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Investigation of Ambient Reactive Nitrogen Emissions Sources and Deposition in the
Columbia River Gorge National Scenic Area

by

Jacinda L. Mainord

A dissertation submitted in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy
in
Environmental Sciences and Resources

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Portland State University
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Abstract

Anthropogenic reactive nitrogen is emitted into the atmosphere from fossil fuel combustion (nitrogen oxides) and agricultural activities (nitrogen oxides and ammonia). Nitrogen oxide emissions have long been controlled for their role in *ambient* air pollution and human health effects. However, reactive nitrogen *deposition* is less understood even though it can play a significant role in altering biodiversity, impairing ecosystem and biogeochemical function and degrading cultural artifacts. Although nitrogen deposition is a natural part of biogeochemical cycling, many ecosystems across the United States are at risk of exceeding the critical nitrogen deposition load. While nitrogen oxides are routinely measured in urban areas, far less is known in non-urban landscapes where ecosystems may be especially sensitive. Regional chemical transport models have been used to predict the impacts of ambient reactive nitrogen deposition in non-urban areas, but models have difficulty simulating reactive nitrogen due to poorly quantified emissions, especially from the agricultural sector.

My research explores the speciated deposition of reactive nitrogen through monitoring and modeling in the unique field setting of the 150 mile Columbia River Gorge (CRG) located along the border of Oregon and Washington. This site is ideally suited for this investigation due to the large sources of reactive nitrogen at either end of the CRG and unique seasonally driven channel wind flow. Seasonally driven wind allowed us to look at the reactive nitrogen emissions flowing through the CRG to assess ambient the reactive nitrogen partitioning and deposition gradient. Using data collected by the United States Forest Service to control ambient haze in the CRG and our co-

located nitrogen oxides (NO_x) gas analyzer, we first characterized the influence of seasonal, bimodal wind distributions on the spatial distribution of reactive nitrogen. We found that during winter months with predominantly easterly winds, particulate nitrate and ammonium and gas-phase nitrogen dioxide levels create a gradient from the eastern end to the western end. Particulate nitrate and sulfate mass concentrations influence the CRG gradient during summer months with predominantly western winds. We also found that the magnitude of the impact from east is greater than the magnitude of impact from the west. When we compared our observations to regional chemistry transport models, we found that models are significantly under-predicting levels of reactive nitrogen in the CRG. This bias is not isolated to a single station within the Gorge, but throughout the whole Columbia Basin. Our results indicate that there are under-represented emissions in the region leading to this bias.

Partly due to the bias in reactive N gas-phase species in the CRG, regional models have been underestimating the impact of gas-phase reactive N on dry N deposition. We conducted field studies at two sites within the CRG monitoring reactive nitrogen species (nitric oxide, nitrogen dioxide, ammonia, nitric acid, particulate nitrate, particulate ammonium, and particulate sulfate) as well as ozone and meteorological parameters. These measurements allowed us to conduct the first comprehensive analysis of reactive nitrogen partitioning and deposition in the CRG.

Through our measurements, we found reactive nitrogen was higher in the spring than the summer. We found concentrations ranging from 0-15 ppbv ammonia, 0-7 ppbv nitric acid, 0-2 µg/m³ ammonium nitrate and 0-1 µg/m³ ammonium sulfate at the sites.

Through the measurements of all these species, we evaluated the limiting gas-phase precursor to inorganic nitrogen particle formation. In the springtime, ammonia limits the formation of particulate reactive nitrogen; while in the summer, nitric acid and oxidized sulfur limit the formation of inorganic nitrogen particles. This suggests that there may be more sources of ammonia in the spring with fertilizer application or perhaps reactive nitrogen reservoirs are renoxified through thermal dissociation during warmer summer months.

Our estimated deposition from gas and particle phase reactive nitrogen ranged from 0 – 0.14 kg N/ha per day. We also found that gas-phase reactive nitrogen plays the largest role in dry N deposition in the CRG with particle-phase contributing less than 15% of total dry N deposition. These results are important for land managers to understand the total impact of reactive nitrogen to non-urban areas. This research can inform mitigation strategies for haze formation, identify the major species and sources involved in dry N deposition and assess the potential impacts to ecosystems and cultural artifacts.

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Introduction

My research focuses on gas and aerosol phase atmospheric pollutants that are classified as reactive nitrogen (Nr) species. Nr is a suite of compounds that contain nitrogen and are biologically, photochemically, or radiatively active in the atmosphere. They include species like nitrogen oxides, ammonia, nitric acid, and inorganic nitrogen particles. The anthropogenic Nr sources into the atmosphere include fossil fuel combustion and agricultural activities (such as fertilizer application and animal husbandry) and further contribute through secondary pollutant formation within the atmosphere. Global and United States emissions of reactive nitrogen species have been on the rise since pre-industrial times (Compton et al. 2011; Houlton et al. 2012), especially within the agricultural sector.

The addition of reactive nitrogen to the atmosphere is a problem due to its role in particle formation, human health effects, role in ozone formation and its role in light scattering leading to decreased visibility. In non-urban landscapes, the addition of reactive N through deposition is a problem: while reactive N is not toxic, it can change ecosystem structure and function (Greaver et al. 2012; Pardo et al. 2011). Additionally, a single molecule of fixed N can be transformed and utilized a number of times before it is denitrified and removed from available N (Galloway et al. 2003). Our ecosystems are at risk of exceeding a critical level of N deposition and can be seen through loss of sensitive species and biodiversity. Specific to this research study area, sensitive species and cultural resources such as rock petroglyphs are in peril from N deposition and associated damages from the increase of available N to the ecosystem.

Figure 1. Schematic of reaction pathways for Nr species. Legend of classifications outlined in the black box. Reactive N reservoirs are in purple circles. Light reactive species are in blue circles. Red dotted arrows represent deposition.

Reactive nitrogen: monitoring stations and networks

Nitrogen dioxide is a National Ambient Air Quality Standard (NAAQS) criteria pollutant in the United States. It is monitored alongside nitric oxide across the nation for regulatory purposes. However, NO_2 is the only Nr criteria pollutant in the US and is monitored at the highest spatial and temporal resolution. The Interagency Monitoring of PROtected Visual Environment (IMPROVE) sites and the Chemical Speciation Network (CSN) monitor for inorganic nitrate and ammonium particles every third day for 24-hour observations. However, the stations do not occur in every state. Wet deposition of nitrate and ammonium are monitored at the National Acid Deposition Program National Trends Network (NTN) and at some NTN locations dry deposition is estimated from nitric acid observations. The spatial resolution of the dry deposition estimates is poor, and the NTN

monitors are mostly located in areas uninfluenced by sources and are meant to show regional trends for deposition. In order to better understand the impacts of dry reactive nitrogen deposition, more monitoring is necessary, especially in the near-source confluence where the impact of these pollutants reach rural areas.

Reactive nitrogen: complex chemistry and poorly constrained emissions

Figure 1 is a schematic of the complex reactions that reactive N species can undergo, mechanisms from CBM-Z and MOSAIC (R. A. Zaveri and Peters 1999; R. A. Zaveri et al. 2008). Each of the reactive nitrogen species is intertwined in the web of possible reactions that can occur at differing rates depending on temperature, relative humidity and interactions with other species. The partitioning from gas to aerosol phase is more complicated, and is dependent upon thermodynamics, temperature, relative humidity, and the mixture of gases and particles present. The partitioning to particulate ammonium sulfate is preferential over the partitioning to particulate ammonium nitrate, so any sulfate present will first be neutralized by ammonium. Remaining ammonium present can neutralize nitrate to form ammonium nitrate (Seinfeld and Pandis 1998).

Reactive N varies spatially and temporally, and each region in the U.S. needs to assess N_r and the N_r deposition impacts for better evaluation in chemical transport models (CTMs). Without understanding nitric acid and NH_3 , we cannot understand partitioning to secondary inorganic aerosols (SIA) and deposition impact to the environment. However, reactive nitrogen species such as ammonia (NH_3) and nitric acid (HNO_3) are sparse and are difficult to measure due to instrument or labor costs (Norman et al. 2009; Williams et al. 1992; Schwab et al. 2007; Harrison and Kitto 1990). Because

of the difficulty of Nr measurements, CTMs are often used to simulate the speciation, partitioning, and deposition of Nr. While models have progressed in terms of availability and computing power through computer clusters, the models can only perform as well as the quality of the inputs such as meteorology, land categories, emissions, and chemical mechanisms. We know that models have difficulty predicting Nr species due to poorly constrained emissions and precursor species (Heald et al. 2012; Walker et al. 2012; Baker and Scheff 2007). Because of poor nitrogen budgets, we need to examine gas-phase HNO_3 and NH_3 to gain a better understanding of N dry deposition and the impact of Nr to surrounding ecosystems.

We will use the Columbia River Gorge (CRG) to investigate the reactive nitrogen partitioning and deposition gradient from distinct sources, bimodal wind flow and transport. Due to the temporal and spatial variability of Nr, it is important to investigate the chemistry dynamics regionally as well as in the near-source confluence. My research aims to:

1. Investigate the gradient of gas-phase nitrogen dioxide and reactive nitrogen and sulfate aerosols in the CRG;
2. Characterize reactive N partitioning and secondary inorganic aerosol formation in the CRG;
3. Characterize total dry N deposition in the CRG; and
4. Determine model performance of the total reactive N problem in the CRG.

Research sites

The CRG lies between the states of Oregon and Washington and encompasses a National Scenic Area, tribal fishing areas, and cultural artifacts such as petroglyphs on the CRG's rocky crags (Figure 2). The Portland-Vancouver metropolitan area and Georgia Pacific paper and pulp anchor the west end of the CRG; while the 550-megawatt coal-fired power plant (Boardman) and the 70,000 cattle-head confined animal feeding operation (Threemile Canyon CAFO) lie on the eastern end.

Figure 2. Location sites and sources in the CRG. From west to east: Portland, Georgia Pacific paper and pulp mill, Mt. Zion IMPROVE, Wishram IMPROVE, Threemile CAFO and Boardman coal-fired power plant. Map made using the leaflet package in R with CartoDB and Stamen tiles.

Seasonal winds from the west in the summer and the east in the winter (Green, Xu, and Adhikari 2008) create bimodal wind distribution (Figure 3) and the unique opportunity to use the CRG as an ambient flow tube with seasonal chemical footprints to investigate the gradient of reactive N emissions and deposition. Transformation of Nr species creates an air pollution gradient spanning over 260 km. The unique use of the CRG as a natural laboratory allows us to investigate the impact of large sources of Nr on nearby non-urban landscapes.

Figure 3. Frequency of wind direction at Mt. Zion and Wishram IMPROVE stations. Figure from (Green, Xu, and Adhikari 2008).

Researchers have used lichen species as bioindicators to ambient pollution over the Pacific Northwest (Figure 4), and have found that pollution sensitive species are absent in the CRG (Geiser and Neitlich 2007; M. Fenn et al. 2007; Geiser et al. 2010; Root et al. 2015). However, surrounding areas in Oregon and Washington have pollutant sensitive species, further suggesting the influence of Nr emissions and deposition on the CRG.

The United States Forest Service monitors for visibility impairments near Wishram, WA at the IMPROVE Wishram, WA at the IMPROVE site. A second IMPROVE station operated near Washougal, WA at Mt Washougal, WA at Mt Zion and is currently an active NTN site. A summary of the measurements and measurements and monitoring schedule can be found in

Table 1, as well as the co-located measurements from this study.

Figure 4. Lichen air score map from Geiser and Neitlich 2007. Lichen air scores are calculated using algorithms from calibrated datasets using lichen community composition and other environmental variables. Green represents good air scores where sensitive species are present and red represents air scores with sensitive species being absent or weedy species enhanced.

Table 1. Monitoring location, monitoring program, and list of measurements related to this project.

Site	Monitoring Network and Schedule	Measurements
Wishram and Mt Zion (historically, 1996-2011)	IMPROVE, 1 in 3 days 24-hour observations	Light extinction, total mass, organic carbon, speciation of the following PM _{2.5} (related to this project): sulfates, nitrates, ammonium
Mt Zion	NTN, continuously, Tues-Tues	Precipitation total, total N, pH, precipitation concentration, wet deposition of the following (related to this project): sulfate, nitrate, ammonium
Wishram, Mt Zion	PSU, continuously every 60 seconds	NO _y , NO _x , O ₃ , wind speed, wind direction, temperature and relative humidity
Wishram, Mt Zion, Portland	PSU, 10 samples for 24 hours	Gas-phase HNO ₃ , NH ₃ , and PM sulfate, nitrate, and ammonium

Investigating ambient reactive nitrogen using the Columbia River Gorge as a natural flow tube

Abstract

The Columbia River Gorge (CRG), located between Oregon and Washington states, is a national scenic area and has distinct sources of pollutants located at each end. The CRG experiences bimodal wind distributions: winter easterlies and summer westerlies. Due to bimodal wind patterns and distinct sources at each end of the CRG, a pollution gradient forms from the east to west in winter and west to east in the summer. Since the pollutants at the east and west end of the CRG are distinguishable, we use seasonal observations of reactive N to show evidence of source impact and characterized the ambient reactive nitrogen gradient within the CRG. The distinct sources and bimodal winds offers a unique opportunity to investigate the gradient and relative impact of reactive nitrogen partitioning downwind and deposition on non-urban landscapes. This project aimed to monitor gas and aerosol pollutants at two locations in the CRG: one located at the western side (Mt. Zion) and one in the east (Wishram) in order to investigate the gradient of reactive nitrogen aerosols and nitrogen oxide gases. We analyzed ambient reactive nitrogen and sulfate concentrations during days with predominantly easterly and predominantly westerly flow. Measurements include continuous gas analyzer observations of NO_x co-located at Interagency MONitoring of PROtected Visual Environment stations that monitor for fine particulate speciation including ammonium nitrates and ammonium sulfates. We found evidence of gas-phase nitrogen dioxide and particle phase ammonium, nitrate and sulfate influence from the east during predominantly easterly winds. Likely eastern sources include the Boardman Coal-fired

Power Plant and Threemile Canyon Confined Animal Feeding Operation. We also found evidence of nitrate and sulfate particulate influence from the west. Likely western sources include Portland-Vancouver metropolitan area and the Georgia Pacific pulp and paper plant located at the western end of the CRG.

