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Investigating the Potential of Land Use Modifications to Mitigate the Respiratory Health Impacts of NO2: A Case Study in the Portland-Vancouver Metropolitan Area

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Investigating the Potential of Land Use Modifications to Mitigate the Respiratory Health Impacts of NO_2:

A Case Study in the Portland-Vancouver Metropolitan Area

by

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Abstract

The health impacts of urban air pollution are a growing concern in our rapidly urbanizing world. Urban air pollutants show high intra-urban spatial variability linked to urban land use and land cover (LULC). This correlation of air pollutants with LULC is widely recognized; LULC data is an integral input into a wide range of models, especially land use regression models developed by epidemiologists to study the impact of air pollution on human health. Given the demonstrated links between LULC and urban air pollution, and between urban air pollution and health, an interesting question arises: what is the potential of LULC modifications to mitigate the health impacts of urban air pollution?

In this dissertation we assess the potential of LULC modifications to mitigate the health impacts of NO_2, a respiratory irritant and strong marker for combustion-related air pollution, in the Portland-Vancouver metropolitan area in northwestern USA. We begin by measuring summer and winter NO_2 in the area using a spatially dense network of passive NO_2 samplers. We next develop an annual average model for NO_2 based on the observational data, using random forest – for the first time in the realm of urban air pollution – to disentangle the effects of highly correlated LULC variables on ambient NO_2 concentrations. We apply this random forest (LURF) model to a 200m spatial grid covering the study area, and use this 200m LURF model to quantify the effect of different urban land use

categories on ambient concentrations of NO_2. Using the changes in ambient NO_2 concentrations resulting from land use modifications as input to BenMAP (a health benefits assessment tool form the US EPA), we assess the NO_2-related health impact associated with each land use category and its modifications. We demonstrate how the LURF model can be used to assess the respiratory health benefits of competing land use modifications, including city-wide and local-scale mitigation strategies based on modifying tree canopy and vehicle miles traveled (VMT).

Planting trees is a common land cover modification strategy undertaken by cities to reduce air pollution. Statistical models such as LUR and LURF demonstrate a correlation between tree cover and reduced air pollution, but they cannot demonstrate causation. Hence, we run the atmospheric chemistry and transport model CMAQ to examine to what extent the dry deposition mechanism can explain the reduction of NO_2 which statistical models associate with tree canopy.

Results from our research indicate that even though the Portland-Vancouver area is in compliance with the US EPA NO_2 standards, ambient concentrations of NO_2 still create an annual health burden of at least $40 million USD. Our model suggests that NO_2 associated with high intensity development and VMT may be creating an annual health burden of $7 million and $3.3 million USD respectively. Existing tree canopy, on the other hand, is associated with an annual health benefit of $1.4 million USD. LULC modifications can mitigate some fraction of this health burden. A 2% increase in tree canopy across the study area may reduce incidence rates of asthma exacerbation by as much as 7%. We also find that increasing tree canopy is a more effective strategy than reducing VMT in terms of mitigating the health burden of NO_2.

CMAQ indicates that the amount of NO_2 removed by dry deposition is an order of magnitude smaller than that predicted by our statistical model. About one-third of the difference can be explained by the lower NO_2 values predicted by CMAQ, and one-third may be attributable to parameterization of stomatal uptake.

“We do not inherit the Earth from our ancestors, we borrow it from our children”
Wendell Berry

Rohan – may our generation give yours the foundation to build beautiful cities on a beautiful Earth.

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Chapter 1: Introduction

In the city, because of the height of the buildings, the narrowness of the streets and all that pours forth from its inhabitants and their superfluities…the air becomes stagnant, turbid, thick, misty and foggy…

12th century philosopher Maimonides
(Finlayson-Pitts & Pitts Jr, 2000)

Urban air pollution

Rapidly rising urbanization (United Nations, 2014) and increasing per capita use of fossil fuel (Figure 1) in the modern era have led to increasing levels of air pollution world-wide, with many pollutants found at much higher levels in cities (Figure 2). Urban air pollutants include primary pollutants that are emitted directly by anthropogenic processes as well as secondary pollutants that are formed by chemical reactions of the primary pollutants with other atmospheric chemical species. Sources of primary pollution include point sources such as manufacturing and industrial sites; on-road mobile sources such as cars; and area sources such as dry cleaners and gas stations. Examples of primary air pollutants emitted into the urban atmosphere by human combustion activity include the oxides of carbon (CO, CO_2), sulfur (SO_2), and nitrogen (NO, NO_2, collectively called NOx), as well as volatile organic compounds (VOCs) such as benzene and dioxins and furans from incinerating waste (U.S. EPA; UNECE, 2014). A host of other air pollutants are also released into the urban atmosphere by non-combustion related human activity, ranging from perchloroethylene (PERC) from dry-cleaning businesses to VOCs from painting to heavy metals from wear and tear of automobiles. Eventually, urban air pollutants are removed from the atmosphere by one of the following mechanisms: transport out of the urban area; deposition to the soil, vegetation, or other surfaces; or chemical transformation into secondary pollutants.

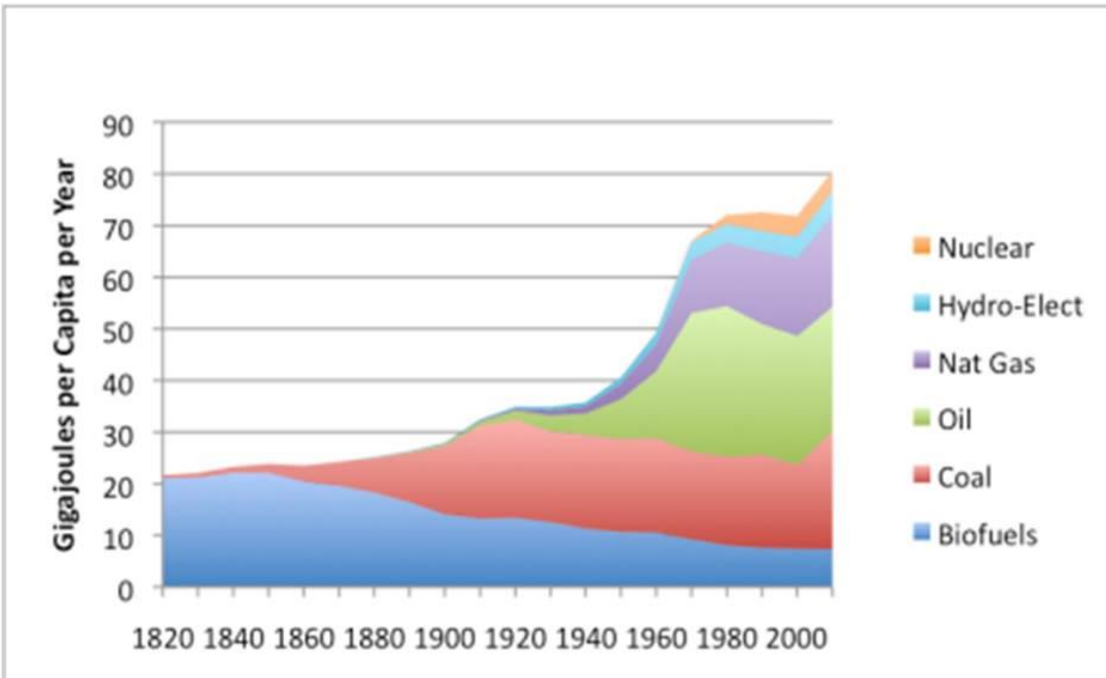
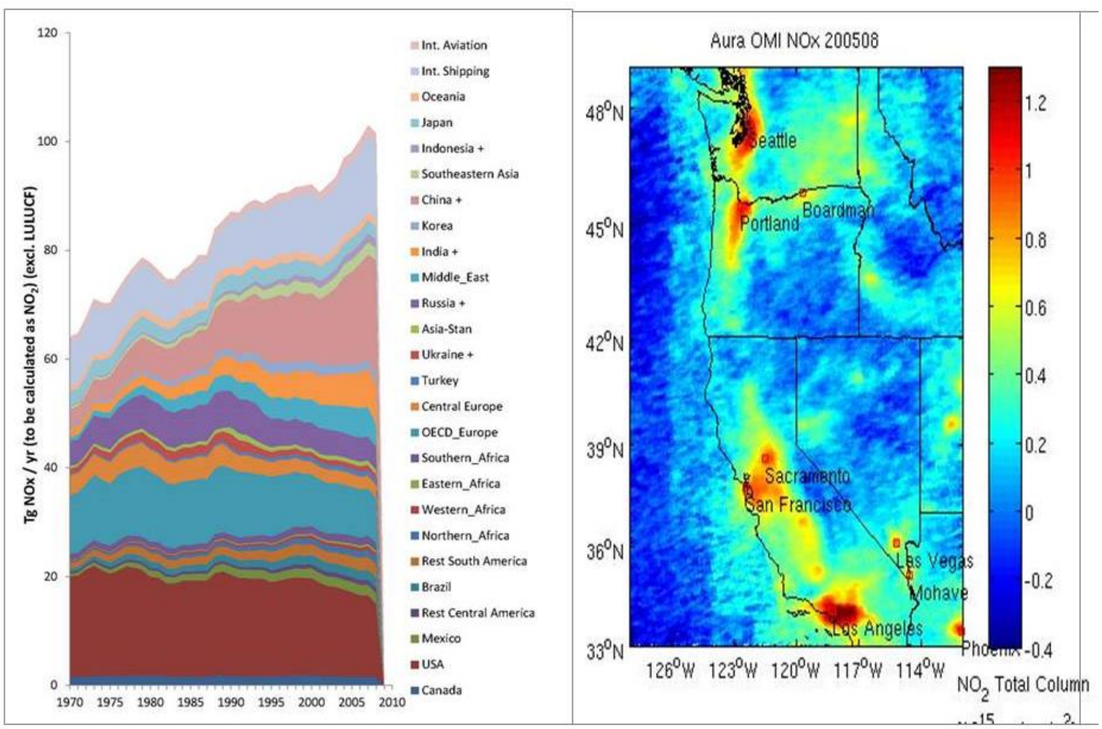


Figure 1: Increase in per capita fossil fuels (Gail Tverberg, 2012, https://ourfiniteworld.com/2012/08/29/the-long-term-tie-between-energy-supply-population-and-the-economy/)

Formation of secondary pollutants is often initiated in polluted urban atmospheres, or in plumes from urban areas carrying reactive chemical species to suburban and rural areas. For instance, ozone, a secondary pollutant that is the principal component of photochemical smog, can often be found at higher concentrations in outlying urban or suburban areas. Smog results when high emissions of urban NO are oxidized to NO_2 through reactions with oxidative species created through the photo-oxidation of volatile organic compounds (VOCs), leading to the formation of ozone and secondary organic aerosols (SOA) (Atkinson, 2000; Finlayson-Pitts & Pitts Jr, 2000; George, 1991; Seinfeld & Pandis, 1998), which are a significant component of $PM_{2.5}$ (Crippa et al., 2013). These secondary by-products resulting from urban photo-oxidative chemistry are even more harmful to human health than the primary pollutant, NOx.



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Right -Cities on the West Coast stand out with their high NO_2 levels. (http://www.temis.nl)

Spatial and temporal variability of air pollutants

Primary anthropogenic emissions and their secondary products are seldom uniformly distributed within cities, either spatially or temporally. Studies show that the distribution of air pollutants within a city shows greater variation than the distribution of air pollution between cities (Jerrett et al., 2005). A meta-analysis by Karner et al (Karner, Eisinger, & Niemeier, 2010) found that air pollutants within cities decay rapidly within 200m of the source, reaching background concentrations between 200m and 1km (Figure 3), creating strong air pollution gradients at short spatial scales within a city. The spatial distribution of air pollutants is influenced by many factors, including distance from source, proximity to sinks such as deposition surfaces, water bodies or rain, reactivity of the pollutants with other chemicals in the air, wind patterns, and temperature. Many of the factors affecting the spatial variability of air pollutants within cities such as local wind patterns, the distribution of sources and sinks, and to a lesser extent temperature, are strongly influenced by urban design (building height and density) and policy (congestion pricing, zoning).

Concentrations of air pollutions also show a diurnal, weekly and seasonal pattern. The temporal patterns of air pollution arise partly due to the patterns of human activity and partly due to the diurnal and seasonal patterns of sunlight, ambient temperature, and weather, which affect the chemistry of the urban atmosphere (Figure 3, RHS). For example, air pollutant levels are typically highest in winter in the northern latitudes as cold temperatures create night-time inversion layers trapping air pollutants.

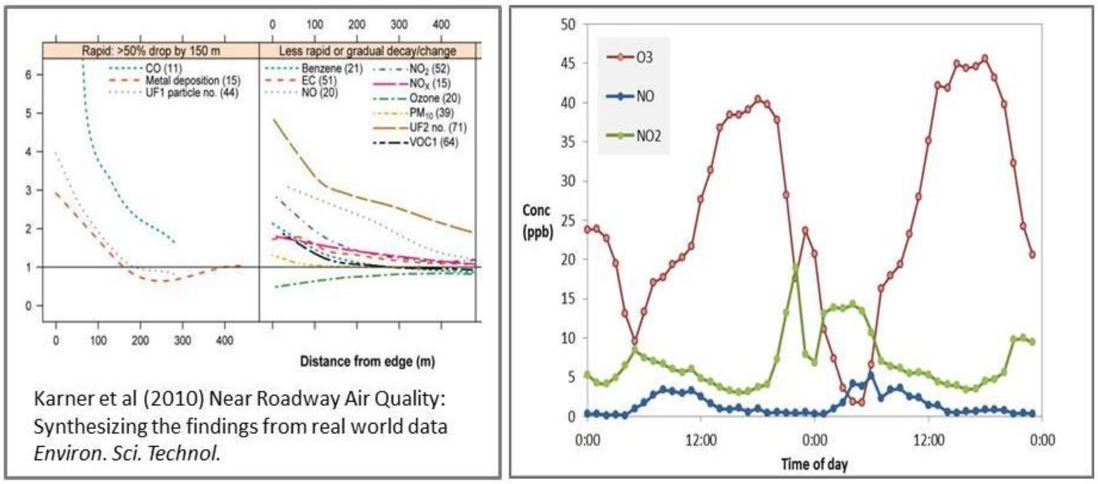


Figure 3: Spatial variation (Karner, A. A., Eisinger, D. S., & Niemeier, D. A. ,2010) and temporal variation (Portland DEQ air monitoring station, SE Lafayette) of air pollutants in cities

Health and environmental impacts of urban air pollutants

Epidemiological research has shown that urban air pollution can be detrimental to human health, with each urban air pollutant having its own set of impacts on human – and environmental – well-being. An increase in the average air pollution in a city is correlated with an increase in cardiovascular disease, strokes and cancer (Brunekreef & Holgate, 2002; Dockery et al., 1993; Nyberg et al., 2000; Pope et al., 2002; Samet, Dominici, Curriero, Coursac, & Zeger, 2000; Samoli et al., 2005). Recent epidemiological research further indicates that the health impacts of air pollution are not uniform across a city. For example, numerous studies show a higher burden of respiratory problems close to major roadways (Brauer et al., 2007; Jerrett et al., 2008; McConnell et al., 2006; Ostro, Lipsett, Mann, Braxton-Owens, & White, 2001), which is not surprising as primary air pollutants levels are greatest near the source and decay rapidly away from it (Faus-Kessler, Kirchner, & Jakobi, 2008; Gilbert, Goldberg, Brook, & Jerrett, 2007; Jerrett et al., 2005; Karner et al., 2010).

Air pollution can have a social impact as well. Smog may lead to corrosive damage to historically significant buildings and monuments (Gauri & Holdren, 1981; Varotsos, Tzanis, & Cracknell, 2009). Studies in the US also document that there is inequity in access to clean air, and that minorities are more likely to be exposed to air pollution, especially children of low-income non-whites (L. P. Clark, Millet, & Marshall, 2014; Rowangould, 2013; Zwickl, Ash, & Boyce, 2014). This inequity may arise in part due to the preferential siting of air pollutant sources in minority neighborhoods (Pastor, Sadd, & Hipp, 2001).

Anthropogenic air pollutants impact not only human health and society, but the environment as well. For instance, ozone exposure causes visible injury to leaves and results in reduced tree growth (US EPA, 2012). Urban emissions of SOx and NOx have led to acidification of rain water, leading to acidification of even remote downwind lakes and increased nitrogen deposition in downwind boreal forests. Emissions of NO_2 are contributing to the “Nitrogen Cascade”(Galloway et al., 2003), a cascading set of impacts as anthropogenic reactive nitrogen moves through the landscape, ranging from changes in successional stages within grasslands and boreal forests to changes in the balance of the global nitrogen cycle (Fenn, Baron, et al., 2003; Schlesinger, 2009; Vitousek et al., 1997). Thus, anthropogenic emissions may threaten the long term sustainability of cities themselves, as urban emissions disrupt the global environment that ultimately sustains all cities.

Current challenges in mitigating urban air pollution

Today, when more than half of humanity lives in cities, and two-thirds of the population is expected to be urban by mid-century (United Nations, 2014), urban air pollution creates a huge public health burden. In the US, where very few areas are in non-attainment of National Ambient Air Quality Standards, Fann et al (Fann et al., 2012) still estimate excess mortality of 130,000 per year associated with $PM_{2.5}$, more than the annual deaths attributable to accidents or diabetes. Globally, the excess annual mortality due to $PM_{2.5}$ was estimated at 800,000 by Cohen et al (A. J. Cohen et al., 2006), approximately half of the estimated excess annual mortality due to indoor air pollution or unsafe drinking water. Thus, there is an urgent need for cities worldwide to mitigate the impact of urban air pollution on human health.

To mitigate the health impact of urban air pollution, cities must be able to (i) assess the health impacts of the existing spatial distribution of air pollution; (ii) to identify and compare diverse mitigation strategies to minimize this exposure to air pollution. However, both these steps present challenges, as discussed below.

Assessing the health impact of urban air pollution

Many urban air pollutants vary at fine-spatial scales within cities (Figure 3, LHS). Epidemiological studies typically assess the health risk of urban air pollution using temporally averaged but spatially resolved data to characterize the health risk of air pollution exposure. The first challenge in understanding the health burden of urban air pollution lies in capturing this spatial variability of intra-urban air pollution. To assess the exposure to urban air pollution, air pollutants must be monitored or modeled at a fine spatial resolution. To date, however, institutional observations, monitoring, and modeling efforts have primarily focused on the regional and global scales. For example, active monitoring stations such as those in the US Environmental Protection Agency (US EPA) monitoring network, satellite observations, and atmospheric transport models provide air pollution data at the 10km or coarser spatial scale. Chemical transport models such as CMAQ and WRF-Chem that could be used to model air pollutant levels at the intra-urban scale lack emissions inventories as well as model validation studies at this scale. Computational fluid dynamics models (Gromke, Buccolieri, Di Sabatino, & Ruck, 2008; Salim, Cheah, & Chan, 2011; Yim, Fung, Lau, & Kot,

2009) that simulate air flow (and hence air pollutant transport) at a very highly spatially resolved scale, are currently too computationally expensive to be applied to an entire city.

Thus, there exists neither a publicly sponsored observation network nor an established protocol for measurement (or modeling) air pollutants for assessing intra-urban exposure in the US today.

Mitigating intra-urban air pollution

Like monitoring, mitigation of air pollution has been driven at a regional scale due to the regulatory framework. Further, regional air pollution mitigation has focused mainly on emissions reduction, through economic (congestion pricing, odd-even license plates access) or technological (catalytic convertors for cars, scrubbers for smokestacks, clean coal for power plants) means. Given our dependence on fossil fuel (Figure 1) to satisfy energy needs and the fact that most of our pollution is related to fossil-fuel combustion, it is probably prudent that we investigate means complementary to emissions reduction to mitigate the impact of urban air pollution. However, complementary strategies for mitigating the intra-urban impact of air pollution have not been identified or investigated.

At the intra-urban scale, urban land use and land cover (LULC) features within a city are known to affect the dispersion of air pollutants by influencing air flow, the location of emissions through zoning and other siting policies, and the quantity of emissions associated with these LULC features through permitting, policies, and urban planning. This role of land use in modulating ambient concentrations of air pollution gives rise to an interesting question: to what extent can urban land use be managed or modified to decrease the human health impact of air pollution? However, the relationship among air pollution, *local* land use decisions, and health impacts has – with few exceptions (Borrego et al., 2006; Nowak, Hirabayashi, Bodine, & Hoehn, 2013; Rao, George, Rosenstiel, Shandas, & Dinno, 2014) – not been systematically investigated or quantified.

To date, cities mostly use emissions reductions as the single strategy for reducing exposure to air pollution, even though intra-urban health benefits of emissions reduction strategies have not been quantified. There exists a challenge of identifying and quantifying strategies to reduce exposure to urban air pollution that are complementary to emissions reductions. In addition, there is a need for a methodology to quantify and compare the health benefits of different mitigation strategies.

The role of trees in the urban environment

One particular urban land cover type deserves especial mention. Trees are an integral part of most urban landscapes, and form a not insignificant percentage of the land cover in most urban areas. Many cities, especially in the USA, have undertaken tree planting projects, to sequester carbon, improve hydrology, as well as to improve air quality (Bureau of Planning and Sustainability, 2015; City of Burlington Vermont, 2014; Morani, Nowak, Hirabayashi, & Calfapietra, 2011). Physiologically speaking, urban forests have the potential to act as sinks of air pollution in urban ecosystems. Additionally, many statistical land use regression (LUR) models find a significant, negative term for trees/vegetation/parks in their air pollution models, indicating that these green spaces are negatively correlated with air pollution (Dijkema et al., 2011; Gilbert, Goldberg, Beckerman, Brook, & Jerrett, 2005; Kashima, Yorifuji, Tsuda, & Doi, 2009; Mavko, Tang, & George, 2008a; Novotny, Bechle, Millet, & Marshall, 2011).

However, quantification of the amount of air pollutants removed by the urban forest at the city level is still imprecise. For instance, leaf-level dry deposition studies have been scaled up to the forest canopy level using big leaf or multi-level canopy models (D. D. Baldocchi, Hicks, & Camara, 1987; D. Baldocchi, 1988; Lovett, 1994; Wesely, 1989); and UFORE, a hybrid big-leaf and multilevel model (Hirabayashi, Kroll, & Nowak, 2012), has been used extensively to estimate air pollutant removal by the urban forest in cities in the USA and the world (Cabaraban, Kroll, Hirabayashi, & Nowak, 2013; Escobedo & Nowak, 2009; Nowak, Civerolo, Trivikrama Rao, Luley, & E. Crane, 2000; Nowak, Crane, & Stevens, 2006; Nowak et al., 2013; Paoletti, Bardelli, Giovannini, & Pecchioli, 2011). The UFORE studies show that on the order of 1% of urban air pollutants are removed by the urban forests in US cities. However, there are some drawbacks to the UFORE studies. For example, in their 2006 deposition study using UFORE, Nowak et al used a single NO_2 value, based on a regional background monitoring station, for each city. Further, UFORE does not incorporate chemistry or transport, and typically uses the same meteorology for the entire city. These approximations in UFORE, while undoubtedly enabling order-of-magnitude estimations of deposition amounts, leave room for improvement.

Landscape level studies have found mixed results. Setälä et al (Setälä, Viippola, Rantalainen, Pennanen, & Yli-Pelkonen, 2012) found no correlation with reductions in NO_2 and presence of trees in the Finnish cities of Helsinki and Lahti. On the other hand, Yin et al found park trees may be removing 1-21% of near-roadway NO_2 (Yin et al., 2011) in Shanghai. We know from Takahashi et al.'s chamber studies (Takahashi et al., 2005) that not only do different species of trees assimilate NO_2 at different rates, but the same species may uptake NO_2 at different rates under different ambient concentrations of NO_2. While this might explain the inconsistency in landscape-level studies, it is clear that the role of the urban forest in removing air pollutants needs better characterization. Complicating the potential of trees as urban sinks of air pollution is the fact that under sunny, hot, and humid conditions, some species of trees emit significantly increased amounts of biogenic volatile organic compounds (BVOCs), dramatically increasing the potential for the creation of the air pollutants ozone and secondary organic aerosols, in the presence of that ubiquitous urban pollutant NOx (Hoyle et al., 2011). Since trees have many human and urban ecosystem benefits and dis-benefits, there is a need to develop a better characterization and quantification of the role of urban trees with regard to urban air pollution (Pataki et al., 2011).

Scope of dissertation research

The dissertation focuses on developing a better understanding and characterization of the impact of urban land use as a driver of urban nitrogen dioxide (NO_2) concentrations in the Portland-Vancouver Metropolitan area. The focus is on the US EPA criteria pollutant NO_2 as it is one of the most ubiquitous urban air pollutant, and a strong marker for other combustion-related air pollutants. It is harmful to human health, and is also a precursor to O_3 and $PM_{2.5}$, both criteria pollutants more harmful to human health than NO_2 itself. From a practical point of view, it can be relatively inexpensively monitored using passive samplers, its gas phase chemistry is well understood, and its health impact functions are available from the US EPA. The urban area we focus on is the Portland-Vancouver Metropolitan area, where Portland State University – with its motto “Let knowledge serve the city” – is located.

This dissertation addresses some of the challenges of assessing and mitigating intra-urban exposure to NO_2 in the study area by developing models and methodologies that can enable citizens and city managers to better assess and mitigate exposure to NO_2 in the Portland-Vancouver Metro area. Specifically, this dissertation aims to:

(1) measure NO_2 at a fine spatial scale in the study area, and develop observationally-based NO_2 models for the region;

(2) assess the association among land use, ambient NO_2 concentrations, and respiratory health for the study area;

(3) evaluate the potential of land-use modification scenarios in mitigating the health impacts of NO_2 at the local and city-wide scale in the Portland-Vancouver (USA) metropolitan region; and

(4) investigate, using the atmospheric chemistry and transport model CMAQ, to what extent removal of NO_2 through deposition onto tree canopy might explain the reduced NO_2 associated with trees.

Chapter 2 of this dissertation describes the NO_2 measurement campaigns undertaken to measure summer and winter NO_2 in the study area. It describes the four models developed: summer and winter NO_2 models based on the standard LUR methodology, using highly resolved land use data (for example, tree canopy data was available at 1m resolution) for the Portland Metro area; and summer and winter models for the Portland-Vancouver area using an ensemble data learning technique called random forest, which is applied here for the first time to air pollution modeling. Further, we critically evaluate the performance of the land use random forest (LURF) model. Highly spatially resolved (200m resolution) annual average NO_2 models are developed using both the LUR and LURF models for their respective study areas. We additionally develop a LUR NO_2 model using the same land use/land cover data sets used for LURF model development in order to compare the NO_2 predicted by the LURF model with LUR predictions.

In Chapter 3, the annual average LURF model is used to assess the demographics and economic impacts of NO_2 exposure in the Portland-Vancouver area; and is further used to explore the association of land use, ambient NO_2 concentrations, and respiratory health.

Chapter 4 further leverages the LURF model to begin characterizing the response of NO_2 concentrations to land use modifications, using a sensitivity analysis. BenMAP, an environmental health benefits mapping tool from the US EPA is used to assess the respiratory health benefits (or damages) attributable to the change in NO_2 associated with each land use modification in the sensitivity analysis. Based on the results of the sensitivity analysis, we construct two city-wide and two neighborhood scale NO_2 mitigation strategies, and compare the health benefits resulting from each strategy.

In Chapter 5, we investigate whether the statistical association between trees and NO_2 reduction seen in both the LUR as well as the LURF models is solely due to the correlation of trees with the absence of sources using statistical methods. Next we compare the NO_2 deposition predicted by the ACTM CMAQ at the 4 km scale, to the estimated amount of NO_2 deposition that would have to occur to correspond to the observed reduction of NO_2 by the LURF model. We also undertake a sensitivity analysis in CMAQ to see if a potential re-parameterizing of stomatal conductance could explain the landscape-level observations of reduced NO_2 associated with trees.

Chapter 6 summarizes the results of the dissertation, and projects how the methodologies developed in this dissertation could be used with emerging sensor technologies and community science programs to develop healthier urban atmospheres.

Chapter 2: Measuring and Modeling NO_2 in the Portland-Vancouver area

To put a city in a book, to put the world on one sheet of paper -- maps are the most condensed humanized spaces of all...They make the landscape fit indoors, make us masters of sights we can't see and spaces we can't cover.

Robert Harbison, *Eccentric Spaces*

Abstract

Annual average NO_2 models are constructed based on NO_2 measured at 174 sites in summer 2013 and 82 sites in winter 2014 in the Portland-Vancouver area, using land use regression (LUR) and the ensemble data learning technique random forest (LURF). The LURF technique makes minimal data assumptions and thus allows us to investigate the relationship between land use and air pollution better than the more traditional LUR approach. Additionally, summer LUR and LURF models based on very fine resolution land use data, including tree canopy at 1m resolution, are also developed for the Portland Metro area.

The LUR and LURF models use national land use data sets but cover the Portland-Vancouver metropolitan area. The LURF model, since it is represents a first application in urban air pollution, is rigorously assessed on three sets of criteria, as well as against the LUR model. The LURF model performs well based on the assessment criteria, and gives results consistent with the LUR model and

existing literature, suggesting that LURF models can be used to investigate the association of land use and ambient concentrations of NO_2.

Introduction

Epidemiological research has established that urban air pollutants such as NO_2, $PM_{2.5}$ and O_3 can be detrimental to human health. An increase in the average air pollution in a city is correlated with an increase in cardiovascular disease, strokes and cancer (Brunekreef & Holgate, 2002; Dockery et al., 1993; Nyberg et al., 2000; Pope et al., 2002; Samet et al., 2000; Samoli et al., 2005). More recent epidemiological research has shown that the health impacts of air pollution are not uniform across a city. For example, numerous studies show a higher burden of respiratory problems close to major roadways (Brauer et al., 2007; Jerrett et al., 2008; McConnell et al., 2006; Ostro et al., 2001), which is not surprising as primary air pollutants levels are greatest near the source and decay rapidly away from it (Faus-Kessler et al., 2008; Gilbert et al., 2007; Jerrett et al., 2005). As mentioned earlier, Karner et al (Karner et al., 2010) found that air pollutants within cities decay rapidly within 200m of the source, reaching background concentrations between 200m and 1km.

To address the challenge of reducing human exposure to urban air pollution, then, we need to monitor or model air pollutants at a spatial resolution of 200m or finer. Epidemiologists have developed land use regression (LUR) (Briggs et al., 2000; Gilbert et al., 2005; Ryan & LeMasters, 2007), a method that successfully captures the fine scale spatial variation in urban air pollutant concentrations (Babisch et al., 2014; Clougherty, Wright, Baxter, & Levy, 2008; Eeftens et al., 2012). LUR is premised on the fact that urban land use and land cover (LULC) features play a significant role in modulating ambient concentrations of air pollutants at these fine spatial scales (~ 1 km or less). LUR combines observational measurements of air pollution and statistical modeling using land use variables obtained through geographic information systems (GIS) to construct predictive models of ambient NO_2 concentrations. The European Union (EU), for example, is currently using LUR in the ESCAPE project, which aims to model the intra-urban variability of several urban air pollutants (Beelen et al., 2013; Cyrys et al., 2012; Eeftens et al., 2012).

Although LUR predicts ambient air pollutant concentrations based on land use such as urban forest, high density development, and roadways in the vicinity of a site, it cannot be used to readily isolate the impact of any one land use category on ambient pollutant concentrations for two key reasons. First, because land use variables are highly correlated, it is difficult to isolate the impact of a single land use predictor. While correlated land use variables can be used to create reliable models, the estimates for the regression coefficients and their standard error are no longer reliable (J. Cohen, Cohen, West, & Aiken, 2003). Thus, though epidemiologists have developed LUR to successfully capture the fine spatial scale variation of urban air pollutants (Babisch et al., 2014; Clougherty et al., 2008; Eeftens et al., 2012; Lakshmanan et al., 2015; Wilhelm et al., 2011), the correlated nature of most land use variables makes it difficult to use the same LUR methodology to isolate the impact of individual land use features on local ambient air pollution concentrations.

