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# Ammonia Sampling using Ogawa® Passive Samplers

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# AMMONIA SAMPLING USING OGAWA® PASSIVE SAMPLERS

by

PAUL TATE

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Science
Department of Chemistry
College of Arts and Sciences
University of South Florida

March 2002

Co-Major Professor: Noreen Poor, PhD
Co-Major Professor: Abdul Malik, PhD

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# Glossary

| Term | Definition |
|---|---|
| ADS | Annular Denuder System |
| Annular Denuder System | A method of sampling for atmospheric gases. |
| Contour Map | A visual display of known and interpolated spatial concentrations. |
| DL | Detection Limit—The detection limit of the analytical technique used |
| Eutrophication | Excess nutrients in a body of water leading to algae blooms and oxygen depletion. |
| Gridding | The process of interpolating unknown values between known values. |
| Interpolation | The process of estimating unknown values that lie between known values. |
| Kriging | A particular method of interpolation. |
| PSD | Passive Sampling Device |
| SDL | Sampling Detection Limit—The detection limit for the overall sampling procedure |
| WWTP | Wastewater Treatment Plant |
| RPD | Relative Percent Difference |
| Relative Percent Difference | The difference of two values divided by their mean times 100. |

# AMMONIA SAMPLING USING THE OGAWA® PASSIVE SAMPLER

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An Abstract

of a thesis submitted in partial fulfillment
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The purposes of this research were to determine the efficacy of using the Ogawa® passive sampling device (PSD) to measure ammonia and to identify significant ammonia sources adjacent to Hillsborough and Tampa Bay. Ninety-four samplers were deployed over a 180-km$^2$ area for two weeks in October 2001. Within the area sampled were located suburbs, an urban center, major highways, port activities, fertilizer manufacturing, wastewater treatment, coal-combustion power plants, warehousing and dairy farming. The sampled locations were arranged in a triangular grid pattern spaced 1.5 km apart. The pattern was designed to locate circular hot spots with a minimum radius of 0.75 km.

The minimum, maximum, mean, and median ammonia concentrations were 0.06, 15, 2.0, and 1.5 $\mu g/m^3$, respectively, and the estimated precision was 16%. Hot spots identified from kriged concentration data coincided with inventoried ammonia sources. The relative bias and precision of the PSD based on collocation with an annular denuder system were ± 30 % and 20 %.

# Chapter I Introduction

This research focused on the question, “Can the Ogawa® passive sampling device (PSD) be used for ammonia sampling of spatial concentrations at ambient levels?” The Ogawa® sampler is advertised for use in sampling of atmospheric $NO_x$, $SO_2$ and $O_3$ (Koutrakis et al., 1993; Liard et al., 1999; Varns et al., 2001). To determine its efficacy, a methodology specific for ammonia sampling was developed, the accuracy and precision of the PSD were determined, and the PSD was assessed using extensive multi-site field deployments that were used to determine spatial concentration gradients.

Current methods of ammonia sampling can be broadly categorized as either passive or active. The active methods of ammonia sampling require at minimum an air pump and either a denuder, coated filter, impinger or reaction chamber. Because of the equipment cost, the need for electricity, and site security, active systems are not preferred for a multi-site deployment necessary for determining spatial concentrations or “hot spots” of ammonia.

A passive sampler typically consists of a small body that holds a filter with a coating designed to react with or to adsorb the target analyte. The size and simplicity of the passive sampler allows the PSD to be made inexpensively and used in an extensive multi-site deployment without the need for security or electricity. For a multi-site deployment, "The large number of measuring sites needed to obtain a representative picture of ammonia concentration in a certain area makes passive samplers the ideal instrument to do the job" (Kirchner et al., 1999).