Introduction

Reactive nitrogen (Nr) is any form of nitrogen that is readily available for radiative, photochemical or biological activity (Galloway et al. 2003). There is currently a lack of spatially resolved monitoring of different reactive N precursor species such as gas-phase ammonia and the oxides of nitrogen. The sparse monitoring has led to increased model comparison to existing networks such as the Interagency MONitoring of PROtected Visual Environments (IMPROVE) sites for particulate matter speciation and evaluating the impacts of reactive nitrogen to deposition. Chemistry transport models (CTMs) over the United States report biases in reactive N species predictions to observations, showing a need to better understand emissions (Walker et al. 2012; Heald, Lee, et al. 2012; Baker and Scheff 2007; Markovic et al. 2014). These incomplete networks cannot validate models and we need more monitoring to characterize reactive nitrogen emissions. The increasing emissions of reactive N, especially ammonia emissions through agricultural activity (Houlton et al. 2012), is creating a need to understand the impact of reactive N species to the surrounding region. This is especially important in areas with projected increases of Nr emissions from agricultural activities because ammonia is an unregulated gas with a significant impact on fine particulate

matter mass concentrations (Deng, Li, and Wang 2015; Behera, Betha, and Balasubramanian 2013).

The Columbia River Gorge (CRG), because of its unique configuration of winds and reactive N emissions, provides a natural laboratory to explore these issues. The cultural and natural resources within the CRG have been at risk from increased pollution located at each end of the CRG. Ecologists have shown that both the eastern and western ends of the CRG have highest N deposition and highest nitrophilous (N tolerant) lichen species and decreased N sensitive lichen species (M. E. Fenn and Poth 2007; Geiser et al. 2010; Root et al. 2015). There have also been studies that have looked at the causes of haze in the National Scenic Area (Green et al. 2006) and the impact of Boardman on the PM_{2.5} levels in the CRG (Jaffe and Reidmiller 2009). While these studies have shown the impact of both western and eastern ends of the CRG on certain ambient parameters or the ecological effect of those parameters, none of these studies have provided insight into the reactive N species and phases present in the total N deposition to the landscape nor provided validation of model performance to ambient observations.

Across the United States, there are over a hundred Interagency MONitoring of the PROtected Visual Environment (IMPROVE) sites that monitor for light extinction, total particulate matter mass (both 2.5 and 10 μm), organic and elemental carbon, and the speciation of fine particulate matter. Observations are made every three days for 24 hours and data is publically available about a year after collection. There have been two IMPROVE stations that have been in operation in the CRG. Located near Wishram, WA

is an active IMPROVE station (monitoring began in 1993) and located near Washougal, WA (Mt. Zion site) is an inactive IMPROVE station that monitored from 1996-2011.

Figure 5. Map of sites and sources. From the west to east: Portland is light blue. George Pacific paper mill is gray. Mt. Zion is dark blue. Wishram is green. Threemile CAFO is purple. Boardman Coal Fired Power Plant is orange. Map of sites made with leaflet package in R with the CartoDB and Stamen tiles.

Our research questions are: (1) What is the reactive N gradient in the CRG (2) can we use models predict gas-phase Nr in the CRG? We aim to provide evidence through the analysis of ambient concentrations of aerosols and gases during predominantly westerly and easterly flow days throughout the CRG sites that a seasonal gradient exists. The Portland-Vancouver metropolitan area and the Georgia Pacific pulp and paper plant (National Emissions Inventory 2011 or NEI11 estimates emissions of 19 tons per year (tpy) SO_2) anchor the west end of the CRG; while the 550-megawatt Boardman coal-fired power plant (NEI11 estimates emissions of 4,049 tpy NO_x & 13,100 tpy SO_2) and the 70,000 cattle-head confined animal feeding operation (Threemile Canyon CAFO, estimated 917-3885 tons NH_3 per year, US EPA Farm Model) lie on the eastern end. Seasonal winds from the west in the summer and east in the winter (Green, Xu, and Adhikari 2008; Sharp and Mass 2004) create an ambient flow tube with unique chemical

footprints in each seasonal flow. These unique sources create an air pollutant gradient spanning over 260 km of transport and transformation of reactive nitrogen and sulfate species. The use of the CRG as a natural laboratory allows us to investigate important chemical processes occurring under environmental rather than chamber conditions, which are often much higher than ambient levels and determine the impacts of Nr sources to downwind areas. This understanding is important to inform models and policies regarding reactive N and the implications from current and future emission scenarios.

Materials, methods and study area

Observations

Ambient measurements were co-located at IMPROVE site COR11 (Wishram) located within the Columbia River Gorge in Washington State (Figure 5). NO_x-NO chemiluminescence gas analyzer measurements started at Wishram in December 2012 to better understand gas-phase reactive nitrogen within the CRG gradient. In order to account for total oxidized nitrogen (NO_y) interference in the molybdenum converter of the NO_x-NO analyzer, the NO₂ concentrations were adjusted according to Steinbacher et al. 2007. This adjustment is especially important in rural areas and is dependent upon other factors such as ambient and shelter temperature and the length on the sample inlet. Meteorological measurements of temperature, relative humidity, wind speed, and wind direction were also measured at Wishram during NO_x measurements.

The EPA's PM_{2.5} National Chemical Speciation Network (CSN) was established in urban areas across the United States to monitor for speciation trends (Agency 1999). At both IMPROVE and CSN sites, surface concentrations of fine particulate (PM_{2.5})

ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$, and ammonium nitrate, NH_4NO_3 , are measured as 24-hour averages every third day. Data from IMPROVE sites Mt. Zion and Wishram was downloaded from 2001-2011 and 2000-2015, respectively. Data from Oregon DEQ's SE Lafayette regulatory station and CSN station was downloaded from 2000-2015. Data from the US EPA's Air Markets Program was downloaded for Boardman Coal-fired power plant hourly emissions.

In order to assess the impact of the sources and bimodal winds on the CRG, we analyzed the gas and aerosol phase measurements within the CRG as well as at each terminus. It is expected that if an influence of source exists, the locations closest to the source will experience higher concentrations of the pollutant in gas or aerosol phase than the downwind location. For example, if an eastern source is suspected to influence the CRG during winter easterly months, we would expect higher concentrations at the site further east (Wishram) than the site located further west (Mt. Zion). Conversely, we expect the urban and industry sources on the western end of the CRG to impact the western site greater than the eastern site. We analyzed IMPROVE data from 2009-2011 and continuous observations at Wishram and continuous emissions monitoring at Boardman coal-fired power plant from 2012. For testing for the western flow gradient, we used 2009-2011 IMPROVE data from summer months (June, July, August). For testing the gradient with predominantly easterly winds, we used 2009-2011 IMPROVE data from winter (November through February). Previous studies have reported that June, July and August have predominantly westerly winds while November through February

have predominantly easterly winds (Green et al. 2006). However, even during months with strong easterlies, there still is westerly wind patterns presents.

Models used

Weather Research Forecasting with Chemistry (WRF-CHEM) regional chemistry transport model was used for model comparisons (Grell et al. 2005). Meteorology inputs came from NCEP North American Reanalysis (NARR). The second generation regional acid deposition model (RADM2) was used to simulate gas-phase chemistry. The aerosol module used was the MADE/SORGAM module (Schell et al. 2001). The model domain used 150 north-south and 150 east-west grid points centered at COR11 in a 4 km by 4 km grid. The National Emissions Inventory 2011 (NEI 11) was used for anthropogenic emissions and the Model of Emissions of Gases and Aerosols from Nature (MEGAN) was used for biogenic emissions.

Results

Historical IMPROVE measurements

Julian day-average PM (particulate matter) nitrate and ammonium concentrations peak with average Julian Day mass concentrations of $4 \mu\text{g}/\text{m}^3$ and $2 \mu\text{g}/\text{m}^3$ (respectively) at Wishram and Mt. Zion during November through February. PM sulfate in Wishram seasonality (higher mass concentrations in November – February) is not as pronounced and mostly ranges from $0\text{--}1 \mu\text{g}/\text{m}^3$. Mt. Zion PM sulfate concentrations are also mostly in ranges from $0\text{--}1 \mu\text{g}/\text{m}^3$ but do show a slight peak during May through September. Portland PM nitrate and sulfate do not show a seasonal pattern, however PM ammonium is elevated slightly November through February (Figure 6).

Figure 6. Plots of Portland CSN (years 2000-2015), Mt. Zion (years 2001-2011) and Wishram (years 2000-2015) IMPROVE stations by average Julian Day mass concentration.

Winter easterly flow tube effect

Evidence of the eastern source influence is supported by our continuous NO_x measurements at Wishram. The NO₂ mixing ratio is elevated at Wishram, WA when the farther east Boardman coal-fired power plant is emitting higher NO_x (Figure 7). If we look at Wishram NO₂ mixing ratios during westerly winds (225 – 315 degrees) and easterly winds (45 – 135 degrees), we find that NO₂ mixing ratios are significantly ($p < 0.01$) lower during westerly (5 ppbv NO₂) than easterly winds (7.8 ppbv NO₂). This

further suggests that Boardman is an eastern influence on the reactive N in the CRG, similar to the Boardman influence on $PM_{2.5}$ as reported by (Jaffe and Reidmiller 2009).

Figure 7. Hourly continuous emissions (kg/hr) from the US EPA Air Markets program from Boardman Coal-fired power plant vs Wishram IMPROVE NO₂ concentrations (hourly ppbv), data from Dec 2012.

The influence of eastern sources such as Boardman coal-fired power plant and the 70,000 animal CAFO on the reactive N gradient is further supported by the higher mass concentrations located in the east when compared to the west. Large fractions of winter easterly winds occur in the CRG during November – February (Green, Xu, and Adhikari 2008). PM species from the predominantly winter easterly months at both Mt. Zion and Wishram are plotted in Figure 8. The $PM_{2.5}$ mass concentrations of nitrate and ammonium (left two plots in Figure 8) are higher in the eastern end (Wishram) than the western end (Mt. Zion) on days with likely winter easterly flow. This suggests an eastern

source of nitrate (Boardman) and ammonium (Threemile CAFO) as evidenced by the gradient of higher mass concentrations to the east than to the west.

There are some instances when sulfate PM is higher at the eastern end, but generally the sulfate PM mass concentrations are just as high at the western end as the eastern end. This suggests that there are sources of sulfate (such as Georgia Pacific and Boardman) that are influencing the sulfate PM levels throughout the CRG. The partitioning of ammonium sulfate is thermodynamically favored over the partitioning of ammonium nitrate. As the western sources of sulfate flow through the CRG with the less frequent westerly winds during cold months, the sulfate is neutralized by any ammonia forming ammonium sulfate particles. There is no evidence of a particulate nitrate influence from the west likely because there are limited ammonia sources on the western end of the CRG to neutralize both the oxides of sulfur and nitrogen.

Figure 8. Fine PM concentrations of nitrate, ammonium and sulfate aerosols at Mt. Zion and Wishram during winter easterly winds. Winter easterlies during November 1 – February 28, as defined by Green et al 2008. Data from 2009-2011 IMPROVE observations. Lines in plots are the 1:1 line.

Summer westerly flow tube effect

Conversely, during months with predominantly westerly winds (June – August, Green et al 2006) there are higher concentrations of nitrate and sulfate aerosol at Mt. Zion which correspond with similar but lower mass concentrations at Wishram, which is located further east (Figure 9). This suggests the western sulfate (Georgia Pacific paper mill) and nitrate (Portland-Vancouver metropolitan area) sources influence the CRG during westerly winds. However, a gradient of particulate ammonium from Mt. Zion to Wishram is not seen, suggesting that there may be more local sources of ammonia within the CRG than on the western end. This gradient of aerosols shows the bimodal wind flow effect on particulate nitrate and sulfate through elevated mass concentrations at the western end; and the addition of ammonia through agricultural activities throughout the CRG illustrates the importance of understanding of agricultural activities on the aerosol activity.

Figure 9. Fine PM concentrations of nitrate, ammonium and sulfate aerosols at Mt. Zion and Wishram during summer westerly winds. Summer westerlies predominantly occur during June 1 – August 31, as defined by Green et al 2008. Data from 2009-2011 IMPROVE observations. Lines in plots are the 1:1 line.

