

AN APPRAISAL OF NO_x PASSIVE SAMPLING

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ABSTRACT

Associated with chronic and short-term health effects, the public health consequences of ambient air pollution are considerable. Accurate measurement of air pollutants is critical for assessing exposure to pollutants as well as an essential step in reducing public health impacts through implementation of regulations and emission controls. Passive sampling devices are often used for the regional-scale determination of pollutants when knowledge of hourly fluctuations in concentrations is unnecessary. Often advantageously described as cost-effective and simple to use, passive samplers are increasingly utilized as an alternative to conventional active sampling. However, the accuracy of these descriptions is challenged by the findings of the subsequent research. The overall objective of this research was to assess the ability of a well-known passive sampler to accurately measure concentrations of nitrogen oxides (NO_x) in the ambient environment. While the passive measurement of numerous pollutants is heavily studied, literature evaluating the use of passive sampling devices for the measurement of NO_x is exceedingly limited. NO_x is a generic term for a group of highly reactive gases composed of oxygen and nitrogen but most commonly NO_x is defined as the sum of nitric oxide (NO) and nitrogen dioxide (NO₂). The trapping of NO_x using filters coated with 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO) for quantitative analysis was investigated using various methods including ambient sampling, electronic absorption spectroscopy, mass spectrometry, and electron paramagnetic resonance. A first of its kind air sampling campaign in New Zealand measured ambient NO_x concentrations at multiple locations using Ogawa passive samplers. High spatial variability in pollutant concentrations was found across the sampling area but accuracy of the concentrations was questioned. At low ambient NO_x concentrations PTIO was found to contribute significantly to the analytical absorbance value. The fraction contributed by PTIO became increasingly difficult to quantitate as the contribution was not uniform across exposed filters. Degradation of PTIO during ambient exposure, evident by the loss of the filter color, was heavily dependent on the sampling environment. Intra- and inter-season variations in the magnitude of degradation are reported. Common limitations of various types of passive samplers are presented as well as challenges currently unaddressed in the literature.

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PREFACE

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DEDICATION

I would like to extend my sincerest thanks and appreciation to everyone who supported me this past year, even during the toughest of times. I dedicate this work to you....

DEFINITIONS & ABBREVIATIONS

Definitions:

An “**unexposed**” filter refers to a filter which was not directly exposed to ambient conditions; this filter was never outdoors.

An “**unmodified**” filter is a purple NO_x filter used for analysis which was not subjected to degradation.

A “**white**” NO_x filter is a NO_x filter which lost the purple PTIO color due to degradation.

Abbreviations:

CO	Carbon monoxide
e ⁻	Electron
EPA	Environmental Protection Agency
EPR	Electron paramagnetic resonance
ESI-MS	Electrospray ionization mass spectrometry
FEM	Federal Equivalent Method
FRM	Federal Reference Method
GIS	Geographic Information Systems
HC	Hydrocarbons
HD	Heavy-duty
HNO ₂	Nitrous acid
H ⁺	Hydrogen ion
IC	Ion chromatography
ISA	Integrated science assessments
LD	Light-duty
LOD	Limit of detection
MoO _x	Molybdenum oxide
m/z	Mass charge
NAAQS	National Ambient Air Quality Standards
NaNO ₂	Sodium nitrite

NEDA	N-(1-Naphthyl)ethylenediamine dihydrochloride
NIWA	National Institute of Water and Atmospheric Research
NO	Nitric oxide
NO [•]	Nitric oxide radical
NO ₂	Nitrogen dioxide
NO ₂ [•]	Nitrogen dioxide radical
NO ₂ ⁻	Nitrite
NO ₃ ⁻	Nitrate
NO _x	Nitrogen oxides
O ₃	Ozone
[•] HO	Hydroxyl radical
PAN	Peroxyacetyl nitrate
PM	Particulate matter
ppm	Parts per million
ppb	Parts per billion
H [⊕]	Proton
PSDs	Passive sampling devices
PTI	2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl
PTIO	2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide
RO ₂ [•]	Peroxy radical
SO ₂	Sulfur dioxide
TEA	Triethanolamine
WoF	Warrant of fitness
VOCs	Volatile organic compounds

1.0 INTRODUCTION – NITROGEN OXIDES (NO_x)

The overall objective of this research was to assess the ability of a well-known passive sampler to accurately measure concentrations of nitrogen oxides (NO_x) in the ambient environment. This chapter presents background information on nitrogen oxides. Chapter 2 introduces all sampling and analytical methods used for the research discussed in Chapters 3 and 4. The results of an air sampling campaign in New Zealand are presented in Chapter 3, which introduces the issues associated with the collection of NO_x using Ogawa passive samplers. The issues, including the interference and degradation of the NO_x filter coating, are discussed in Chapter 4. Finally, Chapter 5 describes passive sampling in detail, along with a discussion of several environmental factors which affect the collection of passive samplers.

The World Health Organization (WHO) reports air pollution has become “the world’s single biggest environmental health risk,” linking pollution to approximately 7 million deaths in 2012 [1]. Ambient air quality depends on (1) the amount of pollution released into the air by human and natural activities (2) the amount of dispersal due to wind and weather conditions and (3) the extent of reactions occurring between pollutants [2]. Although great progress has been made at the local, state, and national levels to control emissions from various sources of air pollution, pollutant levels remain high in many areas throughout the world [3]. One such group of pollutants is oxides of nitrogen, or NO_x. The National Ambient Air Quality Standards (NAAQS) legislation promulgated by the Environmental Protection Agency (EPA) defines NO_x as all forms of oxidized nitrogen compounds, including nitrogen oxide (NO), nitrogen dioxide (NO₂), and all other oxidized nitrogen-containing compounds formed from NO and NO₂. However, within the air pollution research and control communities, NO_x is usually referred to as the sum of its generally major components NO and NO₂ ($NO_x = NO + NO_2$) – this definition being used throughout, unless stated to the contrary. NO_x is emitted through combustion reactions as mainly NO with smaller quantities of NO₂ [4]. NO is considered a primary pollutant as it is emitted directly from a source. NO₂ is classified as a secondary pollutant as this gas is most often formed through chemical reactions occurring in the atmosphere. Emissions of NO_x along with volatile organic compounds (VOCs) can lead to complex reactions resulting in the formation of additional pollutants including ground-level ozone (O₃) [5-7] and particulate matter (PM) [8-10].

NO and NO₂ are frequently used interchangeably and referred to as “NO_x” because they are often emitted together and can quickly interconvert [4]. However, in the ambient environment, from a health standpoint, NO₂ is of most interest as it is known to be directly toxic to the respiratory tract and its acute pulmonary toxicity is thought to be several times greater than NO [11]. Up until 1987 when NO was first identified as a vasodilator of blood vessels [12], it was only considered a toxic gas which led to the formation of photochemical smog, depletion of the O₃ layer, and aided in the formation of acid rain [13]. Today NO is known as a “gasotransmitter” [14] due to its role as an important messenger molecule involved in several pathological and physiological processes within the mammalian body including humans [13]. The roles of NO in the body are numerous including involvement in cardiovascular, nervous and immune systems [15]. Exhaled NO is the most common noninvasive biomarker used to evaluate airway inflammation in asthmatics [16, 17]; however, NO also is reported to exhibit inhibitory effects within the body. Respiration could be regulated by local production of NO which can inhibit the oxygen affinity of cytochrome c oxidase, the enzyme responsible for 90% of oxygen consumption in mammals [18]. Increases in NO can prevent the enzyme from using available oxygen leading to a deficiency in the amount of oxygen reaching body tissues [19]. Similar to carbon monoxide (CO), excess NO in the blood binds to hemoglobin and reduces oxygen transport efficiency. However, atmospheric amounts of NO are typically lower than CO concentrations so the effect of atmospheric NO on hemoglobin is much less [20].

NO₂ is the NO_x component of focus in EPA regulatory networks and in most large-scale NO_x monitoring networks world-wide. However, the importance of accurately measuring its precursor NO should not be overlooked. NO, identified as a primary pollutant, is an odorless gas and a major by-product of combustion processes. NO is formed from the oxidation of nitrogen in air during combustion and from organically bound nitrogen found in certain fuels [21]. The oxidation of nitrogen during combustion primarily occurs through a temperature dependent set of reactions involving nitrogen and oxygen known as the Zeldovich mechanism [21, 22]. Depending on atmospheric conditions, significant amounts of NO₂ can arise from the conversion of NO into NO₂ [21].

NO plays a vital role in the formation of secondary pollutants, including NO₂, which are associated with adverse health effects [23-25]. Although NO is the primary form of NO_x released into the atmosphere, NO can rapidly react to form additional pollutants [20]. While NO in the atmosphere can be oxidized by O₂ to produce NO₂, this reaction is of minor importance in most atmospheric conditions as it is generally too slow to be of importance [21, 26]. The most important route of NO₂ formation in the atmosphere is through oxidation of NO by atmospheric oxidants such as O₃ [27] and the sole known anthropogenic source of tropospheric O₃ is through the photolysis of NO₂ [5]. The inextricable link

between NO, NO₂, and O₃ creates the need to understand the levels of all three atmospheric pollutants especially prior to implementing or assessing the effectiveness of control strategies [28].

The measurement of NO is important for the active (pump) collection of NO₂ and for the measurement of total NO_x using passive (no pump) samplers. For active sampling, NO₂ is most often indirectly measured through the chemical trapping of NO and the concentration of NO₂ determined by the difference in amounts of NO_x and NO alone, i.e., $NO_2 = (NO + NO_2) - NO$ [4]. The collection of NO using passive samplers (no pump) is additionally important for the determination of time-weighted average concentrations of not only NO itself but also total NO_x across space [29]. Generally, for passive sampling, the NO_x sampler collects both NO and NO₂ alongside a sampler collecting only NO₂. The difference between the NO_x and NO₂ collected weights is taken as the amount of NO collected, i.e., Total NO collected = Total NO_x collected – Total NO₂ collected. EPA's units of measure for gas concentrations are given in parts-per notation, specifically parts per million (ppm) or parts per billion (ppb) based upon volume. For gases, 1 ppm equates to one volume of gaseous contaminant per one million volumes of air. Gaseous parts-per notation do not equal the concentration of an air pollutant given by European standards (µg/m³). Conversions are based on the molecular weight of the gaseous pollutant and assumptions of ambient pressure and temperature [30].

1.1 HEALTH EFFECTS OF NO_x

While statistical associations have been reported between levels of individual or combined exposure to secondary pollutants and health outcomes, such as airway inflammation [31], wheezing [32], and medically-diagnosed asthma [24], limited studies focus on associations between NO_x or NO and adverse health effects [33, 34]. The toxicology of NO is not completely understood as the pharmacological properties of NO are not easily separated from its toxicological effects. Weinberger *et al.* recognizes the important role NO plays in the regulation of physiological processes but also the possibility of toxicological effects of this highly reactive gas [34]. Few NO inhalation health outcomes are reported. Reported toxicological effects include increased methemoglobin levels [35] and DNA strand breakage induced synergistically in the presence of an NO-releasing compound and cigarette tar [36].

While the health effects of atmospheric NO may not have been comprehensively studied and/or are less harmful, effects of exposure to pollutants produced through reactions involving NO (i.e. NO₂ and

O₃) are extensive, these pollutants are being regulated by EPA. EPA's Integrated Science Assessments (ISA) [4] for NO_x provides a review and assessment of the health effects associated with NO₂. The ISA concluded that recent scientific evidence is adequate to infer a causal relationship between short-term NO₂ exposure and adverse respiratory effects. Short-term NO₂ exposures, ranging from 30 minutes to 24 hours, have been linked to adverse respiratory effects including airway inflammation in healthy individuals, increased asthma symptoms, more difficulty controlling asthma, and an increase in respiratory illnesses and symptoms in asthmatics [4].

Significant associations were found in children between short term ambient NO₂ exposures and cough incidence [37, 38], reduced lung function [39], and increased asthma symptoms [40-42]. Connections between short-term NO₂ exposure and increased visits to emergency departments and hospital admissions have also been found. Positive associations were found between ambient NO₂ levels and emergency department visits for all respiratory outcomes (asthma, bronchitis, emphysema, pneumonia, upper and lower respiratory infections) [43, 44] and emergency department visits for asthma [45, 46]. Stronger and more consistent associations were seen in emergency department visits in children (<14 years) and the elderly (>65 years) when all respiratory outcomes were analyzed together [4]. Clinical studies reveal increases in allergic responsiveness in the lungs of asthmatics challenged to allergens following NO₂ exposure [47-49]. Asthma affects more than 22 million people in the U.S., including 6 million children. With over 500,000 people hospitalized for asthma each year, a small clinical result can have large public health implications [50]. Other studies have found associations between NO₂ and non-accidental mortality [51, 52] and ischemic stroke [53, 54].

Certain subgroups of the general population are more likely to suffer from adverse health effects associated with NO₂. An increase in risk can occur for a number of reasons. An individual may be affected by lower levels of NO₂ or experience a larger health impact to a given level of exposure as compared to the general population (susceptibility). An individual may also be exposed to a higher concentration of NO₂ than the general public (vulnerability) [55]. Susceptibility refers to innate (i.e. genetic) or acquired factors (i.e. disease) which results in subgroups within the population who are more likely to experience NO₂ related health effects. Vulnerability refers to an increase in risk due to increased exposure as compared to the general population. NO₂ susceptibility factors include age (<18 years and >65 years), preexisting disease (e.g. diabetes), respiratory diseases (e.g., COPD, asthma), adverse birth outcomes (e.g., low birth weight, preterm birth), obesity, and other diseases. NO₂ vulnerability factors include socioeconomic status, geographic location, and proximity to roadways [4].

1.2 PROTECTION AGAINST EXPOSURE TO NO_x

In 1970, the EPA passed the Clean Air Act, giving the federal government power to clean up air pollution. The Clean Air Act requires EPA to set National Ambient Air Quality Standards (NAAQS) for six common air pollutants: ground-level ozone, carbon monoxide, nitrogen oxides, sulfur oxides, and lead. Primary standards serve to protect human health while secondary standards are intended to prevent environmental and property damage [56]. An NO₂ annual mean value of 53 ppb (primary and secondary standard) has been retained without revision since the standard's enactment in 1971. In 2010, EPA passed a 1-hour primary NO₂ standard to complement the existing annual standard. Measured concentrations are averaged over 1-hour increments and are not to exceed 100 ppb. The two NO₂ standards are designed, together, to protect public health. A 1-hour standard allows protection by regulating exposure to short-term peak concentrations of NO₂ predominantly occurring near major roads. In addition, an annual standard limits exposure to community-wide NO₂ concentrations to below levels that have previously been associated with adverse health effects. To determine compliance with the new standard, EPA also ruled for the establishment of an NO₂ monitoring network in areas where the highest NO₂ concentrations are expected to occur, including within 50 meters of major roadways. Monitor placement aims to capture variability in NO₂ concentrations across communities as well as concentrations within communities that are predisposed and vulnerable to NO₂-linked health effects [57].

1.3 AMBIENT SOURCES OF NO_x

Both anthropogenic (man-made) and biogenic (natural) sources emit NO₂. Nationally, 87% of NO_x is anthropogenically emitted [4]. The top 3 categories of NO_x emissions are on on-road mobile sources, electricity generating units, and non-road mobile sources. Mobile sources (on and off road) account for approximately 60% of total anthropogenic NO_x emissions while stationary sources (e.g., electrical utilities, industry) account for the remainder (2002 average US emissions). Natural sources of NO_x include microbial activity in soils, lightning, and wildfires. The breakdown of NO_x sources represents United States averages and does not necessarily reflect contributions of sources at all measured locations [4].

1.4 VEHICULAR SOURCES

1.4.1 The combustion process – NO_x formation in engines

The formation of NO_x has previously been reported in detail [58-60] with three formation processes (e.g., thermal, prompt, fuel) believed to be important [61]. The type of formation depends on the engine and fuel type. Atmospheric (molecular) nitrogen is the main source of nitrogen for NO formation during combustion of typical petroleum- and bio-based fuels [60]. Thermal NO_x formation is thought to be the primary formation type of total NO_x in diesel engines [58, 60, 62, 63] while contributions of non-thermal mechanisms (i.e. prompt and fuel formation) are generally reported to be less significant NO_x contributors [60]. Thermal NO_x is formed through a temperature dependent mechanism, termed the Zeldovich mechanism [22], in which molecular nitrogen and molecular oxygen react at high temperatures (i.e. inside of a diesel engine) [63] on a timescale comparable to the combustion duration in a diesel engine [64]. Any increase in the residence time of the in-cylinder mixture or an increase in the in-cylinder temperature could ultimately result in increased NO_x formation [61]. Thermal NO_x formation occurs at temperatures above 1500 °C with formation increasing as temperature increases [61].

Prompt NO_x formation occurs through a complex pathway where hydrocarbons (e.g., CH, CH₂) react with nitrogen to form species that ultimately react with oxygen to form NO_x [63]. Although previous studies report prompt NO_x formation is negligible during combustion of petrodiesel [58, 65] changes in fuel chemistry or combustion conditions can alter the impacts of NO_x mechanisms of formation [65]. Unlike thermal NO_x formation, prompt formation is sensitive to fuel chemistry as this formation type relies on availability of hydrocarbon fragments. Under fuel rich conditions (i.e. during combustion more fuel is present relative to air resulting in incomplete fuel burning) hydrocarbon species are abundantly available [61]. The third mechanism of NO_x formation, fuel NO_x, involves the reaction of nitrogen-containing fuel species with excess oxygen during combustion. Since usual levels of nitrogen in fuel are extremely low this formation is of most concern when nitrogen-containing fuel additives (e.g., detergents, dispersants) are present in high concentrations [61].

1.4.2 Emissions of NO_x from vehicles

The majority of vehicles operate through the burning of fuel in the vehicle engine. Evaporation of the fuel itself or by-products from the burning (combustion) process (emitted as exhaust from the tail pipe) pollutes the air [66]. During ideal engine combustion, oxygen in the air would convert all hydrogen atoms in the fuel to water and all carbon atoms in the fuel to carbon dioxide leaving atmospheric nitrogen unaffected. In reality, the engine combustion process is not perfect and ultimately leads to the release of pollutants in vehicle exhaust, including NO_x [67]. The estimation of the rate at which a pollutant (in terms of its mass) is released into the atmosphere divided by the level of activity from the emission source is defined as an emission factor [68]. Variables affecting emission factors include vehicle model, age, condition, fuel type, ambient weather conditions, and how the vehicle is driven [69]. Motor vehicles vary in size and fuel type, from light-duty (LD) vehicles, which in the United States are mostly fueled by gasoline, to mostly diesel-powered heavy-duty (HD) vehicles [62].

Currently the majority of vehicles worldwide are fueled by petrol (gasoline) or diesel but more than a dozen alternative fuels (e.g., biodiesel, natural gas, electricity, ethanol) are in production or under development in an effort to reduce vehicle emissions [70]. Petrol and diesel are petroleum-derived liquid mixtures used as fuels. Although both derived from the same base product petrol and diesel fuel each have different properties and usage. Petroleum diesel, also called petrodiesel, is the conventional type of diesel fuel [63]. Biodiesel, an attractive substitute to conventional diesel, is prepared from renewable vegetable oils or animal fats. Positive attributes of biodiesel are considerable, including production from a renewable and domestic feedstock, reduced dependency on foreign petroleum, higher flash point, superior biodegradability, and reduction in most exhaust emissions [63]. However, while biodiesel reduces emissions of PM, CO, and hydrocarbons (HC), NO_x emissions are not reduced [71]. Biodiesel has in fact been reported to increase NO_x emissions more than 10% on average [72-77].

Diesel and gasoline engines are both designed to convert chemical energy into mechanical energy by converting fuel into energy through a series of small explosions or combustions [78]. The manner in which these combustions occur is different in diesel and gasoline engines. In a gasoline engine, fuel is first mixed with air, compressed by pistons and ignited by sparks from spark plugs. On the contrary, in a diesel engine the air is introduced and compressed before the fuel is introduced. The compression of the air causes high heat so once injected the fuel ignites [78]. The extreme temperatures in the combustion chamber help reduce the amount of soot produced by diesel engines but ultimately produce higher levels of NO than gasoline engines [79].

Generally diesel vehicles (compared to gasoline vehicles of similar size and age) will have lower HC and CO but higher emissions of PM and NO_x [69]. Comparatively, diesel engines have been reported to emit over 20 times more NO_x than gasoline engines [80]. Importance of HD diesel truck exhaust as a source of NO_x has gained increased attention as LD vehicle emission standards have become stricter and growth of on-road diesel fuel use surpassed gasoline growth [81]. The ratio of the HD to LD emission factor for NO_x was found to increase from 6±1 to 13±1 between 1997 and 2006 [62]. In diesel exhaust NO is the predominate component of total NO_x [61] but the NO₂/NO_x emission ratio varies among engine types, fuel type, emission mitigation controls, cruising speeds, and accelerations [82-85].

Quantifying emissions from mobile (and other sources) is an important piece of air quality control and management. Particularly important is the quantification of emissions in urban areas where thousands of traffic-related emissions combine, creating one of the greatest, if not the greatest, source of gaseous pollutants [86]. Vehicle emission rates are affected by various factors. Kumares *et al.* classified these factors into the following groups: *travel-related* (e.g., engine operating mode, speed, speed variation), *driver-related* (e.g., severe stops or accelerations), *highway-related* (e.g., presence of ramps or traffic signals), *vehicle-related* (e.g., weight and size, age, mileage, emission control system), *fuel type* (e.g., volatility, contents) and *environmental* (e.g., ambient temperature, humidity, altitude) [87].

Prior to emission regulations, gases from engine combustion were emitted directly into the atmosphere. Since the enactment of the Clean Air Act of 1970, EPA's vehicular emission controls have become increasingly stringent. Today EPA has developed emission standards for almost every kind of engine, from lawnmowers to cruise ships. Engine manufacturers decide themselves how to meet the pollution limits but must follow test procedures specified in the *Code of Federal Regulations* to ensure EPA standards are met [66]. Although engines are initially manufactured to meet emission standards, poorly maintained vehicles or those with malfunctioning controls may release emissions that exceed the standards. State-operated emission inspections are designed to certify a vehicle's emission controls and engine are functioning properly, ensuring standards continue to be met on aging vehicles. The 1990 amendments to the Clean Air Act mandated inspections for specific areas across the country, selecting areas based upon certain criteria, including air quality classification, population, and/or geographic location [88].

1.4.3 Mitigation of vehicle emissions

Engineering strategies to mitigate vehicle emissions include engine modifications, exhaust control technologies, and fuel reformulations. Engine modifications aim to change the combustion process in order to reduce emissions. However, these modifications may result in reduced emissions of a particular pollutant but an increase in others (i.e. lowering the maximum temperature using exhaust gas recirculation valves will reduce NO_x emissions but increase particulate emissions). Examples of additional engine modifications include controlling air-fuel ratios and injection times through the use of fuel injection systems [89].

Catalytic converters are used as an exhaust control technology for the chemical conversion of automotive pollutants. The converter receives all the engine's exhaust gases and a catalyst (causes a chemical reaction without itself being affected) converts pollutants into less harmful emissions before leaving the vehicle's exhaust system. In the case of NO_x, a reduction catalyst is utilized to reduce NO_x to N₂. Various types of reduction catalysts exist (e.g., platinum, rhodium, palladium) as well as various converters. Three-way converters can eliminate all three engine pollutants simultaneously (e.g., HC, CO, NO_x) while dual-bed converters initially convert most of the NO_x present followed by HC and CO removal [90].

Changes in fuel include the reduction of sulfur found in gasoline and diesel. Sulfur impairs the emission control systems, contributing to exhaust emissions. Alternate fuel sources, such as natural gas, propane, alcohol, or electricity offers clean-burning, domestically-produced alternatives to petroleum [91]. Other fuel reformulations include increasing the combustion speed (cetane number) of diesel engines or the addition of fuel additives which reduce combustion temperatures or enhance combustion to reduce exhaust emissions [89].

1.4.4 The NO₂/NO_x ratio

While measuring emissions of total NO_x is important the proportion emitted as NO₂ is possibly more important; especially along roadways close to the source where concentrations are at times reported to exceed standard limits. Continuing concerns over instances of exceeding NO₂ regulatory standards supports the need to maintain an understanding of the trends and sources of NO₂. Recently the possibility of an increase in primary vehicular NO₂ has raised interest as a decreasing trend in NO_x concentrations is

either not accompanied by a similar trend in NO₂ [92] or the reduction rate of NO₂ is slower than that observed in total NO_x [93]. A slower decreasing trend in NO₂ suggests a new source may be contributing to the production of NO₂.

Legislation across the world has progressively reduced the permissible level of pollutants a vehicle can emit. Reduction for some pollutants has been achieved through the implementation of certain emission reduction technology (e.g., diesel oxidation catalyst, diesel particulate filter). However, studies show the use of these types of exhaust after-treatment systems, on diesel vehicles in particular, has increased the proportion of NO₂ directly released through NO_x exhaust emissions [84, 85, 92, 94-98]. These increases are partly due to technology designed to increase the oxidation of NO to NO₂ in order to ultimately reduce emissions of particulate matter [99].

NO_x emission ratios have been found to vary among engine types, exhaust treatment systems, cruising speeds, accelerations, manufacturer, and emission standard manufactured under [83-85, 97]. However, it's generally agreed upon the proportion of NO₂ emitted relative to total NO_x is lowest in petrol-fuelled vehicles (5%) [83, 96, 97], the only vehicle type to have shown a considerable reduction in total NO_x emissions with the introduction of emission control technology (i.e. catalytic convertor) [97]. Diesel vehicles are known to emit more total NO_x with a larger proportion of "primary" NO₂ as compared to petrol vehicles [100]. With increased emission standards the NO₂/NO_x ratio has been reported to increase from 10-15% (pre-Euro 3 (2000)) to between 25 and 30% ((Euro 4 (2005) and Euro 5 (2005, 2008/9)) for diesel passenger cars (n=13,463 vehicles tested) [97]. By time the Euro 5 standard was introduced, emission control technology in diesel vehicles included both diesel oxidation catalysts and diesel particulate filters both of which have been reported to increase primary NO₂ emissions [92, 98, 101]. Vehicles with larger engines (>2.0 L) tended to be associated with higher NO₂/NO_x ratios (+16%) than vehicles with engines <2.0 L [97].

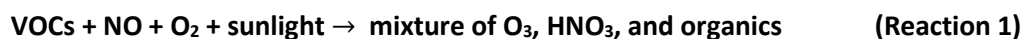
Buses are reported to have wide range of reported NO₂/NO_x ratios, which strongly depend on manufacturer and exhaust control technologies. Higher ratios (mean = 15-20%) were reported for buses fitted with diesel particulate filters (DPF) where NO₂ is deliberately formed to aid in removal of particle emissions. Buses fitted with the most promising technology to comply with Euro IV and V emission standards, selective catalytic reduction, exhibited increasing NO₂/NO_x ratios with the largest proportion of primary NO₂ (mean = 32.9%) reported for buses under the highest Euro class tested (enhanced environmentally friendly vehicle) [97].

1.5 PHOTOCHEMICAL REACTIONS AND THE PRODUCTION OF OZONE

Today in major urban areas air pollution is often characterized by the formation of photochemical oxidants such as O₃ [26]. Tropospheric O₃, produced through reactions involving NO_x and VOCs, is one of the most harmful components of the photochemical air pollution mixture [102]. Exposure to O₃ is widespread and growing in the United States with numerous studies associating this pollutant to various adverse health effects [5, 103, 104]. Short-term O₃ exposures have been linked to adverse health effects similar to those of NO₂ exposures, including increased hospital admissions and emergency room visits, increase in the severity of chronic respiratory conditions (e.g. asthma), decreased lung function [105-109], increased airway reactivity, increased respiratory symptoms [110, 111] and short-term mortality [103, 104].

Several studies have shown associations between O₃ concentrations and daily mortality for both respiratory and cardiovascular causes, identifying elderly subjects [112-116], asthmatic children [117] and women [104] as having higher risks. Exposures to high concentrations of O₃ have been linked to lung irritation and exacerbation of bronchitis, emphysema and asthma [106, 118]. Individuals with preexisting conditions (e.g., asthma, chronic obstructive pulmonary disease, diabetes, atrial fibrillation) have shown a heightened susceptibility to adverse health outcomes due to O₃ exposure [104, 110, 111, 116].

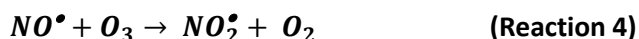
Ozone is found in photochemical smog which forms through hundreds of different reactions, involving dozens of chemicals, occurring concurrently [119]. Photochemical smog has been linked to modern industrialization, and is most commonly found in cities with sunny, dry, and warm climates together with a large number of vehicles [120]. The principal reactants of photochemical smog are nitric oxide (NO) and volatile organic compounds (VOCs), both often referred to as “ozone precursors.” The final products of the smog reaction – ozone, nitric acid (HNO₃) and partially oxidized organic compounds – are more toxic than the reactants (**Reaction 1**) [119].



The generation of photochemical smog relies on the emissions of NO and VOCs from vehicular traffic, or power plants, as well as emissions from trees in the case of VOCs. Sufficient sunlight must also be present for photochemical reactions to occur. Little movement of air ensures reactants are not much diluted [119]. As a secondary pollutant, O₃ levels can be difficult to predict and control. Ozone precursors, released from a variety of sources, can exhibit a non-linear effect on its production [121]; levels can be

heavily influenced by meteorological processes such as long-range transport of O₃ to neighboring areas [122, 123].

During the daytime in the troposphere (lowest layer of earth's atmosphere), interconversion of NO and NO₂ occurs with O₃ on the scale of minutes according to **Reactions 2-4** [121]. A radical symbol (*) indicates the compound has an unpaired electron.



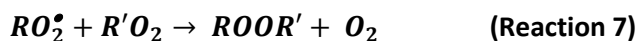
(Where *M* is any non-reactive species that can remove excess energy)

Due to reaction (**Reaction 4**) significant concentrations of NO and O₃ cannot coexist. Levels of O₃ begin to rise in the afternoon hours as NO levels decrease [26]. During this cycle no production or loss of NO_x or O₃ is seen. For O₃ production, an additional pathway is needed to convert NO to NO₂ without the destruction of O₃. Net production of O₃ occurs through the reaction of VOCs and hydroxyl radicals (HO*) to form peroxy radicals (RO₂*). Peroxy radicals react with NO to form NO₂; ultimately O₃ is produced without loss of O₃ occurring throughout the process [121].

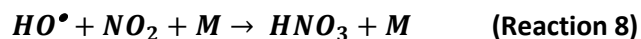


(Where *R* can be hydrogen or any organic group)

The production rate of O₃ is limited by the relative proportions of NO_x and VOCs and varies by time and space. At low concentrations of NO_x, peroxy radicals produced through reactions with VOCs and available for reaction with NO are lost to the following process [121]:



Under these conditions O₃ production becomes independent of VOC concentrations, increasing linearly with increasing NO_x. Conversely, under high concentrations of NO_x, NO₂ competes with VOCs for the reaction with HO* by the following process [121]:



This process removes HO^{\bullet} and as a result minimizes the production of RO_2^{\bullet} via reaction (**Reaction 5**). Under these conditions, O_3 production is inversely proportional to NO_x concentration and more sensitive to VOC levels [121]. Although the formation of NO_2 from NO is understood in theory, determining the amount of NO converted to NO_2 is difficult under atmospheric conditions [124, 125]. The reaction rate of **Reaction 4** assumes NO and O_3 are immediately brought into contact with each other and fully mixed; this may be untrue especially close to a source where mixing may be incomplete. Plumes do not instantaneously mix under normal atmospheric conditions and the efficiency at which they do is dependent on thermal and mechanical atmospheric turbulence down to microscales [124]. Hegg *et al.* reported the oxidation of NO by O_3 is controlled by the rate of plume mixing not gas reaction kinetics [126]. The reaction rate may not hold true for air masses close to the source where mixing rates of the pollutants differ depending on several factors (e.g., location, meteorology, pollutant availability) [124]. Various chemical models exist to aid in prediction of the amount of NO_2 produced through NO - O_3 reactions [125].

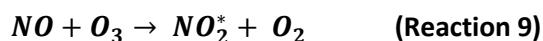
1.6 MONITORING METHODS FOR NO_x

Ambient air monitoring can be divided into two types of sampling systems: active and passive. The conventional method, active monitoring, involves the use of an air sampling pump to draw air through a collection device such as a filter [127]. Active monitors are typically utilized in state and local monitoring surveillance systems where continuously measured short term concentrations are desired, usually to meet environmental regulatory compliance activities [128]. Increasing in use, passive samplers require no electricity, operating on the principle of diffusion. Passive samplers are reported to be inexpensive, easy to use, and unobtrusive [129]. Small in size and lightweight, the use of passive samplers is especially beneficial in regional scale studies where a large number of monitoring locations is desirable. However, passive samplers are not ideal for capturing small exposure periods as these types of samplers provide integrated, not-short term measurements [128].

