

COMPARISON OF AMMONIA MEASUREMENT METHODS INSIDE AND OUTSIDE OF  
TUNNEL VENTILATED BROILER HOUSES

by

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(Under the Direction of Luke P. Naeher)

ABSTRACT

This study compares methods for measuring gaseous ammonia inside and outside of tunnel ventilated broiler houses. Instruments compared were colorimetric passive dosimeter tubes, colorimetric pull tubes, Drager Pac III electrochemical (EC) sensor, Environmental Sensors Inc. ZDL-800 EC sensor and Boreal tunable diode open path laser (OPL). Inside the house with tunnel fans running, all instruments compared well, although the dosimeter tubes indicated higher concentrations. When tunnel fans were shut off and ammonia concentrations increased, so did variation of all instruments, although the increase in variation with the OPL was minimal. During the outside comparison study, NH<sub>3</sub> concentrations were too low and environmental conditions too harsh for the EC sensors and colorimetric tubes. The OPLs performed consistently outside, although the variation between them was higher during the outside comparison than the inside comparison.

INDEX WORDS: Ammonia, Poultry, Broiler, Air quality, Colorimetric tubes,  
Electrochemical sensors, Open-path lasers

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## DEDICATION

I dedicate this thesis to my wife, Courtney. Thank you for your unconditional love and support. You have blessed my life and shown me a love I never knew existed. I could never thank you enough. I love you.

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CHAPTER 1  
INTRODUCTION

Chapter 1 outlines the information contained in each chapter. Chapter 2 is a review of current literature on the subject matter covered in the thesis. Chapter 3 is a manuscript to be submitted to the *Journal of Applied Poultry Research*. It compares different methods of measuring ammonia inside tunnel ventilated broiler houses. It also compares the same methods outside the broiler houses. Chapter 4 summarizes the discussion and conclusions of the study.

## CHAPTER 2

### LITERATURE REVIEW

## **Ammonia and its Fate in the Environment**

Ammonia ( $\text{NH}_3$ ) is a colorless gas comprised of one nitrogen atom covalently bonded with three hydrogen atoms. Its molecular weight is 17.3 g/mol. Ammonia is a known respiratory irritant with a strong, pungent odor [1] with occupational limits set by the Occupational Safety and Health Administration at 50 ppm for 8-hr permissible exposure limit (PEL). The PEL is an 8-hr time-weighted average that will not cause long-term adverse health effects to workers. A 300 ppm concentration is considered immediately dangerous to life and health [2].

Ammonia plays a critical role in the nitrogen cycle and is an essential nutrient for many plants and micro-organisms [3]. It is emitted into the environment from natural and anthropogenic sources; however, anthropogenic sources can overload ecological systems causing deleterious effects to the air, water, and soil. Excess  $\text{NH}_3$  emitted into the environment can lead to smog and overall degradation of air quality [3-5]. The combustion of fossil fuel emits  $\text{SO}_2$  and  $\text{NO}_x$  that are oxidized in the atmosphere to form sulfuric and nitric acid, respectfully [6, 7]. When  $\text{NH}_3$  reacts with these strong acids in the atmosphere, ammonium bisulfate or ammonium sulfate and ammonium nitrate particles are formed [3, 8]. These aerosols partly contribute to decreased visibility and haze. Ammonia and ammonium aerosols can also be transported by the wind and eventually deposited to the earth through wet (precipitation) or dry (particles) deposition [3].

When excess  $\text{NH}_3$  is introduced into aquatic systems, it deteriorates water quality and can be directly toxic to some aquatic organisms at elevated levels [9]. It can also be indirectly toxic by causing nutrient enrichment and cultural eutrophication, which leads

to algal blooms [10]. When these algae decompose, the biological oxygen demand is increased, resulting in anoxic conditions that are toxic to most aquatic organisms [9-11].

Nitrogen deposition, including  $\text{NH}_3$ , is known to increase the acidity of the soil [3, 12-14]. This occurs because  $\text{NH}_3$  is oxidized to  $\text{NO}_3^-$ , which is taken up by plants, leaving behind hydrogen ions that increase the acidity of the soil. Soil acidification results in nutrient leaching, especially Ca and Mg. In addition, lower soil pH can reduce the solubility of some minerals [12].  $\text{NH}_3$  can also be directly absorbed and emitted by plant foliage [15].

### **Technologies, Instruments, and Methods of Measuring Ammonia**

Numerous technologies, instruments and methods have been developed to measure gaseous  $\text{NH}_3$  concentrations [16]. These devices can be divided into several categories and some inherently overlap. Categories include direct vs. indirect reading, point sample vs. path sample, active vs. passive sampling and wet vs. dry chemistry. Direct reading gives a real-time visual display of the concentration while indirect reading must be analyzed to calculate or determine the concentration providing a delayed reading. A point sample can only determine the concentration at one sample location and a path sample averages the concentration over a path length. An active sampler uses a pump to draw air in while a passive sampler allows the air to naturally diffuse. Wet chemistry uses an aqueous solution (usually acidic) to trap  $\text{NH}_3$  molecules and then must be analyzed while dry chemistry determines  $\text{NH}_3$  concentration directly in the gas phase.

Gas detection tubes, diffusion denuders, electrochemical (EC) sensors, chemiluminescence  $\text{NH}_3$  analyzers (CL), Fourier transformed infrared spectroscopy (FTIR), Photo-acoustic spectroscopy (PAS), ultraviolet differential optical absorption

spectroscopy (UV-DOAS), and tunable diode open path laser (OPL) are some of the most common devices and technologies used in research to measure  $\text{NH}_3$  on poultry farms in recent years [16-19]. However, this is not an inclusive list of all available technologies. Each method has advantages and disadvantages that will be discussed in the following paragraphs.

Gas detection tubes are available as passive or active sampling devices. When  $\text{NH}_3$  gas reacts with the acid coated tube, a color change occurs that can be read from a graduated scale printed on the tube. The cost is low at approximately \$5-\$6 per tube and the hand pump can range from \$150 to \$350 depending on the manufacturer. They are easy to use although operator error is still possible. They measure in the ppm range but accuracy is questionable. Accuracy must be better than  $\pm 25\%$  to be sold for use to determine occupational exposures [20, 21].

Diffusion denuders are coated with citric acid or phosphoric acid which reacts with the sample air that is pumped through the system. When  $\text{NH}_3$  reacts with the acid coated denuder it forms a bond and is trapped. The denuder is then analyzed using wet chemistry to determine the  $\text{NH}_3$  concentration. McCulloch and Shendrikar [17] compared citric acid denuders to a CL analyzer and found that 20%  $\text{NH}_3$  was lost from the denuder because the ammonium citrate bond is weak and proposed using phosphoric acid as an alternative coating. Advantages of denuder systems are low cost,  $\text{NH}_3$  and ammonium ions are absorbed, and they are relatively easy to operate. Disadvantages are post-sample analytical chemistry processing that takes extra time, only a TWA concentration can be determined, and loss of  $\text{NH}_3$  if using citric acid coating.



Electrochemical sensors cost in the range of \$1000 and have an accuracy of  $\pm 10\%$  or better, depending on the manufacturer [22, 23]. They operate by having a sensing electrode that reacts with  $\text{NH}_3$  molecules and creates a change in voltage proportional to the concentration. Resolution of EC sensors can vary between 0.1- 1 ppm. Electrochemical sensors are made for use as safety warning devices or short-term measuring of workplace concentrations. They are usually a passive monitor but can be modified as an active sampler [24]. When continuously exposed to high levels of  $\text{NH}_3$ , sensor saturation occurs which can cause erroneous measurements [24, 25]. One advantage of EC sensors is that they are available with data loggers, which show concentration over time. A disadvantage is they must be frequently calibrated to ensure accurate readings [24-26].

Chemiluminescence  $\text{NH}_3$  analyzers convert  $\text{NH}_3$  to NO using a converter kept at  $795^\circ\text{C}$ . They use stainless steel as a catalyst [16]. The NO then reacts with  $\text{O}_3$  to form  $\text{NO}_2$  which has a characteristic luminescence that is detected by the analyzer. This technique requires two phases: the conversion phase, and the analyzer phase. Advantages of this instrument are high sensitivity (1ppb) and precision ( $\pm 0.5$  ppb). Disadvantages include high cost ( $> \$40,000$ ) and maintenance, relatively immobile, the fact that they are made for a laboratory environment, and the need for a highly skilled operator [16].

Fourier-transformed infrared spectroscopy emits an infrared light source (interferogram) that is split and reflected from a fixed mirror and a moving mirror. Both signals are transmitted through the sample air, which can be open-path or an internal cell, and analyzed by a receiver [27]. Using a Fourier transformation, which is a mathematical equation that relates the signal to the frequency content, the absorption spectra of the

sample gas is determined. This spectra can then be used to determine the gases present and their concentration. Advantages of the FTIR are that it can monitor multiple gases and has sensitivity in the ppb range. Disadvantages are high cost (>\$40,000), non-linear response usually not corrected [27], and the need for a highly skilled operator. The FTIR is an EPA approved method of gas analysis for many hazardous air pollutants including NH<sub>3</sub>.

The PAS operates on the principle that when molecules absorb light intermittently, they produce a characteristic acoustic signal. This signal is detected by special microphones which translate the signal into gas. Infrared light is passed by a chopper wheel [16], which is like a spinning fan blade, which pulses the light. The pulsed light is then passed through optical filters which changes the wavelength to widen or narrow the spectrum depending on objectives. The specialized microphones then record the characteristic sounds of molecules present and the computer processes this information to determine concentration. Advantages to PAS systems include the ability to monitor multiple gases, they can detect in the ppb range, and they don't require calibration and maintenance as frequently as instruments with comparable cost and sensitivity [16]. Disadvantages include high cost (>\$40,000), and possible interference from and water and high relative humidity. However, most instruments now automatically compensate for water vapor interferences.

The UV-DOAS is composed of an emitter and a receiver that is used to analyze the path between the two parts. Alternatively, the emitter and receiver can be housed in one unit which uses a reflector to create the path [28]. The emitter uses a xenon lamp to produce UV light which is collected by the receiver. Different molecules in the path

absorb the light in a pattern that is unique to that molecule. The absorption is recorded by a spectroscope and analyzed to determine the gases present and their concentration [16]. Myers et al. [29] determined the detection limit of  $\text{NH}_3$  of the Opsis AR-500 to be 2.8- 5.8 ppb and relative accuracy to be 3.3 -11% over a range of 24- 200 ppb and error to be  $\pm 20\%$ . Advantages are ability to monitor multiple gases, sensitivity in the ppb range, and they are internally calibrated. Disadvantages include high cost ( $> \$40,000$ ), and interference by fog, and haze which prevents the light from reaching the receiver, the need for a skilled operator, and they are relatively immobile.

The OPL operates on the principle that every molecule absorbs light at wavelengths specific to that particular molecule. The laser is tuned to a wavelength that only the molecule of interest will absorb so that there is minimal possibility of interfering gases. The unit emits a laser in the near-infrared spectrum of 1300-1700 nm which is reflected back using a retro-reflector, creating a path of measurement. The OPL uses the units ppm because it is measuring the concentration over a path rather than a point. The concentration in ppm is then divided by the path-length in meters to calculate the average concentration in ppm for the distance measured. For  $\text{NH}_3$ , the laser is tuned to a wavelength of 1512 nm with a fluctuating current used to drive the laser. This causes a slight change in wavelength and induces the laser to scan across the absorption wavelength of 1512 nm [30]. Superimposed on the laser signal is a waveform with a different frequency. This waveform is changed when the laser hits an  $\text{NH}_3$  molecule and energy is absorbed. The change in this waveform in addition to the intensity of the returning laser signal is used to calculate the concentration of  $\text{NH}_3$  molecules that are present in the path. The OPL can measure paths up to 1000m and has a manufacturer's

stated sensitivity of 2.5 ppm with a response time of one second and a range of 0.025 to 1000 ppm [30]. Accuracy is dependent on an internal comparison to a known reference concentration and indirectly dependent on the concentration of the sample air. Accuracy is generally better than  $\pm 5\%$  at concentrations of 1 ppm and it gets better as the concentration increases because the signal-to-noise ratio increases. Disadvantages are high cost and interference of light detection from dense fog, haze, and particulates in the air.

### **Measuring Ammonia on Poultry Farms**

Gaseous ammonia from commercial poultry houses have been of concern to the industry for a number of years [18, 24, 25, 31-35]. The US Environmental Protection Agency (EPA) ranks poultry as the largest contributor to  $\text{NH}_3$  emissions of all animal husbandry operations[36]. Ammonia is produced from the microbial breakdown and conversion of uric acid from poultry excrement [31]. In-house  $\text{NH}_3$  concentrations are dependent on several factors including management practices, bird age, litter moisture content, pH of the litter, humidity and temperature [31, 34, 35].

