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**Preliminary Study Comparing Precipitation Quality Between
Nominal Land Uses in Portland, Oregon**

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Abstract

The purpose of this study is to analyze the precipitation quality in various land use categories throughout Portland. Because of its significance in the removal of atmospheric pollutants, wet deposition is an important component to study (Rocha et al. 2003). In addition to its significant role in cleansing the atmosphere, wet deposition can have a direct impact on the ecosystem due to its potential pollutant load (Khare et al. 2004). Various land uses may provide different emission sources, each uniquely affecting the composition of the atmosphere. A literature review found few studies comparing precipitation quality between local land uses within an urban area. Wet deposition studies seem to be fairly limited in the western United States, specifically in the Pacific Northwest. By collecting wet deposition in four different land uses: industrial, commercial, residential, and open space, precipitation quality is compared between each land use using a chosen group of analytes (ammonia, total phosphorus, copper, lead, mercury, zinc, pH, and conductivity). Significant differences were found between a number of land use category pairs for each of the eight analytes, except pH and conductivity. In order to give more insight into the precipitation quality, the results were also analyzed for differences between sites within each land use and differences between storm events. Differences were found between a number of sites, suggesting local effects in precipitation quality throughout Portland. Differences were also found between events, suggesting the importance of meteorological characteristics.

1. Introduction

1.1 Purpose of Study

The purpose of this study is to analyze the precipitation quality in various nominal land use categories throughout Portland, Oregon. By collecting wet deposition in four different land uses: industrial, commercial, residential, and open space, precipitation quality will be compared between each land use using a chosen group of analytes. The goal is to evaluate whether or not there are differences in precipitation quality occurring within the land uses. The objectives of this study are to evaluate:

- the importance of precipitation as a nonpoint source of pollutants to the environment, particularly for selected heavy metals;
- the local effect on precipitation quality;
- potential sources of atmospheric pollutants within the Portland area; and
- the amount of pollutants entering stormwater from precipitation.

1.2 Definition of Wet Deposition

Wet deposition, as defined by Van Ry et al. (2002), is the removal of contaminants from the atmosphere by precipitation. Atmospheric particles and gases are incorporated into cloud droplets to be deposited as precipitation, or particles and gases are scavenged by raindrops as they fall (Lovett 1994). The composition of wet deposition is an indication of the composition of the atmosphere (Khare et al. 2004). Wet deposition comes from emissions of air pollutants from both natural and anthropogenic sources (USEPA 2001).

Rocha et al. (2003) describe wet deposition to be a significant route of pollutants removal from the atmosphere. Along with dry deposition, wet deposition is the final step in removal of atmospheric trace constituents (Rao et al. 1992). It plays a significant role in cleansing the atmosphere, while also having a direct impact on both the ecosystem and human artifacts (Khare et al. 2004). Impacts include impairment of terrestrial and aquatic ecosystems, and corrosion or degradation of buildings and monuments (Rocha et al. 2003). It is difficult, however, to distinguish between pollutants entering the environment through deposition or through other

pathways such as runoff (USEPA 2001). Examples of this include pollutants found within a waterbody or a stormwater sample. Therefore, it is difficult to determine whether or not the environmental impacts in a given area are caused directly by pollutants found in wet deposition.

It can also be difficult to measure wet deposition inputs accurately due to the sources of air pollution; unlike point sources which are directly discharged into a waterbody, sources of air pollution may be near or distant to the waterbody (USEPA 2001). It is common for atmospheric pollutants to travel great distances and then be deposited by wet deposition. For example, a study done by Sirois et al. (2001) found their study site in the Turkey Lakes Watershed, located in the Algoma Region of central Ontario, Canada, to be highly affected by atmospheric deposition (both wet and dry). With few emission sources within 100 km of the watershed, they determined pollutants to travel hundreds to thousands of kilometers. An additional example is the presence of a significant amount of mercury in the United States due to emissions elsewhere (Seigneur et al. 2004). Twenty-one percent of the total mercury deposition in the contiguous U.S. is contributed by Asia (Seigneur et al. 2004).

Wet deposition has been continuously monitored throughout the United States with the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) (Hooper and Peters, 1989). It was established to determine geographical patterns and temporal trends in atmospheric deposition, focusing specifically on acidic deposition (Hooper and Peters, 1989). Precipitation chemistry was initially developed in response to damage caused by acid rain (Hontoria et al. 2003). Studies are increasing in urban areas specifically due to the effects of pollution on human health (Hontoria et al. 2003). Water resource managers are beginning to realize that atmospheric deposition is important to take into account in order to effectively manage water resources (USEPA 2001). Studies have been increasing over time as technology advances and wet deposition becomes recognized as an important transport mechanism of pollutants to the watershed (e.g. Rao et al. 1992, Shertzer et al. 1995, Landis and Keeler 1997, Patel et al. 2001, Rodhe et al. 2002, Fenn et al. 2003a, Koelliker et al. 2003, Deboudt et al. 2004, Seigneur et al. 2004).

1.3 Atmospheric Chemistry

Contaminants become associated with rain by being dissolved in the raindrop or being incorporated as particles (Ollivon et al. 2002). Water vapor that interacts with pollutant particulate matter in the atmosphere forms very small atmospheric aerosol particles (Manahan 2000). These particles then are incorporated into precipitation. Areas located within or near areas with high levels of air pollution, or areas downwind from a pollution source, will consequently experience higher levels of pollutants in the precipitation.

The most visible form of air pollution is made up of particulate matter. These particles range in size from 0.001 to 10 μm , and are commonly suspended in the air near pollution sources. The most common chemical processes that produce particles are combustion processes (Manahan 2000).

Air pollution dispersal depends on the complicated movement of air across the earth's surface (Manahan 2000). The buildup of atmospheric pollutants in localized regions occurs when the air is stagnant. Temperature inversions, produced by increasing temperature with increasing altitude, are characterized by high atmospheric stability. This atmospheric stability results in the trapping of air pollutants in localized areas, causing inversions to contribute significantly to the effects of air pollution (Manahan 2000).

Precipitation flushes out harmful pollutants from the atmosphere, but rain carrying pollutants can have effects on the environment. Emission sources of aerosol particles include both natural and anthropogenic sources. Natural processes include volcanic eruptions, soil-dust uplift, sea-spray uplift, natural biomass burning fires, and biological materials release. Anthropogenic sources include fugitive dust emissions (from paving, vehicles, construction), fossil-fuel combustion, anthropogenic biomass burning, and industrial emissions. In 1997, 67-71 percent of 37 million short tons of emitted particulates less than 10 μm were of anthropogenic origin (Jacobson 2002).

1.4 Analytes

1.4.1 Common Analytes

The most frequent groups of analytes in precipitation quality studies include dissolved nutrients, dissolved anions, dissolved cations, and pH (e.g. Safai et al. 2003, Shertzer et al. 1995, Rocha et al. 2002, Akkoyunlu and Tayanc 2003). Various organics such as pesticides, Polycyclic Aromatic Hydrocarbons (PAHs), and Polychlorinated biphenyls (PCBs) have also been tested for, but are most often included in studies separate from those testing for nutrients and ions (e.g. Ollivon et al. 2002, Grynkiewicz et al. 2001, De Rossi et al. 2003). Heavy metals are also an important group being tested for, specifically in urban areas (e.g. Siegneur et al. 2004, Patel et al. 2001, Landis and Keeler 1997, Deboudt et al. 2004). All of the above mentioned groups of contaminants have been found in rainfall samples all over the world. Each contaminant can be traced to a potential, if not specific, source category such as an industrial process or an agricultural area utilizing high amount of pesticides. This can be done by looking at possible sources of the analyte near the area, as well as a variety of factors such as meteorological conditions, amounts of the analyte in the air, and air quality trends in the area. The following sections provide information on analytes relevant to the current study.

1.4.2 Ammonia

Sources of Nitrogen emissions include transportation, agriculture, and industry (Fenn et al. 2003b). Nitrogenous emissions include nitrogen oxides (NO_x), ammonia (NH_3), and ammonium ion (NH_4^+). Ammonia is an important pollutant to study because of its increase in emissions in recent years; ammonia emissions have increased 19% in the 11 western states from 1990 to 1999 (Fenn et al. 2003b). It has been found that emissions of N as ammonia are about 50% as great as emissions of N as nitrogen oxides (Fenn et al. 2003b).

The most important variable in predicting an increase in wet deposition of ammonia is proximity to an urban area (Fenn et al. 2003b). In a 2003 study done in the Western United States on Nitrogen emissions by Fenn et al (2003b), N deposition was found to be lower in the Pacific Northwest than the rest of the United States with exception of urban areas within Portland and Seattle.

Small amounts of ammonia are present in air due to natural biochemical and chemical processes (Manahan 2000). Additional sources of atmospheric ammonia include microorganisms, animal waste decay, sewage treatment, coke manufacture, ammonia manufacture, and leakage from ammonia-based refrigeration systems (Manahan 2000).

Ammonia is removed from the atmosphere by its affinity for water and by its action as a base (Manahan 2000).

1.4.3 Total Phosphorus

Atmospheric deposition of phosphorus (and nitrogen) has been shown to be significant in contributing to the total nutrient loading to aquatic ecosystems (Koelliker et al. 2003). Because phosphorus is a limiting nutrient in both aquatic and terrestrial ecosystems, excess amounts can lead to eutrophication (Koelliker et al. 2003). Atmospheric deposition is a non-point source of phosphorus, and is significantly more difficult to control than point sources of phosphorus such as detergents discharged to surface waters (Koelliker et al. 2003).

In a New Jersey Atmospheric Deposition Network (NJADN) study, wet deposition of total phosphorus was collected and analyzed in four different land uses (Koelliker et al. 2003). Both the suburban and rural sites were influenced by the localized application of phosphorus-containing fertilizers, while the urban site was influenced by industrially associated phosphorus loadings. Total phosphorus concentrations in the precipitation samples ranged from 2.0 to 31 $\mu\text{g/L}$, which the authors found comparable to similar studies. It has been pointed out that total P concentrations as high as 200 $\mu\text{g/L}$ have been observed, but most fall within the range of 1 to 50 $\mu\text{g/L}$ (Koelliker et al. 2003).

1.4.4 Heavy Metals

Most heavy metals are introduced to the atmosphere in the form of fine aerosols by human activities (Patel et al. 2001). Once in the atmosphere, these metals may travel long distances before being deposited naturally or by wet deposition (Patel et al. 2001). The dominant removal mechanism for heavy metal atmospheric pollutants is wet deposition, which may be three or four times as large as the dry deposition rates (Deboudt et al. 2004). The magnitude of atmospheric input of metals varies both temporally and spatially due to their short atmospheric residence times and meteorological factors (Deboudt et al. 2004).

A study done in Western Europe by Deboudt et al. (2004), found a high variability of heavy metal concentrations associated with precipitation collected in urban and industrial areas. The authors suggest this to be attributed to the distance of the sources from the sampling locations and the levels of emissions. It can be difficult to determine the source of heavy metals found in precipitation samples; heavy metal particulates may or may not be from direct local sources. As Deboudt et al. (2004) stated, “it is the geographical origin of an air mass and not the location at which it is sampled which constrains the short-term particulate trace metal concentrations in the atmosphere.”

A 2001 study conducted in India by Patel et al. found the concentration of heavy metals in the precipitation to be 1.2 to 1.8 folds higher at the industrial site than the residential site. This finding shows the possible importance of point source emissions. This study also found that heavy metal concentrations were considerably higher in areas where there was operation of several heavy metal industries, combustion of coal and leaded gasoline and dusty atmosphere.

1.4.4.1 Copper

Copper is a widely used heavy metal, but is known to be of low toxicity to humans (Manahan 2005). It is widely used due to its workability, electrical conductivity, and ability to conduct heat. It is used primarily in electrical wire, tubing, copper pipe, shims, gaskets, and other applications (Manahan 2005). Emissions can occur during smelting operations and municipal incinerations (USEPA 2005b). The primary source of copper in the air is copper dust generated by copper processing operations (USEPA 2005b). As for drinking water standards, the secondary maximum contaminant level (MCL) for copper is 1.0 mg/L. Copper levels above this standard, however, are rarely found in raw drinking water supplies or in distributed water (USEPA 2005b). It has been estimated that only 66 water systems have copper levels in source water greater than the Maximum Contaminant Level Goal (MCLG) of 1.3 mg/L (USEPA 2005b).

1.4.4.2 Lead

In an urban atmosphere, lead comes closest to being present at a toxic level, therefore being the heavy metal of greatest concern (Manahan 2005). The primary sources of lead in the atmosphere are industrial use and former use in gasoline (Manahan 2005). In the early 1970s, about 200,000 tons of lead entered the atmosphere each year in the U.S. from car exhaust (Manahan 2005). The initial entry of lead into the environment is via the atmosphere, which it may do so during its mining, ore processing, smelting, refining use, recycling or disposal (USEPA 2005c). Once in the atmosphere, lead can be deposited by precipitation.

Even though lead may be detrimental to several aspects of the environment, the primary concern of elevated lead concentrations in the atmosphere is human health due to the variety of adverse health effects lead causes. Some of these include interference with red blood cell chemistry, developmental delays in babies and young children, slight increases in the blood pressure of some adults, cerebrovascular and kidney disease, and cancer from a lifetime exposure at levels above the action level (USEPA 2005c). A second critical pathway is the ingestion of drinking water. Because of the above adverse effects to humans, concern is great dealing with drinking water. The MCLG is zero mg/L, while the action level is >0.015 mg/L in more than 10 percent of tap water samples (USEPA 2005c).

1.4.4.3 Mercury

Anthropogenic sources of airborne mercury may arise from the operation of metal smelters or cement manufacture (USEPA 2005d). Industrially, mercury comes from coal-fired power plants and municipal waste incineration (Jacobson 2002). Twenty thousand tons of mercury are released into the environment each year by human activities such as combustion of fossil fuels and other industrial release, while 25,000-150,000 ton of mercury per year are released through the natural degassing of the earth's crust (Jacobson 2002). Due to its volatility and bioaccumulation in aquatic species, mercury is of significant concern (USEPA 2005d). A drinking water standard (MCL) has been set at 0.002 mg/L (USEPA 2005d).

1.4.4.4 Zinc

Zinc has a primarily industrial origin. Sources include smelters, coal-fired power plants, municipal waste incineration, and open-hearth furnaces at steel mills (Jacobson 2002). In the air, zinc is present mostly as fine dust particles, which eventually settle over land and water (ECO-USA 2003). In general, levels of zinc in air are relatively low and fairly constant. Air near industrial areas may have higher levels of zinc (Habeck 2003).

Wet deposition plays an important role in cleansing the atmosphere of zinc particles. Zinc entering bodies of water, such as lakes or rivers, either settles on the bottom or remains dissolved in water or as fine suspended particles (Habeck 2003). Some aquatic organisms can collect zinc in their bodies if they live in water containing zinc, but most of the zinc in soil is bound to the soil and does not dissolve in water (Habeck 2003). Depending on the characteristics of the soil, however, some zinc may reach groundwater. Such contamination has been noticed from hazardous waste sites (Habeck 2003). Zinc may be taken up by animals eating soil or drinking water containing zinc, and also can bioaccumulate up the food chain (Habeck 2003). Little is known about health effects in humans, but adverse effects can occur when too little zinc is present in the diet, as well as when excess amounts are present (Habeck 2003). A secondary MCL for drinking water has been set at 5 mg/L (USEPA 2005a).