1.6.1 Active monitoring

NO₂ is the primary component of interest for the EPA regulatory networks as well as most world-wide, large-scale monitoring networks [130]. The mixture of certain air pollutants (e.g., NO₂, NO) with a second reactant (e.g. O₃) is known to produce chemiluminescent reactions, or reactions that produce light emissions without heat. Simplistically, a continuous flow of ambient air mixed with an excess of a second reactant can be used to continuously measure pollutant concentrations [131]. In December 1976, a reference method for the measurement of NO₂, based on chemiluminescent reactions, became a Federal regulation. Today most air quality monitoring agencies use the Federal Reference Method (FRM) gas-phase chemiluminescence (40 CFR Part 50, Appendix F) or Federal Equivalent Method (FEM) for the monitoring of NO₂. Unlike passive samplers, continuous monitors constantly monitor air quality with real time analysis. NO₂ is not measured directly but from the subtraction of the measurement of total NO+NO₂ and NO alone (NO₂ = NO+NO₂ – NO). In 2010, the Environmental Protection Agency ruled any FRM or FEM used for making NAAQS decision-making must have the ability to provide hourly averaged concentration data [132].

Ambient concentrations of NO₂ are measured indirectly by photometrically measuring light emissions generated from the chemiluminescent reaction between NO and O₃ (λ > 600 nm) [131, 133]. Any NO mixed with O₃ results in chemiluminescence characterized by the following reactions:



The amount of light generated by the electronically excited NO₂ returning to its ground state is proportional to the reactant concentration of NO in the sample [134].

For the analysis, an ambient stream of air is pulled directly into the analyzer and a portion is passed through (most frequently) the surface of a molybdenum oxide (MoO_x) substrate, heated between 300 and 400°C to initiate a converter. The converter quantitatively reduces NO₂ in the stream to NO [135, 136]. Any NO in the stream of air is also passed through the converter, unchanged. From the converter, the total NO stream (i.e., the reduced NO₂ + the unchanged NO) is mixed with O₃ and the light emission measured. The resulting measurement is total NO_x concentration equal to NO + NO₂. The remaining portion of the input air, not originally run through the converter, is mixed with O₃ resulting in an NO

concentration. This latter NO measurement is subtracted from the former measurement (NO + NO₂) to yield the final NO₂ concentration [137].

In 2012, the EPA reported their decision to maintain the chemiluminescence FRM following public comments from (Alliance of Automobile Manufacturers, Edison Electric, and the National Petrochemical and Refiners Association) regarding concerns surrounding known interferences relating to NO₂ reduction converters in chemiluminescence analyzers. Specifically the concern addressed the non-specificity to NO₂ of the MoO_x substrate in chemiluminescence FRM. Species of oxides of nitrogen present in ambient air, including nitrous acid, nitric acid, and peroxyacetyl nitrates, are subject to reduction by the converter. Reduction of these species results in “positive artifacts” in the final NO₂ concentrations which results in an over-estimation of the measured NO₂ concentration in ambient air [138].

Larger interferences are more likely to occur during summer afternoons when photochemical activity is greatest with interferences possibly comprising up to 70% of the reported concentrations. Less than 10% of the reported concentration is attributed to interferences during the day in winter months [130, 132]. Urban source areas are subject to less interference than sites further removed from source locations. Quantifying the interferences of NO_x species in the measurement of gas-phase luminescence of NO₂ is quite challenging as the measurement of the interfering species is sparse; the concentration of these species in the sampled air is most likely unknown and variable [130]. Therefore, ever changing, positive artifacts may hinder the accurate measurement of NO₂ concentrations using the chemiluminescence FRM especially in areas where low NO₂ concentrations are accompanied by high concentrations of interfering compounds [130, 134].

1.6.2 Passive monitoring – the Ogawa sampler

Although a variety of passive samplers exist for the collection of NO₂, a limited number of these samplers have the capability of measuring total NO_x (= NO₂ + NO) or NO. One option for the measurement of NO_x is the Ogawa passive sampler, one of the most widely used passive samplers in the U.S. The Ogawa sampler is one of the few methods of simultaneous passive determination of NO and NO₂ in the air; although, details regarding the application of or specifics (i.e., ratios, application) of the absorbing reagents are not readily publicly available. The Ogawa technology was developed by Hirano in Yokohama, Japan, but the complete method has not been published [139]. This sampler is used for the determination of O₃, NO_x, SO₂, and NH₃ in a variety of monitoring settings including personal, indoor and outdoor [140]. This sampler (**Figure 1**) is composed of a cylindrical (2 X 3 cm) plastic body with an air inlet on each end.

A pretreated filter (collection pad) (14.5 mm in diameter) is placed between two screens and covered by an end cap on each end of the sampler body.







Figure 1. Ogawa sampler components

Sampler Components (from left to right): sampler body, backing tab, ring, 1st stainless steel screen, pretreated filter (collection pad), 2nd stainless steel screen, end cap. All components, except for the sampler body itself, are found on both ends of the body. Copyright permission granted by Ogawa & Co. [140].

Filters are specially coated to react with the gas of interest [140]. Without electric power, following Fick's first law, passive sampling is based on the free flow of analyte (i.e. gas) from the sampled medium (i.e. air) to the trapping medium (i.e. filter impregnated with a reagent to trap the gas) at a magnitude proportional to the concentration gradient. Simplistically, the gas will move from an area of high concentration to an area of low concentration [29]. Ogawa NO₂ filters are impregnated with triethanolamine (TEA) only for the trapping of NO₂. TEA traps and reduces NO₂ to nitrite (NO₂⁻). NO_x filters are coated with both TEA and 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO) for the trapping of NO₂ and NO, respectively [140]. PTIO traps and oxidizes NO to NO₂⁻. According to the standard protocol, a fixed quantity of 1.5 mg PTIO is used per filter but no further information is given [141]. **Table 1** summarizes the characteristics of Ogawa NO_x and NO₂ filters in more detail.

Table 1. Ogawa NO_x and NO₂ Filter Characteristics

Filter Type	Filter Coating	Reported Chemical Mechanism	Color of	
			Filter	Extracted Filter in Water
NO ₂	Triethanolamine (TEA)	Traps and reduces NO ₂ to NO ₂ ⁻	White 	Colorless 
NO _x	Triethanolamine (TEA)	Traps NO ₂	Purple 	Purple 
	2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO)	Traps and oxidizes NO to NO ₂		

The goal of NO_x collection is ultimately determining the concentration of NO in air. An initial step in determining the concentration of NO is determining the amount of NO_x and NO₂ collected (Total NO collected = Total NO_x collected – Total NO₂ collected). Therefore, for NO_x collection, one end of the sampler contains a NO_x filter while the other end contains a NO₂ filter. If feasible, two samplers could be deployed side-by-side allowing for duplicate analysis of each filter type (i.e. each sampling site has two NO_x filters and two NO₂ filters). For NO₂ collection, both ends of the sampler contain NO₂ filters. When two of the same filter types are used at the same sampling location, absorbance values are averaged so only one concentration value is determined per sampling location. Assembled Ogawa samplers are stored and transferred to and from sampling locations in air-tight containers. When filters exposed to NO and NO₂ are extracted into Milli-Q water, nitrite ions (NO₂⁻) are produced. Nitrite is the secondary analyte that is actually measured in the case of both filter types. The overall mechanisms of the absorbents are established; PTIO oxidizes collected NO to NO₂ while TEA traps NO₂ on the filter [142]. However, the identification of the reaction mechanisms and products is still a subject of controversy [143, 144]. Ogawa passive samplers were utilized for the research detailed in Chapters 3 and 4. In depth coverage of passive sampling in general is provided in Chapter 5.

1.6.3 Characteristics of active and passive monitors

As with most sampling methods, passive and active monitors are both subject to advantages and disadvantages. It is important that potential sources of error and limitations are recognized prior to selecting a sampling method. Consideration of the characteristics (**Table 2**) of both types of sampling method should be acknowledged prior to planning a study; the chosen method should best meet the needs of the sampling design. Keeping in mind the characteristics of each method may vary depending on the sampling plan. For example, laboratory costs may be high for passive sampling depending on the size of the study and the frequency of collection. However passive sampling analysis costs are generally less than costs associated with purchasing, installing, and maintaining a continuous monitor.

Table 2. Comparative characteristics of passive and active air samplers

Characteristic	Continuous Sampler	Passive Sampler
Ability to detect short-term concentrations (hours), and regulatory noncompliance	Yes	No
Calibration	Periodically	Validation once
Concentration	Continuous real time	Mean value
Cost	High	Low
Field labor requirement	High	Minimal
Flexibility of sampling location	Low	High
Maintenance	Required	Not required
Measurement specificity (other pollutants)	Interference possible	Interference possible
Meteorology Interference	Low	Varies Can be high
Minimum detection limit (in fine-time resolution)	Lower than passive (0.05 ppb)	Higher than continuous but varies within passive samplers
Power Requirement	Yes	No
Sampling Duration	Continuous	Generally 1 day to a month Varies
Size	Large	Small
Spatial measurement	Not suitable	Suitable
Time resolution of pollutant levels	High	Low
Weight	Heavy	Light
Working concentration	Sampler dependent, as low as 0 ppb and up to 1000 ppb for some samplers	Sampler dependent, as low as 0 ppb and up to 500 ppb for some samplers

Characteristics apply to the majority of samplers from each category [128, 143, 145]

2.0 INSTRUMENTATION & METHODS

This chapter details both the sampling and analytical methods used for the research presented in Chapters 3 and 4.

2.1 INSTRUMENTATION

2.1.1 Concentration analysis

Concentration values were determined using electronic absorption spectroscopy (NO_x and NO_2) and ion chromatography (O_3):

Electronic absorption spectroscopy: Ambient NO and NO_2 concentrations were determined colorimetrically using a Genesys 10S UV-vis spectrophotometer. A Shimadzu UV-2501PC spectrophotometer was used for the measurement of electronic absorption spectrum. Spectrophotometry uses light to measure chemical concentrations. The measured compound must absorb light and this absorption should be distinguishable from that of other compounds in the analytical solution. The absorbance value of the analytical solution is directly proportional to the solution concentration according to Beer's Law. To ensure Beer's law is followed, a calibration curve is created prior to sample analysis using a set of standard solutions. The concentration values of the standards are plotted against their absorbance values, determined spectrophotometrically. Standard preparation follows the exact procedure as the samples, except each standard contains a known concentration of analyte. If standards and samples are prepared with both identical solvents and final volumes, then it is possible to calculate the unknown quantity of analyte in each sample based on the linear equation derived from the calibration curve [146].

Ion chromatography: Ozone concentrations were measured by ion chromatography (IC) using a Dionex ICS-2000 Ion Chromatograph. The instrumentation was generously provided by Professor Daniel J. Bain, University of Pittsburgh. Ion chromatography is used to determine the presence and concentrations of ions in samples. The ozone filter is coated with a nitrite-based solution. Ozone oxidizes nitrite to nitrate, and the nitrate ion (NO_3^-) concentration is used to calculate the amount of O_3 collected

[147]. An IC system includes a column in which the sample ions move throughout and adhere to differently depending on the species. Sample ions are identified based on the time at which an ion is extracted from the column, and solution concentrations are determined automatically by the chromatography software [148].

2.1.2 Degradation analysis

PTIO degradation products were identified using mass spectrometry and electron paramagnetic resonance (EPR):

Mass spectrometry: Mass spectrum was obtained using a Finnegan LCQ quadrupole field ion trap mass spectrometer equipped with an electrospray ionization source (ESI-MS). Mass spectrometry provides both qualitative and quantitative information on molecules by the conversion of the molecules to ions. The analytical molecules are ionized to acquire a charge, travel through a mass analyzer, and reach different parts of the detector depending on their mass/charge (m/z) ratio. The Solutions were run under acidic conditions in which an acid is added to aid protonation of the molecule for detection. Output includes the m/z ratio of the molecules present along with the relative abundance of each molecule [149].

Electron paramagnetic resonance: X-band EPR spectrum were recorded on a Bruker ELEXSYS-II E500 spectrometer equipped with an Oxford ESR-910 liquid helium cryostat. The signal was quantified relative to a $\text{Cu}^{(II)}$ (EDTA) spin standard. The microwave frequency was calibrated with a frequency counter and the magnetic field with an NMR gaussmeter. A modulation frequency of 100 kHz was used for all EPR spectrum. This instrument and the software (SpinCount) used to analyze the EPR spectrum were graciously provided by Professor Mike Hendrich, Carnegie Mellon University.

EPR spectroscopy, also referred to as ESR (electron spin resonance) is a technique used for examining compounds containing one or more unpaired electrons. It is analogous to NMR (nuclear magnetic resonance) spectroscopy in that electron spins are excited rather than nuclear spins. EPR spectroscopy is a consequence of Zeeman splitting. When a sample with an unpaired electron is placed in an external magnetic field (B_0), the spin of the electron (m_s) can align either with or against the field. The energy gap, ΔE , is dependent on the size of the applied magnetic field and is generally in the microwave range (*i.e.* the frequency, ν , is ~ 9 GHz). The unpaired electron in the sample can either absorb or emit energy, with a value of $h\nu$, and thus the resonance condition, $\Delta E = h\nu$, is obeyed. The g -factor (relating the magnetic moment μ , the angular quantum number and the bohr magneton, μ_β) of an

unpaired electron is g_e or 2.0023. Thus, the fundamental equation describing EPR spectroscopy, where h is Planck's constant, can be written as:

$$h\nu = g_e\mu_B B_0 \quad \text{(Equation 1)}$$

Again, similar to NMR theory, the unpaired electron is affected by the local magnetic field (σ) of the molecule it resides in and deviations from g_e (2.0023) can be expected. In addition, again analogous to NMR theory, the EPR signal can be split by interactions with nuclear spins. For example, a molecule with a hydrogen atom (I , nuclear spin of $\frac{1}{2}$) next to the unpaired electron will exhibit an EPR spectrum of two lines rather than a single absorption. The unpaired electron is split by the hydrogen nucleus according to $2MI + 1 = 2(1)(\frac{1}{2}) + 1 = 2$ lines, where M is the number of spin $\frac{1}{2}$ nuclei.

Anaerobic conditions: A Vacuum Atmospheres Company Omni-Lab glove box, equipped with an electrolytic fuel cell to measure oxygen levels to below 1 part per million, was used to provide an anaerobic environment when necessary for mass spectrometry and EPR experiments.

2.2 PASSIVE SAMPLING METHODS

Passive samplers and pre-coated filters for NO_x , NO_2 , and O_3 collection were purchased from Ogawa & Co. Gases were measured throughout Auckland, New Zealand as part of a multi-pollutant air monitoring study. Individual Ogawa passive samplers were externally housed in protective shelters fixed to air sampling units originally designed to collect multiple pollutants (i.e., $\text{PM}_{2.5}$, organics) for the New York City Community Air Survey [150]. Unmodified Ogawa shelters purchased directly from the manufacture (Ogawa & Co.) were inserted into a larger completely opaque weather shelter equipped with relative humidity, temperature, and barometric pressure sensors connected to a HOBO micro station data-logging device (Onset Computer Corporation, Pocasset, MA, USA). The Ogawa manufactured shelters are described as opaque but in actuality are semitransparent. About 2 inches of the Ogawa shelter extends out the sampling unit's weather shelter. The entire housing unit (**Figure 2**) is permanently mounted on the exterior of a watertight and crushproof polypropylene case (Pelican Model 1550NF silver case, San Antonio, TX, USA) specifically designed to meet the needs of the multi-pollutant study [150].



Figure 2. Multipollutant air sampling unit

Yellow circles designate area on the sampling unit where gas samplers are housed.

Sampling units were mounted 10-12 feet above street level on utility poles. When collection of additional pollutants was not feasible at all collection sites, gases were collected using Ogawa shelters mounted on utility poles using large cable ties (**Figure 3**). The majority of utility poles were located alongside a road.



Figure 3. Gas samplers housed in Ogawa shelters

At sites where multipollutant sampling monitors were not used, gas samplers were housed in Ogawa shelters and mounted on utility poles using zip ties.

Auckland: NO_x and NO₂ were collected over multiple six day (~ 128 hours) consecutive sessions (n=4) in autumn (April 7th to May 2nd 2014) at a total of 40 spatially distributed sites and one reference site. O₃ was collected at the sites equipped with the sampling monitor (n=12). Over half of the sites were located in Auckland's central business district (Auckland City) bounded by several major highways and the port of Auckland to the north (**Figure 4**). Gas collection was part of the "SpaRTANZ" study or Spatially-Resolved Technique for Source Apportionment in New Zealand carried out in collaboration between the University Of Pittsburgh Graduate School Of Public Health and New Zealand's National Institute of Water and Atmospheric Research (NIWA).

Geographic information system (GIS)-based measures were used to systematically select 40 sampling sites across approximately 50 km² encompassing Auckland's port and most of its major highways. Site selection aimed to capture spatial variability in traffic measures and topographical features deemed to be important in the study area. Each site was classified by three local factors of interest, each of which was dichotomized into two groups representing high or low exposure from (1) total traffic (high or low), (2) diesel (presence or not of bus or traffic route within 50 m² of the site), and (3) uphill road gradient (high or low).

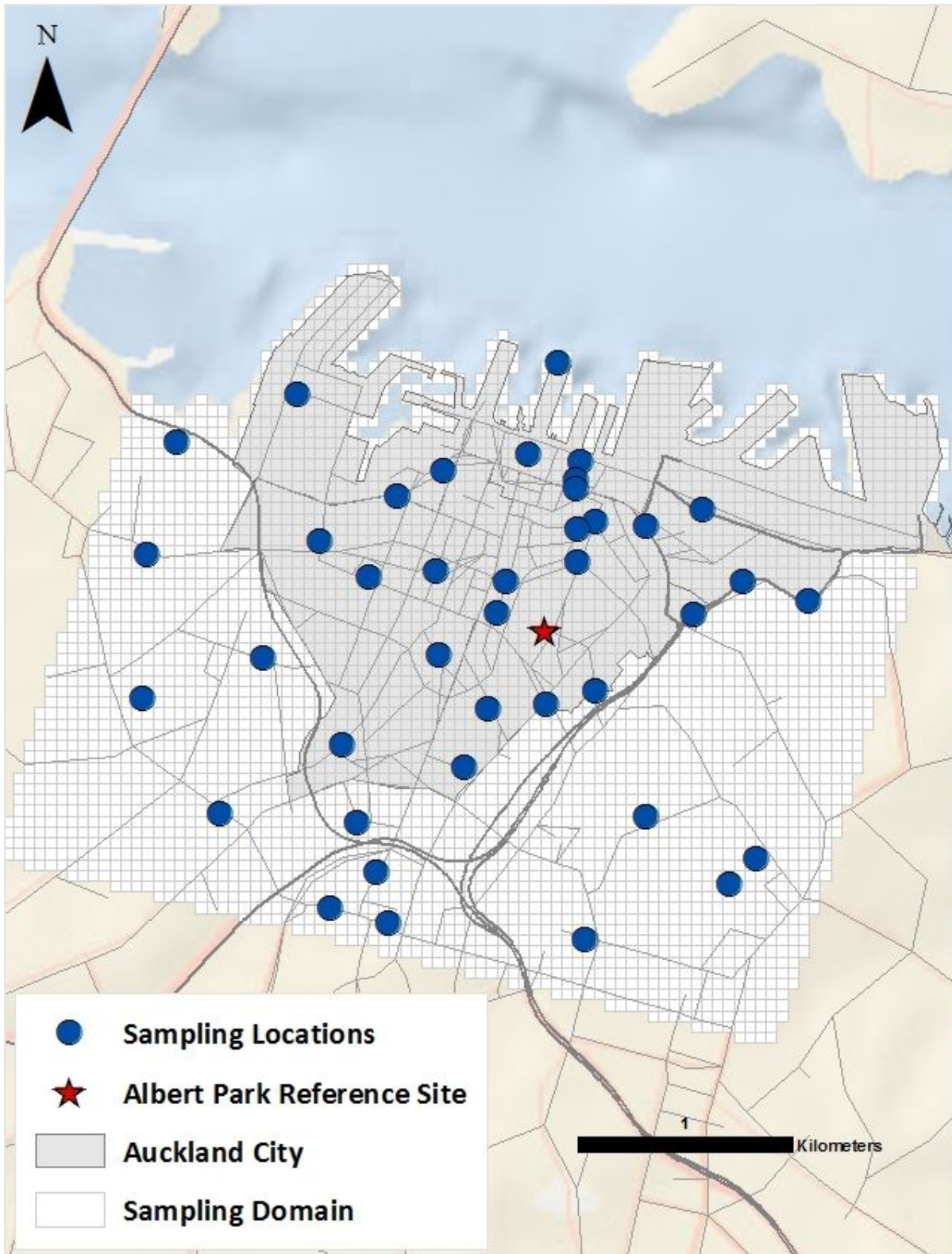


Figure 4. "SpaRTANZ" gas monitoring locations

During each sampling session, NO_x, NO₂, and O₃ were collected at a public park in central Auckland, which served as the study's 'reference' or 'background' site. Unlike the other sampling sites located mostly alongside various roadways, the sampling units were mounted within the park, farther from the roadway. Ideal reference locations are selected away from local sources [151] in an effort to separate pollutant concentrations effected by temporal factors (e.g., meteorology, long-range transport) from those effected by spatial factors (e.g., source locations) [150, 152]. Although the reference site should be "cleaner" than the curbside sampling locations the park was located within the city so traffic is still a main pollutant source somewhat influencing this background site. Since all measurements did not occur at the same time point, calculated concentration values were temporally adjusted to account for variation in temporal-contributing factors occurring between sampling sessions. The adjustment aims to remove the temporal factors as if all measurements were collected at the same time. Raw concentration values measured at each site were temporally adjusted using **Equation 2** derived in Shmool *et al.* [153].

$$[adjConc]_{ij} = \frac{[Conc]_{ij}}{[Ref_{Regional}]} \times [Ref_{Regional}]_{Season} \quad \text{(Equation 2)}$$

Where:

$[adjConc]_{ij}$ =temporally-adjusted concentration at monitoring site i during sampling session j

$[Conc]_{ij}$ =pollutant concentration at monitoring site i during sampling session j

$[Ref_{Regional}]$ =reference site concentration during sampling session j

$[Ref_{Regional}]_{Season}$ =average pollutant concentration at the reference site for the sampling season

A field blank for each gas was used each session. The field blank helps account for possible contamination by subjecting it to the same field processing, transportation, and laboratory handling as the collecting samples. Field blanks were assembled in the laboratory and transported in the same manner as the collecting samplers. During the week-long collection the field blanks were stored at 4°C until analysis. During each session the containers containing the field blanks were opened and immediately closed at one of the sampling sites randomly selected. Following chemical analysis, for each collecting sampler, the difference between the sample absorbance and the field blank absorbance becomes the corrected absorbance used for the concentration calculation.

Christchurch: Following collection in Auckland the "SpaRTANZ" study continued with the measurement of the same pollutants in the city of Christchurch located on New Zealand's southern island. Results for this study will not be discussed in detail; however, one of the passive sampling aims was unique to the current literature. This portion of the study aimed to capture the difference between daytime and

nighttime gas concentrations using passive samplers. In order to collect day and night samples Ogawa passive samplers were swapped between 5:30 AM to 7 AM and again between 5:30 PM to 7 PM. Therefore, a daytime sampler measured from approximately 7 AM to 5:30 PM and a different sampler measured nighttime concentrations from approximately 7 PM to 5:30 AM. The same day or (night) sampler was placed back into the shelter for collection during the respective sampling period for seven consecutive days. At the end of the week each site had at least two sets of filters: one set representative of daytime and the other representative of nighttime concentrations. During each session, at one Christchurch location, passive samplers were co-located next to a fixed active monitor. For both the Auckland and Christchurch studies a total of seven co-located passive measurements were collected for each gaseous pollutant to assess the reproducibility of the sampling and analysis methods. **Sampling results presented in Section 3.2.**

2.3 ANALYTICAL METHODS

2.3.1 NO_x and NO₂ filter preparation for analysis

Following sampler retrieval exposed NO_x and NO₂ filters were individually extracted in 8 ml of Milli-Q water and stored in opaque vials at 4°C until analysis. The day of analysis solutions containing the extracted filters were shaken on a plate shaker for 30 minutes at 4°C.

2.3.2 NO₂ concentration analysis

Sample collection and analysis were performed according to an adaption of the Ogawa & Co., Inc. protocol [141]. A set of 5 standard nitrite (NaNO₂, ReagentPlus®, ≥99.0%, Sigma-Aldrich) solutions (ranging from 0.01 to 3 µg/mL) were prepared in Milli-Q water along with a blank solution (Milli-Q water only). The nitrite concentrations of the samples and standards were determined using a color-producing reagent (an adaptation of the Greiss-Saltzman Reagent [154]) consisting of sulfanilamide (99%, Sigma-Aldrich), N-(1-naphthyl)-ethylenediamine dihydrochloride (NEDA, ACS Grade, >98%, Sigma-Aldrich), phosphoric acid (ACS Grade, Fisher), and Milli-Q water. The sulfanilamide solution was prepared by adding 0.5 g

sulfanilamide to a mixture containing 40 mL Milli-Q water and 5 mL phosphoric acid. Once homogenous, 0.05 g NEDA was added to the sulfanilamide solution followed by dilution to 50 mL with Milli-Q water.

Forty microliters of color reagent was added to a cuvette followed by 1 mL of sample. The same procedure was followed for the standard and blank solutions. Cuvettes sat 10 minutes to allow for color development. Nitrite is detected and analyzed by formation of a pink color through an adaption of the Griess reaction. Under acidic conditions (phosphoric acid), the diazotizing reagent (sulfanilamide) reacts with NO_2^- producing a transient diazonium salt. This intermediate reacts with the coupling reagent (NEDA), to form a stable azo compound (colored) [154, 155]. A pink color gradient was observed in the standard solutions, ranging from a very faint pink in the least concentrated solution to a dark vibrant pink in the most concentrated one. Following the reaction with the color-producing reagent, absorbance values were spectrophotometrically determined at 543 nm with 1 mL Milli-Q water + 40 μL (Griess) colorimetric reagent as the blank. The spectrophotometer automatically subtracts the absorbance value of the blank solution (water + colorimetric reagent, $\text{ABS} \sim 0$) from each standard solution to give a blank-corrected calibration curve. The field blank (**described in Section 2.2**) absorbance value was subtracted from each sample absorbance value prior to the calculation of concentration values.

2.3.3 NO_x concentration analysis

For the accurate analysis of NO_x filters, adaptations were made to the Ogawa & Co., Inc. protocol [141]. Additions to this method include incorporation of a NO_x specific calibration curve and extraction of PTIO from all NO_x solutions including standards, blanks, and exposed filter extract solutions. Extraction was necessary to eliminate the interference of PTIO during analysis (**Discussed in Section 4.2.1**). When a NO_x filter is submerged in water and shaken gently, per the Ogawa & Co., Inc. protocol, the PTIO coating elutes into the water resulting in a white NO_x filter and a purple-colored (PTIO) solution. Diethyl ether ($(\text{CH}_3\text{CH}_2)_2\text{O}$) (CHROMASOLV[®] for HPLC, $\geq 99.9\%$, inhibitor-free, Sigma-Aldrich) was utilized for all extractions. This specific brand of solvent was used for all extractions as other tested brands introduced impurities into the extraction process resulting in unwanted chemical reactions. A liquid-liquid extraction was used to remove PTIO from the analytical solutions. Since water and ether are immiscible, two layers will form with the top removable layer being comprised of ether and PTIO.

NO_x calibration curve: A set of 5 standard nitrite solutions (NaNO_2 , ranging from 0.01 to 3 $\mu\text{g}/\text{mL}$) were prepared in Milli-Q water along with a blank solution (Milli-Q water only). Each standard solution plus the blank was divided into two aliquots. One aliquot was used for the general NaNO_2 calibration

curve (i.e. NO₂ analysis, as described in **Section 2.3.1**) and the second for spiking unexposed filter solutions for a NO_x specific calibration curve to account for any impact the PTIO eluting into solution may have on analysis. An “**unexposed**” filter refers to a filter which was not directly exposed to ambient conditions; this filter was never outdoors – this definition being used throughout, unless otherwise stated. The standard NaNO₂ calibration curve was produced as previously described for determining NO₂ concentrations. For the NO_x calibration curve, individual unexposed NO_x filters were submerged in 8 mL of the five standard nitrite solutions, mentioned directly above, as well as into the Milli-Q water blank solution. These standards, containing the NO_x filters, are referred to as the “NO_x standards.”

Diethyl ether extractions: The exposed NO_x filter extract solutions, NO_x filter extract standards and blanks solutions, were all shaken on a plate shaker (previously described above) the day of analysis. Using an automatic pipette, 2 mL of each solution was transferred to a 15 mL polypropylene conical centrifuge tube and then 2 mL of ether was added to each tube. Vigorous manual shaking of capped tubes was performed until two distinct layers formed with obvious color change to the analytical solution (bottom layer). The top layer was blueish in color while the bottom layer began to lose its purple color. Using individual disposable pipets for each solution, the top (ether + PTIO) layer was removed and discarded from each solution. The shaking and removal process was repeated using 5 mL of ether. The remaining solution in each tube (still ~2 ml) was now colorless. Tubes were heated in beakers containing water on a hot plate (~30°C) for one hour to allow for evaporation of any remaining ether. Following heating, the now ether extracted NO_x filter extract and blank solutions were analyzed to produce the NO_x calibration curve. Standards and sample solutions were analyzed as previously described for NO₂ (**Section 2.3.1**).

Since PTIO interferes with the absorbance measurement, “before extraction” standard absorbance values could not be determined from the NO_x filter extract standard and blank solutions. **Challenges associated with analysis of NO_x filters are presented in section 4.2.1.** Instead, the NO_x calibration curve created post ether extractions was compared to the NO₂ calibration curve to ensure the NO_x calibration aligned on the NO₂ curve. As the NO_x and NO₂ calibration curves were produced from the same stock standard NaNO₂ solutions, it is expected that the NO_x standard curve, following removal of PTIO, should be equivalent to the NO₂ calibration curve.

Following the procedure described above for the production of the NO_x calibration curve, NO₂ calibration curves were also produced using individual NO₂ filters extracted into standard and blank solutions. The NO₂ filter extract solutions were analyzed post ether extraction as described above. However, since NO₂ filters are not coated with purple-colored PTIO, it was found that the addition of the

NO₂ filters was unnecessary as the NO₂ standard solutions absorbance values did not change prior to and after ether extractions (unlike the case when the NO_x filter is added into water – **explained in Section 4.2.1**). Therefore, to eliminate unnecessary use of NO₂ filters, NO_x calibration curves were generally compared to NO₂ calibration curves which did not contain NO₂ filters. However, an example of calibration curves in which both NO_x and NO₂ filters were added during the production of the curves are shown in **Figures 18 and 19**.

2.3.4 Concentration calculations

Calculation of concentration of NO_x, NO₂, and NO were completed according to the Ogawa & Co. protocol [141]. An individual standard curve and analysis was completed for each sampling session (n=4). Each NO₂ calibration curve was compared to the NO_x curve (following ether extractions) to verify no changes due to the addition of ether into the solution. Temperature and relative humidity were measured at sampling sites containing a complete sampling unit equipped with a HOBO micro station data logger designed to measure weather conditions. At each site equipped with a HOBO micro station data logger, temperature and humidity values were recorded every fifteen minutes. At each site values were cropped and averaged to include only the times when gas collection occurred. At gas only sites where a HOBO micro station was not available, averaged temperature and relative humidity values from all sites with a logging device were used. These averaged measurements were used to calculate concentration conversion coefficients (**Equation 3 and 4**). The process for the calculation of concentration data for NO_x, NO₂, and NO is provided in the manufacturer’s protocol [141] and found in **Table 3 and 4**. **Concentration results are presented in section 3.2.1**.