Model performance of reactive N in the CRG

To assess if regional transport models can capture the influence of Boardman coal-fired power plant in the Columbia River Gorge, we ran WRF-CHEM for December 2012 using NEI-2011 and used RADM2 mechanism for gas-phase chemistry. We chose WRF-CHEM over Washington State University's AIRPACT model because the AIRPACT output is unavailable for this time period of observations. The model failed to predict NO₂ concentrations greater than 11 ppbv in the Columbia River Gorge (Figure 10) when the observations included levels up to 19 ppbv NO₂.

Figure 10. Observed Boardman emissions (kg/hr) vs Wishram NO₂ concentrations. Left) Wishram continuous observations. Right) WRF-CHEM predictions. Data from December 2012 observations and WRF-CHEM simulations.

Discussion and conclusion

The results from this study indicate there is a unique opportunity to understand the impact of bimodal wind flow and distinguishable Nr sources at its east and west end

on the gradient of reactive N in the CRG. Eastern sources such as Boardman coal-fired power plant and Threemile CAFO influence gas-phase nitrogen dioxide and particle-phase ammonium and nitrate aerosols during months with predominantly eastern winds (Figure 7, Figure 8). Western sources such as Portland-Vancouver and Georgia Pacific paper and pulp plant influence the levels of nitrate and sulfate aerosols with western winds (Figure 9). This National Scenic Area with distinct emissions and bimodal flow allows researchers to use this area to explore the gradient of atmospheric chemistry occurring in a natural environment and the impact of sources to the non-urban landscape. The impact of these sources and flow impact are not showing up in regional model simulations, as Boardman is a larger influence on eastern nitrogen dioxide mixing ratios than transport models are predicting (Figure 10). Models have difficulty representing areas with complex terrain and biases could be result of either a misrepresentation of transport in this highly complex terrain or misrepresented emissions in the region (O'Neill et al. 2006). Comparing model predictions to observations is important in complex areas to establish better emissions inventories and characterize transport and the total impact of emissions on the non-urban landscapes.

Table 2. Median PM nitrate, ammonium and sulfate aerosols by predominantly winter easterly and summer westerly Julian Days from 2009-2011 IMPROVE data.

Summary Statistic (units of $\mu\text{g per cubic meter}$)	Winter nitrate	Summer nitrate	Winter ammonium	Summer ammonium	Winter Sulfate	Summer Sulfate
Wishram Median (east)	0.88	0.14	0.44	0.33	0.40	0.62
Mt. Zion Median (west)	0.49	0.31	0.16	0.11	0.40	0.83

Beyond the influence of westerly and easterly winds on the air pollution gradient spanning the CRG, the magnitude of the source impact of PM nitrate, sulfate, and

ammonium on the region (Table 2) is different from each source area and may be a result from the proximity of the source as well as the amount of source emissions. While Boardman is farther away from the IMPROVE sites, it emits higher amounts of NO_x and SO₂. Conversely, the paper plant is much closer to Mt. Zion, but emits less. The mass concentrations of winter easterly aerosol nitrate and ammonium are higher than the mass concentrations during summer westerly days. This suggests the impact of the eastern end (Boardman and Threemile CAFO) is a greater influence on mass concentrations of nitrate and ammonium particles than the western end (Portland-Vancouver metropolitan area and the paper mill). With respect to the western influence of the pollutants to the CRG, the western sulfate source (likely the paper mill) is a greater influence on the mass concentrations of sulfate during expected summer westerly flow than Boardman's influence of sulfate with predominantly easterly flow. Understanding these relative source impacts to the CRG is key to understanding the transport and transformation of pollutants as well as management practices for resource protection and haze and acid rain mitigation strategies.

Characterizing the reactive N gradient in the CRG is an important opportunity to investigate the impacts of unique chemical footprints on the transport, transformation, and deposition of ambient pollutants to the rural environment. Additionally, understanding the CRG N_r gradient allows researchers to understand the risks of the sources on the cultural, natural, and recreational resources within the CRG and inform proper management and protection of these valuable resources. This understanding is especially important with the future emissions changes in the region such as the dairy

operation that is permitted to replace the Boardman Poplar Tree farm (“CAFO permit issued to Lost Valley Farm”, 2017). The addition of another animal husbandry operation may amplify the impact of ammonia to the region, especially since the new dairy operation will be closer in proximity to the CRG than the existing Threemile CAFO.

Ambient reactive nitrogen partitioning and deposition in the Columbia River Gorge

Abstract

Measurements of reactive nitrogen species outside urban areas are sparse. Even within the urban environment, only nitrogen oxides (NO_x) are monitored, leaving out important species like nitric acid, ammonia, and inorganic particulate matter. This gap in monitoring leads to uncertainties not only of secondary inorganic aerosol formation, but also in total nitrogen dry deposition. The Columbia River Gorge (CRG), located between Oregon and Washington states, is a national scenic area home to cultural artifacts, tribal treaty rights, and recreational activities such as wind sports and hiking. We monitored ambient reactive nitrogen species at three locations: one located at the western side (Mt. Zion), one in the east (Wishram) and a third at the western end of the CRG in Portland, Oregon. Measurements include continuous gas NO_x analyzer observations and 24-hour annular denuder and filter pack measurements of ammonia, nitrate, and inorganic particulate reactive nitrogen. Average daily nitrogen dioxide at Wishram ranges from 0-15 ppbv. Our 24-hour measurements of HNO₃ ranged from 0 – 8 ppbv at Wishram and NH₃ ranged from 0 – 15 ppbv. Nitrogen dioxide at Mt. Zion ranged from 0-10 ppbv, 24-hour observations of HNO₃ ranged from 0 - 6 ppbv, and NH₃ ranged from 0-7 ppbv. We found that gas to particle partitioning is limited seasonally: ammonia limits particle formation in the spring and nitric acid limits the formation in the summer. We found dry N deposition is dominated by gas-phase reactive N and ranges from 0-0.14 kg N/ha per day and that our daily estimated rates of dry deposition compare well to a throughfall and bulk deposition study conducted within the CRG. We found that gas-phase reactive N is

under-predicted by model simulations. The combination of all these measurements are crucial to managing total dry N deposition, acid deposition and the formation of haze in the National Scenic Area.

Introduction

Reactive nitrogen (Nr) is a suite of compounds in the atmosphere that contain nitrogen (N) and are biologically, photochemically, or radiatively active in the atmosphere and biosphere (Galloway et al. 2003). Global rates of N fixation due to human activity have more than doubled since pre-industrial times (Compton et al. 2011). However, in the contiguous United States, it has been estimated that anthropogenic Nr inputs may have increased at least five times the pre-industrial inputs (Houlton et al. 2012) and it is estimated that inorganic N comprises 15-35% of inorganic fine particulate matter (PM_{2.5}) mass. Inorganic nitrogen particulate matter is projected to increase with increasing precursor emissions (Heald et al. 2012). Even with this increase in Nr emissions, our spatial monitoring of Nr species is sparse and we need to increase our understanding of the impact of Nr in the near source confluence.

Reactive N includes species such as nitrogen oxides (NO_x, the sum of nitric oxide (NO) and nitrogen dioxide (NO₂)), ammonia (NH₃), nitric acid (HNO₃) and inorganic and organic particles containing N. Anthropogenic activity introduces Nr into the atmosphere through fossil fuel combustion, animal husbandry operations such as confined animal feeding operations (CAFO), or through secondary pollutant formation within the atmosphere. The addition of reactive N to the atmosphere is a concern due to its role in secondary inorganic aerosol (SIA) formation (R1, R2) and haze formation, role in ozone

(O₃) formation and from human health effects (Seinfeld and Pandis 1998; Sillman 1999; Pope and Dockery 2006).

Nr also poses a risk to ecosystem health in non-urban landscapes. While Nr is not toxic to an ecosystem, it has been linked to changes in ecosystem structure and function (Greaver et al. 2012; Pardo et al. 2011) and can be amplified within the ecosystem through the phenomenon known as the nitrogen cascade (Galloway et al. 2003). Ammonia, an important Nr species emitted mainly from agricultural (such as CAFOs), is not regulated, unlike NO_x from urban combustion sources.

Figure 11. Schematic of reactive nitrogen pathways. Legend of color and dash code outlined in black box. Purple circles represent reactive nitrogen reservoirs. Circled in dotted blue lines represent species that can photodissociate. Circled in green dashed line represents species monitored in this study.

Without NH_3 , the dominant pathway and products of SIA formation will not occur. However, because NH_3 is not regulated, there are limited monitoring stations for NH_3 across the US. This has led to using chemical transport modelling (CTM) to simulate the impact of NH_3 and other reactive N species have in the US. There are known biases in CTM predictions with regards to Nr species and emissions (Heald et al. 2012; Walker et al. 2012; Markovic et al. 2014; Baker and Scheff 2007). Due to the temporal and spatial variability of Nr and known CTM biases, it is important to investigate the chemistry dynamics regionally as well as in the near-source confluence (Bettez et al. 2013). This paper aims to increase our collective understanding of Nr chemistry impacts to deposition (Figure 11) and address some gaps to effectively manage the Nr problem. We will use the Columbia River Gorge's (CRG) ambient reactive N gradient in order to investigate reactive nitrogen partitioning and deposition to address the following questions:

1. What limits SIA formation in the CRG?
2. What are the rates of dry deposition of reactive N in the CRG and how do they compare to previously reported bulk and throughfall deposition in the CRG?
3. How do models perform across the CRG region when compared to observations?

The United States Forest Service has been monitoring for PM speciation for over 20 years in the CRG. From our analysis of past measurements in the CRG, we found an influence of nitrate, sulfate, and ammonium sources from the east and nitrate and sulfate sources from the west. However, in order to gain an understanding of reactive N

partitioning in the CRG and key species in N deposition, gas-phase measurements of ammonia and nitric acid are necessary.

Fenn et al. 2007 investigated bulk and throughfall deposition at sites throughout the CRG from October 2003-March 2004 (133 days) and found that the ecosystem and cultural resources are likely threatened from the rates of deposition. Fenn reports throughfall deposition rates of 7.87 kg N/ha in western end of the CRG and 13.95 kg N/ha in the eastern end of the CRG. They also reported higher ammonium deposition in the east than the western end (8.01 kg N/ha vs. 2.76 kg N/ha). Fenn reported bulk deposition of 1.71 kg N/ha in the western end and 1.09 kg N/ha in the eastern end. Unlike the throughfall deposition, reduced bulk deposition was highest in the west than the eastern portion of the CRG (0.90 kg N/ha vs 0.48 kg N/ha). While this study has shown the total rates of oxidized and reduced nitrogen deposition throughout the CRG during wet months, these studies do not reveal the role of gas and aerosol phase reactive N in total N deposition, nor does it report deposition rates during dry months.

Materials, methods and study area

The CRG lies between Oregon and Washington States, encompasses a National Scenic Area, tribal fishing areas, and cultural artifacts such as petroglyphs on the CRG's rocky crags. Portland-Vancouver metropolitan area and Georgia Pacific paper mill anchor the western end of the CRG; while the 550-megawatt coal-fired power plant (Boardman); 70,000 CAFO (Threemile Canyon) lie on the eastern end. Seasonal winds from the west in the summer and east in the winter (Green et al. 2006) create an ambient flow tube with unique chemical footprints. Transformation of the Nr species creates an

air pollution gradient spanning 260 km. The unique nature of the CRG as a natural laboratory allows us to investigate source impact to the nearby non-urban landscape (Figure 1). Additional measurements were co-located at the Mt. Zion and Wishram monitoring stations to gain a better understanding of the reactive N in the Columbia River Gorge (see Figure 11 for added measurements circled in dashed green lines). In addition to continuous monitoring in fixed locations, a passive sampling campaign was conducted in the summer of 2016 to gain an understanding of the spatial extent of the reactive N in the CRG.

Observations

Ambient measurements were co-located at IMPROVE site CORI1 (Wishram) and COGO1 (Mt. Zion) located within the Columbia River Gorge in Washington State (Figure 5). NO_x-NO chemiluminescence gas analyzer and an O₃ UV absorbance analyzer was set up at COGO1 from June - October 2010; July – October 2011; and September 2015 – August 2016. NO_x-NO chemiluminescence gas analyzer and an O₃ UV absorbance analyzer was set up at Wishram from December 2012- August 2016. In order to account for total oxidized nitrogen (NO_y) interference in the molybdenum converter of the NO_x-NO analyzer, the NO₂ concentrations were adjusted according to Steinbacher et al. 2007. Meteorological measurements of temperature, relative humidity, wind speed, and wind direction were also collected at Mt. Zion and Wishram at the dates listed above.

