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Analysis of NO\textsubscript{x} Levels in Ambient Air Using Passive Sampling

A Senior Thesis Submitted to:  
The Department of Math-Science  
College of Arts & Sciences

By

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Concordia University  
Portland, OR  
April, 2018
Table of Contents

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title Page</td>
<td>1</td>
</tr>
<tr>
<td>Table of Contents</td>
<td>2</td>
</tr>
<tr>
<td>Acknowledgements</td>
<td>3</td>
</tr>
<tr>
<td>Abstract</td>
<td>4</td>
</tr>
<tr>
<td>Introduction</td>
<td>5</td>
</tr>
<tr>
<td>Experimental</td>
<td>12</td>
</tr>
<tr>
<td>- Undergraduate laboratory procedure</td>
<td>12</td>
</tr>
<tr>
<td>- Field experiment procedure</td>
<td>16</td>
</tr>
<tr>
<td>Results</td>
<td>18</td>
</tr>
<tr>
<td>- Undergraduate laboratory results</td>
<td>18</td>
</tr>
<tr>
<td>- Field experiment results</td>
<td>19</td>
</tr>
<tr>
<td>Discussion</td>
<td>23</td>
</tr>
<tr>
<td>- Undergraduate laboratory discussion</td>
<td>23</td>
</tr>
<tr>
<td>- Field experiment discussion</td>
<td>26</td>
</tr>
<tr>
<td>Conclusion</td>
<td>31</td>
</tr>
<tr>
<td>Supplemental Lab report</td>
<td>32</td>
</tr>
<tr>
<td>References</td>
<td>43</td>
</tr>
</tbody>
</table>
Acknowledgements

The many thanks I owe are far too numerous to capture on this one page. I am so grateful for the constant support that I have received over the past four years. The work on this thesis is due to a large collaboration of efforts by people who have shown me what it truly means to be an academic and a scientist.

Foremost, I would like to thank my advisor and mentor, Dr. Matt Wise. The time and work he has put into this thesis, along with me as a student is irreparable. I am so thankful for the many lessons, opportunities, experiences, and laughs he has afforded me over the past four years. Many thanks are also owed to my other committee members, Dr. Michael Godsey and Dr. Sergei Polozov whose feedback, ideas, and proposals helped shape this work into its final form. I am immensely thankful for each of my professors at Concordia University – Portland. My undergraduate experience has been a constant period of growth and learning due to their expertise and involvement.

I owe thanks to Dr. Linda George, Dr. Jacinda Mainord, Sara Brunk and the Center for Climate Change and Aerosol Research at Portland State University for giving me the opportunity to join this project and learn so much. It is because of them that this work was performed. Words cannot express the growth I encountered during the conduction of this research. Thus, I am immensely grateful for their vital involvement in this project.

Finally, I must thank my parents, Kurt and Theresa, who pushed me from the start to challenge myself and to never settle. I need also to thank Nina, for being by my side through every experience in the past four years and yet never faltering in her support for me.
Abstract

Nitrogen oxides (NO\textsubscript{x}) are gas phase precursors that can lead to excess tropospheric ozone (O\textsubscript{3}). These pollutants are detrimental to human health at concentrations in ambient air. Measurement of these pollutants is generally performed by active sampling. However, this leaves for costly procedures and sparse monitoring networks. Passive sampling is a cost-efficient technique that allows for greater dispersion of sampling networks. In this study, a passive sampling technique developed by Ogawa & CO., USA, Inc. is utilized to study levels of NO\textsubscript{x} on the Concordia University campus in an undergraduate laboratory setting. The same technique is also employed in a field study in collaboration with the Oregon Department of Environmental Quality. Hermiston, OR is a rural town in the Columbia River Gorge that has experienced elevated O\textsubscript{3} precursor levels, such as NO\textsubscript{x}, in previous years. The undergraduate laboratory resulted in a better understanding of critical elements of chemistry vital to the major itself. The field experiment results indicated concentrated NO\textsubscript{x} due to complicated emissions, topographical, and meteorological patterns. This thesis demonstrates the viability of monitoring NO\textsubscript{x} in ambient air in a research setting, as well as an educational setting.
Introduction

This thesis was performed in two separate segments. The first part was conducted at Concordia University – Portland. This part involves writing an undergraduate laboratory experiment that allows for students to test air quality on their campus. The second part of this thesis is a novel scientific study using the same experimental techniques as the undergraduate laboratory. This research was conducted at Portland State University under Dr. Linda George as a part of a grant funded by the National Science Foundation (NSF).

The atmosphere is composed of 4 layers (Figure 1), each of which has a unique chemical makeup separated due to temperature inversions. Ozone (O$_3$) is commonly thought of as being an essential layer in the stratosphere as it absorbs ultraviolet (UV) light. The O$_3$ in the stratospheric layer is formed via photolysis of molecular oxygen, in a process commonly known as the Chapman cycle (Reaction scheme 1). O$_3$ is beneficial to the earth because of the protection it provides from UV light. In recent years, depletion of the stratospheric O$_3$ layer has become an issue of raised awareness. However, when excess O$_3$ is observed in the troposphere, a lower layer of the atmosphere, the effects can be detrimental.

Figure 1: Layers of the atmosphere adapted from Seinfeld and Pandis, 2016.
Acute exposure to excess tropospheric O\textsubscript{3} has been linked to alterations in lung capacity and air flow resistance, epithelial permeability, and difficulty in overcoming bronchoactive challenges (Lippman, 1989). In addition to this, long-term exposure to O\textsubscript{3} is linked to increases in respiratory diseases and discomfort, especially affecting those suffering from asthma (Ebi, McGregor, 2008).

