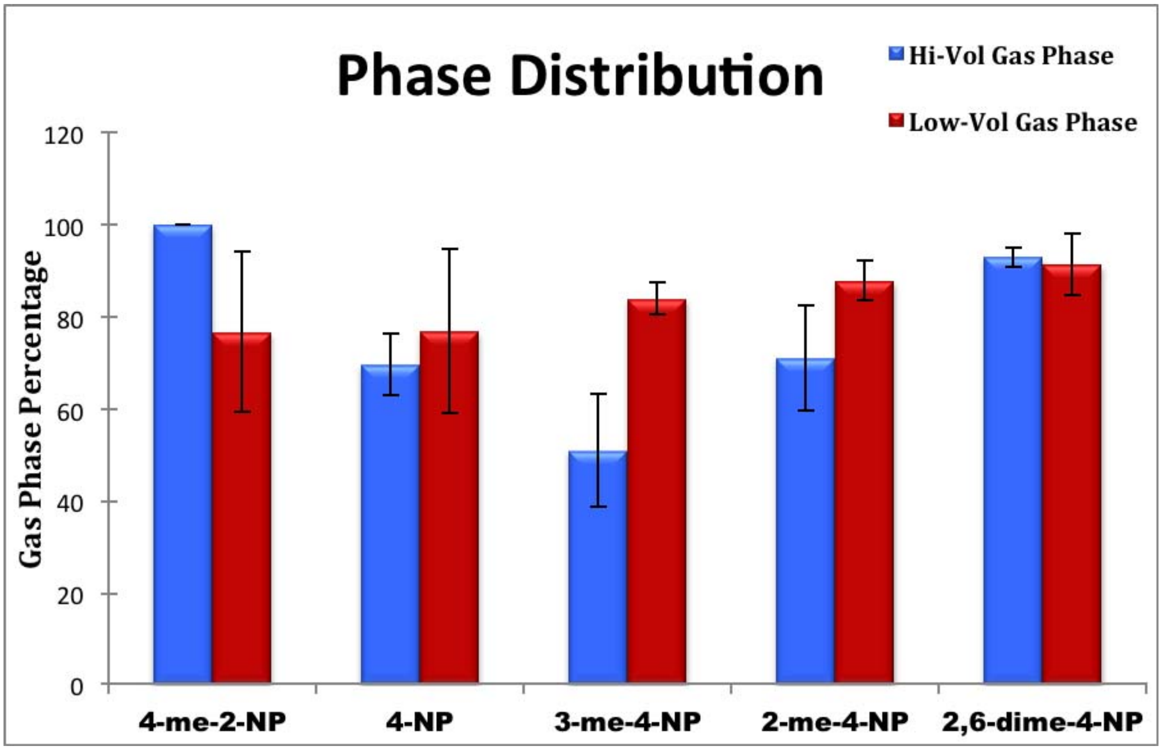


Figure 4.5: Comparison of the average percentage of the gas phase nitrophenols between the High-volume filter sampling and the denuder-filter methods (acquired by Facca). The average gas phase percentages are obtained from four sampling events where the two methods were sampled in parallel. Gas phase = (mass on XAD filter – mass on quartz filter)/ mass on XAD) x 100 %. The error bars represent the standard deviations

4.6 The Impact of Temperature on the Distribution of Nitrophenols

It was hypothesized that the ambient temperature might affect the partitioning of the nitrophenols between the gas and particle phases. To better understand the impact of temperature on the distribution of nitrophenols between these two phases, the total (gas and particle phases) concentration as well as the particle/total ratios of target nitrophenol compounds as a function of temperature was studied.

Figure 4.3 presents the ambient concentrations of total (gas and particle) nitrophenol compounds as a function of temperature. Based on the results presented in Figure 4.3, there is no clear dependence between the concentrations of total nitrophenol compounds and the ambient temperature. However it should be noted that the temperature range is not large, primarily due to the samples having been taken mainly in the fall of 2012 and less in the winter of 2013. Thus, spring and summer samplings, which would provide a considerably larger temperature range, are needed to better understand this correlation.