Annular denuder measurements (Figure 12) in March, April, July and August were collected at co-located Mt. Zion, Wishram, and in Portland, OR. The annular denuder was in-line with a 2-stage filter using Nylasorb and Teflon filters for the

measurement of $\text{NH}_3(\text{g})$, $\text{HNO}_3(\text{g})$, and $\text{PM}_{2.5}$ ammonium sulfate and ammonium nitrate, $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . An annular denuder coated with sodium carbonate solution was used for the collection of HNO_3 and phosphoric acid for the collection of NH_3 . The Teflon filters were extracted for $\text{PM}_{2.5}$ ammonium sulfate and ammonium nitrate and the Nylasorb filters were extracted for any volatilized $\text{PM}_{2.5}$ nitrate. Annular denuder and filter extracts were analyzed using a Dionex Ion Chromatography ICS-5000 using the AS-18 with 39 mM potassium chloride eluent and CS-12 column with 20 mM methanesulfonic acid eluent. We compared our dry deposition estimates to the bulk and throughfall deposition from October 2003-March 2004 reported by Fenn et al. 2007. Bulk deposition is measured in open areas with a funnel and rain collector, and is a measure of dry deposition to the funnel and wet deposition through precipitation. Throughfall deposition was collected using a funnel and an ion exchange column under Ponderosa pine canopies and is during rain events, dry deposition from the funnel and canopy are collected in the column.

Figure 12. Annular denuder and filter pack sample set up.

OgawaUSA passive NO_x and NO₂ samplers were used in four deployments from July through September 2016 at over 20 sites in the Columbia River Basin area (Figure 13). Observations of NO_x and NO₂ were made over 7-14 days. UV-spectrometer was used to analyze the NO_x and NO₂ OgawaUSA sample extracts and perform well against Federal Reference Method for nitrogen dioxide in this region (Rao et al. 2014).

Figure 13. Map of OgawaUSA passive sampler locations in Columbia Basin (black markers). Colored markers reflect Mt. Zion (blue), Wishram (green), Boardman (orange) and Threemile CAFO (purple).

The IMPROVE network was established in 1988 across the United States to monitor trends in visibility (Malm and Hand 2007). The EPA's PM_{2.5} National Chemical Speciation Network (CSN) was established in urban areas across the United States to monitor for speciation trends (Agency 1999). At both IMPROVE and CSN sites, surface concentrations of fine particulate (PM_{2.5}) ammonium sulfate, (NH₄)₂SO₄, and ammonium nitrate, NH₄NO₃, are measured as 24-hour averages every third day. Data from IMPROVE sites Mt. Zion and Wishram was downloaded from 2001-2011 and 2000-2015, respectively. Data from Oregon DEQ's SE Lafayette regulatory station and CSN station was downloaded from 2000-2015. Data from the US EPA's Air Markets Program was downloaded for Boardman Coal-fired power plant hourly emissions.

Model comparison

Washington State University's AIRPACT-5 chemistry transport model (<http://www.lar.wsu.edu/airpact>) was used to compare passive NO_x sampling observations. AIRPACT-5 is a forecast model to predict air quality in the states of

Oregon, Idaho, and Washington. AIRPACT-5 uses Community Model for Air Quality (CMAQ) an EPA chemical transport model with improved emissions and model parameters for the Pacific Northwest. Grid resolution of AIRPACT-5 is 4 km by 4 km.

N partitioning and SIA formation

In order to determine if the Nr SIA formation is limited by gas-phase ammonia or nitric acid, excess ammonia (EA) was determined through R3 (Blanchard et al. 2000), where each reactive N species is in units of $\mu\text{mol}/\text{m}^3$:

$$EA = NH_{3(g)} + NH_4^+ - 2SO_4^{2-} - NO_3^- - HNO_{3(g)} \quad (\text{R3})$$

If EA is > 0 , there is excess reduced N and therefore SIA formation is limited by gas-phase nitric acid or oxidized sulfur. If $EA < 0$, there is excess oxidized N or S and therefore SIA formation is limited by $NH_{3(g)}$.

N deposition

Deposition velocities and measured ambient concentrations from annular denuder with filter-pack and NO_x -NO chemiluminescence analyzer measurements were used to estimate the dry N deposition rates as described by (Wu et al. 2011) where deposition is defined by the concentration of reactive N species multiplied by the species specific deposition velocity. Deposition velocity ranges using from estimates over United States were used (Zhang et al. 2012) (Table 3). The variation in the properties of Nr species lead to a range of deposition velocities. Nitric acid and ammonia deposit at a faster deposition velocity than particulate nitrate and sulfate.

Table 3. Range of deposition velocities used for estimating deposition flux by reactive N species (Zhang et al 2012)

Species	Deposition velocity
Gas-phase NH_3	0.20 - 0.65 cm/s
PM NH_4^+	0.15 cm/s
Gas-phase HNO_3	0.6 – 2.7 cm/s
PM NO_3^-	0.15 cm/s
Gas-phase NO_2	0.3 – 0.36 cm/s

Results

Reactive N partitioning and secondary inorganic aerosol formation

Annular denuder and 2-stage filter pack observations show elevated gas-phase reactive N in March and April, and lower levels in July and August (Figure 14, Figure 15, Table 4). Ammonia peaked at 15 ppbv at Wishram in April and nitric acid peaked in April at 8 ppbv. In Mt. Zion, ammonia ranged from 0-7 ppbv and nitric acid ranged from 0-5 ppbv in the spring. $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 are higher concentrations in March and April, with lower levels in July and August, consistent with historical measurements at the IMPROVE sites. In the summer, Wishram and Mt. Zion nitric acid concentrations were less than 1 ppbv and ammonia measurements were less than 2 ppbv.

Table 4. Annular denuder and filter pack measurements. Spring measurements are shaded in light blue. Summer measurements are shaded in red. <DL denotes concentrations where the observation was less than the detection limit.

Date	Site	HNO ₃ (ppb)	NH ₃ (ppb)	(NH ₄) ₂ SO ₄ (µg/m ³)	NH ₄ NO ₃ (µg/m ³)
3/28/2016	WISH	0.1	1	0.4	NA
3/29/2016	MZ	0.1	2	<DL	<DL
3/29/2016	WISH	0.2	3	0.8	0.9
3/30/2016	MZ	0.4	7	<DL	1.0
3/30/2016	WISH	0.5	4	1.2	1.3
4/6/2016	MZ	2.7	7	0.0	1.3
4/6/2016	WISH	5.5	15	0.3	1.7
4/7/2016	MZ	3.9	5	0.0	1.4
4/7/2016	WISH	6.4	9	0.4	1.5
4/8/2016	MZ	5.3	4	<DL	1.8
4/8/2016	WISH	7.4	6	<DL	1.5
4/9/2016	MZ	3.0	3	<DL	1.9
4/9/2016	WISH	5.8	2	0.1	0.4
7/13/2016	MZ	0.2	2	0.3	<DL
7/13/2016	WISH	0.3	1	0.3	<DL
7/15/2016	MZ	0.2	1	0.6	<DL
7/15/2016	WISH	0.2	0	0.3	<DL
7/31/2016	MZ	0.0	1	0.3	<DL
7/31/2016	WISH	0.1	0	0.0	<DL
8/8/2016	MZ	0.4	0	0.2	<DL
8/8/2016	WISH	0.4	0	0.3	<DL

Figure 14. Wishram spring annular denuder and filter measurements and continuous monitoring during annular denuder sampling period. NOz = NOy – NOx.

Figure 15. Mt. Zion summer annular denuder and filter measurements and continuous monitoring during annular denuder sampling period. $\text{NO}_x = \text{NO}_y - \text{NO}_x$.

Table 5 shows the EA in $\mu\text{mol}/\text{m}^3$ from the annular denuder and filter measurements. During the spring, SIA is mostly limited by gas phase nitric acid or oxidized sulfur. During the summer, SIA formation is limited by gas phase ammonia. The EA seasonality demonstrates the importance of understanding the pre-cursor regimes over the course of a year, as management implications will vary depending on the EA limiting species.

Table 5. Excess ammonia (EA, $\mu\text{mol}/\text{m}^3$) by date and site. Positive values (in black text) represent excess ammonia. Negative values (in red text) represent excess nitric acid or sulfuric acid in SIA formation of ammonium nitrate and ammonium sulfate.

Date	Excess ammonia ($\mu\text{mol}/\text{m}^3$)		
	Portland	Mt. Zion	Wishram
3/28/2016	-0.03	No data	0.17
3/29/2016	0.20	0.06	0.10
3/30/2016	0.67	0.27	0.13
4/6/2016	0.10	0.15	0.36
4/7/2016	0.14	0.03	0.08
4/8/2016	0.32	-0.07	-0.06
4/9/2016	0.12	0.00	-0.19
7/13/2016	-0.09	-0.05	-0.05
7/15/2016	-0.14	-0.04	-0.30
7/31/2016	-0.07	0.00	-0.18
8/8/2016	-0.17	-0.06	-0.02

Dry N deposition in the near source confluence

Daily total dry N deposition, as estimated by deposition velocities and ambient observations of gas and aerosol phase reactive N, ranged from 0 – 0.14 kg N/ha (Table 6)

from our sampling from March through August 2017. Dry deposition was highest in Wishram and Portland and lowest at Mt. Zion. Deposition, like the reactive N concentrations, was higher in March and April than during July and August. Dry deposition estimates from our annular denuder and filter measurements are similar in magnitude at both western and eastern ends of the CRG as bulk and throughfall deposition measurements from Fenn et al. 2007, which ranged from 0.008 – 0.10 kg N/ha per day from October 2003 – March 2004.

Table 6. Estimated daily dry N deposition (kg N/ha) by date and site from this study and Fenn et al 2007. Estimates from this study are calculated ambient concentrations and deposition velocities in Table 3. Estimated daily deposition from Fenn et al 2007 is total deposition divided by number of days of deposition collection at western and eastern sites in CRG.

	This study: Estimated Dry N Daily Deposition (kg N/ha)			Fenn et al 2007: Estimated Daily Deposition (kg N/ha)	
	Portland	Mt. Zion (west)	Wishram (east)	Western CRG	Eastern CRG
Throughfall Oct 2003 – Mar 2004	-	-	-	0.059	0.10
Bulk Oct 2003 – Mar 2004	-	-	-	0.013	0.008
3/28/2016	0.02	No data	No data	-	-
3/29/2016	0.03-0.04	0.04-0.05	0.02	-	-
3/30/2016	0.08-0.09	0.03-0.04	0.03-0.04	-	-
4/6/2016	0.05-0.10	0.03-0.06	0.07-0.14	-	-
4/7/2016	0.05-0.11	0.03-0.07	0.06-0.13	-	-
4/8/2016	0.06-0.11	0.03-0.09	0.05-0.13	-	-
4/9/2016	0.03-0.06	0.02-0.05	0.03-0.09	-	-
7/13/2016	0.02-0.03	0.01	0.01	-	-
7/15/2016	0.02	0.01	0.02-0.03	-	-
7/31/2016	0.01	0.01	No data	-	-
8/8/2016	0.02-0.04	0.01	0.02	-	-

Table 7 shows the mean dry N deposition contribution by species and site from our study and compares to fraction of reduced ($\text{NH}_4\text{-N}$) and oxidized ($\text{NO}_3\text{-N}$) deposition contribution to Fenn et al. 2007 study. NO_2 deposition is roughly a third of the total dry N deposition in Portland and Wishram. Nitric acid dry deposition in Mt. Zion and Wishram were the largest contributor to Nr dry deposition. Gas-phase ammonia deposition was largest fraction in Portland and Mt. Zion during 2017. Mt. Zion was located near a small cattle grazing field and Portland vehicle traffic likely led to the high ammonia deposition in the city. The $\text{PM}_{2.5}$ ammonium nitrate and ammonium sulfate had the lowest contribution to total dry deposition, at less than 15% at all three locations.

Table 7. Dry N deposition mean fraction by site and species from this study and Fenn et al. 2007 fraction of reduced and oxidized N in bulk and throughfall deposition.

	This study: March, April, July, August 2017				Fenn et al. 2007: late October 2003 – early March 2004	
Site	Mean fraction NO_2	Mean fraction NH_3	Mean fraction HNO_3	Mean fraction $\text{NH}_4\text{NO}_{3(s)}$ and $(\text{NH}_4)_2\text{SO}_{4(s)}$	Mean fraction $\text{NO}_3\text{-N}$	Mean fraction $\text{NH}_4\text{-N}$
Portland	0.35	0.30	0.28	0.07	0.65	0.34
Mt. Zion	0.26	0.27	0.39	0.08	0.68	0.32
Wishram	0.34	0.18	0.36	0.12	0.75	0.25
Western CRG	-	-	-	-	0.65 throughfall	0.35 throughfall
					0.47 bulk	0.53 bulk
Eastern CRG	-	-	-	-	0.43 throughfall	0.57 throughfall
					0.56 bulk	0.44 bulk

Fenn et al. 2007 reported 65% $\text{NO}_3\text{-N}$ throughfall deposition and 35% $\text{NH}_4\text{-N}$ throughfall deposition at the western end of the CRG. We reported 68% $\text{NO}_3\text{-N}$ oxidized

and 32% $\text{NH}_4\text{-N}$ at Mt. Zion. Fenn reported 43% $\text{NO}_3\text{-N}$ and 57% $\text{NH}_4\text{-N}$ throughfall deposition at the eastern end of the CRG. We reported 75% $\text{NO}_3\text{-N}$ and 25% $\text{NH}_4\text{-N}$ during our study period. The difference between Fenn's throughfall deposition and our dry deposition is likely due to difference in season: Fenn's study was conducted with predominantly easterly winds and our study was conducted with some easterly in March but more westerly winds in the summer sampling months. Reduced N deposition is more prevalent with easterly winds carrying the CAFO emissions from the east, and the ammonia source contribution is seen more in Fenn's deposition measurements.