The second challenge presented by land use variables is related to the very high number of potential predictor variables. Since the spatial extent of the influence of a particular land use feature on ambient concentrations of air pollution is not known *a priori*, land use predictors are typically extracted in multiple buffers, creating the common, but unfortunate, situation where the potential pool of LUR predictor variables far outnumbers the number of air pollutant concentration observations: a “large P, small N” scenario. Having hundreds of potential land use predictors is not uncommon for an LUR model. Epidemiologists and urban atmospheric scientists using LUR have developed a variety of techniques to reduce the predictor space, but this pruning requires time and expertise, and can lead to biased models in the hands of someone less experienced.

Given the potential of land use modification to mitigate the negative economic and health impacts of air pollution, there exists an urgent demand for developing techniques that will enable urban planners and citizens to more effectively utilize and manage land use while taking into account its influence on intra-urban air pollution and ability to minimize everyday exposure. Here we probe the potential of urban land use modification in mitigating the health impacts of air pollution using a methodology that meets the modeling challenge presented by data sets that have a large number of potentially *correlated* predictors (P) and a comparatively small number of observations (N), and thus add to the repertoire of methodologies available to model urban air pollution concentrations. We employ an ensemble data learning technique, random forest, to assess and quantify the relationship among local intra-urban land use, the concentration of the wide-spread air pollutant nitrogen dioxide (NO_2), and respiratory health. Random forest (Breiman, 2001; James, Witten, Hastie, & Tibshirani, 2006) is a powerful data mining technique that makes minimal assumptions about the independence or underlying distribution of the predictor variables. It is ideally suited to the “large P, small N” situation typical of urban air quality and LUR studies and is widely used in bioinformatics and medical research (X.-W. Chen & Liu, 2005; K. R. Gray, Aljabar, Hammers, Rueckert, & Alzheimer’s Disease Neuroimaging Initiative, 2013; Jiang et al., 2007; Svetnik et al., 2003), land use classification (Pal, 2005; Rodriguez-Galiano et al., 2012), and ecological modeling (Cutler et al., 2007; Prasad, Iverson, & Liaw, 2006).

In this chapter, we describe how we developed land use regression (LUR) and land use random forest (LURF) models for ambient concentrations of NO_2 in the Portland-Vancouver Metropolitan Area. We develop both LUR and LURF models to compare and contrast the results from these two techniques. We study NO_2 as it is the most easily measured of the USA criteria pollutants. It is also a strong marker of anthropogenic combustion-related pollution, and a chemical precursor to two other criteria pollutants, ozone and fine particulate matter. Additionally, it is a respiratory irritant whose health impact and valuation functions are available from the US EPA. The specific goals covered in this chapter are:

(1) development of annual NO_2 LUR and LURF NO_2 models for the Portland-Vancouver area, based on the summer and winter observations, using national datasets;

(2) assessment of the performance of the LURF models; and

(3) a comparison of the annual NO_2 predictions by the LUR and LURF models in the study area.

Vancouver lies in the state on Washington, and Portland in the state of Oregon; hence we were constrained to use national datasets for the Portland-Vancouver area. The national datasets have coarser resolution that city-level datasets. Therefore, we additionally developed LUR and LURF models for summer NO_2 for the Portland Metro based on high resolution land use data from Portland Metro's Regional Land Information System (RLIS) and tree canopy at 1m resolution (from the City of Portland).

Methods and materials

Our study area is the Portland-Vancouver urban area, a mid-size metropolitan area located in the US Pacific northwest. Just over 1.9 million people reside within the study area, which encompasses 2,350 km^2. This area has diverse terrain – two rivers, mountains, and, like other urban areas, a wide mix of current land use. Within the study area, 6% of land area is high intensity development, 7.5% is developed open space, and 13% is under tree canopy, based on the 2011 National Land Cover Database (NLCD) (Homer, C.G., Dewitz, J.A., Yang, L., Jin, S., Danielson, P., Xian, G., Coulston, J., Herold, N.D., Wickham, J.D., and Megown, 2015) and its land use categories (Table 1). According to the National Emissions Inventory (NEI) 2011 data (US Environmental Protection Agency, 2014), there are only three facilities in the study area permitted to emit > 500 tons of nitrogen oxides annually (Portland International Airport, SP Fiber Technologies Northwest, and Georgia-Pacific Consumer Products). Annual average daily traffic (AADT) for the freeways and state highways in the area ranges from 169,500 vehicles/day on stretches of I-84 to 610 vehicles/day on an inner city access ramp (US Department of Transportation, n.d.).

NLCD land use/land cover categories		
Code	LULC	Description
11	Open water	All areas of open water, generally with less than 25% cover or vegetation or soil
12	Perennial Ice/Snow	All areas characterized by a perennial cover of ice and/or snow, generally greater than 25% of total cover.
21	Developed, Open Space	Includes areas with a mixture of some constructed materials, but mostly vegetation in the form of lawn grasses. Impervious surfaces account for less than 20 percent of total cover. These areas most commonly include large-lot single-family housing units, parks, golf courses, and vegetation planted in developed settings for recreation, erosion control, or aesthetic purposes.
22	Developed, Low Intensity	Includes areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 20-49 percent of total cover. These areas most commonly include single-family housing units.

23	Developed, Medium Intensity	Includes areas with a mixture of constructed materials and vegetation. Impervious surfaces account for 50-79 percent of the total cover. These areas most commonly include single-family housing units.
24	Developed, High Intensity	Includes highly developed areas where people reside or work in high numbers. Examples include apartment complexes, row houses and commercial/industrial. Impervious surfaces account for 80 to 100 percent of the total cover.
31	Barren Land (Rocks/Sand/ Clay)	Barren areas of bedrock, desert pavement, scarps, talus, slides, volcanic material, glacial debris, sand dunes, strip mines, gravel pits and other accumulations of earthen material. Generally, vegetation accounts for less than 15% of total cover.
41	Deciduous Forest	Areas dominated by trees generally greater than 5 meters tall, and greater than 20% of total vegetation cover. More than 75 percent of the tree species shed foliage simultaneously in response to seasonal change.
42	Evergreen Forest	Areas dominated by trees generally greater than 5 meters tall, and greater than 20% of total vegetation cover. More than 75 percent of the tree species maintain their leaves all year. Canopy is never without green foliage.
43	Mixed Forest	Areas dominated by trees generally greater than 5 meters tall, and greater than 20% of total vegetation cover. Neither deciduous nor evergreen species are greater than 75 percent of total tree cover.
52	Shrub/Scrub	Areas dominated by shrubs; less than 5 meters tall with shrub canopy typically greater than 20% of total vegetation. This class includes true shrubs, young trees in an early successional stage or trees stunted from environmental conditions.
71	Grassland/ Herbaceous	Areas dominated by grammanoid or herbaceous vegetation, generally greater than 80% of total vegetation. These areas are not subject to intensive management such as tilling, but can be utilized for grazing.
81	Pasture/hay	Areas of grasses, legumes, or grass-legume mixtures planted for livestock grazing or the production of seed or hay crops, typically on a perennial cycle. Pasture/hay vegetation accounts for greater than 20 percent of total vegetation.
82	Cultivated Crops	Areas used for the production of annual crops, such as corn, soybeans, vegetables, tobacco, and cotton, and also perennial woody crops such as orchards and vineyards. Crop vegetation accounts for greater than 20 percent of total vegetation. This class also includes all land being actively tilled.
90	Woody Wetlands	Areas where forest or shrub land vegetation accounts for greater than 20 percent of vegetative cover and the soil or substrate is periodically saturated with or covered with water.
95	Emergent Herbaceous Wetlands	Areas where perennial herbaceous vegetation accounts for greater than 80 percent of vegetative cover and the soil or substrate is periodically saturated with or covered with water.

Table 1: The National Land Cover Database (NLCD) LULC categories and description

NO_2 was measured over two 2-week long field campaigns using relatively low cost passive chemical samplers made by Ogawa Co, Pompano Beach, FL, once during summer and once during winter. Sites were chosen using a spatial allocation model coupled with a stratified random approach to encompass the spatial extent of the Portland-Vancouver Metro area and to capture the effect of roads, railroads and vegetation on ambient NO_2 (Figure 4). A single passive Ogawa sampler, with an NO_2 pad on one side and a NO_x pad on the other, was placed at each site between 2m-3m above ground. Controls were co-located at the Portland State University monitoring station, which actively monitors NO_2 using a calibrated chemiluminescent NO_x monitor (Teledyne NOx Analyzer, Model T200). Lab and field blanks were also deployed to detect contamination during assembling the samplers or excess exposure during transportation.

Samplers were placed in the field between 23rd – 25th Aug 2013 and 14th – 16th Feb 2013; retrieved 3rd – 5th Sep 2013 and 24th – 27th Feb 2014 in summer and winter respectively. Samplers were analysed in the lab on 6th Sep 2013 and 28th Feb 2014 using the methodology outlined in the Ogawa manual (Ogawa & Co., USA, 2006) and corrected for temperature and relative humidity based on measurements at the Portland State University air quality station. The average measured NO_2 in summer was 11 ppb, with observed values ranging from 4 – 23 ppb. The average measured NO_2 in winter was 13 ppb, with observed values ranging from 3 – 29 ppb. Additional details about the field campaign can be found in Rao et al (Rao et al., 2014).

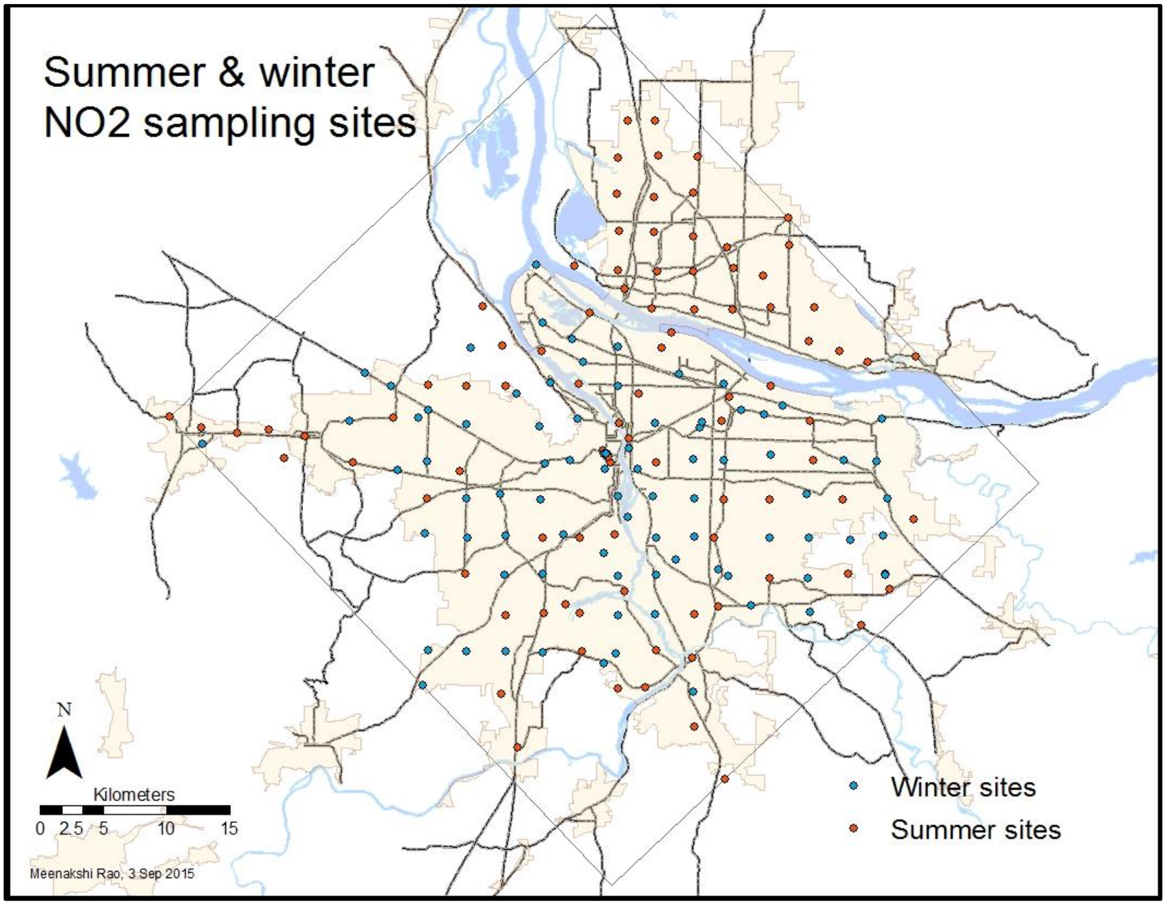


Figure 4: Sites in the Portland-Vancouver Metro area where NO2 was sampled. Orange dots indicate sites that were monitored in summer only, blue dots indicate sites monitored in summer and winter.

Developing annual NO_2 LUR and LURF models for Portland-Vancouver using national datasets

Extracting land use variables

Land use categories to be used as predictors in development of the LUR and LURF models for the Portland-Vancouver area were chosen either because they were known strong proxies for NO_2 (e.g. freeways) or identified based on a literature review and our prior campaigns in the Portland area (Beelen et al., 2013; Henderson, Beckerman, Jerrett, & Brauer, 2007; Kendrick, Koonce, & George, 2015; Mavko et al., 2008a; Rao et al., 2014; Wang et al., 2013). Table 2 lists the land use data sets used, the data source, and the spatial resolution of the data. Land use variables were extracted in 12 buffers, ranging from 100m to 1200m in radius (in 100m increments) for each land use category, at each site (174 sites, as the winter sites were a subset of the summer sites). 100m was picked as the smallest buffer size so that the smallest buffer was sufficiently larger than the resolution of the NLCD data (30m); while the largest buffer (1200m) was chosen as we were interested in local effects, which tend to taper off by ~ 1km. Latitude, longitude and elevation were also associated with each site. The National Land Cover Database (NLCD) categories deciduous, evergreen and mixed forest were added together to create a “trees” category. In all, ~200 land use variables were associated with each site.

Since we planned to use a hold-out validation assessment for both LUR and LURF models, a randomly selected 25% of observations (42/174 for summer, 20/82 for winter) were set aside as a “validation” data set for model evaluation prior to the start of model development. All model development was subsequently done on the remaining 75% “training” data set.

Land Use/Land cover	Data source
Population & housing	US Census Bureau, 2010 (block level)
Land cover classes (developed open space, high intensity development, trees, shrub/scrub, grassland, pasture, cultivated crops)	National Land Cover Database (NLCD), USGS, 2011 (30m)
Permitted NO_2 emissions	National Emissions Inventory, EPA, 2011 (point sources)
Elevation	USGS, 1/3 arc-second
AADT	NHPN (2010)
Roads (primary, secondary and local)	US Census Bureau, Tiger/Line (2013)
Latitude & Longitude	Google Earth, ArcMAP

Table 2: Land use/land cover categories used in LURF analysis, data sources, and spatial resolution.

Developing the LUR model

Briefly, LUR (Briggs et al., 2000; Jerrett et al., 2005; Ryan & LeMasters, 2007) is a statistical modeling technique used to predict air pollutant concentrations at high resolution across a landscape based on a limited number of measurements of the pollutant of interest within the study area. Land use and land cover variables are extracted at each measurement site using a spatial analysis program and a regression model developed, with the air pollutant measurements as the dependent variable and the land use parameters as the independent variables.

Given the very large number of predictors (12 buffers for each of 15 LULC variables), the predictor space was first reduced by selecting the buffer with the highest correlation with NO_2 in each category, separately for summer and winter (Clougherty et al., 2008; Henderson et al., 2007). Using this reduced predictor set (~20 predictors), potential models were identified by stepwise regression using MASS::stepAIC in R (Venables & Ripley, 2002), which bases predictor selection on minimizing the Akaike information criterion, and an exhaustive search of predictor space for the best subset of predictors using leaps::regsubsets (Lumley & Miller, 2009). The final models (one each for summer and winter) were identified as the ones which had the smallest mean square error over a 6-fold cross-validation on the training data. The selected summer and winter LUR models were then each applied to a 200m resolution grid covering the study area to develop the summer and winter fine spatial scale NO_2 models for the Portland-Vancouver urbanized area. These seasonal models were then averaged to develop an estimated annual average NO_2 LUR model, which is the metric required for health impact assessment.

Developing the LURF model

Random Forest

Random forest is an ensemble statistical learning method based on regression trees. Regression trees (James et al., 2006) divide the p-dimensional predictor space into p-dimensional rectangles, such that the total of the residual sum of squares over all the rectangles is minimized. The prediction for any set of predictors P_i is the average of all observations that fall in the rectangle containing P_i. Regression trees tend to over-fit the training data, resulting in large variance, and hence potentially large prediction errors on unseen data. To address this issue, Brieman (Breiman, 2001) developed the random forest methodology in which an ensemble of regression trees is created using bagging, that is by taking repeated samples from the training data set. Further, at each node for each tree in the forest, only a random subset of variables is considered for splitting, which results in decorrelated trees. Predictions are the average over all predictions for all trees in the forest for which the sample is out-of-bag. Strobl et al (Strobl, Hothorn, & Zeileis, 2009) have further refined the methodology by using a conditional permutation scheme that corrects for the inflated variable importance of correlated predictors in random forest (Strobl, Boulesteix, Kneib, Augustin, & Zeileis, 2008), which they call conditional random forest. All random forest model development for this study was done using conditional random forests as implemented in the “party” package (Hothorn, Buehlmann, Dudoit, Molinaro, & Van Der Laan, 2006; Strobl et al., 2008; Strobl, Boulesteix, Zeileis, & Hothorn, 2007) in R (R Core Team, 2014).

Developing the LURF models

Summer and winter random forest NO_2 models were developed using the ~200 land use variables as predictors, in two phases. In the first phase, a conditional random forest, using the "party" package (Hothorn et al., 2006; Strobl et al., 2008, 2007) in R (R Core Team, 2014), was used to identify the buffer size that was the most important predictor within each land use category. Using only the most important buffer size for each land use category reduced the number of potential predictor variables from ~200 to ~20. In the second iteration, we again used conditional random forests, now with the reduced predictor set containing one buffer size for each land use category, together with the point features latitude, longitude and elevation, to develop the observationally-based NO_2 LURF models for summer and winter.

These observationally-based summer and winter random forest models were each applied to the 200m resolution grid covering the study area to develop the seasonal fine-spatial scale NO_2 models for the Portland-Vancouver urbanized area, which were then averaged to develop the annual average NO_2 LURF model.

Assessing the performance of the LURF model

Performance of the summer and winter LURF models was assessed using three sets of criteria: statistical performance measures, predictive ability, and consistency with emissions inventories.

The statistical performance metrics used for model assessment are goodness of fit (R^2); mean bias (= 1/N *Σ {[modeled (NO_2) – observed(NO_2)] / [observed(NO_2)]}); and mean error (= 1/N *Σ { abs[modeled (NO_2) – observed(NO_2)] / [observed(NO_2)]}). The mean bias is an estimate of systematic over- or under-estimation of the LURF models as compared to the observations, while the mean error is the estimate of the average difference in the NO_2 predicted by the models and observations.

The predictive ability of the summer and winter LURF models was gauged by computing the root mean square error (RMSE) of the NO_2 predicted for the validation data with respect to the observations. Since the validation data are not used in model development, the validation RMSEs provide a good estimation of model performance on unseen data. The LURF validation data set RMSEs were further compared with RMSEs reported in the literature for LUR models, as well as the validation RMSEs of the LUR models developed using the same training, validation, and land use data sets as the LURF model.

As a final proof-of-concept check, we compared the rank of the spatially averaged (modeled) NO_2 associated with each land use category with the rank of the county-level emissions of nitrogen oxides (NOx) associated with that land use. To do so, we allocated county-level NOx emissions to the study area based on the fraction of the county that lay in the study area. Each emission sector was then associated with a land use, and emissions were summed and ranked (Table 3).

Emissions based on land use	**NOx emissions (tons/year)**	**% of regional NOx emissions**
Roads	12686	58%
High density development	7045	32%
Commercial	*717*	*3%*
Industrial	*1955*	*9%*
Mobile - Commercial Marine Vessels	*471*	*2%*
Mobile - Aircraft	*607*	*3%*
Mobile - Non-road Equipment	*3296*	*15%*
Railroads	1021	5%
Residential	883	4%
Other	321	1%
Biogenics	*171*	*1%*
Bulk gasoline Terminals	*2*	*0%*
Fires - Agricultural Field Burning	*8*	*0%*
Fires - Prescribed Fires	*118*	*1%*
Fires - Wildfires	*3*	*0%*
Fuel combustion electric generation - natural gas	*11*	*0%*
Fuel combustion electric generation -Oil	*1*	*0%*
Fuel combustion electric generation -Other	*0*	*0%*
Miscellaneous Non-Industrial NEC	*6*	*0%*
Solvent - Graphic Arts	*1*	*0%*

Table 3: NEI 2011 NO_2 emissions, allocated to the study area, and summed by land use.

Comparing the LURF annual NO_2 predictions with LUR

LUR is one of the most widely used methods to capture the fine-scale spatial variations of air pollutants in cities. Thus, it is instructive to compare the annual average NO_2 predicted by LURF with values of annual average NO_2 predicted by LUR for the study area. Towards this end, we examine the correlation between the LUR and LURF NO_2 predictions, as well as the best fit line between the LURF and LUR predicted NO_2. Additionally, we also look at the mean bias and the mean error of the LURF model with respect to the LUR model. The mean bias is an estimate of systematic over- or under-estimation of the LURF model with respect to the LUR model, while the mean error is an estimate of the average difference in the NO_2 prediction of the two models. Systematic under- or over-estimations between the two sets of predictions could be a useful indication of when one methodology could be preferred over the other.

Methodologically, the LURF model predictions are expected to show the greatest deviation from LUR at the highest and lowest NO_2 values. Hence we also undertake a quantile regression for the 0.1 and 0.9 deciles. Finally, we look at the spatial pattern of the mean error between the LUR and LURF models as well as how the mean error varies with land use category, to see if there is a systematic difference in predictions based on land use.

Developing the summer NO_2 LUR and LURF models for the Portland Metro area

For this study, we further constructed summer NO_2 models for the Portland Metro area only, so that we could avail of highly spatially resolved data available for the city. This is especially true in the case of tree canopy, where the 30m resolution of the NLCD data misses small green spaces as well as street and backyard trees. Additionally, the focus of the NLCD is land cover, whereas city-level data includes land use through zoning information.

Land use/land cover variable	**Data source**	**Proxy**
Freeways (length)	RLIS 2012[a]	traffic emissions
AADT[*] (traffic volume)	NHPN 2007[b]	traffic emissions
Major Arteries (length)	RLIS 2012[a]	traffic emissions
Arteries (length)	RLIS 2012[a]	traffic emissions
Streets (length)	RLLIS 2012[a]	traffic emissions
Railroads (length)	RLIS 2012[a]	railroad emissions
Industrial Area (area)	RLIS 2012[a]	industrial point sources
Population (number)	RLIS 2012[a] (based on 2010 census)	area sources
Area under tree canopy (area)	City of Portland, 2010	sink through deposition
Area under shrubs/herbaceous cover (area)	City of Portland, 2010	sink through deposition
Elevation (height)	RLIS 2012[a]	potential sink (wind flow)
Latitude	Measured/Google Earth	spatial variability of sources & sinks
Longitude	Measured/Google Earth	spatial variability of sources & sinks

Table 4: Land use/land cover variables used in LUR, data source and NO_2 source/sink proxy

*** AADT: Annual average daily traffic**

[a] Regional Land Information System, Metro Resource Data Center

[b] National Highway Planning Network

As previously, land use and land cover variables that were known to be strong proxies for urban sources and sinks of NO_2 were identified (Table 4). Latitude, longitude and elevation were added to the predictor set even though they are neither (direct) sources nor sinks of NO_2. However, these terms capture the spatial variability of the sources and sinks in the Portland Metro area, and hence are expected to improve the model fit. As the spatial resolution of the data is finer (1m), each land use and land cover variable was extracted for each of the 144 sites in 24 circular buffers ranging from 50m to 1200m in 50m increments. We considered using wind buffers as was done in the previous Portland LUR study (Mavko, Tang, & George, 2008b). However, we found that the average wind direction varied widely across our study area and could not be modeled using a single wind direction, as was done by Mavko et al, due the smaller spatial extent of their study area.

In all, we extracted more than 200 land-use and land-cover variables. The RLIS-based summer NO_2 LUR and LURF models were constructed using a similar methodology to the model development using the national datasets.

Results and Discussion

Developing annual NO_2 LUR and LURF models for Portland-Vancouver using national datasets

LUR models

The average adjusted R^2 (RMSE) for the summer and winter LUR models was 0.75 (2.8 ppb) and 0.80 (3.6 ppb) respectively. The R^2 for the models is consistent with published R^2 values in the literature which range from 0.50 to 0.90, while the RMSEs are on par with the lowest measured RMSE values (1.4 – 34 ppb) (Hoek et al., 2008).

The summer LUR model:

$$NO_2(i) = 8.5 + 3.3\text{x}10^{-7}*HH_{1200,i} + 2.3\text{x}10^{-8}*VMTf_{700,i} + 1.8\text{x}10^{-3}*HDEV_{1200,i} - 1.3\text{x}10^{-4}*OPEN_{100,i} - 6.8\text{x}10^{-3}*ELEVATION_i + 4.7*LAT_i + 9.1*LONG_i \quad \text{……………………………Equation 1}$$

Adj R^2 = 0.75, training RMSE = 2.3, validation RMSE = 2.8

The winter LUR model:

$$NO_2(i) = 7.3 + 3.5\text{x}10^{-8}*VMTf_{700,i} + 2.9\text{x}10^{-6}*MDEV_{900,i} + 6.8\text{x}10^{-6}*HDEV_{900,i} + 24*LAT_i \quad \text{……………………………Equation 2}$$

Adj R^2 = 0.80, training RMSE = 2.8, validation RMSE = 3.6

Where, at site (i):

NO_2(i) ………………………………..NO_2 ppb, at site (i)
$ELEVATION_i$ ……………………………. Elevation of site
$HDEV_{1200,i}$ ………………………………..High intensity development in 1200m
$HH_{900,i}$ ………………………………..Housing within 900m buffer
$HH_{1200,i}$ ………………………………..Housing within 1200m buffer
$MDEV_{900,i}$ ………………………………..Medium intensity development in 900m
LAT_i ……………………………….Latitude of site
$LONG_i$ ……………………………….Longitude of site
$OPEN_{100,i}$ ……………………..……….Developed open space within 100m
$VMTf_{700,i}$ ………………………………...Freeway vehicle miles traveled within 700m

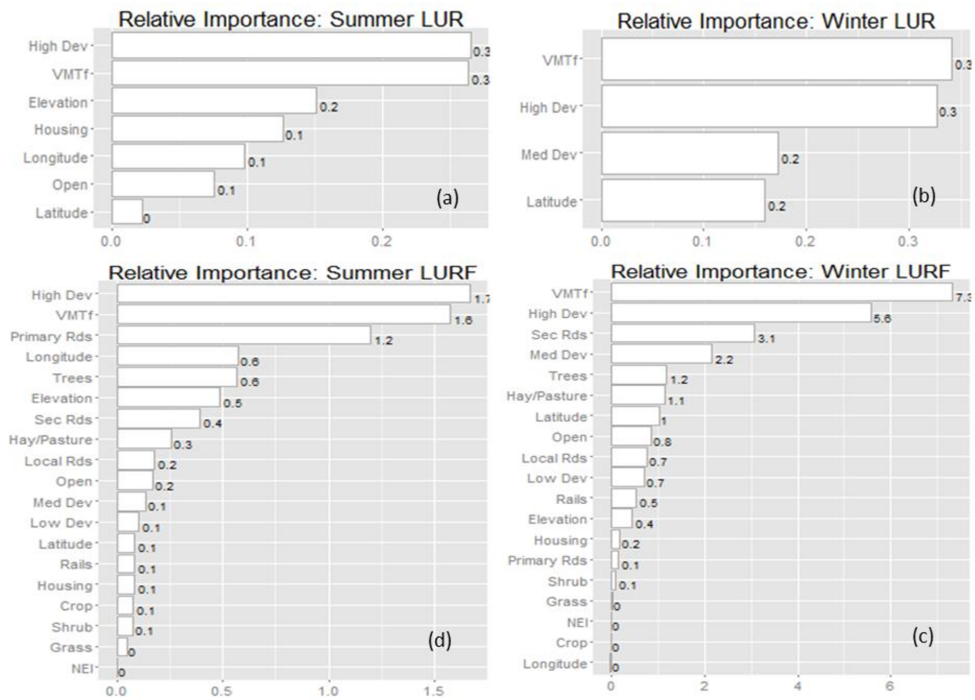


Figure 5: Relative importance of LULC predictors in NLCD-based NO_2 models

Vehicle miles traveled on freeways (VMT*f*) and high intensity development are significant terms in both the summer and winter LUR models (Equations 1 & 2). Elevation and open development are associated with reductions in NO_2 in summer, but do not appear as significant terms in the winter model.

The spatial distribution of the modeled annual NO_2 can be seen in Figure 6. The highest NO_2 concentrations are seen along freeways and in the industrial area in North Portland. The lowest annual NO_2 concentrations are found in Forest Park.

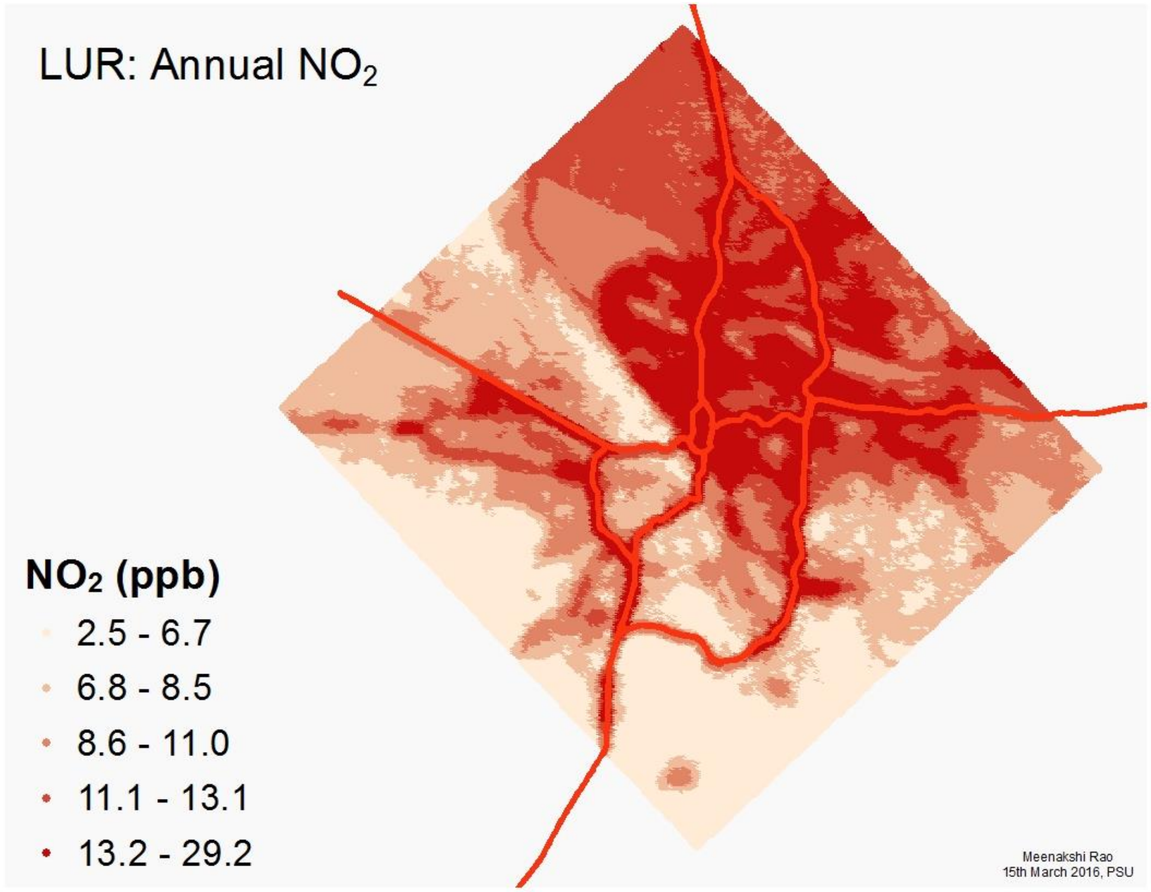


Figure 6: Annual NO_2 in Portland-Vancouver modeled using land use regression (LUR)

LURF models

Given the nature of random forest models, they cannot be tidily encapsulated in one equation like LUR models, but are best represented algorithmically, because the LURF models comprise of many regression trees built using different sets of predictor variables. LURF models are thus best represented indirectly through attributes of the model. Standard statistical measures for the LURF are presented in the next section; here we discuss the relative importance of the

LULC predictors for the summer and winter LURF and LUR (Figure 5). The relative importance of a predictor in LUR is measured by the percentage of total explained model variance that can be explained by the variable. The higher the variance explained by a predictor, the greater the importance of that predictor in the LUR model. In LURF, the importance of a predictor is measured as the difference in the mean square error (MSE) of the data and the MSE when the j^{th} predictor is permuted, i.e., randomized, normalized by the standard error. The greater the decrease in MSE associated with a predictor as compared to randomized data, the greater the importance of the variable in the LURF model.