Several studies have been conducted in Europe and more recently in the US to determine emission rates of  $\text{NH}_3$  from poultry houses [19, 24, 26, 32, 35, 37-39]. Emission rate is simply the product of the  $\text{NH}_3$  concentration and the ventilation rate (VR), however, both of these variables have proven difficult to quantify. Accumulation of dirt and particles on fan blades and inlets, in addition to belt tightness, all affect fan performance and VR [35]. Additionally, temperature and barometric pressure affect VR and must be measured and adjusted for in calculations.

Measuring  $\text{NH}_3$  inside poultry houses has posed problems for flock supervisors, researchers, and poultry companies for years [24, 25, 31]. Many instruments, technologies and methods are available to measure  $\text{NH}_3$  and have been used to try and quantify  $\text{NH}_3$  concentrations. Previous studies have stated that most precision analytical instruments are expensive, susceptible to weather conditions, affected by the quality of air in broiler houses, and are relatively immobile once installed [24]. More affordable electrochemical (EC) sensors and low cost colorimetric tubes have questionable accuracy in the relatively dirty and low ammonia concentrations environment that is found in poultry houses [25]. In addition, EC sensors must be calibrated often and can be saturated with continuous exposure to ammonia resulting in erroneous measurements [24, 40]. Furthermore, pull tubes only give a point reading at a given time and location. EC sensors can show trends over time, but are limited to a specific location. Dosimeter tubes cannot show concentration peaks because they are averaged over the sample time period. Open path lasers (OPLs) are designed to measure the average ammonia concentration over the distance between the laser and a reflector. They are accurate at very low levels of  $\text{NH}_3$ , but comparing the readings with EC sensors is difficult because the ECs are measuring at a point rather in ppm units and OPLs measure a path in ppm units.

Measuring outside and downwind concentrations of  $\text{NH}_3$  on poultry farms is also important and presents some challenges for the instruments. The most notable factor is that the instruments are exposed to weather conditions compared to relatively consistent conditions inside the house. During summer months in the southeastern US, temperatures can exceed  $38^\circ\text{C}$  ( $100^\circ\text{F}$ ) during the day and decrease by  $9\text{-}14^\circ\text{C}$  ( $15\text{-}25^\circ\text{F}$ ) during the night usually reaching the dew point. High relative humidity, condensation,

and high temperatures with large fluctuations are not conditions that are favorable to any  $\text{NH}_3$  monitoring equipment; however, OPLs are much less susceptible to temperature and humidity fluctuations. Adding to this, distant downwind concentrations are much lower than inside concentrations and may be below the accuracy range of many instruments at large distances from the source.

### **Ammonia Measurement Comparison Studies**

Several studies have been conducted comparing  $\text{NH}_3$  measurement methods [24, 25, 39]. Skewes and Harmon [41] compared the Ammonia Quick Test (AQT) distributed by Vineland Laboratories to Gastec dosimeter tubes (model 3D) and Gastec pull tubes (model 3La). The AQT is similar to pH paper that is dropped with distilled water. It is then exposed to the air for approximately 1 minute and compared to a color chart. It has a range of 0-100 and determined by the degree of color change. Gastec 3D reads a time-weighted average and has a range of 25-500 ppm/hr. The Gastec pull tube takes a 50 ml sample and has a range of 0-200 ppm [41]. The authors used the pull tube values as the true  $\text{NH}_3$  concentration that was compared to the AQT and dosimeter tube readings. The authors found that the AQT was only comparable to the pull tube at levels of 20-25 ppm. Below 20 ppm the AQT over-estimated concentrations and above 25 ppm, the AQT underestimated  $\text{NH}_3$  concentrations. Variation of the AQT also increased outside of this range. The dosimeter tube closely compared to the pull tube up to 20 ppm, but became less accurate at higher  $\text{NH}_3$  concentration. The dosimeter tube did underestimate at higher  $\text{NH}_3$  concentrations, but deviations from the pull tube were not as great as the AQT. Skewes and Harmon also evaluated relative humidity (RH) compared to  $\text{NH}_3$  concentration and found that  $\text{NH}_3$  levels increase much more rapidly than RH and

therefore should not be used as an indicator of NH<sub>3</sub> concentration. Lastly, the authors determined that temperature adjustment of the colorimetric tubes did not greatly affect accuracy of the reading under typical poultry house conditions.

Wheeler et al. [25] compared pull tubes (MSA #804405) with a range of 0-100 ppm to passive dosimeter tubes (model 3D, Sensidyne Corp.) with a range of 25-500 ppm\*hr. Also compared was an electrochemical sensor (Polytron 2, Dräger) with a low range of 0-300 ppm and a high range of 0-1000 ppm. The low range was used in this study with an accuracy of  $\pm 3\%$  of the scale (9 ppm). These three instruments were compared in a clean lab, an environmental chamber with caged chickens so that temperature, RH, and NH<sub>3</sub> concentration could be controlled, and in a commercial high-rise layer house. The instruments performed and compared best in the laboratory study at 50 ppm test concentration. All instruments agreed within  $\pm 5$  ppm but the pull tubes tended to underestimate while the dosimeter tubes read both over and under the 50 ppm calibration gas concentration. In the environmental chamber, there was less agreement among all instruments. The NH<sub>3</sub> concentration was maintained at 0 ppm, then 30 ppm, then raised to 90 ppm. The EC sensor agreed closest to the 90 ppm concentration in the environmental chamber, although it was used to control the NH<sub>3</sub> concentration. The dosimeter tube agreed within 10-30% of the concentration, and the pull tube could be as much as 60% off the 90 ppm concentration and mostly underestimating true values. The increased variation in the environmental chamber was possibly due to the presence of interfering gases. The comparison in the commercial high-rise layer house showed the least agreement among the instruments. Differences as large as  $\pm 18$  ppm were found between the pull tube and EC sensor and  $\pm 13$  ppm between the dosimeter tube and EC

sensor. Wheeler et al. concluded that lower  $\text{NH}_3$  concentrations and the relatively dirty environment of the high-rise layer house caused the variation among the instruments. In addition, scale error, EC sensor drift, operator error, and sampling location all were listed as factors that could affect variation.

Xin et al. [40] conducted a study on three EC sensors manufactured by Drager. The Drager Polytron II-LC (low concentration sensor) with range of 0-100 ppm and 1 ppm resolution, the Polytron II-HC (high concentration sensor) with range of 0-300 ppm and 5 ppm resolution, and the Drager Pac III with range of 0-200 ppm and 1 ppm resolution were evaluated. The Pac III has an internal data logger while the Polytron II has a 4-20mA analog output. The first comparison of these  $\text{NH}_3$  sensors was done with 46 ppm calibration gas for a 20 hr study period. All sensors had accurate initial readings but quickly began to vary within 5-15 minutes. Over the 20hr study period the Polytron-HC averaged 37.0 ( $\pm 3.1$ ) ppm, the Polytron-LC averaged 52.8 ( $\pm 5.5$ ) ppm, and the Pac III averaged 50.7 ( $\pm 5.6$ ) ppm. This part of the study concluded that EC sensor saturation quickly leads to inaccurate  $\text{NH}_3$  concentration readings.

A portable monitoring unit (PMU) was developed to reduce EC sensor saturation during continuous monitoring of  $\text{NH}_3$  which was done by purging the sensors with fresh air for a period then sampling for a shorter period. The PMU contains two Pac III  $\text{NH}_3$  sensors enclosed in a case. A tube from a fresh air source and another tube from a polluted air source are connected at a valve. A timer operates the valve to determine which air source enters the PMU. The Pac IIIs are connected to each other in a series configuration so that the air exiting the first unit then enters the second unit. An air pump is positioned last to provide negative pressure. By sampling the polluted air followed by



purging with fresh air, EC sensor accuracy could be sustained for longer sampling periods at accuracy close to that of CL analyzers and other high precision equipment which cost more and are less portable. The next phase of the comparison was done using the Pac III incorporating the sample-purging cycle of 5 min. and 10 min., respectively, over a 48 hr test period using 45.8 ppm calibration gas. The maximum during the first 18hrs of the study ranged from 46-48 ppm, and by the end of the study had reached 51 ppm. The purging period would also return to 0 ppm and drift  $\pm 2$  ppm at the start of the study. At the end of the study during the purging cycle, the reading would return to 0 ppm and drift to 4-5 ppm before the sampling cycle began. The sensor drifted above actual concentrations during both cycles and so maximum readings from the purging cycle was subtracted from the maximum of the sampling cycle to correct for this issue.

The final phase of this study was to conduct a field comparison of the Pac III NH<sub>3</sub> sensors contained in the PMU to a chemiluminescence NH<sub>3</sub> analyzer (model 17C, Thermo-Environmental Instruments). Both instruments were set up in a mobile lab outside a commercial layer house, which is a poultry house that cages the birds so that eggs can be collected. The eggs fall through the cage into a collection system and there are usually several levels of cages to maximize the number of birds per unit of space. Sample air was drawn into the instruments to be analyzed. The maximum value from the 5 min sampling period of the PMU was compared with the 5 min average of CL analyzer. The mean for the PMU was 29.5 ppm while the CL mean was 29.0 ppm over the entire sampling day. The minimum difference between the PMU and CL analyzer was within  $\pm 0.9$  ppm and the maximum agreed within  $\pm 1.3$  ppm. Xin et al. [40] and Gates et al.

[24] reported that the NH<sub>3</sub> concentration and accuracy of the PMU compared very closely to the CL analyzer for a fraction of the cost.

### **Objectives of the Research**

The study presented in the following chapter continues to pursue the efforts to find an affordable and accurate method of measuring ammonia on poultry farms. This study is unique because it compares the average of EC point measurements to OPL path averages inside of tunnel ventilated broiler houses with differing numbers of tunnel fans running and with no ventilation. It also investigates the variability of co-located EC sensors, pull tubes and dosimeter tubes under the same conditions. Additionally, this study evaluates the variability of these instruments outside of tunnel ventilated broiler houses where NH<sub>3</sub> concentrations are much lower and instruments are subject to an uncontrolled environment.

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## CHAPTER 3

### COMPARISON OF AMMONIA MEASUREMENT METHODS INSIDE AND OUTSIDE OF TUNNEL VENTILATED BROILER HOUSES<sup>1</sup>

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<sup>1</sup> Hale, B.D.; Fairchild, B.D.; Worley, J.W.; Harper, L.A.; Ritz, C.W.; Czarick, M.; Naeher, L.P. To be submitted to *The Journal of Applied Poultry Research*

## **Summary**

Accurately measuring ammonia ( $\text{NH}_3$ ) produced from poultry litter and emitted from mechanically ventilated broiler houses continues to be a challenge. There are many technologies and methods available to measure  $\text{NH}_3$  with cost ranging from \$3 for colorimetric tubes to greater than \$40,000 for precision analytical equipment. This study investigated the variability among selected low, mid-range, and high cost instruments. Inter-instrument and intra-instrument comparisons were made using colorimetric pull tubes and dosimeter tubes, electrochemical (EC) sensors from two different manufactures, and tunable diode open path lasers (OPL). The EC sensors evaluated were the Pac III and ZDL-800 (ZDL). This study consisted of inside and outside broiler house components to evaluate instrument performance under different environmental conditions and  $\text{NH}_3$  concentrations. The OPLs showed the least variation during the in-house and outside comparison. The EC sensors and colorimetric tubes performed well at  $\text{NH}_3$  levels of a properly ventilated broiler house. With no ventilation, variation among instruments increased as  $\text{NH}_3$  concentrations increased. With the exception of the OPLs, concentrations on the outside were too low and environmental elements too harsh for these instruments to perform well.

## **Description of Problem**

Gaseous  $\text{NH}_3$  from commercial poultry houses has been of concern to the poultry industry for a number of years [1-8]. Ammonia is a known respiratory irritant [9] with occupational limits set by the Occupational Safety and Health Administration (OSHA) at 50 ppm for 8-hr permissible exposure limit (PEL). A 300 ppm concentration is

considered immediately dangerous to life and health (IDLH) [10]. The US Environmental Protection Agency (EPA) ranks poultry as the largest contributor to ammonia emissions of all animal husbandry operations [11]. Poultry companies not only have to be concerned for worker health, but  $\text{NH}_3$  can also affect bird health and reduce productivity [1]. Complaints from neighbors and the perceived health risk that  $\text{NH}_3$  emissions pose to them and the environment is another issue of growing concern to the poultry industry and regulatory agencies [12].