Using the Ogawa® sampler to measure ammonia concentrations and hot spots was necessary to help determine the contribution of ammonia to the overall deposition of nitrogen to the Tampa Bay Estuary. "…reduced N species[1] can be utilized directly by a variety of microorganisms and higher aquatic plants, including suspended microalgae (phytoplankton), macroalgae and rooted macrophytes" (Paerl et al., 2001). Excessive nitrogen in the Tampa Bay Estuary has contributed to bay eutrophication, which causes excessive algae growth. The algae cloud the water, blocking the sunlight to seagrass, causing them to die (TBEP, 2001). The seagrasses play an important role in the health of the bay, providing both food and shelter to many species of fish. Since the turn of the century, more than half of Tampa Bay's seagrass has been destroyed due to pollution and dredging (TBEP, 2001). Excessive algae also can directly affect fish. As dead algae decay, oxygen is consumed and can lead to hypoxic (little oxygen) conditions that can cause fish kills.

Ammonia/ammonium contributed 58% of the total nitrogen deposited to the Tampa Bay estuary between August 1996 and July 1999 (Poor et al., 2001). Because ammonia/ammonium plays such a significant role in the overall deposition of nitrogen, it

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[1] Reduced nitrogen refers to ammonia/ammonium.

is important to determine ambient concentrations and identify any areas where $NH_3$ concentrations are higher than ambient levels. One location sampled during this research included industrial areas located on Hillsborough Bay (Hillsborough bay is located at the very northern tip of Tampa Bay). The area has known sources of ammonia, such as ammonia docks, fertilizer plants, and a wastewater treatment plant. The proximity of these known sources of ammonia is important. Ammonia/ammonium can deposit close to the source; thus, industries located close to the bay will have a greater impact than if they were located further inland.

Companies that release or store large amounts of ammonia are required to report the amount they release. However, some sources are not included in federal inventories (e.g., wastewater treatment plants). The treatment process releases ammonia but that release is not reported. The type of spatial sampling utilized in this research can assist in confirming inventoried sources as well as discovering uninventoried sources.

To determine if the Ogawa® passive sampling device could be used for ammonia sampling, five steps were followed.

- The development of a method to utilize the Ogawa® PSD for ammonia sampling, i.e., type of coating solution, filter type, extraction and cleaning method (at the beginning of this research Ogawa® had not developed an ammonia protocol)
- The determination of the accuracy and precision of the sampler
- The development of a sampling protocol, i.e., number of samplers and locations necessary for determining hot spots

- The deployment of the samplers, first in a small area and then a much larger area
- The analysis of the data using contour maps to determine if any ammonia hot spots exist in the sampled area

# Chapter II Literature Review

## *Ammonia Sources and Sinks*

Ammonia is the third most abundant nitrogen-carrying compound in the atmosphere behind $N_2$ and $N_2O$. The highest ammonia sources are animal waste, ammonification of humus followed by emission from soils, losses of ammonia from fertilizers use and industrial emissions (Seinfeld, Pandis, 1998).

Table 1 shows an estimate of global ammonia emissions. The anthropogenic (man-made) emissions are twice the naturally occurring emissions.

**Table 1. Estimated Global Ammonia Emissions**

| Source of Ammonia | Emissions Tg (N)/year |
|---|---|
| Anthropogenic | |
| Dairy Cattle | 5.5 |
| Beef cattle/buffalo | 8.7 |
| Pigs | 2.8 |

| | |
|---|---|
| Horses | 1.2 |
| Sheep/goats | 2.5 |
| Poultry | 1.3 |
| Fertilizer | 6.4 |
| Biomass burning | 2.0 |
| Subtotal | 30.4 |
| Natural | |
| Wild animals | 2.5 |
| Vegetation | 5.1 |
| Ocean | 7.0 |
| Subtotal | 14.6 |
| Total | 45.0 |

Source: Dentener and Crutzen (1994) as cited by (Seinfeld, Pandis, 1998)

Figure 1 lists a current ammonia emissions inventory for the Tampa Bay area as compiled by Connie Mizak (2001) of the University of South Florida. In Figure 1, “Point” sources include industries and was taken from the EPA Toxic Release Inventory. The category "Other" is mostly comprised of ammonia releases due to refrigeration.