The summer and winter LURF models show that high intensity development and freeways weighted with AADT (VMT*f*) are the most important predictors of NO_2 in both summer and winter. The relative importance of VMT*f* being comparatively higher in winter is consistent with lower boundary layer in winter. It is also consistent with the LUR findings. Trees have an impact on NO_2 in both summer and winter, which is consistent with our expectations for the mix of trees seen in the Portland-Vancouver area (a mix of evergreen and deciduous). The LURF models show the same directional variation as the LUR models: a longitudinal impact in summer and a latitudinal impact in winter. This is interesting as it is roughly perpendicular to the seasonal prevailing wind directions of NNW in summer and ESE in winter.

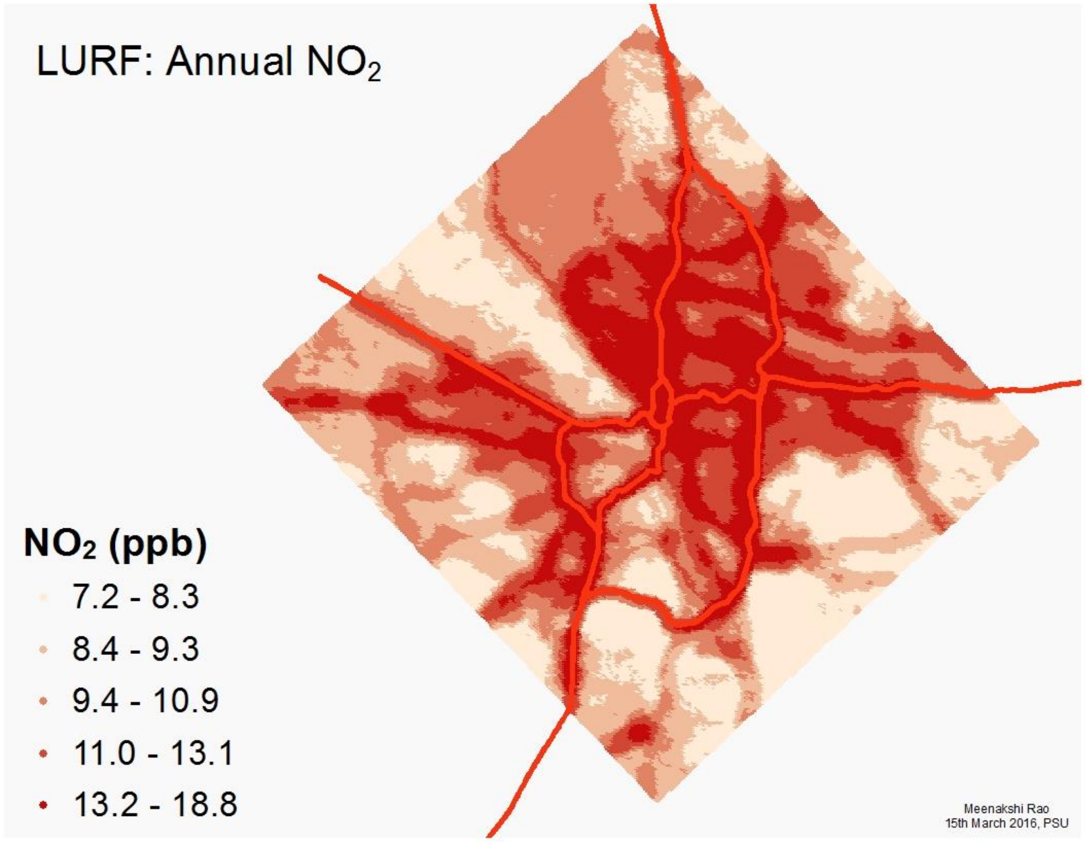


Figure 7: Annual NO_2 in the Portland-Vancouver area modeled using random forest (LURF)

The spatial distribution of the modeled annual NO_2 can be seen in Figure 7. As in the annual NO_2 LUR model, NO_2 concentrations are highest along freeways, and lowest in Forest Park. Modeled ambient concentrations of NO_2 within the study area range from 7-19 ppb, well below the US EPA standard (53 ppb) (US EPA, n.d.) and the World Health Organization standard (20 ppb) (World Health Organization, 2005).

Assessing the NO_2 random forest model

Based on statistical performance metrics, the summer and winter LURF models perform well with R^2 values of 0.80 and 0.83 respectively, indicating that a high degree of variance is captured by these models. Both summer and winter LURF models show non-zero mean bias and mean error: the summer and winter LURF models show mean biases of 9% and 12% respectively; and show mean errors of 20% and 24%. Thus, the LURF models systematically overestimate NO_2 concentrations as compared to the observations, and this bias is larger than for the corresponding LUR models (Table 4). On average, the LURF modeled NO_2 differs by ~22% from the observed NO_2, slightly worse than the LUR model performance.

	Goodness of fit	Model bias		Prediction error	
	Adj R^2	Mean bias	Mean error	Validation MAE (NO_2 ppb)	Validation RMSE (NO_2 ppb)
Summer					
LUR	*0.75*	5%	20%	2.3	2.8
LURF	0.80	9%	20%	2.0	2.4
Winter					
LUR	*0.80*	5%	18%	2.5	3.4
LURF	0.83	12%	24%	2.8	3.8

Table 4: Performance metrics for the NLCD-based summer and winter LUR and LURF models

The predictive ability of the LURF models, as gauged by the validation data RMSEs, indicates that the summer and winter models, on average, predict NO_2

concentrations within 2.4 ppb of the measured NO_2 in summer, and 3.8 ppb in winter (the higher winter validation RMSE being consistent with fewer winter observations). These RMSEs are consistent with RMSEs for NO_2 LUR models in the literature, in fact lying towards the lower end of the reported range of 1.4 – 34 ppb (Hoek et al., 2008). The RMSEs for the summer and winter LURF models of 2.4 ppb and 3.8 ppb are also on par with the validation RMSEs of 2.8 and 3.4 for summer and winter LUR models developed using the same data sets.

Modeled associations of NO_2 with land use are consistent with NOx emissions inventories associated with that land use. Land use associated with roadways – including Vehicle Miles Traveled on freeways (VMT*f*), primary, secondary, and local roads – has the highest average contribution to the NO_2 concentrations in the study area (Table 5), consistent with the fact that about 58% of NOx emissions in the region are from on-road mobile sources. High intensity development has the next largest association with ambient NO_2 concentrations in the study area, an average of about 0.6 ppb across the study area. The land cover class high intensity development in NLCD (Table 1) represents areas where > 80% of the area is impervious surface, typically high density housing, parking lots, and industrial and manufacturing areas. Thus the higher levels of NO_2 associated with this land cover are consistent with NOx emissions sources associated with this land use, which are the second biggest source of NOx emissions (32%). Housing density and railroads are associated with a small average increase in NO_2 concentrations, consistent with NOx emissions from residential fuel combustion and railroads each being 4% of estimated NOx emissions in the region. Permitted facilities, on average, contribute almost nothing to ambient NO_2 concentrations, also consistent with the presence of only 3 facilities with permits to emit more 500 tons NOx/year.

LULC category	NO_2 (ppb) associated with land use	Range NO_2 (ppb)	Typical LULC values within model buffer	Range LULC values within model buffer
High intensity development	0.6	0 – 3.1	28 ha	0 - 7.9 km^2
Roadways	0.9	0 – 6.2		
Vehicle Miles traveled on highways	*0.3*	*0 – 2.8*	1.8×10^7	$0 – 3.6 \times 10^8$
Primary Roads	*0.1*	*0 – 1.2*	0.4 km	0 - 15 km
Secondary Roads	*0.4*	*0 – 1.6*	2.9 km	0 - 38 km
Local Roads	*0.1*	*0 – 0.6*	26 km	0 - 100 km
Railroads	0.1	0 – 0.4	1.6 km	0 - 40 km
Housing	0.1	0 – 0.3	15,000	0 - 230,000
Permitted NO_2 emissions	0.0	0 – 0.0	6 tons/yr	0 - 1,000 tons/yr
Developed open space	-0.2	-0.6 – 0	0.2 ha	0 – 3 ha
Low intensity development	-0.1	-0.4 – 0	0.7 ha	0 – 3 ha
Medium intensity development	0.2	0 – 1.0	33 ha	0 – 170 ha
Trees	-0.3	-0.9 – 0	10 ha	0 – 80 ha
Shrub/Scrub	-0.0	-0.2 – 0	0.5 ha	0 – 28 ha
Grass	-0.0	-0.2 – 0	6 ha	0 – 94 ha
Hay/Pasture	-0.3	-0.7 – 0	60 ha	0 – 335 ha
Crop	-0.0	-0.1 – 0	48 ha	0 – 450 ha

Table 5: Estimated association of land use and annual average NO_2 concentrations, averaged over the study area. The two rightmost columns show average land use values within the model buffers.

Overall, we find that the LURF model performance metrics and predictive ability are on par with the widely used LUR methodology, and that the predicted ambient NO_2 concentrations are consistent with county level emissions.

Comparing the annual NO_2 predictions from LUR and LURF

The annual average NO_2 predicted by LURF and LUR for the Portland-Vancouver metropolitan area is highly correlated (Figure 8a), with a Pearson correlation coefficient of 0.85. The relationship between LUR and LURF predicted NO_2 can be summarized by the best fit regression line which has an adjusted R^2 of 0.72 (Figure 8a), indicating an effective linear mapping from LUR predicted NO_2 to LURF predicted NO_2 concentrations. However, the intercept of 5 ppb, and slope of 0.6 (Figure 8a), indicate that at the origin, the NO_2 estimated by LURF is 5 ppb higher than LUR NO_2, but every subsequent 1ppb increase in LUR predicted NO_2 corresponds to only a 0.6 ppb increase in LURF NO_2.

The positive intercept is an indication that the LURF NO_2 predictions are off-set from the LUR NO_2 predictions. In fact the LURF NO_2 predictions show a systematic overestimation as compared to the LUR predictions, with a 13% mean bias. The mean error is 22%; that is, on average there is a 22% difference between the NO_2 concentrations predicted by the LURF and LUR models. Thus there is a numerical difference between the annual average NO_2 predictions by the LURF and LUR models, but the correlation between the LUR and LURF NO_2 predicted concentrations is high.

Methodologically – and this can also be seen in Figure 8a – one can expect an over-estimation of NO_2 values with respect to LUR at the lower NO_2 quantiles, and an underestimation in the highest quantile. A quantile regression (blue lines in Figure 8a) shows that the discrepancy between LUR- and LURF-predicted NO_2 does vary by quantile. For the lowest decile, the slope = 0.37 and intercept = 5 ppb. At the highest decile, the slope is the same as the best fit line (0.6), but the intercept is higher (6 ppb).

Figure 8b shows the spatial pattern of the bias of LURF NO_2 predictions as compared to the LUR predictions. The strong gradient from south-west to north-east echoes the gradient seen in the LUR annual NO_2 predictions (Figure 6). This may be an indication that the dependence of NO_2 on latitude and longitude is non-linear. Figure 8c shows how the bias in NO_2 predictions varies with land use categories. This is not unexpected, and serves to highlight the correlated nature of land use variables. For example, LURF predicts lower NO_2 concentrations associated with high intensity development. This may be because high intensity development in the LUR model is predicting NO_2 for high intensity development and correlated land use, such as more roads in the vicinity and greater traffic volumes, which are separated out in the LURF model.

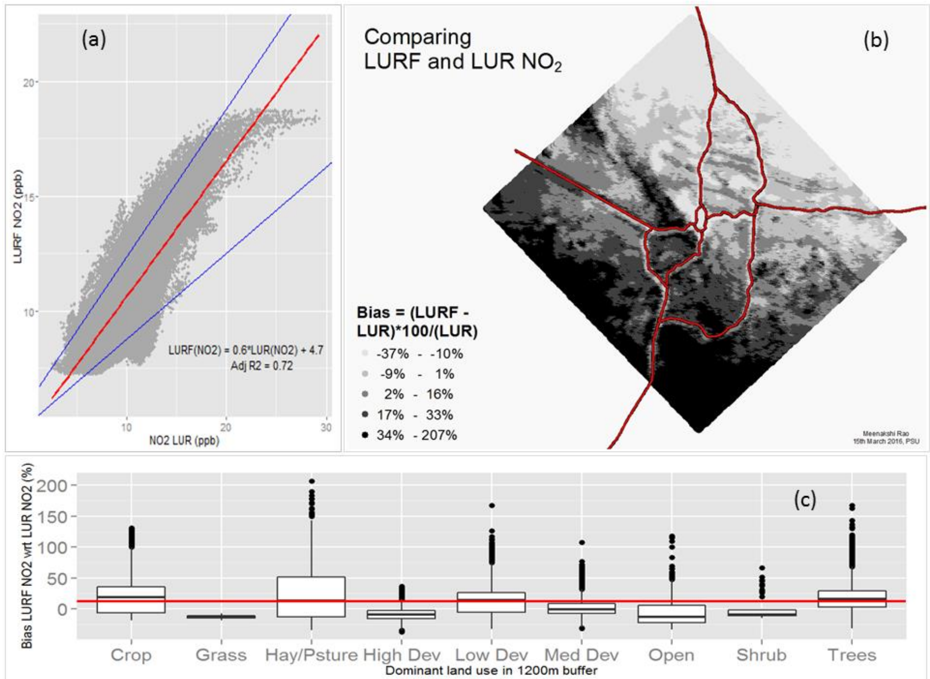


Figure 8: (a) Correlation between LUR- and LURF-predicted annual NO_2 (b) The spatial pattern of the bias of LURF NO_2 as compared to the LUR NO_2 (c) LURF NO_2 bias with land use

Summer NO_2 LUR and LURF models for the Portland Metro area

Since we are especially interested in estimating the potential of trees in mitigating urban NO_2, and the NLCD with resolution of 30m cannot separately capture urban tree canopy, we developed summer NO_2 models using high resolution land use data for the Portland Metropolitan area. The summer LUR NO_2 model is given by equation 3. This model has an adjusted R^2 of 0.80, and an RMSE of 2.2

(note: the RMSE is for the dataset used for model development, as no observations were set aside for validation).

Summer model:

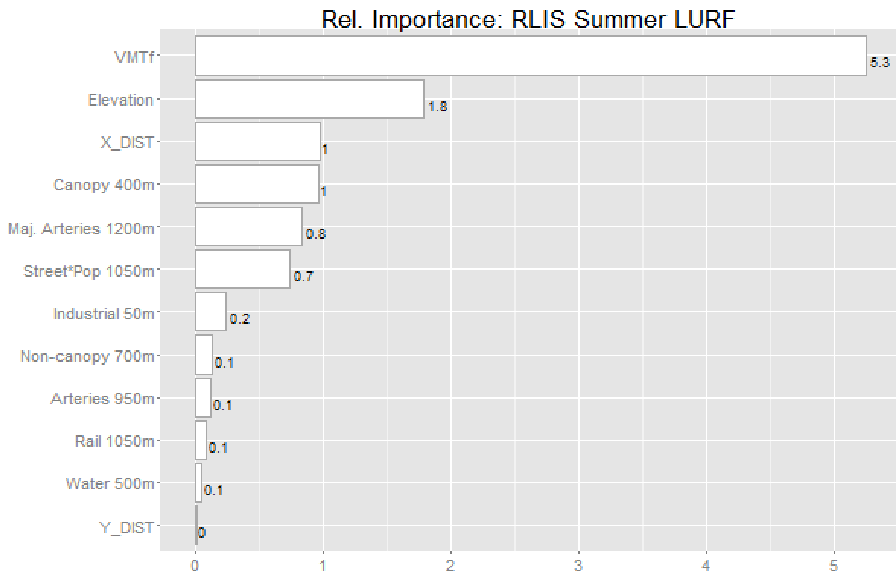
$NO_2(i) =$

$$7.7 + 1.1\text{x}10^{-8}*\text{FWY\_AADT}_{1200,i} + 6.5\text{x}10^{-4}*\text{MAJ\_ART}_{500,i} + 1.7\text{x}10^{-3}*\text{ARTERIES}_{350,i} + 1.8\text{x}10^{-8}*\text{STREETS(POP)}_{800,i} + 1.0\text{x}10^{-3}*\text{RAILS}_{250,i} - 1.0\text{x}10^{-2}*\text{ELEVATION}_i + 1.4\text{x}10^{-5}*(\text{ELEVATION}_i)^2 - 5.73\text{x}10^{-6}*\text{TREES}_{400,i} + 1.1\text{x}10^{-4}*\text{X\_DIST}_i$$

Adj R^2 = 0.80, validation RMSE = 2.2 ……………………..………..Equation 3

Where, at site (i):

NO_2(i) ……………………………….…NO$_2$ ppb, at site (i)
$FWY\_AADT_{1200,i}$ ……………………………freeway (m) in 1200m, weighted with AADT
$MAJ\_ART_{500,i}$ ………………………………..major arteries (m) in 500m
$ARTERIES_{350,i}$ ……………………………… arteries (m) in 350m
$STREETS(POP)_{800,i}$ …………………………streets (m) in 800m, weighted by the population
$RAILS_{250,i}$ ………………………………..railroads (m) in 250m
$ELEVATION_i$ ………………………………..elevation (ft)
$TREES_{400,i}$ ………………………………..tree canopy (m^2) in 400m
X_DIST_i ……………………………….distance from center of city (in m), along E-W axis
Y_DIST_i ……………………………….distance from center of city (in m), along N-S axis



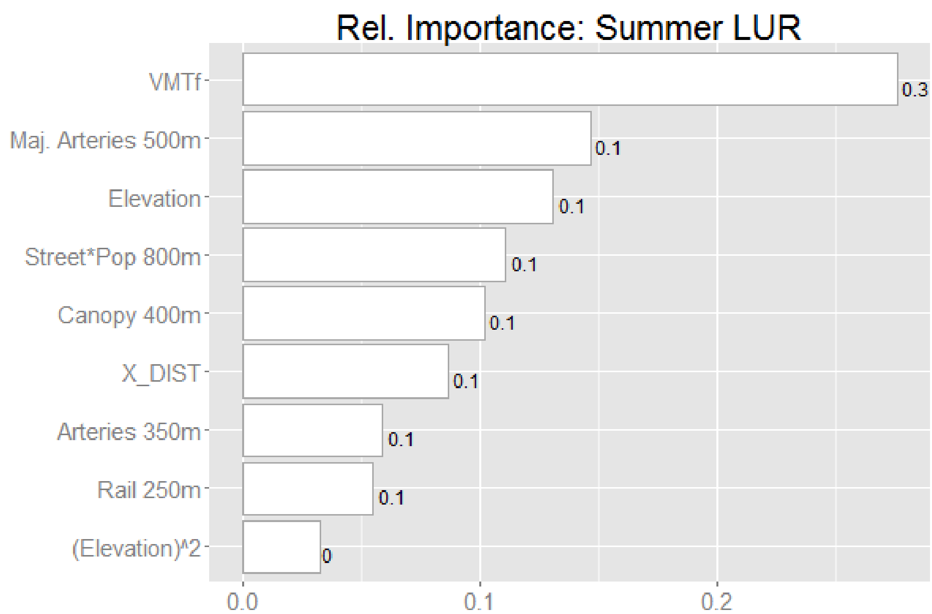


Figure 9: Relative importance of RLIS-based land use variables in the summer LUR and LURF models

Conclusion

In a rapidly urbanizing world, where, according to the World Health Organization, air pollution has become “the single largest environmental health risk,” there is an urgent need to design cities that promote cleaner atmospheres. While reducing emissions remains of paramount concern, modifying or designing urban spaces to mitigate urban air pollution is a good complementary approach. In this chapter, we show that the random forest ensemble learning technique is a viable methodology for modeling the sensitivity of local NO_2 concentrations to urban land use and land cover modifications. We further showed that the summer and winter observationally-based LURF models performed well based on statistical performance metrics, that the prediction error on previously unseen data was on par with the widely used LUR methodology, and that the relative importance of LULC features on modeled NO_2 concentrations was consistent with existing NO_2 emissions inventories. These findings – taken together with the fact that the random forest technique places minimum constraints on the underlying data, can handle correlated predictors, and deal with the “large P, small N” scenario – indicate that the LURF technique is a powerful technique to add to the repertoire of techniques used to model intra-urban variations of air pollution. Critically, this technique is robust in handling noisy and missing data, a not uncommon feature of dense sensor networks, making it ideally suited for analyzing the flood of data from sensor technologies that are currently on the horizon. Since it is relatively easy to use, does not require intense computational support, and the output models are readily interpreted, the use of this technique has the potential to include a wide range of stakeholders, including planners, citizens, and agencies, in the process of better characterizing and managing local LULC to optimize air quality.

In applying the annual NO_2 LURF model, it is important to keep in mind that LURF overestimates NO_2 concentrations both in comparison to observations and the LUR model. Further, the discrepancy between NO_2 predicted by LURF and LUR is greatest for the lowest quantiles of NO_2 concentrations, and least for the highest quantiles. Thus LURF models are perhaps, until better calibrated, best used for determining relative rather than absolute NO_2 concentrations, or limited to applications that are concerned with the highest quantiles of NO_2 concentrations.

Chapter 3: Assessing the relationship between urban land use, ambient NO_2 and respiratory health

Dear future generations: Please accept our apologies. We were roaring drunk on petroleum.

Kurt Vonnegut

Abstract

In this chapter, we apply the annual NO_2 LURF model to understand the health and economic impacts of NO_2 in the mid-sized US metropolitan area of Portland-Vancouver, and compare the demographic characteristics of the population residing in the highest and lowest quintiles of NO_2. We further leverage the LURF model in conjunction with BenMAP to begin assessing the relationship between local land use, ambient concentrations of NO_2, and respiratory health.

We find that there is some disparity in the demographics of the population living in the lowest and highest quintile of NO_2: generally a larger proportion of low-income households, Hispanics and African-Americans can be found residing in the highest NO_2 quintile. Further, although Portland-Vancouver is in compliance with US EPA standards for $NO_{2,}$ there is still a \$40 - \$65 million annual health burden due NO_2-related respiratory problems. The association of high intensity development with ambient NO_2 may be conservatively linked to a \$7 million respiratory health burden annually, while the reduction of NO_2 association with tree canopy may be linked to a \$1.4 million annual health benefit.

Introduction

As we have seen earlier, cities have the unintended consequence of concentrating both people and their emissions into urban areas, creating a huge burden of disease (A. J. Cohen et al., 2006; Fann et al., 2012). In our rapidly urbanizing world – more than half the people live in cities today and two-thirds are expected to be urban by 2050 – we see there is an urgent need for strategies to mitigate the health impact of urban air pollution.

Urban areas are highly managed landscapes. For example, urban policies control building heights, siting of industrial and manufacturing zones as well as commercial and business areas with their higher density of traffic; and the quantity of emissions from industrial or manufacturing units through permitting. These very factors influence the sources, sinks and flows of air pollutants in the urban environment. In our rapidly urbanizing world, this association of land use and ambient concentrations of air pollution brings us back to our overarching question: to what extent can urban land use be managed to decrease the human health impact of air pollution? Globally, managing land use to reduce pollution is not a new concept. Hong Kong requires an air ventilation assessment for all publicly funded construction to mitigate the stagnant wind conditions that arise due to its many urban canyons, which would otherwise lead to an accumulation of air pollutants as well as air-borne diseases like Severe Acute Respiratory Syndrome (SARS) (Ng, 2009). In California, schools are required to be located more than a quarter mile away from sources of potentially hazardous air pollutants (School Facilities Planning Division: California Department of Education, 2015). And many cities actively seek to reduce vehicle miles traveled (VMT) to reduce CO_2 emissions and manage regional air quality (Bureau of Planning and Sustainability, 2015; City of Burlington Vermont, 2014; Seattle Office of Sustainability and Environment, 2013). However, even though land use has been regulated to reduce or avoid exposure to emissions, the relationship among air pollution, *local* land use decisions, and health impacts has – with few exceptions (Borrego et al., 2006; Nowak et al., 2013; Rao et al., 2014) – not been systematically investigated.

In this chapter, we use the annual NO_2 LURF model developed for the Portland-Vancouver area to begin exploring the relationship among local land use/land cover (LULC), ambient concentrations of NO_2, and respiratory health. We begin by evaluating the health impact of current ambient NO_2 concentrations on incidence of NO_2-related respiratory problems in the study area, using BenMAP, an environmental health and benefits mapping program from the US EPA. Many previous studies have shown inequitable access to environmental resources, including clean air, based on income, education, and race (L. P. Clark et al., 2014; O'Neill et al., 2003). Therefore, we also compare the demographics of the population residing in the lowest and highest quintiles of NO_2 concentrations to see how access to the areas with the lowest NO_2 concentrations varies with age, income, race, and educational attainment. Finally, we use the LURF NO_2 model in conjunction with BenMAP, to study the association between air pollution, local land use/land cover, and respiratory health. In summary, in this chapter we use the LURF model to:

(i) characterize and compare the demographics of the populations residing in the areas that fall into lowest NO_2 quintile with those of the population residing in the highest NO_2 quintiles;

(ii) estimate the health and economic impacts of current ambient NO_2 concentrations in the study area; and

(iii) examine the association of the model's land use categories with NO_2 and respiratory health in the study area.

Methods and materials

Our study area remains the Portland-Vancouver urban area, with just over 1.8 million people residing within the 2,350 km^2 that it covers. About 20% of the population in the study area is under 15 years of age, while 11% is 65 years or older. In terms of race, 11% of the population is Hispanic, 3% African-American, and 6% Asian.

The LULC within the study area is summarized in Table 6, and the spatial distribution is shown in Figure 10. Within the study area, the largest proportion of land is low intensity developed space (21%), while 6% of land area is high intensity development, 7.5% is developed open space, and 13% is under tree canopy, based on the 2011 National Land Cover Database (NLCD). There are ~80 permitted facilities within the study area, of which only three are permitted to emit more than 500 tons of NOx annually, the largest emitter being the Portland International Airport, with a permit to emit up to 1,100 tons NOx a year.

NLCD Land Cover Category	Percent of study area
Open Water	4%
Developed, Open Space	7%
Developed, Low Intensity	21%
Developed, Medium Intensity	16%
Developed, High Intensity	6%
Barren Land	1%
Deciduous Forest	2%
Evergreen Forest	6%
Mixed Forest	5%
Shrub/Scrub	2%
Herbaceuous	1%
Hay/Pasture	13%
Cultivated Crops	11%
Woody Wetlands	3%
Emergent Herbaceuous Wetlands	1%

Table 6: Land cover in the Portland-Vancouver area

As described in greater detail below, we begin by using the LURF NO_2 model for the study area to compare the demographics of the population living the lowest and highest quintile of NO_2 concentrations. Next we use the LURF NO_2 model, in conjunction with BenMAP, to assess the incidence of respiratory problems attributable to ambient NO_2 within the study area. Finally, we explore the relationship between individual land use categories, ambient NO_2, and respiratory health, as described in greater detail below.

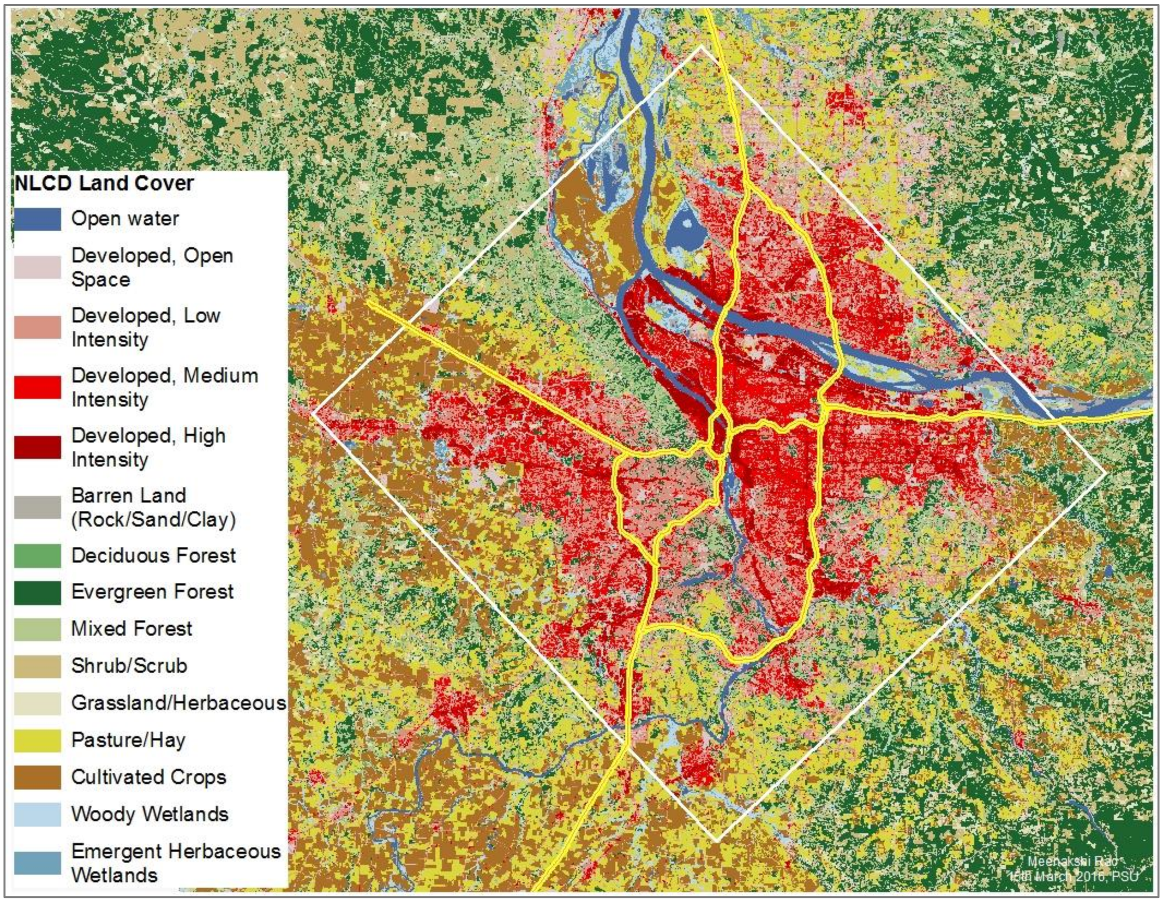


Figure 10: Spatial distribution of the NLCD land cover categories in the Portland-Vancouver area

The demographics of residents in the highest and lowest NO_2 quintiles

Demographic information at the block-group level, including age, household income, educational attainment, and racial diversity, were obtained from the 2011 American Community Survey 5-Year estimate tables (US Census Bureau, 2012). Block-group population was assumed to be evenly spread over the block-group. Block-groups were intersected with the highest and lowest quintiles (80% and 20%) of NO_2 concentrations. The population for each whole or fractional block-group in the quintiles was determined by multiplying the population of the block-group with the fraction of the block-group within the quintile. Then this weighted population was summed over all block groups in the quintile to determine the quintile population and demographics. The demographic categories considered in the comparison are age, as children and seniors have been shown to be more vulnerable to air pollution (L. P. Clark et al., 2014; S. Grineski, 2007; Ostro et al., 2001), and household income, educational attainment, and racial diversity, based on the review by O'Neil et al (O'Neill et al., 2003). Analysis was done in ESRI's ArcMAP 10.3 and R version 3.1.1 (R Core Team, 2014).