Increased O\textsubscript{3} is formed through photochemical reactions involving volatile organic compounds (VOC’s) (e.g. diesel exhaust), and nitrogen oxides (NO\textsubscript{x}), which is the combination of nitrogen monoxide (NO) and nitrogen dioxide (NO\textsubscript{2}) (Figure 2). NO\textsubscript{x} is emitted into the atmosphere via anthropogenic sources such as combustion engines. Photolysis of O\textsubscript{3} with UV radiation (hv) forms hydroxyl radicals, which react with various gas phase species in the troposphere. The majority of the hydroxyl radicals originate from water vapor already present in the air (Seinfeld and Pandis, 2016). As mentioned before, the photodissociation of NO\textsubscript{2} is a major contributor to the formation of tropospheric O\textsubscript{3}. VOC’s play an essential role in the formation of tropospheric O\textsubscript{3} as they oxidize NO. For example, the photooxidation of methanol, a common VOC used as an alternative fuel, is
an example in which VOC’s are precursors to O₃. VOC’s often produce excess hydroxyl radicals, which lead to excess O₃. It may also be noted that the result of the hydroxyl radical with NO₂ is nitric acid (HNO₃), a co-pollutant of O₃ and chemical agent of acid rain. The cyclic nature of these reactions is interfered with when excess precursors are introduced to the system. Increasing levels of NOₓ and VOC’s present the possibility for excess formation of O₃. Therefore, it is important to have a reliable analytical technique to measure NOₓ and VOC concentrations in ambient air.

Gas-phase atmospheric species can be sampled using various passive sampling techniques. Passive sampling, in the context of air quality measurements, is a method that does not require a vacuum pump to pull air through the sampling device. Rather, the pollutant being measured is collected within the sampling system as air naturally flows through it. This technique provides a time averaged, spatial analysis of air quality. One of the most popular and affordable techniques for passive sampling is the technique developed by Ogawa & Co., USA, Inc.

This thesis is broken up into two parts. The first is an undergraduate laboratory study that analyzes nitrogen oxide (NOₓ) levels using a standard passive air sampling technique (Ogawa & Co., USA, Inc., 1997) and UV-Vis spectroscopy. UV-Vis spectroscopy is an analytical technique many first-year chemistry students do not get the opportunity to use. The physical setup utilized for UV-Vis spectroscopy is generally composed of three pieces of equipment: a UV-Vis light source, a cuvette to hold an aqueous solution of the analyte, and a detector (Figure 3). Some analytes absorb energy
in the visible range of the electromagnetic spectrum. It is the absorption of light in the visible range that gives the solution (due to the dissolved molecules) their perceived color.

The UV-Vis spectroscopic technique utilizes the absorption of light to determine the concentration of an analyte in solution. The more light the solution absorbs (e.g. the more intense the color of the solution), the higher the analyte concentration. Absorbance is related to analyte concentration using the Beer-Lambert Law (Equation 1)

\[ A = \varepsilon \cdot b \cdot c \quad \text{Equation 1} \]

where \( A \) is the absorbance of the analyte, \( \varepsilon \) is the absorptivity of the analyte (\( \text{L} \cdot \text{g}^{-1} \cdot \text{cm}^{-1} \)), \( b \) is the length of the light path (cm) and \( c \) is the concentration of the analyte in solution (\( \text{g} \cdot \text{L}^{-1} \)). It is important to note absorbance has no units.

In this experiment gas-phase NO\(_x\) is collected using passive samplers. In order to utilize UV-Vis spectroscopy to determine the amount of NO\(_x\) in the atmosphere, certain tasks must be accomplished. The first task is to collect the samplers from the outdoor locations and quantitatively dissolve the collected NO\(_x\) into water. Unfortunately, merely dissolving NO\(_x\) in water does not result in a colored solution. Therefore, the aqueous NO\(_x\) solution is combined with chemical reagents to produce a color (pink). Although the absorbance of the colored NO\(_x\) solutions can be determined using the spectrophotometer, unknown atmospheric concentrations cannot be determined until the spectrophotometer is.
calibrated with nitrite (NO$_2$) solutions of known concentrations. A calibration curve is constructed by creating nitrite solutions (by dissolving a known quantity of solid sodium nitrite in water), reacting the solutions with a color-producing reagent and plotting the absorbance of each solution versus nitrite concentration (Figure 4).

Typically, universities have several varieties of UV-Vis spectrophotometers. One type of handheld spectrophotometer, manufactured by the Vernier company, is relatively inexpensive (< $500). Other types of spectrophotometers include desktop versions that cost substantially more. In the laboratory experiment described here, one half of the experiments are performed using a Vernier Spectrovis-Plus Spectrophotometer controlled with a Vernier Labquest 2. The other half use a WPA Biowave S2100 diode array spectrophotometer. The spectrophotometers are obviously different, and a calibration curve must be constructed for both. After the calibration curves are created, ambient NO$_x$ concentrations can be determined and the results between the instruments compared. The experiments can elucidate the cost effectiveness of different spectrophotometers by comparing their limit of detection (LOD). In order to assure measured values of ambient NO$_x$ values, LOD for each spectrophotometer must be calculated. The learning outcomes of the experiment are as follows:
(1) Gain experience with analytical techniques used for air quality analysis.

(2) Provide an opportunity to use UV-Vis spectroscopy and create calibration curves

(3) Determine the relationship between LOD and cost of analytical equipment

(4) Provide quantitative evidence of the air quality on an urban college campus

(5) Allow collaboration to reach a sample size with which to interpret data to statistical significance

The second part of this thesis involves the application of the same passive sampling/UV-Vis technique in a field mission. This research was conducted at Portland State University in coalition with the Oregon Department of Environmental Quality (DEQ) in hopes of determining the source of elevated O\(_3\) and NO\(_x\) levels in the surrounding areas of a rural town in Oregon. The field mission used the same sampling techniques as the laboratory experiment but with a greater sample size.