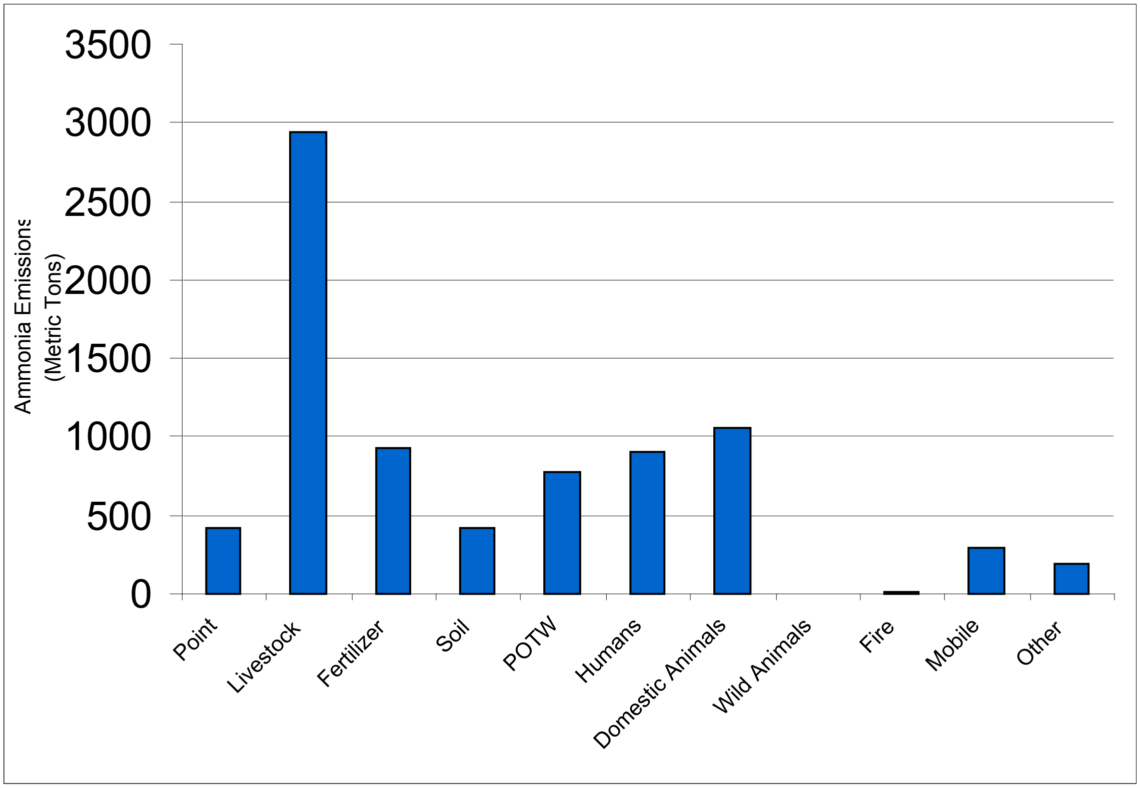

**Figure 1. Ammonia Emissions for Hillsborough County (Mizak, 2001)**

Publically-owned treatment works (POTW) refers to releases due to wastewater processing. The POTW releases were calculated using the Carnegie Mellon University Ammonia Emissions Inventory Program. The area around the Tampa wastewater treatment plant was sampled continuously for a month, and the elevated concentrations demonstrate a strong source of ammonia in the area. The area also has three ammonia terminals where ammonia is transferred from cargo ships to railroad cars so it is difficult to attribute the elevated ammonia concentrations to just the wastewater treatment plant.