Ammonia plays a critical role in the nitrogen cycle and is an essential nutrient for many plants and micro-organisms [13]. However, anthropogenic sources can overload ecological systems causing deleterious effects to the air, water, and soil. Excess  $\text{NH}_3$  emitted into the environment can lead to smog and overall degradation of air quality [13-15]. The combustion of fossil fuel emits  $\text{SO}_2$  and  $\text{NO}_x$  that are oxidized in the atmosphere to form sulfuric and nitric acid, respectfully [16, 17]. When  $\text{NH}_3$  reacts with these strong acids in the atmosphere, it can form ammonium bisulfate or ammonium sulfate and ammonium nitrate [13, 18]. In addition, it deteriorates water quality and at elevated levels causes nutrient enrichment and cultural eutrophication which leads to algal blooms [19]. When these algae decompose, the biological oxygen demand is increased, resulting in anoxic conditions that are toxic to most aquatic organisms [19-21].

Ammonia sensors and concentration indicators have been available on the commercial market for decades, but the accuracy of these devices, especially when exposed to high  $\text{NH}_3$  levels over a period, is questionable (Table 1). Finding an accurate, reliable, and cost effective method for measuring  $\text{NH}_3$  inside and outside of poultry



houses will help to mitigate the problem and benefit the poultry industry, communities, and the environment.

### ***Ammonia Measurement on Poultry Farms***

Measuring  $\text{NH}_3$  inside poultry houses has posed problems for flock supervisors, researchers, and poultry companies for years [1, 3, 7]. Previous studies have stated that most precision analytical instruments are expensive, susceptible to weather conditions, affected by the quality of air in broiler houses, and are relatively immobile once installed [7]. More affordable EC sensors and low cost colorimetric tubes have questionable accuracy in the relatively dirty and low  $\text{NH}_3$  concentration environment that is found in poultry houses [3]. In addition, EC sensors must be calibrated often and can be saturated with continuous exposure to  $\text{NH}_3$  resulting in erroneous measurements [22]. Furthermore, pull tubes only give a point reading at a given time and location. EC sensors can show trends over time, but are limited to a specific location. Dosimeter tubes cannot show concentration peaks because they are averaged over the sample time period. The OPLs are instruments designed to measure the average  $\text{NH}_3$  concentration over the distance between the laser and a reflector. They are accurate at very low levels of  $\text{NH}_3$  concentrations, but comparing the readings with EC sensors is difficult because the EC sensors are measuring a point rather than a path length. The EC sensors measure in ppm units and the OPLs measure in ppmm units. The ppmm can be divided by the path length in meters to obtain an average path concentration in ppm. In poultry houses, high dust levels can affect OPLs by scattering the laser light resulting in a returning signal that is below the light intensity threshold needed to accurately calculate  $\text{NH}_3$  concentrations accurately. Additionally, high  $\text{NH}_3$  levels can cause the waveform used in determining

NH<sub>3</sub> concentrations to become distorted. This saturation effect results in the inability of the OPL to calculate the NH<sub>3</sub> concentration. However, the light scattering and saturation problems can both be overcome by reducing the path length of the OPL [23].

Measuring outside and downwind concentrations of NH<sub>3</sub> on poultry farms is also important and presents some challenges for the instrumentation. The most notable factor is that the instruments are exposed to weather conditions. During summer months in the southeastern US, temperatures can exceed 38° C (100° F) during the day and decrease by 9-14° C (15-25° F) during the night usually reaching the dew point. High relative humidity, condensation, and high temperatures with large fluctuations are not conditions that are favorable to any NH<sub>3</sub> monitoring equipment; however, OPLs are much less susceptible to temperature and humidity fluctuations [33]. Adding to this, distant downwind NH<sub>3</sub> concentrations are much lower than inside concentrations and may be below the accuracy range of many instruments at large distances from the source.

The primary objective of this study was to evaluate inter-instrument and intra-instrument variation among co-located pull tubes, dosimeter tubes, electrochemical sensors, and tunable diode open-path lasers inside a commercial tunnel ventilated broiler house where NH<sub>3</sub> concentrations will tend to be higher. A secondary objective was to evaluate the variation of the same instruments outside the broiler house with lower NH<sub>3</sub> concentrations in an environment that was not controlled.

## **Materials and Methods**

### ***Study Site***

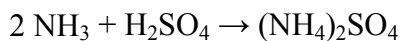
This study was conducted on a commercial broiler farm in northeast Georgia. The farm had four broiler houses that were 152.4m long and 12.2m wide (500ft x 40ft)

and held approximately 24,000 birds each. The houses were tunnel ventilated and had evaporative cooling-pad systems. Environmental controllers regulated temperature, humidity, and air quality. This study consisted of in-house and outside components in order to assess the performance of the instruments under both different environmental conditions and varying ranges of NH<sub>3</sub> concentrations.

### ***Description of Instrumentation***

Low-cost dosimeter and pull tubes were compared with mid-range cost, real time electrochemical sensors from two different manufactures with high-cost open path laser spectrometers (Table 1).

***Colorimetric Tubes.*** Gastec model 3D [24] dosimeter tubes were used in this study. The range for these tubes is from 2.5 to 1000 ppm\*hr. To begin sampling, one end of the tube is broken off and exposed for a measured period of time. When the sulfuric acid coated tube is exposed to NH<sub>3</sub>, the following reaction takes place

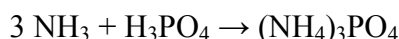


and the color changes from purple to yellow in the tube. The color change proceeds down the length of the tube as more NH<sub>3</sub> is exposed. When sampling is complete, the tube is removed from exposure to NH<sub>3</sub> and then read to obtain the total exposure in ppm\*hr. The reading is taken from the farthest point that the yellow change reached unless the color change is uneven then the midpoint of the uneven line is read. This value is then divided by the sampling time (hours) to give a time-weighted average.

Gastec model 3L pull tubes [25] were used with Gastec model GV-100 hand pump [26] during the outside comparison study. The tubes have a range from 0.5 to 78 ppm. To sample, both ends of the tube are broken off and it is inserted into the hand

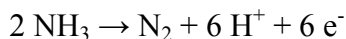
pump with the airflow arrow towards the pump. The handle is set to 100ml sample volume and is pulled once until it locks. After the sample indicator is seen, ensuring the sample volume has been reached; the color change on the tube can be read from the graduated scale to determine the concentration. The same reaction as in the dosimeter tubes causes the color change.

RAE Systems colorimetric pull tubes [27, 28] (RAE Systems, models 10-10-05 and 10-10-10) were used in the in-house comparison (GasTec tubes were not available at this time) in conjunction with the hand pump (RAE Systems, Model LP-1200) [29]. The RAE tube operates on a slightly different reaction principle using phosphoric acid:

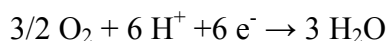


which produces a color change from purple to beige. RAE tube model 10-10-05 has a range of 1 to 30 ppm and was used while tunnel fans were running and the concentration was below 30 ppm. RAE tube model 10-10-10 has a range of 5 to 100 ppm and was used when no fans were running and the NH<sub>3</sub> levels exceeded the 30 ppm range.

***Electrochemical Monitors.*** Electrochemical sensors are designed to measure a single gas, NH<sub>3</sub> in this case, and consist of a selectively permeable membrane, a sensing electrode, and a counter electrode immersed in an organic electrolyte gel. Ammonia undergoes the following oxidation reaction at the sensing electrode:



which releases electrons and creates an electrical current that is proportional to the NH<sub>3</sub> gas concentration. At the counter electrode, oxygen reacts with the hydrogen released to make water according to the reaction:



The Drager Pac III H (Pac III) manufactured by Drager-Safety [30] is a single gas instrument and was used with the DragerSensor XS NH<sub>3</sub>. The H model (Hygiene) comes with an internal data logger that can be set at predetermined time intervals that include 1sec, 30sec, 1min, 2min, 5min, 10min, and 15min averages. The DragerSensor XS NH<sub>3</sub> has a measuring range of 0 to 200 ppm and a manufacturer's stated resolution of 1 ppm. Response time for this sensor is 20 seconds to reach 50% exposed concentration. The manufacturer claims accuracy of  $\pm 3\%$  of maximum full-scale value or better ( $\pm 6$  ppm). The monitors were calibrated before the study with 50 ppm NH<sub>3</sub> gas.

Another EC monitor evaluated in this study was the Environmental Sensors Inc. model ZDL-800 (ZDL) NH<sub>3</sub> sensor with an internal datalogger [31] that contains 5 separate sample logs where data is stored before downloading is necessary. When the capacity for a log is reached, the ZDL stops sampling and the average concentration is calculated. To begin a new sample, the operator must manually start the sensor. From the factory, the ZDL is programmed to collect data every 10 seconds for a total sampling duration of 480 minutes (8 hrs) at which point the capacity for a log is reached. The sampling interval of 10 seconds cannot be adjusted by the user. The user can change to a shorter sampling duration but cannot go longer than 8 hours per sample log. For the purposes of this study, a longer sample duration was needed. The manufacturer re-programmed the ZDLs used in this study to collect a data point every 60 seconds for a total sampling duration of 2880 minutes (48 hrs) per log. The ZDL has a measuring range of 0 to 200 ppm with the nominal range being 0 to 50ppm. The resolution of this sensor is 0.1 ppm with a limit of detection of 2 ppm and overall accuracy of  $\pm 10\%$  of the reading. The response time is 180 seconds or less.

***Open-Path Lasers.*** Boreal Laser Inc. manufactures the Tunable Diode Laser Open-Path Monitor [32] which is referred to as an OPL in this report. These instruments operate on the principle that every molecule absorbs light at wavelengths specific to that particular molecule. The laser is tuned to a wavelength that only the molecule of interest will absorb so that there is minimal possibility of interfering gases. These lasers operate in the near-infrared spectrum of 1300-1700 nm. For NH<sub>3</sub>, the laser is tuned to a wavelength of 1512 nm with a fluctuating current used to drive the laser. This causes a slight change in wavelength and induces the laser to scan across the absorption wavelength of 1512 nm [33]. Superimposed on the laser signal is a waveform with a different frequency. This waveform is changed when the laser hits an NH<sub>3</sub> molecule and energy is absorbed. The change in this waveform in addition to the intensity of the returning laser signal is used to calculate the concentration of NH<sub>3</sub> molecules that are present in the path.

The OPL uses units of parts per million meter (ppmm) because it is measuring along a path and not a point. The reading is divided by the distance of the path (in meters) to obtain a path average concentration in parts per million. This gives the OPL an advantage when measuring narrow NH<sub>3</sub> plumes that might escape a point measurement or large plumes with varying concentrations that would bias point measurements. The OPL can measure paths up to 1000m and has a manufacturer's stated sensitivity of 2.5 ppmm with a response time of one second and a range of 0.025 to 1000 ppm. Accuracy is dependent on an internal comparison to a known reference concentration and indirectly dependent on the concentration of the sample air. Accuracy

is generally better than  $\pm 5\%$  at concentrations of 1 ppm and it improves as the concentration increases because the signal-to-noise ratio increases.

A correction factor was applied to the raw data for each OPL. This is done to adjust for any discrepancies with the internal calibration of the OPLs. Two different concentrations of  $\text{NH}_3$  calibration gas are used to check the OPL reading against the known concentrations to calculate correction factors.

### ***In-House Comparison***

The in-house  $\text{NH}_3$  comparison study was conducted on August 16, 2007. No birds had been present in the house for three days and the litter had not been removed. Real-time instruments compared in this study were 3 OPLs, 8 Pac III EC sensors, and 12 ZDL EC sensors. Colorimetric tubes were also used in this comparison including RAE pull-tubes (with hand pump) and GasTec dosimeter tubes.

The set-up inside the house was 81.0m from the front door. The OPLs were set up 1.40m above the ground with a distance between them of 0.56m. Reflectors were set up across the width of the house with a path length of 10.21m. A 3x3 grid of poles was set up to hold the electrochemical sensors at 1.38m above the ground (See figure 1). Along each laser path, 3 poles were located 2.54m apart, which divided the path length equally. This setup was used to more accurately compare the average EC point measurements to the OPL path average. Sampling stations were labeled #1-#9. Station #5 was at the center position and a small table was used instead of a pole to accommodate all the instruments co-located there. The table was 1.2m above the ground. Each station had at least one electrochemical sensor. ZDLs were placed at each station but due to

limited equipment, no Pac IIIs were placed at stations #1, 2 and 3. Co-located at center station #5 were 4 ZDLs and 3 Pac IIIs.