Table 3. Calculation of NO_x, NO₂, NO Concentrations Part 1

Compound	Blank Absorbance	Slope	Temperature °C	Relative Humidity (%)	Concentration Conversion Coefficient	
					αNO	αNO ₂
NO _x	(1)	(S1)				
NO ₂	(2)	(S2)				

$$\alpha NO = 10,000 / [(-0.78 \times P \times RH) + 220] \quad \text{(Equation 3)}$$

$$\alpha NO_2 = 10,000 / [(0.677 \times P \times RH) + (2.009 \times T) + 89.8] \quad \text{(Equation 4)}$$

Where:

P =vapor pressure coefficient (dimensionless, provided in standard protocol)

RH =relative humidity (%)

T =temperature (°C)

Table 4. Calculations of NO_x, NO₂, NO Concentrations Part II

	Sampling Time (min)	(3)	= (3)
NO _x	Sample Absorbance	(4)	= (4)
	Corrected Absorbance	(5)	= (4) - (1)
	Solution Concentration (µg/mL)	(6)	= (5) / (S1)
	Collected Weight (ng)	(7)	= (6) * 8 * 1000 Where: 8 = solution volume (mL)
	Concentration (ppb)	(8)	= (13) + (15)
NO ₂	Sample Absorbance	(9)	= (9)
	Corrected Absorbance	(10)	= (9) - (2)
	Solution Concentration (µg/mL)	(11)	= (10) / (S2)
	Collected Weight (ng)	(12)	= (11) * 8 * 1000 Where: 8 = solution volume (mL)
	Concentration (ppb)	(13)	= α_{NO_2} * (12) / (3)
NO	Collected Weight (ng)	(14)	= (7) - (12)
	Concentration (ppb)	(15)	= α_{NO} * (14) / (3)

2.3.5 O₃ concentration analysis

Sample collection and analysis were performed according to an adaption of the Ogawa & Co., Inc. protocol [147]. Following sampler retrieval, the two O₃ filters from each sampler were placed together in a storage vial. The day of analysis, 5 mL Milli-Q water was added to each vial. Vials were sonicated for 15 minutes. During sonication the basket holding the vials was turned 180 degrees every five minutes. Ozone concentrations were determined by the detection of NO₃⁻ using ion chromatography. Calibration curves were produced by the IC following the introduction of 1, 10, and 100 ppm standards (containing a variety of compounds). Approximately 1 mL of each sample and standard solution was added to an IC vial. Vials were inserted into the IC and left for automatic analysis. Ozone concentration calculations are not described in detail here but follow the Ogawa & Co., Inc. protocol [147]. **Concentration results are presented in section 3.2.1.**

2.3.6 Degradation analysis

Several experiments were designed to identify the causes and resultant chemical products of PTIO degradation on NO_x filters and in PTIO solutions. Pre-coated NO_x filters, samplers, and shelters were purchased from Ogawa & Co. Ogawa shelters were covered in duct tape to transform the shelters from semitransparent into opaque. **Degradation results are presented in Section 4.2.4.**

2.3.6.1 Influence of specific environmental factors – light and temperature

The effect of light and temperature on the degradation of NO_x filters and PTIO solutions was initially determined through visual inspection. Following each experiment, color was reported as 1) no change or 2) change (purple to white). A portion of the filters and solutions were kept for use in ambient sampling and analytical analysis.

Preparation of PTIO solutions: PTIO purchased from Sigma-Aldrich (SKU# P5084) was added to Milli-Q water to produce PTIO solutions (1.2 mM) which did not contain filters or TEA (as a NO_x filter would). A subset of the solutions were stored in amber vials at 4°C to minimize exposure to light.

Light: To assess the impact of sunlight on NO_x filter color change, filters were placed in a petri dish for 7 days during Pittsburgh's late summer season (August) on an indoor window sill with unrestricted exposure to natural sunlight. This experimental design allowed for the study of sunlight independent of other variables present in the outdoor atmosphere; however the impact of temperature was not eliminated in this design. Although the filters were not exposed directly to ambient temperatures, the placement of the petri dish on the window sill resulted in a heating of the dish during exposure to sunlight. Identical procedures were replicated in autumn and winter. To determine if artificial light had the same effect as sunlight, a petri dish containing NO_x filters was placed under a desk lamp. Similar experiments were tested with PTO solutions. Following these experiments the NO_x filters and PTIO solutions were saved for future analytical experiments described in **Section 2.3.6.3.**

High temperature without light: To establish the effect of temperature independent of light on color change in NO_x filters, a petri dish containing filters was wrapped in a single layer of foil and placed indoors within a few inches of a desk lamp bulb. The dish was exposed to the light for seven days to mimic a typical exposure period. A thermometer placed directly on the dish reported a maximum temperature of 140 °F. As the foil absorbs a portion of the heat the filters would not reach the maximum temperature reported at the top of petri dish. The filters were not checked until the end of the seventh day.

Cool temperature with light: To assess the effect of light exposure at cooler temperatures, a petri dish containing NO_x filters was placed inside a 4 °C (39.2 °F) cold cabinet for 7 days where the filters were exposed to the laboratory light in the daytime and continuous light from the cold cabinet. It is not uncommon for filters to be exposed to a similar temperature during ambient sampling.

2.3.6.2 Influence of storage

Unmodified NO_x filters: Unexposed NO_x filters extracted with Milli-Q were stored in solution in transparent polyethylene vials purchased from Ogawa & Co. Vials were stored inside a 4 °C (39.2 °F) cold cabinet per manufacturer's instructions. Solution absorption values were measured at a wavelength of 543 nm prior to placement in the cold cabinet and again after 50 days two months of storage. Analytical solutions contained only NO_x filter extracts in Milli-Q water (1 mL).

2.3.6.3 Identification of compounds present on NO_x filters

Degraded NO_x filters and PTIO solutions: White NO_x filters extracted with Milli-Q water were stored in solution in transparent polyethylene vials purchased from Ogawa & Co. Vials were stored inside a 4 °C (39.2 °F) cold cabinet. A **"white"** NO_x filter is a NO_x filter which lost the purple PTIO color due to degradation – this definition being used throughout, unless otherwise stated.

Electron absorption spectrum of white NO_x filter extract solutions were recorded in the 200-800 nm range prior to placement in the cold cabinet and 50 days following storage. These filters were unexposed to the ambient environment but had degraded during the previously described window sill experiment. Spectrum were compared to that of an unexposed NO₂ filter extract solution. Solutions were analyzed according to the NO₂ concentration analysis previously described in **Section 2.3.2**. To verify the electronic absorption spectroscopy results, white NO_x filter extract solutions were analyzed for nitrite using ion chromatography.

Preparation of filters through ambient sampling: White NO_x filters, exposed to sunlight on the window sill, as previously described in **Section 2.3.6.1**, were assembled into Ogawa passive samplers (n=4) and deployed alongside samplers containing unmodified (purple) NO_x filters (n=4) for a duration of seven days in November 2014. Unmodified NO₂ filters were deployed as well (n=4). All samplers were housed in duct taped Ogawa manufactured shelters (now opaque) to prevent degradation during exposure. Following sampler retrieval filters were individually extracted in Milli-Q water and stored as previously described in **Section 2.3.1**.

Mass spectrometry: Both NO_x and NO₂ sample solutions were diluted in a solvent consisting of a 50:50 mixture of acetonitrile (HPLC Grade, Fisher) and Milli-Q water plus 1% acetic acid (Optima[®] LC/MS, Fisher). Prior to diluting, the concentrated samples and solvent were each filtered through a syringe filter (0.45 micron PTFE). Analytical solutions were prepared the day of analysis and consisted of 100 μl concentrated sample and 900 μl solvent. Tested solutions included ambient filter extract solutions and unexposed filter extract solutions of each type (i.e., white NO_x filters, unmodified NO_x filters, and NO₂ filters), and PTIO solutions.

Electron paramagnetic resonance: PTIO solutions, ambient NO_x filter extract solutions, and unexposed white NO_x filter extract solutions were analyzed by EPR to complement the mass spectrometry analysis. EPR samples were prepared by placing 200 μL of the appropriate solution in a quartz EPR (3 mm id) tube, freezing the tube in liquid nitrogen and storing the samples in liquid nitrogen until the samples could be analyzed. Quantification of EPR signals was performed by simulating the spectrum using known (or determined) parameters for each sample. Simulations employed a least-squares fitting method to match the lineshape and signal intensity of a selected spectrum. Simulated spectrum were expressed in terms of an absolute intensity scale, which could then be related to sample concentration through comparison with a Cu^{II}(EDTA) spin standard of known concentration.

Effect of oxygen on degradation products (anaerobic conditions): To test the role of oxygen in the degradation of PTIO, a subset of PTIO solutions were produced under anaerobic conditions and analyzed by mass spectrometry. The results were compared to PTIO solutions which were identical in makeup except for being prepared in an aerobic environment. Anaerobic solutions were prepared in a glove box in an argon atmosphere. Nitric oxide (purified with sodium hydroxide) from a nitrogen gas cylinder was added to a subset of the PTIO solutions.

Effect of temperature on degradation products: To test the effect of temperature on the production of degradation products, a subset of PTIO solutions were heated and stored in a water bath at 37 °C for 48-hours. Solutions were analyzed by mass spectrometry and results were compared to the results from PTIO solutions stored at 4 °C for 48-hours.

3.0 PASSIVE NO_x SAMPLING IN AUCKLAND, NEW ZEALAND

3.1 INTRODUCTION

Chapter 3 presents the results of an ambient gaseous monitoring campaign in New Zealand. While concentration values are presented, the main focus of this chapter is the introduction of the first issue associated with Ogawa NO_x passive sampling: the degradation of the NO_x filter coating. The overestimation of NO concentration values using Ogawa passive samplers are discussed as well.

The Auckland urban area, located on the northern island of New Zealand, is the largest and most populated urban area in the country comprising one third of the population. The area is situated on a narrow isthmus (**Figure 5**) characterized by dense population, industrial areas, and high traffic volumes [156]. In 2013, the Auckland region's population ranked first out of New Zealand's 16 total regions comprising 33.4% of New Zealand's population. The central business district of Auckland, Auckland City, ranked first in population size out of New Zealand's 73 districts [157]. In 2006 a continually growing Auckland City comprised 10% of New Zealand's total population [158]. Surrounded by the Tasman Sea to the west and the Pacific Ocean to the east, Auckland is exposed to weather systems from both sides of New Zealand [159]. An interesting feature of the Auckland climate is the high proportion of sunshine during the winter months (as cited in [160]). The prevailing winds are westerly and south-westerly, but north-easterly winds are also present [156]. Relatively high mean wind speeds allows for enhanced dispersion of pollutants keeping Auckland's air quality generally within the national guidelines especially when compared to other major world cities [161]. However, under certain conditions pollution levels can rise substantially.

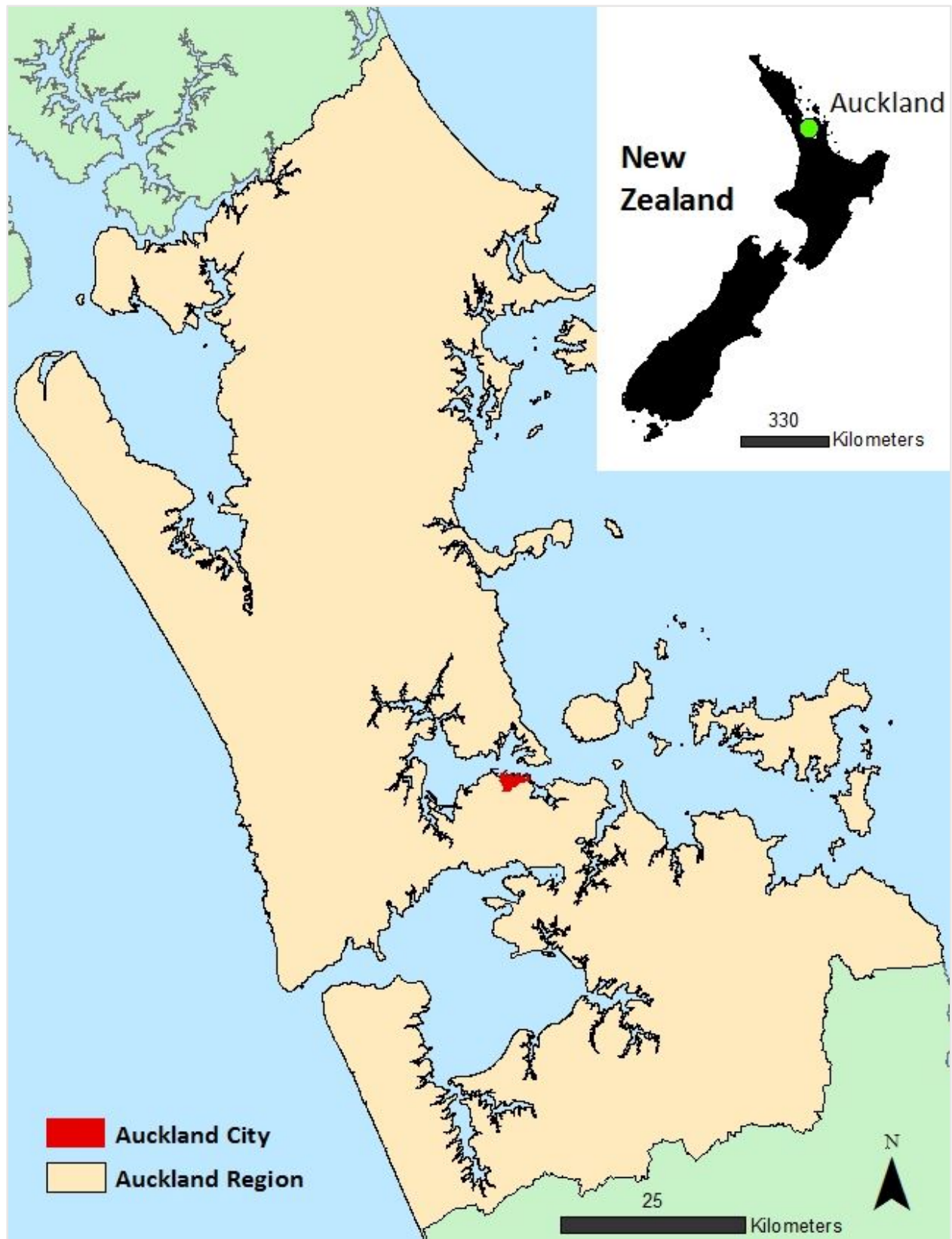


Figure 5. The Auckland Region of New Zealand

Cold, calm, stagnant conditions occur during winter days and nights due to opposing sea breezes [159, 162]. During these conditions, the Auckland Regional Council (1997) reported the city experiences a brown haze that reduces local atmospheric visibility and may be harmful (**Figure 6**) (as cited in [163]). Similar to the haze described in the skyline of major United State cities, reduced visibility is usually most intense in the morning [159], and thought to be a result of NO_x emissions and subsequent reactions with additional pollutants [161].



Figure 6. A brown haze over Auckland

A clear day (top) compared to a winter's morning (bottom) where poor air quality is causing a visible haze. Copyright permission granted by Auckland Council [164].

Although New Zealand's isolated position in the South Pacific gives the country the advantage of receiving fresh, pure air at the coastline, degradation of the air quality is not unusual due to everyday activities throughout the country. Major sources of air pollution in Auckland include combustion of fuels such as wood, gas, and oil, diesel and petrol in vehicles, domestic fires and industrial processes [2]. As New Zealand's main transport hub, emissions from the Auckland's transportation sector is the biggest

contributor to poor air quality [2]. According to Auckland Regional Council (2006a), road traffic is the most significant anthropogenic source of air pollutants in Auckland accounting for about 90% of total NO_x (as cited by [156]) with levels often exceeding air quality standards at peak traffic sites [2]. During the winter months home heating is a significant source of air pollution. Twenty-six percent of surveyed Auckland households ($n=2800$) reported the use of solid-fuel burners (mainly wood) as their most common method of home heating. Seventeen percent of these households reported the use of treated (prohibited) wood [165].

In 2004 the New Zealand government enacted the National Environmental Standards for air quality which contain 14 individual standards which apply to the entire country. Five of these standards define permissible levels of CO , PM_{10} , NO_2 , SO_2 , and O_3 over a specified period of time and the annual allowable exceedances. Unlike the United State standards, only one averaging period for each of the pollutants is specified [2]. The regulated standard for NO_2 is $200 \mu\text{g}/\text{m}^3$ expressed as a 1-hour mean with nine exceedances allowed in a 12-month period [166]. In U.S. concentration units, this value is approximately 106 ppb or 6 ppb higher than the EPA 1-hour standard of 100 ppb. Dissimilar to U.S. standards, annual mean NO_2 levels are not regulated. However, the New Zealand government's principal advisor on the environment, Ministry for the Environment, enacted air quality guidelines which include a 24-hour NO_2 guideline value of $100 \mu\text{g}/\text{m}^3$ [167]. Aimed to protect human health and the environment, this guideline of the maximum acceptable concentration for NO_2 is based on the World Health Organization guidelines and matches the 24-hour EPA NO_2 standard. The annual average guideline for protecting vegetation is $30 \mu\text{g}/\text{m}^3$ [2]. The above conversions from $\mu\text{g}/\text{m}^3$ to ppb are calculated under the assumption of an ambient pressure of 1 atmosphere and a temperature of 25°C .

While some pollutant levels (e.g., O_3 , CO , and SO_2) are within the current air quality standards and guidelines, Auckland Regional Council reports emissions of some pollutants, including NO_2 , need to be reduced significantly [2]. Similar to other regions in the world, there are increased concerns surrounding a possible link between NO_2 exposure and increased prevalence of respiratory [168] and cardiovascular diseases [169]. Although specific studies are limited, New Zealand was reported to have one of the highest prevalence rates of asthma in the world. Notably asthma was also reported as one of the most common chronic diseases in New Zealand children [170]. Nitrogen dioxide was found to be significantly associated with adult cardiovascular hospital admissions, especially in the elderly, at concentrations below the guidelines [169].

Motor vehicles are a significant contributor to Auckland's air pollution [2, 171]. The large quantity of used imported vehicles and New Zealand's relatively new emission standards likely contribute to the

country's current air quality. It wasn't until 2003 that New Zealand introduced vehicular emission standards; over three decades since the enactment of the Clean Air Act. The level of vehicular emissions is heavily dependent on the emission standard under which it was manufactured, but up until the addition of the 2007 Vehicle Exhaust Emissions Rule cars imported into New Zealand did not require compliance with a minimum emissions standard. Vehicles only need be manufactured to a recognized emissions standard according to its manufacture year; it was not required that the vehicle still meet this emission standard [172]. Without import emission standards older vehicles were easily imported including those banned due to air quality reasons in the exporting country [173]. In 2006 the average age of a used petrol vehicle entering the country was 8.1 years, with increasing age for used light diesel and heavy diesel vehicles, 9.3 and 10.4 years, respectively [172]. Today used imported vehicles still make up a large proportion of New Zealand's fleet including a large proportion of which were manufactured in the 1990s. In 2013 the average age of the light fleet, truck fleet, and bus fleet were 13.35 years, 15.7 years, and 15.3 years respectively [173]. The emission standards these vehicles were manufactured under greatly differ from today's standards, i.e., the petrol NO_x emission standard for a European vehicle which entered the fleet in 2001 is over two times the current allowable level [174].

Under the 2007 rule imported new and used vehicles must comply with a certain vehicle emission standard effectively preventing the import of older used vehicles. The standards vary for date of manufacture, new or existing model, fuel type, light or heavy duty vehicles but include a standard for every jurisdiction New Zealand recognizes for imports (i.e., Australia, United States, Europe, and Japan) [172]. Once New Zealand registered, vehicles undergo a "Warrant of Fitness" (WoF) test as often as 6 months (depending the vehicle's registration date). Described as a general safety check, the WoF includes an emissions check as well. Regardless of vehicle age the emissions inspection does not include the actual analysis of tailpipe emissions. The WoF includes an objective noise check as well as a visual check. The noise check verifies the exhaust system does not exceed the legal noise limits. A visible smoke is used as a vehicle emissions proxy; visible smoke from the tailpipe will result in a failed "smoky exhaust test" [175]. Additional emissions testing under the WoF is under currently under consideration [172].

Ideally, New Zealand's adoption of more stringent requirements for imported vehicles would lower the level of NO_x exhaust emissions. As older vehicles leave the fleet and are replaced with new ones, the amount of overall vehicular pollution should, in theory, be reduced. However, the reported increase in diesel NO₂/NO_x ratios [92, 97, 99, 124] due to the implementation of diesel emissions reduction technology could raise a twofold problem for NO₂ emissions in New Zealand. An increasing number of diesel vehicles are entering the New Zealand fleet [173] and the stringency of vehicle importation

requirements have increased (i.e., imported vehicles are built to higher emission standards). By the year 2031 New Zealand's motor vehicle emissions inventory predicts diesel vehicles will contribute 75% of NO_x emissions. Although an additional projection predicts a decrease in NO_x emissions through the year 2031 [176], current literature warns of increasing NO_2/NO_x emissions with newer vehicles and larger vehicle engines (> 2.0 L). In 2013 New Zealand's light fleet engine size class 2.0-2.99 L showed the most growth in terms of vehicle numbers with the 3.0-3.99 L class showing the greatest rate of growth [173]. Recognizing the possibility of a future increase in NO_x or the NO_2/NO_x ratio is crucial as NO_2 from a health standpoint is the more relevant constituent of NO_x . Different control strategies may be adopted if a significant fraction of NO_2 is produced directly from a source rather than through secondary reactions.

In an effort to ensure Auckland's pollutant levels remain below the standards and guidelines, ambient air quality monitoring has been ongoing in the region for several decades. The current monitoring network includes 13 fixed monitoring sites across the Auckland region (urban and rural) along with two mobile monitors. Monitoring sites have been selected to represent various pollutant sources (e.g., industrial, vehicle, home heating, urban plume) and exposures, including traffic monitoring sites 2 to 3 m from the roadside [2, 177]. Auckland Regional Council reports NO_2 concentrations often exceed the standards and guidelines at peak traffic sites. Any reduction in NO_2 concentration at these sites was attributed to local changes in traffic patterns and composition. From 1998 to 2008 no significant changes in NO_2 concentrations were observed; annual average NO_2 concentrations decreased at some monitoring sites but increased at others [2].

To understand spatial patterns of NO_2 concentrations several passive sampling campaigns have been carried out in the Auckland region. Typically, 2 to 4-week sampling durations were chosen [178]. However, a literature review revealed no history of passive sampling campaigns for NO or O_3 in the Auckland region. A passive sampling campaign aiming to capture spatial variability of NO, NO_2 , and O_3 in proposed high and low exposure areas was carried out in New Zealand's fall of 2014.

3.2 RESULTS

3.2.1 Ambient concentrations

Spatial variability in ambient gas concentrations was found across the Auckland study area. NO concentrations adjusted for temporal variability ranged from 8.17 to 133.63 ppb with an average concentration of 37.58 ± 26.64 ppb. (See section 3.4.1 for NO concentration values caveat). Lower in concentration, NO₂ values ranged from 5.33 to 24.21 ppb and averaged 13.67 ± 4.13 ppb. Generally NO and NO₂ values were higher within Auckland city (Figure 7 and Figure 8, respectively). The sampling locations with the highest NO_x concentrations were heavy in diesel sources with the highest NO_x concentration measured at a site alongside a road reserved for bus traffic only (See section 3.4.1 for NO concentration values caveat). Co-located measurements in Auckland and Christchurch of NO_x and NO₂ were highly correlated as a whole across sites (n=7, NO rho= 0.98 and NO₂ rho= 0.96 p<0.05).

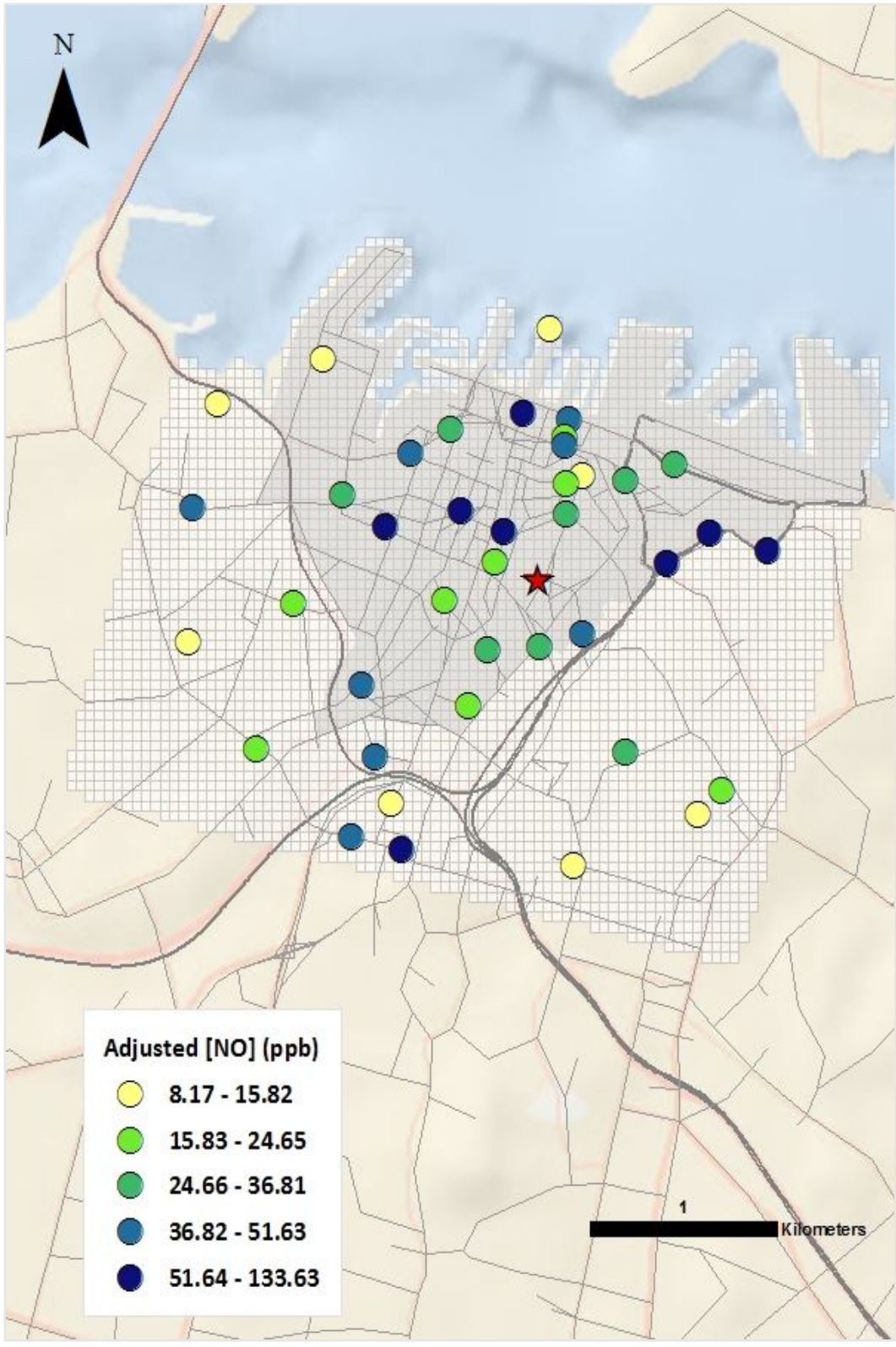


Figure 7. Temporally adjusted [NO] in Auckland, New Zealand

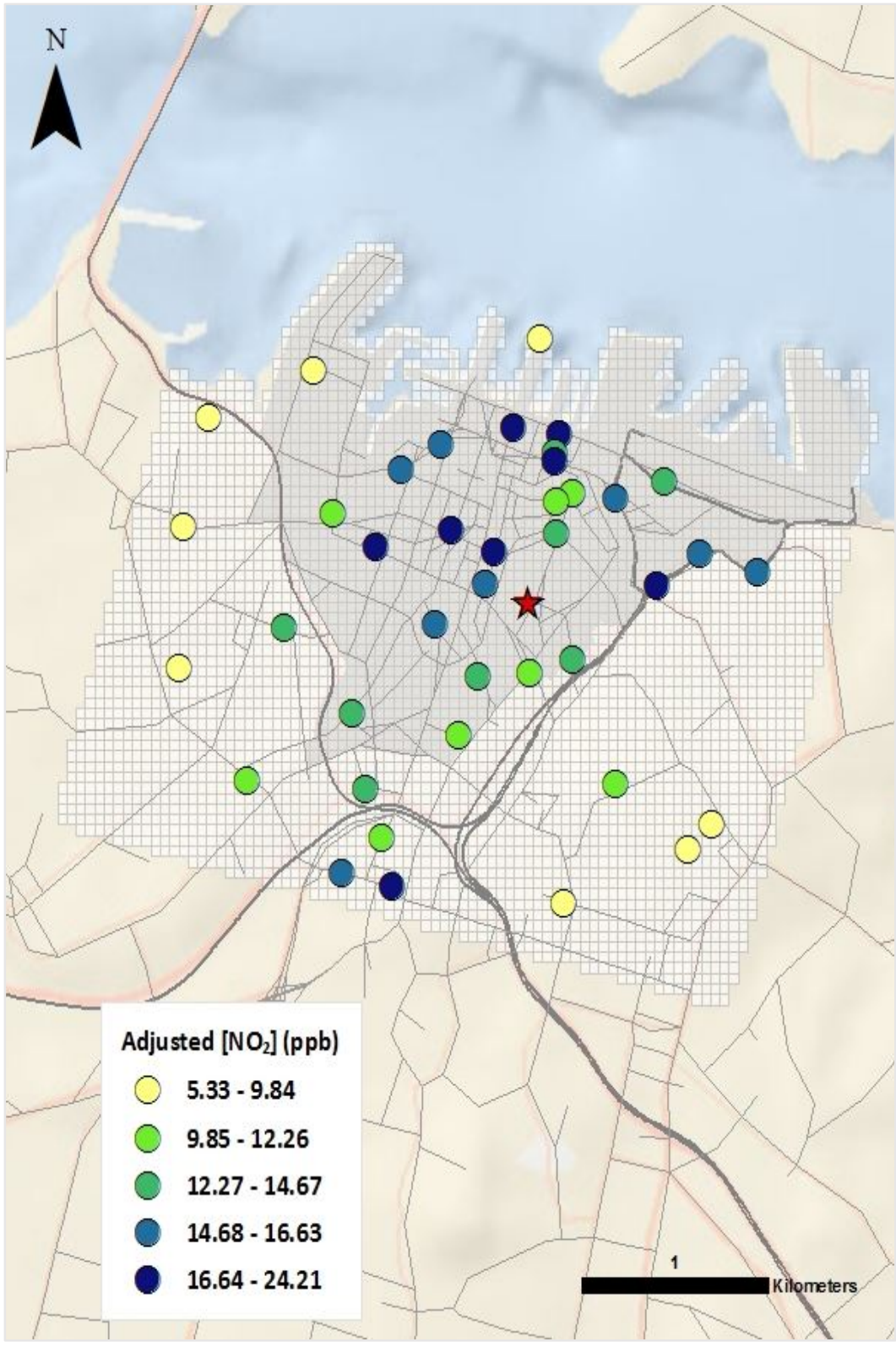


Figure 8. Temporally adjusted [NO₂] in Auckland, New Zealand

In general, NO_x concentrations, including both NO and NO₂ concentrations, tended to be highest at locations nearest a bus stop or on or near roads designated for use by large vehicles (i.e., trucks) (**Figure 9**). Distance from sampling location to diesel source ranged from locations found at the source (0.38 m) up to 630 m from the source.