Model performance of reactive N in the CRG

To determine how well the regional transport models can simulate NO_2 over the broader region, we deployed passive samplers across 20 different sites over 4 deployments in summer and fall 2016. NO_2 was elevated up to 20 ppbv in the greater Columbia Basin. We compared our NO_x results from passive sampling over four deployments to Washington State University's AIRPACT-5, a regional air quality forecasting model with improved emissions for the region when compared to the NEI-2011. NO was under-predicted in AIRPACT-5, with forecasted concentrations ranging from 0-1 ppbv NO, whereas observations ranged from 0-25 ppbv NO. NO_2 was also under-predicted at concentrations ranging from 0-5 ppbv NO_2 when observations ranged 0-20 ppbv (Figure 16).

Figure 16. Ogawa passive O₃, NO, and NO₂ observations from summer 2016 at 20 different sites across the Columbia River Basin vs AIRPACT-5 predictions.

Dry N deposition comparison

Without accurate predictions of reactive N in the CRG, dry deposition simulations cannot be accurate either. Monthly total dry deposition estimate from AIRPACT-5 are on the same order of magnitude as daily dry N deposition estimates from this study (Table 6, Figure 17).

Figure 17. AIRPACT-5 imagery for March 2016 total dry N deposition, legend is average daily N deposition for month of March 2016. Accessed October 2016.

Discussion

The missing gaseous Nr

The results from this study indicate there is a unique opportunity to use the CRG as an environmental flow tube with bimodal wind flow to investigate the gradient of reactive N partitioning and deposition. Our results show that models are missing key reactive N gas-phase species in the CRG which can result in a misrepresentation of impacts such as their role in SIA and in under-predicting dry N deposition. Models are under-predicting NO_x in the whole Columbia River Basin (Figure 16), which can lead to secondary pollutants and their impacts being under-represented as well. This bias could be from emissions in the region or from difficulty in representing the transport in this highly complex river gorge and basin area (O'Neill et al. 2006). The results from the NO_x passive sampling from summer 2016 indicate that gas phase Nr emissions are under-represented across the region, resulting in under-predicted NO and NO₂ and the secondary pollutants in Figure 11.

While ecological studies and CTMs suggest that there is little gas-phase reactive N in the region, our study shows that gas phase Nr is present and often dominating total reactive N. Our data suggests that while lichen air scores may strongly correlate with PM speciation data, that doesn't necessarily suggest that PM dominates dry deposition. PM data may only be used as a proxy for the total reactive N, as the PM speciation data is in thermodynamic equilibrium with gas phase reactive N. There are known biases in CTM simulations of reactive N species (Heald et al. 2012; Walker et al. 2012; Markovic et al. 2014), and without validating the region's reactive N emissions observations, dry N

deposition will likely be under-predicted. Further, it is important to understand both oxidized and reduced Nr species, as the deposition, transformations, and haze implications are dependent upon a complex and dynamic relationship between many players (Figure 11). Monitoring for the contribution of reactive N to deposition and partitioning is especially important with the seasonally driven wind flow with distinct sources at each end of the CRG: there is a seasonal pattern evident in the partitioning of reactive N to particles and the contribution of reactive N to deposition.

Management implications

SIA formation in the CRG is a concern as it is a National Scenic Area. However, to effectively manage the visibility, it is important to understand the contribution of PM speciation to light extinction. During the worst 20% of visibility days at Wishram $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 contribute to roughly half of the light extinction (<http://vista.cira.colostate.edu/Improve>). Without both gas and particle phase reactive N, it is not possible to know what is limiting the formation of more Nr SIA. This study shows there is seasonality in whether SIA formation is nitric acid or ammonia limited. In the spring, there is excess ammonia. This could suggest there are more spring-time sources of ammonia in the region such as fertilizer application. In the summer, the EA for SIA formation is the opposite. There is excess nitric acid and ammonia is limiting further SIA. This could be explained by fewer NH_3 emissions in the summer or a renoxification of Nr reservoirs undergoing thermal dissociation during the warmer summer months.

In order to understand SIA formation in any given region, it is important to have an understanding of the patterns of NH_3 , NO_x , and SO_2 in tandem, as each species plays

an integral role in SIA formation. In addition to haze from the SIA formation, reactive N plays a role in acid deposition. Any HNO_3 left un-neutralized will deposit via wet or dry deposition. This acid deposition could cause damage to ecosystems cultural artifacts in the CRG such as rock petroglyphs and paintings. The important players in reactive N deposition vary not just based on location within the CRG but within each season. Our results suggest higher amounts of oxidized reactive N deposition at the eastern end of the CRG during spring and summer whereas Fenn et al. 2007 results show a more equal contribution of oxidized and reduced N deposition during fall and winter months.

Conclusions

Our 24-hour measurements of HNO_3 ranged from 0 – 8 ppbv at Wishram and 0-6 ppbv at Mt. Zion. NH_3 ranged from 0 – 15 ppbv at Wishram and 0-7 ppbv at Mt. Zion. We found that gas-phase NO and NO_2 is under-predicted by model simulations and that ammonia and nitric acid measurements are crucial in managing acid deposition and the formation of haze in the natural environment. There are temporal variations of precursors to SIA formation and it is important to understand the seasonality of the limiting precursor to SIA formation. In the CRG, SIA is limited by ammonia in the summer and by nitric acid in the spring.

Managers and researchers alike cannot rely on PM speciation data solely to explain N dry deposition and other reactive nitrogen impacts to the ecosystem and visibility. It is crucial to have gas phase reactive N measurements to fully understand the impact of both SIA formation and deposition in the near source confluence. In the CRG, the eastern coal-fired power plant and the CAFO influence ambient reactive N during

November through February when easterly winds dominate. In the summer, there is a western influence on nitrate and sulfate fine particle mass concentrations on the CRG. It is especially important to monitor for ammonia, as it is not a regulated pollutant and NH_3 inputs into a region need to be compared to observations for a more complete understanding of local and regional NH_3 impacts. In the CRG, gas-phase reactive N plays the largest role in dry deposition, with particulate Nr contributing at 12% or less to total daily dry N deposition at all three study sites. Future studies could investigate longer term seasonal and diurnal gas phase NH_3 and HNO_3 in the CRG to better establish patterns of SIA formation in the Columbia River Gorge. This is important with future emission projections from fuel changes to eastern source Boardman Coal-fired power plant and the addition of another CAFO located adjacent to the Interstate-84 along the Columbia River, adding even more ammonia into the region (“CAFO permit issued to Lost Valley Farm”, 2017).

Final discussion and future directions

With the loss of sensitive lichen species in the Columbia River Gorge and the increasing N fixation rates in the United States, it is important to understand the impacts of these rates to our environment and ecosystem services. It is not enough to monitor in urban and remote areas. Measurements and observations in the areas downwind of sources are necessary to understand the consequences of increased ambient reactive nitrogen. This research examined the ambient reactive N gradient within the Columbia River Gorge that was created from a unique bimodal wind distribution and fingerprint of sources to understand Nr pathways to aerosol formation and N deposition as well as comparisons to well-used regional chemical transport models. Our findings are important for understanding reactive N dry deposition and the impacts they may have on critical loads and sensitive ecosystems as well as cultural artifacts throughout the traditional tribal areas.

We found that there is elevated reactive N in the CRG, especially with respect to days with predominantly easterly winds. Located at the eastern ends are Boardman coal-fired power plant and Threemile Canyon CAFO. These two sources influence ammonium, nitrate, and nitrogen dioxide concentrations at Wishram and Mt. Zion, located over 80 and 160 km away, respectively.

We also found that the western sources influence the air pollution gradient during predominantly westerly winds. Located to the west of the CRG are Portland-Vancouver metropolitan area and Georgia Pacific pulp and paper industry. These western sources influence levels of PM_{2.5} sulfate and nitrate at Mt. Zion and Wishram. However, the

magnitude of the western sources to the reactive N in the CRG is not as large as the influence of the eastern sources.

Our results suggest there is seasonality in reactive N partitioning. Depending on season, secondary inorganic aerosol formation may be limited by either nitric acid or ammonia. In the spring, SIA formation is mostly limited by nitric acid and in the summer, it is mostly limited by ammonia. With further exploration into gas and aerosol phase reactive N, we found that gas-phase reactive N is playing a key role in dry N deposition. This contribution to total N deposition has implications for ecosystem biodiversity as well as potential for acid deposition when nitric acid isn't fully neutralized. Sensitive species are already disappearing in the CRG and we need to understand Nr impacts to develop mitigation strategies for the proper emissions and precursors.

Finally, we discovered that models are under-predicting gas-phase reactive N in the region. This difficulty is not isolated to a single site within the CRG, but throughout the whole Columbia River Basin. The missing gas-phase Nr is causing us to under-represent the emissions impacts on dry N deposition throughout the region. Models are biased in this region from poor emission budgets and could be improved from these observations.

Managers can use this information to understand the impacts to the ecosystem as well as developing mitigation strategies for the formation of haze in the CRG's National Scenic Area and in understanding the impacts of acid deposition to the natural landscape. Future work could focus on the diurnal and seasonal patterns of Nr chemistry in this gradient and investigate the impacts of future emissions changes such as the proposed

changes to Boardman coal-fired power plant and the addition of another confined animal feeding operation along Interstate 84 near the Columbia River. Additionally, further research could incorporate observations to improve regional transport models to improve efficiency and decrease bias.

References

- Agency, U.S. Environmental Protection. 1999. "Data Quality Objectives for the Trends Component of the PM 2.5 Speciation Network."
<http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec/dqo3>.
- Baker, Kirk, and Peter Scheff. 2007. "Photochemical Model Performance for PM2.5 Sulfate, Nitrate, Ammonium, and Precursor Species SO₂, HNO₃, and NH₃ at Background Monitor Locations in the Central and Eastern United States." *Atmospheric Environment* 41 (29): 6185–95. doi:10.1016/j.atmosenv.2007.04.006.
- Behera, Sailesh N., Raghu Betha, and Rajasekhar Balasubramanian. 2013. "Insights into Chemical Coupling among Acidic Gases, Ammonia and Secondary Inorganic Aerosols." *Aerosol and Air Quality Research* 13 (4): 1282–96. doi:10.4209/aaqr.2012.11.0328.
- Bettez, Neil D., Roxanne Marino, Robert W. Howarth, and Eric A. Davidson. 2013. "Roads as Nitrogen Deposition Hot Spots." *Biogeochemistry* 114 (1–3): 149–63. doi:10.1007/s10533-013-9847-z.
- Blanchard, C L, P M Roth, S J Tanenbaum, S D Ziman, and J H Seinfeld. 2000. "The Use of Ambient Measurements to Identify Which Precursor Species Limit Aerosol Nitrate Formation." *Journal of the Air & Waste Management Association (1995)* 50 (12): 2073–84. doi:10.1080/10473289.2000.10464239.
- "CAFO permit issued to Lost Valley Farm". www.oregon.gov. 31 Mar 2017. Web. 18 May 2017.
- Compton, Jana E, John a Harrison, Robin L Dennis, Tara L Greaver, Brian H Hill, Stephen J Jordan, Henry Walker, and Holly V Campbell. 2011a. "Ecosystem Services Altered by Human Changes in the Nitrogen Cycle: A New Perspective for US Decision Making." *Ecology Letters* 14 (8): 804–15. doi:10.1111/j.1461-0248.2011.01631.x.
- Deng, Jia, Changsheng Li, and Ying Wang. 2015. "Modeling Ammonia Emissions from Dairy Production Systems in the United States." *Atmospheric Environment* 114. Elsevier Ltd: 8–18. doi:10.1016/j.atmosenv.2015.05.018.
- Fenn, M, L Geiser, R Bachman, T Blubaugh, and a Bytnerowicz. 2007. "Atmospheric Deposition Inputs and Effects on Lichen Chemistry and Indicator Species in the Columbia River Gorge, USA." *Environmental Pollution* 146 (1): 77–91. doi:10.1016/j.envpol.2006.06.024.
- Fenn, Mark E, and Mark A Poth. 2007. "Atmospheric Pollutants and Trace Gases Monitoring Nitrogen Deposition in Throughfall Using Ion Exchange Resin Columns : A Field Test in the San Bernardino Mountains," 2007–14.
- Galloway, James N, John D Aber, Jan Willem Erisman, Sybil P Seitzinger, W Howarth, Ellis B Cowling, B Jack Cosby, and J A N Willem. 2003. "The Nitrogen Cascade." *BioScience* 53 (4): 341–56.
- Geiser, Linda H., and Peter N. Neitlich. 2007. "Air Pollution and Climate Gradients in Western Oregon and Washington Indicated by Epiphytic Macrolichens." *Environmental Pollution* 145 (x): 203–18. doi:10.1016/j.envpol.2006.03.024.
- Geiser, Linda H, Sarah E Jovan, Doug a Glavich, and Matthew K Porter. 2010. "Lichen-