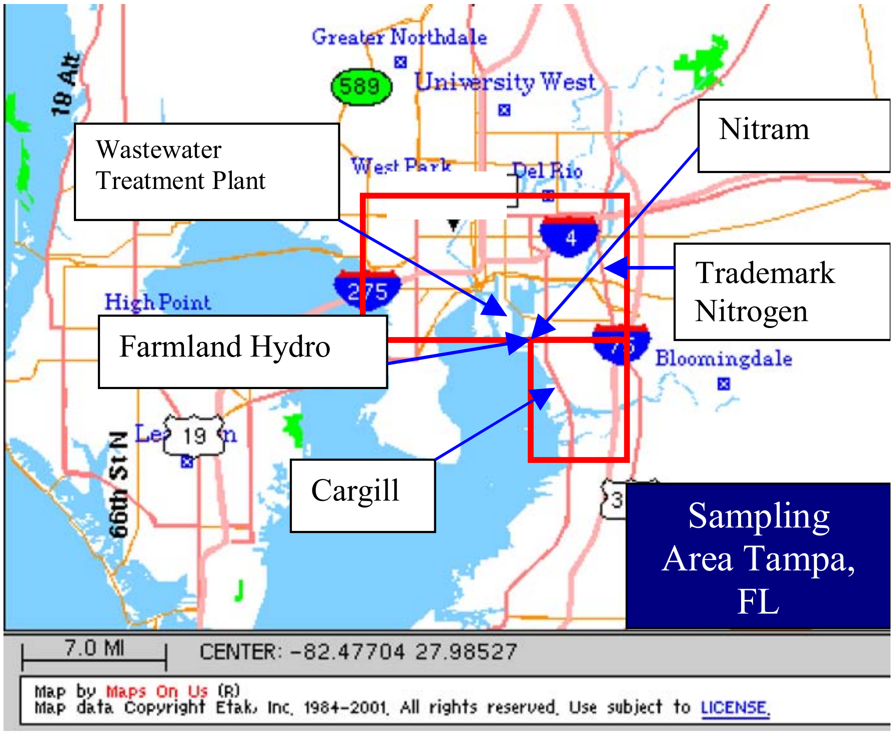

**Figure 2. Tampa Sampling Area (This and all subsequent area maps are reprinted with permission from www.mapsonus.com)**

Once released into the atmosphere ammonia can react with $H_2SO_{4\,(g)}$, $HNO_{3\,(g)}$ and HCl (Atmospheric $SO_2$, $NO_x$ and HCl are primarily emitted during combustion, $SO_2$ and $NO_x$ are further oxidized to form the above acids.) to form fine (< 0.5 µm) particles of $NH_4HSO4_{(s)}$, $(NH_4)_2SO_{4(s)}$, $NH_4NO_{3(s)}$, and $NH_4Cl_{(s)}$. Ammonia/ammonium particles can be deposited directly to the earth's surface (dry deposition) or by interacting with hydrospheres and subsequently deposited via precipitation (wet deposition).

The dry deposition of ammonia is many times higher than the deposition of ammonium particles. Dry deposition is controlled by three mechanisms, transportation down to "…a very thin layer of stagnant air just adjacent to the surface…" referred to as the quasi-laminar layer, transportations across that layer and the uptake by the surface (Seinfeld, Pandis, 1998). The transportation to the quasi-laminar layer is governed by eddy diffusion. Transportation across the layer is governed by molecular diffusion (gases) and Brownian motion (particles). The uptake by the surface is governed by the "stickiness" of the surface and the reactivity of the species with the surface. The diffusion coefficient of ammonia is many times larger than the diffusion coefficient of ammonium sulfate particles (the predominant ammonium particle). This means ammonia gas is more likely to be deposited near its source than ammonium. This regional impact of ammonia deposition provides impetus for determining the regional ammonia concentrations, hot spots, and uninventoried sources.

## *Deleterious Effects of Ammonia*

Besides eutrophication of waterways (discussed in the introduction), ammonia can also have negative effects on land. Ammonia/ammonium is oxidized to nitric acid by soil bacteria. Also, plants can directly absorb ammonium and release a proton ($H^+$) to the soil. Both of these processes acidify the soil. The acidification can lead to "…the loss of important nutrient base cations like calcium and magnesium and an increase in the bioavailability of potentially toxic cations like aluminum (Galloway, 2000)."

## *Measurement of Ammonia*

### *Active Samplers*

One type of active system is the annular denuder system (ADS). In order to determine the PSD's accuracy, the ADS was utilized as the standard for determining ammonia concentrations. The ADS was first described by Possanizini (1983) and refined by Vossler (1988). The ADS pulls air through a cyclone head that removes the particles that are larger than 2.5 μm. The air is then drawn through an annular denuder that removes the ammonia. The denuder contains concentric glass tubes that are coated with an acidic solution (for this research phosphoric acid was used for all but one experiment, citric acid was used for that one). Ammonia flowing through the annular spaces diffuses to and reacts with the acid coating while allowing ammonium particles to pass through. The air is then drawn through a filter that collects particles. One strength of this system is its ability to determine gaseous ammonia concentration separately from particulate ammonium. Prior to use of denuders, many active systems simply pulled air through a solution of acid or a filter coated in acid. This type of collection gives the total ammonia/ammonium collected without differentiating between the two.