Hermiston (population 17,707) is a rural town in Oregon (latitude and longitude 45.828604, -119.259077) located in the Columbia River Gorge (CRG) basin. Sites containing active samplers for O\(_3\) by the Oregon DEQ during peak ozone season (2007-present) in Hermiston revealed O\(_3\) levels approaching non-attainment standards set by the Environmental Protection Agency (EPA). The EPA’s standard for non-attainment ranges from marginal (86ppb) to extreme (175ppb) within an eight-hour window (EPA, 2008). The CRG is a large, winding basin featuring the Columbia River. It contains steep elevation changes and diverse vegetation (Figure 5). The CRG experiences seasonal bimodal wind conditions – westerly winds in the summer and easterly winds in the
winter. With the steep canyons of the CRG, the CRG acts as a natural wind tunnel and serves as a wind funnel for the transportation of pollutants to the region.

The Portland-Vancouver metropolitan area, located on the western end of the CRG, is noted as a possible contributor for the summertime Hermiston O₃ levels, as studies indicate that the CRG may transport O₃ precursors (e.g. nitrogen oxides and VOC’s) under appropriate meteorological circumstances such as: high levels of sunlight, westerly winds, and warm weather (Green et al., 2006). The elevated levels of O₃ in Hermiston are currently not well understood and further study is required to identify major contributors to O₃ precursors in this area.

In rural areas where O₃ measurements may not be available, modeling is relied upon in order to understand variations in O₃ concentrations. Currently, the Oregon DEQ has one station in Hermiston, OR that actively samples for O₃ in the summer months using data loggers and nephelometers, among other active sampling devices. However, O₃ modeling can be increasingly difficult when complex meteorological conditions and topography are present, such as in the CRG basin (Barna et al, 2001). In addition, there may be limited knowledge of past emission inventories for roadways that are not electronically monitored and for small area sources. Thus, making a true comparative verification of the model is difficult for these sparsely monitored areas.

The Pacific Northwest Regional monitoring has been led by Washington State University's AIRPACT-5 airshed model (http://lar.wsu.edu/airpact/). To date, this model has not been able to predict the observed elevated O₃ concentrations in Hermiston. The
underprediction of modeled O₃ suggests that precursor emissions (NOₓ and VOCs) are not being adequately represented. Due to the remote location and the large area of impact, installation of numerous active monitoring stations for NOₓ across the landscape of interest would be cost-prohibitive. The goals of this project are to: provide cost-effective measurements of NOₓ across a relatively large region (4400 square kilometers), to assess potential sources of nitrogen oxide precursors and compare measured values to model predictions to aid in model improvement.

Passive sampling is a technique that can be used for accurate time-averaged measurements of pollutants in the absence of an active monitoring network. Passive sampling for NOₓ is a cost-efficient method for collecting 7-14-day averages of pollutants and provides higher spatial resolution than active sampling (Salem et al. 2009) while providing a strong comparison with active sampling (Rao et al. 2014). This study utilizes passive sampling for NOₓ over four deployments. Passive sampling measurements are investigated and mapped in conjunction with wind trajectories from HYSPLIT and compared to NOₓ point sources from the 2011 National Emissions Inventory data to understand potential O₃ precursors in this region. NOₓ passive sampling data is also be compared to AIRPACT-5 in order to identify the areas with elevated O₃ precursors that were not accounted for in the airshed model.

Experimental

Undergraduate laboratory procedure

The undergraduate laboratory experiment was performed over a two-week time period in a general chemistry laboratory section comprised of twenty-three students. The laboratory section at Concordia University met once a week for two hours. Therefore,
each student spent four hours performing the experiment. During the first week, the
students were separated into groups (not exceeding four students). The samplers, each
containing one NO\textsubscript{x} and one NO\textsubscript{2} collection pad, were pre-assembled by teaching
assistants (TAs). However, the samplers can be assembled by students if there is no time
consideration, or the students are experienced (e.g., in an upper division analytical
chemistry course). The passive sampler consists of seven parts (Figure 6):

1. Chamber
2. Solid pad
3. Pad retaining screen
4. Stainless steel screen
5. NO\textsubscript{2}/NO\textsubscript{x} filter pad
6. Stainless steel screen
7. Diffuser endcap

**Figure 6**: Disassembled passive sampler with labeled components.

The preparation of the reagents described below cannot be performed by general
chemistry students (along with other necessary procedures) in a two-hour laboratory
period. However, reagent preparation can be performed by students if they are more
experienced or the laboratory period exceeds two hours.

The TAs were expected to prepare several aqueous solutions prior to each
laboratory period. The solutions described below were used during both weeks of the
experiment. A sulfanilamide solution was prepared by dissolving 80 g of crystalline
sulfanilamide in a solution of concentrated phosphoric acid (200 mL) and distilled water (700 mL). The solution was then diluted with distilled water to create a 1000 mL solution. A N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA) solution was prepared by dissolving 0.56 g of crystalline NEDA in 100 mL of distilled water. The color-producing reagent was prepared by mixing the sulfanilamide and the NEDA solution in a 10:1 ratio.

Prior to experimentation, the TAs dried crystalline sodium nitrite for approximately four hours at a temperature of 110 °C to avoid unwanted moisture. The TAs then prepared a stock solution of aqueous nitrite ions by dissolving 1.5 g of the sodium nitrite in 1000 mL of distilled water. Using the stock solution, the TAs prepared various concentrations (0.2, 0.4, 0.6, 0.8 and 1.0 µg nitrite/mL) of nitrite solutions for student calibration curves. After the preparation of the reagents, the TAs refrigerated the color producing reagent, the nitrite calibration solutions, and 500 mL of distilled water to a temperature of approximately 6 °C.