1.4.5 pH

The pH of precipitation is measured to determine the rate of deposition of hydrogen ion or bicarbonate ion, and is an estimate of the acid-base status of precipitation (Rodhe et al. 2002). This means that it is a balance of acidifying compounds and alkaline compounds. Low pH values tend to occur in eastern North America, Europe, and China (Rodhe et al. 2002). Shertzer et al. (1995) found pH to be negatively correlated with nitrogen and sulfate. As concentrations of sulfates, nitrates, and ammonium increase, rainfall pH decreases (Shertzer et al. 1995). Therefore, pH is an indirect measure of these substances.

Natural rainwater, in equilibrium with atmospheric CO₂, has a pH of about 5.6. Acid rain, however, has a pH ranging from 2-5.6 (Jacobson 2002).

1.4.6 Conductivity

Conductivity is a measurement of the total ionic concentration within a given sample, and is used to give total ionic strength readings (Ciba Corning). Within precipitation samples, conductivity ranges from 5 to 1000 microsiemens/cm (Garivait 2004). The lowest conductivity readings have been observed at the highest rainfall rates (Laquer 1990). Conductivity varies with the sample temperature and is proportional to the concentration and the species of free ions present in the sample (Garivait 2004).

Within the majority of the studies mentioned in this report, conductivity analyses are not included in determining the chemical composition of precipitation. In studies measuring conductivity, little explanation is given as to the importance of analyzing samples for conductivity (e.g. Hontoria et al. 2003, Rocha et al. 2003, Tuncer et al. 2001). Because conductivity is a measurement of the total ionic concentration within a given sample, it is possible that the importance of conductivity analysis decreases if the major anions and cations have already been analyzed.

1.5 Relating Land Uses to Precipitation Quality

Local land uses have been shown to directly influence precipitation quality. By dividing areas into various land use regimes, comparisons of precipitation quality have been conducted to provide information on local variability and the effects of local sources on precipitation quality (Shertzer et al. 1995). Over recent years, a number of studies have been done relating local land use categories to precipitation quality. A selection of representative studies are given which compare concentrations of certain analytes among various land use categories (Shertzer et al. 1995, Van Ry et al. 2002, De Rossi et al. 2003, Patel et al. 2001, Koelliker et al. 2003, Weathers et al. 2000, Totten et al. 2004, Lee et al. 2000, Jain et al. 2000).

A 2002 study done by Van Ry et al. in New Jersey divided the state into different geographical land-use regimes; urban, suburban, and background areas. Results showed PCBs to be highest at the urban-industrial sites and lowest at sites distant from these. Specifically, concentrations were 7-43 times higher at urban-industrial sites than background concentrations. This shows the effect land use can have on precipitation quality.

Patel et al. completed a study in 2001 looking at heavy metal concentrations within the precipitation of India. In this study, the authors distinguished between urban, industrial, and remote/forest areas. The concentrations within the remote area were found to be 16 to 63% less than within the urban area. In the industrial area, the concentrations were found to be significantly higher than within the other two land use categories (e.g. 1.2-1.8 folds higher than the residential site).

An additional study conducted in India looked at the composition of wet deposition within four urban sites and one rural site (Jain et al. 2000). The concentrations of all measured components, including all major ions, were found to be highest at the rural site compared to the urban sites. The authors attributed this to the influence of the composition of the local soil.

In the region of Trier (Germany), pesticides and PAHs were measured in wet deposition within three different land use categories: urban, industrial, and rural (De Rossi et al. 2003). A significant difference in PAH concentrations were found among the sampling sites, with the lowest concentrations being present within the rural sites. Pesticide concentrations, however, showed no spatial variation.

Wet deposition within a montane ecosystem was compared with adjacent lowlands in the Catskills Mountains of New York by Weathers et al. in 2000. Lead concentrations were found to be significantly higher in the higher elevation areas than within the lowlands. These results were found to be consistent with results of similar studies the authors reviewed for wet deposition within high elevation areas versus lower elevation areas.

In a study looking at inputs to the Hudson River Estuary, Totten et al. (2004) measured the wet deposition of PCBs at nine sites representing various land use regimes, including urban, suburban, forested, and coastal land uses. The authors found significant spatial variations between the sites, with higher PCB concentrations occurring in the urban sites, followed by the next highest within the suburban and coastal areas.

In Korea, a study was done looking at the chemical composition of wet deposition at nine different sites: one urban site, two islands, three coastal sites, and three rural sites (Lee et al. 2000). Seasalt components were found to contribute 60% of the total ionic concentrations at both the island and coastal sites, but less than 10% for inland sites. This shows the effect geographical regions, specifically coastal, can have on precipitation quality. Additionally, the urban area of

Seoul showed the highest levels for all non-seasalt ions, although these levels were not found to be significantly different from the other areas (Lee et al. 2000).

In contrast to the previously mentioned studies showing significant differences in precipitation concentrations between land uses, other studies have found no differences. One study in particular, done by Shertzer et al. in 1995, looked at rainfall quality (concentrations of nutrients, major ions, and herbicides) and the relationship to land uses in a Southcentral Pennsylvania watershed. No differences in analyte concentrations were found among the land uses. This study is an example of the variability of precipitation quality among land uses. It was found that the concentrations of major ions in the precipitation appeared to relate more to regional influences rather than local influences. It was found that the relatively small, localized areas of forest cover, agricultural lands, or urban uses included in the study were not capable of influencing prevailing conditions.

As previously mentioned, a study done by Koelliker et al. (2003) measuring wet deposition of phosphorus as part of the New Jersey Atmospheric Deposition Network (NJADN), compares phosphorus concentration between four different geographical land uses: suburban, urban, urban-industrial, and rural. Even though the land uses were found to have an influence on the wet deposition of phosphorus, such as the influence of phosphorus-containing fertilizers within the suburban and rural sites, it was concluded that there were no significant differences between the four land uses.

1.6 Urban Areas and Significance of Wet Deposition

Because urban areas contain such a high density of emissions sources, wet deposition is an increasing concern. Several recent studies have focused on the quality of wet deposition in an urban area (Shertzer et al. 1995, Van Ry et al. 2002, Safai et al. 2004, Khare et al. 2004, Kim et al. 2001, Rao et al. 1992, Koelliker et al. 2003, Akkoyunlu and Tayanc 2003). In addition to studies already mentioned which include precipitation quality within urban areas compared with other land uses, the following examples are studies done only within urban areas showing how these areas affect the composition of precipitation.

In a long-term study done in Pune, India by Safai et al. (2004), a decrease in precipitation pH was found from 1984 to 2002. There was an increase in both nitrate (NO_3^-) and sulfate (SO_4^{2-}). This was attributed to the rise of industrial, vehicular and commercial activities within the city (Safai et al. 2004). This example shows that urban areas can affect local wet deposition.

An additional study in India, done by Khare et al. (2004), examined the precipitation quality in the urban city of Lucknow. The various pollutants found within the wet deposition were linked to emissions from traditional combustion activities and industrial activities.

Hontoria et al. (2003) completed a study looking at precipitation quality in the urban city of Madrid, Spain. The primary pollution sources within the city are road transport, combustion, and industry. The authors found these sources to greatly influence the chemical composition of the precipitation in Madrid, and concluded that the influence of local conditions was important to the precipitation quality.

In Istanbul, Turkey, the precipitation quality was studied within four urban areas of the city (Akkoyunlu and Tayanc 2003). Results indicate that sulfate, which was the dominant anion, found within the precipitation samples came from urban sources such as combustion processes for domestic heating and industrial activities.

Sources of pollutants are extremely variable throughout urban areas. As already mentioned, sources of wet deposition include natural and anthropogenic sources. These sources vary among regions and study areas. A 1992 study conducted in an urban location in India by Rao et al. suggests that the atmospheric composition is strongly influenced by natural sources rather than anthropogenic sources. On the other hand, Deboudt et al. (2004) found anthropogenic sources to be the cause of the atmospheric composition in Western Europe. Additionally, in a previously mentioned study completed by Jain et al. in 2000, the four urban sites sampled did not show a very clear picture of the influence of sources due to mixed activities within the urban areas.

As previously shown, a large number of recent studies dealing with precipitation quality within an urban area do not divide the urban areas into additional land uses. An urban area is made up of several different land uses, each of which may affect the composition of the local atmosphere. The following example is taken from a study where an urban area is divided up into different land uses and compared for precipitation quality. A thorough literature review found the following study to be most representative of the current study, dividing an urban area into several land uses to compare precipitation quality.

Patel et al. completed a study in 2001 looking at heavy metal concentrations within the precipitation of India. In this study, the authors distinguished between urban, industrial, and remote/forest areas. Within the urban area, three sites were sampled representing residential, commercial, and industrial areas. The concentrations of the metals were found to be 1.8 times higher within the industrial site than the residential site.

1.7 Spatial Patterns

Spatial variation in atmospheric deposition occurs over several different scales (Ollinger et al. 1993). Variation can be seen at both local and regional scales. Specifically, topography and vegetation canopy characteristics can cause variation at local scales. Other fine-scale features, such as local wind exposure, may also affect deposition inputs (Ollinger et al. 1993). At larger scales, however, patterns result from the location of source areas relative to the dominant patterns of atmospheric circulation (Ollinger et al. 1993). One example of the detection of spatial patterns occurred in a study done by Ollinger et al. in 1993 on atmospheric deposition in the northeastern United States. During this study, a steep west to east increasing gradient was found for concentrations of ions whose atmospheric presence is due to industrial activities (e.g. SO_4^{2-} , NO_3^- , H^+).

A second example is taken from a study done by Hooper and Peters in 1989, utilizing data from the previously mentioned NADP/NTN wet deposition monitoring network to determine patterns in three pre-determined categories of solutes : acid, salt, agriculture/soil. The acid component was found to be most dominant within the eastern United States. It was found that the salt component was most important along each coast. The agriculture/soil component was found to be most important within the interior parts of the United States.

Orography (the presence of mountains) may have a significant effect on the spatial patterns of wet deposition (Weston and Fowler 1991). For wet deposition of pollutants, orographic effects are further complicated by the position of the source areas of the pollutants relative to the orography (Weston and Fowler 1991). In a 1991 study on acid rain in Scotland done by Weston and Fowler, geographic patterns in wet deposition were found to be due to two factors: (1) spatial variation of the acidity of rainfall during each event and (2) spatial variation in

the amount of rainfall which occurs on different occasions. In Scotland, the geographic patterns in rainfall acidity were found to show a pronounced gradient from the least polluted areas of the northwest to the most polluted areas in the southeast (Weston and Fowler 1991).

In an Ontario study, spatial patterns were found to differ with each tested parameter, although certain groups of metals displayed similar patterns (Chan et al. 1986). The lead concentration and deposition increased in Southern and Central Ontario compared to Northern Ontario, reflecting the higher density of vehicular emissions within the former areas (Chan et al. 1986).

Short-term studies may not be appropriate for detecting spatial patterns due to the highly random characteristics of these precipitation events. Highly random events cause spatial patterns to be difficult to discern (Ollinger et al. 1993).

1.8 Meteorological Conditions and Precipitation Quality

Meteorological conditions, such as wind direction and precipitation amount, can also affect precipitation quality. For example, a study looking at the variation of wet deposition with meteorological conditions in the Sauerland area in Germany found both conditions to be important in the composition of precipitation (Vautz et al. 2003). By looking at transport directions of certain substances, wind direction was found to significantly affect precipitation quality. The concentration of analytes in precipitation was found to be dependent of precipitation amount, with an increase in precipitation amount corresponding to a decrease in concentrations. The following paragraphs provide additional examples of meteorological conditions affecting precipitation quality.

In the northeastern United States, a spatial model of atmospheric deposition was designed by Ollinger et al. (1993). While developing this model, it was found that the concentrations of nitrogen and sulfur were higher in areas having low precipitation amounts.

Additionally, in a study looking at the ionic composition of precipitation in Turkey, wet deposition fluxes of ions were found to be high in the winter and low in summer (Tuncer et al. 2001). This pattern of ion fluxes was seen to closely resemble the variation in precipitation amount.

In a study done by Lawrence et al. (2000) looking at atmospheric nitrogen in the Mississippi River Basin, the regional patterns of wet deposition of nitrate and ammonium were found to reflect the regional patterns of emissions and atmospheric transport processes. For example, the highest rates of nitrate deposition occur in Ohio and Pennsylvania, downwind of high-emitting power plants and large urban areas with high transportation emissions (Lawrence et al. 2000).

Another example specifically related to wind direction is a study which evaluated the precipitation quality in two different areas within the Central Korean Peninsula (Kim et al. 2001). In this study, the authors concluded that pollution was being transported from the urban area of Seoul to the rural areas of Chunchon, using analysis of pH and major ion concentrations.

1.9 Related Studies in or near Portland

Studies on wet deposition seem to be fairly limited in the western United States, specifically in the Pacific Northwest. Eastern United States studies may be more prevalent due to the higher populations and larger numbers of pollution sources. Three related studies in or near

Portland include (1) a deposition study in the Eastern Columbia River Gorge National Scenic Area done by the USDA Forest Service, (2) an air quality assessment done by the Department of Environmental Quality known as the Portland Air Toxics Assessment (PATA), and (3) sites associated with the NADP/NTN.

The Columbia River Gorge (CRG) study monitored atmospheric deposition at eleven different sites throughout the CRG study area, looking specifically at nitrogen and sulfur deposition (Fenn and Blubaugh 2005). One site in particular, Mt. Zion (MZ), was located at the Portland end of the CRG and was the most westerly site. This site also happens to be a NADP monitoring site.

PATA is the first project of its kind in Oregon. Developed in response to the state Air Toxics Program, it is a local-scale air toxics computer modeling project to estimate local levels of twelve air toxics (formaldehyde, chromium, benzene, polycyclic organic matter, chloroform, 1,3-butadiene, acetaldehyde, perchloroethylene, nickel, arsenic, diesel particulate, and acrolein) (DEQ 2003). The goal of this study is to better understand air toxics in the Portland area by producing a more accurate estimate of the most significant air toxics (DEQ 2003). This study could be important to the current precipitation quality study, as well as future studies, because of documented sources of air pollution.

As previously discussed, the NADP/NTN monitors wet deposition throughout the United States in order to determine spatial and temporal trends in deposition. Five sites are monitored in Oregon, with one site located in the CRG as part of the CRG study previously discussed (NADP 2005). Throughout the United States, wet deposition analysis occurs for pH, sulfate, nitrate, ammonium, chloride, and base cations (NADP 2005).

1.10 Establishing the Need for a Study

While a number of studies have examined the differences in precipitation quality in general land use categories, few have divided urban areas into separate land use categories (e.g. commercial, industrial, residential, open space) when looking at precipitation quality. A number of studies include “urban” as an individual land use, comparing precipitation quality within this land use to other land uses such as suburban and rural. Specifically within the Pacific Northwest, no studies could be found which compare precipitation quality between various land uses within an urban area. Therefore, this type of study done in the urban area of Portland, OR will greatly add to the literature on wet deposition within an urban area.