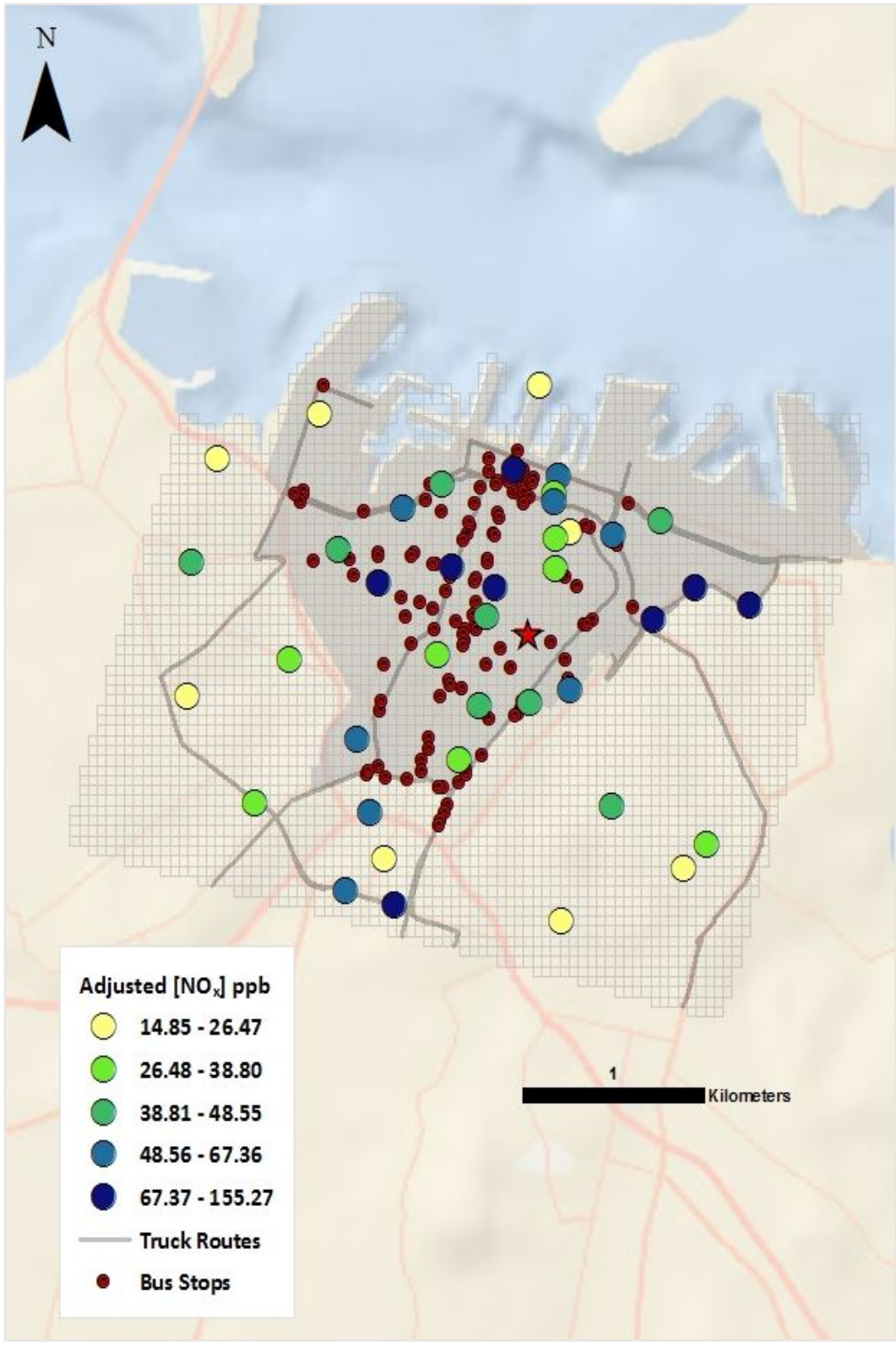


Figure 9. Temporally adjusted [NO_x] in relation to diesel sources

The strongest trend was found for NO₂ ($r = -0.63$, $p = 0.00$) (Figure 10). No significant relationships were found between gas concentrations and the source variables used for site selection (i.e., traffic counts, presence of diesel route, road gradient). This is not surprising as variables are not up to date and more importantly do not reflect changes in traffic patterns or volumes. Site selection variables were meant to be indicative of high and low source areas but in no way foolproof.

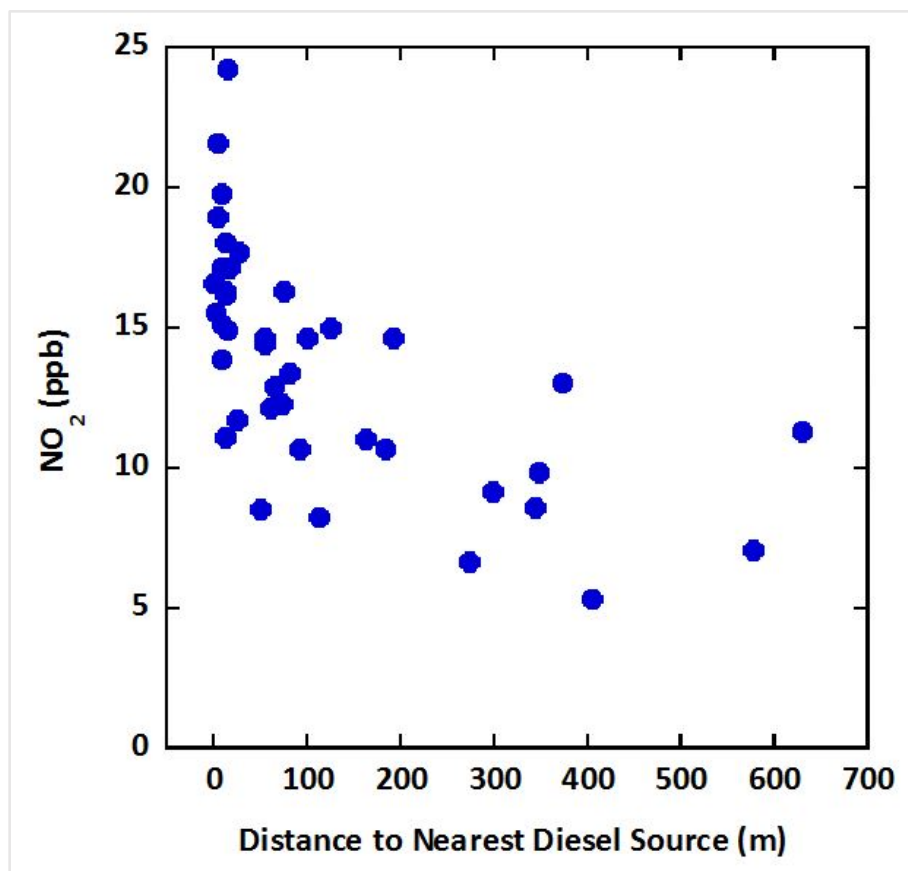


Figure 10. [NO₂] versus distance to nearest diesel source

3.2.2 Passive NO₂/NO_x Ratios

On average NO₂ accounts for 30% of total NO_x measured at each location. NO was the primary component of NO_x at all but two sampling locations. NO₂/NO_x ratios varied spatially from 0.14 to 0.53. Therefore NO comprised 47 to 86% of total NO_x across sampling locations. A significant relationship between NO₂/NO_x ratios and distance to diesel source was not found. A weak positive relationship was observed between NO₂/NO_x ratios and distance to diesel source ($r = 0.28$, $p = 0.08$), opposite of the relationship found with

NO and NO₂ individually. A stronger relationship was found between NO₂/NO_x ratios and concentration of O₃ at each site. Although O₃ was only measured at 12 sites, a strong positive relationship was found between O₃ concentrations and NO₂/NO_x ratios ($r = 0.82$, $p = 0.001$). As the concentration of O₃ increased the ratio of NO₂/NO_x increased as well (**Figure 11**).

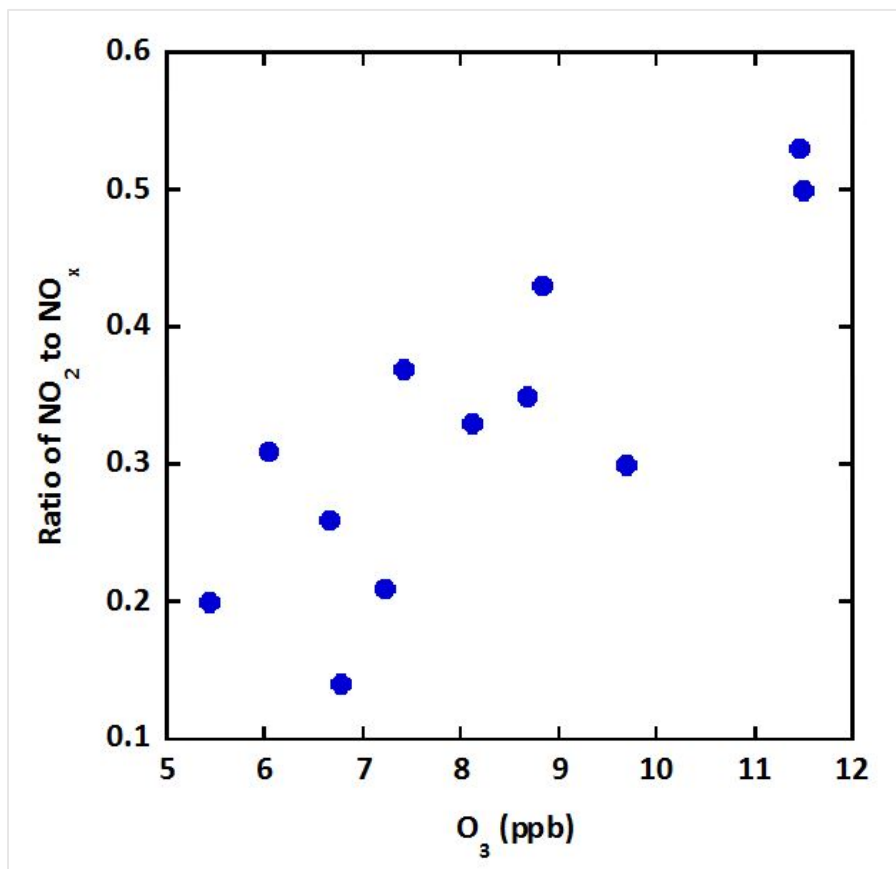


Figure 11. Ratio of NO₂/NO_x versus [O₃]

Sampling locations with higher NO₂ proportions were locations with higher O₃ concentrations as well. The partitioning of NO and NO₂ in this study was better explained by the activity of the oxidation reaction of NO to NO₂ rather than by absolute NO_x emissions from a source. Higher NO_x emissions did not correspond to a higher proportion of NO₂ ($r = -0.87$, $p = 0.002$) (**Figure 12**).

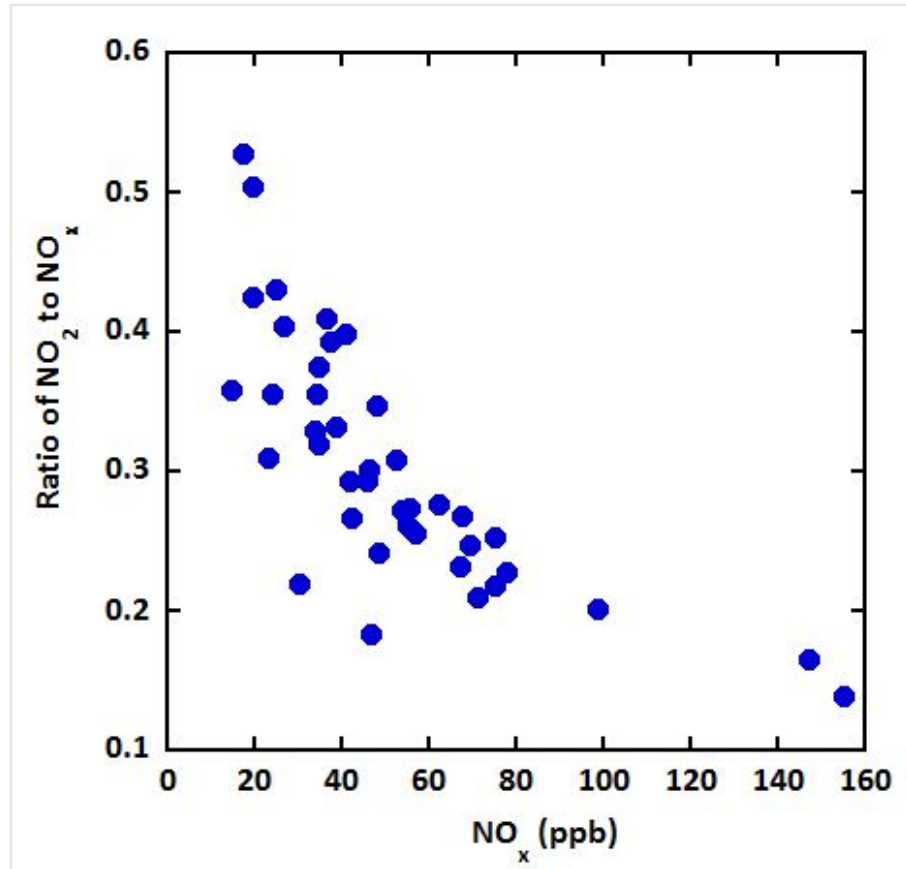


Figure 12. Ratio of NO₂/NO_x versus [NO_x]

The highest NO₂/NO_x ratio (0.59) was measured at the reference site where the average ratio across all sampling sessions was 0.55. These ratios are similar in value to the highest ratio found among the spatially distributed sampling sites (0.53) that was measured in a grassy area where the utility pole was not directly accessible by vehicle. The lowest NO₂/NO_x ratio or the site where NO contributed the most to total NO_x was measured at the previously mentioned buses only site where both the curbside NO_x and NO concentrations were highest among all the sites.

3.2.3 Variation in NO_x filters

Following ambient exposure, a number of NO_x filters exhibited changes in color. The purple color attributed to the PTIO coating on the NO_x filters diminished during sampling. The extent of the loss of PTIO varied between filters in the same sampler and between those at different sites. The variation

ranged from no color change, to partial change, to filters entirely white in color. **Figure 13** illustrates this variation in only a subset of filters.

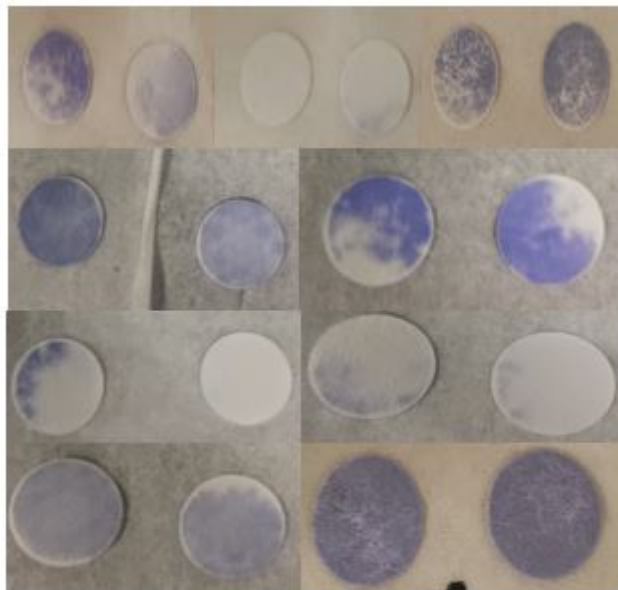


Figure 13. Variation in filter coatings following exposure

Large variation was found in NO_x filter coatings post exposure. This figure represents only a subset of the actual variations seen. The side-by-side filters located within each rectangular block show the deviation found in filters from the same sampler.

Loss of PITO, evident by a color change to white, was greatest at the locations where the sampler was placed under the Ogawa manufactured shelter. Less color change occurred when the sampler was housed under the opaque shelter attached to the air sampling unit. Filters housed under the Ogawa shelter exhibited a splotchy coloring or sometimes a large to complete loss of color. Filters housed in the air sampling unit were less visibly effected, sometimes a lightening of the filter color was observed. Color change did not occur at every sampling location. Variation in color was location specific; differences in color were not uniform between sites even for those samplers housed in the same shelter type. At the conclusion of the Auckland study it was determined sampling site characteristics and shelter type both played a role in the degree of color change but to what extent was still undetermined.

Variability between daytime and nighttime samplers in Christchurch was captured by the passive samplers. On average daytime concentrations were 19 ± 13.54 ppb higher than the nighttime concentrations for NO and 4.41 ± 2.60 ppb higher for NO₂. However, uncertainties arose in daytime specific NO values. Daytime NO_x filters exhibited color changes similar to those observed in Auckland.

Visually the nighttime filters were unaffected. Daytime color change but no change in the nighttime filters held true for each sampling session. During the final session filters were checked for color change during each day and night filter swap. Color change occurred gradually throughout the week; the amount of change was not consistent between all sites.

At the location where passive samplers were co-located with a continuous monitor each session (n=3), *daytime* passive samplers largely overestimated of NO concentrations (**Table 5**). A measurement error of 71% was found for daytime NO values. While a daytime NO₂ measurement error of 39% was found, passive NO₂ concentrations only overestimated continuous concentration values by 2.70 ppb compared to 12.71 ppb for NO_x.

Table 5. Average over (+) or under (-) estimation of concentration (ppb) from passive samplers

Sampling Period	ΔNO (ppb) (% error)	ΔNO_2 (ppb) (% error)
Daytime	+12.71 ± 1.42 (71%)	+2.70 ± 0.88 (39%)
Nighttime	-2.01 ± 1.20 (1%)	-0.26 ± 0.42 (3%)

Continuous monitor values courtesy of Environment Canterbury

3.3 DISCUSSION

3.3.1 Ambient concentrations

The Auckland study revealed large spatial variability of gaseous pollutants concentrations across the study domain with generally higher NO_x values found within Auckland city's boundaries. The average NO₂ concentration of 13.67 ppb, or approximately 25.70 µg/m³ (calculated at a pressure = 1 atm and temperature = 25 °C) was well below New Zealand's 1-hour standard and 24-hour guideline, 200 and 100 µg/m³ respectively. However, measurements were collected during the autumn season which is generally not a typical sampling season. Autumn is not regarded as a "peak" season for pollutant concentrations. The winter season normally produces the highest NO_x concentrations due to an increase in the lifetime of ambient NO₂ along with reduced O₃ activity.

A visual inspection of the concentration maps suggested a link between the measured concentrations and roads known to be heavily traveled by diesel vehicles. However, linking the concentrations to very specific traffic sources was difficult as available data is minimal and the accuracy of this data remains a problem in the Auckland region. The currently available vehicular data is output from a 2006 traffic model which does not reflect current road and traffic patterns. Percentages of diesel vehicles at specific locations are now highly underestimated as portions of certain roads have converted to solely bus traffic. The most recent data includes location based information which identifies roads recommended for use by large vehicles (i.e., trucks) and bus stop locations. A GIS-based analysis using measured gaseous concentrations and the location based data revealed a significant downward trend of NO_x concentrations with increasing distance to the nearest diesel source (i.e., bus stop or designated diesel route). NO₂ exhibited the strongest trend presumably due to reduced diesel emission effects further from the source accompanied by increased mixing of vehicle emissions with ambient air. This trend has commonly been found for roadways in New Zealand [178] and elsewhere [179-182].

Overall the source which was most often closest to the sampling sites was diesel route not bus stop. Overall, distances in the Auckland study ranged from 0.3 (at the source location) to 630 m, but associations between NO₂ and distance have been reported as far as 1500 m from the roadway [182]. Admittedly this relationship did not hold true at all sites. Possible reasons for this relationship break include direction of the site from the source (i.e., down or upwind), position of the site from the source (i.e., location of roads or buildings between), and source volume (i.e., average number of trucks traveling a specific route or average number of stops per day at a bus stop). These variables most certainly differ between sampling locations and were not taken into consideration during analysis. Ultimately these differences as well as others presumably affect the difference in pollutant concentrations found between sites.

Heavy petrol traffic is found in the Auckland region, as well, and often in the same areas heavily occupied with bus and truck traffic. The majority of the sampling sites were at roadside locations; therefore, distance to nearest road was not applicable. Moreover available data did not include location of “real” roads only “model links” which are straight lines abstracted from the roads. Without accurate source data for both diesel and petrol vehicles it is difficult to disentangle these two sources. However the highest gaseous concentrations did visually trend with diesel sources and heavy contribution of diesel vehicles to air pollution in the Auckland region has been previously reported. Wickham *et al.* reported diesel vehicles in Auckland are estimated to be responsible for 81% of all vehicle-related air pollution health costs (as cited in [171]). According to the 2011 Auckland motor vehicle emissions inventory, diesel

exhaust emissions now account for 55% of motor vehicle NO_x emissions despite representing only 25% of vehicle kilometers traveled. Heavy diesel vehicles account for 35% of these emissions and represent only 6% of vehicle kilometers traveled [183]. The diesel fleet in New Zealand continues to grow. The growth includes a change from a commercially oriented diesel fleet to an increase in diesel SUVs and cars [173].

The highest NO_x concentration (155 ppb) measured during the Auckland study was collected at a site 3 meters from the nearest bus stop. This site was unique as it was located along a portion of the roadway designated for bus traffic only. On the same side of the road as the sampling monitors, four bus stops were located within 70 meters of the sampling location. Therefore, the closest representation of NO_x concentrations measured from an isolated diesel source location was collected at this site.

3.3.2 Passive NO₂/NO_x ratios

While NO₂/NO_x ratios can be determined through passive NO_x sampling, the ratios are on-road measurements and not a direct measurement of NO₂ emitted from vehicles. Primary vehicular NO₂ is typically measured using a roadside vehicle emission remote sensing technique [97] or through methods incorporating hourly concentration data [124]. The difficulty in determining primary vehicular NO₂ from passive measurements is the ability to separate the total amount of measured NO₂ into that which is background, transformed, and primary NO₂. Although the majority of Auckland measurements were collected curbside, it is possible for NO_x concentrations in vehicle plumes to decrease substantially in a matter of a few minutes once the plume is in contact with ambient air [184]. During the dilution process NO reacts with an oxidizing agent to form NO₂. This reaction is reported to be controlled by the rate of plume mixing [126] which would not be constant between sites. Therefore NO₂/NO_x ratios measured through passive sampling are likely representative of transformed NO₂ but the presence of primary NO₂ in the ratio cannot be ruled out.

Although passive sampling NO₂/NO_x ratios cannot directly determine the amount of NO₂ emitted from vehicles, the ratios can be used as an additional means to assess the spatial variability of concentrations. It is not surprising NO is the primary NO_x component at the majority of sampling sites in Auckland, accounting for 70% of total NO_x. Even with increasing direct NO₂ emissions NO remains the primary NO_x component emitted from vehicle exhaust [125]. What is more interesting is the variation in ratios across sites; a fourfold difference was found between the lowest and highest NO₂/NO_x ratio.

The lowest NO₂/NO_x ratio was found at the reference site, farther from direct traffic sources, while the highest ratio was found along a bus only roadway. Mavroidis *et al.* found similar results; higher

NO₂/NO_x ratios measured at background sites as compared to traffic-affected sites. The results were reported to be indicative of the lower NO levels at background sites and the increased atmospheric oxidation of NO to NO₂ [185]. While other reactive atmospheric gases can cause this oxidation, O₃ is the typically responsible for the majority of the conversion. New Zealand's isolated geographical location has a profound influence on its low ozone concentrations; values are often close to natural background levels [186]. Episodes of high O₃ concentrations are possible in Auckland but none have been reported during the autumn season; limited studies reported these events in about 32% of summer days (as cited in [160]). Sea breezes and the lack of transport from other regions result in O₃ events short in duration (an hour or two) [160] which is quite different than prolonged O₃ exposures reported in U.S. regions and elsewhere [187].

Similar to the conclusions made by Mavroidis *et al.* [185] the Auckland NO₂/NO_x ratios appeared to be driven by the atmospheric oxidation or lack thereof of NO to NO₂. While NO_x concentrations were found to decline significantly with increasing distance from nearest truck route or bus stop, a weak positive relationship existed between NO₂/NO_x ratios and distance to source. The loss of the source relationship once total NO_x is partitioned into the NO₂/NO_x ratio suggested a difference in the chemical transformations at each site was possibly driving the difference in ratios. Across the Auckland sampling locations, as the concentration of O₃ increased the ratio of NO₂/NO_x also increased. A higher concentration of O₃ at a site allows for a higher production of NO₂ [188]. For low O₃ concentrations, like those found in Auckland, O₃ appears to be the limiting factor for the production of NO₂. In this case an increase in the NO concentration does not affect the NO₂ concentration [83]. When NO_x is high, O₃ is used up more quickly, and increases in NO_x are mainly in the form of NO [184]. This relationship held true in the Auckland study; the more NO_x was emitted the lower was the proportion of NO₂. Therefore, an increase of emitted NO did not correspond to an increase in the production of NO₂ as the lack of O₃ minimizes this reaction. The relationship reported between O₃ concentrations and the NO₂/NO_x ratios further indicates the ratio values are mainly attributable to secondary formation of NO₂ rather than directly emitted NO₂.

Although the age structure of Auckland's vehicle fleet is changing, used imported vehicles currently comprise a large proportion of the total fleet. In 2013 the majority of the light petrol fleet was Japanese vehicles manufactured prior to Japan's 1998 emissions standard. Similarly, for light diesel vehicles the majority was Japanese vehicles manufactured prior to Japan's 1997 diesel emission standard. These vehicles may include those which were banned in the mid-1990s in Japanese cities for air quality purposes [173]. In 2009 New Zealand's Ministry for the Environment reported that close to half the buses

and trucks operating in Auckland (11,000 vehicles) were built either to Euro 2 or an earlier emission standard [189].

Buses built post 2005 only comprise 33% of the bus fleet. Up until the introduction of the 2007 emissions rule the majority of buses entering the fleet were relatively old used imports. While not many buses leave the fleet, the average age when they do exit is high (mean = 24.7 years, in 2013). Heavy duty trucks on average left the fleet at a similar age (22.4 years) [173]. Auckland Regional Council estimates 10% of Auckland's vehicles emit 50% of the region's air pollution. These vehicles are known as "gross emitters" and contain a greater proportion of older vehicles (mainly manufactured pre-1996) [190] some of which may no longer be equipped with emissions control equipment. The Ministry of Transport estimates up to 10% of petrol vehicles may have had their catalytic converters removed in order to "enhance the vehicle's performance." Prior to the 2007 emissions rule there was no rule that required emissions control technologies to remain on a vehicle or work effectively. It is now illegal to tamper with or remove this equipment; however, the rule does not include the inspection of older vehicles for missing equipment [172]. While current vehicular emissions may be a reflection of lenient emission regulations, the introduction of newer vehicles equipped with the latest emissions control technology may not reduce ambient concentrations of NO_x as much as expected. Based on evidence of an increasing NO_2/NO_x emissions ratio from vehicles, Auckland may see higher levels of primary vehicular NO_2 emitted in the future.

3.3.3 Variation in NO_x filters

Ogawa NO_x filters housed in the Ogawa manufactured shelters exhibited a greater loss of PTIO compared to those under the air sampling units' shelters. One of the biggest differences between the two shelters is the amount of sunlight exposure each shelter allows. Samplers housed in the Ogawa shelters were exposed to sunlight from all angles. Samplers within the air sampling unit receive sunlight from the open end of the Ogawa shelter only up to about two inches from the bottom of the shelter. The sampling unit otherwise blocks the sunlight from reaching the sampler. Labeling tape placed on samplers housed in the air sampling unit shelters, faded over time, as well. Therefore, samplers housed in the unit shelters are exposed to sunlight, but not at the level received by samplers in the Ogawa shelters. Although the Ogawa shelters are described as opaque, the shelters are manufactured from a plastic material which is semitransparent. Shelters attached to the sampling unit are constructed from PVC which is completely opaque (**Figure 14**).

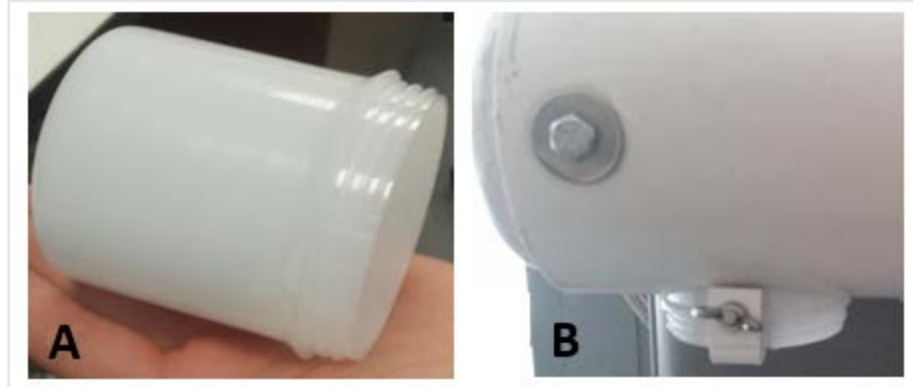


Figure 14. Two types of shelters used in air monitoring studies

Different degrees of color change were seen between filters housed in the two shelter types. (A) Semitransparent Ogawa & Co. manufactured shelter (B) Ogawa shelter inserted into an opaque weather shelter on the air sampling unit. Samplers housed in the Ogawa shelters were exposed to greater amounts of sunlight.

The overestimation of daytime passive NO concentrations collected in Christchurch, New Zealand (obtained from calculations involving collected NO_x and NO₂ values) was thought to be the influence of daytime environmental factor(s) reflected in color change on the NO_x filters. It was acknowledged that inaccurate measurement of NO₂ could result in incorrect NO concentrations. However, this possibility was essentially eliminated by the good agreement between day and night passive and continuous NO₂. In addition, good agreement between passive and continuous NO values were obtained for the nighttime measurements where the NO_x filters did not exhibit color change. From the Auckland study it was determined sampling site characteristics and shelter type both played a role in the degree of color change; the Christchurch study inadvertently narrowed down a possible source of the color change. As the color change was now restricted to a daytime occurrence, it was hypothesized the change was a result of a daytime specific factor (i.e., sunlight, heat, humidity).

Co-located measurements in Auckland and Christchurch of NO_x and NO₂ were highly correlated as a whole across sites (n=7, NO rho= 0.98 and NO₂=0.96). Co-located measurements validate the reproducibility of both sampling and analysis methods; the degree of agreement between two samplers collecting the same pollutant at a single site should be high. At two sites, daytime NO_x samplers were co-located in the two shelter types (i.e., one measurement collected in the Ogawa shelter the other in the unit shelter). Uniformity of values held true for the measurements where color change was not reported. However, at the second location where filters housed in the Ogawa shelter exhibited almost a complete color change to white, the agreement between measurements weakened. The diminished correlation value between daytime NO measurements derived from co-located NO_x samplers in different shelter

types suggested the intensity of color change may relate to a change in the final concentration value. Hard conclusions could not be drawn as a change in the filter color was only reported at one co-located site. To continue narrowing the cause(s) of color change, results from additional studies were considered.

Prior to the SpARTANZ study a similar study conducted in Pittsburgh Pennsylvania, in which NO_x samplers were housed in both Ogawa and the air sampler unit shelters, did not yield noticeable differences in the filter color post exposure. This study took place during winter months (January 13th to February 7th 2014). It is possible lightening of the NO_x filter could have gone unnoticed; the intensity of the purple filter coating varies by batch making it difficult to ascertain if slight changes occurred throughout exposure (**Figure 15**). The same study was repeated during the summer months (July 7th to August 1st). The results of this study, in terms of color change, were similar to the findings in New Zealand. Filters housed in Ogawa shelters exhibited a very obvious color change while the change in those housed in the air sampling units was minimal.



Figure 15. Variation in NO_x filters between batches

The appearance of NO_x filters varies between filter batches. More than one bath may be used during a single sampling session. Due to the variation, often it is difficult to notice slight changes in filters post exposure.

During the summer sampling campaign in Pittsburgh, NO_x samplers were co-located at 16 sampling locations in the two shelter types (i.e., one measurement collected in the Ogawa shelter the other in the unit shelter). Even at the same sampling location, color change occurred for filters housed under the semitransparent Ogawa shelter but not for filters under the sampling unit shelter. These results supported the idea that the change in filter color was occurring as a result of exposure to sunlight. In addition, these results essentially eliminated ambient reactions as the cause of the color change. Color

change was occurring on filters that were exposed to ambient conditions side-by-side at the same sampling location.

Previous studies found an effect of temperature [191-193] and humidity [194-196] on the sampling rate of NO₂ passive samplers. However, these effects were most often reported in extreme atmospheric conditions of cold, dry air and affected NO₂ passive samplers. Nevertheless, to determine if color change was influenced by temperature and/or humidity, values measured at each sampling location during all relevant studies were averaged and compared (Table 6).

Table 6. Measured temperature and humidity values across studies

Location	Sampling Season	Average Temperature (°F)	Average Relative Humidity (%)	Color Change Present
Pittsburgh	Winter	25	66	No
Christchurch	Day	52	86	Yes
	Night	45	89	No
Auckland	Autumn	65	80	Yes
Pittsburgh	Summer	74	67	Yes

Across the four studies presented there was insufficient evidence to infer humidity or temperature *alone* has an effect on the color change of NO_x filters. The average relative humidity across two different Pittsburgh sampling seasons differed by 1% yet color change was seen in only one of those seasons. Similarly between day and night in Christchurch the humidity only differed by 3% yet the day filters exhibited color change. From these results, humidity was ruled out as a major factor of the NO_x filter color change.

Focusing on the Pittsburgh studies it seems plausible the color change or lack thereof could be a result of temperature as the seasonal averages differed by almost 50 degrees. However, Christchurch daytime and nighttime temperatures only differed by seven degrees yet the results measured in terms of color change were opposite. Although it seemed unlikely color change occurred as a result of a seven degree difference in temperature, conclusions could not be drawn with certainty. From the Christchurch data it was not conclusively determined if the seven degree difference between day and night temperature was (1) large enough to result in color change or (2) insignificant and another factor was driving the color change.