Active systems can sample large amounts of air when compared to passive samplers. For example in a 24-hour sampling period an ADS samples 24 $m^3$ of air and a PSD only 0.06 $m^3$. Thus, an active system can be deployed for a much shorter time than can a passive sampler. For instance, the annular denuder system can determine ambient ammonia concentration with a 24-hour integration; passive ammonia samplers need approximately one week to accurately determine ambient concentrations. A researcher can use this shorter deployment time to analyze meteorological data to help determine sources of ammonia.

The biggest drawback to utilizing an ADS system is its cost. One system costs approximately $10,000, independent of the analyses cost and space requirements. This makes using the ADS impractical for multi-unit deployments.

## *Passive Samplers*

In a passive sampler the target compound diffuses to the absorbent. The sampling rate (volume/time) is determined by the diffusion coefficient of the target analyte and the shape and design of the sampler. For this research, phosphoric acid ($H_3PO_4$) was used as the absorbent. The ammonia reacts with the phosphoric acid to form ammonium dihydrogen phosphate ($NH_4H_2PO_4$). This “traps” the ammonia on the filter, which is later extracted using water and analyzed using ion chromatography.

The advantages of passive samplers are cost, size, and ease of deployment. They are inexpensive when compared with active systems, approximately $60 each compared to $10,000 each. This allows for the cost-effective deployment of many samplers at the same time. They are small—2 cm by 3 cm. Because of this small size, they can be easily handled and inconspicuously deployed (see Figure 3).

**Figure 3. Rain cap and PSD attached to a telephone pole support wire**

When used for ammonia sampling, the drawbacks for the Ogawa® PSD are the variability (5-30%), length of deployment time (10-14 days) and accuracy (± 30%).

### *Theory of Passive Sampling*

Passive samplers collect gas based on diffusion. Molecules are in constant motion. This movement causes an analyte to move (diffuse) from an area of higher concentration ($c_1$) to an area of lower concentration ($c_2$). The speed of diffusion is referred to as diffusivity or the diffusion coefficient. The amount diffused is referred to as the flux. Fick's first law mathematically represents this process and is represented by the following expression (Equation 1, **(Britannica, 2001)**)

$$D = -\frac{J}{(c_2 - c_1)/l}$$

**Equation 1**

D is the diffusivity (diffusion coefficient) in $cm^2/s$. $J$ is the flux measured by the amount (mass, molecules, etc) "that passes through an area of one square centimetre (sic) perpendicular to $l$ (length), per second…." (Britannica, 2001) expressed as $g/cm^2$-s. Diffusion continues until the mixture is homogenous ($c_1 = c_2$).

The flux J is equal (Equation 2) to the mass uptake Q (g), sampling time t (s) and area A ($cm^2$). Thus, Equation 1 can be rearranged to give a relationship for the mass uptake Q (Equation 3 , (Brown, Woekenberg, 1989).

$$J = \frac{Q}{At}$$

**Equation 2**

$$Q = (DA)\left(\frac{c_1 - c_2}{l}\right)t$$

**Equation 3**

In the case of passive samplers, $c_1$ is the concentration being sampled and $c_2$ is the concentration at the surface of the collection filter. The collection filter is assumed a perfect sink and should collect 100% of diffused analyte (an assumption that may not hold true as the filter reaches saturation) leaving the gas concentration ($c_2$) of analyte above the filter equal to zero, giving the equation

$$Q = \frac{DAc_1t}{l}$$

**Equation 4**

*DA/l* has the units of $\text{cm}^3/\text{s}$ and is referred to as a sampling rate (r) (Equation 5)[2]

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[2] A sampling rate refers to the movement of a volume of air per time ($\text{dcm}^3/\text{dt}$) and is used for active sampling systems. Since passive samplers do not move air, r is technically not a sampling rate, however, this term plays the same role for passive samplers as it does for active systems in computing air concentrations.

$$r = \frac{DA}{l}$$

**Equation 5**

$$c_1 = \frac{Q}{rt}$$

**Equation 6**

Substituting r into Equation 4 and rearranging yields Equation 6. Using Equation 6 and the amount of analyte collected in grams (Q) and the sampling time in seconds (t), one can calculate the concentration of target gas ($c_1$) in g/cm$^3$.