Health and economic impact of current NO_2

BenMAP

The Environmental Benefits Mapping and Analysis Program version 4.0.35 (BenMAP) (U.S. EPA (US Environmental Protection Agency), 2010), is a Windows-based computer program from the US EPA that uses a Geographic Information System (GIS)-based approach to estimate the health impacts and economic benefits occurring when populations experience changes in air quality. BenMAP comes with multiple built-in regional and national datasets to facilitate health benefits modeling, and has been used to estimate the health benefits of proposed regulatory changes at the regional and national scales (Corbett et al., 2007; Davidson, Hallberg, McCubbin, & Hubbell, 2007; Hubbell, Hallberg, McCubbin, & Post, 2004; Sequeira, 2008).

BenMAP incorporates health impact functions for NO_2 from multiple studies and for multiple outcomes (Abt Associates Inc., 2010a, 2010b). The baseline incidences for all health outcomes at the county level are also part of the BenMAP database. BenMAP includes a built-in county-level population database, based on the 2000 Census, which can be projected up to 2030, using a built-in projection algorithm. Block-group level population is also available through the ancillary program, Popgrid. Using Popgrid, population can also be allocated to a grid of the user's choosing.

Health Impact	Study	Location	Valuation Method
Asthma Exacerbation, Missed school days (4 to 12 years)	O'Connor et al. (2008)	7 inner cities	WTP: 1 symptom-day, Dickie and Ulery (2002) | 0-17
Asthma Exacerbation, One or More Symptoms (4 to 12 years)	O'Connor et al. (2008)	7 inner cities	WTP: 1 symptom-day, Dickie and Ulery (2002) | 0-17
Cough (7 to 14 years)	Schwartz et al. (1994)	Six U.S. cities	WTP: 3 symptoms 1 day, Dickie and Ulery (2002). | 18-99
Emergency Room Visits, Asthma (75 years and older)	Villeneuve et al. (2007)	Edmonton, Canada	COI: Standford et al. (1999) | 0-99
HA, All Respiratory (65 years and older)	Yang et al. (2003)	Metropolitan Los Angeles	COI: med costs + wage loss | 65-99
HA, Asthma (29 years or younger)	Linn et al. (2000)	Metropolitan Los Angeles	COI: med costs + wage loss | 0-64
HA, Asthma (30 years or older)	Linn et al. (2000)	Vancouver, Canada	COI: med costs + wage loss | 0-99
HA, Chronic Lung Disease (less Asthma) (65 years and older)	Yang et al. (2005)	Vancouver, Canada	COI: med costs + wage loss | 65-99

Table 7: BenMAP health impact and valuation functions used for assessing incidence and economic value of NO_2 exposure in the Portland-Vancouver urbanized area (WTP: Willingness to Pay; COI: Cost of Illness)

BenMAP includes several health impact functions for NO_2. We chose a subset of these health outcomes, picking the health impact functions that were based on studies in the Northwest or large urban studies; or ones that were for an outcome for a susceptible population like children or seniors. Table 7 shows the health outcomes and valuation methods considered in our analyses.

The health and economic impact of NO_2 is assessed in BenMAP against a baseline NO_2 of 3 ppb (the lowest observed NO_2 value) and 7 ppb (the lowest LURF modeled NO_2 value). Population is allocated to each 200m grid cell, using 2013 population projections (based on 2000 census data) using Popgrid. Incidences and valuations are summed over the entire study area for reporting.

Association of land use, ambient NO_2, and respiratory health

We leverage the ability of the LURF model to deal with correlated predictors to begin exploring the strength of the association between individual LULC categories and ambient NO_2 concentrations. We estimate the impact of individual LULC category on ambient NO_2 concentrations as follows: each land use category under consideration is set to zero (see Table 5 for typical land use values within the model buffers) over the entire study area, while keeping the remaining land use variables unchanged. Summer and winter NO_2 predictions are calculated using the summer and winter LURF models respectively for each point on the 200m grid covering the study area. These seasonal predictions are then averaged to estimate the annual average NO_2 in the absence of the LULC category. The difference in modeled NO_2 concentrations between the annual NO_2 model and the model with the land use category set to zero is used as an indicator of the NO_2 associated with that land use. In essence, we are using the LURF model to simulate the NO_2 concentrations across the urban landscape when each LULC category is essentially replaced by an NO_2-netural LULC. For example, setting tree canopy to zero is the equivalent of assuming, from the perspective of the model, that tree canopy in the study area has been replaced by a NO_2-neutral land cover; and setting VMT*f* to zero is equivalent to assuming that the current traffic on highways is replaced by non-NO_2 emitting vehicles.

This difference in NO_2 estimated for each LULC category as described above, an indicator of the relative impact of the land use category on ambient NO_2 concentrations, is used as input to BenMAP to estimate the health impact associated with change in NO_2. Using the respiratory health impacts and economic valuations in BenMAP we estimate both the incidence and economic valuation of health impacts associated with differences in NO_2 associated with each LULC. Thus, we are able to assess the relationship between local LULC, ambient NO_2 concentrations and respiratory health. We use the same health impacts and valuation functions (Table 7) as used in the previous analysis.

Results and discussion

The demographics of residents in the highest and lowest NO_2 quintiles

We find (Figure 11c) that approximately 5% of the Portland-Vancouver population lives in the lowest NO_2 quintile (the lowest 20% of NO_2 concentrations, ranging from 7.2 to 8.3 ppb NO_2, shown in Figure 11(b) in green), while 39% live in the highest NO_2 quintile (the highest 20% of NO2 concentrations, ranging from 13.1 to 18.8 ppb NO_2, shown in Figure 11(b) in red). The spatial extent of both the highest and lowest quintiles of NO_2 is ~470 km^2 or roughly one-fifth of the study area; however, from Figures 11(a) and (b), we can see that the highest quintile of NO_2 falls along the area with highest population density, while the lowest quintile of NO_2 lies for the most part along the least densely populated parts of the study area, accounting for the big difference in the population in the two quintiles.

There is a difference in the demographic profile of the people residing in the cleanest or lowest quintile as compared to the highest NO_2 quintile as well. We first see that children under 14 years are slightly less likely than the overall population (34% vs. 39%) to reside in the highest quintile of NO_2 concentrations

(Figure 11c). Based on figures 11(d) – (f), we see that African-Americans and Hispanics, people with a highest educational attainment of a high school diploma or less, and households with annual incomes under $25,000 are slightly more likely to be found residing in the highest quintile of NO_2; while whites and Asians, as well as households with annual income over $100,000 are more likely to be found in the lowest quintile of NO_2.

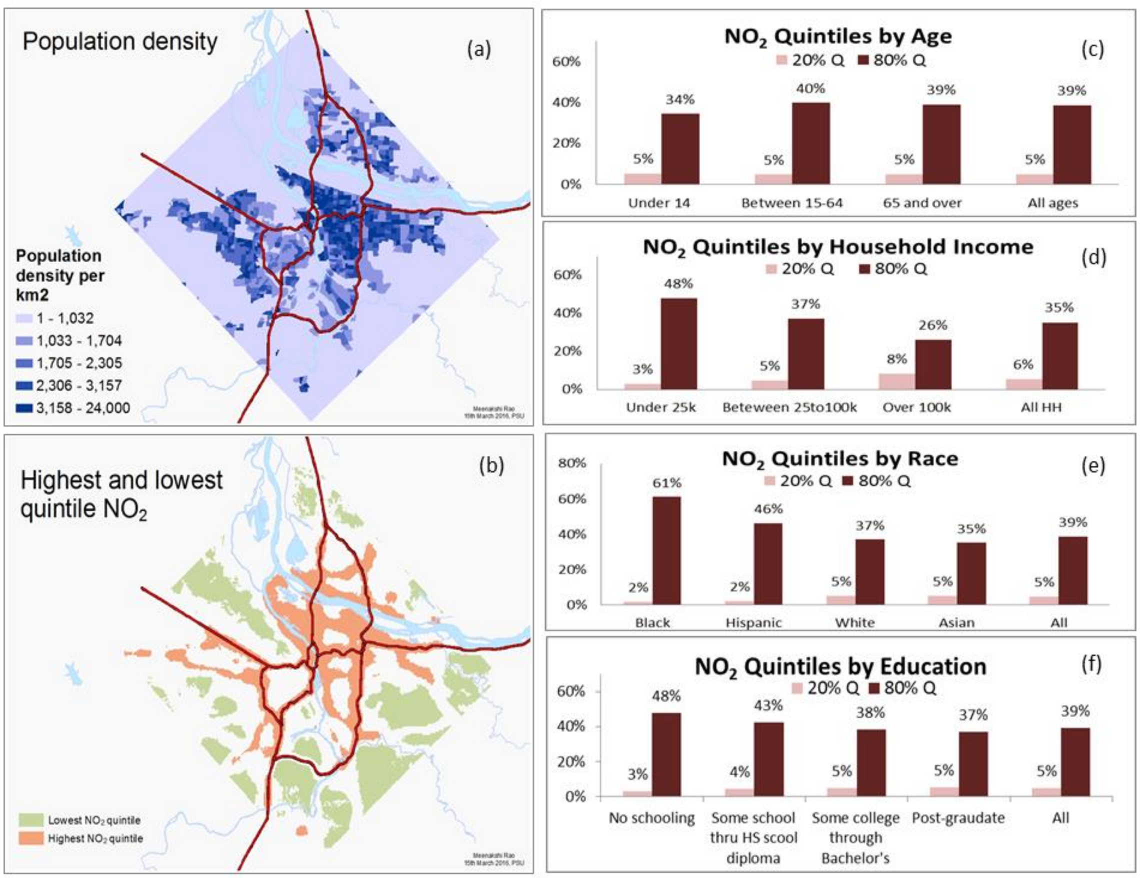


Figure 11: Population density map (a) and the spatial distribution of worst and best NO_2 quintiles in the study area (b). Demographics of people residing in the worst (80% quintile) and best (20% quintile) of NO_2 concentrations by age (c), annual household income (d), race (e), and educational attainment (f).

Our findings that low income households as well as Hispanics and African-Americans disproportionately reside in the worst quintile for NO_2 concentrations is consistent with findings from other studies in the US (L. P. Clark et al., 2014; S. C. Gray, Edwards, & Miranda, 2013; S. E. Grineski, Collins, Chakraborty, & McDonald, 2013; Zwickl et al., 2014).

Health and economic impact of current NO_2

Even though the Portland-Vancouver Metropolitan area is in compliance with the EPA standards for NO_2, our modeling shows an increased incidence of respiratory problems associated with NO_2. This is not surprising, as there is no threshold value for the health impacts of NO_2 – any non-zero level of NO_2 will result in some increased incidence of respiratory problems. In pristine environments, NO_2 concentrations are on the order of 1 ppb (or less), so we have evaluated the increase in incidence of NO_2-related respiratory problems against baseline concentrations of 3 ppb NO_2. Since this concentration level may be hard to achieve in urban areas, especially in the near future, we also evaluate the increase in incidence compared to a more achievable 7 ppb.

We see that in the Portland-Vancouver area, NO_2-related respiratory problems may be creating a burden of $40 - $65 million annually (Table 8). The brunt of this respiratory impact of NO_2, based on the health impact and valuation functions in BenMAP and the LURF modeled NO_2, is borne by children under 15 years of age. BenMAP estimates that between one to two in ten 4-12 year olds miss a day of school annually due to asthma exacerbation attributable to our modeled NO_2; and further estimates between one to two in every ten 7-14 year olds suffer from a cough attributable to NO_2. Seniors are impacted by NO_2-related respiratory problems to a greater extent than adults or young adults. There is an increase in hospital admissions due to respiratory problems in seniors of 100-200 incidents per 100,000 seniors.

Health Impact	**Compared to 3 ppb baseline**			**Compared to 7 ppb baseline**		
	Incidence	**Incidence rate (per 100,000)**	**Valuation (2013 USD)**	**Incidence**	**Incidence rate (per 100,000)**	**Valuation (2013 USD)**
Asthma Exacerbation, Missed school days (4 - 12 year olds)	58,218	24,615	$12,413,037	34,189	14,455	$7,289,729
Asthma Exacerbation, One or More Symptoms (4 -12 year olds)	170,412	72,052	$36,334,706	99,740	42,171	$21,266,297
Cough (7 -14 year olds)	41,084	20,547	$5,479,871	24,134	12,070	$3,219,017
Emergency Room Visits, Asthma (75 years and older)	34	37	$11,948	20	22	$7,171
HA, Asthma (younger than 30 years)	10	1	$109,672	6	1	$64,785
HA, Asthma (30 years and older)	11	1	$130,247	7	1	$76,749
HA, Chronic Lung Disease (less Asthma) (65 years and older)	234	105	$4,398,998	143	64	$2,633,286
HA, All Respiratory (65 years and older)	513	230	$12,980,186	307	137	$7,752,000
Total:			*$67,329,420*			*$39,598,999*

Table 8: Incidence and valuation of the respiratory impact of ambient NO_2 concentrations, compared to idealized baseline concentrations of 3ppb and 7ppb NO_2.

The valuation functions used to estimate the economic cost of respiratory problems are based on either willingness to pay or cost of illness plus lost wages, and may not capture the true economic impact of NO_2-related respiratory problems, especially for children. For example, recent studies show that childhood exposure to traffic-related air pollution may lead to impaired lung function in early adulthood (Z. Chen, Salam, Eckel, Breton, & Gilliland, 2015; Gauderman et al., 2007), and that exposure to air pollution in childhood is linked to poorer performance in school (Clark-Reyna, Grineski, & Collins, 2015), which in turn could lead to lower earnings potential in adulthood.

Findings of the health impacts of NO_2 from the Portland-Vancouver area are likely to be representative of other similar mid-sized cities in the developed world, where NO_2 concentrations are within national and international standards due to strong regulations, and the population density is not too high. However, these findings are unlikely to capture the health impacts of NO_2 in the emerging megacities of the world where both population densities and emission intensities are much higher.

Assessing the association of urban land use, ambient NO_2, and respiratory health

Of the land use categories considered (Table 5), high intensity development, medium intensity development, VMT*f*, primary, secondary and local roads, railroads, housing density, and permitted NO_2 emissions are associated with increasing ambient NO_2. The remaining land use categories (low intensity development, developed open spaces, trees, shrubs, grass, hay/pasture, and cropland) are associated with decreasing ambient NO_2 concentrations (Table 5). Averaged over the urban study area, the changes in ambient NO_2 range from a decrease of 0.3 ppb associated with trees to an increase of 0.9 ppb associated with roadways.

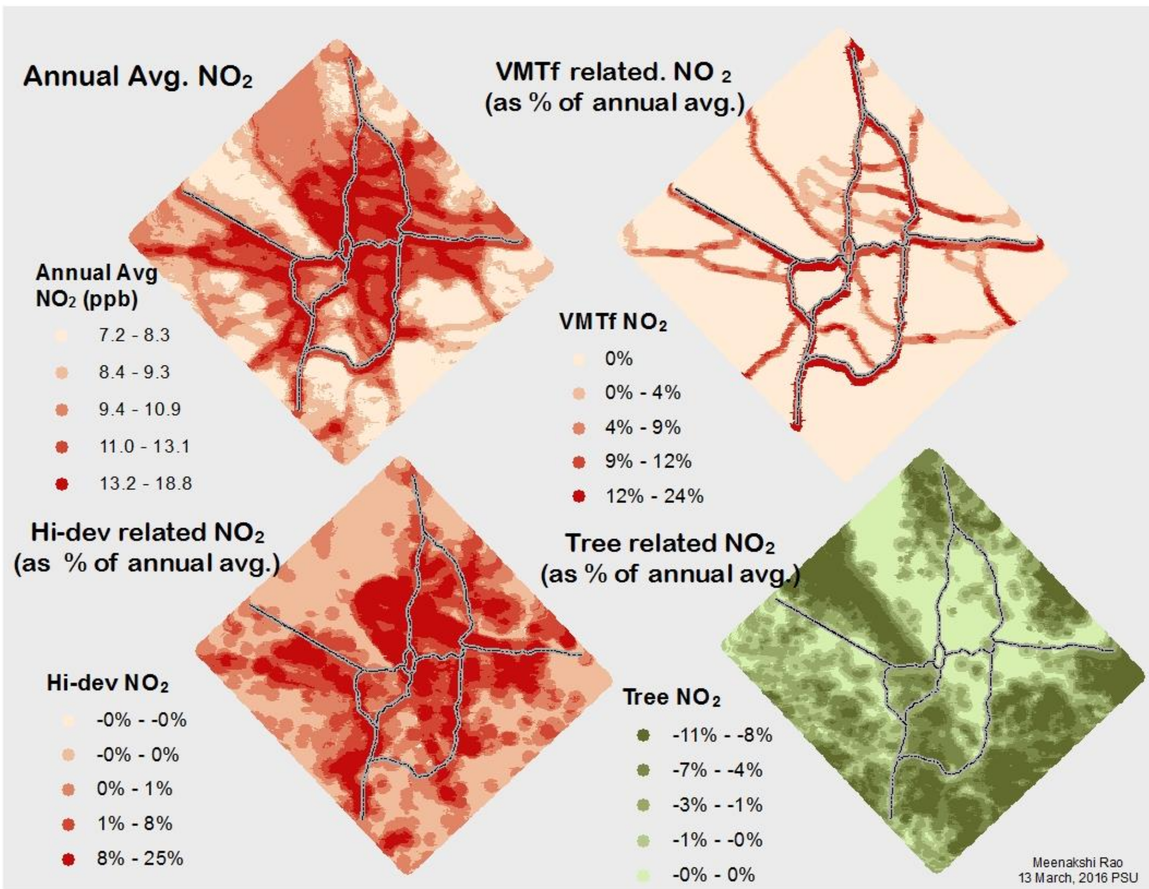


Figure 12: The spatial variation of annual ambient concentrations of NO_2 across the Portland-Vancouver urban area as estimated using random forest.

Figure 12 shows the spatial variation in annual average NO_2 in the Portland-Vancouver area, as well as the spatial pattern of NO_2 associated with LULC categories VMT*f*, high-intensity development, and tree canopy. As can be seen in Figure 12, the impact of VMT*f* is confined to a narrow buffer around the major freeways; where VMT*f* associated NO_2 may be contributing as much as a quarter of the local ambient NO_2 concentrations. The impact of NO_2 associated with high intensity development and tree canopy is much more spatially distributed, as these land cover categories are much more spatially distributed within the study area. High intensity development may contribute as much as 25% of the local ambient NO_2. Tree canopy, on the other hand, is associated with reduced ambient NO_2 concentrations. This finding is consistent with the finding from our LUR model, as well as other observational studies of ambient NO_2 (Dijkema et al., 2011; Faus-Kessler et al., 2008; Gilbert et al., 2005; Kashima et al., 2009; Mavko et al., 2008a; Novotny et al., 2011).

Estimated incidence rates of respiratory health problems linked to individual LULC categories, estimated based on their statistical correlation with ambient NO_2, are shown in Table 9, while the annual economic valuation associated with these health impacts can be found in Table 10.

Health Impact	Incidence rate (per 100,000) associated with LULC category						
	VMT*f*	Sec. rds	High intensity dev	Med. intensity dev	Open dev	Hay	Trees
Asthma Exacerbation, Missed school days (4 -12 year olds)	1,109	1,322	2,393	1,587	-583	-354	-472
Asthma Exacerbation, One or More Symptoms (4 -12 year olds)	3,220	3,837	6,950	4,606	-1,692	-1,027	-1,369
Cough (7 -14 year olds)	926	1,108	1,989	1,338	-503	-304	-414
Emergency Room Visits, Asthma (75 years and older)	2	2	3	2	-1	0	-1
HA, Asthma (younger than 30 years)	0	0	0	0	0	0	0
HA, Asthma (30 years and older)	0	0	0	0	0	0	0
HA, Chronic Lung Disease (less Asthma) (65 years and older)	6	6	11	6	-2	-1	-2
HA, All Respiratory (65 years and older)	12	13	23	13	-5	-3	-4

Table 9: Estimated incidence of respiratory problems per 100,000 population associated with LULC due to local influence on ambient NO_2 concentrations, for the Portland-Vancouver urban area.

The biggest impact on respiratory health comes from high intensity development. Our model suggests that ambient concentrations of NO_2 related to high intensity development may be exacerbating asthma symptoms in ~7,000 per 100,000 4 – 12 year olds in the study area annually, and increasing hospitalizations for respiratory issues by 23 per year per 100,000 seniors. Medium intensity development, VMT*f* and secondary roads all show similar associations with ambient NO_2 and hence, associations with increases in the incidence rates of NO_2-related respiratory problems (see Table 9).

Trees, open development, and hay/pastureland on the other hand show a negative relationship with ambient NO_2, and consequently, respiratory impacts of NO_2 (Table 9). All three land covers are associated with lower ambient NO_2, and hence are associated with lower incidence rates of respiratory problems. For example, tree canopy is associated with ~1,300 fewer incidents of asthma exacerbation per year per 100,000 4-12 year olds, and 4 fewer hospitalizations due to NO_2-related respiratory problems per year per 100,000 seniors.

The economic valuation of the health impacts attributable to each land use category due its association with ambient concentrations of NO_2 is not insignificant, ranging from a benefit of $1.7 million 2013 USD associated with open developed spaces, to a burden of $7 million USD associated with high intensity development (Table 10).

Thus we see that, statistically, different land use/land cover categories affect local NO_2 concentrations differently, and consequently, create a differential effect on the health burdens. For example, high intensity development may be associated with as much as a 25% increase in local ambient concentrations, and, consequently, an annual health burden of $7 million USD, while trees are associated with a decrease in ambient NO_2, and consequently, a health benefit of $1.4 million USD. This characterization of the differential effect of land use on ambient NO_2, and hence NO_2-related health impacts, in urban environments may have the potential to help urban designers and policy makers to create cleaner urban atmospheres.

Health Impact	**Valuation in $1,000s 2013 USD**						
	VMT*f*	Sec roads	High intensity dev	Med intensity dev	Open dev	Hay	Trees
Asthma Exacerbation, Missed school days (4 - 12 year olds)	$559	$667	$1,207	$800	-$294	-$179	-$238
Asthma Exacerbation, One or More Symptoms (4 -12 year olds)	$1,624	$1,935	$3,505	$2,323	-$853	-$518	-$691
Cough (7 -14 year olds)	$247	$296	$531	$357	-$134	-$81	-$110
Emergency Room Visits, Asthma (75 years and older)	$1	$1	$1	$1	$0	$0	$0
HA, Asthma (younger than 30 years)	$5	$6	$11	$7	-$2	-$1	-$2
HA, Asthma (30 years and older)	$6	$7	$13	$7	-$3	-$1	-$2
HA, Chronic Lung Disease (less Asthma) (65 years and older)	$235	$264	$455	$268	-$101	-$52	-$90
HA, All Respiratory (65 years and older)	$667	$758	$1,280	$748	-$281	-$143	-$247
Total:	$3,345	$3,932	$7,001	$4,511	-$1,669	-$975	-$1,380

Table 10: Estimated economic valuation of respiratory health impact associated with LULC due to local influence on ambient NO_2 concentrations, for the Portland-Vancouver urban area.

Conclusion

In this chapter we applied the annual LURF NO_2 model to better understand the impact of anthropogenic NO_2 in the Portland-Vancouver metropolitan area. We found that far more people lived in the highest quintile of NO_2 concentrations (39%) than in the lowest quintile (5%). Further, the pattern of environmental inequity described for other cities and regions in the USA was echoed in the Portland area: Hispanics and African-Americans, people with lower educational attainment, and lower annual household income resided disproportionately in the worst NO_2 quintile in the study area; while whites and Asians, and households with higher annual incomes were slightly more likely to reside in areas with the lowest quintile of NO_2 concentrations. Even though the Portland-Vancouver area is in compliance with the US EPA standards for NO_2, there was an annual health burden of approximately $50 million USD arising from NO_2-related respiratory problems in the study area. The brunt of this health burden was borne by children younger than 15 years of age. Recent research shows that childhood effects of NO_2 on respiratory health and missed school days may persist into adulthood; thus this childhood exposure may potentially impact lung function and earning potential over the rest of an exposed child's lifetime, making the estimates presented here potentially a serious underestimation of the true health burden.

Using the LURF model to investigate the association of different urban LULC categories on NO_2 concentrations, we found that different land use categories impacted ambient NO_2 differently. The biggest impacts on ambient NO_2 were from high intensity developed areas, which was associated with as much as a 25% increase in local NO_2, and a consequent health burden of $7 million 2013 USD. Developed open spaces and trees, on the other hand, were associated with reduced concentrations of NO_2, and hence a health benefit of about $1.5 million USD. Thus the heterogeneity of the land cover together with the uneven distribution of population in the Portland-Vancouver area, have created a highly heterogeneous pattern of NO_2 and its health impacts.

Chapter 4: Assessing the impact of land use modifications on ambient concentrations of NO_2 and respiratory health

It is change, continuing change, inevitable change, that is the dominant factor in society today. No sensible decision can be made any longer without taking into account not only the world as it is, but the world as it will be.

Isaac Asimov, *Asimov on Science Fiction*

Abstract

In this chapter, we use the LURF model to explore the effects of land use modifications on ambient NO_2 concentrations. We first undertake a sensitivity analysis of urban LULC on ambient NO_2. Then, based on the sensitivity analysis, we develop city-wide and local land use modifications options, and use these together with the LURF model and BenMAP to assess and compare the impact of these options on ambient NO_2 concentrations, and consequently, respiratory health. The land use modifications we consider are reducing vehicle miles traveled on highways and planting trees, at the city-wide and targeted local scales. Our results indicate that targeted local tree-planting efforts may have a substantial impact on reducing neighborhood incidence of respiratory distress.

Introduction

Urban land use and land cover features within a city affect the dispersion of air pollutants by influencing air flow, the location of emissions through zoning and other siting policies, and the quantity of emissions associated with these LULC features through permitting, policies, and urban planning. Using the ensemble learning technique random forest, we characterized this association between urban LULC and ambient NO_2 in the Portland-Vancouver area, finding that high intensity development, highway traffic, open developed space and tree canopy all significantly affected local ambient concentrations of NO_2. Further, the impact of these land use categories on NO_2 was large enough to create an appreciable respiratory health impact, estimated at ~$40 million USD annually. Given this impact of current LULC features on ambient NO_2 concentrations, we pose the question: do modifications to existing land use in the city have the potential to mitigate ambient NO_2 concentrations, and are these changes in NO_2 big enough to impact respiratory health?

Urban landscapes are highly managed landscapes, and managing these landscapes for air pollution mitigation and health is not a new concept. However, to date, modifications to urban land use or land cover for air pollution mitigation have been at the regional scale, in large part in response to the regulatory framework which is focused on the regional airshed level. In the last couple of decades, as awareness of the impact of anthropogenic emissions on climate change has risen, many cities have focused on reducing vehicle miles traveled (VMT) by a variety of strategies including promoting public transport, cycling or walking; congestion pricing; and toll ways to reduce combustion-related pollution (Bureau of Planning and Sustainability, 2015; City of Burlington Vermont, 2014; Seattle Office of Sustainability and Environment, 2013). Many cities have also undertaken city-wide projects such as the “million trees” projects with the goal of mitigating emissions of carbon dioxide and other combustion-related air pollutants (for example, New York City, Los Angeles, Denver and Sacramento). These tree plantings are typically implemented in an ad hoc manner, as city planners, especially in smaller cities, do not have access to tools or models to identify optimum locations. And currently there does not exist a framework for choosing between different mitigation strategies, for example reducing VMT vs. planting trees.

In the previous chapters, we have developed a fine spatial scale model of NO_2 using random forest; and using this model, we have demonstrated the impact of the different land use categories within the metropolitan area on ambient concentrations of NO_2. We showed that even in the study area, which is in compliance with US EPA NO_2 standards, there still exists a substantial respiratory health burden, falling mainly on children. In this chapter, we investigate to what extent land use modifications may be able to mitigate the health burden of NO_2.

To determine the potential of land use modifications in mitigating NO_2, we undertake two analyses. We first characterize, using a sensitivity analysis, the response of ambient NO_2 to land use modifications, examining both the magnitude and the spatial pattern of the NO_2 changes arising due to the land use modifications. Next, we demonstrate how BenMAP and LURF can be used in conjunction to assess the respiratory impact of competing land use modification strategies. We examine the two most common land-use modifications strategies used by cities for CO_2 and air pollution mitigation, namely, reducing VMT and increasing tree canopy; and we compare the health benefit arising from implementing these strategies at the city-wide and local-scale.

Methods and materials

Our study area remains the Portland-Vancouver Metropolitan area, with its population of 1.9 million people. We characterize the changes in NO_2 in response to LULC changes through a sensitivity analysis, done in R, using the LURF model. We assess and compare the respiratory benefits of the city-wide and local modifications of VMT*f* and tree canopy using BenMAP and the LURF model. All statistical analyses are in R, while spatial analyses and visualization is done in ArcMAP. The sensitivity analysis and the comparison of health benefits of different mitigation strategies is described in greater detail below.

Sensitivity of NO_2 to land use modifications

We use the annual average NO_2 LURF model to explore the sensitivity of modeled NO_2 to land cover modifications. We focus on four LULC categories – high intensity development, VMT*f*, open development and tree canopy – as these categories showed the greatest impact on NO_2 in the study area and are also amenable to modifications. The purpose of this exercise is to characterize the NO_2 changes, both in terms of magnitude and spatial pattern, for these categories. For each of these categories, we consider modifications of ± 2%, ± 5% and ±10% to the LULC feature. For the land cover categories, high intensity development, open development and tree canopy, the percentage change is based on the buffer size, so that a 2% increase results in an increase even at sites that currently don't have the land cover (high intensity development or tree canopy) in their vicinity. In case of an increase, other land cover in the vicinity of the site is proportionately decreased; while in the case of a decrease, the other land use is proportionately increased. This way, care is taken that the modified land use does not go below 0% or above 100%.

Evaluating the mitigation potential of land use

To explore the potential of managing land use to mitigate the respiratory impact of NO_2, we focused on two land use categories, namely, vehicle miles traveled on freeways and state highways (VMT*f*) and tree canopy. We chose these variables as many city climate action plans (Bureau of Planning and

Sustainability, 2015; City of Burlington Vermont, 2014; Seattle Office of Sustainability and Environment, 2013) already incorporate targets for these two land use categories, and previous research has shown that they have a discernible impact on ambient NO_2 concentrations. To better understand and characterize the mitigation potential of these two categories, we first estimate the maximum potential benefit that could be derived by changing VMT*f* and tree canopy. For VMT*f*, the maximum benefit will be derived under the (unrealistic) scenario that there is no freeway/highway traffic, i.e. zero VMT*f* in the area. Trees provide maximum benefit when the entire study area is under tree canopy, that is, 100% tree cover in the region (as compared to 13% today).