2. Methods

2.1 Study Area

Portland, OR is located in the Northwestern United States, about 65 miles east of the Pacific Ocean. It is situated at 20 feet above sea level, and lies midway between the lower Coast Range to the west and the high Cascades Range to the east, each about 30 miles distant (Rockey 2004). Moderate rainfall is received each year due to the steep slope of the Cascades to the east, providing orographic lift of moisture-laden westerly winds (Rockey 2004). Precipitation falls primarily as rain, with about 90 percent of the annual rainfall occurring from October through May (Rockey 2004).

For the purposes of this study, Portland is divided up into four different land uses: industrial, commercial, residential, and open space. These land use categories are nominal and were chosen based on generalized zoning classifications obtained from Metro's Regional Land Information System (RLIS) database. Four sites were chosen within each land use, creating a total of 16 sites. A map of the study area, including sampling locations, is shown in Figure 2.1.

Figure 2.1. Map of study area, including sampling locations and land use classifications.

2.2 Choosing Analytes for the Analysis

A group of analytes were examined for each precipitation sample. These analytes include pH, Conductivity, Ammonia, Total Phosphorus, Copper, Lead, Zinc, and Mercury. Previous sections provide information on why each analyte was chosen, a description of each, individual roles in precipitation quality, and the potential effect each may have on the environment. Chloride and turbidity were both analyzed for the first sampling event, but were not included in the proceeding samples due primarily to funding issues, as well as the high number of non-detects and little variation among the sampling locations.

2.3 Field Sampling

Sampling, which was completed in Portland, Oregon, consisted of wet deposition samples collected at 16 sites throughout the city (Table 2.1). Precipitation samples were collected at four locations each within four land use categories: industrial, commercial, residential, and open space. Five storm events were sampled from December 2004 to June 2005.

Wet deposition samples were collected using a 12.6-inch diameter polyethylene funnel fitted to a 2-L polyethylene bottle (Figure 2.2). For each storm event sampled, decontaminated bottles were provided by the lab prior to sampling. The funnels were rinsed and scrubbed thoroughly before attachment to remove any remaining particles from previous storm events. The same funnel was used for a given sampling location to further reduce the risk of cross contamination. The funnels were then rinsed with distilled water prior to attachment to the bottles. Attachment was done using duct tape, and was done no more than 12 hours before deployment. The bottles and attached funnels were stored in clean plastic bags until delivered to the site to prevent the influence of dry deposition.

At each of the 16 sites, one wet deposition collector was attached to a sign, post, or railing using cable ties to anchor the bottle in place. The attachment site was chosen based on what was available at each location. At sites where there was no sign, post, or railing to attach the collector to, the collector was placed on the ground and anchored in place using bricks around the bottle. At each site, the collector was placed in an area far enough away from buildings or vegetation in order to protect the funnel opening from allowing runoff or debris into the bottle. One duplicate collector was placed at a different site for each storm event to provide field quality control.

The Water Pollution and Control Laboratory of the Bureau of Environmental Services provided forecasts during the extent of the study. Storm events were chosen based on predicted precipitation amounts, amount of time in between events, and availability. Forecasts were additionally followed using online sources such as Accuweather (<http://www.accuweather.com>), The Weather Channel (<http://www.weather.com>), and National Weather Service (<http://www.wrh.noaa.gov/pqr/rain.php>). The collectors were deployed 12 to 24 hours prior to a predicted storm event in order to prevent significant amounts of dry deposition from influencing the samples. At the conclusion of each storm event, the collectors were retrieved within 12 to 24 hours. The samples were then placed in coolers on ice until taken to the laboratory for analysis.

Table 2.1. Description of Sampling Locations

Category/Site ID	Location	Address	Description
Open Space			
OS1	Mt. Tabor	Off SE 69 th and SE Yamhill	Amphitheater, attached to fencing near basketball courts
OS2	Oaks Bottom	Off SE Milwaukie	Oaks Park entrance, first path on right, attached to post
OS3	Forest Park	Off W Burnside	Pittcock Mansion parking lot, attached to low sign
OS4	Powell Butte Park	Off SE 162 nd and SE Powell	Open field near parking lot, attached to fencing
Residential			
R1	North	7608 N Fiske Ave	Emily Skoro residence, on back porch
R2	Northeast	3024 NE 61st Ave	Chris Prescott residence, attached to front railing
R3	Southeast	5336 SE 50th Ave	Joel Bowker residence, in driveway
R4	Southwest	9818 SW 6th Ave	Amin Wahab residence, in front yard
Commercial			
C1	NW Natural Gas Co.	220 NW 2nd Ave	4th floor courtyard, attached to railing
C2	Hamilton Building	1212 SW Clay St	Ecoroof
C3	Matrix Integrated	4000 SW Macadam Ave	Across from building, attached to a stop sign
C4	Providence Office Park	Hollywood District- Halsey & 44th	Parking lot fencing
Industrial			
I1	Gunderson	4350 NW Front Ave	Across from Gunderson, railroad side, attached to post
I2	Indoor Billboard	5140 N Channel Ave	Across from Indoor Billboard, attached to sign
I3	Oregon Humane Society	1067 NE Columbia Blvd	Parking lot, attached to fence
I4	Schnitzer Steel	12005 N Burgard Rd	Across from Schnitzer, attached to post on bridge fence

Figure 2.2. Precipitation collector

2.3.1 Determination of Precipitation Amount

The amount of precipitation that fell during a given storm event was determined using the City of Portland HYDRA Rainfall Network, which is operated and maintained by the City of Portland Bureau of Environmental Services. A reference HYDRA station was chosen for each of the 16 sampling locations based on proximity to each location (Table 2.2). Figure 2.3 shows a map of the HYDRA Network.

Immediately following retrieval of the samples, the amount of precipitation collected in the bottles was measured in centimeters using a basic ruler. The volume of precipitation collected was then calculated.

Table 2.2. HYDRA Stations used to determine precipitation amounts at each site

Site ID	HYDRA Station #
C1	1
C2	164
C3	120
C4	12
I1	121
I2	122
I3	115
I4	167
OS1	6
OS2	64
OS3	173
OS4	21
R1	48
R2	72
R3	174
R4	10

Figure 2.3. City of Portland HYDRA Rainfall Network Station Map (http://or.water.usgs.gov/non-usgs/bes/raingage_info/clickmap.html)

2.3.2 Duplicates

Duplicates were placed at a different site, within a different land use, for each storm event. Table 2.3 summarizes the duplicates for each storm event. The concentrations of analytes found within the duplicate sample were averaged with the concentrations of analytes found within the original site sample.

Table 2.3. Duplicates

Event	Duplicate
1	R2
2	C1
3	OS1
4	I4
5	R1

2.4 Laboratory Analysis

Immediately after retrieval of the samples, pH and conductivity were measured in the field using the Checkmate pH Set and Checkmate Conductivity Set. Measurements of conductivity for events 2 and 3 only were taken using the BES Field Operations Conductivity Meter due to complications with the Checkmate Conductivity Set in the field. In the laboratory, samples were analyzed for ammonia, total phosphorus, copper, lead, mercury, and zinc. Table 2.4 summarizes the lab methods used to test for each analyte.

Table 2.4. Lab Methods

Analyte	Method	Method Detection Limit (MDL)	Units
Ammonium	EPA 350.1	0.02	mg/L
Total Phosphorus	EPA 365.4	0.03	mg/L
Copper	EPA 200.8	0.2	µg/L
Lead	EPA 200.8	0.1	µg/L
Mercury	EPA 200.8	0.002	µg/L
Zinc	EPA 200.8	0.5	µg/L

2.5 Data Analysis

After data from the last storm events sampled were received from the laboratory, statistical analyses were performed on the data using the Minitab statistical software package (Minitab, Inc. 2004). Each dataset consists of the total concentration of the analyte at each site for all five events. The first step in the analysis was to perform basic statistics on the data to determine whether or not the data fit a normal distribution. If the dataset fit a normal distribution before or after transformation, parametric statistical methods were used. If the data did not fit a normal distribution, nonparametric statistical methods were used.

For those datasets fitting a normal distribution, an analysis of variance (ANOVA) was run on the data to determine differences in analyte concentrations between land use categories across all events. Bonferroni pairwise comparisons were used to determine which pairs of land uses are significantly different. Next, each land use was analyzed to determine if there are any

significant differences between concentrations during different storm events. This was also done using an ANOVA (to detect differences) and Bonferroni pairwise comparisons (to determine which pairs of events were significantly different). Finally, each land use was analyzed to determine if there were any significant differences in concentration between sites (across all events). This was also done using an ANOVA and Bonferroni pairwise comparisons. An alpha value of 0.05 was used to determine significance. If the ANOVA indicated “near significance” ($0.05 < p < 0.1$), the pairwise comparison was performed to see whether a significant difference between pairs exists.

For those datasets not fitting a normal distribution, a nonparametric equivalent of the ANOVA, the Kruskal-Wallis test, was used to evaluate differences in analyte concentrations among both land use categories and storm events. Bonferroni pairwise comparisons were used to evaluate which pairs of land uses were significantly different. Next, each land use was analyzed to evaluate whether there are any significant differences between concentrations during different storm events. This was also done using a Kruskal-Wallis test and Bonferroni pairwise comparisons. Finally, each land use was analyzed to evaluate if there are any significant differences in concentration between sites (across all events). This was also done using a Kruskal-Wallis test and Bonferroni pairwise comparisons. An alpha value of 0.05 was used to determine significance.

Within the Kruskal-Wallis analysis, Bonferroni pairwise comparisons are the default comparisons when running the analysis. Within the ANOVA, however, additional choices exist, including Tukey pairwise comparisons. The Bonferroni method is more conservative than the Tukey method, but was used throughout the analysis in order to stay consistent.

2.6 Interpreting Figures

2.6.1 Box plots

Figure 2.4 is an example of a box plot from the study, and will be used to explain how to interpret such figures. The box represents the middle 50% of the data, or the interquartile range (IQR), with the whiskers extending out to the highest/lowest data values within the upper/lower limit. The line within the box is the median, and the point within the box is the mean. Outliers are represented with the symbol “*” and extend beyond the whiskers. An outlier is equal to 1.5 times the IQR. The letters above the whiskers (e.g. (a) and (b) within Figure 2.4) have been inserted to allow the reader to easily evaluate which land uses (in this example) are different from each other. Data with different letters mean they are different from each other. In Figure 2.4, commercial and industrial land uses (both marked “a”) have different ammonia concentrations than open space and residential land uses (both marked “b”).

Figure 2.4. Example of a box plot used in the study; used to explain how to interpret box plots

2.6.2 Pairwise Comparisons

Figure 2.5 will be used as an example for how to interpret the pairwise comparison charts created as part of a Kruskal-Wallis analysis. First of all, the labels for charts showing comparisons between land uses are as follows:

- 1 = Commercial
- 2 = Industrial
- 3 = Open Space
- 4 = Residential

The labels for charts showing comparisons between events correspond to the event number (e.g. 1 = Event 1). If the horizontal lines go past the z-values (dotted lines), then there are significant differences in concentrations between the parameters being compared. For example, in Figure 2.5 the second horizontal line from the top of the graph points to the left, past the z-value line. Therefore, the concentration of ammonia within the commercial land use (1) is significantly different from the open space land use category (3). Because the horizontal line points to the left, the concentration within the commercial land use (1) is significantly higher than within the open space land use (3).

Figure 2.5. Example of a pairwise comparison used in the study; used to explain how to interpret pairwise comparisons

3. Results and Discussion

3.1 Summary Tables for Each Storm Event

Tables 3.1-3.5 summarize the characteristics of each of the five sampled storm events; including precipitation amount, date/time of deployment and retrieval, and the volume of precipitation available for analysis.

Table 3.1 Storm Summary for Event 1

Site ID	Time of		Water Level	Approx. Volume	Precip. Amount	Hydra Station
	Deployment	Retrieval				
	12/8/2004	12/12/2004	(cm)	(mL)	(inches)	(#)
OS1	1425	810	10.8	1080	0.74	6
OS2	1345	945	10.4	1040	0.62	64
OS3	1840	810	6.0	600	0.73	173
OS4	1455	755	14.5	1450	0.90	21
R1	1625	905	10.8	1080	0.84	48
R2	1755	855	7.1	710	0.78	72
R3	1405	825	9.8	980	0.72	174
R4	1330	955	9.8	980	0.77	10
C1	1530	825	6.7	670	0.67	1
C2	1340	935	8.3	830	0.50	164
C3	1315	930	8.5	850	0.63	120
C4	1730	840	9.5	950	0.65	12
I1	1815	835	11.9	1190	0.79	121
I2	1705	1010	8.2	820	0.80	122
I3	1555	955	10.0	1000	0.80	115
I4	1640	855	8.6	860	0.69	167
R2-D	1755	855	7.7	770	0.78	72

Table 3.2 Storm Summary for Event 2

Site ID	Time of		Water Level	Approx. Volume	Precip. Amount	Hydra Station
	Deployment	Retrieval				
	3/18/2005	3/20/2005*	(cm)	(mL)	(inches)	(#)
OS1	1210	1305	7	700	0.44	6
OS2	1115	1235	6.1	610	0.36	64
OS3	945	1125	6.1	610	0.45	173
OS4	1240	1345	6.2	620	0.44	21
R1	855	2115	7.1	710	0.67	48
R2	1220	1320	5.5	550	0.44	72
R3	1150	1250	6.3	630	0.45	174
R4	1900	1205	6	600	0.46	10
C1	600	1145	5.5	550	0.48	1
C2	1400	1300	8.4	840	0.58	164
C3	1050	1220	7.3	730	0.44	120
C4	955	2200	7.8	780	0.62	12
I1	1040	2040	8	800	0.62	121
I2	845	2100	8.1	810	0.61	122
I3	935	2145	8.9	890	0.63	115
I4	920	2130	7.5	750	0.57	167
C1-D	600	1145	6	600	0.48	1

* 10-C2 was retrieved 3/21/2005 due to limited accessibility

Table 3.3 Storm Summary for Event 3

Site ID	Time of		Water Level	Approx. Volume	Precip. Amount	Hydra Station
	Deployment	Retrieval				
	3/31/2005	4/3/2005*	(cm)	(mL)	(inches)	(#)
OS1	1040	1555	5.1	510	0.36	6
OS2	1005	1520	6.1	610	0.27	64
OS3	855	1650	4.2	420	0.40	173
OS4	1110	1640	7.2	720	0.43	21
R1	1400	1530	4.5	450	0.28	48
R2	950	1625	4.0	400	0.35	72
R3	1020	1545	6.0	600	0.38	174
R4	945	1500	5.2	520	0.34	10
C1	600	1440	3.7	370	0.33	1
C2	1325	1130	5.0	500	0.31	164
C3	955	1510	8.9	890	0.38	120
C4	940	1615	4.7	470	0.34	12
I1	1055	1505	4.3	430	0.40	121
I2	1115	1520	3.7	370	0.35	122
I3	1000	1600	4.1	410	0.29	115
I4	1035	1550	4.0	400	0.24	167
OS1-D	1040	1555	5.2	520	0.36	6