To use the above equations, the diffusion coefficient is needed. The diffusion coefficients for common analytes have been determined experimentally and can be found in papers and textbooks. Table 2 lists a few published values for ammonia.

**Table 2. Diffusion Coefficients for Ammonia**

| Diffusion Coefficient At 25 °C cm$^2$/sec | Source |
|---|---|
| 0.23 | (Shelley, 1986) |
| 0.236 | (Coulson,Richardson, 1954) |
| 0.28 | (Logan, 1999) |
| 0.249 | Average of the three given. |

Diffusion coefficients are a function of temperature and pressure. Equation 7 shows this dependency (Brown, Woekenberg, 1989).

$$D = f\left(\frac{T^{3/2}}{P}\right)$$

**Equation 7**

However, from the ideal gas law, concentration is proportional to pressure and inversely proportional to temperature (Equation 8).

$$c = \frac{n}{v} = \frac{P}{RT}$$

**Equation 8**

Inserting these relationships into Equation 4 yields Equation 9.

$$Q = f\left(\frac{P}{T}, \frac{T^{3/2}}{P}\right)$$

$$Q = f(T)^{1/2}$$

**Equation 9**

Q, is the uptake rate in mass, and "is independent of pressure but proportional to the square root of the absolute temperature. In practice, the temperature dependence of the sampling rate at ambient temperature levels (about 0.2%/°C) may be ignored."(Brown, Woekenberg, 1989) For rate calculations pertaining to the Ogawa® sampler, see the section titled Sampling Rate.

### *The Ogawa® PSD and Other Analytes*

Petros Koutrakis (1993) of the Harvard Public School of Health wrote the first published report on the use of the Ogawa® sampler. In the Harvard study, Dr. Koutrakis tested the Ogawa® sampler in a controlled laboratory chamber and outdoors using ozone. He determined that the sampling rate did not change with temperature or humidity. Wind, however, did have an affect. Wind blowing directly at one end of the PSD caused the sampling rate to increase exponentially with increasing wind velocity. Preliminary testing showed that these effects were mitigated by the use of a protective raincap.

The Ogawa® PSD was used to determine ozone concentrations in Dallas over an eight-week period (Varns et al., 2001). The samplers were mailed to homeowners who were instructed on how to deploy the samplers. This sampling was rather unique because the public was used to deploy the samplers. Each resident received a week's supply of samplers by mail. This allowed the daily sampling at 30 sites covering a 24,000-km$^2$ area. To attempt this deployment with paid personnel traveling to each site daily would have been impractical and cost prohibitive. The measurements taken with the passive samplers correlated with collocated continuous monitors (r range = 0.95-0.97). The precision was reported as 1.83 ppb $O_3$ absolute difference between duplicates without a dependence on concentration. Using a mean concentration of 30 ppb $O_3$ (an approximate mean of their reported data) yields a relative percent difference of 6%.

The Ogawa® PSD has also been used in an attempt to measure the affects of air pollution on the health of asthmatics. The PSD was used in Paris to determine asthmatics' exposure to $O_{3,}$ NO, and $NO_2$ (Liard et al., 1999). The amount of pollution an individual is exposed to can vary greatly from the nearest fixed monitoring site, which causes great difficulty in conducting epidemiological studies of healthy versus asthmatic persons. This study involved 94 adults and children who were asked to wear two samplers for 3 days at a time. Researchers concluded that the sampler did a good job at determining NO and $NO_2$ but not $O_3$. It was determined that the $O_3$ concentrations were too low to be determined using a three-day deployment.