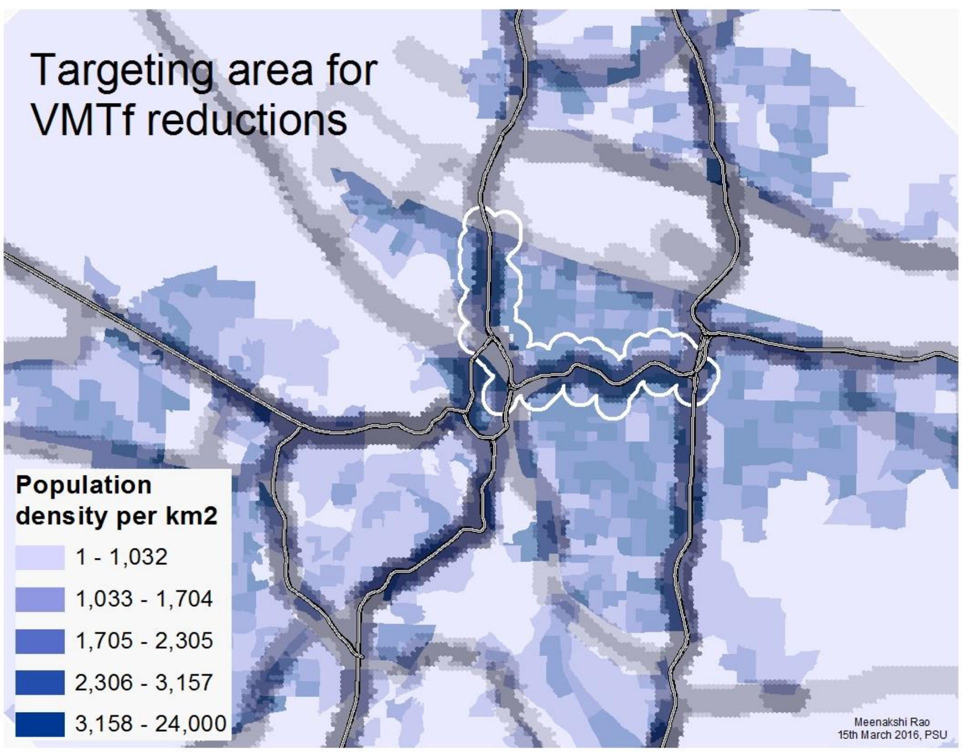


Figure 13: Area (outlined in white) with high VMT*f*-associated NO_2 and high population density, targeted for a local mitigation strategy of 5% decrease in VMT*f*.

We next assess the benefits of two city-wide strategies frequently mentioned in city climate action plans: reducing VMT*f* 2% annually over a decade, as well as increasing tree canopy by 2% annually over a decade. We estimate NO_2 under the 2% change scenario by uniformly decreasing VMT*f* by 2% or adding 2% of tree canopy to all sites within the study area. Tree canopy is capped to not exceed 100% of the buffer. BenMAP is used to estimate the respiratory health and economic valuations by comparing the change in NO_2 associated with land use change at the end of the first year (2% change) and the end of the decade (a cumulative 20% land use change) to the current annual average NO_2 impacts.

We further estimate the benefits of three local mitigation scenarios. In the first scenario, we reduce VMT*f* by 5% for two stretches of freeways that lie in the highest quintile of both VMT*f*-related NO_2 and population density. We do this by reducing VMT*f* by 5% in all grid cells within a 700m buffer of the identified stretches of transportation corridors (Figure 13). We also assess the potential of using trees as an alternate mitigation strategy in the same area by increasing tree canopy 5% within the area identified above. Finally, we assess the benefits of increasing tree canopy by 5% in four high population density neighborhoods that lie within the worst NO_2 quintile (Figure 14). BenMAP is used to estimate the health benefit and economic valuation, using current annual average NO_2 impacts as the baseline.

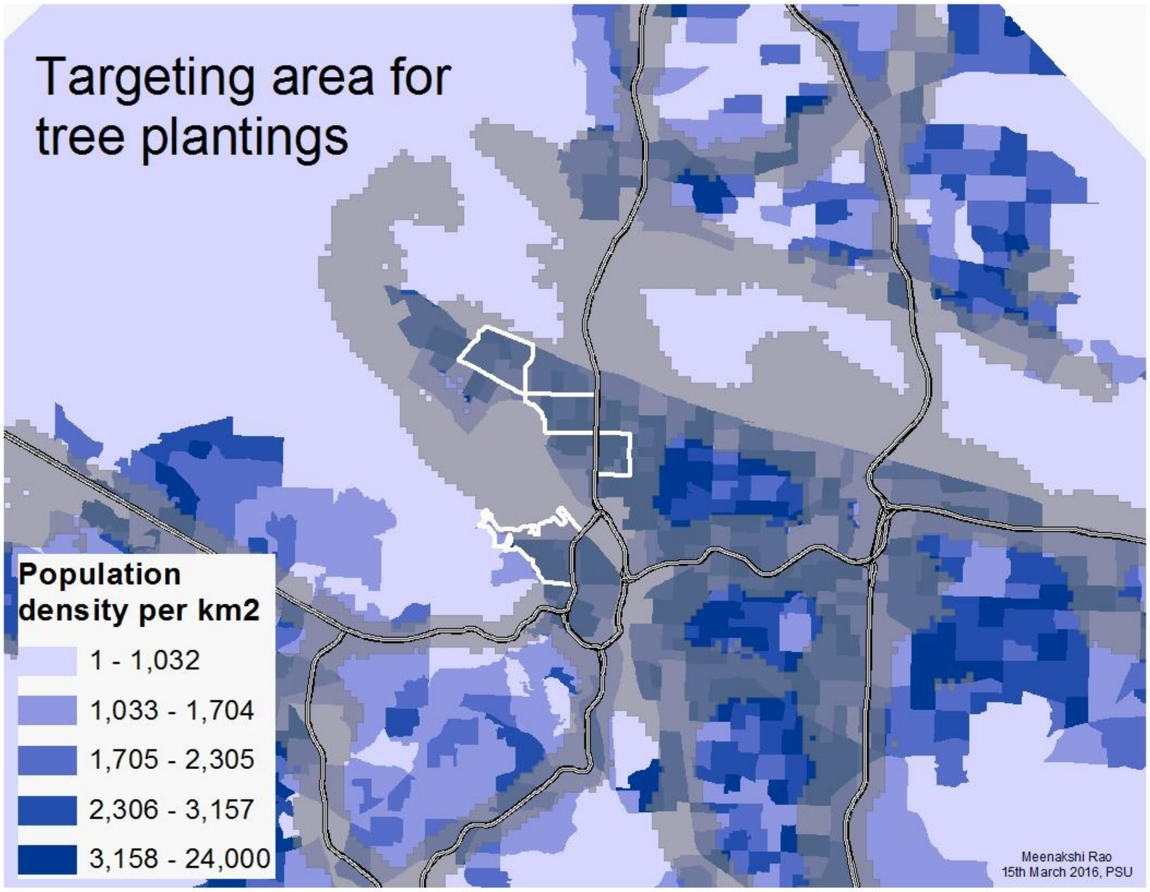


Figure 14: Neighborhoods (outlined in white) with high population density and high NO_2, targeted for a local mitigation strategy of 5% increase in tree cover.

Results and discussion

Sensitivity of NO_2 to land use modifications

Table 11 and Figure 15 present the results of the sensitivity of ambient NO_2 to modifications to VMT*f*, high intensity development, open development and tree canopy. Table 11 summarizes the percent change in annual NO_2 (averaged over the study area) in response to ± 2%, ± 5% and ±10% changes in VMT*f*, high intensity development, and tree canopy. We see that ± 2-10% change in VMT*f* has relatively little impact on the region-wide average of NO_2, although the local impact can be greater: a 5% decrease in VMT*f* decreases ambient NO_2 concentrations by as much as 8% in some localities (Figure 15a). Decreases of 2% to 10% in high intensity development show a 1% - 3% decrease in NO_2 concentrations, averaged over the study area.

However there is a relatively large increase in regionally averaged NO_2 (2% - 11%) when high intensity area is increased (Table 11). The reason for this is partly methodological, in that high intensity area is increased as a percentage of the buffer area, and not of the high intensity development area within the buffer, leading to increases in high intensity development across the entire study area. Locally, the model shows as much as a 12% decrease in NO_2 concentrations when high intensity development is reduced by 5% (Figure 15d). Similarly, modifications to area under tree canopy result in a 1 % increase (for a 10% decrease in tree canopy) to a 3% decrease in region-wide average of ambient NO_2 concentrations (for a 10% increase in tree canopy). Locally, a 5% increase in tree cover can result in up to an 11% decrease in modeled local NO_2 concentrations (Figure 15c). Similarly, changes to developed open space result in a 3.3% decrease in NO_2 for a 10% increase in developed open space, to a 2% increase in NO_2 if developed open space is decreased by 10%. Locally, a 5%

increase in developed open space may result in as much as 12% reduction in annual NO_2 concentrations.

LULC change	VMT*f* average % change in NO_2	HDEV average % change in NO_2	TREE average % change in NO_2	OPEN average % change in NO_2
Zeroed	-2.2%	-4.1%	3.6%	2.2%
10% decrease	-0.2%	-2.7%	1.4%	1.8%
5% decrease	-0.1%	-1.8%	0.9%	1.1%
2% decrease	-0.0%	-0.9%	0.4%	0.5%
2% increase	0.0%	1.7%	-1.0%	-1.1%
5% increase	0.1%	5.9%	-1.9%	-2.1%
10% increase	0.1%	10.9%	-3.1%	-3.3%

Table 11: The percent change in NO_2, averaged over the Portland-Vancouver area, in response to land cover modifications.

Looking at Figure 15, we see that spatial pattern of NO_2 response to LULC modifications is distinct for the four LULC categories considered. The NO_2 change in response to changes in VMT*f* is constrained to a narrow buffer around the freeways, while the response of NO_2 to modifications in the other three categories is much more spread out across the study area. The greatest percentage change in NO_2 is towards the center of the study area for high intensity development, and on the periphery of the study area for developed open space.

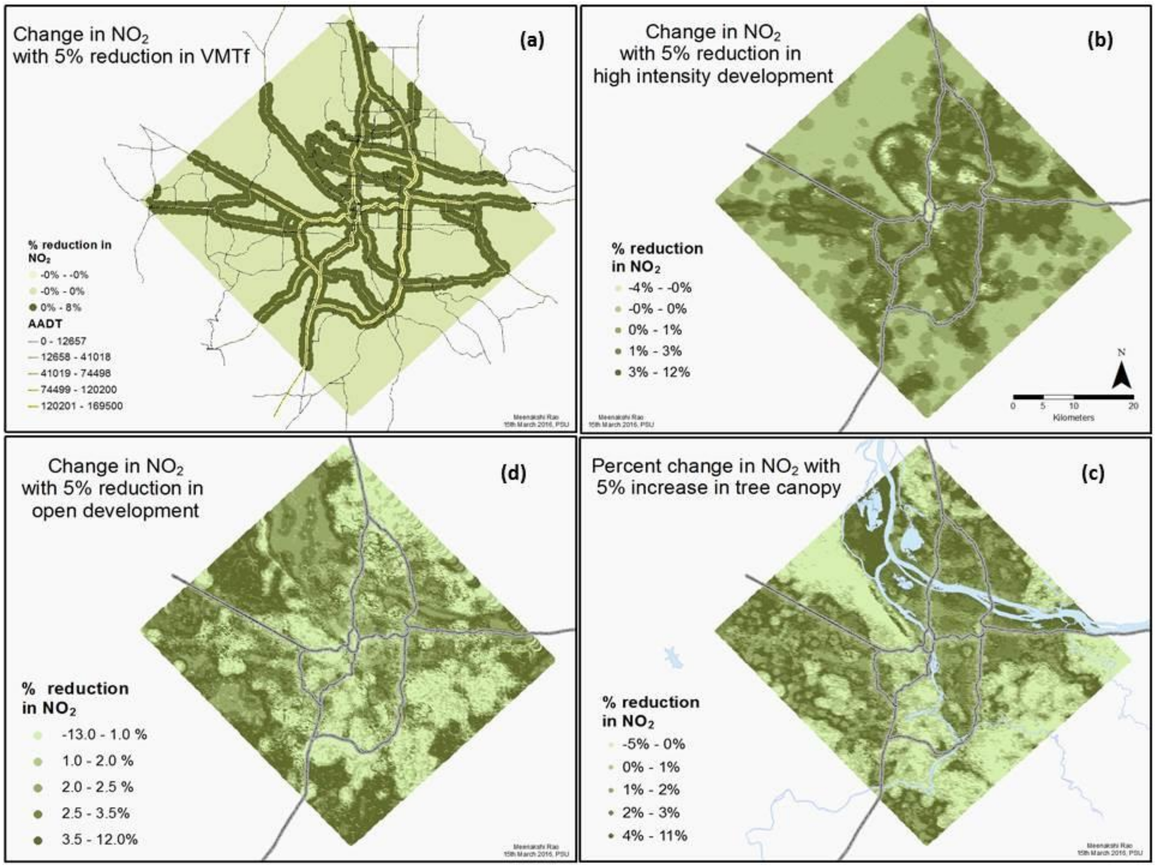


Figure 15: The spatial distribution and magnitude of the change in modeled NO_2 concentrations in response to a ± 5% change in (clockwise from top left) (a) VMT*f* (b) high intensity development (c) tree canopy (d) open development.

Air quality mitigation potential of urban land use

The maximum potential respiratory health benefit through NO_2 mitigation from VMT*f* –realizable if traffic on freeways and highways is completely curtailed or emissions from freeway traffic are reduced to zero – is $3 million on an annual basis (Table 13). Similarly, the maximum potential respiratory benefit that can be achieved by unrealistically planting trees at 100% canopy cover is about $11 million annually.

Health Impact	Decrease in incidence of respiratory issues due to land use change *(decrease in incidence per 10,000 population)*					
	2% dec in VMT*f*	20% dec in VMT*f*	100% dec in VMT*f*	2% inc in tree canopy	20% inc in tree canopy	100% tree canopy
Asthma Exacerbation, Missed school days (4 -12 year olds)	32 *(14)*	350 *(148)*	2,623 *(1,109)*	1,069 *(452)*	4,271 *(1,806)*	9,561 *(4,043)*
Asthma Exacerbation, One or More Symptoms (4 -12 year olds)	93 *(39)*	1,015 *(429)*	7,617 *(3,220)*	3,102 *(1,311)*	12,369 *(5,241)*	27,791 *(11,750)*
Cough (7 -14 year olds)	23 *(11)*	248 *(124)*	1,852 *(926)*	766 *(383)*	3,042 *(1,521)*	6,715 *(3,358)*
Emergency Room Visits, Asthma (75 years and older)	0 *(0)*	0 *(0)*	2 *(2)*	1 *(1)*	2 *(3)*	5 *(6)*
HA, Asthma (younger than 30 years)	0 *(0)*	0 *(0)*	0 *(0)*	0 *(0)*	1 *(0)*	2 *(0)*
HA, Asthma (30 years and older)	0 *(0)*	0 *(0)*	1 *(0)*	0 *(0)*	1 *(0)*	2 *(0)*
HA, Chronic Lung Disease (less Asthma) (65 years and older)	0 *(0)*	2 *(1)*	13 *(6)*	4 *(2)*	17 *(8)*	40 *(18)*
HA, All Respiratory (65 years and older)	0 *(0)*	3 *(2)*	26 *(12)*	9 *(4)*	35 *(16)*	83 *(37)*

Table 12: Decrease in incidences and incidence rates per 100,000 individuals of NO_2-related respiratory problems associated with city-wide land-use modifications.

Using more realistic scenarios, a city-wide NO_2 mitigation strategy of an annual 2% decrease in VMT*f* each year for a decade provides an annual respiratory benefit of $37,000 2013 USD at the end of the first year, and a benefit of $411,000 2013 USD at the end of the decade, when VMT*f* has cumulatively declined by 20%. At the end of the decade, this can potentially lead to an annual decrease in asthma exacerbation by as much as 148 incidents per 100,000 4-12 year old children.

Health Impact	Valuation of health impact (in $1,000s 2013 USD)					
	2% dec in VMT*f*	20% dec in VMT*f*	100% dec in VMT*f*	2% inc in tree canop y	20% inc in tree canopy	100% tree canopy
Asthma Exacerbation, Missed school days (4 -12 year olds)	$7	$75	$559	$228	$911	$2,039
Asthma Exacerbation, One or More Symptoms (4 -12 year olds)	$20	$216	$1,624	$661	$2,643	$5,926
Cough (7 -14 year olds)	$3	$33	$247	$102	$406	$896
Emergency Room Visits, Asthma (75 years and older)	$0	$0	$1	$0	$1	$2
HA, Asthma (younger than 30 years)	$0	$1	$5	$2	$8	$19
HA, Asthma (30 years and older)	$0	$1	$6	$2	$8	$21
HA, Chronic Lung Disease (less Asthma) (65 years and older)	$3	$30	$235	$81	$315	$744
HA, All Respiratory (65 years and older)	$7	$86	$667	$224	$881	$2,098
Total:	**$37**	**$411**	**$3,103**	**$1,218**	**$4,849**	**$10,978**

Table 13: Economic valuation of health benefits accruing from a decrease in NO2-related respiratory problems associated with city-wide land-use modifications.

Similarly, an annual city-wide increase in tree cover by 2% over a decade results in an annual mitigation benefit of $1.2 million 2013 USD at the end of the first year, and an annual benefit of $5 million 2013 USD at the end of the decade when tree cover has increased by 20%. At the end of the decade, the increased tree cover may potentially reduce the incidence of asthma exacerbation in 4-12 year old children by as many as 1,800 incidents per 100,000 children, roughly half the maximum potential benefit associated with conversion to 100% tree canopy.

Health Impact	Decrease in incidences of respiratory issues due to local land use change *(decrease in incidence per 100,000 population)*		
	5% decrease in local VMT in high VMTf	5% increase in tree canopy in high VMTf	5% increase in local tree canopy in high NO_2
Asthma Exacerbation, Missed school days (4 -12 year olds)	3 *(28)*	72 *(765)*	32 *(880)*
Asthma Exacerbation, One or More Symptoms (4 -12 year olds)	2 *(83)*	209 *(2220)*	92 *(2553)*
Cough (7 -14 year olds)	8 *(25)*	52 *(656)*	22 *(748)*
Emergency Room Visits, Asthma (75 years and older)	0 *(0.01)*	0 *(0.89)*	0 *(1.11)*
HA, Asthma (younger than 30 years)	0 *(0.00)*	0 *(0.01)*	0 *(0.03)*
HA, Asthma (30 years and older)	0 *(0.00)*	0 *(0.02)*	0 *(0.03)*
HA, Chronic Lung Disease (less Asthma) (65 years and older)	0 *(0.12)*	0 *(3.79)*	0 *(4.43)*
HA, All Respiratory (65 years and older)	0 *(0.24)*	1 *(7.50)*	0 *(8.56)*

Table 14: Decrease in incidences and incidence rates per 100,000 individuals of NO_2-related respiratory problems associated with local land-use modifications.

Local mitigation strategies provide comparable or better decreases in incidence rates, though total decrease is small, given the smaller population base. A 5% increased tree cover along the targeted highway corridors is seen to be more effective in reducing the health impacts of VMT*f*-related NO_2 than decreasing VMT*f* by 5% (Table 14). Local tree plantings provide an annual benefit of $35,000 - $85,000 2013 USD (Table 15).

Health Impact	Valuation of health impact (in 2013 USD)		
	5% decrease in local VMT in high VMt*f*	5% increase in tree canopy in high VMT*f*	5% increase in local tree canopy in high NO_2
Asthma Exacerbation, Missed school days (4 -12 year olds)	$572	$15,394	$6,767
Asthma Exacerbation, One or More Symptoms (4 -12 year olds)	$1,660	$44,656	$19,632
Cough (7 -14 year olds)	$265	$6,984	$2,957
Emergency Room Visits, Asthma (75 years and older)	$0	$16	$5
HA, Asthma (younger than 30 years)	$6	$156	$74
HA, Asthma (30 years and older)	$9	$224	$88
HA, Chronic Lung Disease (less Asthma) (65 years and older)	$230	$6,922	$2,295
HA, All Respiratory (65 years and older)	$596	$18,500	$5,956
Total:	$3,099	$85,705	$35,391

Table 15: Economic valuation of health benefits accruing from a decrease in NO_2-related respiratory problems associated with local land-use modifications.

Conclusion

Many issues of exposure to urban air pollutants are at the local (i.e. neighborhood) scale. However, municipalities often engage in city-wide VMT reduction and “greening” campaigns, both to reduce emissions and improve human health, without being able to avail of a clear assessment methodology to identify optimum strategies. Again using the random forest model, we were able to compare the respiratory health benefits of both city-wide and local-scale LULC management strategies, finding that different VMT*f* and tree canopy management strategies can mitigate the health burden of NO_2 to substantially different extents, reducing incidence of asthma exacerbation in 4-12 year olds anywhere from 28 to 1,800 incidents/100,000 children/year. Surprisingly, we find that modest tree plantings efforts appear to provide close to half of the maximum potential benefits even at only 20% increase in canopy coverage.   Furthermore, model outcomes suggest that a 20% increase in canopy coverage city-wide may reduce the incidences of childhood asthma ~10 times more than a city-wide 20% reduction in VMT*f*. These intriguing, spatially-informed results highlight the potential power of the random forest approach in making strategic LULC decisions aimed at mitigating air pollution exposure and improving human health in urban landscapes.

To the extent that the Portland-Vancouver metropolitan area is representative of other mid-size cities in the USA, we can expect a similar burden of respiratory health due to NO_2, borne disproportionately by children, in other cities as well (Z. Chen et al., 2015; Lemke et al., 2013; Penard-Morand et al., 2010; Son, Kim, & Bell, 2015). As we have seen earlier, childhood exposure to traffic-related air pollution may lead to impaired lung function in early adulthood as well as poorer performance in school and lower earnings potential in adulthood. Given the increasing number of studies that suggest the role of the urban forest in promoting physical and mental well-being (Donovan et al., 2013; Donovan, Michael, Butry, Sullivan, & Chase, 2011; Maas, Verheij, Groenewegen, de Vries, & Spreeuwenberg, 2006; Takano, Nakamura, & Watanabe, 2002; Ulrich, 1984), it seems likely that small-scale strategic tree planting campaigns in either high NO_2 areas and/or near roadways, or city-wide greening campaigns, may well play an important role in mitigating respiratory distress. However, these statistical results serve to highlight the need for future research to better understand the mechanisms that determine how different LULC categories shape the intra-urban patterns of air pollution within our cities. Combining the sophistication of new sensor technologies with advanced modeling techniques such as random forest will clearly contribute to accelerating our understanding of the linkages between land use and urban air pollution and lead to creating healthier cities and more sustainable urban atmospheres for all, especially our most vulnerable populations.

Chapter 5: The role of trees in removal of NO_2 through deposition

Forests are the lungs of our land, purifying the air and giving fresh strength to our people.

President Franklin D. Roosevelt

Abstract

In this chapter we explore to what extent the reduction in NO_2 found by the statistical summer LUR and LURF models can be linked to removal of pollutants through dry deposition by trees.

We first use a hierarchical nested analysis on the LUR model to determine to what extent the reduction in NO_2 associated with trees is simply due to absence of sources. Further, we compare reduction in NO_2 predicted by the statistical LURF model in association with trees with the reduction in NO_2 attributable to dry deposition as predicted by the CMAQ model. We also undertake a sensitivity analysis to determine if any discrepancy between CMAQ and the statistical models can be explained by a different parameterization of bulk stomatal resistance.

We find that our different analyses all provide strong support that the reduction in NO_2 associated with trees in the Portland area is likely due to dry deposition.

Introduction

Trees are an integral, albeit shrinking, part of the urban landscape (Nowak & Greenfield, 2012; Nowak et al., 2010). Research has established a robust relationship between urban vegetation (including tree canopy) and human health. Ulrich's seminal work (Ulrich, 1984) demonstrated that just the view of a tree from a hospital window reduced post-surgery recovery times. Since then, presence of trees and vegetation has been associated with longevity (Takano et al., 2002), better health and well-being (de Vries, Verheij, Groenewegen, & Spreeuwenberg, 2003; Donovan et al., 2013; McCracken, Allen, & Gow, 2016; Pope, Ezzati, & Dockery, 2009), better birth outcomes (Dadvand et al., 2012; Donovan et al., 2011) and improved mental health (Hansmann, Hug, & Seeland, 2007; Mitchell, 2013); also see van den Berg et al for a review (Van Den Berg et al., 2015). However, the mechanism (or mechanisms) through which trees and green spaces influence human health and well-being remains unclear, although studies postulate that at least some of the health benefits are due to the removal of air pollutants by trees (Frumkin, 2013; Hartig, Mitchell, de Vries, & Frumkin, 2014).

Many landscape-level studies, including this one, see an association of tree canopy with reduced NO_2, PM_{10}, or $PM_{2.5}$ (Kashima et al., 2009; Mavko et al., 2008b; Nowak et al., 2006; Rao et al., 2014; Yin et al., 2011), lending credence to the hypothesis that air pollution removal is one of the possible mechanisms through which trees influence human health. Yet, although these landscape-level studies establish and quantify a correlation between trees (or green spaces) and reduced pollutant levels, they are not sufficient to demonstrate causation. It has been shown, based on theoretical models of leaf physiology (Sparks, 2009) and further supported by leaf-level and chamber observations (Breuninger, Oswald, Kesselmeier, & Meixner, 2012; Takahashi et al., 2005), that vegetation – including grasses, crops, shrubs, and trees – removes air pollutants through dry deposition, predominantly via leaf stomatal uptake. A semi-empirical framework has extended these well-established leaf-level models to the landscape-level using a "big-leaf" conceptualization (D. Baldocchi, 1988; Lovett, 1994; Wesely, 1989; Zhang, Brook, & Vet, 2003). In this conceptualization, a vegetated region is treated as a single "big-leaf" surface. Flux of an air pollutant to the big-leaf surface is modeled as a set of resistances in series and parallel (Figure 16). In this conceptualization, the aerodynamic flow layer, determined only by meteorological conditions, transports air pollutants (or other chemical species of interest) above the big leaf. Some of the pollutants in this aerodynamic layer are transferred to the layer of air directly in contact with the big leaf, called the quasi-laminar boundary layer. The amount of pollutant transferred from the aerodynamic layer to the quasi-laminar layer depends on the aerodynamic resistance, R_a. This quasi-laminar flow in turn transfers some fraction of the pollutant to the leaf surface, depending on the quasi-laminar resistance R_b. The pollutants arriving at the big-leaf surface can go through one of three routes (resistances in parallel). They can go through the “canopy” and reach the soil layer (resistances in series, R_{ac} and R_g), or they can enter the big-leaf stomata and then the mesophyll (resistances in series, R_{st}, R_m), or they can be deposited on the bark and cuticles (R_w) of the big-leaf. We will refer to these three routes collectively as R_{surf}. The big-leaf resistances, also referred to as bulk resistances, are typically inferred based on scalings from leaf to bulk or big-leaf level coupled with empirical studies (D. D. Baldocchi et al., 1987; Wesely, 1989). It is important to note that the scalings for the bulk parameters are based on observations in fields and pristine forests.

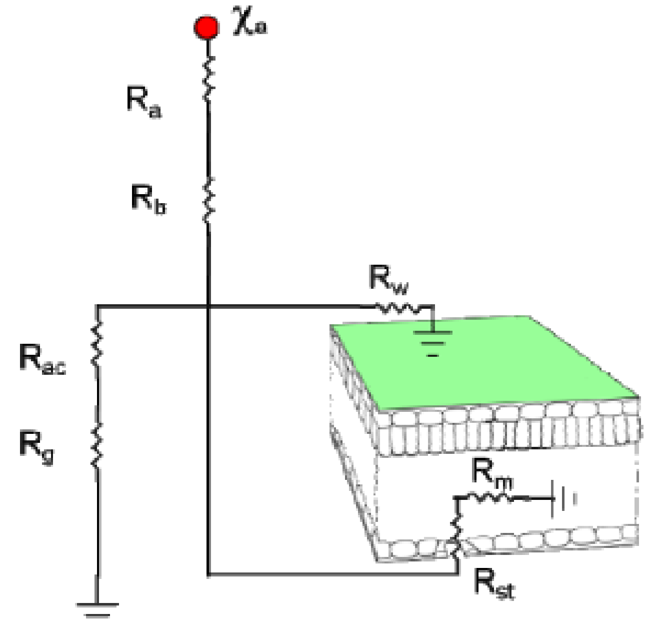


Figure 16: Schematic of dry deposition model for soil and leaf (from Pleim and Ran, 2011). Ra is aerodynamic resistance, Rb quasi-laminar flow resistance, Rac in-canopy resistance, Rg ground resistance, Rw cuticular resistance, Rm mesophyllic resistance and Rst stomatal resistance.

This semi-empirical framework based on the big-leaf model has been incorporated into the Community Multi-scale Air Quality (CMAQ) model (CMAS, 2015; J. E. Pleim & Xiu, 2003; J. Pleim & Ran, 2011), an open source development project of the US EPA; and into i-Tree Eco /UFORE (Hirabayashi et al., 2012), a public domain model developed by the USDA Forest Service; both of which are widely used models. The focus of CMAQ deposition models has been to examine the impact of deposition of air pollutants emanating from urban areas on the natural environment (C. M. Clark, Morefield, Gilliam, & Pardo, 2008; Fenn, Haeuber, et al., 2003; Simkin et al., 2016). i-Tree Eco/UFORE, on the other hand, has been applied at the city-scale (Morani et al., 2011; Nowak et al., 2000; Nowak & Dwyer, 2007; Paoletti et al., 2011), but shows that trees may be removing < 1% of NO_2 in urban areas (Nowak et al., 2006).

In the previous chapter, using LURF, we saw that the existing tree canopy may be associated with as much as an 11% reduction in local NO_2 concentrations; and that increasing tree canopy was an effective mitigation strategy for respiratory health. Given the findings from UFORE, a mechanistic model, we are faced with the question: is the reduction in NO_2 we see in the LURF – and other statistical models – due to deposition, or merely a reflection of trees displacing sources of NOx emissions, and therefore, leading to reduced NO_2 concentrations? And, if the reduction in NO_2 shown by the statistical models is, at least to some extent, linked to trees, can this reduction be explained by deposition to the tree canopy?

In this chapter, we attempt to answer these questions, drawing upon our statistical models as well as simulations in CMAQ. Specifically, we first estimate the extent to which the reduction in NO_2 associated with trees is due to trees themselves and to what extent it is due to the correlation of trees with absence of sources. Next, we compare the reduction in ambient NO_2 from the statistical LURF model to the reduction in ambient NO_2 due to dry deposition based on a CMAQ simulation; examining the similarity and differences between the two. Finally, we run a sensitivity analysis in CMAQ to determine whether realistic changes in dry deposition bulk resistance parameterizations can approximate the tree-related reductions in NO_2 seen in the summer LURF model.

Methods and materials

Briefly, to attempt to answer the questions raised above, we draw upon the summer LURF as well as the RLIS-based summer LUR models of the Portland-Vancouver and the Portland area respectively. We use the Portland area only LUR model as we have access to 1m resolution tree canopy data for the Portland area, in contrast to the NLCD data used in the LURF models, which is at 30m resolution, and thus may not capture the full effect of trees as it does not resolve street and backyard trees. We focus on the summer models only, as trees are most photosynthetically active in this season.