The experiment started with all 8 tunnel fans running with a designed air movement capacity of 160,000 cfm. Two fans were shut off every two hours. At the beginning of the two-hour period, three dosimeter tubes were placed at station #5 with the open end facing the fans at a height of 1.2m. They were retrieved and recorded at the end of that period and three more dosimeter tubes were deployed. Three pull-tube samples were taken one hour after each period began. These samples were also taken at station #5 at a height of 1.2m. This procedure was repeated until all fans were shut off. Final pull-tube samples were taken after all fans had been off for 1.75 hours, all instruments were turned off, and the experiment was ended.

For consistency, all EC sensors were oriented with the sensing element facing the fans, parallel to the air flow. Dosimeter tubes and pull tube samples were also taken with the open-end oriented towards the fans, parallel to the air flow.

### ***Outside Comparison***

The outside NH<sub>3</sub> comparison study was conducted on October 1, 2007, and ended on October 4, 2007. The birds were 40 days old when the study began. Real-time instruments compared in this study were 3 OPLs, 4 Pac III EC sensors, and 13 ZDL EC sensors. Colorimetric tubes were also used in this comparison including pull-tubes (GasTec, Model 3L) with pump (GasTec, Model GV-100) and dosimeter tubes (GasTec, Model 3D). Each morning and evening 3 pull-tube samples were taken at center location #5 (Fig. 2) at a height of 1.4m. Three dosimeter tubes were deployed each morning and retrieved the following morning.



The outside set-up was located at the exhaust end of the house and centered on fan #4. The closest laser was 6.1m from the house (see Fig. 2). The distance between each laser was 1.5m and each was at a height of 1.3m. The path length between laser and reflector was 6.0m. A 3x3 grid of poles was set up to hold the electrochemical sensors at 1.34m above the ground. Along each laser path, 3 poles were located 1.50m apart, which divided the path length equally. These sampling stations were labeled #1-#9 with station #5 being in the center. Each station had at least one electrochemical sensor. One ZDL was placed at each station with the sensor facing away from the fans. Due to limited equipment, all 4 Pac IIIs were co-located at station #5 with sensors facing away from the fans. Also co-located at center station #5 were 5 ZDLs.

### ***Statistical Analysis***

All real-time instruments compared in this study (OPL, ZDL, Pac III) were analyzed using SAS statistical software [34]. Procedures used in data analysis of inside comparison are Analysis of Variance (ANOVA) with sources of variation for instrument type, instrument ID with type (InstID(type)) and number of fans running (fans). Interactions between type\*fans and InstID\*fans were also included. Sources of variation for InstID, InstID\*fans, and error were further partitioned into separate terms by type of instrument. InstID and InstID\*fans are treated as random effects. Furthermore, estimates of variance components were determined for InstID, InstID\*fans, and error and separated by each instrument type. For the outside comparison, variance component estimates for InstID and error were determined and separated by each instrument type.

## Results and Discussion

### *In-House Comparison*

*Comparison of All Real-Time Instruments.* Table 2 summarizes the descriptive statistics for all instruments evaluated in the in-house component of this study and is separated into study periods by number of fans. Table 3 shows the sources of variation of real-time instrument NH<sub>3</sub> concentrations. Shaded sources of variation (InstID, InstID\*fan, and error) are partitioned by instrument type. This shows the contribution of each instrument type to a source of variation. Mean squared values for each instrument show that the OPL has the least intra-instrument variation of NH<sub>3</sub> concentrations. The Pac IIIs variation is an order of magnitude larger than the OPL, and the variation of NH<sub>3</sub> reading among the ZDLs is 85 times the OPL variation.

Table 4 shows the estimates of variance components for each source of variation. InstID is interpreted as intra-instrument variability (between instrument) and error is interpreted as variability within one instrument. The interaction of the number of fans running on variability is indicated by the InstID\*fan term. Between instrument variation is estimated at 0.00, 0.07, and 3.31 for the OPL, Pac III and ZDL, respectively. This indicates that throughout the study the OPLs show little variation among each other and all react similarly. The between instrument source of variation contributed very little to the Pac IIIs 0.07 (0.3%), indicating these instruments respond similarly to each other. The ZDL between instrument source of variation was estimated to be 3.31, which is 47 times more than the Pac IIIs for this source. The ZDLs had the most variation between the instruments over the study period.

The variation from the interaction InstID\*fan showed the highest contribution to variation in the ZDL, estimated at 32.28. The Pac III estimate of variation from the fan interaction was 3.23, which is an order of magnitude less than the ZDL. The OPLs were not affected by this interaction. The majority of the variation from the InstID\*fan interaction is most likely occurring when 0 fans are running and the NH<sub>3</sub> concentration is increasing rapidly. When comparing the SD in table 2 from 2 fans and 0 fans running, the Pac III increases by 3.7 ppm and the ZDL increases 11.5 ppm. The increasing variation for the 0 fan period can also be visualized by the SEM bars in figure 3. The variation in the Pac IIIs for this interaction could be underestimated because of the plateau effect that is observed at approximately 40 ppm.

The within instrument variation for the OPL is estimated at 105.9 (100%), indicating that almost all variation is because of changes in NH<sub>3</sub> concentration over time. The within instrument variation contributed 88% of total variation in the Pac IIIs, although the estimated value 24.12 is relatively small compared to the other instruments for this source of variation. This is consistent with the plateau effect seen in the Pac IIIs which reduce the total range of NH<sub>3</sub> concentration over the study and result in a low estimate for this source. The ZDL estimate of 77.42 is also consistent with the change in NH<sub>3</sub> concentration over time when compared to the OPLs and Pac IIIs. This is because over the entire study day, the OPLs had the greatest range (46.2 ppm), the ZDLs were in the middle (39 ppm), and the Pac IIIs had the smallest range (28.2 ppm). The range was calculated by subtracting the lowest average NH<sub>3</sub> reading for a 15 minute period from the highest average NH<sub>3</sub> reading during the study.

***Co-located Electrochemical Sensors and Colorimetric Tubes.*** Figure 3

illustrates the temporal variability among the different instruments co-located at location #5. The Pac IIIs and ZDLs compared very closely ( $\pm 3$ ppm or less) with the ZDLs, reading slightly higher for all fan periods until no fans were running and the  $\text{NH}_3$  levels began to increase. The Pac IIIs plateaued at approximately 40 ppm with 0 fans running although the standard error of the mean was small indicating little variation between the three instruments. This is possibly due to sensor saturation. The dosimeter tubes read consistently higher than the EC sensors and the pull-tube for the study period. The pull-tube readings compared very closely to the EC sensors and were consistent for the 8-fan ( $\pm 2$ ppm,  $\text{SD}=0$ ), 6-fan ( $\pm 2$ ppm,  $\text{SD}=0.6$ ), and 4-fan ( $\pm 3$ ppm,  $\text{SD}=0.6$ ) periods when the  $\text{NH}_3$  concentration was approximately 8 ppm. During the 2-fan period, with slightly elevated  $\text{NH}_3$  concentrations (10ppm), the pull-tube read higher than the EC sensors ( $>10$ ppm,  $\text{SD}=1.5$ ) and had greater variation than the previous fan periods. For the 0-fan period, the pull-tube was drastically higher than the EC sensors ( $>30$  ppm) and the dosimeter tube ( $>24$  ppm).

***Averaged Electrochemical Sensors Compared to OPL Path Average.*** Figure 4 illustrates the path-average concentration of OPL 1 and the average of 3 ZDL sensors placed along that path. Figures 5 and 6 illustrate the path average of OPLs 2 and 3, respectively, in addition to the ZDL and Pac III line averages for the corresponding OPL. Overall, the ZDL line averages compare well to the OPL path average ( $\pm 4.4$ ppm) for all fan periods with the exception of 0-fans. For the same fan periods, the Pac III line averages compare more closely ( $\pm 2.4$  ppm) to the OPLs than the ZDL (Table 5 and Table 6). For the 0-fan period, in which  $\text{NH}_3$  levels increase to levels greater than 40

ppm, the ZDL line averages compare more closely ( $\pm 9.9$  ppm) to the OPLs than the Pac III line averages ( $\pm 16.9$  ppm). During this period, Z2 line average difference is 2.6 ppm and Z3 line average is 1.4 ppm with Z1 line average difference being the greatest at 9.9 ppm. The Pac III line averages P2 and P3 both exhibit a greater difference (15.2 ppm, 16.9 ppm, respectively) when compared to the OPL path. This is due to the fact that all Pac IIIs used in this study plateau at approximately 40 ppm. The ZDLs do not seem to exhibit this behavior at the observed  $\text{NH}_3$  concentrations.

When comparing EC sensors to OPLs, the Pac III readings are more similar and less variable than the ZDL readings at  $\text{NH}_3$  concentrations that are likely to be found in broiler houses. When levels above 40 ppm are reached, the ZDL is then more comparable to the laser, although the variation between instruments is high.

### ***Outside Comparison***

***Comparison of All Instruments.*** Table 7 summarizes the descriptive statistics for the instruments evaluated in the outside comparison averaged for each day. For the pull-tube comparison, the 3 morning and the 3 evening samples were averaged for reporting in this table. The Pac IIIs had a small standard deviation (SD) for the intra-instrument differences on all days ( $< 0.5$  ppm), indicating little variation between the instruments. However, the resolution of the Pac III is 1 ppm and on three of the four study days the average  $\text{NH}_3$  concentration was less than 1 ppm, meaning that these instruments were reading 0, 1 ppm or negative the majority of the time. Worley et al.[35] found that Pac IIIs were not sensitive enough to accurately report  $\text{NH}_3$  concentrations downwind from poultry houses and suggested using an instrument with higher resolution between 0 and 1 ppm. The ZDL sensors had the highest SD on all study days indicating the most intra-

instrument variability. The OPLs had the most consistent SD over the 4-day study period and ranged from 0.20 to 0.33 ppm. Generally, as average daily NH<sub>3</sub> concentrations increased, variability among the lasers decreased. This was not the case with the other instruments and is most likely because the OPL signal-to-noise ratio increases with concentration resulting in higher accuracy of the OPL.

Table 8 shows the estimates of variance components for each instrument type. For the OPL, the variation between the instruments was estimated at 0.019 (5.55%). The Pac III estimate indicates nearly three times more variation between instruments than the OPL, and the ZDL show 69 times more variation than the OPL. The OPLs within instrument variation was estimated at 0.329 (94.5%) indicating most of the variation resulted from change in NH<sub>3</sub> concentration over time. The Pac III seemed to exhibit a smoothing effect compared to the OPLs and is probably because of the low readings of the Pac III. The ZDL between instrument variation (61.28%) was greater than the variation within the instrument (38.72%). This suggests that the ZDLs had the least consistent performance of the instrument evaluated during the outdoor study.

Overall, the OPLs and the Pac IIIs had small SD throughout the outside study. The Pac III SD can be misleading because the small variation is due to readings rarely reaching higher than 1 ppm, its limit of detection.

***Co-located electrochemical sensors and colorimetric tubes.*** Figure 7 illustrates the EC sensors and colorimetric tubes co-located in the middle of the grid at location #5. The pull tubes have readings that are similar to the Pac III while the dosimeter tubes show concentrations NH<sub>3</sub> that are more similar to the ZDL, keeping in mind that the dosimeter is a time-weighted average. The trend of concentration peaks and valleys are

generally the same for the EC sensors, although the ZDL is much more exaggerated. This is most apparent on the last day of the study at 6:30am when the ZDL average is reading 10.3 ppm and the Pac III average is 0 ppm. The smallest difference between Pac IIIs and ZDLs during a 15 minute peak concentration event is 5.4 ppm. This is an extremely large difference considering the maximum concentration during the study is approximately 10 ppm, according to the ZDL, and less than 5 ppm according to the OPLs, which are much more sensitive to NH<sub>3</sub> and affected very little by temperature and humidity.

With the co-located instruments at location #5, the ZDLs show the most variation and then the Pac III, Pull tube and dosimeter tube with the least variation. With all these instruments, as the concentration increases, so does the intra-instrument variation.

ZDL line averages compared to OPL path average. Figure 8 compares the line average of three ZDL EC sensors to the collocated OPL path average. This figure is similar to the other ZDL line/OPL path comparisons, which are not depicted. It is very concerning that when the ZDL increases the laser decreases and vice versa. The only time that the instruments appear to be showing the same NH<sub>3</sub> concentration trend is the morning of the last day when they both increase until approximately 6:30am and then sharply decrease. Although the average OPL and ZDL NH<sub>3</sub> concentrations are reacting similarly at this time, there is a substantial difference in concentration between the two instruments of  $\pm 5$  ppm. Even more puzzling is the fact that the variation of the three ZDL line averages is less than 1 ppm the majority of the time indicating that the ZDLs are consistent with one another, however, trends of increasing and decreasing NH<sub>3</sub> concentrations for the ZDLs do not compare with the OPLs. During times when OPL

NH<sub>3</sub> concentrations are rising, ZDL NH<sub>3</sub> concentrations are declining. Most likely, the ZDL sensors are being affected by decreasing temperature and increasing humidity during the night causing erroneous readings.