* 10-C2 was retrieved 4/4/2005 due to limited accessibility

Table 3.4 Storm Summary for Event 4

Site ID	Time of		Water Level	Approx. Volume	Precip. Amount	Hydra Station
	Deployment	Retrieval				
	5/7/2005	5/10/2005	(cm)	(mL)	(inches)	(#)
OS1	1100	655	16.7	1670	1.76	6
OS2	1045	910	14.6	1460	1.31	64
OS3	930	910	12.1	1210	1.47	173
OS4	1130	750	12.6	1260	1.30	21
R1	950	1055	14.4	1440	1.24	48
R2	1120	715	8.4	840	1.18	72
R3	1110	815	10.8	1080	1.65	174
R4	1010	1150	14.2	1420	0.97	10
C1	1600	600	16.6	1660	1.34	1
C2	1400	915	15.0	1500	1.11	164
C3	1035	920	18.7	1870	1.35	120
C4	1040	710	6.9	690	1.89	12
I1	925	1030	15.9	1590	1.40	121
I2	940	1110	10.4	1040	1.24	122
I3	1020	1125	12.5	1250	1.39	115
I4	1005	1045	14.5	1450	1.18	167
I4-D	1005	1045	14.6	1460	1.18	167

Table 3.5 Storm Summary for Event 5

Site ID	Time of		Water Level	Approx. Volume	Precip. Amount	Hydra Station
	Deployment	Retrieval				
	6/15/2005	6/18/2005	(cm)	(mL)	(inches)	(#)
OS1	2015	2000	7.4	740	0.44	6
OS2	1955	1705	5.8	580	0.54	64
OS3	1840	1600	6.0	600	0.42	173
OS4	2110	2045	9.8	980	0.63	21
R1	1800	2035	3.7	370	0.35	48
R2	1920	2115	6.9	690	0.58	72
R3	2020	1730	4.9	490	0.40	174
R4	1920	1630	4.6	460	0.37	10
C1	1910	1620	5.4	540	0.38	1
C2	1655	1630	5.9	590	0.33	164
C3	1935	1645	3.7	370	0.32	120
C4	1910	2110	6.9	690	0.45	12
I1	1935	2010	3.4	340	0.44	121
I2	1745	2020	4.6	460	0.50	122
I3	1855	2100	5.6	560	0.37	115
I4	1840	2045	7.9	7900	0.55	167
R1-D	1800	2035	4.2	4200	0.35	48

Tables 3.6-3.10 summarize the wet deposition concentrations of all analytes for each of the sampled storm events.

Table 3.6. Wet deposition concentrations of analytes for Event 1.

Site ID	Ammonia (mg/L)	Total Phosphorus (mg/L)	Copper (µg/L)	Lead (µg/L)	Mercury (µg/L)	Zinc (µg/L)	pH (pH units)	Conductivity (µmhos/cm)
C1	0.54	<0.03	2.2	0.7	0.0038	21.1	6.3	13.7
C2	0.43	0.036	2.97	1.5	0.0038	18.5	6.2	13
C3	0.33	<0.03	1.48	0.7	0.0031	8.67	6.3	10.1
C4	0.42	<0.03	2.89	0.93	0.0041	12.4	5.8	11.2
I1	0.55	0.031	31.2	3.96	0.0039	47	5.5	13.2
I2	0.31	<0.03	9.99	1.03	0.0035	39.6	6.5	11.9
I3	0.27	0.034	2.07	0.77	0.0044	12.7	7	9.8
I4	0.32	0.044	28.9	5.91	0.0077	92.2	5.9	12.9
OS1	0.13	<0.03	2.15	0.97	0.0092	7.1	5.4	8.5
OS2	0.18	<0.03	1.17	0.41	0.0026	5.63	5.9	8.7
OS3	0.12	0.075	4.72	1.16	0.009	32.4	6	12.8
OS4	0.11	<0.03	0.49	0.22	<0.002	3.3	6.1	5.5
R1	0.25	0.14	3.41	0.61	0.0065	14.8	6.2	9.8
R2	0.25	0.13	4.42	7.24	0.014	23.3	5.8	24.3
D-R2	0.31	0.23	5.67	8.69	0.016	24	5.8	28.5
R3	0.18	0.052	1.42	1.03	0.0039	9.03	6.2	10.5
R4	0.11	0.11	1.26	0.61	0.0041	10.5	5.6	7.2

Table 3.7. Wet deposition concentrations of analytes for Event 2.

Site ID	Ammonia (mg/L)	Total Phosphorus (mg/L)	Copper (µg/L)	Lead (µg/L)	Mercury (µg/L)	Zinc (µg/L)	pH (pH units)	Conductivity (µmhos/cm)
C1	0.46	0.040	2.70	1.43	0.004	35.6	5.63	7.1
D-C1	0.46	<0.030	2.51	1.02	0.004	21.1	5.63	7.2
C2	0.48	0.033	1.88	1.06	0.005	14.9	5.11	8.2
C3	0.95	0.041	3.45	2.71	0.006	1200.0	5.39	18.6
C4	0.30	0.045	1.81	1.24	0.004	12.7	5.76	5.6
I1	0.41	0.046	62.00	2.58	0.006	22.8	5.59	7.7
I2	0.38	0.040	3.54	1.36	0.006	16.5	5.68	7.6
I3	0.44	0.044	2.86	1.26	0.005	12.4	5.66	7.1
I4	0.40	0.074	4.00	5.15	0.014	103.0	5.68	9.3
OS1	0.22	0.100	3.19	1.32	0.009	13.1	5.18	5.5
OS2	0.26	0.058	2.42	0.79	0.006	6.5	5.29	5.8
OS3	0.25	0.053	1.65	0.71	0.006	9.2	4.78	6.9
OS4	0.14	<0.030	0.93	0.31	0.002	4.5	4.99	4.0
R1	0.35	0.034	6.45	0.92	0.005	10.9	5.68	6.1
R2	0.25	0.086	2.35	2.08	0.006	11.8	5.73	6.0
R3	0.18	0.066	1.88	2.04	0.005	9.3	5.71	5.2
R4	0.03	0.210	2.30	1.22	0.005	10.9	5.54	8.0

Table 3.8. Wet deposition concentrations of analytes for Event 3

Site ID	Ammonia (mg/L)	Total Phosphorus (mg/L)	Copper (µg/L)	Lead (µg/L)	Mercury (µg/L)	Zinc (µg/L)	pH (pH units)	Conductivity (µmhos/cm)
C1	0.34	0.05	4.03	1.78	0.0072	35.5	5.3	8.6
C2	0.38	0.044	2.5	1.43	0.0069	20.5	5.7	9.8
C3	0.47	0.04	2.67	2.28	0.0096	1570	6	13
C4	0.4	0.044	3.46	1.47	0.011	28.3	5.5	9.9
I1	0.36	0.071	16.5	7.39	0.01	71.5	5.6	10.1
I2	0.27	0.081	7.29	2.21	0.0082	47.3	5.3	10.5
I3	0.35	0.055	7.54	2.02	0.012	24.3	5	9.9
I4	0.35	0.16	99.2	46.2	0.05	346	5.3	20
OS1	0.27	0.32	1.98	0.77	0.015	9.88	5.4	10.5
D-OS1	0.2	0.14	1.58	0.83	0.042	8.55	5.2	9.7
OS2	0.27	0.062	1.9	3.94	0.0085	8.52	5.6	8.3
OS3	0.21	0.12	1.74	0.48	0.0077	8.32	5.6	8.7
OS4	0.23	0.03	1.3	0.36	0.0062	4.79	5.8	7.9
R1	0.38	0.03	2.44	0.1	0.002	13.8	5.4	16.7
R2	0.27	0.17	3.5	2.33	0.012	17.5	5.5	10.8
R3	0.17	0.24	3.17	4.34	0.015	15.7	5.6	7.9
R4	0.03	0.32	1.97	0.54	0.012	10.4	5.3	7.4

Table 3.9. Wet deposition concentrations of analytes for Event 4

Site ID	Ammonia (mg/L)	Total Phosphorus (mg/L)	Copper (µg/L)	Lead (µg/L)	Mercury (µg/L)	Zinc (µg/L)	pH (pH units)	Conductivity (µmhos/cm)
C1	0.23	<0.03	1.16	0.48	0.0034	5.04	5.9	5.9
C2	0.19	<0.03	0.99	0.5	0.0025	5.71	5.8	5.1
C3	0.17	0.041	0.56	0.22	0.0023	14.6	5.6	5.5
C4	0.2	<0.03	1.66	1.03	0.0028	5.64	5.4	5.8
I1	0.16	<0.03	2.13	1.56	0.0039	7.69	5.4	5.4
I2	0.16	0.12	2.83	1.09	0.006	11	4.8	15.4
I3	0.24	<0.03	1.25	0.52	0.0031	5.07	5.2	7.1
I4	0.18	0.048	34	4.41	0.0086	26.2	5.5	6.5
D-I4	0.16	0.036	13.4	5.87	0.0072	26.8	5.6	6.1
OS1	0.11	<0.03	0.72	0.36	0.0039	3.06	5.7	15.3
OS2	0.36	0.36	3.38	0.93	0.012	16.9	5.9	8.8
OS3	0.25	2.21	8.56	0.89	0.011	26.2	6	50.9
OS4	0.12	<0.03	0.96	0.38	0.0038	5.9	6.4	5.5
R1	0.16	<0.03	49.1	0.53	0.0055	33.5	6	6.4
R2	0.12	2.52	14.9	1.51	0.018	60.9	5.2	94.2
R3	0.15	<0.03	0.8	0.87	0.015	3.98	5.4	10.8
R4	0.3	0.53	3.04	0.38	0.0085	14.4	5.8	19

Table 3.10. Wet deposition concentrations of analytes for Event 5

Site ID	Ammonia (mg/L)	Total Phosphorus (mg/L)	Copper (µg/L)	Lead (µg/L)	Mercury (µg/L)	Zinc (µg/L)	pH (pH units)	Conductivity (µmhos/cm)
C1	0.38	0.033	3.23	1.69	0.0079	17.7	5.9	7.62
C2	0.33	0.05	4.06	2.22	0.01	27.8	5.6	8.37
C3	0.29	0.063	4.93	2.57	0.0067	37	5.8	7.94
C4	0.31	0.032	2.06	1.23	0.0047	12.7	5.7	6.07
I1	0.42	0.12	14.9	9.83	0.012	93.5	5.9	11.6
I2	0.38	0.073	12	3.53	0.0086	63.8	5.8	9.58
I3	0.28	0.039	3.38	1.41	0.015	15.2	5.6	7.22
I4	0.2	0.12	21.2	32.1	0.033	156	5.7	16
OS1	0.22	0.095	1.45	0.52	0.0087	6.21	6.4	9.95
OS2	0.38	0.15	2.02	0.74	0.0087	7.86	6.4	6.92
OS3	0.24	0.12	3.24	0.8	0.0085	8.12	6.2	6.73
OS4	0.13	0.033	0.83	0.34	0.0044	3.62	5.8	5.5
R1	0.49	0.072	31.7	1.65	0.0078	32.2	6	9.96
DUP-R1	0.5	0.067	18.1	2.23	0.0096	40.7	5.7	10.2
R2	0.16	0.06	4.24	24.2	0.012	19.2	5.7	6.18
R3	0.36	0.09	3.35	2.73	0.013	13.5	5.5	21.2
R4	0.19	0.083	1.38	0.47	0.0079	6.49	5.8	6.38

3.2 Duplicates

Because the datasets for site concentrations and corresponding duplicate concentrations were nonnormally distributed, a Mann-Whitney test was used to test whether or not significant differences exist between concentrations at each site and the corresponding duplicate. The null hypothesis is that there are no differences between the two concentrations. Using total concentrations (across all events), no significant differences were found between concentrations at the site and duplicate samples ($p = 0.9616$). For each individual event, which were compared using parametric two-sample t-tests on lognormal distributions, no significant differences were found between concentrations at the site and duplicate samples. Table 3.11 shows the p-values for each event.

Table 3.11. P-values for two-sample t-tests for detecting differences between site concentrations and corresponding duplicate concentrations

Event	P-value
1	0.888
2	0.920
3	0.933
4	0.920
5	0.993

In Tables 3.6-3.10, the duplicate sample concentrations are presented along with the concentrations at the corresponding sites. For simplicity, Table 3.12 summarizes this data. As previously discussed within the methods section (2.3.2), the duplicates and corresponding site samples were averaged to have one value per site to analyze. Even though one value may appear higher than the other (e.g. Event 4 concentrations for Copper at the duplicate site, Table 3.12),

the values were still averaged in order to have consistency. Based on the above analysis, no significant differences between samples were found within any events.

Table 3.12. Analyte concentrations for sites and duplicates for each event

Event	Site ID	Analyte	Site Concentration	Duplicate Concentration	Average Concentration (Site + Duplicate)	Relative Percent Difference (RPD)
1	R2	NH4	0.25	0.31	0.28	21
1	R2	Total P	0.13	0.23	0.18	56
1	R2	Cu	4.42	5.67	5.045	25
1	R2	Pb	7.24	8.69	7.965	18
1	R2	Hg	0.014	0.016	0.015	13
1	R2	Zn	23.3	24	23.65	3
1	R2	pH	5.8	5.8	5.8	0
1	R2	Cond	24.3	28.5	26.4	16
2	C1	NH4	0.46	0.46	0.46	0
2	C1	Total P	0.040	0.03	0.035	29
2	C1	Cu	2.70	2.51	2.605	7
2	C1	Pb	1.43	1.02	1.225	33
2	C1	Hg	0.004	0.004	0.004	0
2	C1	Zn	35.6	21.1	28.35	51
2	C1	pH	5.63	5.63	5.63	0
2	C1	Cond	7.1	7.2	7.15	1
3	OS1	NH4	0.27	0.2	0.235	30
3	OS1	Total P	0.32	0.14	0.23	78
3	OS1	Cu	1.98	1.58	1.78	22
3	OS1	Pb	0.77	0.83	0.8	8
3	OS1	Hg	0.015	0.042	0.0285	95
3	OS1	Zn	9.88	8.55	9.215	14
3	OS1	pH	5.4	5.63	5.515	4
3	OS1	Cond	10.5	7.2	8.85	37
4	I4	NH4	0.18	0.16	0.17	12
4	I4	Total P	0.048	0.036	0.042	29
4	I4	Cu	34	13.4	23.7	87
4	I4	Pb	4.41	5.87	5.14	28
4	I4	Hg	0.0086	0.0072	0.0079	18
4	I4	Zn	26.2	26.8	26.5	2
4	I4	pH	5.5	5.6	5.55	2
4	I4	Cond	6.5	6.1	6.3	6
5	R1	NH4	0.49	0.5	0.495	2
5	R1	Total P	0.072	0.067	0.0695	7
5	R1	Cu	31.7	18.1	24.9	55
5	R1	Pb	1.65	2.23	1.94	30
5	R1	Hg	0.0078	0.0096	0.0087	21
5	R1	Zn	32.2	40.7	36.45	23
5	R1	pH	6	5.7	5.85	5
5	R1	Cond	9.96	10.2	10.08	2

3.3 Meteorological Conditions

Tables 3.1-3.10 summarize the key elements of each of the five storm events. Additional aspects, however, are worth discussing separately. These include precipitation amount, sample volume, and wind direction.