### *Atmospheric Ammonia Concentrations*

Table 3 list ammonia concentrations found at various sites. The first four are concentrations that were determined at locations very near to known sources. The last six were determined in non-source areas and can be considered ambient. The first highlighted line is the mean value determined by the PSD sampling discussed in this thesis. The second highlighted line is the average of 4 years of data collected at a Tampa site using an ADS.

**Table 3. Atmospheric Ammonia Concentrations**

| Concentration $\mu g/m^3$ | Type | Instrument | Location | Reference |
|---|---|---|---|---|
| 50-200<br>0-24 hours | Pig Slurry/Wheat Field | FTIR | Goteborg, Sweden | (Galle et al., 2000) |
| 4-75 | Live Stock Facility | Impinger | Japan | (Kawashima, Yonemura, 2001) |
| 10-25 | Ammonia emissions areas | Continuous | Netherlands | (Buijsman et al., 1998) |
| 10. | Hog Farm | ADS | Eastern North Carolina | (McCulloch, Shendrikar, 1998) |
| 2-4 | Background | Continuous | Netherlands | (Buijsman et al., 1998) |
| 2.4 | Urban | ADS | Nara, Japan | (Matsumoto, Okita, 1998) |
| 2.0 | Tampa Deployment | PSD | Tampa, Florida | Tate |
| 1.7 | Gandy Site | ADS | Tampa, Florida | (TBADS, 2001) |
| 1.4 | Rural | Rotating Denuder | Scotland | (Burkhardt et al., 1998) |
| 0.32 | Research Triangle Park | ADS | North Carolina | (Vossler et al., 1988) |

# Chapter III Methods

## *Statistical Methods Used*

To determine hot spots, a criterion for considering a particular value as elevated above ambient level had to be established. By definition, a hot spot would be a value or values statistically above the rest of the population. The question is, “What test of statistically above the rest should be used?”

The null hypothesis used was that no hot spots exist of the selected size and shape, and the alternative hypothesis used was that one or more such hot spots exist. One method to test the null hypothesis is to compute the Z-scores for each sample. The Z-score was computed by subtracting the mean from the sample value and then dividing by the standard deviation. If the computed Z-score was larger than the critical Z-value then we reject the null hypothesis. Two problems exist with this approach. One is that it assumes the distribution is Gaussian. The distribution of ammonia concentrations may not have been symmetric. The other concern is that a few high values can result in a positively skewed mean and a large standard deviation. This would result in smaller Z-scores and lead to the possibility of missing elevated values. Another approach for determining elevated values is to look at the higher values as outliers. There seems to be much debate and disagreement about determining outliers.

Two common approaches are the Grubbs test and the box plot. The Grubbs test was computed exactly as the above Z-score was calculated; however, the critical values are different. Special tables have been created especially for determining outliers. The Grubbs test was computed and if an outlier existed, it was discarded and the test was run again. This method was iterated until no outliers were found (Handbook, 2001). This method also assumes a Gaussian distribution. This test has an advantage over using calculated Z-scores because as outliers are removed their values no longer distort the mean and standard deviation thus allowing additional outliers to be determined.

The box plot can be used to determine outliers (Pagano, Gauvreau, 2000). The box plot is simply a graphical representation showing the spread of the data and is based on percentile. Any value higher than the 90th percentile is considered an outlier. This method has the advantage that it makes no assumptions based on the shape of the distribution.