Figure 9 shows all of the real-time instrument-types' average reading over the entire study period. Instruments of the same type (OPLs or Pac IIIs or ZDLs) followed the same NH<sub>3</sub> concentration trends over the study period, however, none of these trends from one type of instrument matched the trend of another instrument type. For example, on 10/1/2007 from 8:15 to 9:30pm, the Pac III shows a steady decrease in average concentration from 2.8 ppm to 0.4 ppm. During the same time period, the average ZDL concentration increases from 6.3 ppm to 7.8 ppm. Also, the EC sensors generally show peak concentrations during the night from 8:00pm to 6:00am and the OPL generally peaks during the afternoon from 11:00am to 5:00pm. Numerous studies have shown that peak ammonia concentrations from poultry houses occur during the afternoon when temperatures are hot, the birds are more active, and more ventilation is needed [6, 7, 36, 37]. The increase in NH<sub>3</sub> by the EC sensors during cool or nighttime conditions could be the result of temperature, humidity, or even wind turbulence on the EC sensors. These data suggest that humidity and condensation increase the reading on the EC sensors and increased wind turbulence decreases readings. This is consistent with the results of the EC sensor showing higher concentrations during the night and lower concentrations during the day when the fans are blowing on them. Direct sunlight and high temperatures could also be causing erroneous readings with the EC sensors. The OPLs are not affected by this, although if condensation is heavy enough on the reflectors, it will diffuse the light resulting in no reading.



### ***Instrument Performance in-house compared to outside.***

Overall, the instruments showed less variation and performed better during the in-house comparison. This is the result of several factors including higher concentrations, smaller temperature and humidity fluctuation, and protection from precipitation and direct sunlight. Outside, the  $\text{NH}_3$  concentrations are near the limit of detection of these instruments while they are also exposed to extreme temperatures, condensation at night, and direct sunlight during the day. In both the in-house and outside comparison, the OPL showed the least variation, then the Pac III, and the ZDL showed the most. The small variation of the Pac III during the outside comparison is misleading because the concentrations were barely at the instrument's limit of detection. Inside the house, the ZDLs performed better at higher concentrations (>40ppm) than the Pac IIIs as the Pac IIIs leveled off at approximately 40 ppm, which is probably because of sensor saturation. Other possibilities that could cause the plateau effect in the Pac IIIs were investigated. Battery voltage was within normal operating range and batteries had been in the Pac IIIs for 1-2 weeks. This is important because EC sensors require a warm-up period when batteries or sensors are replaced, which can be as long as 48 hours. Sensor age could be another possible cause but this was ruled out because sensor age ranged from 2 weeks to 1.5 years, yet all Pac IIIs exhibited a similar plateau effect. The morning of the in-house study the EC sensors were zero calibrated and span calibrated with 50 ppm gas in the lab. With all these possibilities being ruled out, other causes for this phenomenon must be addressed. One possibility is that the 8 hr continuous exposure to approximately 10 ppm  $\text{NH}_3$  saturated the sensor so that as concentrations increased to 40 ppm and above, the

sensor could not perform properly. Additional research needs to be conducted to investigate this phenomenon.

The pull tubes performed well inside at concentrations typical of a poultry house but the variation increased as the concentration increased. Outside, the pull tubes were also consistent but concentrations were near the limit of detection. The dosimeter tubes read higher than the other instruments in the house even though the variation between them was small. Outside the dosimeter tubes also performed well with little variation even though they were exposed for longer than the manufacturers' recommended 10hr exposure. Because of the lower concentration outside and the possibility that a small shift in wind direction can cause instantaneous point measurements to vary, the dosimeter tube most likely gave a better estimation of the actual concentration than the pull tubes.

For in-house applications for growers, the pull tube and/or the dosimeter tube perform comparably with the EC sensors at a much lower cost; however, colorimetric tubes cannot give real-time data and show concentration trends over time like the EC sensors. Colorimetric tubes are much easier to deal with, as EC sensors require frequent calibration and maintenance. For measuring downwind concentrations, instruments such as the OPL are needed, despite their expense, to ensure accurate measurements at low  $\text{NH}_3$  concentrations. The OPL is also less affected by the humidity, wind, precipitation and temperature compared to EC sensors.

### **Conclusions and Applications**

1. All instruments evaluated performed better inside the broiler house compared to outside due to higher  $\text{NH}_3$  concentrations inside and lower  $\text{NH}_3$  concentrations outside.
2. The OPL showed the least variation during the in-house and outside comparisons.

3. The Pac III and the ZDL performed well with little variation under in-house conditions but did not do well outside or at high concentrations.
4. The colorimetric tubes are a good choice for growers because they cost less, are easier to use, and compare closely to ECs under inside conditions. Their limitation is that they only measure NH<sub>3</sub> concentrations at one point in time and location.
5. For outside and downwind NH<sub>3</sub> measurements, the OPLs were the only reliable instrument tested at concentrations that are essentially below the limit of detection of the other instruments.

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CHAPTER 4  
CONCLUSIONS

### **In-house Comparison**

During the in-house comparison, instruments were evaluated under typical house conditions with 2-8 tunnel fans running which provided adequate ventilation.

Instruments were also evaluated under extreme house conditions with 0 tunnel fans running and no ventilation which resulted in a steady increase of  $\text{NH}_3$  concentrations.

Under typical house conditions, the OPLs, Pac IIIs, ZDLs, and pull tubes, all performed consistently and accurately. Dosimeter tubes tended to overestimate the average concentration of the 2 hour fan period by approximately 10 ppm. Of the real-time instruments, the OPLs had the least intra-instrument variation.

Under extreme house conditions, with no ventilation,  $\text{NH}_3$  concentration increased steadily. With all instruments, as the concentration increased so did the variation. The Pac III sensors all plateaued at approximately 40 ppm, which is possibly due to sensor saturation. When comparing the ZDL line average with the OPL path average, there was not much difference between the line average and path average although the variation among the 3 ZDLs used in the line average increased. This could indicate that the  $\text{NH}_3$  concentration is not uniform along the path. The pull tube overestimated the  $\text{NH}_3$  concentration under these extreme conditions.

Further research is needed to investigate the behavior of the EC sensors. Particularly, the plateau effect seen in the Pac IIIs during the in-house comparison. Continuous exposure to  $\text{NH}_3$  at low concentrations could cause sensor saturation in the Pac III and therefore, cause inaccurate readings at higher concentrations. However, this is only speculation. Exposing the Pac IIIs to a 10 ppm  $\text{NH}_3$  calibration gas for 8 hours

and then switching to a 100 ppm NH<sub>3</sub> calibration gas could be a way to test for the plateau effect in a laboratory setting.

### **Outside Comparison**

During the outside comparison, the NH<sub>3</sub> concentrations were much lower and close to the limit of detection of all instruments. In addition, all instruments were subjected to all weather conditions with little protection. With the exception of the OPLs, ammonia concentrations were too low and weather fluctuation too extreme for instruments to perform consistently and accurately. EC sensors are especially sensitive to temperature and humidity fluctuations and should be operated under conditions similar to when calibrated. Also, condensation formed on these instruments overnight which affects their performance and is advised against by the manufacturers. The OPLs showed the least intra-instrument variation during the outside comparison and was the only instrument evaluated that the author had confidence in its performance.

For measuring downwind NH<sub>3</sub> concentrations, the OPLs should be compared UV-DOAS, PAS, CL analyzers, and FTIR to determine which of these high cost, high sensitivity instruments is most accurate and precise at very low NH<sub>3</sub> levels. In addition, this would compare ease of use, performance, and reliability in the field.



Table 3.1. Summary of instruments evaluated during in-house and outside ammonia comparison study.

Manufacturer	Model	Technology	Cost	Limit of Detection	Range	Resolution	Accuracy
Drager	Pac III	Electrochemical	\$1,200.00	1ppm	0-200ppm	1ppm	+/- 3%
Environmental Sensors Inc	ZDL-800	Electrochemical	\$1,000.00	2ppm	0-200ppm	0.1ppm	+/- 10%
Boreal OPL Inc	GasFinder	Tunable Diode OPL	\$40,000.00	2.5ppmm	0-1000ppm	.025ppm	variable
Rae	10-10-05	Colorimetric Pull Tube	\$3.00		1-30ppm		+/- 25%
Rae	10-10-10	Colorimetric Pull Tube	\$3.00		5-100ppm		+/- 25%
GasTec	3L	Colorimetric Pull Tube	\$5.70 per tube	0.5ppm	0.5-78ppm		+/- 25%
GasTec	3D	Dosimeter Tube	\$6.50 per tube	0.5ppm *10hrs	2.5-1000ppm * hr		+/- 25%
GasTec	GV-100	Piston Hand Pump	\$375.00	N/A	N/A	N/A	N/A
Rae	LP-1200	Piston Hand Pump	\$180.00	N/A	N/A	N/A	N/A

Table 3.2. Mean NH<sub>3</sub> concentration of real-time instruments and colorimetric tubes during in-house comparison.

<b>No. Fans Running</b>	<b>Instrument</b>	<b>n</b>	<b>Period Mean NH<sub>3</sub> Concentration(ppm)</b>	<b>Std Dev</b>
8	OPL	3	6.1	0.4
	Pac III	8	7.1	1.0
	ZDL	12	8.5	2.3
	Pull Tube	3	9.0	0.0
	Dosi Tube	3	20.8	1.4
6	OPL	3	6.6	0.2
	Pac III	8	5.8	1.3
	ZDL	12	7.9	2.5
	Pull Tube	3	8.7	0.6
	Dosi Tube	3	15.0	3.1
4	OPL	3	7.2	0.3
	Pac III	8	6.4	1.9
	ZDL	12	8.4	3.2
	Pull Tube	3	11.7	0.6
	Dosi Tube	3	21.7	2.9
2	OPL	3	9.1	0.5
	Pac III	8	7.4	1.4
	ZDL	12	10.4	2.9
	Pull Tube	3	19.3	1.5
	Dosi Tube	3	21.0	3.1
0	OPL	3	52.3	1.0
	Pac III	8	34.0	5.1
	ZDL	12	46.9	14.4
	Pull Tube	3	93.0	3.5
	Dosi Tube	3	67.9	7.5

Table 3.3. ANOVA sources of variation of real-time instrument NH<sub>3</sub> concentrations during in-house comparison. Shaded sources are partitioned by type of instrument.

Source	DF	Type III SS	Mean Square
type	2	3640.56	1820.28
<b>InstID(type)</b>	<b>20</b>	<b>5564.34</b>	<b>278.22</b>
OPL	2	10.98	5.49
Pac III	7	374.28	53.47
ZDL	11	5179.08	470.83
fan	4	140256.30	35064.07
type*fan	8	5161.08	645.13
<b>InstID(type)*fan</b>	<b>80</b>	<b>15381.92</b>	<b>192.27</b>
OPL	8	11.07	1.38
Pac III	28	1388.96	49.61
ZDL	44	13981.89	317.77
<b>Error</b>	<b>782</b>	<b>49862.35</b>	<b>63.76</b>
OPL	102	11835.90	116.04
Pac III	272	6530.03	24.01
ZDL	408	31496.41	77.20

Table 3.4. Variance components estimates and percentages (%) for the sources of variation of real-time instrument NH<sub>3</sub> concentrations during the in-house comparison.