- Based Critical Loads for Atmospheric Nitrogen Deposition in Western Oregon and Washington Forests, USA.” *Environmental Pollution (Barking, Essex : 1987)* 158 (7). Elsevier Ltd: 2412–21. doi:10.1016/j.envpol.2010.04.001.
- Greaver, Tara L, Timothy J Sullivan, Jeffrey D Herrick, Mary C Barber, Jill S Baron, Bernard J Cosby, Marion E Deerhake, et al. 2012a. “Ecological Effects of Nitrogen and Sulfur Air Pollution in the US: What Do We Know?” *Frontiers in Ecology and the Environment* 10 (7): 365–72. doi:10.1890/110049.
- Green, Mark, Narendra Adhikari, Jin Xu, and George Nikolich. 2006. “Columbia River Gorge Haze Gradient Study.”
- Green, Mark C., Jin Xu, and Narendra Adhikari. 2008. “Transport of Atmospheric Aerosol by Gap Winds in the Columbia River Gorge.” *Journal of Applied Meteorology and Climatology* 47 (1): 15–26. doi:10.1175/2007JAMC1561.1.
- Grell, Georg A, Steven E Peckham, Rainer Schmitz, Stuart A Mckeen, Gregory Frost, William C Skamarock, and Brian Eder. 2005. “Fully Coupled “online ” Chemistry within the WRF Model” 39: 6957–75. doi:10.1016/j.atmosenv.2005.04.027.
- Harrison, Roy M., and a.-M.N. Kitto. 1990. “Field Intercomparison of Filter Pack and Denuder Sampling Methods for Reactive Gaseous and Particulate Pollutants.” *Atmospheric Environment. Part A. General Topics* 24 (10): 2633–40. doi:10.1016/0960-1686(90)90142-A.
- Heald, C. L., J. L. Collett, T. Lee, K. B. Benedict, F. M. Schwandner, Y. Li, L. Clarisse, et al. 2012. “Atmospheric Ammonia and Particulate Inorganic Nitrogen over the United States.” *Atmospheric Chemistry and Physics* 12: 10295–312. doi:10.5194/acp-12-10295-2012.
- Heald, C. L., T. Lee, K. B. Benedict, F. M. Schwandner, Y. Li, L. Clarisse, D. R. Hurtmans, et al. 2012. “Atmospheric Ammonia and Particulate Inorganic Nitrogen over the United States.” *Atmospheric Chemistry and Physics* 12 (21): 10295–312. doi:10.5194/acp-12-10295-2012.
- Houlton, Benjamin Z., Elizabeth Boyer, Adrien Finzi, James Galloway, Allison Leach, Daniel Liptzin, Jerry Melillo, Todd S. Rosenstock, Dan Sobota, and Alan R. Townsend. 2012a. “Intentional versus Unintentional Nitrogen Use in the United States: Trends, Efficiency and Implications.” *Biogeochemistry* 114 (1–3): 11–23. doi:10.1007/s10533-012-9801-5.
- Houlton, Benjamin Z, Elizabeth Boyer, Adrien Finzi, James Galloway, Allison Leach, Daniel Liptzin, Jerry Melillo, Todd S Rosenstock, Dan Sobota, and Alan R Townsend. 2012b. “Intentional versus Unintentional Nitrogen Use in the United States: Trends, Efficiency and Implications.” *Biogeochemistry* 114 (1–3): 11–23. doi:10.1007/s10533-012-9801-5.
- Jaffe, D. a., and D. R. Reidmiller. 2009. “Now You See It, Now You Don’t: Impact of Temporary Closures of a Coal-Fired Power Plant on Air Quality in the Columbia River Gorge National Scenic Area.” *Atmospheric Chemistry and Physics Discussions* 9 (3): 14235–61. doi:10.5194/acpd-9-14235-2009.
- Malm, William C., and Jenny L. Hand. 2007. “An Examination of the Physical and Optical Properties of Aerosols Collected in the IMPROVE Program.” *Atmospheric Environment* 41 (16): 3407–27. doi:10.1016/j.atmosenv.2006.12.012.

- Markovic, M.Z., T.C. VandenBoer, K.R. Baker, J.T. Kelly, and J.G. Murphy. 2014. "Measurements and Modeling of the Inorganic Chemical Composition of Fine Particulate Matter and Associated Precursor Gases in California's San Joaquin Valley during CalNex 2010." *Journal of Geophysical Research: Atmospheres* 3 (3): 6853–66. doi:10.1002/2013JD021408. Received.
- Norman, M, C Spirig, V Wolff, I Trebs, C Flechard, A Wisthaler, R Schnitzhofer, and A Hansel. 2009. "Intercomparison of Ammonia Measurement Techniques at an Intensively Managed Grassland Site (Oensingen , Switzerland)." *Atmospheric Chemistry and Physics* 4: 2635–45.
- O'Neill, Susan M, Brian K Lamb, Jack Chen, Candis Claiborn, Dennis Finn, Sally Otterson, Cristiana Figueroa, et al. 2006. "Modeling Ozone and Aerosol Formation and Transport in the Pacific Northwest with the Community Multi-Scale Air Quality (CMAQ) Modeling System." *Environmental Science & Technology* 40 (4): 1286–99. <http://www.ncbi.nlm.nih.gov/pubmed/16572788>.
- Pardo, Linda H., Mark E. Fenn, Christine L. Goodale, Linda H Geiser, Charles T. Driscoll, Edith B. Allan, Jill S. Baron, et al. 2011a. "Effects of Nitrogen Deposition and Empirical Nitrogen Critical Loads for Ecoregions of the United States." *Ecological Applications* 21 (8): 3049–82.
- Pardo, Linda H, Mark E Fenn, Christine L Goodale, Linda H Geiser, Charles T Driscoll, Edith B Allan, Jill S Baron, et al. 2011b. "Effects of Nitrogen Deposition and Empirical Nitrogen Critical Loads for Ecoregions of the United States." *Ecological Applications* 21 (8): 3049–82.
- Pope, C. Arden, and Douglas W. Dockery. 2006. "Health Effects of Fine Particulate Air Pollution: Lines That Connect." *Journal of the Air & Waste Management Association* 56 (6): 709–42. doi:10.1080/10473289.2006.10464485.
- Rao, Meenakshi, Linda a George, Todd N Rosenstiel, Vivek Shandas, and Alexis Dinno. 2014. "Assessing the Relationship among Urban Trees, Nitrogen Dioxide, and Respiratory Health." *Environmental Pollution (Barking, Essex : 1987)* 194 (November). Elsevier Ltd: 96–104. doi:10.1016/j.envpol.2014.07.011.
- Root, Heather T., Linda H. Geiser, Sarah Jovan, and Peter Neitlich. 2015. "Epiphytic Macrolichen Indication of Air Quality and Climate in Interior Forested Mountains of the Pacific Northwest, USA." *Ecological Indicators* 53. Elsevier Ltd: 95–105. doi:10.1016/j.ecolind.2015.01.029.
- Schell, Benedikt, Ingmar J. Ackermann, Heinz Hass, Francis S. Binkowski, and Adolf Ebel. 2001. "Modeling the Formation of Secondary Organic Aerosol within a Comprehensive Air Quality Model System." *Journal of Geophysical Research: Atmospheres* 106 (D22): 28275–93. doi:10.1029/2001JD000384.
- Schwab, James J., Yongquan Li, Min-Suk Bae, Kenneth L. Demerjian, Jian Hou, Xianliang Zhou, Bjarne Jensen, and Sara C. Pryor. 2007. "A Laboratory Intercomparison of Real-Time Gaseous Ammonia Measurement Methods." *Environmental Science & Technology* 41 (24): 8412–19.
- Seinfeld, John H, and Spyros N. Pandis. 1998. *Atmospheric Chemistry and Physics*. New York: John Wiley and Sons.
- Sharp, Justin, and Clifford F. Mass. 2004. "Columbia Gorge Gap Winds: Their

- Climatological Influence and Synoptic Evolution.” *Weather and Forecasting* 19 (6): 970–92. doi:10.1175/826.1.
- Sillman, Sanford. 1999. “The Relation between Ozone, NO_x and Hydrocarbons in Urban and Polluted Rural Environments.” *Atmospheric Environment* 33 (12): 1821–45. doi:10.1016/S1352-2310(98)00345-8.
- Steinbacher, Martin, C. Zellweger, B. Schwarzenbach, S. Bugmann, B. Buchmann, C. Ordóñez, A. S H Prevot, and C. Hueglin. 2007. “Nitrogen Oxide Measurements at Rural Sites in Switzerland: Bias of Conventional Measurement Techniques.” *Journal of Geophysical Research Atmospheres* 112 (11): 1–13. doi:10.1029/2006JD007971.
- Walker, J. M., S. Philip, R. V. Martin, and J. H. Seinfeld. 2012. “Simulation of Nitrate, Sulfate, and Ammonium Aerosols over the United States.” *Atmospheric Chemistry and Physics* 12 (22): 11213–27. doi:10.5194/acp-12-11213-2012.
- Williams, E.J., S.T. Sandholm, J.D. Bradshaw, J.S. Schendel, A.O. Langford, P.K. Quinn, P.J. LeBel, et al. 1992. “An Intercomparison of Five Ammonia Measurement Techniques.” *Journal of Geophysical Research* 97 (D11): 11591–611.
- Wu, Zhiyong, Xuemei Wang, Fei Chen, Andrew a. Turnipseed, Alex B. Guenther, Dev Niyogi, Umarporn Charusombat, Beicheng Xia, J. William Munger, and Kiran Alapaty. 2011. “Evaluating the Calculated Dry Deposition Velocities of Reactive Nitrogen Oxides and Ozone from Two Community Models over a Temperate Deciduous Forest.” *Atmospheric Environment* 45 (16). Elsevier Ltd: 2663–74. doi:10.1016/j.atmosenv.2011.02.063.
- Zaveri, Rabul A., and Leonard K. Peters. 1999. “A New Lumped Structure Photochemical Mechanism for Large-Scale Applications.” *Journal of Geophysical Research* 104 (D23): 30387–415.
- Zaveri, Rahul a., Richard C. Easter, Jerome D. Fast, and Leonard K. Peters. 2008. “Model for Simulating Aerosol Interactions and Chemistry (MOSAIC).” *Journal of Geophysical Research* 113 (D13): D13204. doi:10.1029/2007JD008782.
- Zhang, L., D. J. Jacob, E. M. Knipping, N. Kumar, J. W. Munger, C. C. Carouge, a. van Donkelaar, Y. X. Wang, and D. Chen. 2012. “Nitrogen Deposition to the United States: Distribution, Sources, and Processes.” *Atmospheric Chemistry and Physics* 12 (10): 4539–54. doi:10.5194/acp-12-4539-2012.

Appendix A: Supplemental plots from CRG monitoring

As part of this dissertation, the co-located monitoring stations were established outside beyond the previous sections. This appendix section will provide more context of the continuous hourly observations from Mt Zion and Wishram, WA monitoring stations.

Figure A 1. Continuous monitoring from Mt Zion 2010. Data captured as part of Holly Neill's Master's thesis.

Figure A 2 Continuous monitoring from Mt Zion 2011. Data captured as part of Holly Neill's Master's thesis.

Figure A 3. Continuous monitoring from Wishram 2013.

Figure A 4. Continuous monitoring from Wishram 2014

Figure A 5. Continuous monitoring from Wishram 2015.

Figure A 6. Wishram hourly NO_x concentrations and Hourly Boardman NO_x emissions (kg/hr) for all data, data with easterly winds, and data with westerly winds.

Appendix B: Special case study: Mosier train derailment

On 6/3/2016 at 12:30 PM, a 96-car train unit carrying Bakken crude oil derailed at Mosier, Oregon. Sixteen cars derailed at a portion of the tracks that are within 600 feet of the Columbia River. Of the 96 trains, 3 rail cars caught fire (Figure A 7). Rather than allowing crude oil to enter the Columbia River, responders allowed the oil to combust. The oil train cars were under fire from about 12:30 PM on 6/3/2016 and finally extinguished at 2:05 AM 6/4/2016, lasting nearly 10 hours.

Figure A 7. Crude oil plume from Mosier train derailment June 3, 2016.

The Wishram co-located monitoring station was measuring NO_x, O₃, and estimated PM_{2.5} from bscat during this time. The monitoring station is approximately 30 kilometers east of the Mosier train derailment site. Unfortunately, the co-located

measurements were not running at Mt Zion. The estimated PM_{2.5} was calculated using slope and intercept from a Radiance Nephelometer vs a beta attenuation mass monitor in Seattle, WA during the summer, as described in Chow et al. 1995.

The winds at Wishram were NNW and SSE primarily on June 4. On June 5, a larger component of winds were originating in the NNW, SSW, and SWW. Because the winds were not originating from the Mt Zion area on June 3 or June 4, elevated NO₂ and PM_{2.5} was not observed at Wishram until June 5 and June 6 (Figure A 8).

It is estimated that 16,000 gallons of crude oil burned (US EPA PowerPoint). NO₂ and PM_{2.5} are not the only pollutants released during a crude oil fire, however, they can serve as a proxy for other products of crude oil combustion. Nitrogen dioxide at Wishram slowly built up to a broad peak of 27 ppb NO₂ on June 5 and estimated PM_{2.5} had two peaks: one of 34 µg/m³ on June 5 and a second peak on June 6 of 32 µg/m³.