In the first week of the experiment, each student group was assigned a passive sampler containing one NOx and one NO2 collection pad. Each group was also assigned an additional NOx and an additional NO2 collection pad to act as field blanks. Each group took the first 15 minutes of the laboratory period to select an outdoor location for their samplers and field blanks. The sampler and the field blanks (sealed in separate brown plastic container) were left outdoors for a period of one week. Locations were chosen to avoid weather exposure and tampering. Since rain-water contamination was anticipated, the passive samplers were attached to the underside of a PVC end cap for protection.
After deploying the samplers and field blanks, each group returned to the laboratory and created a nitrite calibration curve for two spectrophotometers: a Vernier Spectrovis-Plus Spectrophotometer controlled with a Vernier Labquest 2 and a WPA Biowave S2100 diode array spectrophotometer. 8 mL of each chilled nitrite solution (0.2, 0.4, 0.6, 0.8 and 1.0 µg nitrite/mL) and four 8 mL aliquots of chilled distilled water were added to separate vials (9 vials total) using separate pipets. 2 mL of chilled color producing reagent was added to each vial and the solutions were mixed thoroughly. Each solution was then refrigerated for an additional 30 minutes. After refrigeration, the solutions were warmed to room temperature and the absorbance of each solution was determined using each UV-Vis spectrophotometer set at 545 nm. The students then created two nitrite calibration curves, noting the slope and $R^2$ values. Each calibration curve was forced through the origin according to the protocol provided by Ogawa & Co., USA, Inc. If the $R^2$ values were <0.95, the students repeated the procedure to create their calibration curve.

In the second week of the experiment, the students retrieved their samplers and field blanks from the outdoor locations. The students disassembled the samplers and placed the NO$\textsubscript{x}$ and NO$\textsubscript{2}$ collection pads into separate vials containing 8 mL of room temperature distilled water. The NO$\textsubscript{x}$ and NO$\textsubscript{2}$ field blanks were also placed into separate vials containing 8 mL of distilled water. The vials were agitated by shaking periodically for 30 minutes. After mixing, the vials were refrigerated until a temperature of approximately 6 °C was achieved. After refrigeration, 2 mL of chilled color producing reagent were added to each vial and mixed. The vials were then refrigerated for an additional 30 minutes. After the second refrigeration period, the samples were warmed to
room temperature and the absorbance measured using the UV-Vis spectrophotometers set at 545 nm. The Supplemental Section of this thesis describes the mathematical procedures required to calculate spectrophotometer LOD and to convert absorbance values into parts per billion (ppb) of NO\textsubscript{x}, NO\textsubscript{2} and NO. Additionally, the supplemental section outlines and describes the steps students and instructors must follow to perform the experiment.

*Field experiment procedure*

For this study, passive Ogawa samplers were used to measure concentrations of O\textsubscript{3} precursors, such as NO\textsubscript{x} in the CRG. Approximately 20 sites were chosen near and within Hermiston, OR and samplers were deployed four times for 7-14-day sampling periods (**Table 1**). The sites were chosen based on proximity to Hermiston and likely O\textsubscript{3} problem areas or precursor source emissions (**Figure 7**). Each site was selected in collaboration with Oregon DEQ. At each site, passive Ogawa samplers were fastened in sampler housings approximately 2m off the

<table>
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<th>Dates of Deployment</th>
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<td>D4: 9/24 - 9/30/16</td>
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**Table 1:** Dates of deployment and number of samplers.
ground. Field blank samplers were placed at two locations each deployment in a sealed Nalgene container. Lab blank samplers were also sealed and left in the lab. Each Ogawa sampler was extracted and analyzed using the Ogawa & Co., USA, Inc. protocol for NO\textsubscript{x}, which is the same procedure used in the undergraduate laboratory experiment. NO\textsubscript{x} extracts were analyzed using a double-beam Shimadzu UV spectrophotometer. The results were then mapped using a spatial mapping program ARC-GIS, in order to show the spatial relevance of NO\textsubscript{x} precursors. HYSPLIT was utilized in displaying significant wind patterns. The results were compared with fixed site monitors, as well as compared to NO\textsubscript{x} predictions from the modeling system AIRPACT-5. Comparing results with modeled expectancies allowed for determination of whether a site was affected by Portland’s emissions, or whether there were local sources impacting the ambient air.

**Figure 7**: Map designating sampler locations for the four deployments.
**Results:**

*Undergraduate laboratory results:*

This lab was performed in an undergraduate general chemistry lab at Concordia University – Portland for its pilot session. The students followed the procedures outlined in the experimental section, and their data was saved in order to quantify their capabilities to perform the lab.

Students effectively constructed calibration curves on both the Vernier and Biowave spectrometers (Figure 8). The student calibration curves showed positive correlations of >0.95 regardless of the spectrophotometer the students used. The student measured NO$_3$, NO$_2$, and NO concentrations of the lab are shown in Table 2. The results indicated a measured concentration of NO from 14-26ppb, while NO$_3$ concentration fell in the range of 30-32ppb.