Source	Estimates of Variance Components		
	OPL	ZDL	Pac III
Between instrument (intra) InstID* Fan	0 (0%)	3.31 (2.9%)	0.07 (0.3%)
Within instrument (Error)	0 (0%)	32.28 (28.6%)	3.23 (11.7%)
	105.9 (100%)	77.42 (68.5%)	24.12 (88.0%)

Table 3.5. OPL path average with corresponding electrochemical line average for each fan period in ppm. (n=3 for each line average)

<b>Fans</b>	<b>OPL 1 Path</b>	<b>ZDL 1 Line Avg (SD)</b>	<b>OPL 2 Path</b>	<b>ZDL 2 Line Avg (SD)</b>	<b>PacIII 2 Line Avg (SD)</b>	<b>OPL 3 Path</b>	<b>ZDL 3 Line Avg (SD)</b>	<b>PacIII 3 Line Avg (SD)</b>
<b>8 Fans</b>	5.7	6.4 (0.9)	6.0	8.3 (1.5)	7.1 (0.9)	6.5	9.7 (2.4)	6.5 (0.9)
<b>6 Fans</b>	6.3	5.4 (0.8)	6.8	7.6 (1.0)	5.5 (1.6)	6.6	10.2 (2.5)	5.4 (1.0)
<b>4 Fans</b>	7.3	5.3 (0.9)	7.5	7.8 (1.2)	5.9 (2.6)	6.9	11.4 (3.3)	5.9 (1.2)
<b>2 Fans</b>	8.5	7.5 (0.5)	9.4	10.4 (2.4)	7.2 (1.4)	9.3	13.0 (3.5)	6.9 (6.9)
<b>0 Fans</b>	45.9	35.9 (10.0)	47.3	49.8 (21.0)	32.0 (6.3)	47.6	46.2 (8.9)	30.7 (3.8)

Table 3.6. Absolute difference (in ppm) between OPL path average and corresponding EC sensor line averages.

Fans	Z 1-L1	Z 2-L2	Z3-L3	P2-L2	P3-L3
8 Fans	0.7	2.3	3.2	1.0	0.0
6 Fans	0.9	0.8	3.6	1.4	1.2
4 Fans	2.0	0.3	4.4	1.6	1.0
2 Fans	1.0	1.0	3.7	2.2	2.4
0 Fans	9.9	2.6	1.4	15.2	16.9

Table 3.7. Daily mean NH<sub>3</sub> concentration of real-time instruments and colorimetric tubes during outside comparison.

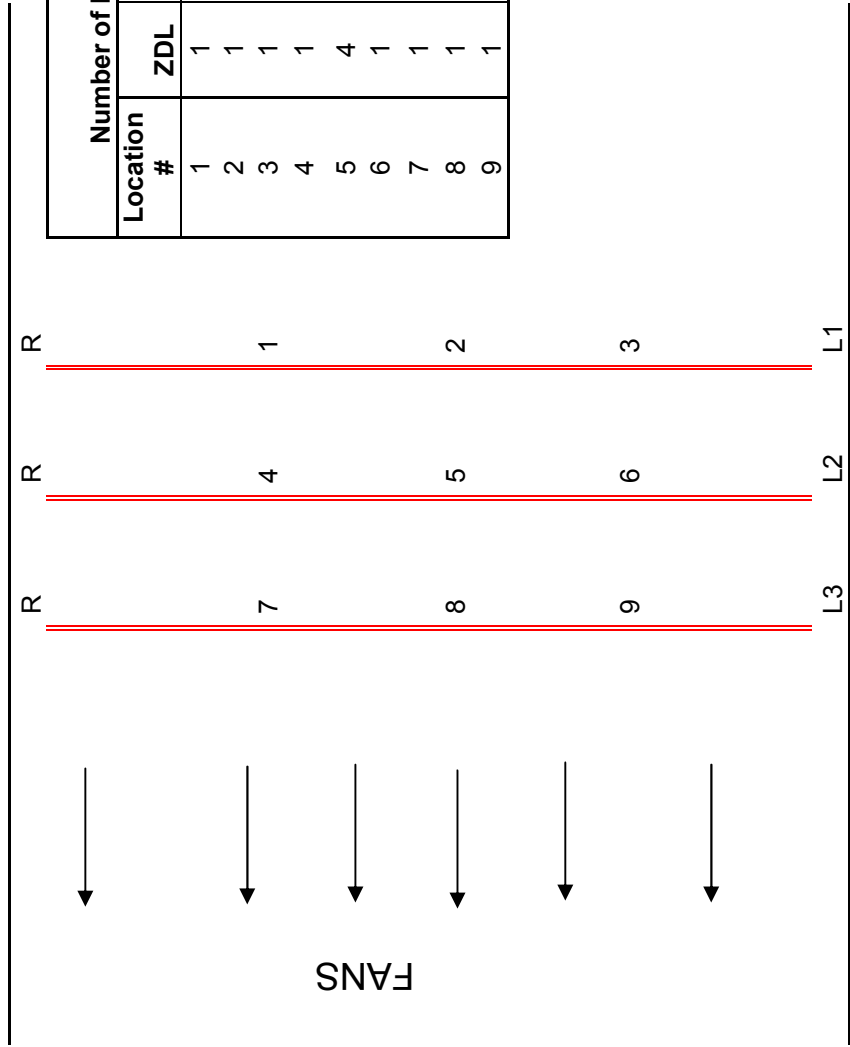
Date	Instrument	n	Mean	Std Dev
9/30/2007	OPL	3	1.5	0.33
	Pac III	4	0.1	0.16
	ZDL	13	2.7	1.06
	Pull Tube*	6	2.7	1.21
	Dosi Tube	3	1.4	0.15
10/1/2007	OPL	3	1.1	0.20
	Pac III	4	0.6	0.30
	ZDL	13	3.8	0.98
	Pull Tube*	6	0.8	0.88
	Dosi Tube	3	2.0	0.00
10/2/2007	OPL	3	2.4	0.23
	Pac III	4	0.6	0.17
	ZDL	13	4.2	1.11
	Pull Tube*	6	0.5	0.55
	Dosi Tube	3	2.4	0.12
10/3/2007	OPL	2	2.9	0.20
	Pac III	4	1.2	0.46
	ZDL	13	6.3	1.80
	Pull Tube*	6	1.7	1.60
	Dosi Tube	3	6.2	0.26

\*Pull tube averages are based on 3 morning and 3 evening point samples and therefore do not represent true daily averages.

Table 3.8. Variance components estimates and percentages (%) for the sources of variation of real-time instrument NH<sub>3</sub> concentrations during the outside comparison.

<b>Estimates of Variance Components</b>			
<b>Source</b>	<b>OPL</b>	<b>Pac III</b>	<b>ZDL</b>
<b>Between Instruments</b>	0.019 (5.55%)	0.054 (17.44%)	1.315 (61.28%)
<b>Within Instrument</b>	0.329 (94.45%)	0.255 (82.56%)	0.831 (38.72%)





Number of Instruments by Location				
Location #	ZDL	Pac III	Pull Tube	Dosimeter Tube
1	1	0	0	0
2	1	0	0	0
3	1	0	0	0
4	1	1	0	0
5	4	3	3	3
6	1	1	0	0
7	1	1	0	0
8	1	1	0	0
9	1	1	0	0

Legend	
Air flow	←
OPL	L
Laser path	====
Reflector	R

Figure 3.1. Schematic of in-house layout. (Not to Scale)

Instruments at Location 5	
Instrument	Number
ZDL	5
Pac III	4
Dosimeter Tube	3 per day
Pull Tube	3 morning & evening

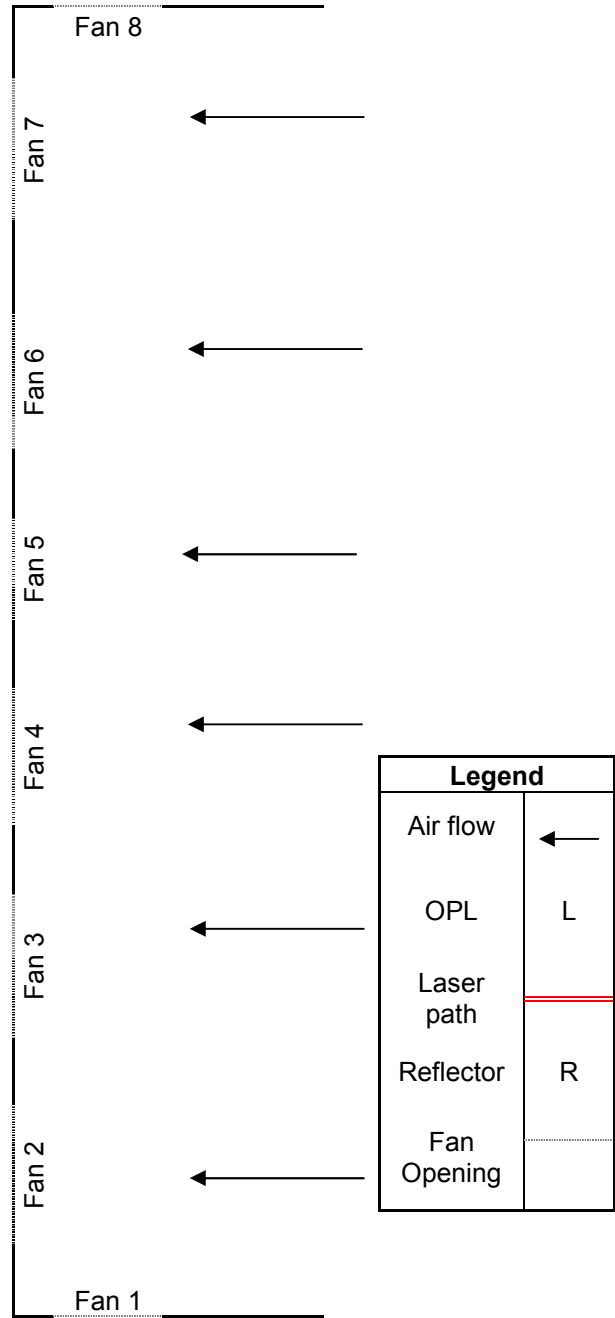
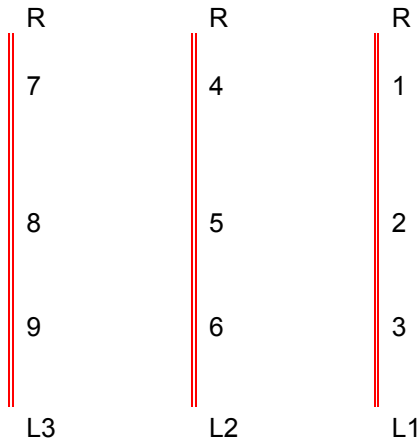


Figure 3.2. Schematic of outside layout. (Not to scale)

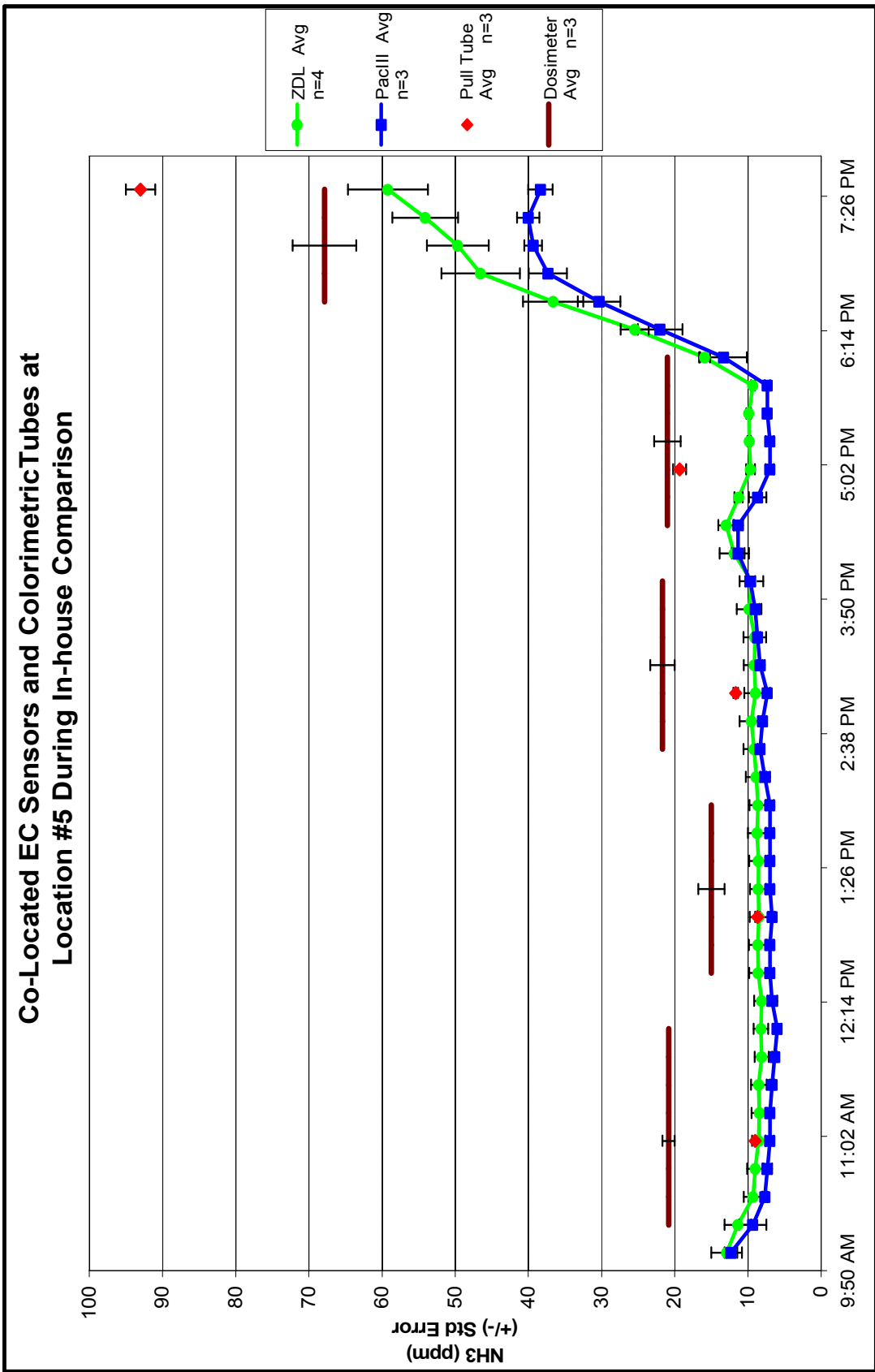


Figure 3.3. NH<sub>3</sub> concentrations of instruments co-located at location #5. Dosimeter tube line indicates fan period.