The trail derailment did appear to impact areas even 20 km away from the source, and the broad spike in NO₂ lasted for nearly 24 hours before returning back to lower levels of NO₂. The estimated PM_{2.5} remained elevated for longer than 24 hours after the plume arrived at Wishram.

Figure A 8. Continuous monitoring NO_x, estimated PM_{2.5}, and ozone at Wishram. The first vertical line marks the crude oil ignition and the last vertical line marks the crude fire extinguishing time.

Figure A 9. Wind Roses from June 4 (top), 5 (bottom) at Wishram.

Figure A 10. Wind Rose from June 6 at Wishram.

Figure A 12. Hysplit forwards trajectory from Mosier on June 5, 2016.

Appendix C: Technical report to OR DEQ

Hermiston area ozone study: Using passive samplers to assess ozone and nitrogen oxides in the Columbia River Gorge Basin

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Abstract

Hermiston, a rural town in Oregon, has recently experienced elevated ozone (O_3) concentrations. Due to the limited monitoring in the area, there are no measurements of precursors such as nitrogen oxides (NO_x) in the region. In this study, passive Ogawa samplers were used to measure NO_x and O_3 levels at twenty sites over four deployments from July through September 2016. The measurement campaign revealed areas of elevated NO_x concentrations that were not accounted for in regional model AIRPACT-5. Ozone averages greater than 20 ppbv are represented well in AIRPACT-5, however the model does not represent ozone concentrations ranging from 5-20 ppbv well. This study demonstrates the viability of using passive samplers in order to ground-truth airshed models, especially in remote areas with an absence of monitoring networks.

Introduction

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. Continuous sampling by Oregon Department of Environmental Quality during peak ozone season (2007-present) in Hermiston revealed O₃ levels approaching non-attainment standards set by the Environmental Protection Agency (EPA). The CRG is a large, winding basin featuring the Columbia River. It contains steep elevation changes and diverse vegetation. 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 volatile organic compounds) 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. 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 emission inventories for roadways that are not electronically monitored and

for small area sources. 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 capture the observed elevated O₃ concentrations in Hermiston. The under-prediction of modelled ozone suggests that precursor emissions (NO_x 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 nitrogen oxides across the landscape of interest would be cost-prohibitive. The goals of this project are to: provide cost-effective measurements of nitrogen oxide and ozone across a relatively large region (4400 square kilometers), to assess potential sources of nitrogen oxide precursors and compare measured values to model predictions in order 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 O₃ and NO_x 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 will deploy passive sampling for O₃ and NO_x over four deployments. Passive sampling measurements will be investigated and mapped in conjunction with wind trajectories from HYSPLIT and compared to NO_x point sources from the 2011 National Emissions Inventory data to understand potential O₃ precursors in this region. NO_x passive sampling data will 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.

Methods

For this study, passive Ogawa samplers were used to measure concentrations of ozone and nitrogen oxides in the CRG. Approximately twenty sites were chosen near and within Hermiston, OR and samplers were deployed four times for 7-14 day sampling periods. The sites were chosen based on proximity to Hermiston and likely ozone problem areas or precursor source emissions (Figure A 13). At each site, passive Ogawa samplers were fastened in sampler housings approximately 2m off the 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 U.S.A protocol for NO_x and O₃. Ozone extracts were analyzed using a DIONEX Ion Chromatograph. NO_x extracts were analyzed using a double-beam Shimadzu UV spectrophotometer. The results were then mapped in order to show the spatial extent of ozone and its NO_x precursors. HYSPLIT was utilized in displaying significant wind patterns. The results were compared with fixed site continuous monitors for O₃ as well as compared to NO_x and O₃ 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.

Table A1. Dates of deployment and number of samplers.

Dates of Deployment	Number of Sites	Number of O ₃ samplers	Number of NO _x samplers
D1: 7/11/2016 - 7/18/2016	19	12	19
D2: 7/28/2016 - 8/4/2016	22	21	21
D3: 8/12/2016 - 8/26/2016	21	21	21
D4: 9/24/2016 - 9/30/2016	19	19	19

Figure A 13. Map of NOx emitters in region from 2011 National Emissions Inventory.

Figure A 14. Temporal plot of ozone at the Hermiston Airport. Shaded areas represent D1-D4 deployments.

Results

Precursor nitric oxide ranged from 0-25 ppbv during the sampling periods. The highest levels of nitric oxide were observed in Prosser, WA; Pasco, WA; Wallula, WA; Pendleton, OR and along the Columbia River off US-Highway 730 (Figure A 15, Figure A 16, Figure A 17) during D4. Precursor nitrogen dioxide levels ranged from 0-20 ppbv over the course of the sampling period. Highest levels of nitrogen dioxide were observed in Benton City, WA; Pasco, WA, Hermiston, OR and Pendleton, OR (Figure A 18, Figure A 19) and occurred during D2-D4.

Figure A 15. Nitric oxide concentrations from D2.

Figure A 16. Nitric oxide concentrations from D3.

Figure A 17. Nitric oxide concentrations from D4.

Figure A 18. Nitrogen dioxide results from D1 and D2.

Figure A 19. Nitrogen dioxide results from D3 and D4.

The highest levels of ozone were observed in the Horse Heaven Hills just west of the Columbia River; the Tri-Cities, WA area; Pendleton, OR and Boardman, OR. The

highest level of ozone occurred during D2, 7/28/2016-8/4/2016 in Boardman, eastern side of Horse Heaven Hills, and Pendleton (Figure A 20, Figure A 21). D3 was the second highest ozone period, with highest ozone in the Wallula Gap, the eastern side of Horse Heaven Hills, and the Tri-Cities area. The temporal ozone plot from the Hermiston Airport shows that ozone peaked in late July during in the Hermiston area (Figure A 22).

Figure A 20. Ozone results from D1 and D2.

Figure A 21. Ozone results D3 and D4.

The Columbia River Gorge Basin area was dry and warm during the sample period (Figure A 22). The warmest temperature was during D3. The average temperature for D1, D2, D3, and D4 was 22, 23.9, 24.5, and 17.5 degrees Celsius, respectively.

Figure A 22. Temperature during deployments D1 through D4.

AIRPACT-5 predictions were low for the region during all deployments (Figure A 23) for NO_x . Nitric oxide predictions for the sites were all 0-1 ppbv whereas observations ranged from 0-25 ppbv. NO_2 predictions for the sites were all less than 5 ppbv whereas observations ranged from 0-20 ppbv. Ozone predictions were 25-40 ppbv whereas observations ranged from 0-40 ppbv. Of all species, ozone 7-14 day averaged predictions do fairly well at the greater than 20 ppbv O_3 . However, at 5-20 ppbv O_3 , AIRPACT is over biased.

Figure A 23. AIRPACT predictions vs observations by species and deployment.

Discussion

During D1 and D2, there were some field contamination of the O₃ passive samplers. Condensation built up inside the sampling containers during transport, which is why there are higher limit of detections for D1 and D2. More precaution was taken with D3-D4 with additional sample bags and minimizing exposure to fast temperature differences. Future studies could test using silica packets to help minimize moisture.

The results of this study indicate that there are multiple and complex factors that contribute to the elevated O₃ concentrations in Hermiston and the surrounding area. There

is evidence of a large amount of NO_x in the area that may contribute to the formation of O₃. Additionally, VOCs in the area also contribute to O₃ formation, and to gain a better understanding of the spatial extent of precursors to O₃, VOCs 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.

Figure A 24. D1 HYSPLIT trajectories from Hermiston at 500 m above ground level. Left) Forwards Right) Backwards.

Figure A 25. D2 HYSPLIT trajectories from Hermiston at 500 m above ground level. Left) Forwards Right) Backwards.

The wind in this area constantly shifts, combining O₃ precursors from multiple sources. HYSPLIT model results (Figure A 24, Figure A 25, Figure A 26, Figure A 27) show that the wind for all four deployments come from NW, SW, and NE directions at different heights, allowing for pollutants to be carried in from the CRG and also from Washington and California. The polar plot of mean O₃ by wind direction and wind speed from the Hermiston airport during peak ozone sampling season (July – September 2016), reveals that O₃ formation may actually be traveling in from the northeast and the northwest (Figure A 28). 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.

Figure A 27. HYSPLIT trajectories from Hermiston at 500 m above ground level. Left) Forwards Right) Backwards.

The O_3 problem in the Hermiston area may further be explained by two different regimes regarding NO_x . The two-part regime could be from the transport of NO_x from non-local sources and from local emissions and NO_x sources. Both of these regimes act on this area by contributing to the formation of O_3 in different ways. The 2011 NEI reveals that there are several large NO_x sources near Hermiston. Furthermore, there is also the possibility of unaccounted for NO_x sources in the area from a variety of sources (area or mobile). The NO_x observations in this study suggest that there is a mixture of O_3 precursors traveling via the CRG and as well as localized emissions.

Figure A 28. Polar plot of mean ozone by wind direction and wind speed.

The remote sites in the Horse Heaven Hills represent the first regime. These sites contain relatively low NO_x averages but higher O₃ averages, suggesting that the O₃ precursors are coming from elsewhere. With no point source or heavy mobile sources of NO_x 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.

Figure A 29. Maximum ozone concentration as a function of mean deployment temperature.

Sites in more populated areas like Hermiston and Pendleton represent the second NO_x regime: the local production of NO_x contributing to O_3 . These sites maintain both high O_3 and high NO_x averages, suggesting that there are O_3 precursors local to those areas. A site having concentrated O_3 and NO_x simultaneously would suggest that there is production of both pollutants occurring concurrently. The NEI reports the largest point NO_x 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_3 averages. Local NO_x sources may also contribute to elevated O_3 levels at other sites, thus combining both factors of these two regimes.

Finally, the missing 5-20 ppbv ozone predictions in AIRPACT-5 could be from missing emissions or the complex terrain leading to difficult representation of meteorology and transport and ozone titration. Because the samplers are time averaged over 7-14 days, peak ozone concentrations cannot be observed and compared to AIRPACT-5 peak ozone concentrations. The missing emissions is best seen in the comparisons of NO during the deployments (Figure A 23). When emissions are not represented, the O₃ 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 where the river width is less than the 4 km model grid. When transport isn't accurately modeled, the non-local source regime for O₃ production in the region will not be modeled correctly.

This study shows the complexity involved in the Hermiston area's pollution problems and the usefulness of using ozone and nitrogen oxides Ogawa passive samplers in rural areas. The multifaceted conditions work in and out of conjunction with one another, resulting in various scenarios. O₃ precursors are greatly affected by temperature, wind patterns, and the from local and transported NO_x sources.

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Literature Cited

"AIRPACT." *Air-Quality Forecasting for the PNW*. Washington State University, n.d. Web. 01 Sept. 2016.

Barna M, Lamb B, & Westberg H. (2001) Modeling the Effects of VOC/NO Emissions on Ozone Synthesis in the Cascadia Airshed of the Pacific Northwest. *Journal of the Air & Waste Management Association*, 51(7), 1021-1034, DOI: 10.1080/10473289.2001.10464330

Green, M. C., Xu, J., & Adhikari, N. (2008). Transport of Atmospheric Aerosol by Gap Winds in the Columbia River Gorge. *Journal of Applied Meteorology and Climatology*, 47(1), 15–26. <http://doi.org/10.1175/2007JAMC1561.1>

Koutrakis, P.; Wolfson, J.M.; Bunyaviroch, A.; Froehlich, S.E.; Hirano, K.; Mulik, J.D. Measurement of Ambient Ozone Using a Nitrite-Coated Filter; *Anal. Chem.* 1993, 65, 209-214.

Rao, M., George, L. a, Rosenstiel, T. N., Shandas, V., & Dinno, A. (2014). Assessing the relationship among urban trees, nitrogen dioxide, and respiratory health. *Environmental Pollution* (Barking, Essex : 1987), 194, 96–104. <http://doi.org/10.1016/j.envpol.2014.07.011>

Rolph, G.D. (2016). Real-time Environmental Applications and Display sYstem (READY) Website (<http://www.ready.noaa.gov>). NOAA Air Resources Laboratory, College Park, MD.

Salem, A. A., Soliman, A. A., & El-Haty, I. A. (2009). Determination of nitrogen dioxide, sulfur dioxide, ozone, and ammonia in ambient air using the passive sampling method associated with ion chromatographic and potentiometric analyses. *Air Quality, Atmosphere and Health*, 2(3), 133–145. <http://doi.org/10.1007/s11869-009-0040-4>

Stein, A.F., Draxler, R.R, Rolph, G.D., Stunder, B.J.B., Cohen, M.D., and Ngan, F., (2015). NOAA's HYSPLIT atmospheric transport and dispersion modeling system, *Bull. Amer. Meteor. Soc.*, **96**, 2059-2077, <http://dx.doi.org/10.1175/BAMS-D-14-00110.1>

Appendix D: GK-12 Curriculum

Cascades to Coast GK12 Curriculum

Air Parcel Trajectory Inquiry: Modeling Atmospheric Transport to Determine Potential Impacts in Your Community

Fellow: Jacinda Mainord (Environmental Science)

Teacher: Steve Scannell (Gresham High School)

Learning Goal:

Model air parcel trajectory in your community and use the model to predict potential impacts of a proposed metals foundry.