Finally, NO$_2$ showed two-week concentrations from 6-17ppb. The

<table>
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<th>PPB NO$_2$</th>
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*Figure 8: Biowave and Vernier calibration curves created by students in a general chemistry course.*

*Table 2: Data from the pilot study of the laboratory experiment.*
groups all selected different sampling locations at Concordia University -Portland’s campus. It must be noted that group 4’s data in this experiment was not included in the concentration ranges due to difficulties involved in micro-pipettes that may have skewed the data. The groups pooled their field blank data in order to achieve a statistically significant sample size for the LOD calculations. LOD for this experiment was 0.072 ppb of nitrite for the samples run on the Biowave spectrophotometer, while the samples tested via the Verner spectrometer had an LOD of 0.037 ppb of nitrite.

Field experiment results:

NO\textsubscript{x} concentrations ranged from 0-25 ppb during the sampling periods. The highest levels of NO were observed in Prosser, WA; Pasco, WA; Wallula, WA; Pendleton, OR and along the Columbia River off US-Highway 730 (Figure 9a-9c). Deployment 4 (9/24-9/30) had the most consistently high levels of measured NO. NO data from deployment 1 was not included do to contamination. Precursor NO\textsubscript{2} levels ranged from 0-20 ppb over the course of the sampling period. Highest levels of NO\textsubscript{2} were observed in Benton City, WA; Pasco, WA, Hermiston, OR and Pendleton, OR (Figure 10a-10d) and occurred during from deployment 2 to deployment 4.
Figure 9a-9c: NO concentrations (ppb) during deployments 2-4
Figure 10a-10d: NO$_2$ concentrations (ppb) during deployments 1-4
The Columbia River Gorge Basin area was dry and warm during the sample period (Figure 11). The warmest temperature was during deployment 3. The average temperatures for deployments 1-4 was 22.0, 23.9, 24.5, and 17.5 degrees Celsius, respectively. This data was reported by the DEQ at the Hermiston airport.

Figure 11: Dates and temperature spread for each deployment.
AIRPACT-5 predictions were low for the region during all deployments (Figure 12) for NO\textsubscript{x}. NO predictions for the sites were all 0-1 ppb, whereas, observations ranged from 0-25 ppb. NO\textsubscript{2} predictions for the sites were all less than 5 ppb, whereas, observations ranged from 0-20 ppb.

![Figure 12: AIRPACT predictions versus observations by species and deployment.](image)

**Discussion**

*Undergraduate laboratory discussion*

This lab was performed first as a pilot lesson to test the validity of the experiment. All parts were carried out with exactness in relation to the procedure and timeline above. These were compared with the predicted model, AIRPACT-5 and showed similarity for what was expected for the area. Calibration curves were constructed for each method and limit of detection was calculated for each method. The pilot lab was run within the time parameters and was able to be completed with some time to spare. This lab affords
students the opportunity to enhance practical and scientific knowledge through the
practice of instrumental techniques, calculations, and real-world application.

This lab proves to be both effective and efficient for the students and university.
The results of this experiment fall easily within the proposed timeline, especially if
certain parts of the experiment are prepared prior to the laboratory period. This
experiment demonstrates analytical and statistical techniques that are vital to a myriad of
undergraduate chemistry courses, ranging from simple pipetting and unit measurement to
calibrating a spectrophotometer and calculating LOD. The cost of this experiment is also
relatively low ($200-300), provided the university performing the experiment has
equipment necessary for UV-Vis spectroscopy. The pads and samplers are relatively
inexpensive ($100), and the samplers are reusable. For a larger class size, the ability to
achieve statistical significance with the blanks is relatively easy and proves to be a vital
lesson when considering LOD, especially for upper division classes. Calculating LOD
also allows for a cross-curriculum approach along with many of the calculations in this
experiment such as the calibration curve measurements. For lower division courses, the
unit conversion calculations that allow for absorbance measures to be converted to parts
per billion provide a practical application of dimensional analysis techniques.

Class collaboration is a vital facet to this lab as it is unlikely that sampler volumes
will achieve statistical significance without the pooling of data. The goal for this setup is
to achieve data pooling along with the collaboration among students in comparing
calibration curves, techniques etc. The outcome will be the error analysis that allows for
students to reflect on their group’s work in comparison to their classmates to see where
they may have made some mistakes or where they performed techniques correctly. The
comparison between sampling techniques is also compared with the difference in methods being used. For the trial run, the data suggests that the Vernier and the Biowave spectrophotometers are relatively similar in LOD despite the difference in prices. Discussion of price and affordability of the devices may follow the lab as this experiment is aimed in some respect to demonstrate low-cost science.

This laboratory experience proved to be an effective teaching tool for undergraduate chemistry students. Of the four learning outcomes, three were completed in week one of the experiment. During the first week of the experiment, there was a 30-minute period of time during which the students were waiting for their calibration curve solutions to cool. Instead of allowing the students to do nothing, a discussion of the Beer-Lambert Law was initiated. After the discussion of the Beer-Lambert Law, the students created their calibration curves and proved that the concentration of nitrite ions was linearly proportional to absorbance. Additionally, the LOD of each spectrometer was calculated. It was proven that both spectrometers behaved similarly.

During the second week of the experiment the 30-minute period of down time was used for students to share calibration curves and LOD values. This gave the students an opportunity to see if their calibration curves and LOD values were similar to other students in the section. The fourth learning goal of the experiment was completed in the second week. Although not all groups calculated reasonable NOx values, they compared their results with the AIRPACT-5 model to determine if mistakes were made. The write-up for the lab was due one week after the students completed their experiment. Specific questions were asked to determine if the students understood Beer’s Law, construction of calibration curves, determination of LOD and the calculations necessary to calculate
ambient NO\textsubscript{x} concentrations. The students answered the questions with a 79\% success rate.