3.3.1 Precipitation Amount

Figure 3.1 summarizes the precipitation amount during each of the five storm events. The distribution of precipitation amount is neither normal nor lognormal. Therefore, a nonparametric Kruskal-Wallis analysis was used on the data to determine whether or not there are differences in precipitation amount between the five storm events.

Figure 3.1. Precipitation amount measured during each storm event.

Pairwise comparisons detected 8 pairs of significant differences between the storm events (Figure 3.2). The most relevant differences are those between event 4 and the other storm events. Pairwise comparisons show the precipitation amount during event 4 to be significantly greater than the precipitation amount during any of the other storm events. The precipitation amount during event 1 is also significantly greater than the precipitation amount during the other storm events, with the exception of event 4. This may hold significance when analyzing analyte concentrations due to possible dilution effects.

Figure 3.2. Results of a Kruskal-Wallis analysis for precipitation amount during each storm event.

Significant correlations were detected between the concentrations of analytes and precipitation amount, specifically for the nutrients and heavy metals. The concentrations were found to be negatively correlated with the precipitation amount; as precipitation amounts increase, concentrations decrease. The correlation for copper and precipitation was near significant, with a p-value equal to 0.059. No significant correlations were detected between precipitation amounts and pH or conductivity. Table 3.13 summarizes the correlation values and p-values for each analyte.

Table 3.13. Correlations between concentrations and precipitation amount

Analyte	Correlation Value*	p-value
NH ₃	-0.347	0.001
Total P	-0.305	0.005
Cu	-0.212	0.059
Pb	-0.336	0.002
Hg	-0.224	0.045
Zn	-0.263	0.018
pH	0.068	0.555
Cond	-0.073	0.521

*Correlations are Spearman's Rho values (nonparametric), except for Hg and pH which are Pearson's R values (parametric)

3.3.2 Wind Direction

Table 3.14 summarizes the dominant wind direction and average wind direction for each of the 5 storm events. Hontoria et al. (2003) defined the dominant wind direction to be the wind direction on the first day of the storm event. They supposed this direction was related to the

origin of the mass of air causing the precipitation. The dominant wind direction for the length of the study was SW, followed in second place by SE.

Table 3.14. Wind directions for each storm event.

Event	Dominant Wind Direction	Average Wind Direction
1	SW	SE
2	SE	SE
3	SW	SW
4	SW	SE
5	SE	SE

3.4 Ammonia

3.4.1 Exploratory Data Analysis

Exploratory data analysis shows the ammonia concentration dataset (across all events and land uses) to be non-normal. A histogram and box plot of the original data (Figure 3.3) shows the data to be positively skewed, with a sharper than normal peak (Skewness = 1.43, Kurtosis = 5.36). A probability plot (Figure 3.4) gives a p-value of 0.040, rejecting the null hypothesis that the data follow a normal distribution.

Figure 3.3. Histogram and box plot of ammonia concentration, showing a positive/right skew with a sharper than normal peak.

Figure 3.4. Probability plot of ammonia concentration ($p = 0.040$, rejecting the null hypothesis that the data come from a normal distribution).

A log transformation of the data produces a negatively skewed distribution (Skewness = -1.23, Kurtosis = 3.57) (Figure 3.5). A probability plot (Figure 3.6) concludes that the transformed data is non-normally distributed ($p < 0.005$). Additional transformations produced similar results. Therefore, the distribution of the data was determined to be non-normal and a nonparametric test is needed for analysis.

Figure 3.5. Histogram and box plot of the log transformation of ammonia concentration, showing a negative/left skew with a sharper than normal peak.

Figure 3.6. Probability plot of the log transformed ammonia concentration ($p < 0.005$, rejecting the null hypothesis that the data come from a lognormal distribution).

3.4.2 Land Use Analysis

Ammonia concentrations within each individual land use are summarized in Figure 3.7. Results of a Kruskal-Wallis test indicate that there is a difference in concentrations among land uses. Pairwise comparisons showed significant differences between four pairs of land uses (Figure 3.8). Differences were detected between commercial and open space, commercial and residential, industrial and open space, and industrial and residential land use categories. Specifically, ammonia concentrations within both the commercial and industrial areas are significantly greater than concentrations measured in both the open space and residential areas (Figure 3.7).

Figure 3.7. Box plots comparing ammonia concentration within each land use.

Figure 3.8. Pairwise Comparisons from a Kruskal-Wallis analysis of ammonia concentration within each land use.

3.4.3 Event Analysis

Ammonia concentrations during each event within each land use are summarized in Figure 3.9. Figure 3.10 shows the concentrations during each event across all land uses. The results of a Kruskal-Wallis test indicate a significant difference in concentrations between events. Pairwise comparisons indicated significant differences in ammonia concentrations between events 1 and 4, 2 and 4, 3 and 4, and 4 and 5 (Figure 3.11). Ammonia concentrations sampled during event 4 are significantly lower than the four other events sampled.

Figure 3.9. Box plots comparing ammonia concentration during each event within each of the four land uses.

Figure 3.10. Box plots comparing ammonia concentration during each event across all land uses.

Figure 3.11. Pairwise Comparisons from a Kruskal-Wallis analysis of ammonia concentration during each storm event.

Significant differences between events were found within two out of the four land use categories: commercial and industrial. Within the commercial land use, a significant difference was found between events 2 and 4. Within the industrial land use, differences were found between three sets of events: events 1 and 4, events 2 and 4, and events 4 and 5. Event 4 showed significantly lower concentrations than the other events mentioned.

3.4.4 Site Analysis

Ammonia concentrations at each site within each of the four land uses are summarized in Figures 3.12-3.15. Significant differences between sites occurred within the open space land use category only.

Pairwise comparisons showed the differences within the open space to occur between sites 1 and 2 and sites 2 and 4. Concentrations at site 2 are significantly higher than at sites 1 and 4. Even though the concentrations at site 3 are not significantly different from those at site 2, Figure 3.14 indicates concentrations at site 2 to be slightly greater than those at site 3.

Figure 3.12. NH₃ concentration at each site location within the commercial land use category

Figure 3.13. NH₃ concentration at each site location within the industrial land use category

Figure 3.14. NH₃ concentration at each site location within the open space land use category

Figure 3.15. NH₃ concentration at each site location within the residential land use category

3.4.5 Summary and Conclusions for Ammonia

- Concentrations within commercial and industrial land uses are significantly greater than within open space and residential land uses
- Concentration differences between three pairs of events, across all land uses:
 - Event 4 significantly lower than all other events
- Concentration differences between events within the commercial and industrial land use categories only:

- Commercial: event 4 significantly lower than event 2
 - Industrial: event 4 significantly lower than events 1, 2 & 5
- Concentrations between sites are different within open space land use only
 - Open space: site 2 significantly greater than sites 1 & 4

Ammonia concentrations within both the commercial and industrial areas are significantly greater than concentrations measured in both the open space and residential areas. As Fenn et al. (2003b) suggest, proximity to an urban area is the most important variable in predicting an increase in wet deposition of ammonia. Potential sources causing increased levels of ammonia concentrations in these specific areas may include transportation emissions and emissions from industrial activity (Fenn et al. 2003b). This supports the results obtained from the land use analysis, with commercial and industrial areas showing greater concentrations of ammonia than both open space and residential areas.

Specifically within Portland, ammonia emission levels from highway vehicles are greater than all other ammonia emission sources within the area (563 tons/year in 1999) (USEPA 2004). Fuel combustion (industrial) accounted for 35.6 tons of ammonia per year in 1999 (USEPA 2004). Other ammonia sources within the Portland area include other sources of fuel combustion, waste disposal and recycling, off-highway vehicles, and miscellaneous sources (USEPA 2004).

Precipitation amount during event 4 was determined to be significantly greater than during all other events (Figure 3.1), therefore possibly explaining the results of the events analysis. The significantly lower concentrations during event 4 could be due to a dilution of the samples from the high amount of precipitation.

In addition to differences seen between events across all land uses, differences were also seen between events within two individual land use categories: commercial and industrial. One possible explanation for these differences is that the higher concentration of ammonia present in these land uses cause the dilution of event 4 to be greater than within the open space and residential land uses, where concentrations were not observed to be as high. The effect of event 4 did not seem to be too critical, however, because concentrations within the commercial and industrial land uses are still greater than within the open space and residential land uses.

A difference in concentrations between sites was observed only within the open space land use, showing fairly uniform concentrations across sites within the other three land uses. It is difficult to explain why the Oaks Bottom site showed higher ammonia concentrations than both the Mt. Tabor and Powell Butte sites, but speculation will be made. Powell Butte is the most remote site within the open space land use, which possibly explains why the concentration would be lower (if sticking with the theory that transportation emissions and emissions due to industrial activities are the cause of increased ammonia concentrations within the precipitation). Mt. Tabor seems to have a fair amount of traffic compared to Powell Butte (due to recreation activities), but is at a higher elevation like Powell Butte and is more forested than the sampling point at Oaks Bottom. The sampling point at Oaks Bottom is located near Oaks Amusement Park, which receives a considerable amount of traffic from cars and school buses. Another possibility is meteorological conditions carrying pollution plumes with high ammonia concentrations. Meteorological conditions and traffic densities were not monitored in this study, however, making it difficult to provide accurate explanations for local differences seen within the open space land use category.

3.5 Total Phosphorus

3.5.1 Exploratory Data Analysis

Exploratory data analysis shows the total phosphorus concentration dataset, across all land uses and events, to be non-normal. A histogram and box plot of the original data shows the data to be positively skewed, with a sharper than normal peak (Skewness = 5.80, Kurtosis = 34.20) (Figure 3.16). A probability plot (Figure 3.17) gives a p-value of <0.005 , rejecting the null hypothesis that the data follow a normal distribution.

Figure 3.16. Histogram and box plot of total phosphorus concentration, showing a positive right skew with a sharper than normal peak.

Figure 3.17. Probability plot of total phosphorus concentration ($p < 0.005$, rejecting the null hypothesis that the data come from a normal distribution).

A log transformation of the data produces a positively skewed distribution as well (Skewness = 1.92, Kurtosis = 4.73). This is illustrated in the histogram a box plot in Figure 3.18, and is supported with the probability plot in Figure 3.19 ($p < 0.005$). This is most likely due to the large number of nondetects in this dataset. Additional transformations produced similar

results. Therefore, the distribution of the data was determined to be non-normal, needing a nonparametric test for analysis.

Figure 3.18. Histogram and box plot if the log transformation of total phosphorus concentration, showing a positive/right skew with a sharper than normal peak.

Figure 3.19. Probability plot of the log transformation of total phosphorus concentration ($p < 0.005$, rejecting the null hypothesis that the data come from a normal distribution).

3.5.2 Land Use Analysis

Total phosphorus concentrations within each individual land use are summarized in Figure 3.20. Results of a Kruskal-Wallis test indicate a difference in total phosphorus concentration among land uses ($p = 0.002$). Pairwise comparisons show significant differences between two pairs of land uses: commercial and residential, and commercial and open space (Figure 3.21). The box plots in Figure 3.20 and pairwise comparisons in Figure 3.21 indicate significantly higher levels of phosphorus within the residential and open space areas than within the commercial areas.

Figure 3.20. Boxplots comparing total phosphorus concentration within each land use.

Figure 3.21. Pairwise Comparisons from a Kruskal-Wallis analysis of total phosphorus concentration within each land use.

3.5.3 Event Analysis

Total phosphorus concentrations during each event within each land use are summarized in Figure 3.22, while Figure 3.23 shows the concentrations during each event across all land uses. The results of a Kruskal-Wallis test indicate a nearly significant difference in total phosphorus concentration between storm events, taking into account all of the sites ($p = 0.052$). Pairwise comparisons indicated significant differences between three pairs of events: events 1 and 3, events 1 and 5, and events 3 and 4 (Figure 3.24).

Differences between events were found within the commercial and industrial land use categories only. Within the commercial land use, differences in total P concentration were found between events 1 and 3, events 1 and 5, and events 3 and 4. Within the industrial land use, differences were found between events 1 and 3 and events 1 and 5. The differences observed within both the commercial and industrial land uses seem to drive the differences observed between events across all sites, due to the corresponding pairs of significant events. Figure 3.24 appears almost identical for pairwise comparisons within the commercial land use and industrial land use, with the exception of events 3 and 4 being equal within the industrial land use.

Figure 3.22. Box plots comparing total phosphorus concentration during each event within each of the four land uses

Figure 3.23. Box plots comparing total phosphorus concentration during each event across all land uses.

Figure 3.24. Pairwise Comparisons from a Kruskal-Wallis analysis of total phosphorus concentration during each storm event.

3.5.4 Site Analysis

Total phosphorus concentrations at each site within each of the four land uses are summarized in Figures 3.25-3.28. Differences between sites were found within the open space and residential land uses only. Within the open space, differences were found between sites 3 and 4 and sites 2 and 4. Within the residential land use, differences were found between sites 1 and 4.

Figure 3.25. Total P concentration at each site location within the commercial land use category

Figure 3.26. Total P concentration at each site location within the industrial land use category

Figure 3.27. Total P concentration at each site location within the open space land use category

Figure 3.28. Total P concentration at each site location within the residential land use category

3.5.5 Summary and Conclusions for Total Phosphorus

- Concentrations within both residential and open space land uses significantly greater than within commercial land use
- Concentration differences between three pairs of events, across all land uses:
 - Event 4 concentrations significantly lower than event 3
 - Event 1 concentrations significantly lower than events 3 & 5
- Concentration differences between events within the commercial and industrial land use categories only
 - Commercial: event 4 significantly lower than event 1; event 1 significantly lower than events 3 & 5
 - Industrial: event 1 significantly lower than events 3 & 5
- Concentration differences between sites within open space and residential land use categories only:
 - Open space: site 4 significantly lower than sites 2 & 3
 - Residential: site 1 significantly lower than site 4

In a New Jersey Atmospheric Deposition Network study, wet deposition of total phosphorus was analyzed in four land uses (Koelliker et al. 2003). It was found that the urban sites were more influenced by industrially associated phosphorus loadings, while both rural and suburban sites were influenced by the localized application of phosphorus-containing fertilizers (Koelliker et al. 2003). In the current study, significantly higher phosphorus levels were found within the residential and open space land use categories than the commercial land use category. This may suggest that locally applied phosphorus-containing fertilizers, or additional rural and suburban sources such as the re-suspension of biogenic material or the incineration of biomass, are of greater importance in the Portland area than industrially associated loadings (Koelliker et al. 2003).

Examining events across all land uses, differences in concentrations were observed between three pairs of events, with event 1 being significantly lower than events 3 and 5 and event 4 being significantly lower than event 3. Event 4 showed a significantly higher amount of rainfall than the other events, possibly causing dilution of the samples (Figure 3.1). Event 1 showed the second highest amount of rainfall compared to all other events, possibly causing

dilution of the samples as well. Both of these observations may explain the differences seen in concentrations between events. When looking at differences between events within specific land use categories, differences were seen within commercial and industrial land use categories only.

Even though differences in concentrations were seen between pairs of events within the commercial land use, with specific events showing significantly greater concentrations than others, it does not seem to influence the relationships between land uses. Concentrations within the commercial areas are significantly lower than within the open space and residential areas.