Learning Objectives:

Introduce students to basic meteorology

Introduce air parcels and trajectories

Introduce students to modeling

Introduce students to air quality impacts of industrial areas on residential and urban areas

Target Grade: 9th Grade

State Standards

HS-ESS3-3.

Create a computational simulation to illustrate the relationships among management of natural resources, the sustainability of human populations, and biodiversity.

H.3E4.

Evaluate the impact of human activities on environmental quality and the sustainability of Earth systems.

HS-ESS3-4.

Evaluate or refine a technological solution that reduces impacts of human activities on natural systems.

Activity Plan:

These activities are designed to take place over four 50-minute class periods

Period One (50 min):

Give students a quick overview of air movement and meteorology. Introduce key vocabulary such as trajectory, modeling, and atmospheric emissions. Discuss the potential impacts of industry on air quality of residential and urban areas. Introduce the proposed metals foundry and location near the students' school.

Period Two (50 min):

Re-introduce the proposed metals foundry. Give the students a quick overview of the Hysplit model (https://ready.arl.noaa.gov/HYSPLIT_traj.php). Discuss the parameters, starting location, trajectory settings, and meteorological inputs. Students will work in appropriately sized groups according to the available computers and begin the simulated activity. Students will learn the seasonal air movement (trajectories) specific to their community and start to think if the proposed plant will affect their school.

Period Three (50 min):

Students begin to synthesize their findings from the Hysplit modeling. Discuss the air parcel trajectory modeling. Students will make predictions of whether or not the proposed plant will have an impact on the air quality of their school and residential community.

Period Four (50 min):

Students present their findings to the class. Each student group will have modeled a different school within their region.

Materials: Computers with Internet connection.

Possible Extensions:

Students can provide ideas on how to mitigate the impact of the proposed plant.

Students can investigate other options and locations that would minimize the impact.

Students can investigate existing plants in their region to determine if an air quality study should be designed to determine impact on their community.

Assessment and Worksheet Questions:

Day One:

What are potential emissions from a metals foundry?

What are the potential health concerns related to these emissions?

Who is most affected by the air quality concerns?

Day Two:

Why does air move?

What does trajectory mean?

What is an air parcel trajectory model?

Day Three:

What is Hysplit model?

Who uses the model?

What are the required inputs to the model?

How does air movement change throughout the day?

Day Four:

Are there potential concerns for the proposed plant?

Suggest a regulation on emission for this proposed plant to help lower the transport of pollution to community members.

Cascades to Coast GK12 Curriculum

Smog City Inquiry: Modeling Air Pollution in Your Community

Fellow: Jacinda Mainord (Environmental Science)

Teacher: Steve Scannell (Gresham High School)

Learning Goal:

Model ozone concentrations at Smog City and use the model to predict levels of ozone in the local environment. Compare with regional background air pollution.

Learning Objectives:

Introduce the students to the air quality index

Introduce the concepts of photochemical reactions and environmental and health impacts

Introduce the students to stratospheric and tropospheric ozone

Introduce students to modeling

Introduce students to a Portland air quality database

Interpret graphs

Target Grade: 9th Grade

State Standards:

HS-PS1-5 Apply scientific principles and evidence to provide an explanation about the effects of changing the temperature or concentration of the reacting particles on the rate at which a reaction occurs.

H.3E4 Evaluate the impact of human activities on environmental quality and the sustainability of Earth systems.

Activity Summary:

Students will learn about the air quality index and the health concerns associated with each index. Students will learn about ozone, and through modeling, investigate how ozone concentrations relate to meteorological conditions. Students will use the modeled results to predict ozone levels in the different seasons in their local environments, and then use online air quality databases to compare their predictions with the real data.

Activity Plan:

These activities are designed to take place over four 50 minute class periods.

Period One (50 min):

Give students a quick overall view of the Air Quality Index from Air Now (www.airnow.gov). Discuss health impacts of increased air pollution. Allow students to navigate the Air Now webpage and answer questions about the different levels of air pollution.

Period Two (50 min):

Give students a quick tour of the Smog City (<http://www.smogcity.com/>) model. Show them the different parameters that can be changed. Students will work in appropriately sized groups according to available computers and begin to model ozone concentrations in Smog City.

Period Three (50 min):

Students begin to synthesize their findings from Smog City modeling. Discuss the parameters that lead to high and low levels of ozone. Students make predictions on local ozone concentrations.

Period Four (50 min, optional):

Introduce students to online air quality databases. For Portland, students can go to www.horizons.pdx.edu. Students will graph ozone concentrations from local air quality monitoring stations and compare their predictions to the real data.

Materials: Computer with internet access and Java

Possible Extensions:

Students can provide ideas to mitigate ozone pollution

Students can investigate environmental effects of ozone pollution

Students can use the air quality database to investigate downwind effects of ozone pollution

Assessment and Worksheet Questions:

Day One:

What is the Air Quality Index?

How many levels of health concern are there in the Air Quality Index?

Who is most affected by air quality concerns on an orange AQI day?

Day Two:

What is ozone?

Is there good and bad ozone?

What makes ozone dangerous to human health?

What are sources to ozone?

Day Three:

What is Smog City?

What factors can be changed?

Which of these factors appears to have the greatest influence on ozone concentrations?

How does ozone change throughout the day?

Which is a greater influence on ozone concentrations: emissions or weather conditions?

Explain.

Day Four:

Name an example of when weather may influence changes in emissions.

Suggest regulations that could help lower smog in cities. What is a possible outcome?

How did your ozone predictions compare with the real data?

Appendix E: Calibration curve for denuders and passive sampling in the Columbia River Gorge.

Table A2. Calibration curves for denuders (noted by date) and passive Ogawa NO_x and O₃ by deployment.

Date or Deployment	Calibration Curve (y = peak area (uS/min), x = mol/L)	Analyte
4/14/2016	$y = 7.165E-04x - 6.1E-05$, $R^2 = 0.995$	Ammonium
7/25/2016	$y = 7.165E-04x - 6.1E-05$, $R^2 = 0.995$	Ammonium
8/2/2016	$y = 8.94E-04x - 9E-05$, $R^2 = 0.999$	Ammonium
8/11/2016	$y = 6.45E-04x - 2E-05$, $R^2 = 0.994$	Ammonium
4/1/2016	$y = 1.779E-04x + 5.7E-06$, $R^2 = 0.998$	Nitrate
4/11/2016	$y = 1.789E-04x + 7.2E-06$, $R^2 = 0.999$	Nitrate
D1	$y = 1.06E-04x - 1.7E-06$, $R^2 = 1.000$	Nitrate
D2	$y = 1.05E-04x + 5E-06$, $R^2 = 0.998$	Nitrate
7/19/2016 & D3	$y = 1.06E-04x + 2.0E-06$, $R^2 = 0.9999$	Nitrate
8/2/2016 & D4	$y = 1.20E-04x + 5.5E-06$, $R^2 = 0.999$	Nitrate
8/5/2016	$y = 2.172E-04x + 4.0E-06$, $R^2 = 0.999$	Nitrate
8/11/2016	$y = 2.11E-04x + 1.8E-06$, $R^2 = 0.999$	Nitrate
10/1/2016	$y = 1.23E-04x + 5.8E-06$, $R^2 = 0.999$	Nitrate
4/1/2016	$y = 8.839E-05x + 5.6E-07$, $R^2 = 0.999$	Sulfate
4/11/2016	$y = 9.146E-05x + 3.9E-06$, $R^2 = 0.999$	Sulfate
8/5/2016	$y = 5.9E-05x + 5E-06$, $R^2 = 0.993$	Sulfate
8/11/2016	$y = 4.98E-05x + 1.3E-06$, $R^2 = 0.999$	Sulfate
D1	$y = 0.57x - 0.002$, $R^2 = 1.000$	Nitrite
D2	$y = 0.54x - 0.006$, $R^2 = 0.999$	Nitrite
D3	$y = 0.56x - 0.005$, $R^2 = 0.999$	Nitrite
D4	$y = 0.57x - 0.001$, $R^2 = 1.000$	Nitrite

Table A3. Nitrogen dioxide passive sampling results from Columbia Basin study by site and deployment.

Site	lat	long	NO2 D1 (ppbv)	NO2 D2 (ppbv)	NO2 D3 (ppbv)	NO2 D4 (ppbv)
CBA	45.820589	-119.694017	NA	4.5	5.5	9.8
CBB	45.855791	-119.6474	NA	8.5	7	9.1
CB1	45.882915	-119.504951	2.1	4.4	6.3	7.1
CB2	45.890078	-119.504625	NA	10.3	5.4	8.3
CB3	45.801754	-119.435138	6.2	4	5.3	7.4
CB4	45.893725	-119.347827	7	12.4	7.5	11.4
CB5	45.864761	-119.34208	2.7	13.5	13.7	18.4
CB6	45.828958	-119.26299	4.8	8.8	9.3	13.4
CB7	45.784155	-119.205205	4.7	3.7	7.1	9
CB8	45.660314	-118.741689	7.6	9.5	10.5	NA
CB9	45.928899	-119.098517	5.6	12.8	8.1	13.1
CB10	46.053712	-118.933714	6.6	10.2	8.1	13.5
CB11	46.046624	-118.894597	6.2	5.4	2.5	3.6
CB12	46.343339	-119.090824	7.6	15	NA	15.4
CB13	46.209029	-119.772027	6.7	11.6	10.3	17
CB14	46.249253	-119.475303	9.3	9.6	11.5	13.9
CB15	46.170436	-119.201763	4.4	7.8	7.5	9.3
CB16	46.066695	-119.048655	1.2	1.9	1.9	NA
CB17	46.018046	-119.230869	6.4	9.9	6.9	13.2
CB18	45.991273	-119.603683	5	8.5	8	9.8
CB19	45.93921	-119.60965	3.8	7.3	6.6	0
CB20	46.058302	-119.601836	NA	NA	4.5	NA

Table A4. Nitric oxide passive sampling results from Columbia Basin study by site and deployment.

Site	lat	long	NO D1 (ppbv)	NO D2 (ppbv)	NO D3 (ppbv)	NO D4 (ppbv)
CBA	45.82059	-119.694017	NA	0	2.3	10.1
CBB	45.85579	-119.6474	NA	0	1.6	2.5
CB1	45.88292	-119.504951	NA	0	0.2	5.2
CB2	45.89008	-119.504625	NA	0	1.8	7
CB3	45.80175	-119.435138	NA	1.3	3.6	9.6
CB4	45.89373	-119.347827	NA	1.9	1.5	3.6
CB5	45.86476	-119.34208	NA	1.8	2.4	14.8
CB6	45.82896	-119.26299	NA	0	0.7	5.6
CB7	45.78416	-119.205205	NA	2.4	4.4	9.1
CB8	45.66031	-118.741689	NA	5	8.8	NA
CB9	45.9289	-119.098517	NA	3.1	4.9	0
CB10	46.05371	-118.933714	NA	6.1	8	19
CB11	46.04662	-118.894597	NA	0	0.9	NA
CB12	46.34334	-119.090824	NA	8.4	NA	17
CB13	46.20903	-119.772027	NA	4.9	8.6	21.3
CB14	46.24925	-119.475303	NA	2.8	5	17.8
CB15	46.17044	-119.201763	NA	0	0.8	2.4
CB16	46.0667	-119.048655	NA	0	0.6	NA
CB17	46.01805	-119.230869	NA	2.6	5.2	21.6
CB18	45.99127	-119.603683	NA	5	5.5	4.4
CB19	45.93921	-119.60965	NA	0	1.3	2.6
CB20	46.0583	-119.601836	NA	NA	1.5	NA

Table A5. Ozone passive sampling results from Columbia Basin study by site and deployment.

Site	lat	long	O3 D1 (ppbv)	O3 D2 (ppbv)	O3 D3 (ppbv)	O3 D4 (ppbv)
CBA	45.820589	-119.694017	NA	54	30	10
CBB	45.855791	-119.6474	NA	45	9	14
CB1	45.882915	-119.504951	5	20	13	6
CB2	45.890078	-119.504625	NA	17	20	10
CB3	45.801754	-119.435138	14	17	11	9
CB4	45.893725	-119.347827	NA	14	13	12
CB5	45.864761	-119.34208	NA	36	20	8
CB6	45.828958	-119.26299	5	6	23	10
CB7	45.784155	-119.205205	NA	NA	13	6
CB8	45.660314	-118.741689	27	43	20	NA
CB9	45.928899	-119.098517	NA	7	17	11
CB10	46.053712	-118.933714	12	29	30	15
CB11	46.046624	-118.894597	NA	12	29	21
CB12	46.343339	-119.090824	NA	22	NA	7
CB13	46.209029	-119.772027	8	12	19	9
CB14	46.249253	-119.475303	3	26	18	9
CB15	46.170436	-119.201763	29	NA	34	14
CB16	46.066695	-119.048655	NA	41	36	NA
CB17	46.018046	-119.230869	NA	4	8	8
CB18	45.991273	-119.603683	5	NA	16	12
CB19	45.93921	-119.60965	22	10	19	10
CB20	46.058302	-119.601836	NA	NA	16	NA