We begin by examining the statistical models for more information on the role of trees with respect to NO_2 concentrations. We first look at the relative importance of the land use parameters in the summer model using conditional random forest (LURF), and also carry out a nested hierarchical regression with the summer LUR model in order to identify the extent to which the effect of trees on ambient concentrations of NO_2 might be correlated to the absence of sources.

Next, we examine to what extent the mechanism of dry deposition might account for the reduction of NO_2 observed in association with trees. To do so, we run CMAQ simulations for the 2-week summer period corresponding to the field campaign, and compare the reduction in NO_2 due to dry deposition predicted by the CMAQ model with the reduction in NO_2 associated with trees predicted by the summer LURF model. We focus on comparing the LURF model with the CMAQ model as both these are based on the NLCD land cover data.

Finally, after a quick simulation in CMAQ to verify that dry deposition in the study area is mainly due to bulk stomatal resistance, we undertake a sensitivity analysis, examining the response of NO_2 deposition to re-parameterizing of bulk stomatal resistance (R_{st}) to determine whether realistic parameterization changes to R_{st} can align the CMAQ results with those of the LURF model. A realistic parameterization change to R_{st} to align the landscape-level observational LURF model to the mechanistic CMAQ model would provide strong support for reduction in NO_2 associated with trees being caused by dry deposition. Each of these analyses is described in greater detail below.

LURF and LUR: is it the trees or the absence of sources?

We describe here the additional statistical tools used to dissect our models and better understand whether trees directly influence NO_2 concentrations, or influence NO_2 concentrations only indirectly due to their correlation with absence of sources.

We chose the random forest methodology for modeling NO_2 in the Portland-Vancouver area specifically because of its ability to deal with correlated predictors. Additionally, all random forest analyses were done using conditional random forest (Strobl et al., 2008, 2007, 2009) , which permutes the variables in order to ensure that the importance of a variable in explaining the variance in the dependent variable is not inflated due to its correlation with other predictors. Thus the relative importance of trees compared to the other predictor variables in the summer (NLCD) LURF model (which was developed using conditional random forest) can provide a good indication of the importance of trees in explaining the ambient concentrations of NO_2, after adjusting for the correlation of trees with other land use predictors in the model.

Additionally, using a different statistical model and approach, we analyze the summer LUR model, and quantify the direct vs. indirect effects of trees on urban NO_2. The summer RLIS LUR model (Equation 3) includes tree canopy, roadways, as well as elevation as predictors. These predictors are somewhat correlated, although the variance inflation factors (VIFs) in the regression model are low: < 5 for all variables, and < 2 if the terms elevation and its square are excluded. We carry out a nested hierarchical regression analysis (J. Cohen et al., 2003) to partition the effects of the land use predictors in Equation 3 into direct and indirect effects. This method can be used in in certain constrained circumstances to partition variation, including, knowing a priori the interaction model amongst the predictors. Using this method, we examine the effect of trees on ambient NO_2 concentrations by partitioning the total effect of trees into its direct and indirect effects on NO_2 (i.e. through other predictors).

NO_2 reduction based on CMAQ and LURF

CMAQ inputs and configuration

In this section, we explore to what extent our statistical finding of the correlation of trees with reduced NO_2 concentrations is compatible with the mechanism through which trees are known to remove air pollution, namely dry deposition. To do this, we run a mechanistic model, the air chemistry and transport model CMAQ, which incorporates the mechanism of dry deposition. We chose to run the CMAQ model rather the UFORE model as the CMAQ model is a full chemistry and transport model which incorporates a big-leaf deposition model. The UFORE model is a deposition model only, and thus would have to run in conjunction with a chemistry and transport model to determine hourly meteorological conditions and ambient NO_2 concentrations.

We provide here a brief description of CMAQ and the configuration used for the CMAQ simulations in this study. CMAQ is an air quality modeling framework and tool developed by the US EPA. CMAQ's flexible framework allows for multiple ways to configure CMAQ, including a choice of weather, chemistry, and physics options.

Input data for the CMAQ simulations was as follows:

(i) Meteorological data was from the National Center for Environmental Prediction's Global Forecasting System (NCEP GFS), at 3-hourly intervals.

(ii) Terrain data was the NLCD 2011 (the same data sets used in the Portland-Vancouver LURF and LUR model development).

(iii) Emission inventories were from the NEI 2011, supplemented for mobile sources and wildfires.

(iv) Biogenic emissions were from the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (A. B. Guenther et al., 2012; A. Guenther et al., 2006).

WRF was used for weather simulations, the carbon bond mechanism was used for chemistry, and the Pleim-Xu model for land-surface interactions. The CMAQ deposition simulations were run for the 2-week period corresponding to the summer field campaign with a 4 day spin-up period. All simulations were over a 4km domain nested within a large 12 km domain.

Comparing NO_2 reduction based on CMAQ and the statistical models

The CMAQ simulations output hourly NO_2 concentrations as well as amount of NO_2 deposited for each 4 x 4 km^2 grid cell in the domain. We extract the ambient NO_2 concentrations and the amount of NO_2 deposited hourly for the CMAQ grid cells that lie within the bounding rectangle of the study area. In addition to the hourly ambient NO_2 concentrations and the deposited NO_2, we also extract the hourly boundary layer height and the temperature for each grid cell in our domain of interest. Using the boundary layer height and temperature we estimate the higher ambient NO_2 concentrations that would have resulted if the deposited NO_2 had remained in the atmosphere. For each grid cell, the increase in NO_2 concentrations C_{inc}, in ppb, if there were no dry deposition, is computed by:

$C_{inc} = n_{no2}/n_{air}$

$= [D_{no2} / MW_{no2}] / n_{air}$

$= [DA_{no2} * A_{cell} / MW_{no2}] / n_{air}$

$= [DA_{no2} * A_{cell} / MW_{no2}] / [P_{air}V_{air} / R T]$

$= [DA_{no2} * A_{cell} / MW_{no2}] * R T / [P_{air}* A_{cell}*pbl]$ ………….Equation 4

where:

n_{no2} ≡ moles of NO_2

n_{air} ≡ moles of air

D_{no2} ≡ NO_2 deposited in grid cell

MW_{no2} ≡ molecular weight of NO_2 (46 g)

DA_{no2} ≡ Areal deposition rate of NO_2 for grid cell

A_{cell} ≡ Area of grid cell

P_{air} ≡ Pressure of air in grid cell

V_{air} ≡ Volume of air into which the deposited NO_2 would disperse

R ≡ Gas constant

T ≡ Temperature (in Kelvin)

pbl ≡ boundary layer height

Putting in the values and unit conversions, we get:

$C_{inc} \equiv DA_{no2}\,(kg/ha)*10^5*(0.08206)*T/ (46)(pbl)$ …………………….Equation 5

The increase in NO_2 that would occur in each grid cell if there was no dry deposition to trees is calculated for each hour of the CMAQ output using Equation 5.

This then allows us to estimate the NO_2 in the presence and absence of dry deposition of NO_2 to trees based on CMAQ data. The NO_2 values for each grid cell, both with and without the dry deposition to trees, are averaged over the 2-week period to determine the average 2-week NO_2 concentration for each cell, as well as the NO_2 concentrations in the absence of deposition. We also sum up the hourly deposition amounts to derive the total amount of NO_2 deposited over the two-week period. For each grid cell, we further calculate an effective deposition velocity (to be used later with the LURF model predictions) for the two week period using Equation 6:

$V_{eff}(NO_2) = F(NO_2)/C(NO_2)$ ……………………………….Equation 6

where:

$V_{eff}(NO_2)$ ≡ effective deposition velocity for the 2 weeks, calculated for each grid cell

$F(NO_2)$ ≡ the total deposited NO_2, for each grid cell

$C(NO_2)$ ≡ the 2-week average concentration of NO_2, for each grid cell

In parallel, we use the summer LURF model to predict NO_2, the improvement in NO_2 due to trees, and the estimated NO_2 that must be deposited to trees to explain that reduction. The NO_2 predictions are a direct application of the summer LURF model, and this represents the ambient NO_2 concentrations in the presence of trees. To estimate NO_2 concentrations in the absence of trees, we set the predictor tree canopy area to zero, and re-run the LURF model, giving us the higher ambient NO_2 values in the absence of trees. Our working hypothesis is that the reduction in NO_2 associated with trees (captured here as a difference between predicted LURF NO_2 concentrations in the presence and absence of trees) can be explained by dry deposition. Since the LURF model is evaluated over a 200m point grid, the NO_2 concentrations (both with and without trees) for all LURF points lying within a CMAQ grid cell are averaged to determine the LURF NO_2 values corresponding to the CMAQ cell. Again, this difference in NO_2 calculated based on the presence and absence of trees using the LURF model for each grid cell is assumed to correspond to the amount removed by trees through dry deposition. The NO_2 concentration (expressed as ppb, a mixing ratio) is converted to a two-week deposition amount using the effective deposition velocity, namely v_{eff}, calculated for the two-week period for each cell earlier, using the CMAQ output.

The analyses above allow us to compare the ambient NO_2 concentrations predicted by the CMAQ and LURF models (the 200m resolution LURF predictions being averaged up to the 4km CMAQ grid cell); the reduction in NO_2 associated with trees estimated by the two models; and the amount of NO_2 deposited to trees estimated by CMAQ and LURF.

Sensitivity of NO_2 deposition to bulk stomatal resistance parameterization

Realistically, we do not expect the NO_2 deposition predicted by CMAQ and LURF to match perfectly. Therefore, we undertake a sensitivity analysis in CMAQ, characterizing the change in NO_2 deposition in response to changes in the rate of bulk stomatal uptake. We choose to change bulk stomatal uptake as dry deposition is mainly driven by stomatal uptake. Further, stomatal uptake at the leaf level is highly variable, depending as it does on angle of the sun, meteorology (wind speed, humidity, temperature), tree species (uptake rates can differ widely between species), as well as ambient NO_2 concentrations. Thus parameterizations scaling leaf-level to bulk level uptake are likely to include large uncertainties. The purpose of this exercise is to see how big (and realistic) are the changes that need to be made to bulk stomatal uptake in order to align the reduction in NO_2 estimated by the LURF model with the NO_2 deposition estimated by the CMAQ simulations.

Before beginning the sensitivity analysis, we first verify that NO_2 deposition is indeed responsive to changes in bulk stomatal resistance (R_{st}). This analysis basically asks whether NO_2 deposition in the study area is dominated by deposition to trees or to the ground. Based on Figure 17, we can see that in the absence of trees, NO_2 is effectively being deposited to the ground. In urban areas, where only a small fraction of the land is under vegetation, it is reasonable to ask whether NO_2 deposition is driven by deposition to the ground (in which case it will not be particularly responsive to changes in stomatal resistance) or tree canopy. These two analyses are described in greater detail below.

Is it the trees or the ground?

In urban areas, areas without tree canopy dominate. Even in the absence of trees, some NO_2 is deposited to the ground. To determine whether deposition to ground or "big-leaf" dominates, we modify the deposition code in CMAQ (m3dry.F) such that the vegetation fraction in each cell is set to zero (see Figure 17). The output from this run gives us the deposition of NO_2 to ground in the absence of tree cover. We can compare this deposition of NO_2 to the NO_2 deposition from the unmodified CMAQ run, to estimate the deposition of NO_2 to trees as compared to the ground.

Conceptually, the resistance/deposition model we are looking at can be seen in Figure 17, with the resistances associated with tree canopy grayed out (or removed from the circuit).

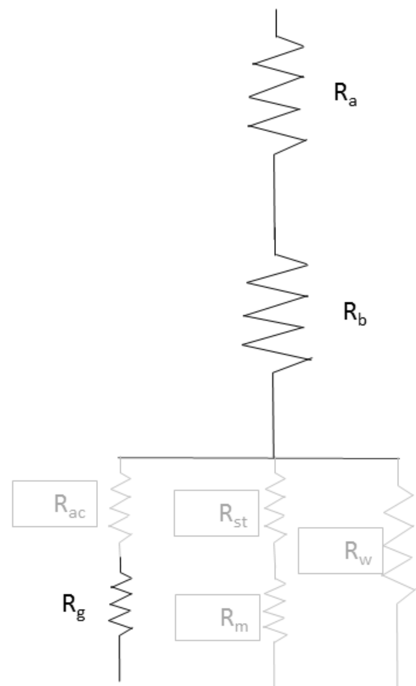


Figure 17: Deposition model assuming ground, no trees

Sensitivity of NO_2 deposition to parameterization of stomatal uptake rates

Finally, we compare the amount of NO_2 deposited under different parameterizations of R_{st}. We modify the R_{st} (in m3dry.F) to take values of 10x, 2x, 1x, 0.5x, and 0.1x of its original value (see Figure 18 for context of R_{st} changes). Change of NO_2 deposition in response to changes in R_{st} parameterizations is non-linear, so these values are meant to determine the range parameterizations of R_{st} (for the big-leaf) that bracket the reduction in NO_2 determined by the summer LURF model rather than an attempt to match the

LURF reductions in NO_2 exactly. The same comparisons are undertaken (NO_2, % decrease in NO_2 due to trees, deposited NO_2) as when comparing NO_2 for the LURF and CMAQ models, in an attempt to bracket the values of R_{st} within which we get the best estimate for LURF estimated NO_2 deposition.

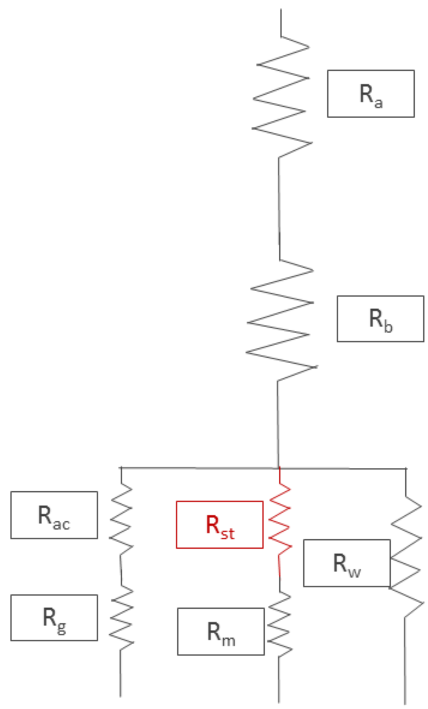


Figure 18: Stomatal resistance in the context of the dry deposition resistance model

Results and discussion

LURF and LUR: is it the trees or the absence of sources?

The summer NLCD LURF model using conditional random forest shows that tree canopy is relatively important, ranking only behind VMT*f*, elevation and longitude (Figure 9, Chapter 2). In fact, it ranks higher in relative importance than in the LUR model, supporting the conclusion that trees independently affect ambient NO_2 concentrations.

We next look at the results from the hierarchical nested regression analysis on the LUR model. The hierarchical analysis shows that 56% of the reduction in NO_2 associated with trees is directly associated with tree canopy, while 14% is due to fewer area sources and 30% due to fewer roadways and lower traffic volume.

These two analyses, coming at the question from different methodological angles, coupled with the existence of a known tree mechanism to reduce ambient NO_2, strengthen the case that the reduction in NO_2 observed by the LUR and LURF models is associated with trees, and possibly even dry deposition (although we examine this in greater detail below).

NO_2 reduction based on CMAQ and LURF

Figure 19 compares the ambient summer NO_2 concentrations as estimated using LURF and CMAQ. As can be seen, both the pattern and the magnitude of summer NO_2 under both CMAQ and LURF are similar, and the correlation between the LURF and CMAQ predicted NO_2 is high (correlation coefficient =

0.85, adjusted $R^2 = 0.73$). However, even though the correlation is very good, the CMAQ NO_2 values are systematically lower than those predicted by the LURF model.

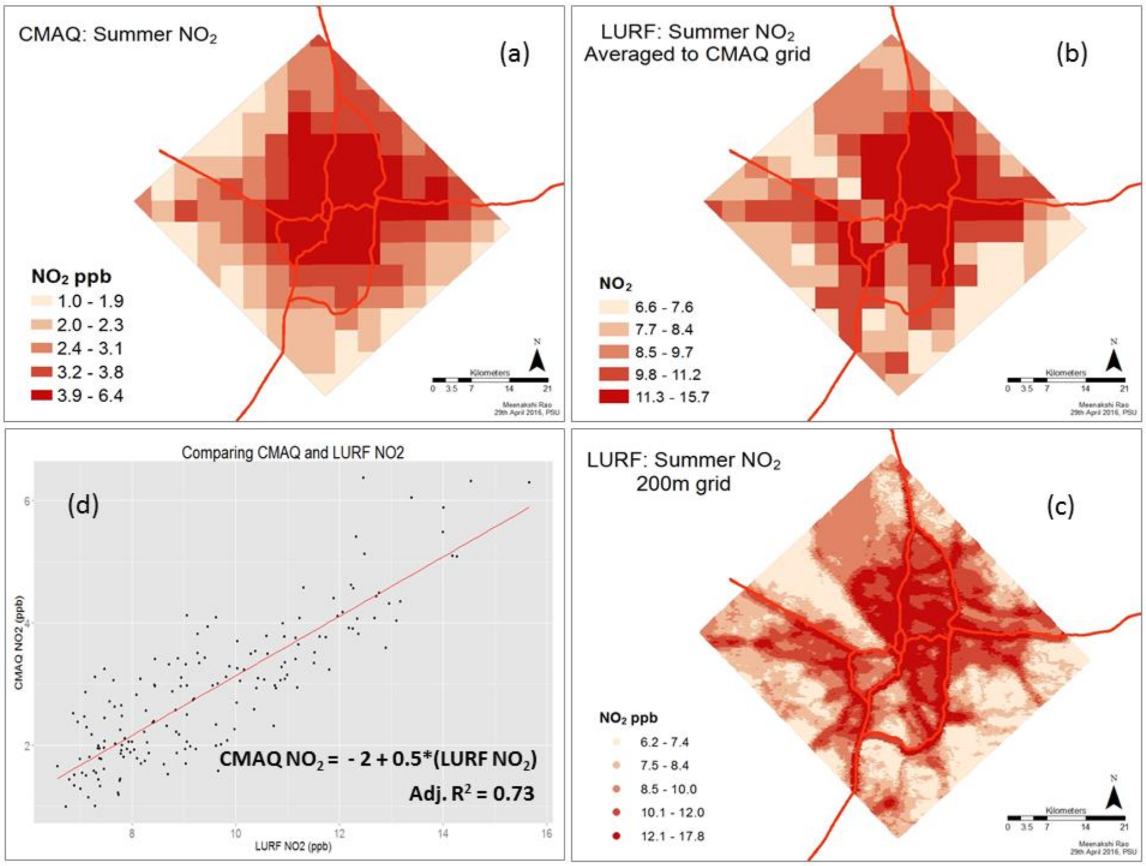


Figure 19: Comparing the NO_2 surfaces from the LUR and CMAQ applications. (a) Summer NO_2 estimates for the 2-week period corresponding to the winter field campaign using CMAQ. (b) NO_2 predictions for a 200m grid based on the summer LURF model averaged up to the 4km CMAQ grid. (c) NO_2 predictions for a 200m grid based on the summer LURF model. (d) Plot showing fit of the summer LURF and CMAQ predicted NO_2 values (at the CMAQ grid level).

The percent reduction in local ambient NO_2 concentrations due to deposition is shown in Figures 20a & 20b, while Figures 20c & 20d show the estimated NO_2 deposition for the summer CMAQ and LURF models. Note, unlike the %

reduction on NO_2 associated with trees, which are independently computed in the CMAQ and LURF models, the LURF deposition estimation is not totally independent. It uses CMAQ data to convert LURF modeled reductions in NO_2 associated with trees into estimated dry deposition. The LURF model predicts 1-5 times the deposition estimated by the CMAQ model. Overall, the CMAQ model estimates that 24 tons NO_2 were deposited in the study area over the 2-week period, which is approximately 0.1 kg/hectare/2-week NO_2 deposition, as compared to the LURF estimate of 82 tons NO_2 deposited over the study area in the same period, for a deposition rate of 0.3 kg/hectare/2-week NO_2, or roughly 300% of the CMAQ estimate.

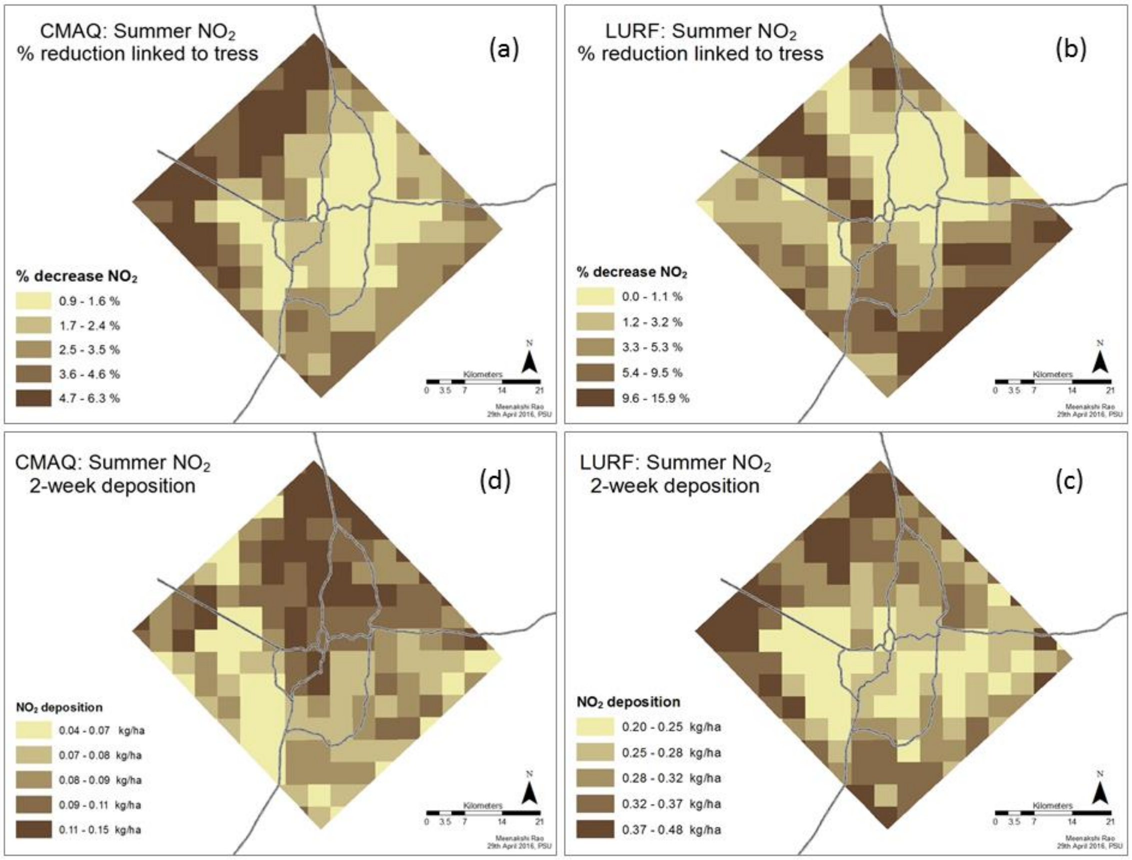


Figure 20: NO_2 deposition estimated based on CMAQ and LURF summer models. (a) The percent reduction in ambient NO_2 as predicted by the CMAQ model. (b) Percent reduction in NO_2 predicted by the LURF model, averaged up to a CMAQ grid cell. (c) Estimated deposition for the LURF model, based on v_{eff} calculated from the CMAQ data for each cell. (d) The pattern of NO_2 deposition in the CMAQ model.

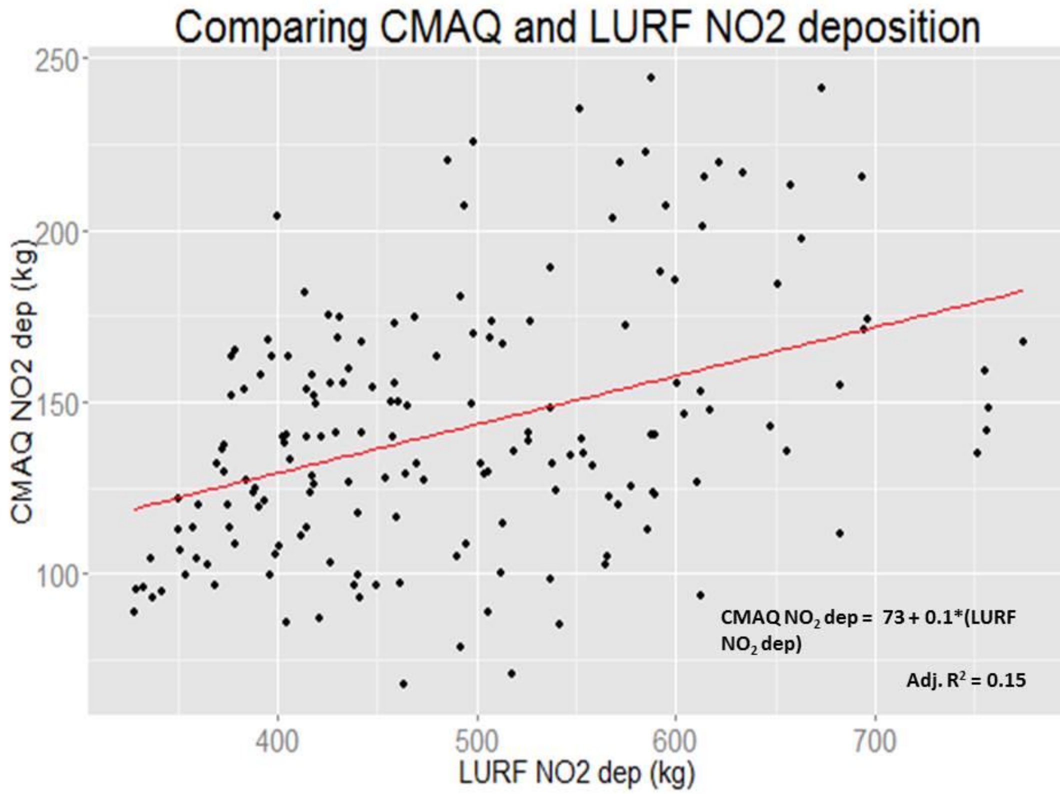


Figure 21: Correlation between 2-week NO_2 deposition estimated by CMAQ and LURF

The difference between the NO_2 deposition estimated by the two models, while not insignificant, is still well within an order of magnitude. Part of the difference could potentially arise just due to the higher ambient NO_2 concentrations reported by the LURF model (~2ppb higher than the CMAQ estimates, based on the intercept of the best-fit line in Figure 19d). However, the pattern of deposition is somewhat different between the CMAQ and LURF models, as is further borne out by the relatively weak correlation between CMAQ and LURF NO_2 deposition values (Figure 21). The CMAQ model shows higher deposition levels in downtown and north Portland, while the LURF model shows the highest deposition in the north of the study area and the west (patterns that are seen weakly in the CMAQ deposition model as well) (Figure 20c and 20d).

The comparison of the reduction in NO_2 in association with trees, as well as the amount of NO_2 deposited as estimated using CMAQ and the LURF model are well within an order of magnitude, and the spatial patterns are not too disparate. Given the very different methodologies and the very different scales of analysis, we believe this is a very positive finding.

Sensitivity of NO_2 deposition to stomatal resistance parameterization

We next look at the response of ambient NO_2 concentrations as well as NO_2 deposition to the parameterization of stomatal resistance in CMAQ.

Our preliminary analysis, which aimed to identify whether the ground or the trees were the dominant route for NO_2 depositions, showed that the dominant deposition route is indeed deposition to trees, and not to ground. The CMAQ results show that approximately 2 tons of NO_2 is deposited daily (or 8 g/ha/day) to the trees plus ground in the study area, while only 167 kg is deposited to the ground daily (0.6 g/ha/day). Thus, we can conclude that stomatal uptake of NO_2 is an important mechanism associated with removal of NO_2, and further that changes in the stomatal uptake rate (or stomatal resistance) will impact the resultant NO_2 concentrations in urban areas. This finding is consistent with what is reported in the literature as well (Dennis et al., 2013).

Based on a coarse sensitivity analysis (Table 16), we find that increasing the stomatal uptake by an order of magnitude increases NO_2 deposition rates from 2 tons/day of NO_2 deposited to about 8 tons/day of NO_2 deposited for the study area; or equivalently, from an NO_2 deposition rate of 8gm/ha/day to 30 g/ha/day. A NO_2 dry deposition amount of 82 tons in 2-weeks over the study area is equivalent to a dry deposition rate of 22 g/ha/day, and is thus consistent with an increase in stomatal uptake by a factor between 2 and 10.

	No uptake by trees	0.1 x Current uptake	0.5 x Current uptake	Current uptake	2x current uptake	10x current uptake	LURF
NO_2 (ppb)	5.1	5.0	4.9	**4.8**	4.7	4.0	9.5
NO_2 dep g/ha/day	0.6	2	5	**8**	13	30	22
NO_2 deposited in study area daily (kg)	167	7725	3382	**2110**	1287	492	5837
O_3 (ppb)	8.7	7.5	7.2	**6.6**	6.5	4.8	---

Table 16: Sensitivity of NO_2 deposition to stomatal uptake rate

Taken together, the CMAQ analysis indicates that the reduction in NO_2 associated with trees as estimated by the summer LURF model is consistent with the mechanism of dry deposition as estimated via CMAQ, contingent upon a 2-10x increment in bulk stomatal resistance. Interestingly, Cabaraban et al (Cabaraban et al., 2013), in their comparison of NO_2 removal through dry deposition in i-Tree Eco and CMAQ, found that CMAQ underestimated NO_2 deposition by a factor of 1-3 due to the difference in the parameterization of deposition velocity (which is equivalent to the inverse of resistance). Cabaraban et al. ascribe this difference to the fact that i-Tree Eco uses parameterizations for deposition velocity at the upper end of the range of values prescribed by Lovett et al., while CMAQ uses the lower end of the range. Thus, the NO_2 deposition rate required in CMAQ to fit the LURF estimated decrease in NO_2 due to trees is within the range of valid resistance (or deposition velocity) parameterizations.

Thus we have shown that the estimated reduction of NO_2 associated with trees seen in the LURF model is consistent with removal of NO_2 from the urban atmosphere through dry deposition. However, whether dry deposition is the mechanism through which trees actually reduce NO_2 still remains to be unambiguously demonstrated. Alternative mechanisms associated with trees that could affect NO_2 concentrations include the change in transport due to the effect of trees on wind flow as well as emissions of VOCs that react with and transform

NO_2. With recent advances in measuring chemical fluxes in the urban environment (Marr, Moore, Klapmeyer, & Killar, 2013), we may soon be able to resolve this question empirically.

Conclusion

Trees play an integral part in urban ecosystems; and numerous studies underscore the health and environmental benefits that accrue from the urban forest. Specifically, as we saw in earlier chapters, increasing urban canopy could be an effective means to mitigate the health impacts of NO_2. In this chapter we explored the extent to which the reduction in NO_2 seen by statistical models, including many LUR models and the LUR and LURF models developed for the Portland-Vancouver areas and presented here, could be (i) linked to trees, rather the mere absence of sources; and (ii) associated with the causal mechanism of dry deposition. Nested hierarchical analysis and conditional random forest both indicate that the association of trees with reduced NO_2 exists above and beyond the correlation of trees with the absence of sources. Further, the amount of NO_2 deposition estimated based on the CMAQ model (8 g/ha/day) is about 300% higher than that required by LURF model (22 g/ha/day). Given the semi-empirical nature of the CMAQ parameterizations, and that these parameterizations are typically based on studies in fields and pristine forest environments, this order of magnitude compatibility emphasizes that the mechanism behind the statistically observed reduction in NO_2 associated with trees might well be the dry deposition mechanism. This is confirmed by the sensitivity analysis, which indicates that a 2-10 fold increase in stomatal uptake rates would be enough to align the findings from the LURF model with the CMAQ model, which is consistent with the findings of Cabaraban et al. (Cabaraban et al., 2013). Thus, this chapter, makes a compelling case both for planting trees to mitigate the health impacts of NO_2 in the Portland-Vancouver area, and also for the role of accessible models such as the LURF model as potentially powerful tools in managing urban landscapes for mitigating the respiratory impacts of NO_2.