The execution of this experiment fell within the timeline presented above. The experiment demonstrates analytical and statistical techniques vital to a myriad of undergraduate chemistry courses, ranging from simple pipetting to calibrating a spectrophotometer and calculating LOD. In lower division courses, unit conversions used to convert absorbance into concentration units is a practical application of dimensional analysis. The real-life application of this lab makes it both fun and exciting as students get the opportunity to compare their data with models and other peer-reviewed research articles.

*Field experiment discussion*

The results of this study indicate that there are multiple and complex factors that contribute to the elevated O\textsubscript{3} concentrations in Hermiston and the surrounding area. There is evidence of a large amount of NO\textsubscript{x} in the area that may contribute to the formation of O\textsubscript{3}. Additionally, VOC’s in the area also contribute to O\textsubscript{3} formation, and to gain a better understanding of the spatial extent of precursors to O\textsubscript{3}, VOC’s need to be monitored in the region. VOC emissions will vary with meteorological conditions and season. Each factor must be studied individually in order to assess the overall problem.

The wind in this area constantly shifts, combining O\textsubscript{3} precursors from multiple sources. HYPLIT model results show that the wind for all four deployments come from NW, SW, and NE directions at different heights (*Figures 13a-16b*), allowing for pollutants to be carried in from the CRG and also from Washington and California.
Combining this with wind data suggests that O₃ precursors are not being carried away from this area but are instead holding to their local location and forming O₃ over time.

**Figures 13a-13b:** HYSPLIT trajectories for deployment 1 (forwards and backwards) measuring wind trajectories from left to right. Colors designate specific elevations.
Figures 14a-14b: HYSPLIT trajectories for deployment 2 at Hermiston, OR (forwards and backwards) measuring wind trajectories from left to right. Colors designate specific elevations.

Figures 15a-15b: HYSPLIT trajectories for deployment 3 at Hermiston, OR (forwards and backwards) measuring wind trajectories from left to right. Colors designate specific elevations.
Changes in the atmospheric temperature are important in the formation of O₃.

Temperature affects photolysis rates of sources and sinks in the atmosphere. One of the key players in reactive nitrogen chemistry that could be affecting O₃ formation is peroxycetyl nitrate (PAN). PAN thermally decomposes at higher temperatures (25-72 °C) and can alter the NOₓ-VOC regime for O₃ formation. Additionally, VOC emission rates vary with temperature (Seinfeld and Pandis, 2016). The observed O₃ concentrations rose considerably from the deployment 1 to deployment 2, despite just a 1°C increase in weekly temperature. Likewise, deployment 3 showed an increase in mean temperature, but resulted in less overall O₃ formation. Deployment 4 was the coolest sample period and had the lowest amount of O₃ formation. Daytime temperatures in this area frequently exceed 37°C, which in turn expedites the rate at which O₃ is formed. The difference in
average O₃ concentrations from the 4 deployments highlights the effect that a temperature change can have on concentrations of O₃.

The O₃ problem in the Hermiston area may further be explained by two different regimes regarding NOₓ. The two-part regime could be from the transport of NOₓ from non-local sources and from local emissions and NOₓ sources. Both of these regimes act on this area by contributing to the formation of O₃ in different ways. The 2011 National Emissions Inventory (NEI) reveals that there are several large NOₓ sources near Hermiston. Furthermore, there is also the possibility of unaccounted for NOₓ sources in the area from a variety of sources (area or mobile). The NOₓ observations in this study suggest that there is a mixture of O₃ precursors traveling via the CRG and as well as localized emissions.

The remote sites in the Horse Heaven Hills (Latitude and Longitude 46.0001275, -120.4428333) represent the first regime. These sites contain relatively low NOₓ averages but higher O₃ averages, suggesting that the O₃ precursors are coming from elsewhere. With no point source or heavy mobile sources of NOₓ nearby, it suggests that transported pollutants affect these sites. The remote sites in this study suggest that part of the O₃ problem stems from the precursors that traverse the CRG.

Sites in more populated areas like Hermiston and Pendleton represent the second NOₓ regime: the local production of NOₓ contributing to O₃. These sites maintain both high O₃ and high NOₓ averages, suggesting that there are O₃ precursors local to those areas. A site having concentrated O₃ and NOₓ simultaneously would suggest that there is production of both pollutants occurring concurrently. The NEI reports the largest point NOₓ emitter in Boardman, with two of the largest five in Hermiston. When wind patterns
are overlaid on the maps, it is evident that many of these local emissions are actively contributing to the O\textsubscript{3} averages. Local NO\textsubscript{x} sources may also contribute to elevated O\textsubscript{3} levels at other sites, thus combining both factors of these two regimes.

Finally, the missing 5-20 ppb O\textsubscript{3} predictions in AIRPACT-5 could be from missing emissions or the complex terrain leading to difficult representation of meteorology and transport and O\textsubscript{3} titration. Because the samplers are time averaged over 7-14 days, peak O\textsubscript{3} concentrations cannot be observed and compared to AIRPACT-5 peak O\textsubscript{3} concentrations. The missing emissions are best seen in the comparisons of NO during the deployments. When emissions are not represented, the O\textsubscript{3} formation regime from local sources will not be accurately represented. Second, transport in the region is highly complex, and the 4 km by 4 km grid cells in this area could be too coarse, especially in areas such as the Wallula Gap (Latitude and Longitude 46.0445782, -118.9466686) where the river width is less than the 4 km model grid. When transport isn’t accurately modeled, the non-local source regime for O\textsubscript{3} production in the region will not be modeled correctly.