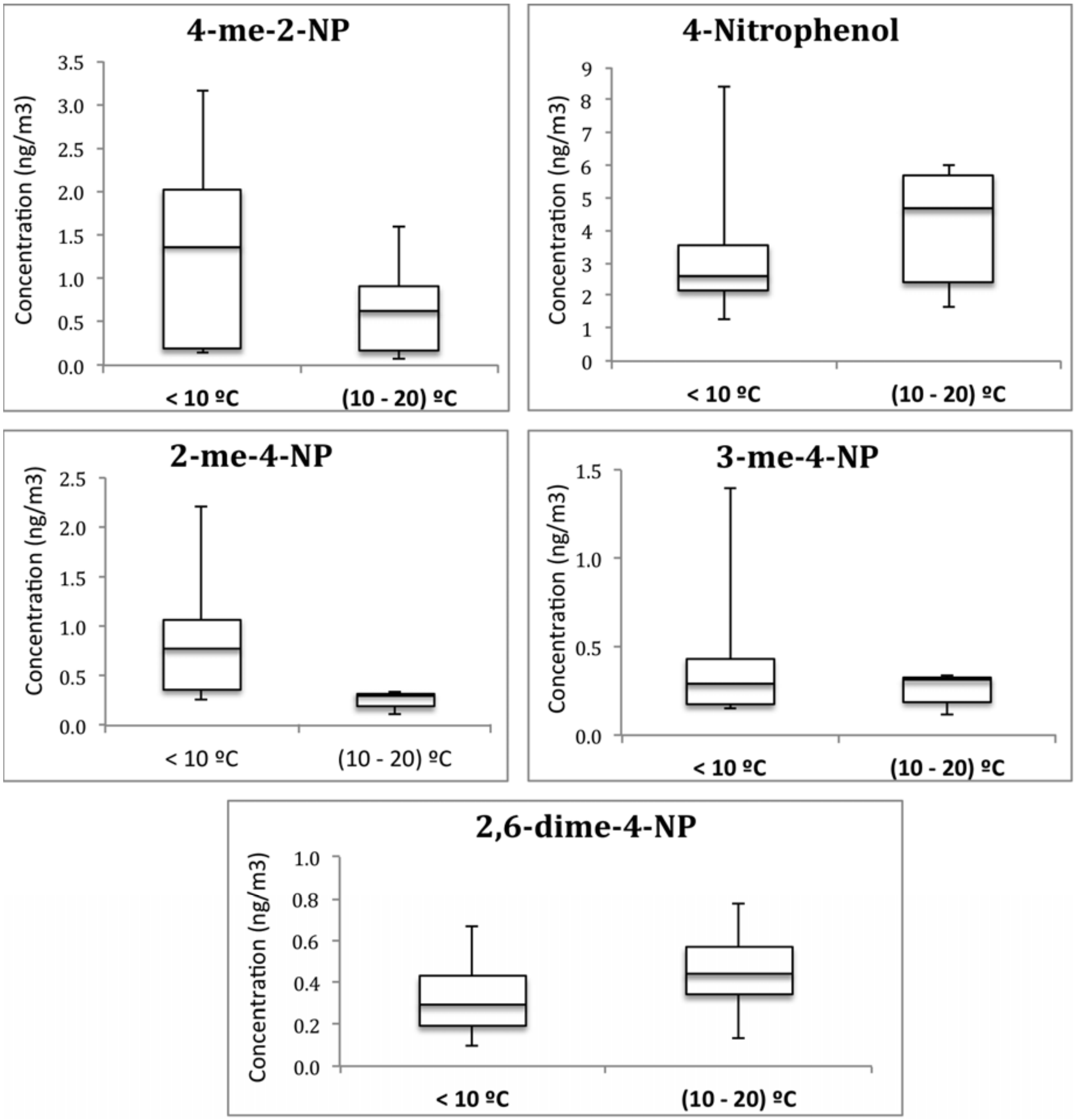


Figure 4.3: Illustrates the average concentrations of total (gas and particle phase) nitrophenol compounds (ng/m^3) as a function of maximum daily temperature (ºC). The average concentrations are obtained from a total of 15 XAD coated filters. In each graph 9 data points were used for temperature group less than 10 ºC and 6 data points were used for temperature group 10-20 ºC.
The small horizontal lines extending above and below the boxes show the maximum and minimum concentrations, respectively. The bottom line of each box represents the 25 percentile and the top line of each box represents the 75 percentile. The lines inside each box represent the median.