Chapter 6: Summary and Conclusions

The Athenians had an oath for someone who was about to become a citizen. They had to swear that "I shall leave the city not less but more beautiful than I found it".

Richard Rogers, Architect

Summary

In this increasingly urban world, the juxtaposition of people and anthropogenic air pollutants has created a huge public health burden. Nations are addressing this problem through a regulatory framework that couples emissions reductions with technological (or economic) innovations. Cities, on the other hand, motivated to a large degree by climate change, have focused on managing the intensity or scale of urban land use within their boundaries. The two most common land use modification strategies employed by cities are reducing VMT and increasing tree canopy. However, cities appear to be lacking a methodological framework to assess both the current health impact of air pollutants in the city and the health benefits accruing from land use modification strategies.

In this dissertation, we developed a methodological framework that would enable cities to monitor and model air pollutants, assess their health impacts, as well as evaluate the relative health benefits of different land use modification strategies.

Developing this framework necessitated not only drawing upon methods and data from diverse domains but also identifying and applying a methodology (namely random forest) that could handle large, correlated predictor sets. This framework is modular, and can readily adapt to air pollutant input from a variety of sources, including on-the-ground-observations, satellite observations, or even new emerging sensor technologies. The random forest technique is robust even in the face of large, noisy data sets that are typically of large sensor arrays. Similarly, health economic impact functions, as well as population data, can either come from the US EPA BenMAP database or be customized as needed.

We specifically applied the framework developed in this dissertation to the Portland-Vancouver area, focusing on one particular urban air pollutant, NO_2 – a US EPA criteria pollutant and a strong marker of combustion-related air pollution, as well as a respiratory irritant. Using extensive on-the-ground measurements and LURF, we were able to examine the effect of correlated land use variables on ambient concentrations of NO_2. We found that even in the mid-sized Portland-Vancouver metropolitan area, which is in compliance with US EPA standards for NO_2, there was still a respiratory health burden of at least $40 million 2013 USD, and that this health burden was disproportionately borne by children. Further, African-Americans, Hispanics, and household with annual income under $25,000 were more likely to be found in the worst quintile of NO_2 as compared with white and high income households. Planting trees emerged as a viable and effective way of mitigating the respiratory effects of NO_2, based on the LURF models.

The statistical finding of reduction of NO_2 associated with trees, however posed a challenge as current literature has not effectively linked the statistically observed reduction of NO_2 with the dry deposition mechanism through which trees are known to remove air pollutants. Thus, before advocating planting trees as an effective mitigation strategy, we investigated to what extent the statistical correlation of reduced NO_2 with tree canopy could be explained simply by the absence of sources of NO_2 in high-canopy areas. Using several different perspectives, namely conditional random forest, nested hierarchical analysis, and comparison with CMAQ deposition output, we concluded that the reduction of NO_2 associated with trees seen by landscape level studies is consistent with the mechanism of dry deposition.

In summary, the key contributions of this dissertation are:

- The development of a methodological framework for analysis of health impacts related to urban land use modifications;
- Introducing the random forest technique to the domain of urban air pollution modelling;

- Applying the methodological framework to assess the health impacts of NO_2 in the Portland-Vancouver area; and further assessing the health benefits accruing from different land use modification strategies.
- Demonstrating that the dry deposition mechanism is consistent with the reduced NO_2 concentrations associated with tree canopy in the Portland-Vancouver area.

Future research

While this research addressed new and interesting questions about the impact of land use on ambient NO_2 concentrations, the framework developed as part of the research is robust and flexible enough to adapt to emerging sensor technologies, data mining techniques, and improvements in satellite observations of air pollution as well as land use data. As air pollution monitoring sensor networks become ubiquitous in the near future, data mining techniques such as random forest, boosted trees, and neural networks can be used to visualize real-time maps of air pollution in urban areas, while temporal data can be mined for trends and used as a basis for predictive models. An added benefit of new sensor technology coupled with data mining techniques like random forest is the ability to actively engage students and community members in process of developing and understanding the science of cities. As a step in this direction, we have developed air quality curriculum for middle school students that can be easily adapted to other grade levels as well as to community members in general (see Appendix).

This research, although making a compelling case for the association of the reduced NO_2 concentrations linked with trees in statistical models, has still not provided a convincing case that it is the trees and nothing but the trees. Thus, a critical future research project would be establishing the relationship between deposition of NO_2 and the reduction of ambient NO_2 concentrations.

Other future research includes establishing the pattern of the spatial distribution of NO_2 with the size, shape, and land use configuration of a city, based on a comparative analysis of multiple cities. Knowledge of the spatial distribution of air pollutants in relation to land use could play an important role in designing and building resilient cities.

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Appendix

Cascades to Coast GK12 Curriculum and Lesson Plans: What is in our air?

CASCADES TO COAST GK12 CURRICULUM: WHAT IS IN OUR AIR?

Meenakshi Rao
Portland State University
Chad Honl
Vestal Middle School

Learning goals:
Upon completion of this curriculum, students will:

i. understand the key concepts about air, air pollution, and the health impacts of air pollution;
ii. develop a habit of observation and inquiry;
iii. participate in a student-directed, authentic inquiry project in air quality.

Objectives:

- Understand the properties of air and how they are measured.
- Describe how human activities are changing the composition & properties of air.
- Understand the sources and sinks of the criteria pollutant, nitrogen dioxide (NO2) in the urban environment
- Describe the influence of NO2 on human health.
- Design and carry out an inquiry on NO2 in their environment.
- Communicate scientific findings of their NO2 inquiry using PowerPoint, posters and oral presentations.

Target Grade:
7th grade

State Standards:

- **6.1P.1**
  Describe physical and chemical properties of matter and how they can be measured.
- **7.2E.3**
  Evaluate natural processes and human activities that affect global environmental change and suggest and evaluate possible solutions to problems.

- **8.2P.1**
  Compare and contrast physical and chemical changes and describe how the law of conservation of mass applies to these changes.
- **8.2P.2**
  Explain how energy is transferred, transformed and conserved.

Activity Summary:
We describe a curriculum designed and implemented to enable 7th grade students to understand the basic ideas about air, air pollution, and scientific inquiry. The curriculum was implemented over the course of a year as three 6-7 week units comprising background information, scaffolded inquiry, and student-directed inquiry. Each unit consisted of about 6-8 contact hours. The entire curriculum could also be covered in a 6-week period.

UNIT 1
Background: Concepts about Air:
We identified five key concepts that students had to learn about air and air pollution:
- What is air?
- Physical properties of air
- Composition of air
- Understanding parts per million and parts per billion
- Nitrogen dioxide – sources, sinks and health effects.

Each concept was introduced through a hands-on activity. The habits of inquiry and observation were encouraged by asking students to hypothesize what would happen in the activity and what observations would support or disprove their hypothesis.
After the key concepts were introduced, one period was dedicated for students to reflect on what they had learned and to develop questions. While this activity empowered students to sharpen their curiosity, it also provided us with an opportunity to address students' misconceptions.

Week 1: 1 period: What is air?
Week 2: 1 period: Physical properties of air: Pressure
Week 3: 1 period: Composition of air
Week 4: 1 period: Understanding parts per million and parts per billion
Week 5: 1 period: Nitrogen dioxide – sources, sinks and health effects
Week 6: 1 period: Ask-a-Scientist (questions and debrief)

UNIT 2
Scaffolded Inquiry:
We introduced a scaffolded inquiry activity to prepare the students for the final student-directed air quality inquiry project. In this first inquiry, the students were given the research question: where will NO_2 levels be the highest – the front of the school along a major street, the back of the school (where there is a community garden), or inside the classroom?

Week 1: 1 period: Review procedure and data sheet for scaffolded inquiry.
Week 1: 2 periods: Assemble NO_2 samplers, deploy samplers, fill in data sheets.

Week 3: 1 period: Pick up samplers, fill in data sheets. Review and note any observations that would affect NO_2 readings (sampler was on the ground; spider in sampler; etc.).
Week 4: 2-4 periods: Review results; discuss implications.
Week 5-6: (as needed): Work on posters.
Week 7: 2 periods: Student presentations of results.

UNIT 3
Student-directed Inquiry:
In the student directed inquiry project, the research goal and protocol were developed by the students themselves. Since communicating one's science is an important part of the scientific process, students presented their results after both the scaffolded and student-directed inquiry projects in either poster or slide (PowerPoint or PREZI) format, both in the classroom and at the GK12 conference.

Week 1: 2-4 periods: Develop goals, methods and observation sheet with students.
Week 2: 1 period: Assemble and deploy NO_2 sampling tubes. Make sure all students have a log book/observation sheet and understand the observation protocols!
Week 4: 0.5 period: Pick up NO_2 samplers.
Week 5: (as needed): Discuss results, have students do research to better understand the results.
Week 6: (as needed): Work on presentations.
Week 7: Students present their results.

Activity Plans

UNIT 1
Background: Concepts about Air

Key learning goal:

> At the end of the unit, students will have developed a better understanding of the basic concepts related to air and air pollution. They will be able to develop a hypothesis (what they expect to happen based on prior knowledge), hone their observational skills, and be able to reason whether their observations support their hypothesis or not.

We had identified 5 key concepts to teach students about air and air pollution:

- What is air?
- Physical properties of air: Pressure
- Composition of air
- Understanding parts per million and parts per billion
- Nitrogen dioxide – sources, sinks and health effects.

Each of these concepts was introduced in a 1-period class (typically). Each period used the same format: a review of existing student knowledge, introduction of the new concept building on students' existing knowledge, solidifying the new concept through a hands-on activity or demo, and further reinforcing retention of the new concept through a debriefing discussion and note-taking.

1. *Review*
   The first several minutes were used to review what was learned in the previous class.
2. *Introduction of the new concept*
   The new concept was introduced, typically by asking the students how they would explain a phenomenon within their experience. For example, to introduce the concept of air, we asked the students how they knew there was air around us. To introduce the concept of the physical properties of air, we asked the students how they would describe air to a friend on a different planet.
3. *Hands on activity or demo to demonstrate concept*
   Following the introduction of the concept, we either had a demo or a hands-on activity based on the concept.
   This section was used to introduce the students to and reinforce their practice of the scientific method. The students hypothesized on the outcome of the demo/activity based on their existing knowledge. They were required to make observations and fill out a data sheet during the demo/activity. They worked in small groups to determine whether the observations supported their hypothesis or not.
4. *Wrap-up*
   Finally, we debriefed as a group and summarized what we had learned about the concept.

Ask-a-Scientist
We used the last period in this unit for students ask the fellow any unanswered questions they had about air. Each student was given an index card, with the expectation that each student would write down at least one question. The remainder of the class was a free-flowing discussion that resulted in a lot of great questions.
This period served two useful purposes. First, it gave us (the teacher and the fellow) an opportunity to observe what the students had learned and to correct any misconceptions. Second, it gave the students a chance to review and integrate their knowledge about air and air pollution.

See Appendix I for detailed lesson plans for:
- What is air?
- Physical properties of air: Pressure
- A sampling of questions about air from students; and some answers.

Extensions

Properties of air – temperature, relative humidity
Wind
Chemical properties of air
Pollutants – ozone, PM2.5

Assessment Questions

Review and wrap-up, data sheets and science notebook were used for formative assessment.
Ask-a-Scientist

UNIT 2

Scaffolded Inquiry: What are the Nitrogen Dioxide(NO2) levels around the school?

Key learning goal:

At the end of the unit, students will have a better understanding of the air pollutant nitrogen dioxide – its sources, its sinks and its effects on human health. They will get a hands-on opportunity to follow the scientific method, as well as to practice communicating their science.

1. *Prior to Week1 (for fellow and teacher)*
    a. Prepare map of classroom (using PowerPoint) and vicinity of school (using Google Earth).
    b. Walk the area identifying spots where students can safely place NO2 samplers.
    c. Prepare sampler materials (see Appendix II materials needed and procedures for preparing TEA solution and analyzing the NO2 passive samplers).
    d. Divide students into groups and work out the logistics of how many samplers each group will place and where.
    e. Prepare datasheet.
    f. Prepare packet for each group:
        i. Instructions for assembling and labeling tubes.
        ii. Indoor & outdoor map, with marked with the sampler sites for each group.
        iii. Datasheet for noting time of deployment.
2. *Week 1: 1 period: Introduce experiment*
    a. Review experiment.
    b. Have each group write down their hypothesis.
3. *Week 1: 1 period: Review procedure and data sheet*
    a. Do a dry run through the deployment procedure.
    b. Make any changes needed to datasheets and procedures.
4. *Week 1: 2 periods: assemble NO2 samplers, deploy them, fill in data sheets*
    a. Assemble NO2 samplers.
    b. Place samplers indoors and outdoors.
    c. Note timings of deployment.
    d. If possible, co-locate 2-3 samplers with a NO2 monitor. We co-located 2 samplers at the Portland DEQ air monitoring station to serve as an experimental control.
5. *Weeks 2-3: Samplers accumulating NO2*
    a. Samplers need to be deployed for about 2 weeks.
    b. Students should monitor the samplers (especially if any are in busy places such as the playground).
    c. Students may optionally want to track weather conditions and wind directions during the two weeks samplers are in the field.
6. *Week 3: 1 period: Pick up samplers*

    a. Pick up samplers
    b. Note time of picking up samplers. Students should additionally note any relevant observations of the samplers (spider in the sampler; thrown on the ground, missing, etc.).
    c. Retrieve DEQ controls, if any.
7. *Week 3/4 (fellow): Analyze samplers, retrieve wind and weather data*
    a. Analyze the samplers.
    b. Retrieve wind and weather data.
    c. Map the data.
8. *Week 4: Discuss results*
    a. Hand back to each group of students the NO2 levels for their samplers.
    b. Show students the NO2 map for indoors and outdoors.
    c. Discuss results, implications.
9. *Week 5-6: (as needed): Research & presentation preparation*
    a. Students do background research.
    b. Work on posters.
10. *Week 7: 2 periods: Students communicate their science*
    a. Students present the results of the scientific inquiry both as posters and oral presentations.

See Appendix I for NO2 samplers assembling instructions (for students), maps given to students for placing their tubes, and maps showing the measured NO2 levels.

Assessment Questions

Posters and oral presentations

UNIT 3

<u>*Student-directed Inquiry:*</u>

Key learning goal:

At the end of the unit, students will have designed a scientific inquiry to answer a question about NO2 levels that is of interest to them.

1. *Week 1: 1 period: What is the question?*
    a. Review NO2 information, especially air pollutant standards and impact of air pollutants on human health.
    b. Prompt the students: if they had access to a reasonably large number of NO2 tubes, what would they want to measure?
    c. Settle on one question. If necessary, take a vote.
    In our class, students pretty quickly concurred that they wanted to measure NO2 around their homes.
    d. Discuss why the question is important to students, what do they expect to find and why. Encourage students to summarize the discussion and write it up in their science notebooks.
2. *Week 1: 2 periods: How can we answer the question?*

    a. Work with the students to decide on:
        i. How many samplers?
        ii. Where will the samplers be placed?
        iii. What other variables need to be observed?
        iv. What is the protocol for measuring the other variables?
    b. Form a hypothesis
3. *Week1/2 (for fellow and teacher): Getting sampler materials and preparing data sheets*
    a. Get materials together for assembling the required number of samplers.
    b. Prepare any maps that might be needed.
    c. Prepare inquiry packet:
        i. datasheet/observation booklet that students have designed.
        ii. Observation protocols.
        iii. Space for NO2 tube deployment & pick-up timings.
4. *Week 2: 1 period: Deploy samplers*
    a. Review observation protocols and datasheet.
    b. Deploy samplers.
    c. Co-locate 2-3 samplers with a calibrated NO2 monitor as experimental controls, if possible.
5. *Weeks 2-3: Samplers accumulating NO2*
    a. Samplers need to be deployed for about 2 weeks.
    b. Check in with students that they are monitoring the samplers and keeping up with their observation protocols (teacher).
6. *Week 3: 1 period: Pick up and analyze samplers*
    a. Students turn in samplers and completed datasheets.
    b. Analyze the samplers (fellow).
    c. Consolidate class datasheets.
    d. Prepare any relevant maps.
    e. Retrieve wind and weather data (if relevant).
7. *Week 4: Discuss results*
    a. Hand back to each group of students the NO2 levels for their samplers.
    b. Discuss results, implications.
8. *Week 5-6: (as needed): Research & presentation preparation*
    a. Students do background research.
    b. Work on PREZIs.
9. *Week 7: 2 periods: Students communicate their science*
    a. Student presentations of results.

See Appendix I for the question, data sheets, and protocols designed by the students.

Assessment Questions

PREZIs (or PowerPoint) and the accompanying oral presentations

Materials

See the section *Making Palmes Tubes* (pg. 165)

Handouts and worksheets

Seethe section *Lesson Plans* (pg. 145).

Extensions

Students can extend their experiments for science fair projects.

Lesson Plans

Activity Plan

<u>What is Air?</u>

Key learning goal:
What is air? What state of matter is air in? Does air have mass? What are the physical properties of air?

1. Begin by prompting students with questions such as:
   - what is air?
   - how do they know there is air around us?

   The goal is to guide students to draw conclusions based on their own observations about air. Are there observations from their own experience that they can use to confirm that there is air around us? If students seem at a loss, show them a sheet of paper floating down or ask them what happens when they breathe out on a cold day.
   In my classroom, I prompted the students to describe how they could use their 5 senses to observe air – Can you see air? Can you hear air? Can you feel air? Can you smell air? Can you taste air?
   At the end of the discussion period summarize the discussion and have the students write it in their science notebooks.
2. What state of matter is air in?
   This is a chance to review the three states of matter, and may be get the students thinking about liquid air and solid air – and what that might mean for life on Earth.
   Wrap-up, and have students write in their notebooks.
3. Does air have mass?
   My class was divided on this – most students said air did not have mass, because if it did, we would be crushed. A few students said air had mass (without giving a very good reason for why they thought so). I prompted the students to describe how they would find out who was right.
4. What are the physical properties of air?
   Prompt the students to say how we describe things. Typically, we use color, shape, size, smell, name, etc. to identify things. How would we describe air? If students have studied temperature and pressure, these can be added to the list.

Related Concepts

Scientific Method

Materials

None

Handouts and worksheets

None

Extensions

Measuring the density of air

Assessment Questions

How do we know there is air around us?

How can we describe air?
Does air have mass? How would you measure it?

Activity Plan

Physical Properties of Air: Pressure

Key Learning goal:
At the end of the activity, students will have a better understanding of atmospheric pressure and how it affects us in everyday life.

1. Review the physical properties of air that have been covered so far (color, state of matter, does it have a shape?, Does air have mass? Density). Tell the students that they will be learning about another physical property of air.
2. Do the following demo
   (here is a link: http://www.youtube.com/watch?v=XfFdNNiIAJw)
   a. Fill a plastic glass half to three-quarters full of water.
   b. Place a plastic lid on the glass.
   c. Holding the lid with one hand, slowly turn the glass over, so the open end of the glass is facing down.
   d. Ask the students what they expect to happen when you let go of the lid - ask them to support their answers.
   e. Remove your hand that is holding up the lid.
   f. The water does not fall.
3. Give the students a minute or two to think about it, and then ask them how they would explain their observations of the demo. Write the students' hypotheses on the board. Ask them how they might test their hypotheses. For example, one hypothesis might be that the lid stays on the glass due to suction and thus prevents the water from falling. A follow-up question would be what causes the suction? If water is causing the suction, what would happen when the amount of water in the glass was changed?
4. Let the students work in groups repeating the experiment and testing their hypothesis. Give the students about 20-30 minutes to explore what happens. Make sure they record their observations in a simple observation sheet.
5. Some things the students may explore to test or strengthen their hypothesis:
   a. Using different amounts of water in the glass
   b. Comparing what happens when hot and cold water are used
   c. Seeing what happens when the upside-down glass is squeezed
   d. Seeing what happens when the upside-down glass is shaken
   e. Using different materials for the lid (cardboard, paper, metal, wood…)
   f. Whatever else (that is safe) they would like to test. For example, some students added crumpled paper to the cups; others put in pencil stubs. Make sure the students tie back their "experiment" to their hypothesis.
6. After students have done the experiment, let the students discuss their observations in their groups to determine if their observations support their hypothesis.
7. Come together as a class, debrief. Explain to the students that air has a property called "atmospheric pressure". It is atmospheric pressure that pushes up against

the lid and keeps the water from spilling. Atmospheric pressure is about 15 pounds per square inch (psi). Air exerts this pressure everywhere – on the table, the floor, our heads…and that is why astronauts need to wear spacesuits.

Related Concepts:

Air has mass
Air is made up of molecules
Air is a gas

Materials:

Plastic tubs (to catch water in case of spillage)
Clear plastic glasses
Yogurt container lids (preferably clear)
Water
Towels for mopping up

Handouts and worksheets:

(attached)

Extensions:

The soda can demo makes a good extension.
(here is a link: http://www.youtube.com/watch?v=skhSfFz28g0)

- Add about a tablespoon or two of water in an empty soda can.
- Place the soda can on a burner or hot plate till the water starts steaming.
- Count till 10 once the water starts steaming. Then, using tongs, turn the can into a bowl of cold water.
- Atmospheric pressure will crush the can.
  (Heating the can causes the water to vaporize. As the steam rises, it pushes the air out of the can. Dunking the can in the cold water converts the steam to water, reducing the pressure inside the can. The greater atmospheric pressure outside the can causes the can to implode).

Assessment Questions:

If doing the soda can extension, ask the students to write a one paragraph explanation of why the soda can in the soda can demo was crushed. The clarity of the explanation can provide an assessment of how well the student has understood the concept of atmospheric pressure.
If not doing the extension, ask students to explain why astronauts wear spacesuits.

Date: ________________

Names:

---

1. What is your hypothesis?

2. Describe in words and draw a picture showing how you did the experiment.

3. Write down what you observed when you were doing the experiment.

4. Do your observations support your hypothesis? How would you explain your observations after doing the experiment?

Ask-a-Scientist : Sample Questions

1. How do humans filter out the NO_2 from the air?
2. When you breathe air and breathe it out, how does it turn into carbon dioxide?
3. What all is in the air?
4. How do people measure air?
5. Will air ever run out on Earth?
6. How long can we live without air?
7. Does air pressure change around the world?
8. Can too much air kill you?
9. Is there a way to bring NO_2 levels down?
10. What state has the cleanest air?
11. Will we ever be able to see air, because it is colorless?
12. How can we know if there is anything bad in the air?
13. Can air be liquid or solid?
14. How much air do you need to hear sound?
15. Can oxygen be bad for us?

Ask-a-Scientist : Sample Answers

1. How long has air been on the Earth?
   Air, similar to what we know today, has probably been on Earth for only about 1.5 billion years. Oxygen did not appear in the Earth's atmosphere till about 2 billion years ago, and it took at least another 500 million years for the amount of oxygen in the air to reach the amount we see in the atmosphere today. Scientists think that the atmosphere we see today is probably the third atmosphere the Earth has had. The first atmosphere (about 4.5 billion years ago) was likely mostly hydrogen, and Earth lost it all in the heavy solar winds of that time. The Earth's second atmosphere was formed about 4.4 billion years ago by the release of gases by volcanoes and meteor strikes. It was mainly made up of CO2, N2, water vapor, ammonia and methane, and no oxygen. The second atmosphere was transformed into our current atmosphere by the action of cyano-bacteria. Our current atmosphere still has a lot of nitrogen (78%), very little carbon dioxide (0.04%) and quite a bit of oxygen (21%).

2. If air is colorless, how do we know it is there?
   Although we cannot see air, we can sense it using our sense of touch, smell and hearing. Also, using our sight, we get some clues that air exists as we see smoke rising, clouds floating and birds flying.

3. How do we know what air is made of?
   It took scientists centuries and centuries to figure out what air is made of. More than 2000 years ago, the ancient Greeks thought that air was an element, not a mixture of gases. People believed the idea that air was an element for a very long time. It was only in the 1700s that experiments by famous chemists such as Lavoisier, Priestley, Cavendish and others showed that air is a mixture of gases. Priestley discovered oxygen in 1770s, and Cavendish showed that air is 21% oxygen. Daniel Rutherford discovered that nitrogen was a part of air in 1772. It was more than a hundred years later, in 1864, that William Ramsay discovered argon.

4. Can air have a chemical reaction?
   Air is a mixture of many compounds like nitrogen, oxygen, argon, carbon dioxide, nitrogen dioxide, etc. Other than Argon (which is very chemically un-reactive), all compounds that make up air can and do take part in chemical reactions under the right conditions. For example, a forest fire is a chemical reaction between carbon in the forest and oxygen in the air. The nitrogen and oxygen in the air also react chemically when heat energy is supplied to form NO and NO2.

5. How does air stay in Earth, but not in space?
   The reason why air stays on Earth, but not in space is the same reason why a ball thrown in the air comes back down to Earth and does not go off into space: gravity. All gases that make up the atmosphere, like the ball, have mass, and therefore "fall" towards the Earth because of gravity. However, all molecules in

the air have some energy which depends on the temperature. Hydrogen molecules, which are the lightest, often get enough energy to escape Earth's gravity and go off into space. Planets with stronger gravity, like Jupiter, can hold on to even the hydrogen in their atmosphere. Small planets or moons may not have enough gravity to hold on to any gases.

6. Can air pressure and temperature change the sound of air?
   The speed of sound does change with temperature: sound travels faster in warmer air. Temperature can change the pitch (or frequency) of the sound in musical instruments. In wind instruments like the trumpet or flute, warmer air makes the sound slightly higher in pitch. Pressure does not change the speed of sound in the air.

7. Where does N2 go after it enters our body?
   The nitrogen that we breathe in is breathed out unchanged. Nitrogen is an important component of proteins, but humans cannot use the nitrogen in the air to make proteins. This is because the nitrogen bond in the nitrogen molecule is very strong and we cannot break it.

8. When Earth runs out of air, is there another planet with a similar context of air?
   Scientists are very interested in finding an earth-like planet outside our solar system. Scientists have defined a "Goldilocks" zone - the orbital distance from a sun where the temperature is not too hot or too cold so that liquid water can exist. NASA scientists have found several planets in our galaxy that are in the Goldilocks zone, but we do not know what their atmospheres are made of - yet.

9. When you breathe air and breathe it out, how does it turn into carbon dioxide?
   The air that we breathe in goes into our lungs. From the lungs, the arteries absorb the oxygen and carry it to the cells in the body. Each cell uses this oxygen to "burn" fuel - just like we burn wood - to generate energy. And, just like when we burn wood, burning the fuel in the cell uses up O2 and produces CO2. The carbon dioxide (and remaining oxygen) is collected by veins and taken back to the lungs, where it is breathed out. The air we breathe in has 21% O2 and 0.04% CO2. The air we breathe out has about 17% O2 and 4% CO2.

10. How many molecules are inside the human body?
    There are approximately 1.22 x 10^27 molecules in a 12-year-old’s body. Another way of saying this is that a 12-year-old has [(one billion) times (one billion) times (one billion)] molecules – which is a humongous number!
    If we imagined that each molecule was the size of a small sphere with a diameter of 1 cm (like a ball bearing), then:
    One billion molecules would fill 2 big classrooms.
    If we began piling (one billion times one billion) of these 1 cm diameter-size molecules over the entire city of Portland, the pile would rise to the height of Mt. Hood!
    And if we wanted to pack (one billion times one billion times one billion) of theses 1 cm diameter size molecules, we would need two spheres – one the size of Earth, the other the size of the Moon (and we would still have a few molecules left over)!

It is a good thing molecules are much, much, much, smaller than 1 cm!
This is how I estimated the number of molecules in a 12-year-old's body: Let us say that the 12-year old weighs about 45 kg (about 100 lbs). To make the calculation simple, let us say that the body is made up of only water (actually the body is only 2/3 water). One mole of water is 18 g. So, 45 kg of water will be [(45 x 1000) / 18] moles. Each mole has Avogadro's number (6 x 10^23) molecules. So 45 kg will have [(45 x 1000 x 6 x 10^23) / 18] molecules = 1.5 x 10^27 molecules. Since the body is only 2/3 water, we can guesstimate that there will be 1 x 10^27 molecules of water + the molecules in the remaining 1/3 of the body. Since these molecules are heavier than water, there will be fewer than 0.5 x 10^27 of them – let us say 0.2 x 10^27. This leads us to guesstimate that an average 12-year-old has about 1.2 x 10^27 molecules in his/her body.

NO_2 sampler assembly instructions for scaffolded inquiry

Names:____

Date:________________________

Group #:_____________________

Procedure:

Each group will make 6 (3 pairs) of NO2 samplers according to the following steps:

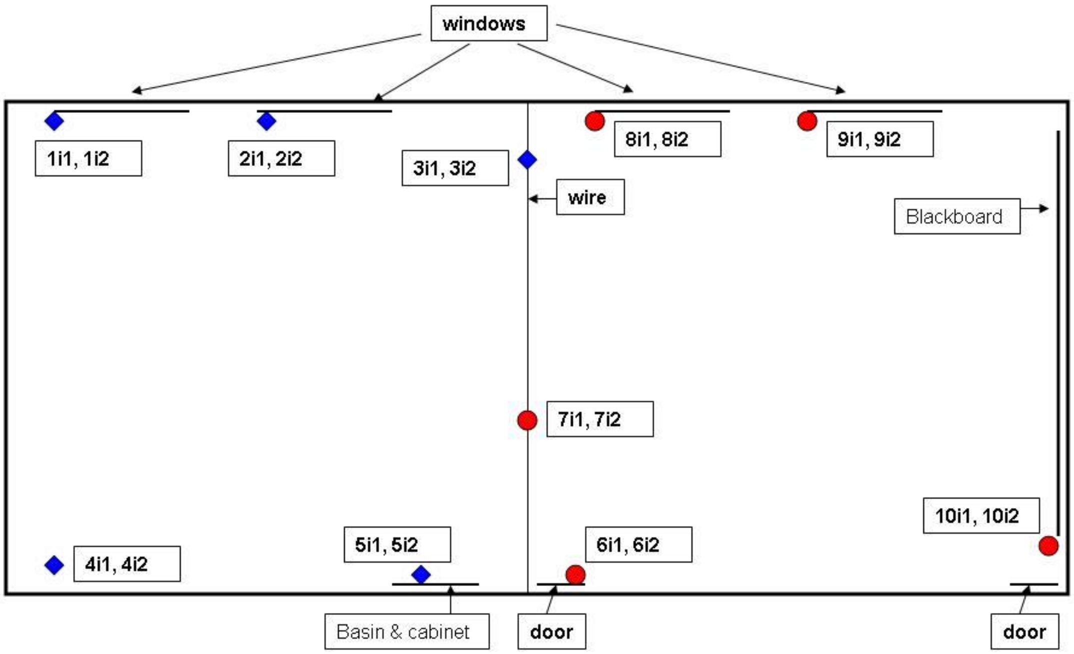
1. Place 2 wire meshes in six red caps. The wire meshes should be flat and at the bottom of the cap. You may need to use a clean metal rod to tap them in.
2. Once 6 caps have meshes, place them in the tray and bring them to the teacher or the scientist to add TEA (triethanolamine) to the meshes in the 6 red caps.
3. Once the TEA solution is placed in the cap, put a tube in each cap. Push it till it reaches the bottom of the cap.
4. Label the samplers (on the caps with the meshes and TEA solution):
   grp# i1 (so group 1 will label <u>1i1</u>)
   grp# i2 (so group 1 will label <u>1i2</u>)
   grp# f1
   grp# f2
   grp# b1
   grp# b2
5. Place another empty cap loosely on the open end of each sampler.
6. First place the samplers labeled i1 & i2 inside the classroom, using zip ties and blue tape. The classroom map shows you where to place your tubes. Once the samplers are put up, remove the loose caps and note the time the caps were removed.
7. Next we will place the samplers labeled f1 and f2 in front of the school. The samplers in the front will be placed on either trees or poles along the front of the school. The school map shows where your tubes will be placed.
   Remove the caps that were loosely put on.
   Note the time you removed the caps.
8. Finally, samplers labeled b1 and b2 will be placed in the back of the school. The school map shows you where to place your group's tubes. Remember to remove the loose caps.
   Remember to note the time you took off the caps!