3.4 CONCLUSIONS AND LIMITATIONS

Vehicular emissions are known to be a large contributor to air pollution in Auckland's urban area. The analysis of passive gaseous data from monitoring sites in and around Auckland city shows large variability in NO_x concentrations near roadways. From available limited source data, a significant relationship was found between concentrations of NO and NO₂ and proximity to nearest bus stop or heavy diesel route with decreasing concentrations further from the source. While emissions from petrol vehicles contribute to NO_x emissions as well, previous studies support the notion that diesel vehicles are increasingly contributing to air pollution in Auckland.

NO₂/NO_x ratios, assumed to reflect the proportion of NO₂ produced through secondary reactions, were incorporated to provide an additional approach to assess the variability of concentrations between sites. NO was found to be the primary component of total NO_x at all but two sampling locations. The amount of NO₂ at each site seemed to be controlled by the concentration of O₃ rather than the absolute NO_x emission level. An increase in NO_x did not result in higher NO₂ concentrations; O₃ was the limiting factor for the oxidation reaction of NO to NO₂. Improvements have been made to Auckland's vehicle emission regulations forcing the introduction of newer vehicles into the fleet. As the composition of the fleet begins to change, including a higher proportion of diesel vehicles, it will become increasingly important to understand how vehicle emissions are changing over time. With increasing reports of disagreement between emission inventory estimates and projections when compared to actual vehicle emissions, the need for the direct measurements of on-road emissions is growing. Recognizing an increase in primary NO₂ emissions could lead to new strategies or policies necessary to protect human health.

Measurements were made in autumn which is typically not a prime season for measuring air pollutants as concentrations are generally low. Ideally measurements should be collected in summer or winter when exposures to pollutants are highest. Additionally one sampling session took place over a holiday which presumably altered typical traffic patterns therefore possibly altering typical pollutant concentrations. In future studies additional collocation of passive samplers with continuous monitors would be beneficial to validate passive measurements. The development and incorporation of more variables possibly predictive of gaseous pollutants (i.e., traffic counts, land use, population density) as well as additional meteorological factors (i.e., wind speed, wind direction) could be considered as a next step in understanding sources and measured concentrations in Auckland.

3.4.1 NO_x and NO concentration values caveat

It must be acknowledged that some of the NO_x filters used to calculate final NO concentrations did exhibit a loss of PTIO, evident by changes in the filters purple color, over the course of the sampling period. These filters were treated in the same manner as those visibly unaffected; no corrections were applied to final concentration values. Data concerns due to sampling and methodological inaccuracies in manufacturer's protocols are present. The assessment of the validity of the New Zealand datasets reveals a promising number of findings which are conventional in this type of study. These findings include (1) characteristically low field blank values (2) lowest NO_x concentrations at the reference site (3) highest NO_x concentrations at diesel heavy sites (4) distance to roadway relationship with pollutant concentrations (5) a significant relationship with O₃, and (6) good agreement between co-located passive samplers. Concerns over data validity are currently centered on filters which exhibited a noticeable color change (e.g., partially or completely white); although the concentrations measured from filters with less obvious color change may be affected as well. **Tests aimed to determine the effect of the loss of PTIO on the ability of Ogawa NO_x filters to accurately measure NO_x and NO concentrations are presented in Chapter 4. New Zealand NO_x and NO concentration values presented in Chapter 3 should be interpreted with consideration of the complications detailed in Chapter 4. The difficulty of applying a correction factor, accounting for the loss of the PTIO, in order to accurately determine NO_x and NO concentrations is also discussed in Chapter 4. Concentration values reported for NO₂ and O₃ were unaffected by the NO_x filter issues; no evidence was found to suggest NO₂ or O₃ concentration values are inaccurate.** For future NO_x studies, it is recommended an alternative sampler is used for ambient collection. If Ogawa NO_x filters are chosen, opaque shelters are suggested to minimize both color change and the variability in the color change across sites.

4.0 DEGRADATION OF PTIO COATED NO_x FILTERS

4.1 INTRODUCTION

Chapter 4 addresses, in detail, the issues associated with Ogawa NO_x passive sampling. Issues include the interference and degradation of the NO_x filter coating. The results of several experiments aimed to assess the causes and effects of this interference and degradation are presented.

While nitric oxide is a contributor in many beneficial physiological processes [197], it can induce negative biological outcomes as well [198-200]. Nitronyl nitroxides, such as derivatives of 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (PTIO) are used to selectively scavenge and convert nitric oxide radicals ($\bullet\text{NO}$, written as NO) in the body to nitrogen dioxide radicals ($\text{NO}_2\bullet$, written as NO₂) [144]. Manufacturers do not report on the use of PTIO in ambient conditions. One manufacturer lists the application of PTIO as “a nitric oxide radical scavenger used to inhibit physiological effects of NO” [201].

It is reported that PTIO oxidizes NO, yielding one mole each of NO₂ and 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl (PTI) (Figure 16) [202]. However, other reaction schemes are possible. In sampling environments which are high in humidity, it is possible the reaction product, NO₂ will react with itself and produce NO₂⁻ as well as NO₃⁻ [144]. Reactions involving PTIO are typically described in the literature on short time scales, i.e. minutes [144, 203, 204]. This is the first study to analyze PTIO reactions on time scales more representative of reactions taking place during ambient sampling, i.e. hours to days.

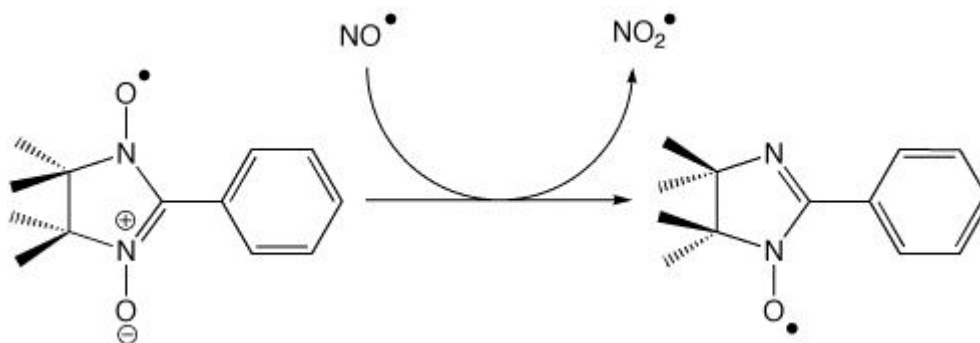


Figure 16. Reaction between PTIO and NO

The oxidation of a nitric oxide radical (NO[•]) by 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl 3-oxide (PTIO) to form 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl (PTI) and a nitrogen dioxide radical (NO₂[•]).

While many studies focus on the use of PTIO as a NO scavenger *in vivo* [144, 202, 203, 205], literature on the development of and decision to use PTIO in the ambient environment is not available. Maeda *et al.* [202] report PTIO has been used to detect NO_x in a polluted atmosphere as a solid stable indicator exposed to air in a canister, but no source was reported. There are no peer reviewed reports supporting the decision to use PTIO for ambient environmental sampling. In fact, previous findings evoke questions regarding the applicability of PTIO for the collection of NO in the ambient environment. PTIO on NO_x filters has been shown to degrade over the course of a sampling period. The extent of the degradation is not uniform amongst filters, varying between sites and sampling seasons. Day and nighttime sampling across 24 sites in Christchurch, New Zealand revealed the most concrete pattern of degradation found to date (**Section 3.2.3**). The presence, or not, of PTIO degradation was shown to vary by the time of day with degradation occurring only in filters exposed during daylight hours. Visually nighttime filters showed no change in the PTIO coating. The results of the Christchurch study suggested the cause of the degradation was rooted in environmental factors present during daytime hours; one of the most obvious factors is sunlight. However, as the amount of sunlight and variation in temperatures are strongly intertwined, it is yet to be determined if the color change is a result of one or both of these factors.

Based on the ambient sampling results presented in **Chapter 3**, it was hypothesized the degradation of PTIO is predominantly catalyzed by light with temperature having a smaller effect. This hypothesis was supported by similar studies focused on NO₂ passive sampling. Several studies reported diminished sampling efficiency of NO₂ passive samplers due to degradation of the collection media as a result of sunlight or heat. Explanations of altered sampling efficiency include *in situ* photolysis of NO₂ or the TEA-nitrite complex [129, 206, 207], degradation of the TEA-NO₂ reaction product [208, 209], and transmission of UV light through the sampler walls causing a chemical breakdown of trapped NO₂ [207]. The conditions and findings of the previously described studies suggest a similar degradation of the NO_x filters could be possible. Degradation of the NO collecting media, indicated by the loss of the purple NO_x filter color, would result in inaccurate concentration measurements. Hauser *et al.* report a similar finding of the degradation of the PTIO-coating on NO_x filters as a result of the exposure environment (e.g. heating during exposure) [210]. The idea that sunlight and temperature play a role in PTIO degradation is implicitly supported by PTIO manufacturers which recommend the chemical is stored at -20 °C [201, 211] or 2-8 °C [212] almost certainly guaranteeing dark storage.

Up until this point, despite the variability in the degradation of PTIO, all NO_x filters had been treated the same throughout the analytical procedure. This is the first study to document the

investigation of the causes and effects of the degradation of NO_x filters. The usefulness of the manufacturer's analytical protocol is also addressed.

4.2 RESULTS

4.2.1 Challenges ensuing from the measurement of NO_x filters

When a NO₂ filter is submerged in water during analysis, the filter coating extracts into the water and produces a colorless solution. However, following the same process, a NO_x filter produces a purple solution due to its chemical coating, PTIO, which is purple. A NO_x filter extract solution absorbs in the visible region, with a maximum absorbance at 560 nm, resulting in interference at the analytical wavelength of 543 nm. Without the addition of the colorimetric reagent, an unexposed NO_x filter extract solution was found to absorb as high as 0.651 at the analytical wavelength (543 nm, 1 cm pathlength). Electronic absorption spectrum collected in the 200-800 nm range for a 1 ppm NaNO₂ standard solution and an unexposed NO_x filter extract solution depict the interference of PTIO at the analytical wavelength of 543 nm (**Figure 17**). Colorimetric reagent was added to the NaNO₂ standard solution, while the NO_x filter extract solution did not contain colorimetric reagent.

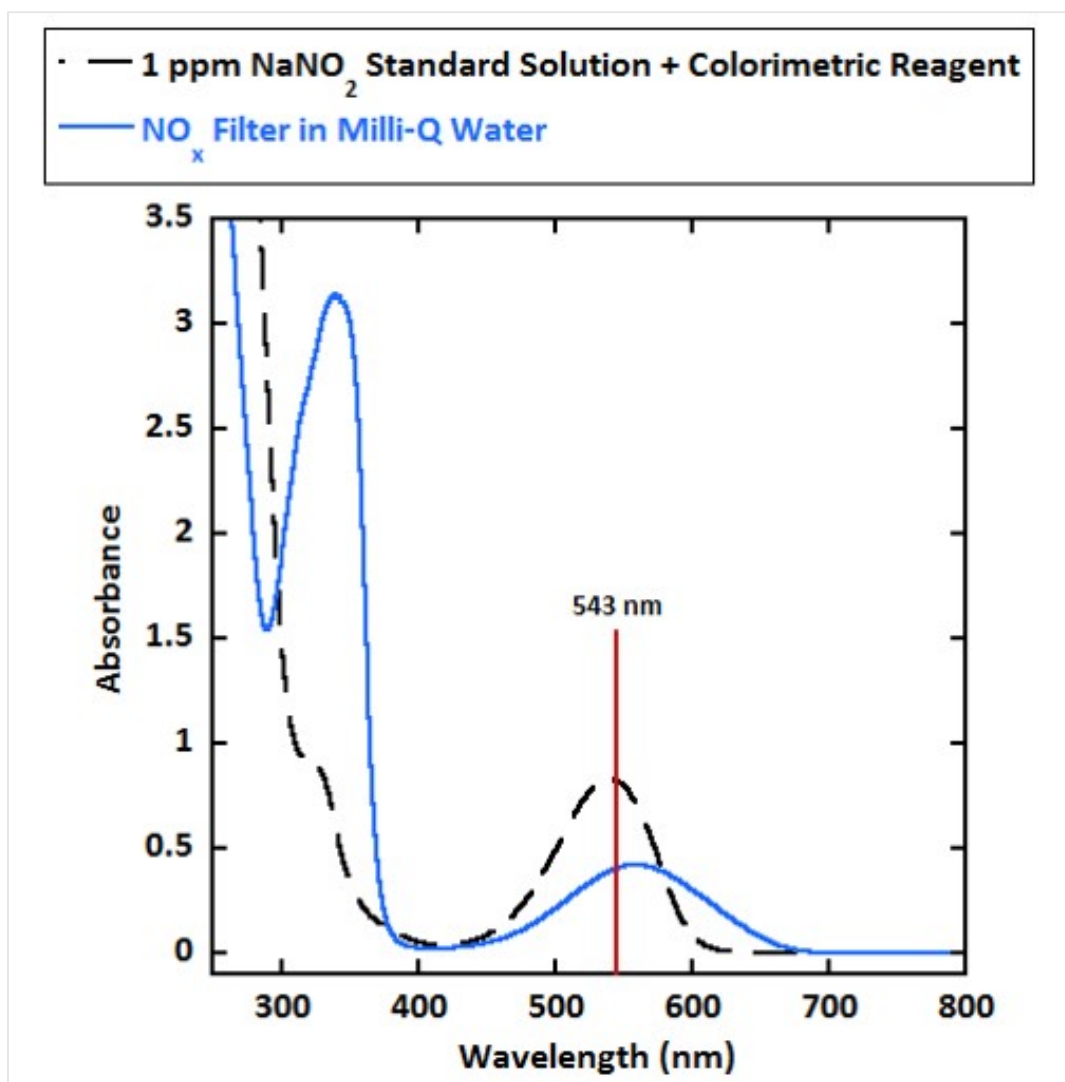


Figure 17. Electronic absorption spectrum: NO_x filter extract solution and a standard NaNO₂ solution

Electronic absorption spectrum of a 1 ppm sodium nitrite (NaNO₂) standard solution and an unexposed NO_x filter extract solution collected in the 200-800 nm range (1 cm pathlength). The NaNO₂ standard solution contained NaNO₂, colorimetric reagent composed of sulfanilamide, N-(1-Naphthyl) ethylenediamine dihydrochloride (NEDA), phosphoric acid, and Milli-Q water (dashed black). The NO_x filter extract solution was comprised of an unexposed NO_x filter submerged into Milli-Q water (solid blue spectrum). The filter extract solution did not contain colorimetric reagent.

The contribution of PTIO to the analytical absorbance value interferes with the accurate measurement of nitrite (NO₂⁻). To test if the interference of PTIO would be overcome by the reaction between the colorimetric reagent and NO₂⁻, colorimetric reagent was added to standard NaNO₂ solutions containing PTIO extracted from unexposed NO_x filters as well as into NaNO₂ solutions containing NO₂ filter extracts (no PTIO). Each calibration curve was blank-corrected. Absorbance at the analytical wavelength from the filter coatings should be accounted for by the blank solutions (containing only filter extracts in

water + colorimetric reagent, no NO_2^-). Therefore, the NO_x and NO_2 calibration curves should align. However, the addition of the colorimetric reagent to the NO_x filter standard solutions did not produce a calibration curve which aligned with the NO_2 filters calibration curve, as expected (**Figure 18**).

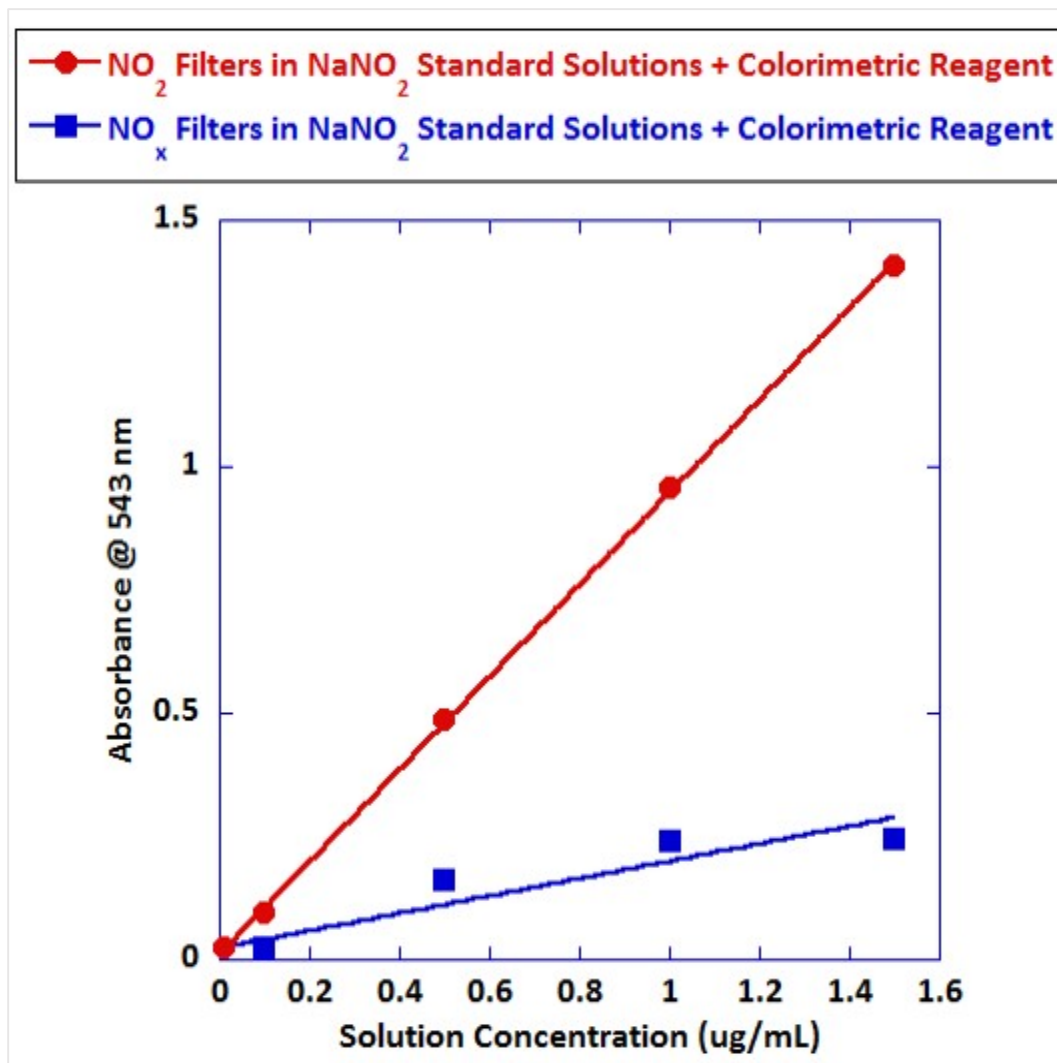


Figure 18. Blank-corrected NO_2 and NO_x calibration curves

An example of the difference between blank-corrected NO_2 and NO_x calibration curves. Both curves were derived from the same standard sodium nitrite (NaNO_2) stock solutions. Each standard solution was divided into two aliquots. Individual NO_2 filters were extracted into the first set of standard aliquots (top, red line) and NO_x filters extracted into the second set (bottom, blue line). All standard solutions contained colorimetric reagent composed of sulfanilamide, N-(1-Naphthyl) ethylenediamine dihydrochloride (NEDA), phosphoric acid, and Milli-Q water. Standard solutions were measured at 543 nm, 1 cm pathlength. The absorbance value of the blank solution (NO_x filter, colorimetric reagent, and water) or (NO_2 filter, colorimetric reagent, and water) was subtracted from each standard absorbance value to create blank-corrected calibration curves. (The NO_2 curve did not change with or without the addition of NO_2 filters into the standard solutions.)

The goodness of fit for the NO_x calibration curve ($R^2 = 0.8679$) was below the value ($R^2 \geq 0.99$) that confidently indicates the relationship between concentration and absorbance is linear, as defined by the Beer-Lambert law, with a margin of tolerable error [213]. At the higher standard concentrations the NO_x calibration line begins to curve which is a deviation from Beer's law. It was hypothesized that this deviation was a result of a chemical interference between PTIO and the colorimetric reagent. This hypothesis was supported by the NO₂ and NO_x calibration curves aligning following the extraction of PTIO from the NO_x filter extract solutions with diethyl ether (Figure 19). Without the interference of PTIO, on average, the slope of the curves differed by < 1%.

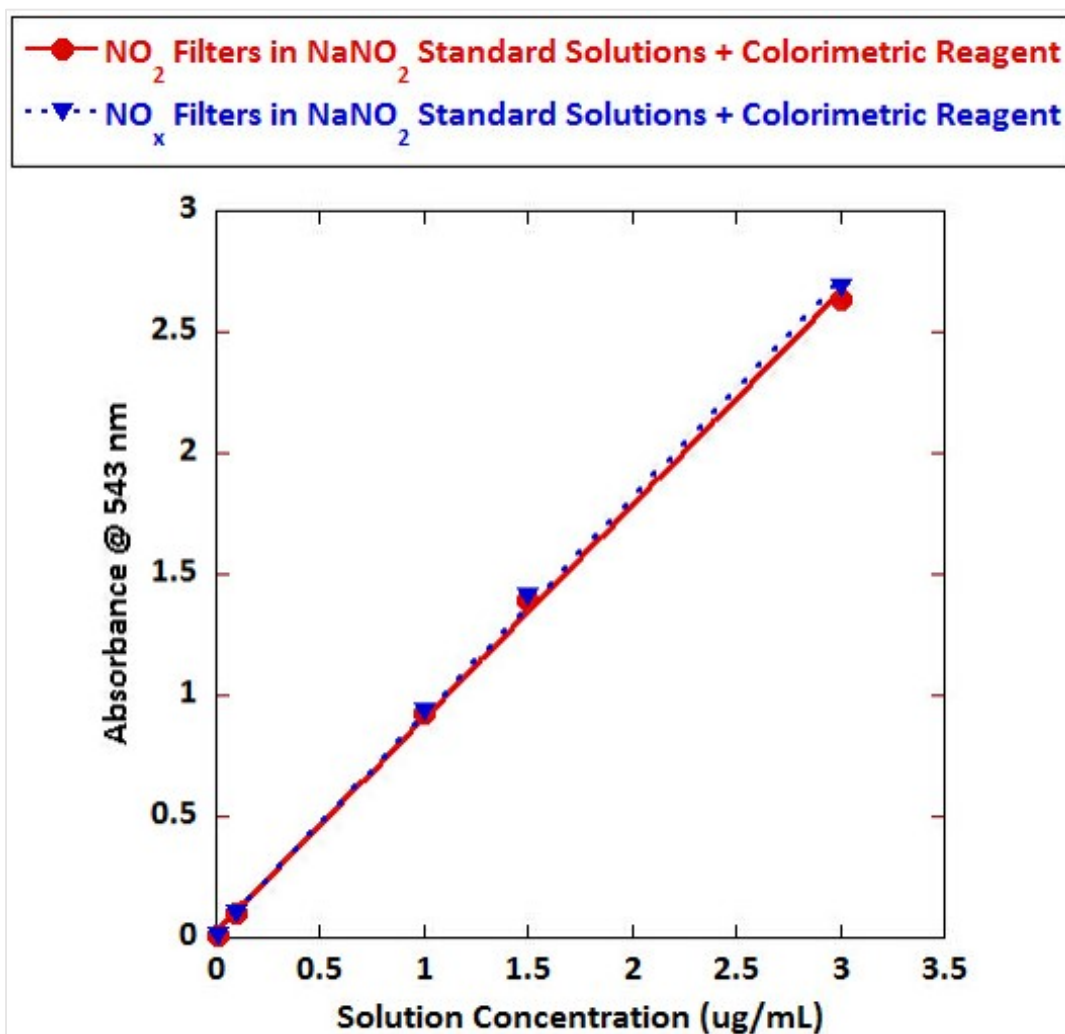


Figure 19. Blank-corrected NO₂ and NO_x calibration curves post ether extraction

An example of the difference between blank-corrected NO₂ and NO_x calibration curves post ether extraction. Both curves were derived from the same standard sodium nitrite (NaNO₂) solutions. Standard solutions contained either NO_x (dotted, blue line) or NO₂ (solid, red line) filters. Calibration curves were produced following extraction

of the filter coatings from the standard filter solutions using diethyl ether. Prior to analysis colorimetric reagent composed of sulfanilamide, N-(1-Naphthyl) ethylenediamine dihydrochloride (NEDA), phosphoric acid, and Milli-Q water was added to all solutions. Standard solutions were measured at 543 nm, 1 cm pathlength. The absorbance of the blank solution (comprised of a NO_x filter, colorimetric reagent, and water) or (NO₂ filter, colorimetric reagent, and water), measured following ether extractions, was subtracted from each standard absorbance value to create blank-corrected calibration curves. (The NO₂ curve did not change with or without the addition of NO₂ filters into the standard solutions.)

4.2.2 Influence of specific environmental factors – light and temperature

In addition to the complications arising from the contribution of the PTIO at the analytical wavelength, PTIO was found to degrade throughout exposure to the ambient environment (**See Section 3.2.3**). PTIO degradation was visually detected through the loss of the purple color on the NO_x filter following ambient exposure. The change varied from a partial to a complete loss of color. When a purple NO_x filter loses its color completely, the filter is then white. A series of indoor experiments involving NO_x filters revealed degradation of the PTIO coating was not unique to the ambient environment.

Light: The placement of NO_x filters in a petri dish on an indoor window sill in the summer resulted in a complete loss of the purple filter color. Filters were left in the dish for a full seven days but complete color change occurred prior to the seventh day. Within a timespan comparable to previously described sampling durations (approximately 5 days), all NO_x filters were completely white on both sides of the filter. During the autumn season, as ambient conditions became increasingly cloudy and cooler, it was necessary to find an alternate means to produce the color change. A distinct change was not observed during the seven day exposure period. Placing the petri dish approximately a foot under artificial light from a desk lamp resulted in the filters turning white quicker than observed during the summer window sill experiment (< 5 days). When a dish was placed within a few inches of the lamp bulb, all filters exhibited a complete loss of color within 24 hours. Similar results were found when PTIO (purchased from Sigma-Aldrich) solutions, which did not contain NO_x filters, were placed on the window sill or under the lamp.

High temperature without light: Filters stored in a foil wrapped petri dish placed within a few inches of a lamp bulb exhibited complete loss of color by the end of the seventh day of exposure. While the foil reached a maximum temperature well above ambient levels (140 °F), the ability of the foil to absorb some of the heat should be considered and suggests that the filters did not reach as extreme of a temperature. Nevertheless, although light was blocked from reaching the filters, exposure to heat alone resulted in complete loss of color.

Cool temperature with light: All filters stored in a petri dish within an illuminated 4 °C cold cabinet exhibited complete color change within a seven day exposure period.

4.2.3 Influence of storage

Unmodified filters: The average absorbance of an unmodified, unexposed NO_x filter extract solution, measured the same day it was extracted into water, was 0.651 (543 nm, 1 cm pathlength). Following storage at 4 °C for 50 days in an Ogawa & Co. semitransparent vial, the average absorbance dropped to 0.420. The storage duration was within the 90 day lifespan of the extracted solution in water reported by the manufacturer [141]. This same loss in absorbance was exhibited in a previously measured 1 ppm NO_x filter extract standard solution similarly stored. Measured prior to storage, PTIO prevented the accurate measurement of the solution's absorbance value (**Figure 18**). However, 50 days following the original measurement, the standard solution's absorbance value was accurately measured due to the partial loss of PTIO from the NO_x filter extract standard solution. The absorbance value of the 1 ppm solution now matched the expected absorbance value (~ 0.9) measured for a 1 ppm standard solution without PTIO. Unexposed white NO_x filter extract solutions were also affected by storage (**Discussed in Section 4.2.4**).

4.2.4 Identification of compounds present on NO_x filters

Several experiments were designed to identify the causes and resultant chemical products of PTIO degradation on NO_x filters and in PTIO solutions. Tested samples included NO_x filter extract solutions (unmodified and degraded, exposed and unexposed) as well as PTIO solutions (unmodified and degraded). Results included here are representative of each sample type, i.e., results were reproducible among samples of the same type.

4.2.4.1 Electronic absorption spectroscopy

Degraded NO_x filter extract solutions and PTIO solutions: Following degradation on the window sill, NO₂⁻ was detected in colorless PTIO solutions which did not contain filters and in unexposed white NO_x filter extract solutions. **At the analytical wavelength, the absorbance value of an unexposed NO₂ filter extract solution (i.e., NO₂ filter extracted in Milli-Q water + colorimetric reagent) is zero, as expected.** However, the absorbance of an unexposed white NO_x filter extract solution was found to be

0.158. For the same solution, the amount of NO_2^- increased over time. Following the 50 day storage period the absorbance value increased to 0.772, almost a five times increase in NO_2^- during storage. An absorbance value of 0.772 would correspond to ~ 0.85 ppm NO_2^- in solution. This concentration of NO_2^- would fall near the top of a NO_x calibration curve. **Figure 20** depicts the absorption spectrum of the three filter extract solutions described above.

Ion chromatography, which does not require the use of colorimetric reagent to detect NO_2^- , verified the presence of NO_x^- in unexposed white NO_x filter extract solutions. An increase in the amount of NO_2^- present in stored NO_x filter extract solutions was detected by ion chromatography, as well. In addition, NO_2^- was detected under anaerobic conditions in degraded PTIO solutions, as well. Without the presence of the NO_x filter, oxygen or nitrogen, NO_2^- was detected (by the colorimetric reagent, only) in PTIO solutions following degradation by light.

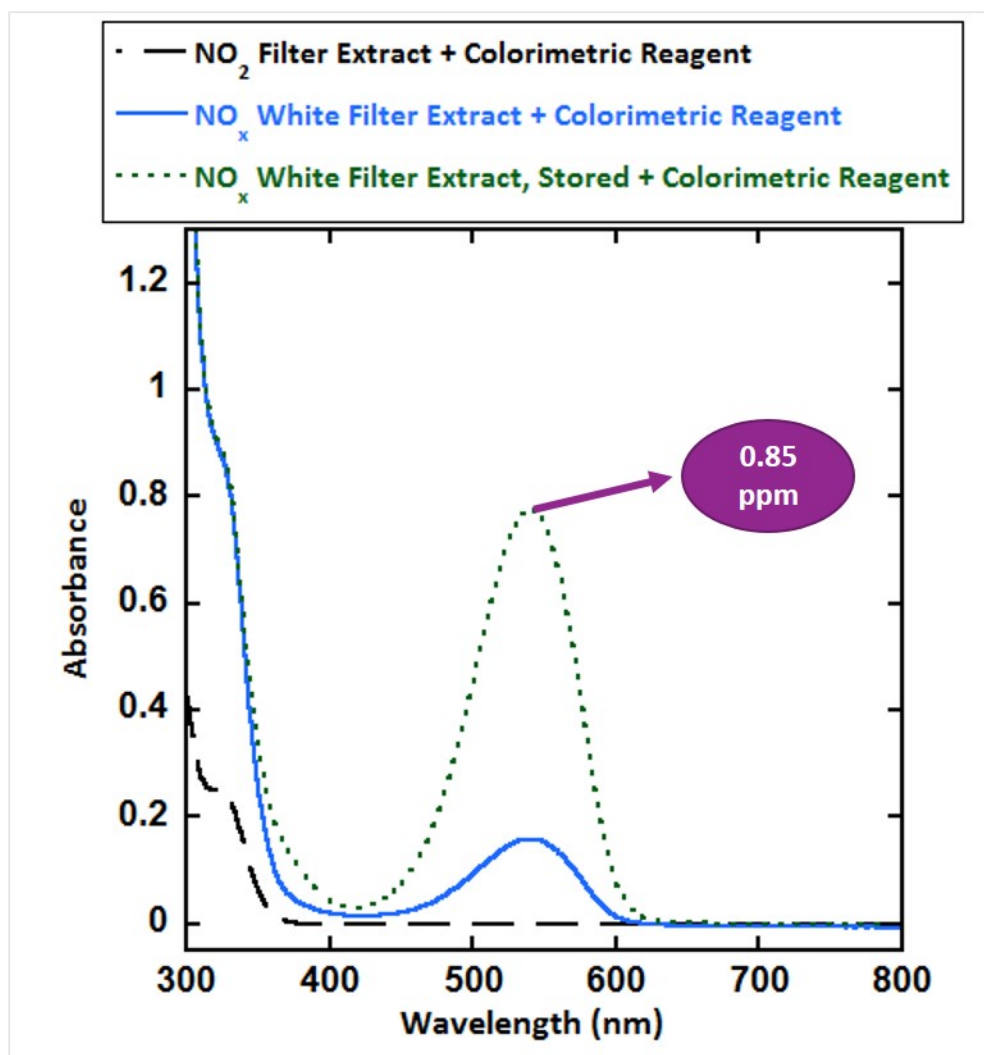


Figure 20. Detection of NO_2^- in filter extracts unexposed to the ambient environment

Electronic absorption spectrum of various unexposed filter extract solutions collected in the 200-800 nm range (1 cm pathlength). The NO_2 filter extract solution contained an unexposed NO_2 filter, Milli-Q water, and colorimetric reagent (dashed black spectrum). The unexposed white NO_x filter extract solution contained a white NO_x filter extracted into water the day of analysis, and colorimetric reagent (solid blue spectrum). The same solution was re-measured 50 days following the original analysis (dotted green spectrum). The colorimetric reagent is composed of sulfanilamide, N-(1-Naphthyl) ethylenediamine dihydrochloride (NEDA), phosphoric acid, and Milli-Q water. Filters used during analysis were unexposed to ambient conditions.