The results presented in Figure 4.4 show the particle/total ratios as a function of temperature for each target nitrophenol compounds. Clearly the number of samples as well as the temperature range obtained during this project was insufficient to elucidate the impact of ambient temperature on distribution of nitrophenol compounds between the two phases. However a general trend can be observed. As seen in Figure 4.4, although the dependence is not very strong, the particle/total ratios are higher at lower temperature for all target nitrophenol compounds studied in this project. This correlation may indicate that particle phase nitrophenol compounds are favored at lower temperatures. Nevertheless due to the limited number of samples and small temperature range, the impact of the temperature on the distribution of the target nitrophenols are not as clear as expected. There also might be some other meteorological factors such as the variety of air masses or changes in wind directions, which may impact the temperature, and, by extension, the distribution of nitrophenols in the atmosphere.

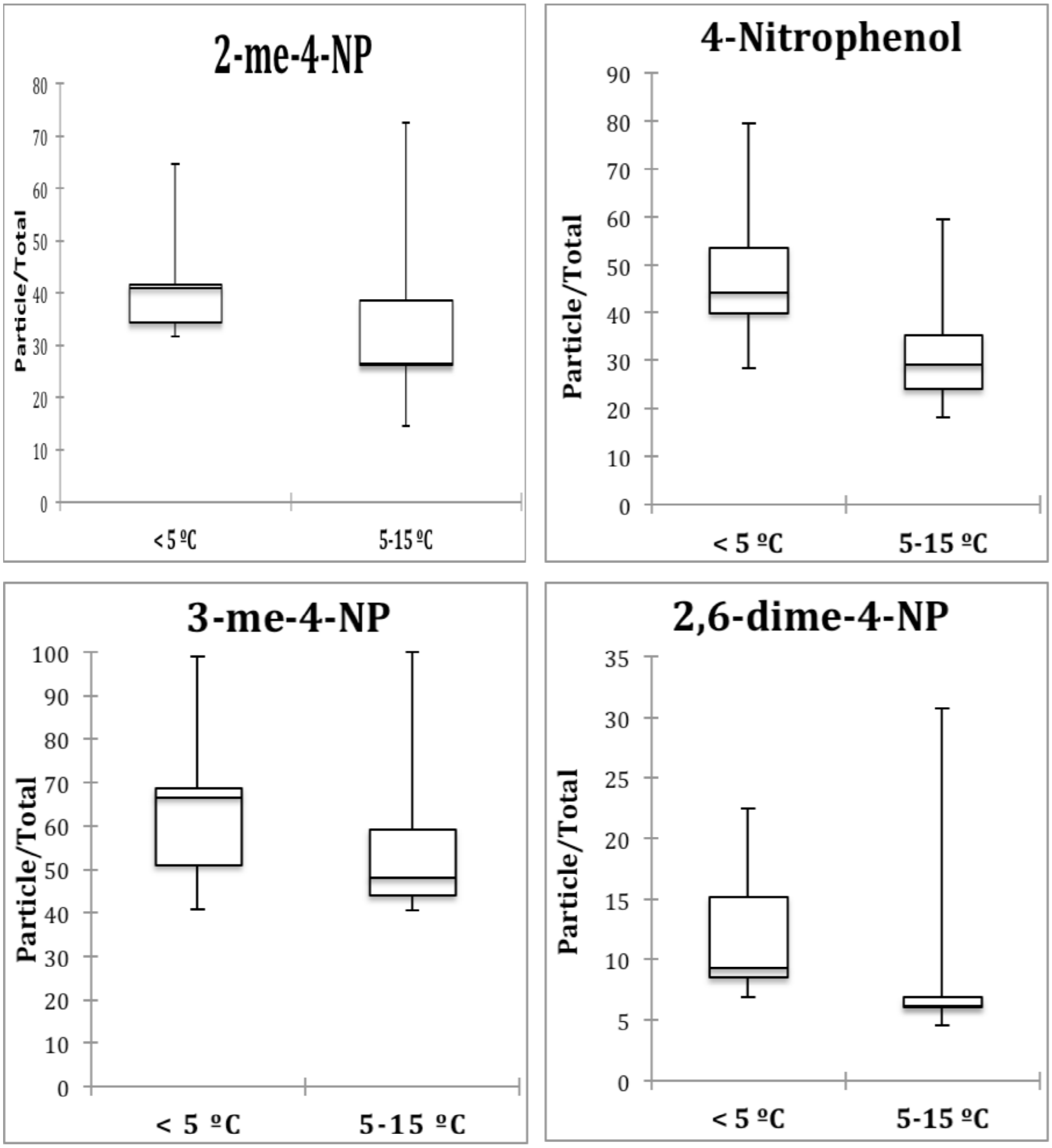


Figure 4.4: Shows the average of particle/total ratios of nitrophenol compounds from ten ambient measurements as a function of maximum daily temperature (ºC). The particle/total ratios for each compound are calculated from each individual measurement shown in Table 4.5 and their averages are plotted against temperature. In each graph 5 data points were used for each temperature group.
The small horizontal lines extending above and below the boxes show the maximum and minimum concentrations, respectively. The bottom line of each box represents the 25% confidence limits and the top line of each box represents the 75% confidence limits. The lines inside each box represent the median

5. CONCLUSION AND FUTURE WORK

The main objective of this research project was to study the ambient concentrations as well as the distribution of nitrophenols in the gas and particle phases using a method recently developed by Busca (2010) and modified by Saccon et. al. (2013). Although this new method was demonstrated to be suitable to measure the separate gas and particle phases of nitrophenols in the atmosphere, some modifications have been made to improve the efficiency of XAD coated filters in sampling ambient gas phase nitrophenols (Saccon et. al. 2013). The breakthrough tests performed in this project indicated an overall sampling efficiency of larger than 90% for the target nitrophenol compounds as a result of the recent method modifications.

The preliminary ambient nitrophenol measurements obtained in this project, when compared with some literature work, indicate that the high-volume filter sampling method has the potential of being used as a sampling technique for measuring the separate gas and particle phases of semi-volatile organic compounds such as nitrophenols in the atmosphere. Nevertheless, there is still some work that needs to be done in order to improve the sampling efficiency of this method. For example, the