Sampler uncapping time:

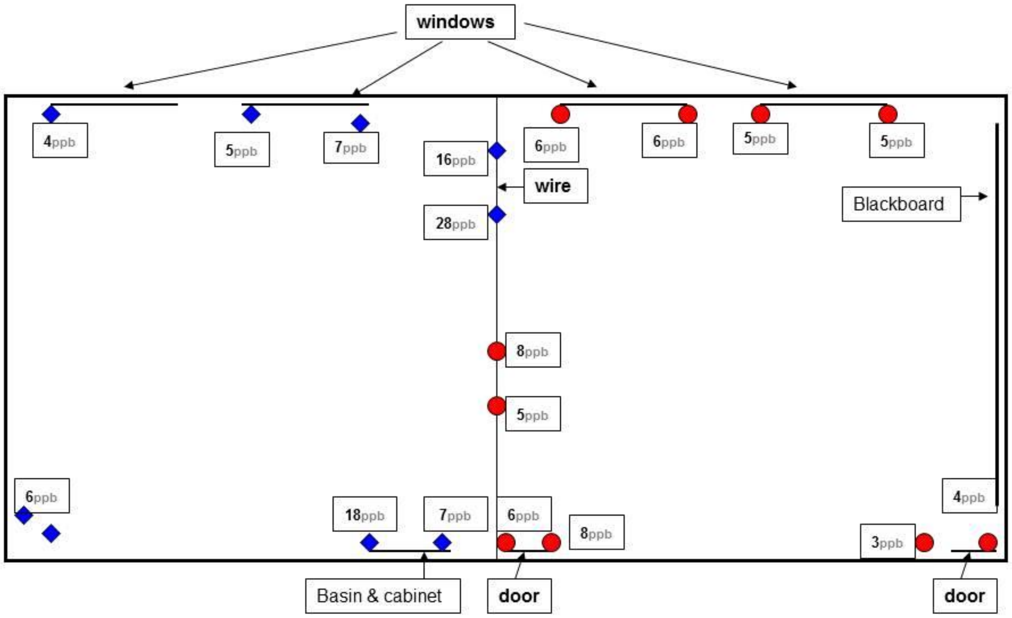
Inside:________________

Outside front:____________

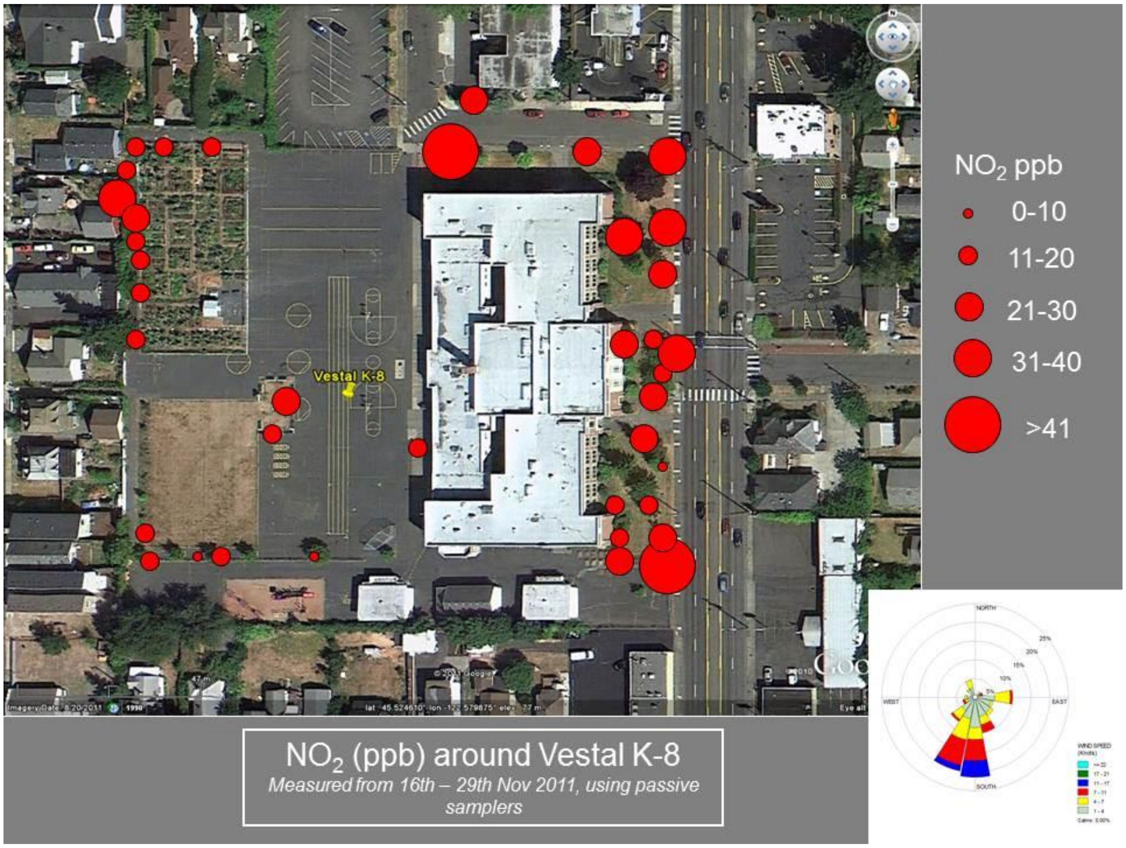
Outside back:______________


windows
1i1, 1i2
2i1, 2i2
3i1, 3i2
wire
8i1, 8i2
9i1, 9i2
Blackboard
7i1, 7i2
10i1, 10i2
4i1, 4i2
5i1, 5i2
6i1, 6i2
Basin & cabinet
door
door


1b1, 1b2
2b1, 2b2
3b1, 3b2
4b1, 4b2
5b1, 5b2
10b1, 10b2
Vestal K-8
6b1, 6b2
9b1, 9b2
7b1, 7b2
8b1, 8b2
5f1, 5f2
4f1, 4f2
3f1, 3f2
2f1, 2f2
1f1, 1f2
6f1, 6f2
7f1, 7f2
8f1, 8f2
9f1, 9f2
10f1, 10f2
Google



Vestal K-8 7[th] grade science classroom NO_2 map


NO$_2$ ppb
0-10
11-20
21-30
31-40
>41
Vestal K-8
NO$_2$ (ppb) around Vestal K-8
Measured from 16th – 29th Nov 2011, using passive samplers

Student-directed inquiry

Research Question:
What are the NO_2 levels inside and outside students' homes?

Hypotheses:

(1) NO_2 levels inside students' houses will be less than outside, unless people use fireplaces during the sampling period.
(2) NO_2 levels will be higher at student homes where people cook a lot, do not open windows, or there is a smoker in the house.
(3) Students who live close to freeways or major streets will have higher NO2 levels than students who live further away from busy streets.

Lickert scale for ranking indoor and outdoor NO2 levels at student homes:

Outdoor NO_2:

- Distance from freeway
  - 5 - More than one freeway 1 block from house
  - 4 - One freeway 1 block from house
  - 3 - Freeway 2 blocks from house
  - 2 - Freeway 3 blocks from student house
  - 1 – Freeway more than 3 blocks from student house
- Distance from busy street
  - 5 - More than one busy street 1 block from house
  - 4 - One busy 1 block from house
  - 3 - Busy street 2 blocks from house
  - 2 - Busy street 3 blocks from student house
  - 1 – Busy street more than 3 blocks from student house
- Gas station nearby?
  (Students reasoned that a gas station would increase the idling, and hence increase NO2 emissions)
  - 3 - More than one gas station within a block of house
  - 2 - One gas station within a block of the house
  - 1 - One gas station within 2 blocks of the house

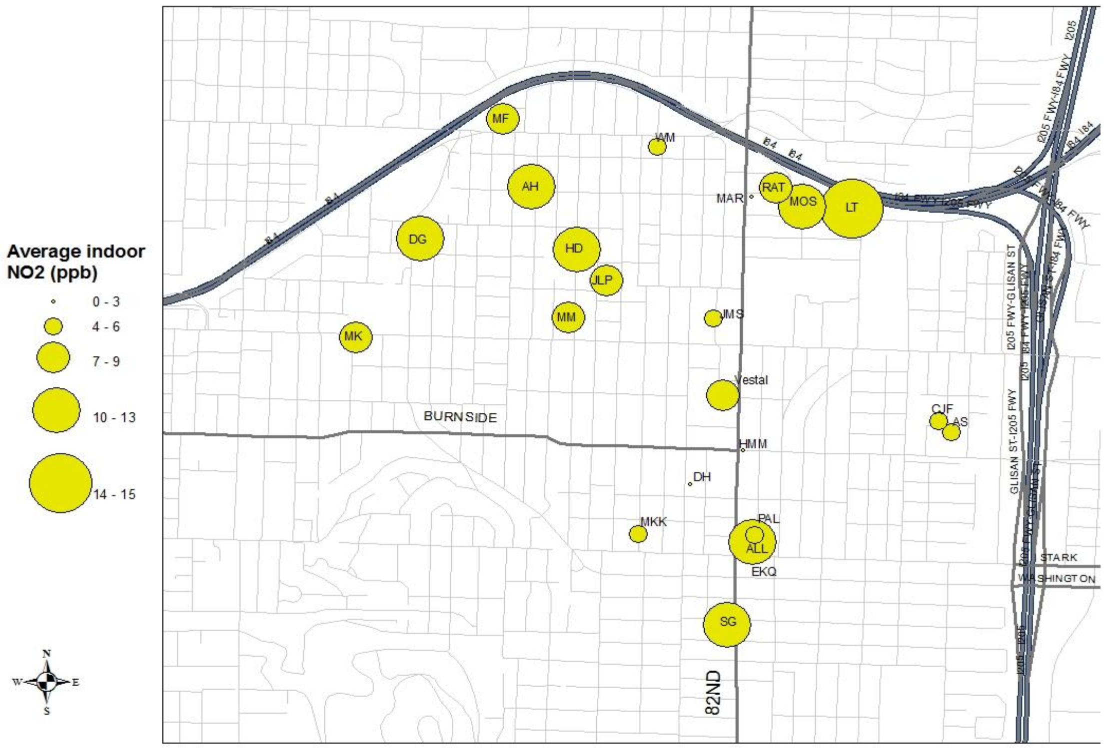
Indoor NO_2:

- Gas or electric cooking range?
  - 2 – Gas cooking range
  - 1 – Electric cooking range
- Cooking time
  - 5 – 1.5 hours cooking daily, on average
  - 4 – one hour of cooking daily, on average
  - 3 – 45 mins of cooking daily, on average
  - 2 – 30 mins of cooking daily, on average
  - 1 – 15 mins of cooking daily, on average
- Ventilation during cooking
  - 5 – almost always
  - 4 – most of the times

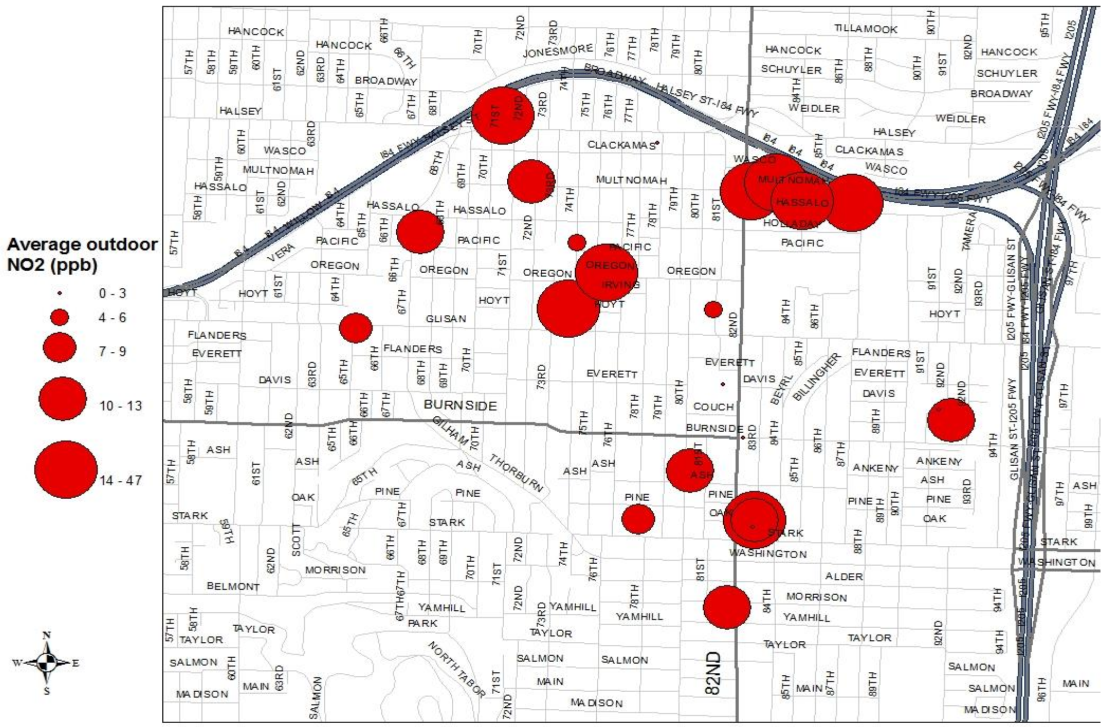
3 – sometimes
2 – rarely
1 – almost never

- Open windows?
  5 – almost always
  4 – most of the times
  3 – sometimes
  2 – rarely
  1 – almost never
- Fire in fireplace?
  5 – always
  3 – sometimes
  1 – rarely
- Indoor smoking
  5 – always
  3 – sometimes
  1 – rarely

	NO2: Outdoor factors				NO2 Indoor factors						
Initials	Distance from freeway	Distance from busy streets	Gas station nearby?	Outdoor Total	Gas or Electric?	Cooking time	Ventilation during cooking	Open windows	Fireplace	Indoor smoking	Indoor Total
CJF	5	5	3	13	1	2	3	4	0	1	11
MK	5	5	2	12	1	0	3	5	0	0	9
JMS	4	4	2	10	1	3	0	1	0	0	5
Steph	4	4	2	10	1	2	0	4	3	0	10
LDE	5	4.5	0	9.5	2	1	3	0	0	0	6
HMM	2	5	2	9	2	4	1	5	1	0	13
MOS	5	4	0	9	1	4	3	2	0	0	10
EKQ	2	5	2	9	1	4	2	4	0	0	11
PAL	1	4	4	9	2	3	2	5	0	0	12
RAT	5	4	0	9	1	3	1	4	0	0	9
LT	5	3	0	8	3	4	5	0	0	0	12
MM	2	4	0	6	1	3	3	4	0	2	13
MKK	1	3	2	6	1	5	2	0	0	0	8
DG	4	1	0	5	0	4	0	0	0	0	4
JLP	1	3	0	4	1	4	3	1	3	3	15
WIL	2	2	0	4	1	3	3	4	0	0	11
Arf	1	5	0	6	1	1	3	2	0	0	7
DH	2	5	0	7	1	5	4	3	0	0	13
Chr	5	5	1	11	1	2	1	0	5	0	9
HD	3	3	2	8	1	5	4	3	0	0	13
AS	5	5	0	10	1	4	3	2	0	0	10
AH	1	1	1	3	2	5	1	2	5	0	15
LuisM	5	5	0	10	2	4	2	2	0	0	10
TL	2	4	0	6	2	3	3	3	0	0	11
MAR	5	2	0	7	1	4	4	5	0	0	14
Lar	1	5	2	8	2	5	1	3	0	0	11
Cam	4	5	1	10	1	3	4	4	0	0	12
ALL	3	4	1	8	2	4	2	3	0	0	11
MF	5	4	0	9	1	4	2	2	0	0	9
WM	4	4	2	10	4	5	3	0	0	0	12
SG	1	4	0	5	4	5	0	1	0	0	10
MR	1	5	0	6	1	4	4	2	0	0	11
CH	1	4	0	5	1	4	4	2	0	0	11
Vestal	1	5	0	6	2	4	4	4	0	0	14



NO2 levels inside students homes



NO2 levels outside students homes

MAKING PALMES TUBES

Passive Nitrogen Dioxide Sampler: Preparation and Analysis

Created by Matthew Mavko, Portland State University

This page provides instructions for preparing and analyzing passive samplers for measuring gaseous nitrogen dioxide. This method was originally described by *Palmes, et al.* (1976). It is highly recommended you read through all of the instructions once before beginning, as there are many side notes.

Washing Components

It is essential that all of the parts of the diffusion tube are clean before construction. The stainless screens are best cleaned by soaking in phosphoric acid and distilled water, then rinsed at least three times. Caps and tubes ideally are washed in a sonic bath with distilled water and a detergent such as automatic dishwashing soap or Sparkleen. I have also had luck with generic dishwashing soap, but these have a tendency to leave behind residue and odors. If using a sonic bath, the parts should be left for at least one hour; otherwise, soaking in detergent for several hours will work. After either the bath or soaking, RINSE, RINSE., RINSE with distilled water. All components may be laid out on paper towels to air dry, and should be thoroughly dry before construction.

Constructing tubes

Components necessary for tube construction. See Shopping List at end of document for relevant catalog numbers and pricing.

Two (orange) polyethylene caps, 0.5" ID
Two Stainless steel mesh screens, 0.5" diameter
One acrylic tube: 0.5" OD; 3/8" ID
Triethanolamine (TEA)
Brij-35 (Wetting agent)
Distilled water
Scale
Cleaning detergent (see below)
Phosphoric acid
Clean glassware: 100ml graduated cylinder, 25ml and 200ml beakers
100-1000uL micro-pipettor
20-50uL micro-pipettor (optional)
clean paper towels

There are two methods for preparing the tubes which achieve satisfactory results, although one is preferred over the other. If you have access to micro-pipettors capable of 25-50uL, use the preferred method. Both are illustrated below. Before putting the tubes together, however, the TEA solution must be prepared.

- Weigh out 1 gram of Brij-35 on a scale. Place in a small beaker and add 9mL distilled water. Heat briefly on a hot-plate to dissolve the solution; the boiling point of Brij-35 is near 110 degrees F.

- In another beaker, combine distilled water and TEA in a 80:20 solution. That is, for 80ml of distilled water, add 20ml of TEA.
- To the 100ml total water/TEA solution, add 167uL (that's *micro*-liters) of Brij-35. Stir to mix thoroughly.

NOTE: it does not take much to prepare even a large number (e.g. 200) of tubes. If you want, you may cut down the total amount of solution by scaling appropriately. The limiting factor in the solution preparation will be how little Brij-35 solution you are accurately able to measure.

Preferred method

For one cap in each pair of caps you have, arrange open side up. Into each cap, place two stainless steel mesh screens, pushing them *all the way to the bottom* so they lay flat, one on top of the other. Into each cap that now has a pair of screens, use a micropipettor to put 25-50uL (again, *micro*-liters) onto the surface of the screens.
NOTE: the reason a range is given is that not all micro-pipettors have the same volume increments. I always put in 50uL, but any more than that can cause excess to run down the sides of the tube. Choose a volume in the range that will allow you to only have to put solution in each tube once.

Alternative method

If you do not have a micro-pipettor that will measure down to 50uL, use this method. Take a pair of stainless steel screens and sandwich them together. Using a pair of tweezers or needle-nose pliers, grip the screens together and dip into the TEA solution. Lightly dab off the screens on a clean cloth or paper towel and put into the bottom of a cap. Repeat for one cap in each pair of caps.

At this point, there are two options. One is to shove an acrylic tube into each cap that now has a screen, making sure the tube makes contact with the screens, and cap the open end of the tube. It is crucial here not to shove the closing cap on too hard or too far, as it can force excess TEA up into the crack between the outside of the acrylic tube and the inside of the cap with the screens. Placing the closing cap on about half way is good enough. Once all tubes are capped, put them in a sealable bag, label the outside with the date and method of preparation, and put them in cold storage (a normal refrigerator is fine) until ready to use.

Alternatively, if one has access to a clean-air source (i.e. air that is scrubbed clean of ozone, NOx, VOCs and other hydrocarbons, and water), an enclosed chamber can be rigged up to dry out the solution in the open caps before the tubes and closing caps are put on. This will ensure that no excess TEA will run down the inside or outside of the tubes, potentially skewing the analysis. After drying (about 24 hours is sufficient), finish construction as described in the previous paragraph.

Tube Deployment

The following are some general guidelines to consider when deploying tubes in the field.

The cap without the screen should be removed upon deployment. Tubes should be placed at

least 10cm (4 inches) away from any surfaces—a good way to achieve this is with wire. Placing tubes out in pairs or triplets may help increase the accuracy of your data and reduce anomalous results.
ALWAYS put out a few capped tubes with your measurement set as blanks as a check against contamination. They are also used in the calculation of NO_2.
Be creative: wire, duct tape, zip ties, and fishing line are your friends. Be sure to place the tubes out of reach and line of sight, 2.5 – 3 meters (8 – 10 feet) off the ground.

Analysis

Components necessary for analysis

- Exposed passive samplers
- Sulfanilimide
- Naphthylethylenediamine Dihydrochloride (NEDA)
- Phosphoric acid
- Sodium Nitrite (solid)
- Distilled water
- Scale
- Spectronic-20
- Cuvette that fits into Spectronic-20
- Five test tubes
- Nine 250ml Volumetric flasks; 500ml Erlenmeyer flask; 25ml graduated cylinder
- 20ml, 10ml, 5ml, 1ml glass pipettors
- 100-1000uL micro-pipettor
- clean paper towels

*****Turn on the Spectronic-20 and set the wavelength to 540nm. The instrument needs to warm up for one hour before use.*****

Preparation of Reagent Solution

Using the scale, weigh out 0.35 grams of NEDA; put into a 250ml volumetric flask and fill with distilled water to the line. Weigh 5.0 grams of sulfanilamide; put into a 250ml volumetric flask. Add to the sulfanilamide 15ml phosphoric acid; fill the flask to the line with distilled water. Note: combining water and phosphoric acid triggers an exothermic chemical reaction; do not be alarmed if the flask becomes warm. When filling each flask with distilled water, add about half the necessary amount and agitate the solution to encourage mixing. Do not fill to the line until the mixture has completely dissolved.

Once both mixtures are completely dissolved, pour the entire contents of the volumetric flask containing the sulfanilamide solution into the 500ml Erlenmeyer flask. Next, add 35.7ml of the NEDA solution to the 500mL flask. Mix well, and cover with a rubber stopper until ready to use.

Making a Calibration Curve

The method of analysis to determine the amount of NO_2 captured by the tubes involves measuring the absorbance of NEDA that has reacted with NO_2. To determine the mass of NO_2 relative to absorbance, a calibration curve must be done using known amounts of NO_2 in solution.

Weigh out 0.70g (0.01mol) of sodium nitrite and add to a 250mL volumetric flask. Fill with distilled water to the line, making sure the solution completely dissolves. Take 1ml of solution and add it to a second volumetric flask and fill with distilled water to the line. This second solution is the stock solution. From the stock solution add the following amounts into each of 5 volumetric flasks:

Solution #	ml of Stock	$[NO_2]$ mol/L	$[NO_2]$ diluted
1	20	1.28×10^{-5}	5.97×10^{-6}
2	15	9.60×10^{-6}	4.48×10^{-6}
3	8	5.12×10^{-6}	2.39×10^{-6}
4	3	1.92×10^{-6}	8.96×10^{-7}
5	1	6.40×10^{-7}	2.99×10^{-7}

After making your standard solutions, add 1.4 ml from each into its own test tube, and add 1.6 ml of sulfnilamide-NEDA solution to each test tube. Let sit 15 minutes. To find the absorbance for each standard solution, follow the steps outlined in the section, "Spectroscopic Analysis of Analyte".

Plot your obtained absorbance values versus $[NO_2]$ and apply a simple linear regression. A valid curve will have $r^2 \approx 0.999$ and an intercept near zero. You now have a way to convert absorbance to mass of NO_2. See "Calculation of $[NO_2]$ in Parts Per Billion" for more details.

(An example calibration absorbance curve is shown at the end of the document).

Preparation of Tubes for Analysis

Uncap the non-screen end of your exposed tubes and arrange open end up. Using your 100-100uL micro-pipettor (having more than one is helpful here), measure out 1.6ml of the combined sulfanilamide-NEDA solution into each tube AND into the cuvette. Next add 1.4ml distilled water to each tube for a total of 3ml of liquid in each tube AND into the cuvette. The solution will become pink. This coloring is the result of NEDA dye reacting with NO_2 captured by the tubes during exposure. The solution in the cuvette, however, is the blank and should be clear; if it is pink, your sample is contaminated. Let stand for 15 minutes.

Spectroscopic Analysis of Analyte

You will now measure the absorbance of each tube. First, the Spectronic-20 needs to be calibrated so we are only measuring the absorbance of the reacted NEDA. This is accomplished by placing the cuvette into the Spectronic-20 with the blank solution and turning the offset dial until the needle reads zero ON THE ABSORBANCE SCALE, NOT THE TRANSMITTANCE SCALE. If the cuvette has a label or marking near the top, always orient the cuvette the same way relative to the marking as the glass will have slight variations in absorbance depending on its orientation. If there is no marking, make one. Remove the cuvette, then empty, rinse, and dry the cuvette.

Now, pour the contents from a tube into the cuvette and measure the absorbance using the Spectronic-20, remembering to orient it the same way for each reading (and the same as the balnk reading at the beginning). Record both the absorbance and the tube number. Empty, rinse, and dry the cuvette after each absorbance reading.

Blank tubes should be analyzed in the same manner. The results of all blank absorbance readings may be combined into an average blank absorbance, *b*, to be used the calculation of NO_2.

Calculation of [NO_2] in Parts Per Billion

Equation 1 below is derived from Fick's law of diffusion. Several assumptions are made in the calculation of the diffusion rate:
-Constant with temperature
-Not affected by wind or other turbulent flow
-Density of air does not include water vapor, and is for an average temperature of 17°C.

For further discussion of the effects of environmental parameters on diffusion tubes, see *Heal, et al.* (2000) and *Kirby, et al.* (2001).

Definition of relevant variables:

A_b = Absorbance
b = Average blank absorbance
l = Length of tube [cm]
d = Volume of solution [3 mL]
M_w = Molecular weight of NO_2 [47 g mol^{-1}]
s = Slope of calibration curve [A L mol^{-1}]
r = Inner radius of tube [cm]
D_L = Diffusion coefficient, 0.154 cm^2 s^{-1}
t = Time of exposure [sec]
ρ_a = Density of dry air (@ 290 K) [1.21 kg m^{-3}]

$$[NO_2]\ (\text{ppb}) = [(A_b - b)\ l\ d\ M_w\ (10^9)] / [s\ \pi\ r^2\ D_L\ t\ \rho_a] \qquad (1)$$

Sources

Heal, M.R., C. Kirby, J.N. Cape, "Systematic biases in measurement of urban nitrogen dioxide using passive diffusion samplers." *Enivron. Monitoring and Assessment*, **62**: 39-54, 2000.

Kirby, Carolyn, Malcolm Fox, John Waterhouse, Tim Drye, "Influence of environmental parameters on the accuracy of nitrogen dioxide passive diffusion tubes for ambient measurement." *Journal of Environmental Monitoring*, **3**: 150-158, 2001.

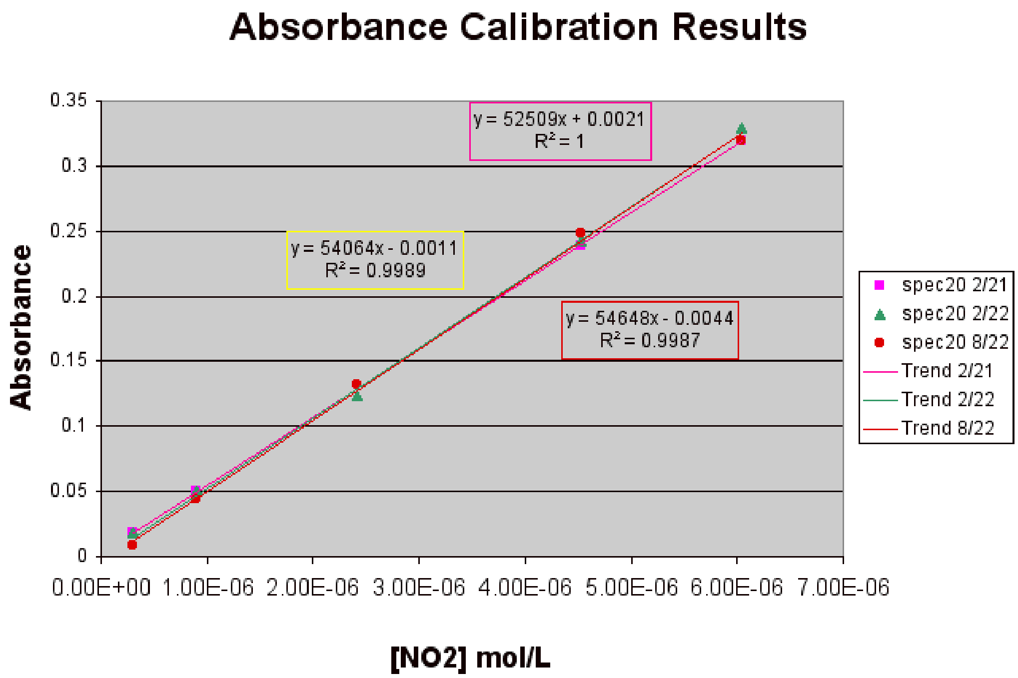
Palmes, E.D., A.F. Gunnison, J. DiMattio, and C. Tomczyk, "Personal sampler for the measurement of nitrogen dioxide." *Am. Ind. Hyg. Assoc. J.* **37**, 570-577, 1976.

Shopping List

Prices and catalogue numbers last checked on 21 November 2005.

Sigma-Aldrich		
T58300 – 1000g	Triethanolamine	31.30
P1254 – 500g	Brij-35	29.70
59251 – 100g	Sulfanilamide	20.80
510912 – 100g	Sodium Nitrite (s)	25.30
N9125 – 100g	N-1-Naphthylethylenediamine Dihydrochloride (NEDA)	145.50
P5811 – 500g	Phosphoric Acid 85% (aq)	28.85
Fisher Scientific		
S66800	20-50uL Pipettor	207.05
S66802	100-1000uL Pipettor	207.05
21-197-8G	2-200uL pipettor tips (1000)	50.16
21-278-52	101-1000uL pipettor tips (1000)	18.00

Calibration Curve


Absorbance Calibration Results
y = 52509x + 0.0021
R² = 1
y = 54064x - 0.0011
R² = 0.9989
y = 54648x - 0.0044
R² = 0.9987
Absorbance
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0.00E+00
1.00E-06
2.00E-06
3.00E-06
4.00E-06
5.00E-06
6.00E-06
7.00E-06
[NO2] mol/L
spec20 2/21
spec20 2/22
spec20 8/22
Trend 2/21
Trend 2/22
Trend 8/22