**Conclusion**

This thesis shows the complexity involved in the Hermiston area’s pollution problems and the usefulness of using NO\textsubscript{x} Ogawa passive samplers in rural areas. The multifaceted conditions work in and out of conjunction with one another, resulting in various scenarios. O\textsubscript{3} precursors are greatly affected by temperature, wind patterns, and the from local and transported NO\textsubscript{x} sources. Furthermore, these techniques are easily utilized by undergraduate chemistry students as they move through their degree. The topics covered in the laboratory portion of this thesis are translatable to other educational
areas such as mathematics, environmental sciences, and engineering. In addition to this, the laboratory technique is suitable and modifiable for different levels of classes.

**Supplemental lab report**

Investigating NO\textsubscript{x} concentrations on an urban university campus using passive air samplers and UV-Vis spectroscopy

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\textsuperscript{1}Math and Science Department, Concordia University, Portland, OR

**Instructor note**

This laboratory experience is applicable to a lower division general chemistry course or an upper division analytical chemistry course. The experiment can be assigned during any semester the instructor chooses. A typical textbook utilized in a general chemistry course is “Chemistry: The molecular nature of matter and change” by Silberberg (2018). If this textbook is used, the laboratory is appropriate when discussing solutions in Chapter 3. In an analytical chemistry course the UV/Vis instrumental technique is important. “Principles of Instrumental Analysis” by Skoog, Holler and Crouch (2018) presents a discussion of molecular spectroscopy in Chapter 13.

**Instructor and student note**

Review the MSDS for each chemical and be familiar with their hazards (see Table S-1) prior to working in the laboratory. The effects of sulfanilamide have not been studied in humans; however, it has been shown to cause thyroid cancer in mice. Sulfanilamide also has the potential for toxicity if inhaled or ingested. This experiment
requires the use of concentrated phosphoric acid. Be sure to avoid direct skin/eye contact.

All chemicals used in this experiment have warnings for targeted organ toxicity. Sodium nitrite has been shown to cause genetic defects in fetuses and may cause other pregnancy related damage. Use care when handling. It is recommended that protective eyewear and nitrile gloves be worn during sample preparation. Waste should be disposed of according to OSHA safety regulations. All chemicals are purchased from Sigma Aldrich.

Table S-1. CAS numbers and hazard overview for each chemical used in this experiment.

*All Safety and Hazard Information was collected using the website https://pubchem.ncbi.nlm.nih.gov/

<table>
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<tr>
<th>Chemical</th>
<th>CAS</th>
<th>Hazard overview</th>
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<tr>
<td>sulfanilamide</td>
<td>63-74-1</td>
<td>• Harmful if swallowed: Acute oral toxicity.</td>
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<td>• Causes skin irritation: Skin corrosion; irritation.</td>
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<td>• Causes serious eye irritation: Serious eye damage/eye irritation.</td>
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<td>• Harmful if inhaled: Acute toxicity, inhalation.</td>
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<td>• May cause respiratory irritation: Specific target organ toxicity, single exposure; respiratory tract irritation.</td>
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<td>• May cause damage to organs: Specific target organ toxicity, single exposure.</td>
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<tr>
<td>Phosphoric acid</td>
<td>7664-38-2</td>
<td>• Harmful if swallowed: Acute toxicity, oral.</td>
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<td>7664-38-2</td>
<td>• Causes severe skin burns and eye damage: Danger skin corrosion/irritation.</td>
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<td>• Causes serious eye damage: Danger serious eye damage/eye irritation.</td>
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<td>• Toxic if inhaled: Danger acute toxicity, inhalation.</td>
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<td>• Causes damage to organs: Danger specific target organ toxicity, single exposure.</td>
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<td>N-(1-Naphthyl)-ethylendiamine dihydrochloride</td>
<td>1465-25-4</td>
<td>• Causes skin irritation: Warning skin corrosion/irritation.</td>
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<td>(NEDA)</td>
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<td>• Causes serious eye irritation: Warning serious eye damage/eye irritation.</td>
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<td></td>
<td>• May cause respiratory irritation: Warning specific target organ toxicity, single exposure; respiratory tract irritation.</td>
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<tr>
<td>Sodium nitrite</td>
<td>7632-00-0</td>
<td>• May intensify fire; oxidizer: Danger oxidizing liquids; oxidizing solids.</td>
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</table>
Experimental procedure

Week 1 – Instructor note: NO\textsubscript{x} sampler and field blank setup

Typical laboratory sections have approximately twenty-four students. If each laboratory section has six Ogawa passive air samplers, the laboratory section is divided into six groups of four students. Each group receives one Ogawa & Co., USA, Inc. sampler. The samplers contain a NO\textsubscript{2} and a NO\textsubscript{x} collection pad (be sure to label which side of the sampler each pad is on). The samplers are pre-assembled with the NO\textsubscript{x} and NO\textsubscript{2} collection pads mounted inside by the laboratory instructor. Samplers are placed in campus locations chosen by each laboratory group. The sampler location should be easy to access, immune to unfavorable weather conditions and in a location that discourages tampering. The samplers are attached inside a PVC end cap to shelter it from rain. Each group also has one NO\textsubscript{x} and one NO\textsubscript{2} collection pads, which act as field blanks. The field blanks are contained inside a re-sealable zipper storage bag and are placed inside a protective brown plastic case near the samplers. After securing the samplers and the field
blanks to the selected location, students record the location and the time and date of sampler dispersal.

**Week 1 – Instructor note: Spectrophotometer assignment**

Each laboratory group uses two spectrophotometers (e.g., Vernier spectrophotometer and Biowave diode array spectrophotometer). Each group creates one calibration curve for each spectrophotometer. Therefore, at the conclusion of the experiment twelve calibration curves are created. Each laboratory group calibrates their spectrophotometers with solutions containing known nitrite concentrations. The same calibration solutions (described in the next section) are used for each spectrophotometer. The calibration curves are used for the analysis of ambient NO\(_x\) concentrations and the determination of spectrophotometer LOD.