Within the open space land use, differences between sites were seen between sites 2 and 4 and sites 3 and 4, with site 4 being significantly lower than both sites 2 and 3. A possible explanation for this is the remoteness of Powell Butte (site 4) causing a lower concentration than at Oaks Bottom and Forest Park. This, however, does not fit the theory that concentrations within the residential and open space are greater than within the commercial areas due to the influence of rural and suburban sources.

Within the residential land use, differences were seen between sites 1 and 4; site 1 showing significantly lower concentrations than site 4. This could be due to a site specific influence, but without further analysis of the sites it is difficult to determine why this difference occurred.

3.6 Copper

3.6.1 Exploratory Data Analysis

Exploratory data analysis shows the copper concentration dataset to be non-normally distributed and, thus nonparametric statistics will be used. A histogram and box plot of the original data (Figure 3.29) shows the data to be positively skewed, with a sharper than normal peak (Skewness = 4.34, Kurtosis = 22.14). A probability plot (Figure 3.30) gives a p-value < 0.005, rejecting the null hypothesis that the data follow a normal distribution.

Figure 3.29. Histogram and box plot of copper concentration, showing a positive/right skew with a sharper than normal peak.

Figure 3.30. Probability plot of copper concentration ($p < 0.005$, rejecting the null hypothesis that the data come from a normal distribution).

A log transformation of the data produced a positively skewed distribution as well (Skewness = 1.07, Kurtosis = 1.09) (Figure 3.31). A probability plot indicates that the transformed data is from a non-normal distribution ($p < 0.005$) (Figure 3.32). Additional transformations produced similar results.

Figure 3.31. Histogram and box plot of the log transformation of copper concentration, showing a positive/right skew with a sharper than normal peak.

Figure 3.32. Probability plot of the log transformed copper concentration ($p < 0.005$, rejecting the null hypothesis that the data come from a normal distribution).

3.6.2 Land Use Analysis

Copper concentrations within each individual land use are summarized in Figure 3.33. Results of a Kruskal-Wallis test indicate that there is a difference in copper concentrations among land uses. Pairwise comparisons showed significant differences between four pairs of land uses (Figure 3.34). Differences were detected between industrial and open space, commercial and industrial, open space and residential, and industrial and residential land use categories. The copper concentrations found within the industrial land use are significantly greater than concentrations found in the other three land use categories. In addition, copper concentrations were found to be significantly higher in residential areas than open space areas.

Figure 3.33. Box plots comparing copper concentration within each land use.

Figure 3.34. Pairwise Comparisons from a Kruskal-Wallis analysis of copper concentration within each land use.

3.6.3 Event Analysis

Copper concentration during each storm event within each land use is summarized in Figure 3.35a. The results of a Kruskal-Wallis test indicate no significant difference in concentration between events (Figures 3.36 and 3.37).

Figure 3.35a. Box plots comparing Cu concentration during each event within each of the four land uses.

Figure 3.35b. Box plots comparing Cu concentration during each event within the commercial land use.

Figure 3.36. Box plots comparing copper concentration during each event across all land uses.

Figure 3.37. Pairwise Comparisons from a Kruskal-Wallis analysis of copper concentration during each storm event.

Even though no significant differences were found between events as a whole, differences were detected within the commercial land use category (Figure 3.35b). Within this land use, differences were found between events 4 and 5 and events 3 and 4. Specifically, concentrations during event 4 were found to be significantly lower than during events 3 and 5.

3.6.4 Site Analysis

Copper concentrations at each site within each of the four land uses are summarized in Figures 3.38-3.41. Differences between sites occurred within three out of four land use categories: industrial, open space, and residential. Pairwise comparisons showed the differences

within the industrial land use to occur between sites 3 and 4 and sites 1 and 3. Specifically, concentrations at sites 1 and 4 are significantly higher than at site 3.

Within the open space, differences occurred between sites 3 and 4 and sites 2 and 4. Specifically, the concentrations are significantly lower at site 4 than sites 2 and 3.

Within the residential land use, differences occurred between sites 1 and 4, 1 and 3, 2 and 4, and 2 and 3. Specifically, concentrations at sites 1 and 2 are significantly higher than at both sites 3 and 4.

Figure 3.38. Copper concentration at each site location within the commercial land use category

Figure 3.39. Copper concentration at each site location within the industrial land use category

Figure 3.40. Copper concentration at each site location within the open space land use category

Figure 3.41. Copper concentration at each site location within the residential land use category

3.6.5 Summary and Conclusions for Copper

- Concentrations within the industrial land use are significantly higher than within the other three land use categories
- Concentrations within the residential land use are significantly higher than within the open space land use category
- No significant concentration differences between events, across all land uses
- Concentration differences between events within the commercial land use only:
 - Events 3 & 5 significantly greater than event 4

- Concentration differences between sites within the industrial, open space, and residential land use categories:
 - Industrial: sites 1 & 4 significantly greater than site 3
 - Open Space: site 4 significantly lower than sites 2 & 3
 - Residential: sites 1 & 2 are significantly higher than sites 3 & 4

Focusing on land uses only, concentrations are significantly higher within the industrial areas compared to the other three land uses. Additionally, concentrations are significantly higher in residential areas than within open space areas. These results support the belief that the primary source of copper in the air is copper dust generated by copper processing operations, which takes place in industrial areas (USEPA 2005a). Additional sources of copper in the atmosphere may include fuel combustion, burning, and vehicle brake pads (Pun and Seigneur 2004).

The EPA does not provide data on copper emissions within the city. Data on particulate matter emissions, however, are available (USEPA 2004). Within Portland, the primary sources of particulate matter are fugitive dust and the metal works industry (USEPA 2004). Fugitive dust within the city originates primarily from unpaved roads and construction sites. This, along with emissions from the metal works industry, may explain the high levels of copper seen in the industrial areas.

Because significant differences between events occurred within the commercial land use category only, it is likely that the individual storm events did not greatly affect the results of the land use analysis. Specifically, concentrations during event 4 were found to be significantly lower than during events 3 and 5. This could be due to the higher amounts of precipitation received during event 4 compared to the other events (Figure 3.1).

Within the industrial land use, copper concentrations at sites 1 and 4 were found to be significantly higher than at site 3. According to the land use classifications found on The City of Portland's PortlandMaps.com, the Oregon Humane Society site (I3) is classified as general industrial rather than heavy industrial like Gunderson (I1) and Schnitzer Steel (I4). This could be a possible explanation for the lower concentrations of copper found at site 3.

Within the open space land use, concentrations are significantly lower at site 4 than sites 2 and 3. This could be due to Powell Butte (site 4) being much more remote than both Oaks Bottom and Forest Park.

Within the residential land use, concentrations at sites 1 and 2 are significantly higher than at both sites 3 and 4. There is no specific explanation for this; differences could be due to site specific influences such as vegetation type or proximity to a copper source. Additionally, sites 1 and 2 are geographically located in the northern part of Portland, while sites 3 and 4 are located in the southern part of the city. A geographical influence could be the cause of the difference between sites. Industrial activities predominate within the northern part of the city (Figure 2.1), therefore possibly causing higher copper concentrations in the north. However, more research needs to be done on specific sources of copper within the city and meteorological conditions that would bring higher amount of copper to certain areas within the city.

3.7 Lead

3.7.1 Exploratory Data Analysis

Exploratory data analysis shows the lead concentration dataset to be from a non-normal distribution. A histogram and box plot of the original data (Figure 3.42) shows the data to be positively skewed, with a sharper than normal peak (Skewness = 4.99, Kurtosis = 27.03). A probability plot (Figure 3.43) gives a p-value < 0.005, rejecting the null hypothesis that the data follow a normal distribution.

Figure 3.42. Histogram and box plot of lead concentration, showing a positive/right skew with a sharper than normal peak.

Figure 3.43. Probability plot of lead concentration ($p < 0.005$, rejecting the null hypothesis that the data come from a normal distribution).

A log transformation of the data produced a positively skewed distribution as well (Skewness = 0.88, Kurtosis = 1.65) (Figure 3.44). A probability plot indicates that the transformed data is from a non-normal distribution ($p = 0.012$) (Figure 3.45). Additional transformations of the data produced similar results. Even though the log transformation

produced a distribution that was close to normal, it was decided that the data did not entirely fit a normal distribution and therefore a nonparametric test was used.

Figure 3.44. Histogram and box plot of the log transformation of lead concentration, showing a positive/right skew with a sharper than normal peak.

Figure 3.45. Probability plot of the log transformed lead concentration ($p = 0.012$, rejecting the null hypothesis that the data come from a normal distribution).

3.7.2 Land Use Analysis

Lead concentrations within each individual land use are summarized in Figure 3.46. Results of a Kruskal-Wallis test indicate that there is a difference in lead concentrations among different land use categories. Pairwise comparisons showed significant differences between five pairs of land use categories (Figure 3.47). Differences were detected between industrial and open space, commercial and open space, open space and residential, industrial and residential, and commercial and industrial land use categories. No differences were found between commercial and residential land uses.

Lead concentrations within the industrial land use are significantly higher than within the other three land uses. Additionally, the concentration within the open space land use is significantly lower than within the other land uses.

Figure 3.46. Box plots comparing lead concentrations within each land use.

Figure 3.47. Pairwise Comparisons from a Kruskal-Wallis analysis of lead concentration within each land use.

3.7.3 Event Analysis

Lead concentrations during each storm event within each land use are summarized in Figure 3.48. The result of a Kruskal-Wallis test indicates a significant difference in lead concentration between storm events. Pairwise comparisons indicate differences between three

pairs of storm events (Figure 3.50). There are differences detected between events 4 and 5, events 3 and 4, and events 2 and 4 (Figure 3.49). The lead concentration found in samples during event 4 is significantly lower than that found during 3 out of the 4 other events.

Figure 3.48. Box plots comparing lead concentration during each event within each of the four land uses.

Figure 3.49. Box plots comparing lead concentration during each event across all land uses.

Figure 3.50. Pairwise Comparisons from a Kruskal-Wallis analysis of lead concentration during each storm event.

Differences in lead concentrations among events were also found within individual land uses, specifically within the commercial land use category. Within this land use, differences were found between events 4 and 5, events 3 and 4, and events 2 and 4. Specifically, event 4 was significantly lower than the other mentioned events.

3.7.4 Site Analysis

Lead concentrations at each site within each of the found land uses are summarized in Figures 3.51-3.54. Differences between sites occurred within three out of four land use categories: industrial, open space, and residential.

Pairwise comparisons showed the differences within the industrial land use to occur between sites 3 and 4, sites 2 and 4, and sites 1 and 3. Concentrations at sites 1 and 4 are both significantly greater than at site 3.

Within the open space, differences occurred between sites 2 and 4, sites 3 and 4, and sites 1 and 4. Concentrations at site 4 are significantly lower than at all other sites within the open space.

Within the residential land use, differences occurred between sites 2 and 4, sites 1 and 2, and sites 3 and 4. Specifically, concentrations at site 2 are significantly higher than at sites 1 and 4, and concentrations at site 3 are significantly higher than at site 4.

Figure 3.51. Lead concentration at each site location within the commercial land use category

Figure 3.52. Lead concentration at each site location within the industrial land use category

Figure 3.53. Lead concentration at each site location within the open space land use category

Figure 3.54. Lead concentration at each site location within the residential land use category

3.7.5 Summary and Conclusions for Lead

- Concentrations within the industrial land use are significantly higher than within the other three land use categories
- Concentrations within the open space land use are significantly lower than within the other three land use categories
- Concentration differences between three pairs of events, across all land uses:
 - Event 4 concentrations significantly lower than events 2, 3, & 5
- Concentration differences between events within the commercial land use category only:
 - Event 4 concentrations significantly lower than events 2, 3, & 5
- Concentration differences between sites within the industrial, open space, and residential land use categories:
 - Industrial: sites 1 & 4 significantly higher than site 3; site 4 significantly higher than site 2
 - Open space: site 4 significantly lower than all other sites
 - Residential: site 2 significantly higher than sites 1 & 4; site 3 significantly higher than site 4

Focusing on land uses only, concentrations are significantly higher within the industrial areas compared to the other three land uses. Because the primary source of lead in the atmosphere is due to industrial activities (Manahan 2005), these results seem reasonable. Industrial sources of lead may include mining, smelting and refining, manufacture of lead products, metal works, and incinerators of waste.

Within the Portland area, 19,680 pounds of lead compounds are emitted per year, looking at total emission sources (USEPA 2004). Major source emissions, or point sources/facilities (primarily industrial), account for about 82% of the total emission sources (USEPA 2004).

Additionally, concentrations are significantly lower in the open space areas than within the other three land uses. It seems reasonable to expect lead concentrations to decrease in the atmosphere in the more remote areas due to the greater distance from potential sources of atmospheric lead. However, due to a lack of analysis of distance from potential sources, this is just a speculation rather than a conclusion.

The lead concentration found in samples during event 4 is significantly lower than that found during 3 out of the 4 other events. This could be due to the fact that the greatest amount of precipitation fell during event 4 (Figure 3.1), possibly diluting the samples. Because significant differences between events occurred within the commercial land use category only, it is likely that the individual storm events did not greatly affect the results of the land use analysis.

Within the industrial land use, concentrations at sites 1 and 4 are both significantly greater than at site 3. This could be due to the fact that the Gunderson (I1) and Schnitzer Steel (I4) sites are considered heavy industrial, while the Oregon Humane Society site (I3) is classified as general industrial (according to PortlandMaps.com).

Within the open space, concentrations at the Powell Butte site (OS4) are significantly lower than at all other sites within the open space. This may be due to Powell Butte being the most remote site monitored within this land use type.

Within the residential land use, concentrations at site 2 are significantly higher than at sites 1 and 4. Concentrations at site 2 may be greater than at sites 1 and 4 because of possible contamination of two out of the five samples. These specific samples were discolored and contained excess debris. There is no reasonable explanation for why concentrations at site 3 are greater than site 4. Further analysis of the residential sites is needed to determine exactly why these differences occurred.

3.8 Mercury

3.8.1 Exploratory Data Analysis

Exploratory data analysis shows the mercury concentration dataset to be from a lognormal distribution. A histogram and box plot of the original data (Figure 3.55) shows the data to be positively skewed, with a sharper than normal peak (Skewness = 3.52, Kurtosis = 16.83). A probability plot (Figure 3.56) gives a p-value < 0.005, rejecting the null hypothesis that the data follow a normal distribution.

Figure 3.55. Histogram and box plot of mercury concentration, showing a positive/right skew with a sharper than normal peak.

Figure 3.56. Probability plot of mercury concentration ($p < 0.005$, rejecting the null hypothesis that the data come from a normal distribution).

A log transformation of the data produced a normal distribution, with Skewness = 0.39 and Kurtosis = 0.61 (Figure 3.57). A probability plot further verifies the lognormal distribution, with a p-value of 0.092 (Figure 3.58). The null hypothesis that the log transformed data come from a normal distribution cannot be rejected.

Figure 3. Histogram and box plot of the log transformation of mercury concentration, showing a lognormal distribution.

Figure 4. Probability plot of the log transformed mercury concentration ($p = 0.092$, failing to reject the null hypothesis that the data come from a normal distribution).