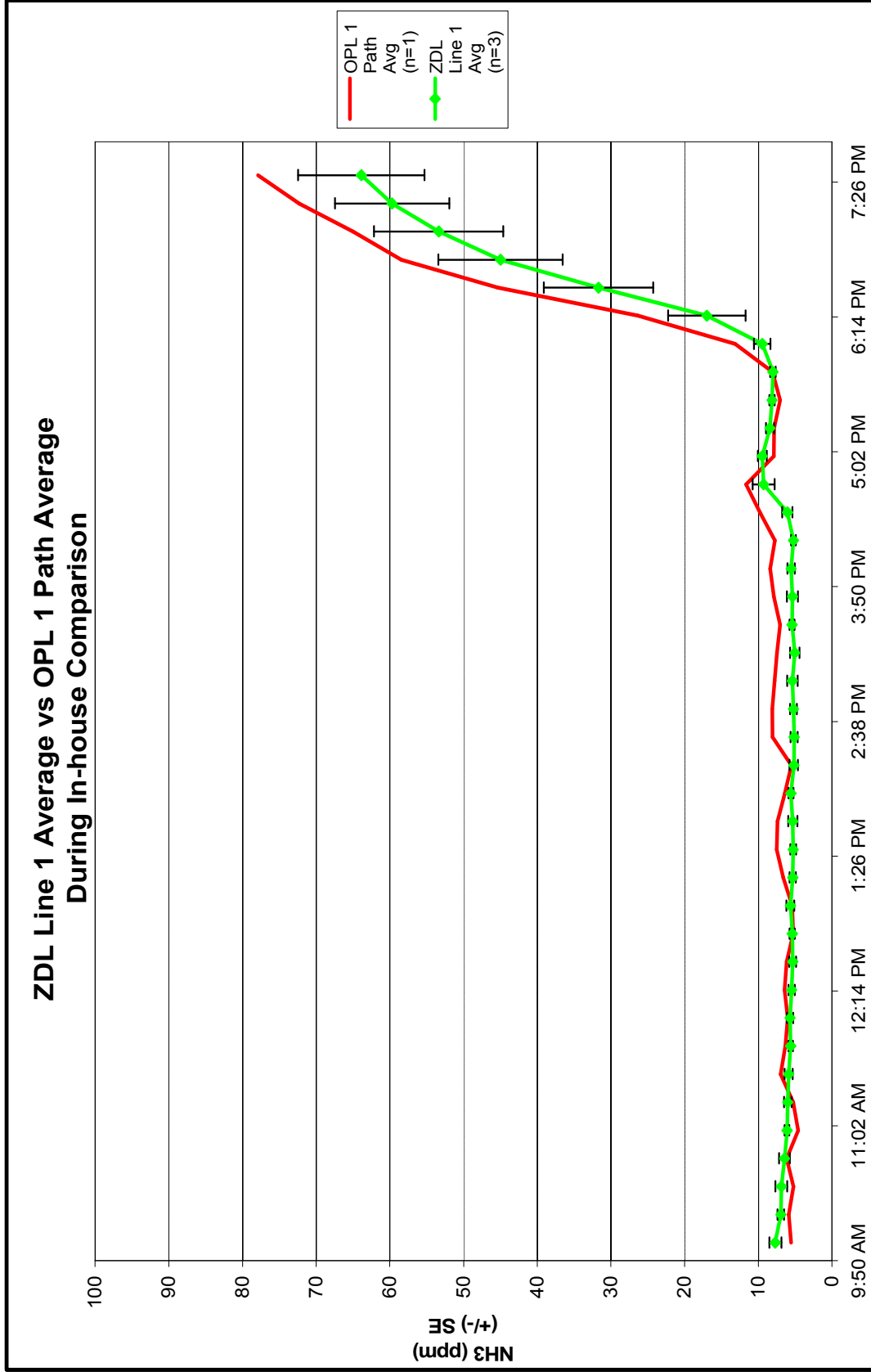


Figure 3.4. OPL1 path average compared to ZDL line 1 average during in-house comparison.

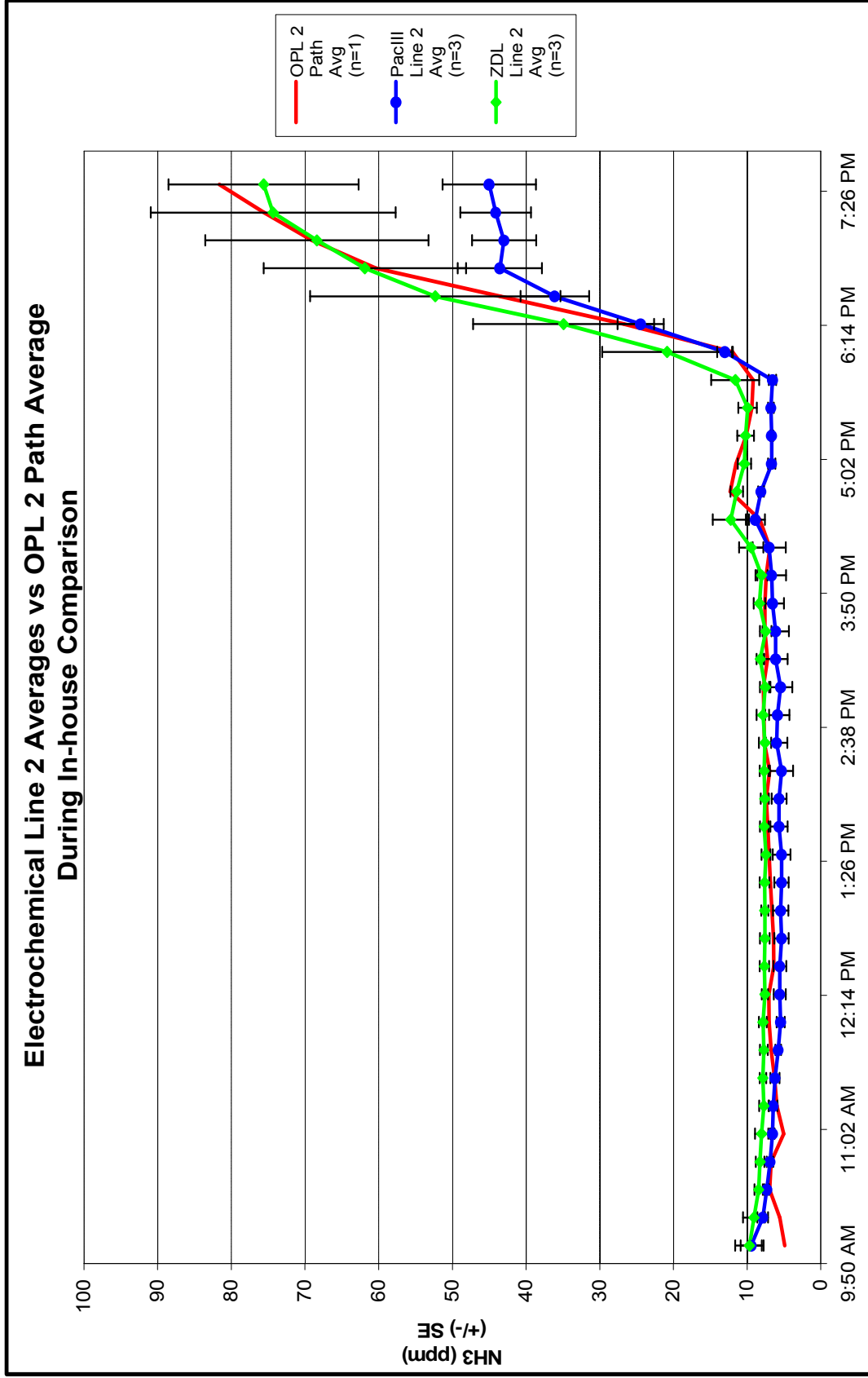


Figure 3.5. NH<sub>3</sub> concentrations OPL 2 path average compared to ZDL and Pac III line 2 average during in-house comparison.

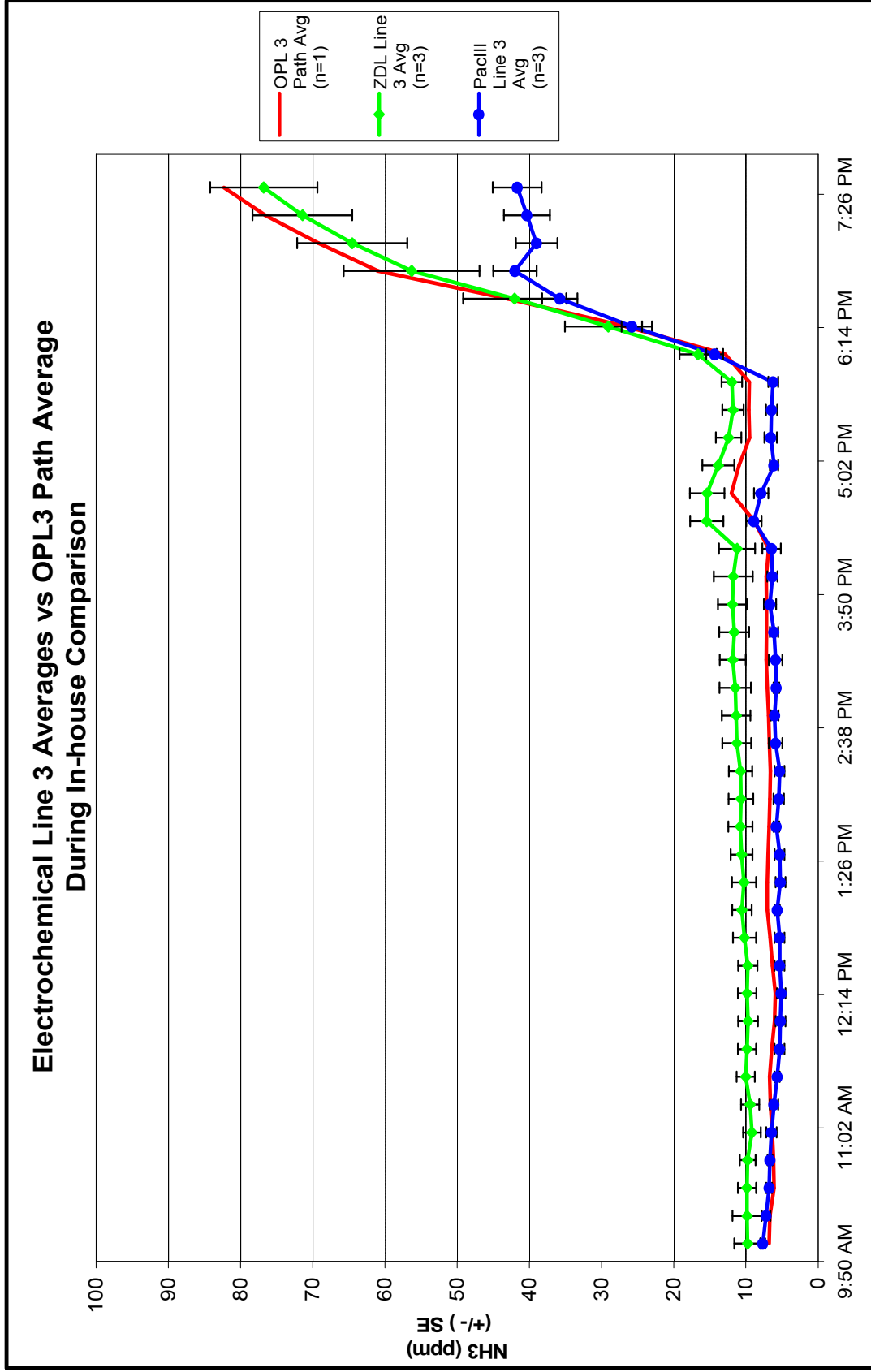


Figure 3.6.  $\text{NH}_3$  concentrations of OPL 3 path average compared to ZDL and Pac III line 3 average during in-house comparison.