4.2.4.2 Mass spectrometry

Results from the mass spectrometry analysis are found in **Tables 7-10** below. The most abundant ion in each sample solution is defined as the “base peak” and is set to 100% relative abundance. All other peaks are recorded relative to the value of the base peak. The base peak for each sample is highlighted in grey in the tables below. Solutions were run under acidic conditions; therefore, the protonation of tested compounds is expected. For example, PTIO has a molecular weight of 233 and an overall neutral

charge. Under acidic conditions, PTIO picks up a proton (**Figure 21**). The addition results in the formation of PTIO-H with a molecular weight of 234 and an overall positive charge. Therefore, the presence of PTIO in solution is detected as PTIO-H with a peak at $m/z = 234$. Additional protonation is possible depending on analytical conditions (e.g., time until analysis, flow rate).

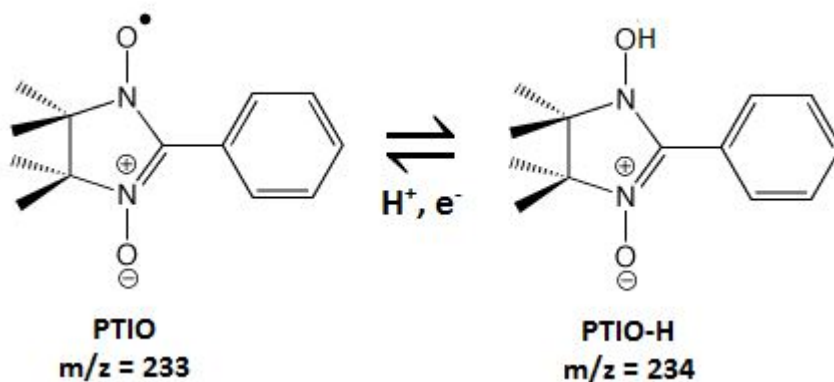


Figure 21. Protonation of PTIO

Running mass spectrometry under acidic conditions results in the protonation of PTIO to PTIO-H. PTIO-H is detected at an $m/z = 234$. That is, mass-to-charge ratio: $m/z = (233 + 1) / 1 = 234$.

PTIO solutions: For the PTIO solution created from Sigma-Aldrich PTIO, the PTIO peak corresponded to PTIO with the addition of **1** (m/z 234, base peak, $[PTIO + H]^+$) or **2** (m/z 235, $[PTIOH + H]^+$) **protons (Table 7)**, as described above. Following exposure to sunlight, the degraded solution, now colorless, was reanalyzed. The base peak shifted to an ion with an m/z of 219, referred to as the PTIO degradation product, or “Compound A.” Compound A was present in the original PTIO solution but in small quantities relative to PTIO. The PTIO signal, m/z 234, dropped to a relative abundance of 2% in the degraded PTIO solution. **Figures 22 and 23** illustrate the spectrum from the PTIO solution minus (purple) and plus light (colorless), respectively.

Table 7. Mass spectrometry results: Sigma-Aldrich PTIO solution

	m/z	Relative Abundance (%)	
		PTIO solution – $h\nu$ (Purple)	PTIO solution + $h\nu$ (Colorless)
PTIO	234	100	2
	235	75	37
Compound A	219	17.5	100

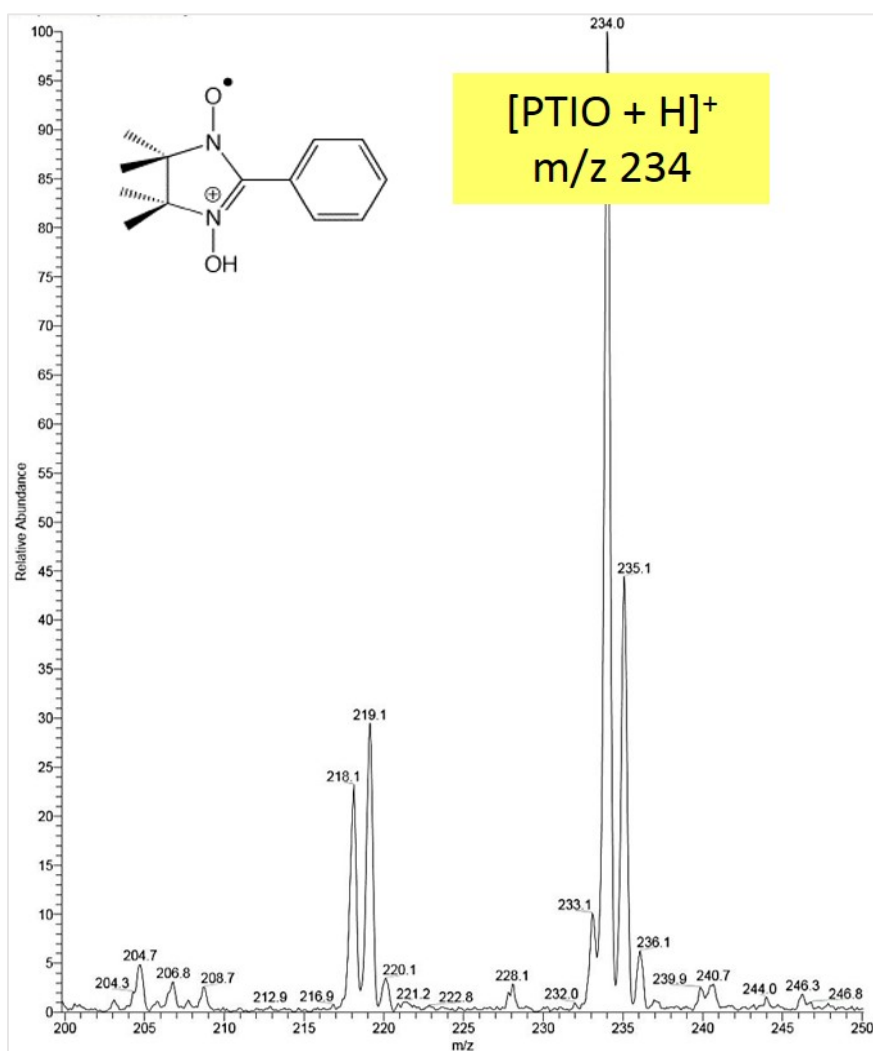


Figure 22. Mass spectrometry: PTIO solution – $h\nu$

Mass spectrometry spectrum of a PTIO solution minus exposure to light. PTIO purchased from Sigma-Aldrich was added to Milli-Q water (1.2 mM). Solutions were diluted in a solvent consisting of a 50:50 mixture of acetonitrile (HPLC Grade, Fisher) and Milli-Q water plus 1% acetic acid (Optima® LC/MS, Fisher). Prior to diluting, the

concentrated samples and solvent were each filtered through a syringe filter (0.45 micron PTFE). Analytical solutions were prepared the day of analysis and consisted of 100 μl concentrated sample and 900 μl solvent. The solution was unexposed to light; therefore, purple at the time of analysis. Protonated PTIO is detected at 100% relative abundance at $m/z = 234$.

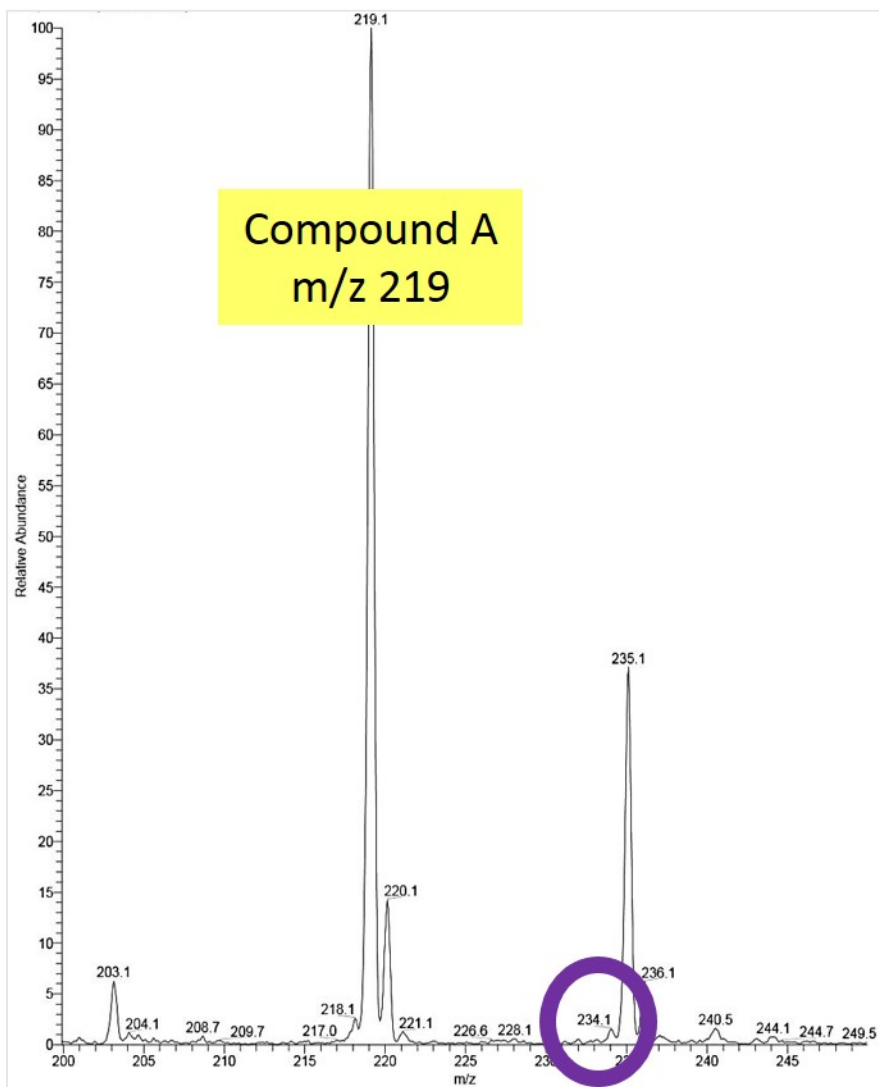


Figure 23. Mass spectrometry: PTIO solution + $h\nu$

Mass spectrometry spectrum of a PTIO solution plus exposure to light. PTIO purchased from Sigma-Aldrich was added to Milli-Q water (1.2 mM). Solutions were diluted in a solvent consisting of a 50:50 mixture of acetonitrile (HPLC Grade, Fisher) and Milli-Q water plus 1% acetic acid (Optima[®] LC/MS, Fisher). Prior to diluting, the concentrated samples and solvent were each filtered through a syringe filter (0.45 micron PTFE). Analytical solutions were prepared the day of analysis and consisted of 100 μl concentrated sample and 900 μl solvent. The solution was exposed to light on a window sill and degraded to a colorless solution. The degradation product, Compound A, is present at 100% relative abundance at $m/z = 219$. PTIO is *barely* detected (2%) at $m/z = 234$ (purple circle).

Storing a PTIO solution in an amber vial minimized the production of the degradation product. Following exposure to light, the PTIO peak ($m/z = 234$) remained the most abundant ion in solution.

Compound A was present but at a relative abundance of only 30%. The results (**Table 8**) were similar to those of the PTIO solution unexposed to light (**Table 7**); the PTIO signal was the base peak.

Table 8. Mass spectrometry results: Sigma-Aldrich PTIO solution in amber vial

	m/z	Relative Abundance (%)
		PTIO solution in amber vial + $h\nu$ (Purple)
PTIO	234	100
	235	45
Compound A	219	30

Unexposed filter extract solutions: Filters unexposed to ambient conditions were extracted into Milli-Q water and stored for 17 days prior to mass spectrometry analysis. White (degraded) NO_x filters were obtained through methods previously described (**Section 2.3.6.1**). Results from filters unexposed to ambient conditions (**Table 9**) were similar to the results found for the degraded PTIO solutions (solutions in which the degradation product, Compound A, was the base peak). The only filter extract solution not containing Compound A was the solution from a NO₂ filter (lacks PTIO coating). For the NO₂ filter, the only peak present correlates to TEA (the chemical coated on NO₂ filters) with the addition of 1 proton (m/z 150). Both types of NO_x filters, unmodified and white filters, presented peaks indicative of Compound A (m/z 219, m/z 220). Presumably, PTIO was not detected in unmodified NO_x filter extract solutions due to the degradation of PTIO during the 17-day storage period. The only peak correlating to PTIO was present at a relative abundance of 6%.

Table 9. Mass spectrometry results: Filters unexposed to ambient conditions

	m/z	Relative Abundance (%)		
		NO ₂ filter extract solutions	NO _x filter extract solutions	White NO _x filter extract solutions
TEA	150	100	100	100
PTIO	234	0	0	0
	235	0	6	0
Compound A	219	0	82	95

Ambient exposed filter extract solutions: Filters exposed to ambient conditions under opaque shelters, including unmodified NO₂ filters, unmodified (purple) NO_x filters and degraded (white) NO_x filters, did not produce peaks representative of PTIO (**Table 10**). The base peak for NO_x filters which were white (degraded) at the start of ambient exposure correlate to Compound A. NO_x filters which were purple (unmodified) at the time of exposure exhibited similar results; no PTIO detected. A peak representative of Compound A was detected (m/z 219) with a relative abundance of 82%.

Table 10. Mass spectrometry results: Filters exposed to ambient conditions

	m/z	Relative Abundance (%)		
		NO ₂ filter extract solutions	NO _x filter extract solutions	White NO _x filter extract solutions
TEA	150	100	100	94
PTIO	234	0	0	0
Compound A	219	0	82	100

Effect of oxygen on degradation products (anaerobic conditions): PTIO solutions (no filters) created under anaerobic conditions in a glove box were also analyzed by mass spectrometry to test the effect of oxygen on the degradation of PTIO. The solutions were almost colorless at the time of analysis. The use of the glove box removed the possibility of unwanted reactions between PTIO and trace amounts of NO indoors, as well. A significant difference in results were not found between anaerobic and aerobic

degraded solutions. Anaerobic results were similar to those presented in **Tables 7, 9-10** where Compound A was present in degraded NO_x solutions in large relative abundance compared to other ions present. Removing oxygen from the solutions did not inhibit the degradation of PTIO or minimize the production of Compound A. An m/z of 323 was detected for all PTIO solutions exposed to light without the addition of NO. A discussion of this peak is not presented here but ongoing analysis is occurring in an effort to identify this ion.

Similarly, Compound A was formed from the reaction between PTIO and NO in both the presence and absence of light. When NO was added to PTIO solutions Compound A was formed at 100% relative abundance. No effect of oxygen was found (**Table 11**).

Table 11. Mass spectrometry results: PTIO solutions + NO

	m/z	Relative Abundance (%)	
		PTIO solution + $h\nu - O_2 + NO$	PTIO solution - $h\nu - O_2 + NO$
PTIO	234	0	0
Compound A	219	100	100

Effect of temperature on degradation products: Using mass spectrometry, no temperature effect (over a 2-day period) was found. Results did not differ between PTIO solutions heated and stored at 37 °C versus solutions stored at 4 °C.

Identification of Compound A: Compound A (m/z = 219) correlates to PTI detected in its reduced and protonated form, [PTIH + H]⁺. PTI is formed through the reaction between PTIO and NO (**Figure 16**). Following the production of PTI from the reaction between PTIO and NO, the formation of [PTIH + H]⁺ in is depicted in **Figure 24**. The mechanism was confirmed by the addition of PTIO and NO into deuterium (D₂, ²H) water. The solution heavy in hydrogen shifts the PTI signal to m/z = 220.

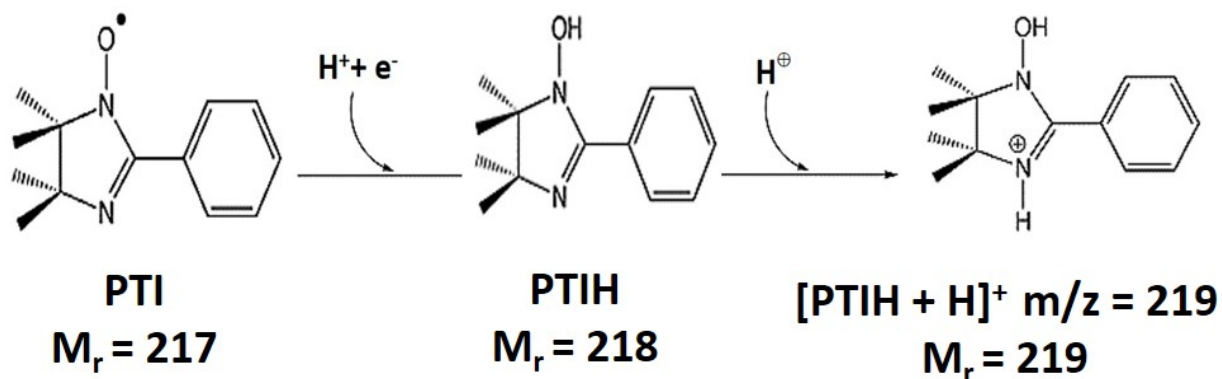


Figure 24. Formation of $[\text{PTIH} + \text{H}]^+$ in the presence of NO

A mass spectrometry signal at $m/z = 219$ was detected in degraded NO_x filter extract solutions, degraded PTIO solutions, and PTIO + NO solutions. PTI (molecular weight = 217) is formed through the reaction between PTIO and NO. In water PTI picks up a hydrogen ion (H^+) and an electron (e^-) to form PTIH (molecular weight = 218). Under mass spectrometry acidic conditions PTIH picks up a proton (H^+) and forms reduced and protonated PTI: $[\text{PTIH} + \text{H}]^+$. With a +1 charge and a molecular weight of 219, $[\text{PTIH} + \text{H}]^+$ is detectable at $m/z = 219$.

4.2.4.3 Electron paramagnetic resonance

A five line (*) EPR spectrum indicative of PTIO (**Figure 25, A**) was found for PTIO solutions produced from Sigma-Aldrich manufactured PTIO. A five line spectrum is produced through an interaction between PTIO's unpaired electron and its nitrogen atoms. A similar, but broadened, spectrum was found for the unexposed NO_x filter. The signal greatly diminished beginning with the exposed white NO_x filters (**C** and **D**) and is absent for the white filters unexposed to ambient conditions (**E** and **F**). A stronger signal was found for filters housed under an opaque shelter (**C**).

Compound A was not detected by EPR which indicated it is EPR inactive. The identification of Compound A as reduced, protonated PTI ($[\text{PTIH} + \text{H}]^+$) by mass spectrometry was in fact confirmed by the EPR results. Although $[\text{PTIH} + \text{H}]^+$ was detected using mass spectrometry, it would not be detected by EPR because it does not have an unpaired electron.

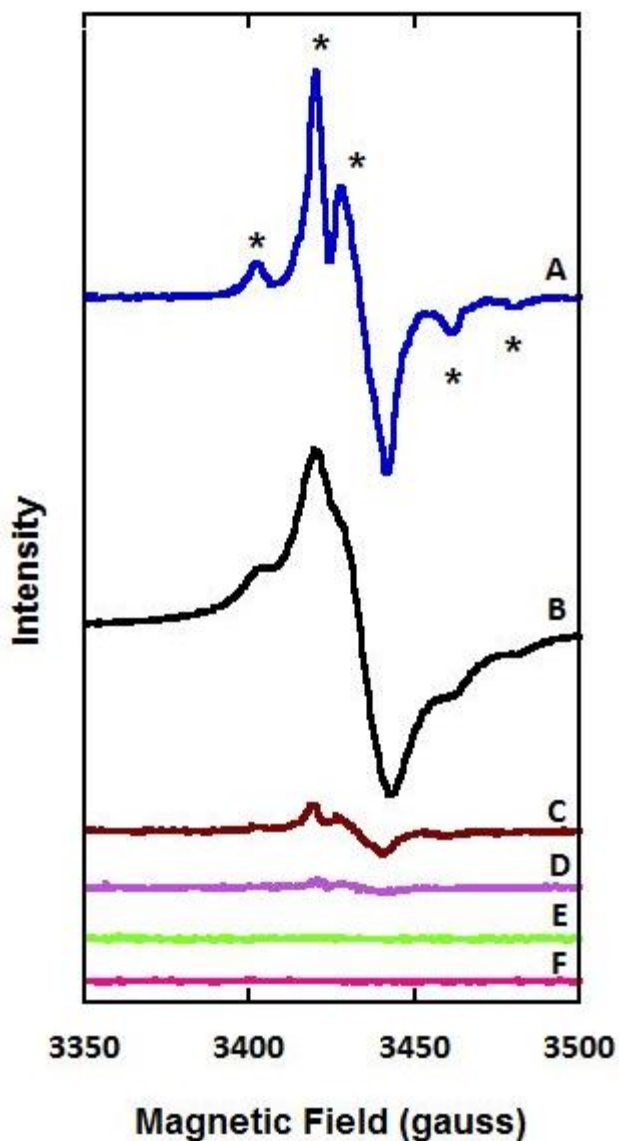


Figure 25. Electronic paramagnetic resonance of various PTIO solutions

EPR samples were prepared by placing 200 μ L of the appropriate solution in a quartz EPR (3 mm id) tube, freezing the tube in liquid nitrogen and storing the samples in liquid nitrogen until analysis. Spectra include: (A) PTIO solution produced from Sigma-Aldrich manufactured PTIO (B) Unexposed NO_x filter extract solution (C) Exposed white NO_x filter extract solution. Filters were housed under an opaque shelter (D) Exposed white filter extract solution. Filters were housed under a semitransparent (Ogawa manufactured) shelter (E) Unexposed white NO_x filter extract solution (F) Unexposed white NO_x filter extract solution

4.3 DISCUSSION

4.3.1 Challenges ensuing from the measurement of NO_x filters

The interference of PTIO prevents the accurate measurement of NO₂⁻ extracted from Ogawa NO_x filters. If this interference is not addressed, NO_x and NO concentration values are inaccurately reported. However, despite the contribution of PTIO and the inability to accurately measure NO and NO_x concentrations following the standard protocol, there is limited literature reporting this interference. Hauser *et al.* reported similar issues with the analytic procedure and attempted to correct for the interference of PTIO without truly understanding the causes and effects of the interference [210]. In addition Hauser *et al.* did not investigate the effect PTIO degradation would have on NO collection [Cindy Hauser, personal communication, July 15, 2014]. Singer *et al.* reported several “inconsistencies” in NO_x masses for samples and blanks, attributing the discrepancies to a possible mix-up of sample filters or vials [214].

Ogawa & Co. report a higher blank absorbance value for NO_x compared to NO₂ but reported values are lower than those found in this study. Suggestions from the company to correct for this absorbance include removing PTIO from the blank solutions through extraction with ethyl ether [141]. However, removing PTIO from the blank solution only does not adjust for the contribution of PTIO in the exposed filter extract solutions. In the analytical protocol, a single point subtraction of the blank absorbance value is recommended [141]. However, in this study a single blank correction was shown to inaccurately account for the contribution of PTIO at the analytical wavelength (**Figure 18**).

A method was developed to remove PTIO from all filter extract solutions. Removal of PTIO allows for the accurate measurement of NO₂⁻ concentrations. Housing NO_x samplers in Ogawa manufactured semitransparent shelters results in the degradation of PTIO during ambient sampling. Intra- and inter-season variations in the magnitude of degradation was found. Elimination of PTIO removes this variation, allowing for uniformity between filters prior to analysis. Previous studies have reported removing PTIO through various extraction methods. Methods previously reported include a copperized cadmium reduction column [215], chloroform followed by filtration through a C₁₈-cartridge [216], and ethyl ether [217]. Most often the extraction is utilized prior to ion chromatography analysis as PTIO is reported to have a detrimental effect on the instrument’s column.

Spiking unexposed NO_x filter solutions with known concentrations of NaNO₂ prior to ether extractions allowed for detection of variations in NO₂⁻ concentrations before and after ether extractions.

Changes in concentration values following extraction would suggest an unwanted reaction between NO_2^- and ether or with a contaminant produced as a result of extraction. A < 1% difference, on average, between NO_2^- concentrations prior to and following ether extractions suggests ether does not affect the NO_2^- measurement.

4.3.2 Influence of specific environmental factors – light and temperature

Similar to the results found in ambient conditions, indoor exposure to ambient sunlight resulted in a complete loss of color from NO_x filters. PTIO degradation was observed as a result of exposure to both natural and artificial light. Typically, NO_x filters within a sampler under a shelter would not receive as much direct light as exposed to during the indoor experiments. Although indoor exposure conditions were likely more extreme than ambient conditions, the purpose of the indoor experiments was to identify the causes of degradation.

The NO_x filters were enclosed in a petri dish suggesting secondary reactions specific to the ambient environment did not contribute to the loss of PTIO. Indoor PTIO degradation diminished as the amount of sunlight present diminished as well. The difficulty in producing a color change during times of reduced sunlight exposure supports the hypothesis that PTIO degradation is light-catalyzed. In addition, the hypothesis is also supported by the findings of ambient studies where degradation did not occur during the winter season or during nighttime hours, neither of which were abundant in sun exposure (**Chapter 3**).

The exposure of foil wrapped NO_x filters to direct heat without light was used to mimic a sampling environment where temperatures were high but sunlight was not present. Degradation of these NO_x filters suggested an increase in temperature alone could result in the loss of PTIO. However, when PTIO solutions were heated to 37 °C and compared to solutions at 4 °C no effect of temperature was found over a 2-day period. Degradation products, identified by mass spectrometry, did not differ between solutions stored at different temperatures. Although mass spectrometry results suggested no effect after a 2-day exposure, a temperature effect on the degradation of PTIO cannot be eliminated. The degradation of PTIO by heat could require a longer time period than degradation catalyzed by light. In addition, it is possible degradation catalyzed by heat is not through the mechanism detected by mass spectrometry but through an alternative mechanism not yet determined.

Loss of PTIO on NO_x filters stored in a cooled cabinet (4°C) while exposed to artificial light implied degradation was possible during exposure to cooler temperatures. However, previous findings suggested

cooler temperatures alone would not result in a loss of PTIO as nighttime filters visually showed no visual signs of degradation. The temperature inside the cold cabinet was about five degrees cooler than the average nighttime temperature during which sampling occurred (**Section 3.3.3**). Therefore, it was concluded that PTIO degradation can occur from light exposure independent of elevated temperature and therefore degradation during colder sampling months is possible when ample sunlight is present. Future investigations into the amount of heat and/or light required to induce color change would be informative.

While the results of indoor experiments and ambient monitoring found sunlight to have a direct role in PTIO degradation, it is possible other environmental factors contribute to the degradation (e.g. humidity). Previous studies reported a negative effect of low humidity values on the uptake rate of TEA-coated NO₂ filters due to a drying effect [194, 196, 218, 219]. Therefore, it is possible humidity could have an effect on NO_x collection as well. An effect of humidity on degradation was not directly tested; however, results of ambient monitoring imply humidity does not affect degradation. Sampling locations with relative humidity values within 1 to 3% of each other exhibited opposite degradation outcomes. Nevertheless, it is recommended that future studies test a direct effect of humidity on degradation.

4.3.3 Influence of storage

The manufacturer's protocol reports a storage time of 90 days for a refrigerated filter extract solution, sealed in an 8 mL semitransparent vial [141]. The vial referenced in the protocol is sold by Ogawa & Co. and is the same vial in which stored NO_x solutions exhibited PTIO degradation and NO₂⁻ production (**discussed further in Section 4.3.4**). Filter extract solutions were stored for 50 days which is less than the 90 day lifetime reported by the manufacturer. If solutions are stored for different time periods, presumably the concentration of PTIO remaining and the amount of NO₂⁻ produced will vary between solutions. Therefore, if the standard protocol is followed (i.e., PTIO is not extracted prior to analysis), the contribution of PTIO at the analytical wavelength would also vary between solutions. Hauser *et al.* also reported this variation in PTIO concentrations with varying storage periods [210]. Therefore, degradation of PTIO not only occurs during exposure but in solution while stored in Ogawa & Co. vials. **The manufacturer's vials were only used for testing purposes. Filters used during ambient monitoring (Chapter 3) were protected from light, stored in opaque vials purchased from an alternative supplier.**

4.3.4 Identification of compounds present on NO_x filters

4.3.4.1 Mass spectrometry

The mass spectrometry results revealed the production of Compound A (m/z 219) as a result of 1) the degradation of the PTIO solution and 2) the reaction between PTIO and NO. Compound A was identified as PTI, detected in its reduced and protonated form. It remains unclear how PTI is produced when NO is not present (i.e. unexposed NO_x filters stored in water or PTIO solutions). PTIO was not detected (or detected in small amounts relative to PTI) in degraded NO_x filter extract solutions or degraded PTIO solutions. Therefore, exposure of Ogawa NO_x filters to sunlight results in the loss of the collection medium, PTIO, during ambient sampling. The loss of PTIO on NO_x filters results in the loss of the ability of filters to collect NO. The amount of NO collected at the end of an exposure period would depend on the extent of the degradation or the time at which degradation occurred during the exposure period. If the degradation of PTIO and the production of NO₂⁻ are occurring simultaneously it is difficult to determine whether or not NO concentrations will be over or underestimated.

4.3.4.2 Electron paramagnetic resonance

EPR results supported the mass spectrometry results with the strongest PTIO EPR signal in the freshly made PTIO solutions. The signal broadened, but was still present, in the unexposed NO_x filter extract solution. Broadening of the signal could possibly be due to an interaction with other compounds on the filter or PTIO reacting with itself. The PTIO signal was minimal to absent in the white NO_x filters, indicating a loss of PTIO in degraded filters, this was supported by the mass spectrometry results. A signal indicative of reduced and protonated PTI was not present, suggesting the degradation product does not have an unpaired electron or it would have been detected through the EPR analysis. Therefore, this finding supports the identification of Compound A as reduced and protonated PTI, [PTIH + H]⁺ (**Figure 24**).

4.3.4.3 Electronic absorption spectroscopy

Perhaps one of the most interesting findings was the detection of NO₂⁻ in unexposed, degraded (white) NO_x filter extract solutions and in degraded PTIO solutions. Enclosed in a petri dish or vial, minimal exposure to indoor air and no exposure to ambient air occurred yet NO₂⁻ was produced. Nitrite was detected PTIO solutions produced under anaerobic conditions as well. Oxygen and nitrogen were removed from the atmosphere under which the PTIO solutions were produced. Therefore, NO was not

initially present but was produced during the degradation process. This finding is supported by the production of NO_2^- during the storage of unexposed white NO_x filter extract solutions stored in screw-top vials. The detection of NO_2^- in the PTIO solutions, which did not contain NO_x filters, eliminated the possibility that the production of NO_2^- was attributed to the filter itself.

Ion chromatography results verified the detection of NO_2^- in unexposed white NO_x filter solutions. Typically, NO_x filters are not analyzed using IC because PTIO is reported to damage the instrument's column [215, 216]. However, following the removal of PTIO from filters during exposure to sunlight (while indoors), the solutions could be analyzed using IC. The analytical procedure for the detection of NO_2^- using IC does not require the addition of colorimetric reagent. Therefore, the detection of NO_2^- by IC confirmed that NO_2^- production is not a result of a reaction between the colorimetric reagent and compounds present on degraded NO_x filters.

At this time the production of NO_2^- in degraded solutions is not thought to be a direct result of the degradation of PTIO to PTI. Although NO_2^- production may be through a minor degradation mechanism, it can have large impacts on ambient sampling since the analyte of interest is produced without exposure to the ambient environment. When compared to continuous monitors, daytime passive NO_x samplers overestimated NO concentrations (**Section 3.3.3**). Nighttime NO_x concentrations matched well with the continuous monitor. Daytime NO_x filters consistently exhibited color change while nighttime NO_x filters visually showed no degradation. The overestimation of NO concentrations from daytime NO_x filters could be the result of the production of NO_2^- during PTIO degradation.