3.8.2 Land Use Analysis

Mercury concentrations within each individual land use are summarized in Figure 3.59. Results of an ANOVA, using log transformed data, show a difference in mercury concentrations found in precipitation between land uses. Bonferroni pairwise comparisons showed no true significant differences among specific pairs of land uses ($p > 0.05$), but concentrations found within commercial and industrial land uses were close to being significantly different ($p = 0.0617$). This p -value decreased slightly below 0.05 when a Tukey pairwise comparison was performed, so it will be called near significant, with the industrial areas having a higher concentration than commercial areas.

Figure 3.59. Box plots comparing mercury concentration within each land use.

3.8.3 Event Analysis

Mercury concentrations during each storm event within each land use are summarized in Figure 3.60. The results of an ANOVA indicate significant differences in mercury concentration between five pairs of events. These differences, as detected by Bonferroni pairwise comparisons, occurred specifically between events 1 and 3, events 1 and 5, events 2 and 3, events 2 and 5, and events 3 and 4 (Figure 3.61). Events 1 and 4 typically had the lowest mercury concentrations, while events 3 and 5 had the highest.

Figure 3.60. Box plots comparing mercury concentration during each storm event within each of the four land uses.

Figure 3.61. Box plots comparing mercury concentration during each event across all land uses.

Differences were also detected in mercury concentrations between events within the commercial land use category only. Specifically, differences within the commercial land use occurred between events 1 and 3, events 1 and 5, events 2 and 3, events 2 and 4, events 3 and 4, and events 4 and 5. Similar to the above analysis for events across all land uses, events 1 and 4 typically had the lowest mercury concentrations, while events 3 and 5 had the highest.

3.8.4 Site Analysis

Mercury concentrations at each site within each of the four land uses are summarized in Figures 3.62-3.65. Differences between sites occurred within the open space land use category only. Pairwise comparisons (Bonferroni) showed differences within the open space land use to occur between sites 1 and 4, and somewhat significant differences to occur between sites 3 and 4 ($p = 0.0638$), with concentrations at site 4 being less than those at both sites 1 and 3.

Figure 3.62. Mercury concentration at each site location within the commercial land use category

Figure 3.63. Mercury concentration at each site location within the industrial land use category

Figure 3.64. Mercury concentration at each site location within the open space land use category

Figure 3.65. Mercury concentration at each site location within the residential land use category

3.8.5 Summary and Conclusions for Mercury

- Concentrations within industrial land use are significantly higher than within the commercial land use category
- Concentration differences between five pairs of events, across all land uses:
 - Event 1 concentrations significantly lower than events 3 & 5
 - Event 2 concentrations significantly lower than events 3 & 5
 - Event 4 concentrations significantly lower than event 3
- Concentration differences between events within the commercial land use only:
 - Event 1 concentrations significantly lower than events 3 & 5
 - Event 2 concentrations significantly lower than event 3
 - Event 4 concentrations significantly lower than events 2, 3, & 5
- Concentration differences between sites within the open space land use category only:
 - Open space: site 4 significantly lower than sites 1 & 3

The higher concentration within the industrial areas compared to the commercial areas is to be expected due to the high amounts of mercury put into the atmosphere from industrial activities (Jacobson 2002). Industrial sources of mercury may include incinerators, electric utilities, waste combustors, and coal-fired boilers.

Within Portland, 2,380 pounds of mercury are emitted per year, as total mercury emissions (USEPA 2004). Major source emissions (point sources/facilities) account for about 96% of the total emissions (USEPA 2004). Because of this, it seems that mercury concentrations should be higher within the industrial areas compared to all other land use types (not just commercial). In this study, however, that is not the case. The literature actually shows that a higher amount of mercury (25,000-150,000 tons per year) is released through the natural degassing of the earth's crust, compared to the 20,000 tons per year released by industrial activities and fossil fuel combustion (Jacobson 2002). Therefore, specific land uses may not have such a significant effect on mercury concentrations detected in precipitation.

As far as specific storm events are concerned, events 1 and 4 typically had the lowest mercury concentrations. This is reasonable due to the highest precipitation amount seen during these two events compared to other events (Figure 3.1). The high amount of precipitation could cause a significant amount of dilution.

Examining differences between events within specific land use categories, the commercial land use was the only one to show differences. These differences are similar to the ones detected across all land uses, and may be due to some sort of meteorological pattern within the areas of the commercial sites.

Differences between sites were detected within the open space land use category only. This means the other land uses had fairly consistent mercury concentrations across all sites. Specifically within the open space, the Powell Butte site (O4) was significantly lower in mercury concentration than either Mt Tabor (OS1) or Forest Park (OS3). This could be due to Powell Butte being the most remote site within this land use.

3.9 Zinc

3.9.1 Exploratory Data Analysis

Exploratory data analysis shows the zinc concentration dataset to be non-normal. Therefore, a nonparametric test is needed for analysis. A histogram and box plot of the original data (Figure 3.66) show the data to be positively skewed, with a sharper than normal peak (Skewness = 6.02, Kurtosis = 37.07). A probability plot (Figure 3.67) gives a p-value of <0.005, rejecting the null hypothesis that the data follow a normal distribution.

Figure 3.66. Histogram and box plot of zinc concentration, showing a positive/right skew with a sharper than normal peak.

Figure 3.67. Probability plot of zinc concentration ($p < 0.005$, rejecting the null hypothesis that the data come from a normal distribution).

A log transformation of the data produced a positively skewed distribution as well (Skewness = 1.62, Kurtosis = 3.99) (Figure 3.68). A probability plot concludes the transformed data to be from a non-normal distribution ($p < 0.005$) (Figure 3.69). Additional transformations produced similar results. Therefore, the distribution of the data was determined to be non-normal and a nonparametric analysis was needed.

Figure 3.68. Histogram and box plot of the log transformation of zinc concentration, showing a positive/right skew with a sharper than normal peak.

Figure 3.69. Probability plot of the log transformed zinc concentration ($p < 0.005$, rejecting the null hypothesis that the data come from a lognormal distribution).

3.9.2 Land Use Analysis

Zinc concentrations within each individual land use are summarized in Figure 3.70. Results of a Kruskal-Wallis test showed a difference in zinc concentrations between land uses. Pairwise comparisons showed significant differences among four pairs of land uses: industrial and open space, commercial and open space, open space and residential, and industrial and residential land use categories (Figure 3.71).

The concentration of zinc within the open space land use is significantly lower than the concentration within the other three land uses. The industrial land use has a significantly higher concentration of zinc present than both the open space and residential land uses.

Figure 3.70. Box plots comparing zinc concentration within each land use.

Figure 3.71. Pairwise Comparisons from a Kruskal-Wallis analysis of zinc concentration within each land use.

3.9.3 Event Analysis

Zinc concentrations for each event within each land use are summarized in Figure 3.72. Figure 3.73 summarizes the concentrations for each event across all land uses. The results of a Kruskal-Wallis test indicate no significant difference in zinc concentration between events across all land uses. However, pairwise comparisons indicate a significant difference between events 3 and 4, with event 4 showing significantly lower concentrations than event 3 (Figure 3.74).

Figure 3.72. Box plots comparing zinc concentration during each event within each of the four land uses.

Figure 3.73. Box plots comparing zinc concentration during each event across all land uses.

Figure 3.74. Pairwise Comparisons from a Kruskal-Wallis analysis of zinc concentration during each storm event.

Differences between events were found within two out of the four land use categories: commercial and industrial. Within the commercial land use, differences were found between events 2 and 4, events 3 and 4, and events 4 and 5. The concentrations during event 4 are significantly lower than events 2, 3, and 5. Within the industrial land use, differences were found between events 3 and 4 and events 4 and 5, with event 4 being significantly lower than the other two events.

3.9.4 Site Analysis

Zinc concentrations at each site within each of the four land uses are summarized in Figures 3.75-3.78. Differences between sites occurred within the industrial, open space, and residential land use categories.

Pairwise comparisons showed the differences between the industrial land use category to occur between sites 3 and 4 only, with site 4 having significantly higher concentrations than site 3.

Within the open space, differences occurred between sites 3 and 4 and sites 2 and 4. Specifically, site 4 showed significantly lower concentrations than sites 2 and 3.

Within the residential land use, differences occurred between sites 2 and 3 and sites 2 and 4. Specifically, site 2 showed significantly higher concentrations than sites 3 and 4.

Figure 3.75. Zinc concentration at each site location within the commercial land use category

Figure 3.76. Zinc concentration at each site location within the industrial land use category

Figure 3.77. Zinc concentration at each site location within the open space land use category

Figure 3.78. Zinc concentration at each site location within the residential land use category

3.9.5 Summary and Conclusions for Zinc

- Concentrations within industrial land use are significantly higher than within the open space and residential land use categories

- Concentrations within the open space land use are significantly lower than within the other land use categories
- Concentration differences between events 3 and 4 only
 - Event 4 concentrations significantly lower than event 3
- Concentration differences between events within commercial and industrial land use categories
 - Commercial: event 4 concentrations significantly lower than events 2, 3, & 5
 - Industrial: event 4 concentrations significantly lower than events 3 & 5
- Concentration differences between sites within industrial, open space, and residential land use categories
 - Industrial: site 3 significantly lower than site 4
 - Open space: site 4 significantly lower than sites 2 & 3
 - Residential: site 2 significantly higher than sites 3 & 4

Because zinc has a primarily industrial origin, it is reasonable for concentrations to be highest in the industrial areas compared to the open space and residential areas (Jacobson 2002). Air near industrial areas is likely to have higher levels of zinc, meaning that concentrations found in the precipitation could potentially be higher as well. Possible industrial sources of zinc include the galvanization of metals, rubber industry, zinc oxide in paints, and die castings by the automotive industry. There is no explanation as to why concentrations within the industrial areas are not greater than those found within the commercial areas. This could be due to possible local influences at sites within the commercial areas.

As with copper emissions, the EPA does not provide data on zinc emissions within the city. Data on particulate matter emissions, however, are available (USEPA 2004). Within Portland, the primary sources of particulate matter are fugitive dust and the metal works industry (USEPA 2004). Fugitive dust within the city originates primarily from unpaved roads and construction sites. This, along with emissions from the metal works industry, may explain the high levels of zinc seen in the industrial areas.

Significant differences between events were found within both the industrial and commercial land use categories. Within both land uses, concentrations during event 4 were significantly lower than events 3 and 5. This can potentially be explained by the higher precipitation amounts during event 4 causing dilution of the samples (Figure 3.1)

Within the industrial land use, the Oregon Humane Society site (I3) was found to have significantly lower concentrations than the Schnitzer Steel site (I4). This could be due to the classification of the Oregon Humane Society site as general industrial, compared to the heavy industrial classification of Schnitzer Steel (according to PortlandMaps.com). Increased levels of zinc are potentially released in areas where industrial activities dominate.

Within the open space land use, concentrations found at Powell Butte (OS4) are significantly lower than at both Oaks Bottom (OS2) and Forest Park (OS3). Powell Butte is the most remote site within the open space land use category, therefore potentially having a lower influence of zinc sources.

Within the residential land use, concentrations at site 2 are significantly higher than at sites 3 and 4. Concentrations at site 2 may be greater than at sites 3 and 4 because of possible contamination of two out of the five samples. These specific samples were discolored and contained excess debris.

There were no significant differences in zinc concentrations between sites within the commercial land use, but extreme values were observed at site 3 during two events. The site is located near automotive repair shops, which could have been the source of zinc in the samples.

3.10 pH

3.10.1 Exploratory Data Analysis

Exploratory data analysis shows the pH dataset to follow a normal distribution. A histogram and box plot of the data (Figure 3.79) supports this distribution (Skewness = 0.36, Kurtosis = 1.10). A probability plot further supports a normal distribution, with a p-value equal to 0.084 (Figure 3.80).

Figure 3.79. Histogram and box plot of pH, showing a normal distribution.

Figure 3.80. Probability plot of pH ($p = 0.084$), unable to reject the null hypothesis that the data come from a normal distribution.

3.10.2 Land Use Analysis

The pH data within each individual land use are summarized in Figure 3.81. Results of an ANOVA indicate no significant differences in pH of the precipitation among land uses.

Figure 3.81. Box plots comparing pH within each land use.

3.10.3 Event Analysis

The pH data during each storm event within each land use are summarized in Figure 3.82. The results of an ANOVA indicate significant differences between five pairs of events ($p = 0.000$). Pairwise comparisons indicate differences to occur between events 1 and 2, events 1 and 3, events 1 and 4, events 2 and 5, and events 3 and 5. Specifically, the pH during event 1 is significantly higher than during events 2, 3, and 4 (Figure 3.83). Additionally, the pH during event 5 is significantly greater than during events 2 and 3 (Figure 3.83).

Figure 3.82. Box plots comparing pH during each storm event within each of the four land uses.

Figure 3.83. Box plots comparing pH during each storm event across all land uses.

Significant differences in pH were also detected between events within specific land use categories. These differences occurred within commercial, industrial, and open space land use categories. Within the commercial land use, differences occurred between events 1 and 2 only. Within the industrial land use, differences occurred between events 1 and 3 and events 1 and 4. Within the open space land use, differences occurred between events 1 and 2, events 2 and 3, events 2 and 4, and events 2 and 5.

3.10.4 Site Analysis

The pH data at each site within each of the four land uses are summarized in Figures 3.84-3.87. There are no significant differences to report between sites within any of the four land use categories.

Figure 3.84. pH at each site location within the commercial land use category

the industrial land use category

Figure 3.86. pH at each site location within the open space land use category

the residential land use category

3.10.5 Summary and Conclusions for pH

- No significant differences in pH between land uses
- pH differences between five pairs of events, across all land uses:
 - pH during event 1 significantly higher than during events 2, 3, & 4
 - pH during event 5 significantly higher than during events 2 & 3
- pH differences between events within the commercial, industrial, and open space land use categories:
 - Commercial: event 1 significantly higher than event 2
 - Industrial: event 1 significantly higher than events 3 & 4
 - Open space: event 2 significantly lower than all other events
- No significant differences in pH between sites within the land use categories

The only significant differences for pH occurred between a few pairs of events. These differences could be attributed to a difference in meteorological conditions among the events, but sufficient analysis has not been done to determine this. Because no differences in pH were detected between land use categories or between sites within the land use categories, it seems reasonable that the differences between events did not have much effect.

3.11 Conductivity

3.11.1 Exploratory Data Analysis

Exploratory data analysis shows the conductivity dataset to be non-normal. The data do not follow a normal or lognormal distribution. A histogram and box plot of the original data (Figure 3.88) shows the data to be positively skewed, with a sharper than normal peak (Skewness = 5.80, Kurtosis = 39.51). A probability plot (Figure 3.89) gives a p-value of <0.005, rejecting the null hypothesis that the data follow a normal distribution.

Figure 3.88. Histogram and box plot of conductivity, showing a positive/right skew with a sharper than normal peak.

Figure 3.89. Probability plot of conductivity ($p < 0.005$, rejecting the null hypothesis that the data come from a normal distribution).

A log transformation of the data produced a positively skewed distribution as well (Skewness = 1.89, Kurtosis = 5.99) (Figure 3.90). A probability plot concludes the transformed data to be from a non-normal distribution ($p < 0.005$) (Figure 3.91). Additional transformations produced similar results. Therefore, a nonparametric test is needed for analysis.