### Co-located EC Sensors and Colorimetric Tubes During Outside Comparison

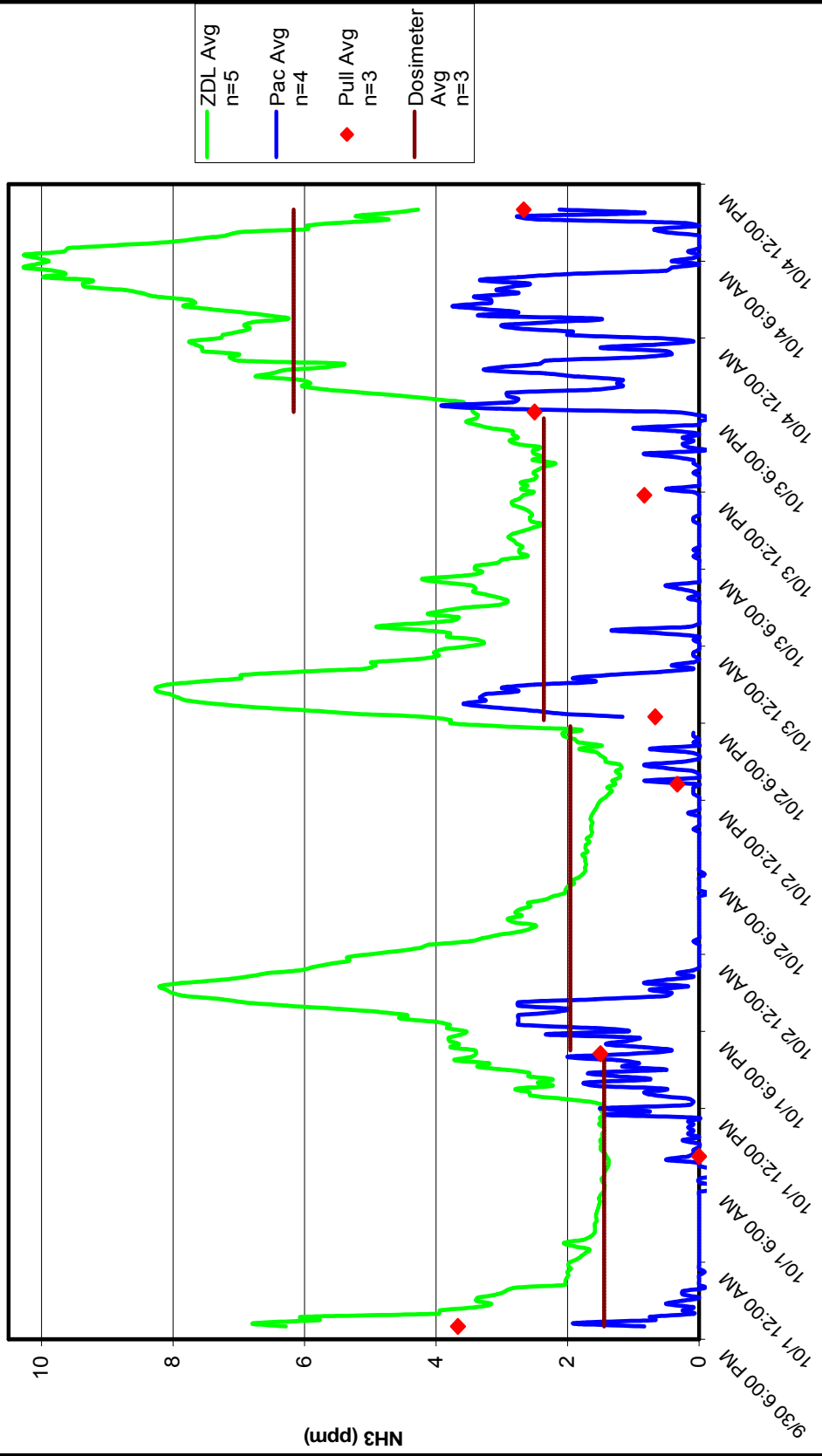


Figure 3.7. NH<sub>3</sub> concentrations of co-located EC sensors and colorimetric tubes during outside comparison.

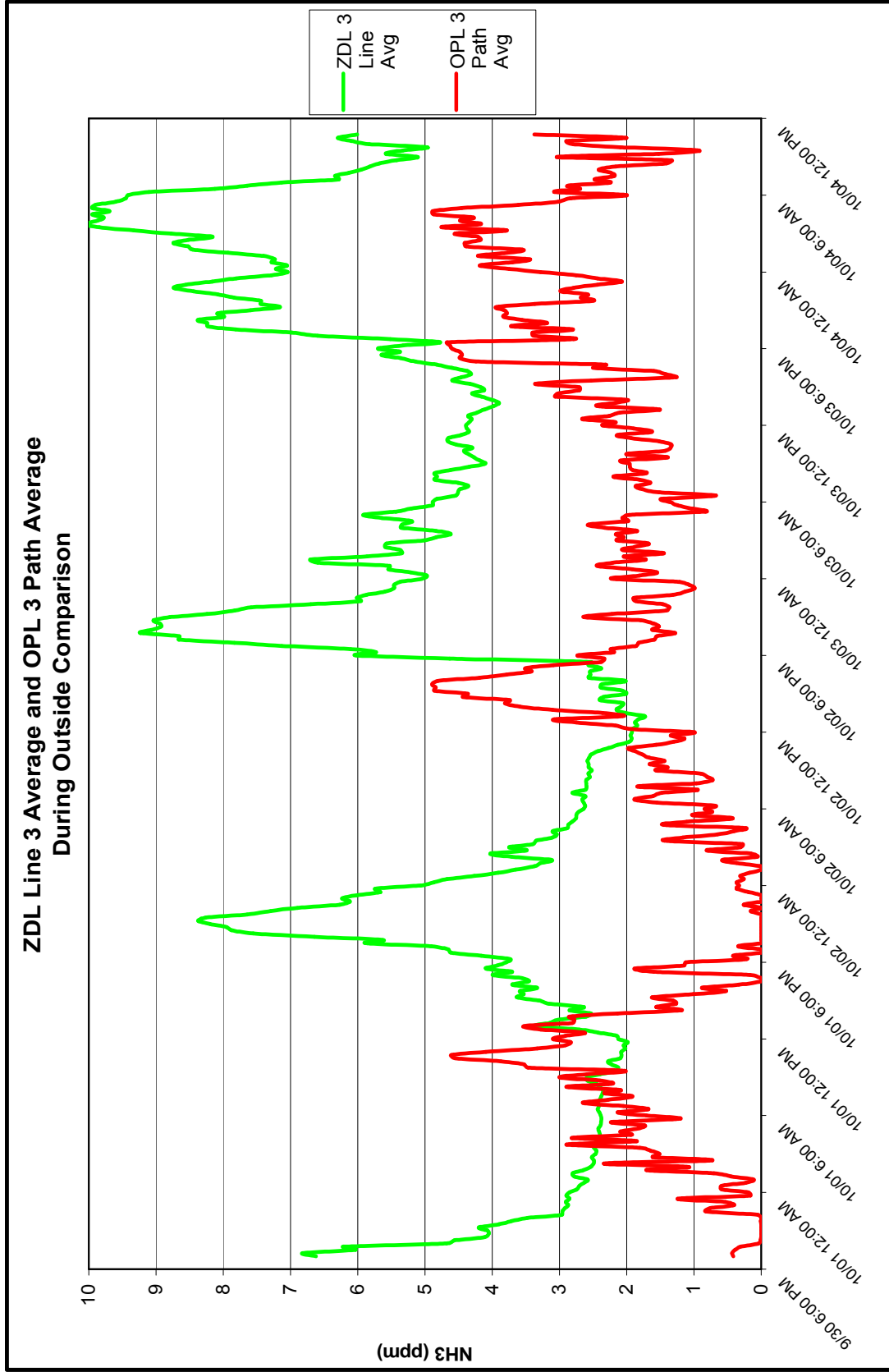


Figure 3.8. NH<sub>3</sub> concentrations OPL 3 path average compared to ZDL line 3 average during outside comparison.



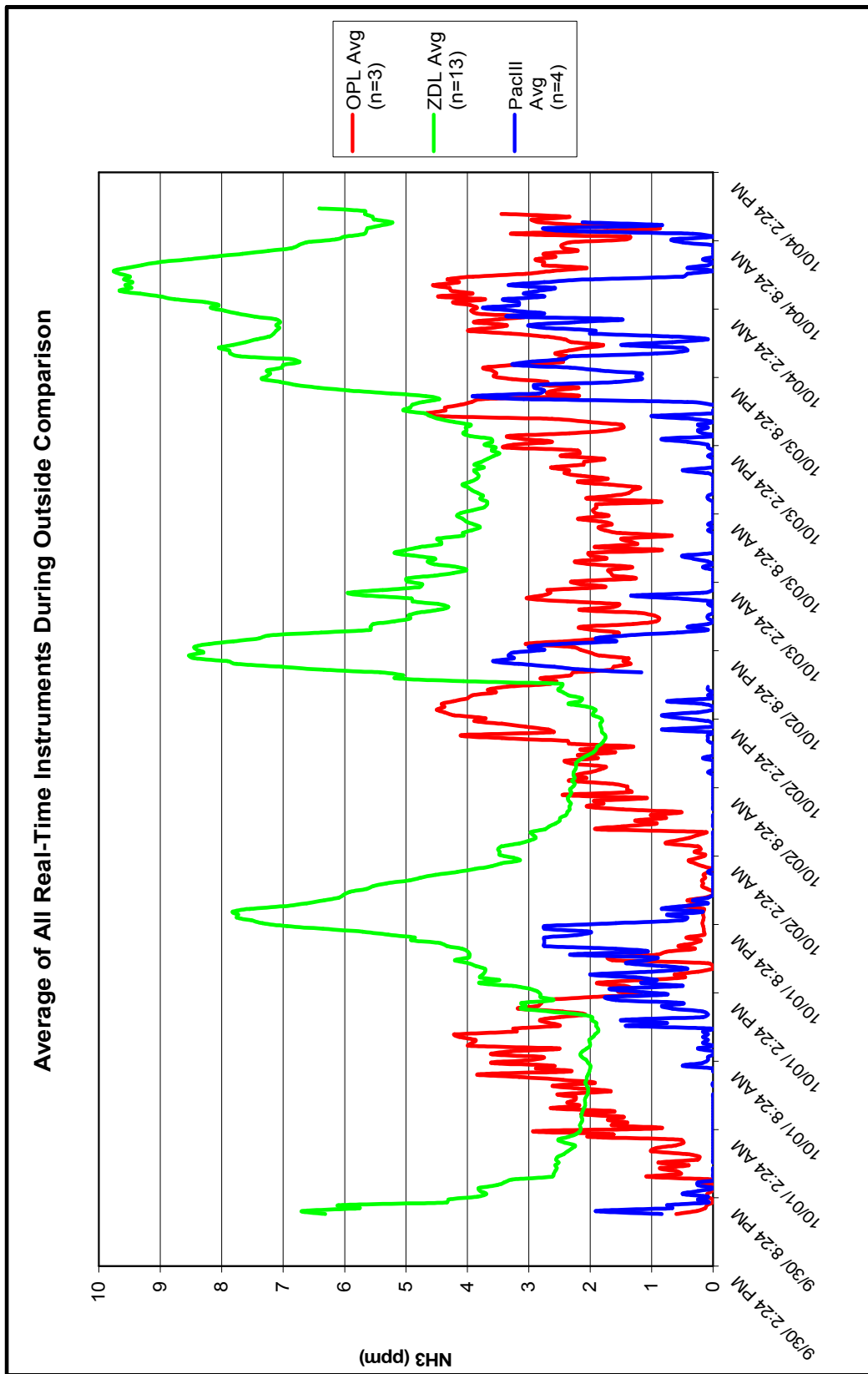


Figure 3.9. Average NH<sub>3</sub> concentrations of all real-time instruments during outside comparison study.