**Week 1 – Student note: Spectrophotometer calibration**

Each laboratory group must create a calibration curve for their spectrophotometers. The steps below describe the creation of the calibration curve.

- Six beakers labeled “distilled water, 0.2 µg NO\(_2\)/mL, 0.4 µg NO\(_2\)/mL etc.” are located at the front of the laboratory. The laboratory instructor prepares the distilled water and the nitrite working solutions prior to the start of the laboratory. The solutions are chilled in a refrigerator prior to experimentation.

- Pipette four 8 mL aliquots of distilled water and 8 mL of each nitrite solution out of the beakers into nine separate vials.

- Pipette 2 mL of chilled color producing reagent into each vial and mix. The color producing reagent is a 10:1 ratio of aqueous sulfanilamide solution combined aqueous NEDA.
• Cool the vials for approximately 30 minutes in a refrigerator, and then allow the vials to equilibrate to room temperature.

• Determine the absorbance of the twenty-four distilled water samples (from the entire laboratory section) and each working solution using the Vernier and the Biowave UV-Vis spectrophotometer pre-set to an absorbance wavelength of 545 nm. Record the average water absorbance value along with the working solution absorbance values.

• Input the absorbance values and the nitrite solution concentrations into Microsoft Excel and create a scatter plot (absorbance on the y-axis and concentration on the x-axis). Fit a linear trend line through the data, force the trendline through the origin and report the $R^2$ value the equation of the line.

• The $R^2$ should be as close to 1 as possible, if value is < 0.95, repeat the above steps to create a new calibration curve.

• Rinse and replace materials.

Week 2 – Student note: NO$_x$ and NO$_2$ field blank analysis

• Retrieve the NO$_2$ and NO$_x$ field blanks and record the retrieval time.

• Place each NO$_2$ and NO$_x$ collection pad in separate vials containing 8 mL of water and shake periodically for 30 minutes.

• Refrigerate the vials until a temperature of approximately 6 °C is achieved.
- Add 2 mL of chilled color producing reagent, mix and cool for an additional 30 minutes.

- Allow samples to equilibrate to room temperature.

- Determine the absorbance of each NO₂ and NOₓ field blank using the UV-Vis spectrophotometer at 545-nm and record the values in the laboratory notebook.

**Week 2 – Student note: Sampler retrieval and ambient NOₓ analysis**

- Retrieve the samplers and record the retrieval time.

- Disassemble the samplers

- Place each NO₂ and NOₓ collection pad in separate vials containing 8 mL of water and shake periodically for 30 minutes.

- Refrigerate the vials until a temperature of approximately 6 °C is achieved.

- Add 2 mL of chilled color producing reagent, mix and cool for an additional 30 minutes.

- Allow samples to equilibrate to room temperature.

- Determine the absorbance of the ambient NO₂ and NOₓ samples using the UV-Vis spectrophotometer at 545 nm and record the values in the laboratory notebook.

**Week 2 – Instructor note: NOₓ concentration calculations**

It is important to create organized Excel spreadsheets to calculate ambient NOₓ concentrations. The headings of the Excel spreadsheets should be labeled in correlation with the tables in the Supplemental Section.
Week 2 – Student note: Field blank and sample spreadsheets

Begin by creating three tables in an Excel spreadsheet: two “Field blank” tables (Tables S-2a and S-2b), two “Sample” tables (Table S-2c and S-2d) and one table to calculate parts per billion (ppb) of NO, NO₂ and total NOₓ (Table S-2e). In the tables fill in the information recorded in the laboratory notebook (e.g., field blank/sample number, absorbance, date/time out, date/time in).

NO₂ field blank table (Table S2-a)

- Record the absorbance value for the NO₂ field blank.

NOₓ field blank table (Table S2-b)

- Record the absorbance value for the NOₓ field blanks.

NO₂ sample table (Table S-2c):

- Calculate the µg/mL of NO₂ in the ambient samples using Equation S2.

\[
\frac{(\text{Absorbance} - \text{NO₂ field blank absorbance})}{\text{Slope of the calibration curve}} \quad \text{Equation S2}
\]

- Convert to ng of NO₂ by multiplying µg/mL by 8000.

NOₓ sample table (Table S-2d)

- Calculate the µg/mL of NOₓ in the ambient samples using Equation S3.

\[
\frac{(\text{Absorbance} - \text{NOₓ field blank absorbance})}{\text{Slope of the calibration curve}} \quad \text{Equation S3}
\]

- Convert to ng of NOₓ by multiplying µg/mL by 8000.

- Calculate the ng of NO using Equation S4.
\[
\text{LOD} = \frac{(S_m - S_{bl})}{m} \quad \text{Equation S8}
\]

where \(S_m\) is the minimum distinguishable absorbance signal, \(S_{bl}\) is the mean field blank absorbance signal and \(m\) is the slope of the calibration curve. \(S_m\) is calculated using Equation S9.

\[
S_m = S_{bl} + k s_{bl} \quad \text{Equation S9}
\]

where \(k\) is a constant (3) and \(s_{bl}\) is the standard deviation of the pure water absorbance signal.
Table S-2f: Calculation sheet for NO₃, NO₂, and NO conversions to ppb.

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<td>Sample #</td>
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Optional - Compare Results with AIRPACT-5

http://www.lar.wsu.edu/airpact/gmap/ap5/ap5smoke.html

Visit the Website above:

• Select “Layers” in the top right corner of the screen

• Select the “species” tab

• Click the circle that specifies for NOx

• Compare Concordia area values with predicted values from the map (make sure to adjust the time on the right side of the screen!)