Figure 3.90. Histogram and box plot of the log transformation of conductivity, showing a positive/right skew with a sharper than normal peak.

Figure 3.91. Probability plot of the log transformed conductivity data ($p < 0.005$, rejecting the null hypothesis that the data come from a lognormal distribution).

3.11.2 Land Use Analysis

Conductivity within each land use is summarized in Figure 3.92. Results of a Kruskal-Wallis test determined that there is no significant difference in conductivity of the precipitation between land uses (Figure 3.93).

Figure 3.92. Box plots comparing conductivity within each land use.

Figure 3.93. Pairwise Comparisons from a Kruskal-Wallis analysis of conductivity within each land use.

3.11.3 Event Analysis

Conductivity during each event within each land use is summarized in Figure 3.94. The conductivity during each event across all land uses is summarized in Figure 3.95. The results of a Kruskal-Wallis test indicate a significant difference in conductivity between events. Pairwise comparisons detect differences between events 1 and 2, events 1 and 4, events 1 and 5, and events 2 and 3 (Figure 3.96). Specifically, event 1 is significantly higher than events 2, 4, and 5, and event 3 is significantly higher than event 2.

Figure 3.94. Box plots comparing conductivity during each event within each of the four land uses.

Figure 3.95. Box plots comparing conductivity during each event across all land uses.

Figure 3.96. Pairwise Comparisons from a Kruskal-Wallis analysis of conductivity during each storm event.

Differences between events were found within the commercial land use category only. Within the commercial land use, pairwise comparisons detected differences between events 1 and 4, events 1 and 5, and events 3 and 4. Specifically, event 1 is significantly higher than events 4 and 5, and event 3 is significantly higher than event 4.

3.11.4 Site Analysis

Conductivity at each site within each of the four land uses is summarized in Figures 3.97-3.100. Differences between sites occurred within the open space land use category only. Within the open space, pairwise comparisons determined differences between sites 1 and 4 and sites 3 and 4, with site 4 showing significantly lower conductivity than sites 1 and 3.

Figure 3.97. Conductivity at each site location within the commercial land use category

Figure 3.98. Conductivity at each site location within the industrial land use category

Figure 3.99. Conductivity at each site location within the open space land use category

Figure 3.100. Conductivity at each site location within the residential land use category

3.11.5 Summary and Conclusions for Conductivity

- No significant differences in conductivity between land uses
- Conductivity differences between four pairs of events, across all land uses:
 - Event 1 significantly higher than events 2, 4, & 5
 - Event 3 significantly higher than event 2
- Conductivity differences between events within the commercial land use category only:
 - Commercial: event 1 significantly higher than events 4 & 5; event 3 significantly higher than event 4
- Conductivity differences between sites within the open space land use category only:
 - Open space: site 4 significantly lower than sites 1 & 3

Conductivity was fairly uniform across all land uses, with no significant differences detected between land use categories. However, differences did occur between events and between sites, specifically within the commercial land use category. These differences did not seem to affect the differences between land uses, however.

3.12 Influence of Industrial Land Use

The results suggest the importance of the industrial land use within Portland in regard to precipitation quality. Because of this, the concentrations of analytes between the industrial land use and all three general land use categories (all lumped together) were compared to see if the industrial areas really do have a significant impact on the precipitation quality.

The analysis was completed using the same methods as within individual analyte sections looking at differences between land use categories. Significant differences were seen between concentrations within the industrial land use category versus the category including all three other land uses for all analytes except total phosphorus, mercury, pH, and conductivity. In the initial analysis, total phosphorus concentrations were not higher within the industrial areas, and mercury concentrations were seen to be more variable throughout the land uses; differences were not detected for pH or conductivity between any of the pairs of land uses.

3.13 Relating Stormwater to Precipitation

One of the main objectives of this study is to look at the amount of pollutants entering stormwater from precipitation. By summer of 2006, The City of Portland will have a more comprehensive stormwater quality dataset which will be used to look at this issue in more detail. This section provides a preliminary review of this relationship, showing possible patterns and providing an indication of why this type of analysis is important.

Stormwater data gathered by the City from 2000 to 2005 (personal communication 11-15-2005) is used in correlation with the precipitation data collected during the course of this study. The medians were used for comparison, rather than the means, due to the non-normality of the datasets. Table 3.15 summarizes the stormwater and precipitation data. It is important to note that data is available for only three out of the four land uses for both stormwater and precipitation (commercial, industrial, and residential). The ratio of stormwater to precipitation has been calculated to indicate what percent of the analyte concentration within the stormwater samples is contributed by precipitation.

Heavy metal concentrations show similar patterns for both stormwater and precipitation, with the highest concentrations detected within the industrial land use (Figures 3.103-3.106). Concentrations of heavy metals in stormwater are greater than those found in the precipitation, which is expected due to the numerous possible sources in stormwater.

Concentrations of ammonia are generally higher in the precipitation than in the stormwater, except within the commercial land use (Figure 3.101). This can be rationalized by looking at the chemistry of ammonia; ammonia is the volatile form of nitrogen which is easily converted to nitrate. Therefore, it makes sense that more ammonia is seen in precipitation, while possibly more nitrate is seen in stormwater.

Total phosphorus shows similar results between stormwater and precipitation, although the stormwater shows a stronger trend with higher concentrations seen within the industrial land use (Figure 3.102).

In general, across all analytes, precipitation has the greatest impact on the stormwater in residential areas. The concentrations are consistently lower in stormwater within the residential land use than the other land uses, with concentrations similar to those found in precipitation samples. Looking at the ratios, precipitation contributes about 50 percent of the stormwater pollutant load in residential areas and 10 to 30 percent in industrial and commercial land uses.

Table 3.15. Comparing Concentrations of Analytes between Stormwater and Precipitation

			Stormwater Land Use				Precipitation Land Use				Ratios Land Use			
		Year	C	I	R	T	C	I	R	OS	C	I	R	OS
TP (mg/L)	Mean	2005	0.23	0.83	0.17		0.04	0.06	0.25	0.19				
		1996	0.40	0.61	0.34	0.37								
	Median	2005	0.19	0.52	0.15		0.04	0.05	0.09	0.06	5.4	11.6	1.7	
		1996	0.23	0.55	0.20	0.31								
Pb, T (µg/L)	Mean	2005	20	37	3	12	1.35	6.75	2.82	0.82				
		1996	35	48	10	63								
	Median	2005	14	19	3	9	1.24	2.40	1.13	0.73	11.3	8.1	2.3	
		1996	17	30	10	40								
Cu, T (µg/L)	Mean	2005	19	35	6	12	2.53	17.82	6.85	2.23				
		1996	17	45	14	35								
	Median	2005	15	23	5	11	2.55	8.77	3.11	1.76	5.9	2.7	1.7	
		1996	13	31	10	26								
Zn, T (µg/L)	Mean	2005	138	247	30	82	155	61	17	10				
		1996	155	339	105	234								
	Median	2005	101	121	24	62	18	33	14	7	5.6	3.6	1.8	
		1996	90	276	80	185								
Hg, T (µg/L)	Mean	2005	0.026	0.033	0.018	0.009	0.006	0.011	0.009	0.008				
		1996												
	Median	2005	0.011	0.011	0.010	0.007	0.005	0.008	0.008	0.009	2.4	1.3	1.2	
		1996												
NH3 (mg/L)	Mean	2005	1.17	0.25	0.05		0.38	0.32	0.22	0.21				
		1996	0.46	0.64	0.46	0.73								
	Median	2005	1.14	0.22	0.02		0.36	0.34	0.19	0.22	3.2	0.6	0.1	
		1996	0.17	0.50	0.21	0.60

Figure 3.101. Comparing ammonia concentration in stormwater and precipitation using data from 2005.

Figure 3.102. Comparing total phosphorus concentration in stormwater and precipitation using data from 2005.

Figure 3.103. Comparing copper concentration in stormwater and precipitation using data from 2005.

Figure 3.104. Comparing lead concentration in stormwater and precipitation using data from 2005.

Figure 3.105. Comparing mercury concentration in stormwater and precipitation using data from 2005.

Figure 3.106. Comparing zinc concentration in stormwater and precipitation using data from 2005

4. Conclusions

4.1 Summary of Results

Differences in concentrations were found between pairs of land use categories for all analytes except pH and conductivity.

The two nutrients sampled, ammonia and total phosphorus, were found to behave differently when looking at concentrations found within precipitation samples. Ammonia concentrations were found to be significantly greater within commercial and industrial areas than open space and residential areas. Total phosphorus showed differences between the commercial land use and both the open space and residential land uses as well, but the phosphorus concentrations detected within the commercial land use were found to be significantly less than those found within the open space and residential land uses.

The results for ammonia are supported by previous studies, as well as known emission sources within the Portland area. It is reasonable for the concentrations to be higher within the commercial and industrial areas than the open space and residential areas. Generally, sources of ammonia are traffic emissions and industrially-associated emissions. Within Portland, the primary sources of ammonia emissions are highway vehicles and industrial activities such as fuel combustion.

The results for total phosphorus concentrations are also supported by previous studies. The results suggest that emission sources within rural and suburban areas are more important in Portland than emissions due to industrial activity.

Within the heavy metals sampled, concentrations within the industrial land use were found to be significantly greater than within all other land use categories except for mercury, where concentrations within the industrial land use were not significantly greater from those within the open space or residential land uses; and zinc, where concentrations within the industrial land use were not different from those within the commercial land use. Additional differences were found, but no significant patterns were detected.

Based on the literature for heavy metals, concentrations within the atmosphere are generally higher within industrial areas. Primary emission sources of these metals are industrially-associated.

Emission sources of lead and mercury compounds are specifically monitored in Portland. Within Portland, 19,680 pounds/year of lead are put into the atmosphere. Most of these emissions come from major source emissions, which are stationary sources such as point sources and facilities (USEPA 2004). On a smaller scale, 2,380 pounds/year of mercury are put into the atmosphere. As with lead, most of these emissions come from major source emissions.

Emission sources of copper and zinc are indirectly monitored in Portland through Hazardous Air Pollutants (HAPs) monitoring and monitoring of particulate matter. Approximately 30,000 tons of particulate matter was emitted in 1999 (USEPA 2004). Sources of particulate matter in Portland include fuel combustion (both industrial and other), industrial processes, waste disposal and recycling, vehicles (both highway and off-highway), and miscellaneous sources (USEPA 2004). In 1999, 188 HAPs were released to the Portland area, totaling 13,650,643 pounds/year (USEPA 2004). A significant amount of these emissions come from industrial sources.

For copper, lead and zinc, differences between sites were found within industrial, open space, and residential land use categories. Similar differences were detected within each land use

for all three metals. For example, concentrations of all three metals were significantly lower at site 3 (Oregon Humane Society) than at site 4 (Schnitzer Steel) within the industrial land use. Within the open space land use, the Powell Butte site (OS 4) was consistently lower in concentrations than the other three sites within the open space. Similarities such as this found within the group of metals suggests common sources throughout the study area.

For a number of analytes, differences in concentrations were also found between storm events within land use categories. The main pattern which seems to be relevant for all analytes is the decrease in concentrations during event 4. One possible explanation for this is the significantly greater amount of precipitation, and therefore sample volumes, for event 4 compared to the other events. This shows the possible effect meteorological conditions can have on wet deposition.

As discussed in the introduction materials, additional factors may affect the rates/composition of wet deposition in a given area (e.g. wind direction, orography, topology, vegetation type). Due to limited resources, all of these factors were not taken into consideration when analyzing the differences in precipitation quality among sites. Further analysis of pollution sources and meteorological conditions is needed at each site in order to provide explanations for all of the observed results. Speculation can be made about possible explanations, but presented here are the observed results for this preliminary study.

According to Khare et al. (2004), precipitation quality is highly sensitive, varying considerably from site to site and region to region. This stands true for this current study. There is considerable variation throughout the sites and between events for each of the land uses. Even though patterns were detected, which seem reasonable based upon the literature, further studies completed in the area would be useful to solidify the results and conclusions drawn from the study. The study would benefit from further analysis, specifically looking at additional meteorological conditions and specific sources near each site.

4.2 Future Studies

This study can be thought of as a preliminary study examining precipitation quality in Portland. In the near future, a goal is for The City of Portland to be able to use this data in correlation with stormwater quality data to determine the approximate quantity of pollutants entering the stormwater from precipitation. A preliminary look at this relationship was shown previously in section 3.13. However, the City will further examine this issue in greater detail.

As previously discussed, the land use categories used in this study are nominal, chosen based on classifications already developed within the city. Taking into account wind direction and location of specific sources of analytes, the sites used in this study could be reclassified to more accurately represent chosen land uses. For example, a residential site located on the edge of an industrial area which is influenced by emissions from industrial activities may be reclassified as an industrial site. The reclassification of each site could possibly provide more accurate results to the study.

It would be interesting to expand the study to include the outskirts of Portland, including suburbs and rural areas. This may give a better idea of where exactly the pollutants are coming from; from local sources or from distant sources.

This study is not meant to pinpoint exactly where the sources of pollutants found within the precipitation are coming from, but instead to give a preliminary look at what is found in the

precipitation and patterns found across the city. It is of interest to determine whether or not there are differences in precipitation quality between land uses, suggesting possible local sources.

GLOSSARY OF TERMS

Analysis of Variance (ANOVA):

One-way: performs a one-way analysis of variance and performs multiple comparisons of means

Two-way: performs a two-way analysis of variance for balanced data

General Linear Model: analyzes balanced or unbalanced ANOVA models with crossed or nested and fixed or random factors; can include covariates and perform multiple comparisons of means

Kruskal-Wallis test: nonparametric alternative to the one-way analysis of variance; tests the null hypothesis that there are no differences among the population medians (for two or more populations)

Kurtosis: measure of whether the data are peaked or flat relative to a normal distribution

High K: distinct peak near mean, rapid decline, heavy tails

Low K: flat top near mean rather than sharp peak

Mann-Whitney test: nonparametric alternative to the 2-sample t-test; tests the null hypothesis that there is no difference between the two population medians

Maximum Contaminant Level (MCL): the highest level of a contaminant that is allowed in drinking water; enforceable standards

Maximum Contaminant Level Goal (MCLG): the level of a contaminant in drinking water below which there is no known or expected health risk; allow for a margin of safety and are non-enforceable public health goals

Nonparametric: no assumption of a specific distribution for the population

Pairwise Comparisons: used to examine which pairs of means are different

Bonferroni pairwise comparisons: most conservative

Tukey pairwise comparisons: all pairwise differences only, not proven to be conservative

Parametric: a distribution is assumed for the population

Pearson's R: measure of the linear relationship between two variables (parametric correlation)

Probability Plot: used to determine whether a particular distribution fits the data; if the distribution fits the data, the Anderson-Darling statistic will be small and p-value > 0.05

Skewness: a lack of symmetry; a distribution is skewed if one tail extends farther than the other

Negative/left skew: negative values indicate a left-skewed distribution

Positive/right skew: positive values indicate a right-skewed distribution

Normal: value close to zero

Spearman's Rho: measure of the linear relationship between two variables; calculated on ranked data (nonparametric correlation)

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