4.4 CONCLUSIONS

Despite the obvious degradation of the PTIO on NO_x filters, reports of this degradation in the literature are nearly absent. Hauser *et al.* reported partial degradation of PTIO [210] but does not elaborate on this degradation. This study aimed to determine the causes and effects of the degradation as well as to elaborate on the problems associated with the manufacturer's analytical protocol.

Electronic absorption spectrum revealed the interference of PTIO at the analytical wavelength. A method was developed to remove this interference by extracting PTIO from filter extract solutions using diethyl ether. The contribution of PTIO at the analytical wavelength is inconsistent between filters. The interference is greater for filters that did not undergo degradation during exposure. Storage of filter

solutions also minimizes this interference. The removal of PTIO eliminates this variation and allows for uniformity between analytical solutions prior to analysis.

Ambient and indoor experiments revealed light to be the driving factor of degradation as both ambient and artificial light resulted in degradation. Depending on the light intensity, complete degradation can occur as quickly as 24 hours from the beginning of exposure. A temperature effect on degradation is under consideration, but no effect was found over a 2-day period. Storage of solutions in amber vials minimized degradation even during exposure to ambient light. The presence or absence of oxygen did not affect degradation. Therefore, at this time, light was the only tested factor to have an effect on PTIO degradation.

Mass spectrometry revealed the presence of a compound, typically at a relative abundance of 100%, in degraded filter extract solutions, degraded PTIO solutions, and PTIO + NO solutions. This compound was present in small quantities in fresh PTIO solutions. The relative abundance of the compound increased through degradation and following the reaction between PTIO and NO. The product was also present in unmodified (purple) NO_x filters stored in solution for less time than the solution lifetime reported by Ogawa & Co. Compound A was identified as PTI in its reduced and protonated form, [PTIH + H]⁺. The mechanism to produce PTI when NO was present was identified, but future tests will also aim to determine the mechanism when NO is absent.

Interestingly, NO₂⁻ was detected in both degraded filter extract solutions and PTIO solutions unexposed to the ambient environment. Production of NO₂⁻ in the filter extract solutions was confirmed by ion chromatography and by colorimetric reagent detected by electronic absorption spectroscopy. The presence of NO₂⁻ in the PTIO solutions was only confirmed by a color change in the solutions (colorless to pink) following the addition of the colorimetric reagent. The production of NO₂⁻ in filters unexposed to NO_x suggested degraded NO_x filters could overestimate ambient concentrations. Production of NO₂⁻ increased for degraded NO_x filter extract solutions stored prior to analysis. Future studies will aim to determine the source of NO₂⁻, as well.

A limitation of this study was unmodified (purple) NO_x filters were stored in Milli-Q water prior to analysis. Due to limited materials, it was not possible to submerge the filters in water and analyze the solutions the day of analysis. Although PTIO was present on the filter during ambient exposure (under opaque shelters) it was not detected in the stored solutions. PTIO was shown to degrade in solution; therefore, the lack of a PTIO signal was most likely due to storage degradation.

Ideally a correction factor would be applied to account for the loss of PTIO. However, as the degradation is not uniform between filters, it is difficult to apply such a factor. A further complication in

applying a correction factor is the production of NO_2^- in degraded NO_x filter extract solutions unexposed to the ambient environment. Therefore, the current method uses a collection medium which degrades in light and produces the analyte of interest, NO_2^- .

Recommendations for future NO_x collection would be to utilize an alternative mechanism. If Ogawa filters are used it is recommended the samplers are housed under opaque shelters during ambient exposure. Opaque shelters would minimize the degradation of PTIO and minimize the variation in degradation between filters. Ether extractions are necessary during the analytical procedure to remove the interference of PTIO. Finally similar storage times of filter extract solutions are recommended in an attempt to keep the amount of degradation and production of NO_2^- during storage consistent between solutions.

5.0 A REVIEW OF PASSIVE SAMPLING WITH SPECIAL REGARD TO NO_x ANALYSES

5.1 INTRODUCTION

Reliably measuring pollutant concentrations in a variety of atmospheres is a necessary step in linking pollutant levels to possible health and ecological effects [128]. Passive sampling devices (PSDs) provide an alternative to conventional sampling wherein air is actively pumped through a collection device. PSDs are useful to measure average pollutant concentrations when real-time concentrations from active monitors are not necessary, available, or feasible. Originally designed as a personal monitoring device for gaseous pollutants over 4 decades ago [220], the use of PSDs have expanded to a variety of environmental media including ambient air, water, soil, and sediment [221]. Passive sampling of gaseous pollutants has proven to be a feasible substitute to active monitoring of ambient pollutants offering high spatial resolution in a variety of monitoring situations at a lower cost [215, 222-224]. The cost-effectiveness, ease of use, sensitivity, flexibility of placement and non-intrusive nature of passive samplers make them appropriate candidates for assessment of air quality on a regional-scale [143, 145, 221, 225, 226].

Originally developed as a personal monitor for SO₂ and adapted for NO₂ monitoring in an occupational setting [227] Palmes tubes paved the way for the development of commercially available passive samplers with broad measurement capabilities, including volatile organic chemicals, benzene, nitric oxide, ozone, carbon monoxide, and sulfur dioxide [143]. Palmes tubes remain one of the most extensively used passive samplers, especially in Europe [128]. Although different types of passive samplers exist (e.g., tube, badge, and radial types), all samplers operate under the same governing principle of diffusion according to Fick's law. Samplers operate by the unidirectional flow of analyte from the sampling area across a measurement area of known dimensions onto an absorbing medium [226].

According to Fick's law, diffusion, or small scale turbulence, transports the sampling substrate (e.g., NO_x, SO₂, O₃) on to a sorbent (e.g. filter) [145]. The sorbent can be physically sorptive (e.g. active carbon) or as in the case of NO_x chemisorptive. In the case of a chemisorptive sorbent, a reagent (e.g., triethanolamine, potassium iodide + sodium arsenite) coated on a filter is designed to chemically react with a specific substrate; ultimately through this reaction the analyte of interest is trapped on the sorbent. Detailed discussions of the theory behind passive sampling is thoroughly documented [139, 145, 221];

briefly, a description of the amount, M , of the analyte transported by diffusion in time, T , is given by the following relationship (**Equation 5**) [29]:

$$M = D \left(\frac{A}{L} \right) C T \quad (\text{Equation 5})$$

Where:

M =amount collected (ng)

D =molecular diffusion coefficient of the analyte (cm²/min)

A =cross-sectional area of the diffusion path (cm²)

L =diffusive path length (cm)

C =analyte concentration in the medium examined (mg/m³)

T =sampling time (min)

The product of $D \times (A/L)$ is the theoretical sampling rate or uptake rate for a specific compound. Uptake rates are a function of both the sampler geometry (A/L) (**Figure 26**) and the sorbent material being used. Rates are compound dependent, not always determined for every compound for a given sampler, and may vary by literature source [228]. The diffusion coefficient, D , is a function of temperature, humidity and pressure [129, 229]. Although widely studied, the diffusivities of gases such as O₃, NO₂, and NO remain relatively uncertain, often differing from manufacturer-reported values [192, 193, 228, 230].

Fick's law in relation to uptake of gaseous pollutants is well documented [29, 143, 145, 206, 221]; however, the law assumes ideal stable conditions. Under actual sampling conditions the theoretical and actual sampling rate of a pollutant may differ due to environmental influences [128]. Several assumptions are made in calculating the theoretical sampling rate: the molecular diffusion coefficient is known for the gas in air (in conjunction with its dependence on environmental factors); the absorbent surface is a perfect sink, once absorbed, the gas can be measured quantitatively; there is no adsorption on or absorption to the sampler walls; no unwanted chemical reactions occur during sampling that would affect final concentrations; and a constant concentration is maintained at the entrance of the sampler [129]. Sampler design should aim to keep the above assumptions valid or at least sufficiently close that the error introduced from any deviations from the assumptions is minimal [128, 129].

According to Fickian diffusion, the theoretical uptake rate of a sampler is a function of the length, L , and the internal cross-sectional area, A , of the sampler (**Figure 26**) [206, 226]. Movement of a gas to the absorbent is proportional to the surface area over which diffusion takes place and inversely proportional to the diffusion path length. Therefore, altering the geometry of the sampler body can

ultimately optimize the sampling uptake rate (i.e. reducing the diffusion path length and/or increasing the diffusion cross-sectional area) [231].

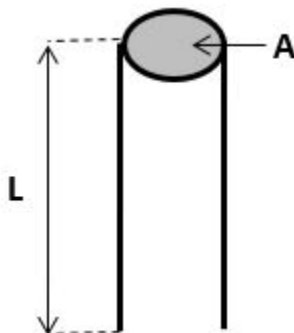


Figure 26. Schematic diagram of a tube-tube diffusion sampler

The uptake rate of a diffusive sampler depends partially on the total length (L) of the diffusion path and the cross-sectional area (A) of the diffusion tube. L and A are defined by the geometry of the sampler. L : the distance between entrance of the air at the sampler and the absorbent surface. A : the cross-sectional area of the narrowest portion of the sampler [139].

Current passive air samplers include modifications of the original Palmes tube design which aim to minimize meteorological effects on collection (e.g., wind speed, temperature, humidity) as well as improve collection specificity and efficiency [128, 145]. Several reviews detail the variety of commercially available passive samplers including sampler designs, environmental influences, advantages, disadvantages, and analytical methods [29, 128, 129, 143, 145, 206, 221, 226]. Generally, passive air samplers can be grouped into three design types: tube, badge, and radial. For the measurement of NO_x the analytical method is visible spectrophotometry at 545 nm. An alternate more expensive technique is ion-chromatography, reported to improve the analytical sensitivity and precision of analysis. The absorbent most used is triethanolamine (TEA), but other absorbent types exist for various sampler types (e.g. sodium carbonate + glycerol: Analyst™ passive sampler; potassium iodide + sodium arsenite: IVL sampler; CHEMIX™: Maxxam PASS) [128]. Varying preparations within absorbent types also exist (e.g. 20% TEA in de-ionized water, 50% TEA in acetone) [232]. Most commercially available passive samplers are axial (cylindrical) in shape while the newest models offer an improvement in geometry with a radial design. Arguably, most of the literature surrounds the oldest type of passive samplers, tube-type, followed by badge-type samplers with limited studies on the newest passive sampler type, radial.

5.2 TYPES OF PASSIVE SAMPLERS

5.2.1 Tube-type samplers

Much of the literature is centered on tube-type samplers which are closest in design to the original Palmes tubes. Tube-type samplers are hollow cylindrical acrylic tubes suspended vertically during sampling. A fixed cap at the top of the tube holds either filter paper or stainless steel screens, which are treated with an absorbent that collects the gas of interest [206]. Tube-type samplers exhibit a long, axial (longitudinal) diffusion length and a relatively small cross-sectional diffusion area [128] generally resulting in relatively low sampling rates [225]. Typically a cap is removed from the bottom of the tube at the beginning of collection. A modification of the original Palmes tube includes the addition of a fitted membrane at the tube's open end to minimize wind effects on sampling [128]. This widely used (especially in Europe) tube-type sampler is referred to as the Gradko sampler, manufactured by Gradko Environmental [128]. Gradko samplers are available for both NO_2 and NO collection, but unlike the other Gradko samplers the NO_2 and NO_x samplers are not equipped with a fitted membrane. The membrane introduces resistance to molecular diffusion which adds a challenge in determination of the uptake rate as the estimation of diffusion impedance is not easily estimated [129, 233]. This resistance should be accounted for in the sampling uptake rate provided by the manufacturer.

The TEA absorbent used in Gradko samplers for collection of NO_2 is available in two options: 20% TEA/water absorbent and 50% TEA/acetone absorbent. For the collection of NO_x a two-tube pack is available. The first is a conventional tube designed to only absorb NO_2 . NO_x is taken up into the second tube which contains two absorbent caps. NO_2 is absorbed into the first cap by TEA. NO_x enters the tube. NO_2 is absorbed by the first cap while NO passes through the first cap into the second cap containing a proprietary absorbent. The proprietary absorbent oxidizes NO to NO_2 which is then back diffused into the first cap [234]. The concentration of NO is ultimately determined by taking the difference between NO_2 collected in each sampler. Similar in theory to Gradko NO_x samplers, in principle, the original Palmes tube could be used to monitor personal exposure to NO . NO (along with any NO_2 collected) diffuses through the tube's TEA-coated screen, where it hits an oxidizing layer comprised of chromic acid. The chromic acid converts NO to NO_2 which is trapped quantitatively by the TEA. The Palmes version consists of a chromic acid-coated screen which gives accurate and reliable results if in place for 24 hours or less; making it necessary, therefore, to insert immediately before and remove immediately after sampling. Due to the sampling duration restrictions the Palmes sampler is not feasible for ambient collection of NO_x [235].

A variety of additional tube-type samplers exist commercially. These samplers vary in dimensions (diffusion length x diffusion area), absorbent, sampling rate, and analytical method. Tube-type samplers are generally not suitable for short-term monitoring although new developments are now allowing for shortened sampling periods. Recommended sampling time of tube-type samplers is generally 2-4 weeks, although times may be shorter or longer depending on sampler manufacture (type) [128]. The Passam sampler (membrane equipped), derived from the Palmes tube, is designed for two different sampling periods. The short term Passam sampler (2.0 cm x 4.15 cm²) is applicable for daily measurements (8 to 48 hours) while the long sampler (7.4 cm x 0.75 cm²) is designed for a more typical tube-type sampling period (1 to 4 weeks). Passam samplers are available for NO_x collection but come with both an increase in the sampling period (2 to 4 weeks) and measurement uncertainty [236]. Sampling duration has been shown to have an effect on concentrations determined from passive samplers, especially those of the tube-type variety [129]. TEA absorbent tube-type samplers are analyzed by visible spectroscopy at 545 nm; however, to improve analytical sensitivity and precision ion chromatography is now the preferred analytical method [128].

5.2.2 Badge-type samplers

Badge-type samplers typically have shorter diffusion path lengths and larger surface areas which allow for higher sampling rates (**Figure 27**) [139]. Higher sampling rates allow for shorter sampling durations. Without the large air gap between the collection medium and the sampler face, badge-type samplers may be more affected by air velocity than other sampler types, reportedly requiring a minimum face velocity [139, 237-239]. A layer of microporous material separating the collection medium from the outside air usually defines the diffusion barrier of badge samplers. The length of the diffusion barrier, L , is approximated by the thickness of the porous layer [29]. Typically the diffusion length of badge-type samplers range from 0.6 cm up to 1 cm which is much smaller than the 7.0 cm length of common tube-type samplers [128]. The cross-sectional area of the diffusion path, A , is the total area of the pore openings [29].

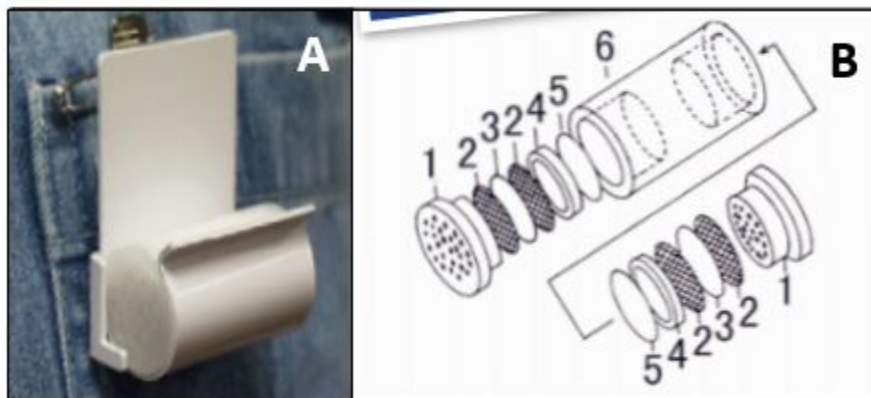


Figure 27. Badge-type sampler

The Ogawa passive sampler is an example of a badge-type sampler. (A) An assembled Ogawa badge. (B) The components of the Ogawa badge. The path length is minimal as there are no large gaps (~6 mm) between the inlet (1) and the collection filter (3). The only separation is a very thin stainless steel screen (2). Copyright permission granted by Ogawa & Company [140].

Similar to tube-type samplers, various badge-type samplers (e.g., Yanagisawa filter badge, Ogawa sampler, Willems badge, IVL sampler, and Maxxam PASS sampler) of differing geometry exist, but their basic geometry is the same. TEA absorbent is used in the majority of badge-type samplers for the collection of NO₂. The Maxxam PASS sampler collects NO₂ with a proprietary pre-treated solid collection medium, CHEMIX™, rather than the typical TEA absorbent. Information on the performance of this sampler is limited as the composition of CHEMIX™ is not publicly accessible and field evaluation data is limited. Badge-type sampling durations range from hours to days with options up to one month depending on the specific sampler. The ability to measure hourly or daily concentrations allow for personal, indoor, and/or occupational monitoring. Like tube-type samplers, TEA absorbent badge-type samplers are analyzed by visible spectrophotometry around 545 nm but analysis using ion chromatography is also possible [128].

5.2.3 Radial-type samplers

The newest variety of passive samplers developed and patented in the mid 1990's is one of radial design. As previously discussed, altering the geometry of a sampler, can increase the sampling rate. The radial design, now registered trademarked as Radiello, offers a larger diffusive surface as compared to the axial design of tube and badge-type samplers without an increase in the amount of adsorbing media. The radial sampler typically exhibits a cylindrical, coaxial design for both the diffusive and adsorbing surface. The

Radiello® sampler's cylindrical outer diffusive surface acts as a diffusive membrane, gaseous pollutants move axially parallel to a cylindrical adsorbent bed coaxial to the diffusive surface (Figure 28) [240].

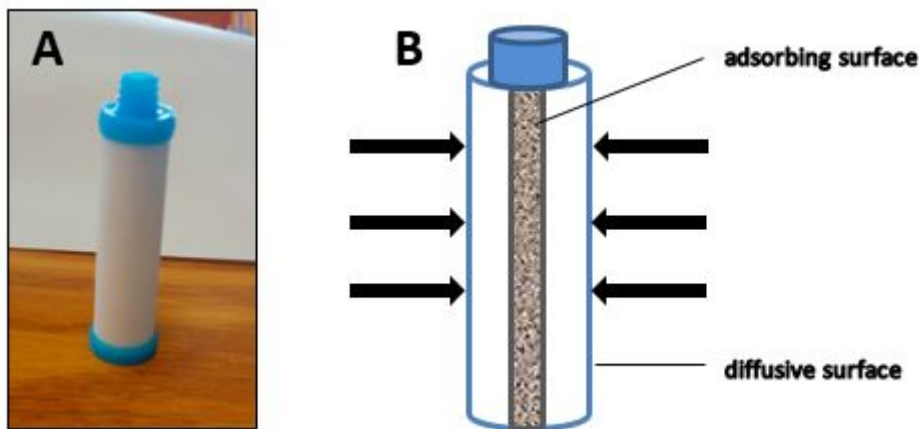


Figure 28. Radial-type sampler

The Radiello® sampler is an example of a radial-type sampler. (A) The diffusive body of the Radiello® sampler. Prior to sampling, the adsorbent cartridge is inserted into the opening at the top. The body screws onto a supporting plate which clips into a protective weather shelter. (B) Depiction of the sampler highlighting the adsorbing and diffusive surfaces. Analytes can access the adsorbent material throughout the 360° diffusive barrier/body allowing for at least three times higher uptake rates than for tube or badge-type samplers. (B) Adapted from [241].

The diffusive body used for the collection of NO₂ is opaque to light (suited to the sampling of light-sensitive compounds) and made of microporous polyethylene (1.7 mm thick). The Radiello® sampler can collect a variety of compounds (e.g., aldehydes, VOCs, O₃, and NO₂) but does not have the ability to measure NO. For the collection of NO₂ the adsorbent cartridge is coated with TEA. Prior to collection the adsorbing cartridge is inserted into the diffusive body and screwed onto a supporting plate. While the manufacture reports the sampler is not affected by inclement weather conditions because of its water-repellant diffusive body, a mountable polypropylene shelter is recommended for outdoor exposures. The shelter which is reported to offer the best compromise between protection against inclement weather and adequate ventilation has the capacity to house up to four samplers [240]. The sampler is not suitable for long-term ambient monitoring but is applicable for shorter durations of sampling (1 to 24 hours or 1 to 7 days). Similar to badge-type samplers an advantage of radial-type samplers is their ability to monitor short term exposures in an indoor or occupational setting [128]. According to the Radiello® manual, NO₂ is chemisorbed by TEA and quantified as nitrite (NO₂⁻) ions by visible spectrophotometry at 537 nm [240]. Currently Radiello® appears to be the only commercially available radial-type sampler.

5.3 ANALYTICAL METHODS

The method originally used by Palmes *et al.* for the measurement of trapped NO_2^- on passive filters involved the photometric determination of NO_2^- with quantification of concentration through electronic absorption spectroscopy at a wavelength of 540 nm [227]. Spectrophotometry is the procedure used to analyze the concentration of colored compound in solution by measuring the absorbance of the compound at a specific wavelength. Nitrite does not absorb light in the visible region. Therefore, to measure a photometric signal, a compound must be added to the analyte solution that will react with the NO_2^- to produce a chromophore (colored solution). The intensity of the color can be used to determine the amount of NO_2^- in solution through application of the Beer-Lambert Law [242]. An ideal colorimetric reaction should include initially colorless reagents which react to form a colored, stable, soluble, and quantitative product [243]. The colorimetric reagent used by Palmes *et al.* during the analysis of NO_2^- filters, known as the 'Saltzman reagent,' is reported to react specifically to NO_2^- [154]. This photometric method is still recommended in today's sampler protocols, but with slight alterations to the original reagent.

Ion chromatography (IC), when available, rather than colorimetry has been used in studies to quantify NO_2^- collected by a variety of passive sampler types [195, 244-246]. Gair *et al.* found the limit of detection (LOD) for Palmes tubes to be over eight times lower using IC analysis compared with colorimetric methods [247] while Plaisance *et al.* reported a 14-fold decrease in LOD using IC [248]. Therefore, although more costly, the ion chromatographic determination of NO_2^- provides greater analytical sensitivity and precision of analysis, so it may be better suited for detection in areas of low concentrations [128, 129].

5.4 INFLUENCE OF ENVIRONMENTAL FACTORS ON PASSIVE SAMPLING

5.4.1 Influence of air velocity

Ambient air movement can alter a sampler's effective diffusion path length affecting its uptake rate. Depending on environmental circumstances, the effective path length may be greater or less than the path length calculated from the sampler geometry [129, 139, 145, 226]. High external wind speeds can

lead to a reduction in the effective diffusion path length, known as 'wind shortening' [139] resulting in an increased sampling rate. High air flow into the sampler opening disturbs the static air layer within; ultimately this disturbance reduces the effective path length [139]. Air concentrations will be overestimated if the theoretical uptake rate is used [139, 235, 248-250]. To the contrary, without sufficient external air movement at the sampler, gas molecules close to the sampler opening that are diffusing into the sampler will not be replaced. A 'boundary layer' (L_b) is created between the stagnant air within the sampler and the moving air outside the sampler; the effective diffusion path length is increased. This boundary layer must be included in the value of the effective diffusion path length ($L + L_b$) [139, 206]. The significance of the boundary layer is partially dependent on the sampler's nominal path length. A sampler with a long path length and a small cross-sectional area should be relatively unaffected by the air velocity outside the sampler while a sampler opposite in design will be more greatly affected [139]. Therefore, badge-type samplers will be affected more than tube-type samplers as badge-type samplers exhibit a higher ratio of the boundary layer to effective diffusion length ($L_b / (L + L_b)$) [206].

However, even in studies where the same types of samplers are tested, discrepancies exist on the extent of the effects of wind. Findings between studies are hard to associate as test parameters (e.g. ranges of wind velocity) differ. To eliminate the variance in test parameters, Plaisance *et al.* investigated the effect of wind on six different diffusive samplers at varying air velocities in a laboratory exposure chamber (tested samplers did not all collect NO_2 although samplers of the same brand are available for NO_2 collection) [251]. At least one sampler from the three major types of passive samplers was tested (i.e., tube-type, badge-type, and radial-type). The change in uptake rate due to changes in air velocity was compared to the rate found under standard conditions (40-50% relative humidity, 20 °C temperature, and 0.5 m s^{-1}). A systematic increase in uptake rate with increasing wind speed was reported for all diffusive samplers following a logarithmic function. At 2 m s^{-1} , tube-type samplers without a diffusive membrane at the open end of the tube exhibited a 40-50% increase in uptake rates. Other studies reported similar results for open ended tube samplers [248, 249].

Badge and radial-type samplers equipped with a diffusion membrane exhibited lesser effects from changing air velocities (8 to 18% changes in uptake rate at higher velocities). The porous diffusion membrane may actually limit the reduction in the effective diffusion path length induced by higher wind velocities. For lower air velocities (close to 0 m s^{-1}) a decrease of uptake rates between -13 and -30% compared to those under standard conditions was reported. Of all samplers tested, the Radiello® samplers (collecting benzene), especially those with the thicker diffusion membrane, were found to be the most effective at resisting effects of wind. The radial design of these samplers may favor the upholding

of uptake rates at varying wind velocities [251]. Plaisance *et al.* recommend an increase in the use of membranes in tube-type samplers [251], as the membrane reduces the effect of high wind velocities which particularly affect these types of samplers [233].

Discrepancies also exist between results of air velocity tests performed in laboratory exposure chambers or wind tunnels versus those performed under field conditions. Previous laboratory experiments using tube-type samplers report average sampling rate increases of 3% for an increase in wind speed of 0.05 m s^{-1} [235] up to a 104% increase between 0 and 2.5 m s^{-1} [248], while samplers of 6 different lengths mounted outdoors showed no effects of wind speed in the range of 2.3 to 4.5 m s^{-1} [252]. The relationship between wind speed and the effective sampling rate under real field conditions is difficult to determine as the majority of field studies use wind speed estimates from nearby wind stations rather than at the sampler itself [129].

Wind speeds at the sampling site may differ compared to conditions at the meteorological station, depending on the location of and distance to the station. Location of and distance to the meteorological station will also differ between studies possibly accounting for discrepancies in results. A laboratory test found that the placement of protective shelters over tube-type samplers significantly minimized the effect of wind speeds up to 4.5 m s^{-1} . This result highlights that the effects of wind at the face(s) of a sampler may be quite different than a measured wind speed near the sampling location [253].

Badge-type samplers may be more greatly affected by wind speeds as these types of samplers have shorter diffusion path lengths [128, 129, 139, 239, 244]. The high sampling rate of badge-type samplers can result in a standstill of air (boundary layer) outside the sampler ultimately increasing the effective diffusion path length. This layer creates an increased diffusion resistance, that is the sampling rate and estimated concentration are decreased [254]. At low wind speeds badge-type samplers exhibit a 'starvation' effect as air outside the sampler comes to a standstill and gas molecules are not replenished at the sampler face(s) [244]. The minimum wind speed required to replenish air at the sampler has been reported at 0.25 to 1 m s^{-1} [237-239].

The use of shelters over samplers deployed in ambient air to protect against wind and other meteorological factors (e.g., precipitation, sunlight) is common [145, 193, 218, 224, 255]. Shelters should not prevent free air movement around the sampler [129]. Plaisance *et al.* found a cylindrical protective box placed over tube-type samplers was an effective and practical option to protect against effects on sampler performance due to wind [248]. Sheltered tube-type samplers have shown smaller sampling uptake rates compared to adjacent unsheltered samplers which may be wind affected [249, 256]. However, limited literature is available on shelters especially in relation to non-tube-type samplers [129, 257].

For samplers equipped with diffusion membranes, thickness of the membrane has been shown to alter the effect of wind velocity. An axial-sampler (Radiello®) with a thick diffusion membrane exhibited the highest resistance to air velocity in a closed chamber test as compared to samplers without membranes and those with thinner membranes. The added resistance of the membrane results in altered uptake rates. These rates should be measured, not calculated, as Fick's law is no longer applicable without modification. Uptake rates could be calibrated against a standard gas mixture in the laboratory or against active monitors in the field [244]. The effect of a membrane on sampling rate should be reflected in the calculations provided by the sampler manufacturer.

5.4.2 Influence of temperature

Temperature can cause variation in sampling rates throughout the sampling period. Therefore, understanding the role temperature plays is a necessary step in the validation of the performance of passive samplers [221]. According to the kinetic theory of gases, for an ideal passive sampler, the effect of temperature and pressure on the uptake rate of the analyte should be accounted for by the diffusion coefficient (D) of the analyte. The diffusion coefficient is temperature dependent and will increase with increasing temperature resulting in higher uptake rates [139]. Nevertheless understanding the effects of temperature is important in determining the uptake rate of samplers, especially in extreme weather conditions. As with wind speed, experimental measurements of sampling rates may show greater dependence on temperature than calculated by theoretical estimations [129] and different sampler designs may have different temperature responses.

A previous field study using Ogawa badge samplers determined NO_x concentrations in two cold climate cities (mean annual temperatures of 4 and 8 °C) with two calculation methods (1) using uptake rates determined in the field and (2) calculated according to the Ogawa manufacturer's protocol. For NO_x , the theoretical uptake rate of NO_2 was used as previous work assessing the uptake rates of NO_x is exceedingly limited. The calculated NO_x uptake rate for temperatures above 0°C was reported at 9.88 ml min^{-1} and 7.17 ml min^{-1} at temperatures below 0°C [192]; both rates are lower than the reported NO_2 rate of 12.1 ml min^{-1} [128]. Temperature was found to account for 60% of the variability in uptake rate. The uptake rate increased 0.178 ml min^{-1} with every 1 °C increase in temperature [192].

The field calculated uptake rates for NO_2 differed slightly from those determined for NO_x . The uptake rate for NO_2 was determined to be in the range 6.0-9.4 ml min^{-1} for average temperatures between -13.8 and 17.3°C. The rate was reported as 8.60 ml min^{-1} for temperatures above 0°C and 6.64 ml min^{-1}

for temperatures below 0°C [192]; both rates are lower than the reported theoretical uptake rate of 12.1 ml min⁻¹ [128]. Similar to NO_x, temperature was found to significantly affect uptake rate; accounting for 34% of uptake rate variability. The uptake rate increased with temperature (0.109 ml min⁻¹ per °C) [192].

An evaluation of tube-type samplers found almost constant uptake rates from 20 to -8°C but a strong temperature dependence below -8°C [191]. The effect of low temperatures on sampling rates was reported in other studies, including those testing radial-type samplers [191, 193, 248, 258, 259]. Explanations for the decrease in the uptake rate at colder temperatures include structure changes of the absorbent (TEA,) which would remove active sites for NO₂, or the rate constant for the reaction between TEA and NO₂ may be significantly temperature dependent [191]. However, findings on the effect of temperature on uptake rates may actually be confounded by simultaneous changes in humidity [195, 218].

5.4.3 Influence of humidity

A review of the use of diffusive samplers in the European Union for the monitoring of NO₂ in ambient air, with TEA as the absorbent, concluded humidity is perhaps the most important variable affecting sampler performance [260]. Absolute humidity is a measure of the water vapor (moisture) content in the air and is often used equally with relative humidity [261]. The effects of humidity on the uptake rate appear to be related to the reaction of NO₂ with TEA rather than the diffusion process [129]. The amount of water in the sampled air is an important factor in the reaction between NO₂ and TEA. The reaction will not occur in completely dry air [194, 218]. Therefore, reported effects of low NO₂ uptake rates due to cold temperatures may actually be caused by low water vapor pressures rather than the temperature [192] as colder air contains less water vapor than warm air [262].

In a laboratory experiment Tang *et al.* found little effect of relative humidity using a non-TEA collection medium (CHEMIX™) but a significant reduction in uptake rate (80%) at low humidity (and temperatures) when testing alongside a TEA coated collection medium (Ogawa samplers) [196]. Similarly, a drying effect on the TEA collection medium was shown by Palmes *et al.* [194] by lowering total pressure during sampling. The reduction in pressure induced a reduction in the sampling rate of TEA absorbent Palmes tubes. According to the theory of diffusional sampling, lowering pressure (to simulate increasing altitude of the sampling environment) should not affect sampling rate. The sampling rate was not affected when experiments were repeated with water vapor as the gas and molecular sieve as the absorbent, suggesting the results were NO₂/TEA dependent. The hypothesized reason for decreased sampling rate

at low pressures was the dehydration of TEA. The hypothesis was tested by simultaneous exposure to identical concentrations of NO₂ at a pressure of 1 atm and 50% or 0% relative humidity. The amount of nitrite formed in the dry environment, by the reaction of NO₂ and TEA, was significantly different to that in the humid environment [194]. Reduction in sampling rate was similar to previous findings of reduced sampling rates at low pressures (approximately 1/10 atm) [219]. Therefore, the reduction of sampling rates at reduced pressures is most likely not a direct result of pressure reduction, but rather the loss of humidity at reduced pressure [194]. This finding is consistent with the report of a greater effect of pressure reduction on sampling tubes shorter in length, from which drying would occur more quickly [219].