contamination problems must become more controlled. The few blank tests that were performed in this study showed higher blank values for 4-nitrophenol than previously observed in Busca's study, indicating the presence of some contamination. This shows that further investigation is needed in order to determine the source of this contamination. One potential solution may be to perform diagnostic tests on some of the major steps of the extraction procedure. One such test could be to run the extract from a clean XAD coated filter into the GC-MS before the HPLC cleanup step to test whether or not this step contributes to the contamination. Diagnostic tests on some of the components of the extraction procedure such as the solvent and the derivatizing agent used may also be useful in finding the source of contamination. Although there is variability in the blank values for nitrophenol compounds due to the one outlying high blank value, looking at both DLs the one including the outlier and the one without the outlier, they do not seem to effect the ambient concentration measurements of these compounds in any significant way.

The parallel filter test performed in this project pointed to some potential sources of error in the simultaneous sampling of coated and uncoated filters, which may have resulted in some bias in the concentration as well as the partitioning measurement of nitrophenols in the atmosphere. This uncertainty may be attributed to the indirect calibration of the flow rate in the case of sampler B, as explained in section 4.3. But more parallel tests need to be performed to provide more detail about the discrepancy in the concentration of filters sampled parallel to one another.

Another significant outcome observed in this research project was that the distribution of the semi-volatile organic compounds such as the nitrophenols studied in this project did not necessarily depend on their vapor pressure. Thus, factors affecting the partitioning of these compounds in the atmosphere still remain unclear. It may be speculated that other factors such as the temperature, humidity and the concentration of particulate matter in the atmosphere may be responsible for the partitioning of nitrophenols in the atmosphere, and these relationship can be investigated in future to gain more knowledge about the partitioning of these nitrophenols in the atmosphere.

The impact of the temperature on the partitioning of the nitrophenols was also studied in this project. Although a weak dependence between the particle/total ratio and ambient temperature was observed, the statistical significance of this correlation however remains unclear due to the limited number of tests as well as the small temperature range obtained in this project. Conducting more samples during the spring and summer will help in substantiating the data on the temperature range, which may be helpful in determining to which extent the ambient temperature may impact the distribution of the nitrophenols between the two phases.

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