While many studies use relative humidity as a measure of water vapor concentration [193, 263-265], absolute humidity may be a better marker [129, 192] as it gives the amount of vapor actually present at a given temperature [266]. Absolute humidity is independent of temperature while relative humidity (expressed as a percent) measures water vapor relative to the temperature of the air. Specifically relative humidity is the amount of water vapor in the air (absolute humidity) divided by the total amount of vapor that could exist in the air at its current temperature. Therefore, although relative humidity is usually used as a direct measure of water vapor concentration in passive sampler calculations it does not directly indicate the actual amount of water vapor in the sampled air [262].

Previous laboratory studies reported no effect of relative humidity >20% at room temperature [264] or at ambient temperatures [253, 263] on uptake rates of short-path passive samplers. However, between 20 and 80% relative humidity changes in uptake rates for Palmes tubes [265] and membrane-capped samplers [233] were reported as 18 and 23%, respectively. On the other hand, Plaisance *et al.* found changes in sampling rate $\pm 10\%$ for Palmes tubes only at “unusual” temperature and humidity field conditions ($T > 30^\circ\text{C}$ and $\text{RH} > 80\%$) [248].

Hagenbjörk-Gustafsson *et al.* reported absolute humidity to be a significant predictor of NO₂, accounting for 35% of the variability in the uptake rate of badge-type (Ogawa) passive samplers. The uptake rate increased for increasing absolute humidity (range 0.9 to 8.7 g H₂O kg⁻¹) for both NO₂ and NO_x measurements. A greater effect of humidity on uptake rate was reported for NO_x concentrations with absolute humidity explaining 63% of the variability in uptake rate. In contrast, relative humidity (range 68 to 96%) was negatively associated with both the uptake rate of NO₂ and NO_x accounting for less variability than absolute humidity, 6% and 25% of uptake rate, respectively. The negative association is perhaps a reflection of the highest relative humidity being found at the lower temperatures [192]. At the

same amount of absolute humidity, colder air will have a higher relative humidity because lower temperatures cannot retain as much water vapor as higher temperatures [262].

Similar to the previously discussed effects of wind speed and temperature, reported effects of humidity on uptake rates vary between studies. Contrary to the minor effect of relative humidity reported by Hagenbjörk-Gustafsson *et al.*, [192] Swaans *et al.* found a strong negative relationship between uptake rate and high relative humidity (80%) at three tested temperatures (-5, 10, 30 °C) at 24 hour experiments in a laboratory exposure room. Results between the two studies may be difficult to discern as Swaans *et al.* tested the effect of relative humidity on axial-type (Radiello®) passive samplers at differing temperatures and sampling times [193], reiterating the difficulty in drawing hard conclusions between studies which differ in test parameters. Continuous samplers are reported to also have a dependence on humidity. Plaisance *et al.* report a chemiluminescence NO_x monitor response typically decreases by 0.5% per g H₂O m⁻³ absolute humidity, equivalent to a change of 5% between 20 and 80% relative humidity at 20 °C [248].

Hansen *et al.* showed evidence of a loss of TEA absorbent efficiency below -8 °C, equivalent to an air concentration of water vapor of 2.9 g m⁻³ (0.35 kPa), or 35% RH at 5 °C [191]. While this effect would most likely hinder sampler performance in areas with cold, dry climates, regions which experience fluctuations during a sampling period to cold, dry conditions will also be affected. Seasonal differences may unknowingly be partially a result of environmental influences such as humidity. While Gold *et al.* demonstrated TEA will react with NO₂ under completely dry conditions; the experimental NO₂/TEA ratio was several orders of magnitude larger than those used in air sampling. Therefore, the results are not directly applicable to air sampling studies [267]. Although laboratory evidence shows an effect of humidity on sampler performance, humidity is understudied. There have been limited field studies assessing the effects of humidity [192, 249, 253] and a systematic study of its interaction with TEA has not been reported [129].

Table 12 provides reported environmental factor influences for a variety of NO₂ passive samplers whose absorbent is TEA. This list provides an idea of the manufacturer's (when provided) reported effects of environmental factors on NO₂ uptake rates. As seen in the table the effect of certain environmental factors are not tested, or at least not reported by the manufacturer. The lack of reported influence of these factors confirms the importance of field and laboratory evaluation studies. Fick's law of diffusion is based on steady state conditions; however, under field conditions environmental factors can affect passive sampler performance. Theoretical uptake rates may differ from field calculated rates resulting in the over or under estimation of concentrations. Varshney *et al.* reported uptake rates determined under

standard conditions may even vary during a sampling period and should be assessed under a wide range of environmental conditions [143].

Reported analytical results may differ between sampler types, sampling location, and with shelter or protective membrane use. Furthermore, not all sampler types have been studied equally. Unsurprisingly more findings are reported on the oldest passive sampler design (tube-type) compared to badge or radial-types. Although not always feasible (as certain types of passive samplers may be readily available for a specific study), consideration of environmental factors as well as other factors (e.g., sampling duration, analytical methods, known interferences) should be taken into account before commencing a study. Careful assessment of both the manufacture's recommendations and the literature is important; performance information or other caveats may be lacking or not provided by the manufacture.

Hagenbjörk-Gustafsson *et al.* found the Ogawa sampler consistently underestimated the NO₂ concentration and overestimated the NO_x concentration (compared to a chemiluminescence monitor), especially if concentrations were determined according to the manufacture protocol rather than using field-determined uptake rates [192]. These findings establish the importance of field studies when determining the uptake rate of a passive sampler. Theoretical uptake rates may inaccurately estimate a pollutant concentration especially in extreme climates. If possible, it is recommended to test passive samplers in field tests under the conditions in which they will be used.

Table 12. Effect of meteorological factors on a variety of TEA absorbent NO₂ passive badges

Passive Sampler Type	Sampler Manufacture		Meteorological Factors, Effect of:			References
			Temperature	Relative Humidity	Wind Speed	
Tube-Type	Palmes (Gradko Intl., without membrane)		N.R.	N.R.	<10%, 1.0-4.5 m/s	[232]
	Passam	Short	No influence between 10 to 30 °C	No influence between 20 to 80% RH	<10% up to 10 m/s	[268, 269]
		Long	No influence between 5 to 40 °C		<10% up to 4.5 m/s	
Badge-Type	Yanagisawa		Deviation occurs <0 or >30 °C for 24-h exposure	±30% accuracy between 40 to 80% RH	±30% accuracy between 0 to 9 mph	[270, 271]
	Ogawa		Operable between -10 to 40 °C	Operable between 50 to 80% RH	N.R.	[141]
Radial-Type	Radiello®		Operable between -10 to 40 °C	Invariant from 15 to 90% RH	Invariant between 0.1-10 m/s	[240]

N.R. designates those factors not reported by the manufacturer
Adapted from Yu *et al.* [128]

5.5 CHEMICAL INTERFERENCES DURING PASSIVE SAMPLING

As the acrylic bodies of open diffusive tubes (Palmes tubes) are effective in blocking UV wavelengths which destroy NO₂ [230] (only <20% of integrated NO₂ photolysis occurs within the tube [272]) the effect of within-tube chemical reactions on NO₂ passive sampling is most likely due to the diffusion of and consequently the reactions between existing NO and O₃ [129, 206]. In ambient daylight conditions a photostationary equilibrium theoretically exists between NO, O₃, and NO₂. However, this equilibrium rarely exists in the ever-changing atmosphere of a city, or in weather conditions where sunlight intensity changes quickly [206]. The extent to which within tube reactions occur rely heavily on the local pollutant

concentrations during sampling and most crucially on the proportion of NO_x components [206]. Excess NO₂ will not be formed when the atmosphere becomes limited in NO or O₃ [273]. In rural areas where O₃ concentrations are generally in excess and NO₂ concentrations are generally greater than concentrations of NO, within-tube reactions between O₃ and NO are limited and diffusion tubes will measure NO₂ effectively. As the majority of NO_x present in rural areas is comprised of NO₂, diffusive tubes are an accurate tool for measuring NO₂ in this type of environment [230].

Opposite in makeup, the urban environment generally consists of larger amounts of NO, which may lead to an overestimation of NO₂ using diffusion tubes. NO is generally the predominant species of NO_x in the urban environment while O₃ varies. The within-tube reaction of excess NO with O₃ can lead to an overestimation of NO₂ [206]. Within-tube chemical reactions most likely cause the greatest alteration in sampler performance during daylight hours when photolysis and the chemistry between NO and O₃ is most active. At nightfall within-tube reactions should be reflective of those reactions occurring in the ambient atmosphere. Therefore, in the urban environment tube-type samplers may be most efficient at capturing true concentrations during night hours [273].

Heal *et al.* reported passive diffusion tubes cannot be used with confidence in urban areas. The authors' modeled results showed NO₂ concentrations are systematically overestimated in urban areas due to chemical reactions in the tube, mainly the reaction between NO and O₃. The model incorporated real atmospheric data as input in order to evaluate chemical concentrations and reactions in ever-changing atmospheric conditions [272]. In two independent studies, the overestimations were close in value to the average difference between concentrations of NO₂ measured from diffusive tubes and continuous analyzers [207, 230]. This result supports the idea that within-tube reactions may partially account for inconsistencies between passive and continuous monitors.

At curbside sampling locations NO measured as NO₂ due to within-tube reactions has been shown to give errors up to 28% for 1-week exposures. While the greatest uncertainty occurred when the fraction of NO₂ was on average 0.5 of NO_x, the relationship between sampler overestimation and the ratio of NO₂ to NO_x was found to be non-linear. Chemical overestimation rose to a maximum as the proportion of NO to NO₂ increased, but ultimately declined when NO concentrations were in large excess compared to NO₂. Under excess conditions the reaction between NO and O₃ becomes limited by the amount of O₃ available. The amount of O₃ outside the sampler tube is likely to become depleted as a result of the rapid reaction between O₃ and excess NO, inhibiting excess NO₂ formation [207].

Adjusting for within-tube reactions is difficult as the chemistry can vary temporally, seasonally, and spatially. At an urban location Heal *et al.* reported a 28% overestimation of NO₂ using diffusion tubes

as compared to concentrations measured by a continuous monitor. The predicted overestimation decreased to between 8 and 14% at a rural site during the same summer month and at the urban site in winter [272]. Heal *et al.* report accurate quantifiable corrections of overestimation is not feasible due to inconsistency in atmospheric conditions. However, despite the overestimation, the authors report the correlations between passive samplers and continuous measurements suggests that passive samplers do retain a qualitative measure of NO_x variations across a sampling area [230].

The approximate residence time for the diffusion of molecules along a sampler is also an important determinant in the extent of within-tube reactions. The residence time for a typical tube-type sampler (7.1 cm in length) is 2.8 minutes, comparable to the reaction time of NO with O_3 at representative atmospheric concentrations [272]. Therefore samplers with shorter residence times (i.e., badge-type and radial-type) would not be expected to incur NO_2 overestimations, at least from reactions between NO and O_3 [129, 206]. This idea is supported by studies reporting an increase in NO_2 overestimation with increasing diffusion length [273, 274].

Within-tube chemical reactions have been found to overestimate the amount of NO_2 in the air sampled; however, other findings such as the shortening of the effective path length due to wind speed have also been reported to overestimate NO_2 concentrations. Therefore, it is possible some of the previously reported effects of wind speed may, in part, be attributed to excess chemical reactions within diffusive tubes [272]. If wind was the only factor attributing to NO_2 overestimation, it would be expected that co-located sampler tubes of the same length but varying in material would exhibit no difference in measured NO_2 . Standard acrylic-tubes were co-located next to quartz-tubes and foil-wrapped tubes all measuring 7.1 cm in length [230]. Quartz tubes transmit ~90% of the wavelengths of light necessary for NO_2 photolysis while acrylic and foil-wrapped tubes are UV blocking [272]. A significant discrepancy was found reported measurements collected with the quartz tubes and those collected with the acrylic and foil-wrapped tubes. At identical tube lengths, the differences in concentrations found between sampler types supports the notion that within tube chemistry, not wind speed, is responsible for overestimation of NO_2 [230]. However, studies providing evidence that additional factors (e.g. wind effects) may contribute to overestimation prevents these factors from being completely ruled out [273]. If both wind speed and within-tube chemical reactions are individually responsible for the overestimation of NO_2 concentrations, the combination of both causes could potentially increase overestimations especially in urban environments [272].

5.6 THE USE OF SHELTERS AND PROTECTIVE MEMBRANES

There are inconsistent results amongst investigations on the effect of wind on the performance of passive samplers. One possible solution to minimize possible wind effects is fitting a porous membrane barrier at the opening of the sampler. The addition of a membrane alters the theory behind passive sampling, as uptake is consequently not only controlled by diffusion but is also limited by diffusion through the membrane. The resistance to diffusion introduced by the membrane must be measured experimentally and adjusted for in subsequent concentration calculations [244]. Another option to deter wind effects is the use of a protective shelter over the passive sampler [193, 206, 224, 259]. Additionally, the shelter is designed to protect against precipitation. While some sampler manufactures recommend the use of the manufactured shelter [140, 240], others list the shelter as optional [234]. The size of the shelter should be designed so as not to limit the free flow of air to the sampler [249, 259, 275]. Minimal information is available regarding the effects of shelters on the performance of samplers [257].

An investigation evaluating the extent of differences between measurements collected using various commercially available passive samplers found certain samplers to be affected by lack of a shelter while other samplers were not affected even in high exposure conditions [259]. Plaisance *et al.* tested the use of a protective shelter for tube-type samplers by collocating sheltered samplers next to fully exposed samplers. Concentrations from the exposed and unexposed samplers were compared against concentrations measured by continuous monitors. High degrees of linearity ($r = 0.9$) were reported between the passive samplers and the continuous monitors with an increase in the correlation coefficient for the sheltered samplers. The investigators concluded the shelter appeared to limit the wind effects on the sampler. Additionally, the authors reported estimations of the overall uncertainties for the NO_2 measurements collected by passive tube samplers with and without a shelter. The use of a protective shelter decreased the overall measurement uncertainties [257].

Kirby *et al.* found sheltered tube-type passive samplers performed better than those which were unsheltered. Both exposure modes correlated well with continuous monitors; however, exposed samplers overestimated NO_2 by 16% on average compared to 3% for sheltered samplers. A highly significant difference ($P=0.0005$) of mean concentrations were found between unsheltered samplers and the continuous monitors while no significant difference was found for sheltered samplers and continuous monitors. Although sheltered and unsheltered data correlated well, a highly significant difference ($p=0.0005$) was also found between the means of these two modes of exposure. Although these differences in NO_2 values may suggest wind turbulence was responsible for the overestimation of

unsheltered samplers, additional statistical tests incorporating wind speed revealed an increase in NO₂ uptake was not a direct result of wind [273]. As previously suggested [129, 249] it is possible this disconnect between overestimation and wind speed could be a result of inappropriate wind measurements. In a laboratory experiment Hangartner *et al.* used a protective shelter to emphasize the importance of assessing the wind conditions at the sampler entrance rather than speeds at the nearest measurement station. At up to 4.5 m s⁻¹ the use of the protective shelter greatly reduced the effect of wind speed [253].

Other explanations for differences in measured concentrations between protected and unprotected samplers, besides wind turbulence, could be due to perturbations in photochemical equilibrium at the face of the sampler. Differences were reported in measured NO₂ concentrations between sheltered and unsheltered tube-type samplers; variations attributed to the use of protective screens, screen type, and sampler locations were seen. Concentrations of photochemical pollutants rely heavily on the state of the equilibrium between NO, NO₂, and O₃. During the day this equilibrium is often disturbed at near roadway locations where fresh NO_x emissions are common. As distance to roadway increases concentrations of pollutants are more representative of background concentrations due to atmospheric dilution and additional chemical reactions [273]. Background NO₂ concentrations have been reported as close as ~20 m from the roadway [276, 277]. This same background effect can be created through the use of protective screens at the face of passive samplers most often used in badge-type samplers. The protective screen impedes natural air flow which may create extra turbulence at the sampler face resulting in increased chemical mixing and a delay in the entrance of pollutants into the sampler. An increase in atmospheric dilution, chemical reactions, and delay in reaching the absorbent can result in the sampler ultimately receiving concentrations near background levels. Analytic levels may vary depending on the extent of the use of sampler screens and/or shelters.

Kirby *et al.* reported results supporting this effect of protective screens on tube-type sampler uptake. For equivalent exposures, the concentration of NO₂ collected reflected the level of protection of samplers collecting within ~20 m of a main road. The most protected sampler recorded NO₂ concentrations matching those at an urban background site. Contrary to these results, no difference in collected NO₂ was found between protected and unprotected samplers at the background site. Away from direct NO_x sources the atmosphere at the background site should be equilibrated resulting in no reduction in NO₂ concentrations regardless of the level of sampler protection. Protection of samplers may alter the composition of the air at the sampler face resulting in reduced accuracy of measurement depending on the type of protection used and the proximity to direct NO_x sources [273].

5.7 TRIETHANOLAMINE (TEA) ABSORBENT

The most commonly used absorbent in the collection of NO₂ dating back to the 1970s [278] is triethanolamine. Triethanolamine (2,2',2''-Nitrilotriethanol (C₆H₁₅NO₃), referred to as TEA, is a hygroscopic colorless to pale yellow liquid with a melting point of 21.6 °C [129]. The TEA-coated collection surface traps and reacts with NO₂ which is ultimately converted to nitrite ions (NO₂⁻) for analysis [218, 226]. Palmes *et al.* reported the advantages of using TEA to capture NO₂ in the atmosphere: (1) it captures NO₂ very efficiently, (2) it has a high viscosity and a low vapor pressure making it possible to stably coat the NO₂ collection surface, and (3) the TEA-NO₂ complex is stable enough so trapped NO₂ can be stored for substantial periods prior to analysis [227].

Although TEA may remove NO₂ from the atmosphere with 90 to 100% efficiency, not all absorbed NO₂ is necessarily available as NO₂⁻ for analysis. Cape *et al.* report stages in the trapping and analysis process that should be noted in order to understand the sampling efficiency of TEA for NO₂ (1) ability to remove NO₂ from the atmosphere, (2) reaction with TEA to produce a product capable of freeing NO₂⁻ upon extraction into solution, and (3) losses of trapped NO₂ during and after sampling prior to analysis [129].

Previous studies have shown TEA is an efficient absorbent (near 100% at typical ambient NO₂ concentrations) unless high NO₂ concentrations or sampling rates surpass the capability of TEA to react [278, 279]. Greater uncertainty surrounds the overall stoichiometry of the reaction between TEA and NO₂ to form a product that liberates NO₂⁻. Early studies of the reaction process reported various stoichiometric factors of NO₂ to NO₂⁻, including 0.63 [278] 0.85 [279] and 1 [218] with conversion increasing as the concentration of sampled NO₂ decreases [280]. Reported reaction products, include triethanolamine nitrite and triethanolamine nitrate [281], nitrite and triethanolammonium nitrate (with concentrated NO₂ gas as the reactant) [267], nitrosodiethanolamine [282, 283], and triethanolamine N-oxide [218].

As previously discussed in detail temperature and humidity may be important factors in the reaction of TEA with NO₂. Prior studies investigated the efficiency at which TEA can collect at low temperatures. Girman *et al.* reported a 15% loss of TEA efficiency at a temperature change from 27 to 15 °C; attributing the loss as a result of a liquid to solid phase change of TEA [284]. However, a more recent study showed for a range of aqueous TEA solutions (0-20% H₂O) no freezing occurred as low as -10 °C [285]. The proposed effect of temperature on the reaction of TEA and NO₂ may actually be a dependence on the availability of sufficient amounts of water to ensure conversion of trapped NO₂ to NO₂⁻. Humidity has been shown to play an important role in the direction of the reaction pathway, with higher NO₂ to

NO₂⁻ conversion efficiency at higher relative humidities [286]. Glasius *et al.* demonstrated the role of water in the TEA/NO₂ reaction to give a conversion coefficient of 1 [218]. However, in the case of excess water (i.e. liquid water in the trapping medium) equal production of NO₂⁻ and nitrate (NO₃⁻) was reported [287] thus limiting the amount of NO₂⁻ available for analysis. Unless sampling in very cold, dry weather temperature and humidity effects should be minimal [129] as 100% conversion of absorbed NO₂ to NO₂⁻ is reported at 75% relative humidity and 26 °C (18 g H₂O m⁻³) [194]. A minimum of 3 g H₂O m⁻³ is reported as the requirement for TEA to be effective in passive sampling [191].

Previous findings suggest the conditions under which the TEA/NO₂ products form are important [129]. Kirby *et al.* compared four sampler preparation methods to assess differences in NO₂ uptake. All methods used TEA-absorbent material transferred by dipping collection screens in a TEA-acetone solution or pipetting a TEA-H₂O solution directly on the screens. TEA solutions varied by % v/v and by solvent used. No significant difference was found between NO₂ concentrations using three out of the four preparation methods; however, the fourth method, a 50% v/v TEA in deionized water solution, yielded consistently lower NO₂ concentrations varying significantly from the three other methods. The authors suggested the 50% v/v TEA in deionized water hindered the absorption of NO₂ and ultimately its conversion to NO₂⁻ [285].

To minimize differences arising from variations in manufacturers and consumers procedures, Europe's AEA Energy and Environment consultancy recommended the TEA solution used for tube-type samplers should be nominally 50% or 20% TEA v/v. If absorbent screens are to be dipped into the solution the recommended formula is 50% TEA in acetone, whereas for pipetting the solution a 20% TEA in H₂O solution is preferred [288]. Preparations of the TEA solution for major manufacturers of badge-type (e.g. Ogawa USA) or radial-type (e.g. Radiello®) samplers are not reported.

Concerns regarding the loss of trapped NO₂ prior to analysis have been raised following studies of longer exposure lengths. Multiple studies report consistently lower NO₂ concentrations collected from tube-type samplers during 1-month exposures than concentrations from successive samplers exposed for 1-or 2-week durations [207, 208, 230, 289]. The mechanism for this time-dependent loss of NO₂ is not known; although in situ photolysis of NO₂ or the TEA-nitrite complex may be a possible explanation for loss of trapped NO₂ [129, 206, 207]. Losses of NO₂ over exposure periods of several months suggest the degradation of the TEA-NO₂ reaction product leading to the potential use of an alternate NO₂ trapping medium (e.g., iodide + hydroxide, iodide + arsenite) [208, 209]. Transmission of UV light through the sampler walls or by internal reflections from the sampler entrance could cause a chemical breakdown of trapped NO₂ over exposure periods of days to weeks [207]. Smith *et al.* investigated seasonal effects of

NO₂ collection, reporting the largest NO₂ losses occurring during the summer months possibly a result of NO₂ photolysis [290].

Much of the work investigating TEA absorbent performance has focused on tube-type samplers. The chemistry behind the TEA-coated collection medium should be the same for all passive sampler types; however, sampler efficiency as it relates to the TEA absorbent may differ between samplers due to sampler geometry (e.g. allows for more sunlight), use of opaque end caps, sampler placement (e.g. shaded versus sunny area), absorbent preparation, or use of shelters.

5.7.1 Chemical interferences with TEA

TEA absorbent passive samplers are subject to positive interferences due to chemical reactions aside from the targeted reaction with NO₂. Besides the reaction between NO and O₃ previously discussed, the two chemical interferences of concern are nitrous acid (HNO₂) and peroxyacetyl nitrate (PAN) [129]. Sickles *et al.* reported HNO₂ (21-78 ppb in the sampled air) to be a direct interference in the measurement of NO₂ using TEA-coated filters as reacted HNO₂ was recovered as solely NO₂⁻ [291]. However, HNO₂ is a short-lived intermediate of NO_x produced from combustion processes and present in the atmosphere in very small quantities [292]. It is unlikely HNO₂ will significantly affect the measurement of NO₂, as its level in the atmosphere is usually insignificant [247].

PAN is formed photochemically in air through reactions involving NO_x and VOCs [293] and is quantitatively converted to NO₂⁻ upon reacting with TEA [294]. For TEA coated filters, Sickles *et al.* found the majority of reacted PAN (tested at 500 ppb) was in the form of NO₃⁻ but still 15-25% was present as NO₂⁻ [291]. Interference from PAN for tube-type samplers has been reported at <5% [247]. Likewise, Heal *et al.* reported PAN is less than a few percent of the total collected NO₂ concentration even when the concentration of PAN exceeds 20% of NO₂ input [272]. High atmospheric concentrations of PAN are reported to greatly interfere with accurately measuring NO₂ [294]. Although PAN is abundant in regions heavily associated with anthropogenic pollutants [295], its ability to transport long range contributes to its presence in rural areas as well [296]. Reported NO₂ concentrations from continuous monitors are also reported to contain a small fraction of PAN and HNO₂. Therefore, a potential overestimation of NO₂ from TEA absorbent passive samplers is likely offset as continuous monitors would include this overestimation as well [129, 207].

5.8 COMPARISON OF RESULTS – ACTIVE VERSUS PASSIVE MONITORING

Tube-type samplers have been shown to overestimate NO₂ concentrations in field comparisons; reported overestimations ranging from 10% to 30% compared to active chemiluminescent monitors [230, 247, 297] suggesting unagreed-upon interferences from environmental factors or other reacting species. Some authors report measurements within ±10% of chemiluminescent values [191, 256, 274] while others report no significant differences [218, 298]. Overestimation of measurements collected with badge-type samplers is not as commonly reported.

A review of the application of diffusive samplers in the European Union reported average ratios ([Passive sampler NO₂]/[Active sampler NO₂]) ranging from 0.90 to 1.07 for concentrations collected from Ogawa samplers and continuous monitors [260]. Sather *et al.* collected NO₂ using Ogawa passive samplers at sites equipped with a federal reference monitor and found good correlation ($r = 0.95$) between the two monitoring types for 107 paired measurements [223]. Likewise, Mukerjee *et al.* found a correlation of $r = 0.91$ for 16 paired measurements [224].

A limited number of studies have assessed comparisons between radial-type samplers and continuous monitors. Some investigations found Radiello® samplers range from underestimating concentrations to matching collected from continuous monitors. Measurement ratios ranged from 0.58 to 0.99, with a larger effect seen for shorter (7-day) exposure period [260], 0.67 to 1.06 [193] and 0.69 to 1.08 [249]. It should be noted chemiluminescent monitors may not be specific to solely NO₂ in ambient air; therefore, NO₂ concentrations from these monitors may be overestimated as well [297]. Moreover, there is variation in results found by different labs using different methods under different conditions in studies comparing tube-type passive samplers to continuous monitors; not all studies can be given equal weight when drawing final conclusions [129].

5.9 CONCLUSIONS AND CONSIDERATIONS

Passive sampling offers an attractive alternative to conventional monitoring especially for studies where determining the spatial variability of pollutants is desired. Present monitoring networks typically employ a small number of monitors as it is impracticable to use this type of monitor at a large number of sites. Passive samplers provide the opportunity for monitoring to occur simultaneously at a larger number of

locations. Compared to active monitors, passive samplers are cheap and highly portable. Nitrogen dioxide concentrations are often measured passively but few passive sampler types are capable of measuring total NO_x . A variety of passive samplers exist, each with their own advantages and disadvantages. Recently developed samplers offer an increase in sampling rate and the ability to measure pollutants over shorter time periods. However, validation studies of these samplers are limited.

Passive samplers are often used because they do not require power and compared to active monitors are reported as easier to use, easier to handle, cost-effective, and require no calibration. The accuracy of these samplers is often reported to be similar to that of active monitors but in actuality may depend on the atmospheric conditions in which sampling is taking place. Measurement biases are often reported but are difficult to interpret. Results frequently differ between studies due to variations in sampler types and test conditions.

Passive sampler users should familiarize themselves with the limitations of the study sampler. Relying solely on the manufacturer's protocol may not always be sufficient. The possible limitations of passive sampling reported in this review, especially the potential for environmental interferences, demonstrate the importance of field-determined uptake rates. Undoubtedly field studies for the determination of these rates is not always feasible. At the minimum, collocation of passive samplers with active monitors is an ideal way to test the performance of passive samplers in the environment where they are to be used. However, at the very least, it is important to acknowledge field measurements may be over- or underestimated due to the conditions of the sampling environment. Nonetheless, despite the limitations, a variety of passive samplers have been shown to accurately measure NO_2 concentrations. Passive samplers are the best available option and provide most detailed assessment of the variation in NO_2 concentrations across a study area.

6.0 OVERALL CONCLUSIONS AND RECOMMENDATIONS

The overall objective of this research was to assess the ability of a well-known passive sampler to accurately measure concentrations of nitrogen oxides in the ambient environment. While passive samplers are an attractive alternative to conventional monitoring, studies suggests the passive collection of pollutants can be affected by environmental interferences. Passive samplers are so often described as cheap, quick, and easy to use that disadvantages of passive sampling are typically not considered. Atmospheric conditions can alter a sampler's theoretical uptake rate, yet field-determined uptake rates are seldom tested. Although rarely reported, the loss of PTIO on Ogawa & Co. NO_x filters, evident by the loss of the filter's purple color during ambient exposure, ensures the disadvantages of this sampler are readily apparent. Over multiple ambient exposure periods of five to seven days, NO_x filters exhibited color changes ranging from partial to a full loss of color.

The degradation of PTIO varied within samplers and between sites. Degradation was greatest for filters housed under Ogawa & Co. manufactured semitransparent shelters. Through a series of indoor tests and ambient sampling, with certainty, it can be concluded the degradation of PTIO is catalyzed by light and is unaffected by oxygen. A temperature effect was not present over a 2-day testing period but is possible, and will be investigated, for longer time periods representative of ambient exposure. The amount of PTIO on degraded filters was shown to be minimal or in most sample solutions completely absent. Degradation of PTIO led to the production of PTI identified in its reduced and protonated form. In addition, interestingly, NO₂⁻ was detected in the solutions of filters unexposed to the ambient environment as well as in degraded PTIO solutions. At this time the source of the NO₂⁻ is unknown but is under investigation.

Not only is PTIO a disadvantage under ambient conditions, it poses a problem during analysis as well. The PTIO coating interferes with the measurement of NO₂⁻ because the absorbance of PTIO is significant at the analytical wavelength. Variation in absorbance values, due to the extent of degradation, further complicates the accurate measurement of NO₂⁻. To accurately measure NO₂⁻ the interference from PTIO must be removed through diethyl ether extractions. Extractions add a cumbersome step to the analytical procedure.

Based on the results of this study, it is concluded that Ogawa & Co. passive NO_x samplers do not accurately measure ambient NO_x concentrations. The use of these samplers in a variety of ambient environments resulted in the loss of PTIO on NO_x filters. The chemical responsible for collection NO is

now minimized, or absent, resulting in a possible underestimation of NO present in the sampling environment. However, the loss of PTIO resulted in the detection of NO₂⁻ on filters which had not been exposed to the ambient environment. Therefore, it is difficult to determine whether or not and over or underestimation of NO₂⁻ is expected. It likely varies by filter. In addition, the manufacturer's analytical protocol, as is, will not accurately measure the amount of collected NO₂⁻.

The results of this study suggest the Ogawa sampler should not be used in future studies for the collection of NO_x as it does not accurately measure NO. It is difficult to accurately measure NO in the ambient environment using filters which degrade in sunlight and when unmodified interfere at the analytical wavelength. However, if the Ogawa sampler is chosen it is recommended samplers are housed under opaque shelters. Although these shelters will not prevent complete protection from light, this shelter type has been shown to minimize the degradation of PTIO. Moreover, the use of an opaque shelter will also minimize variation in filter coatings post exposure. To ensure the analysis is not affected by PTIO, extraction by diethyl ether should occur prior to analysis. Extraction is especially important when opaque shelters are utilized as the PTIO color will be strongest in this instance. Additionally, to account for production of NO₂⁻ during storage, filter extract solutions should be stored for a consistent time.

Studies will continue in an effort to identify any additional degradation products as well as the source of NO₂⁻ in filter extract solutions unexposed to ambient conditions. Examples of ongoing studies include further testing of the effects of temperature on the degradation of PTIO and the use of nuclear magnetic resonance (NMR) to aid in the identification of unknown compounds.

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