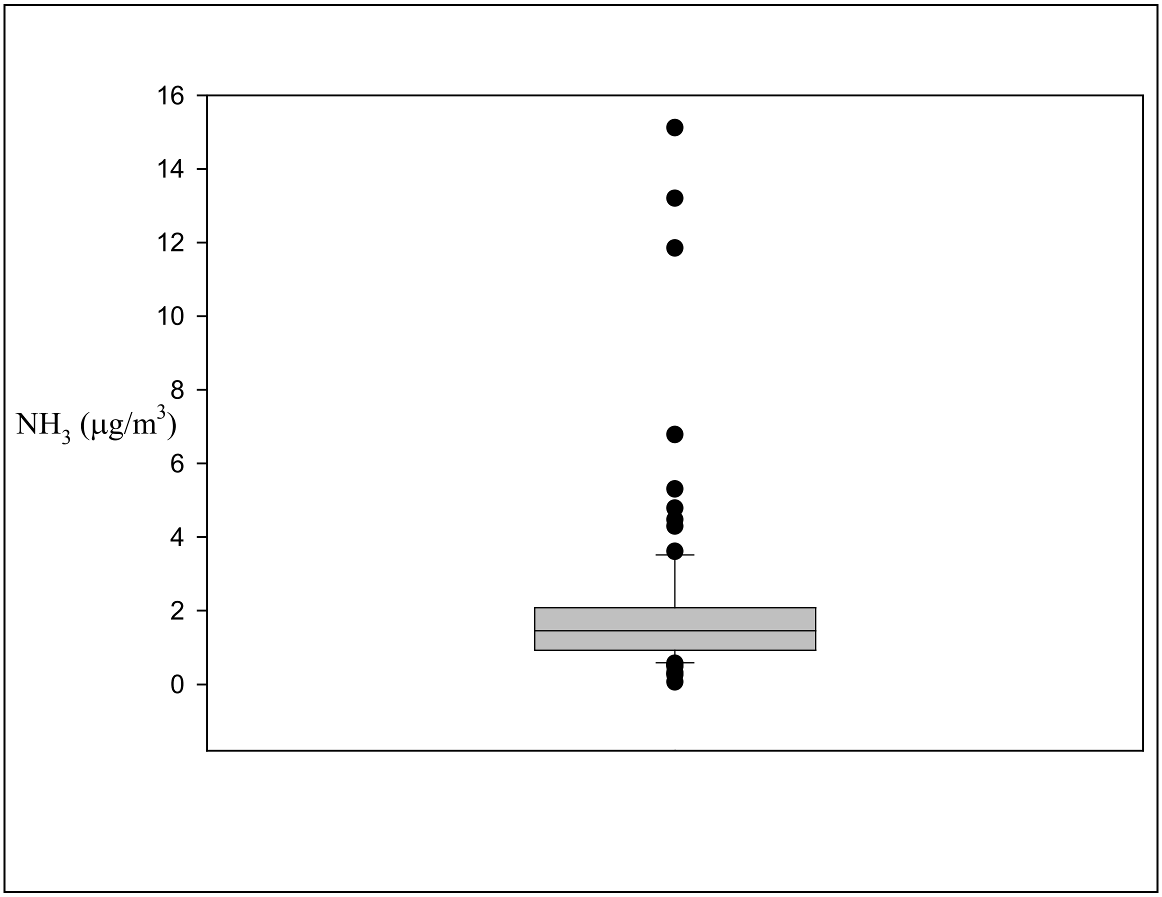


**Figure 4. Box Plot of Tampa Data**

Figure 4 shows a box plot of the Tampa data. The gray box represents the range between the 25th and 75th percentile. The short bars (whiskers) above and below this box represent the 90th and 10th percentile respectively. This graph shows that all values above 3.4 µg/$m^3$ are considered "outliers" or far enough from the rest of the data to be considered different.

All three methods were used to test the null hypothesis and the results are tabulated in Appendix IV—Tables of Data. Each method demonstrated that the null hypothesis should be rejected and the alternative hypothesis should be accepted—that hot spots do exist in the sampled area. The only differences between the three methods are the number of points that are considered elevated.

For all experiments concerning accuracy or precision, outliers were determined using the Grubbs test at 95% confidence level. All statistics reported were with outliers removed unless otherwise noted.

### *Gridding*

Gridding of the data was done using Surfer®(2000) software program. The Surfer® contour maps were made using kriging to interpolate ammonia concentrations between sample locations.

All gridding techniques available in Surfer® were used and compared. Many methods attempted had drawbacks. For instance, inverse distance to a power displayed contour bulls-eyes around each data point and interpolated higher values between points of almost equal value. Using the nearest neighbor method assumes the concentration does not change until midway between points, thus, it draws "boxes" of one concentration around each point, in effect not interpolating at all. Kriging was selected because it best represented the data. Kriging interpolates smoother transitions between points of differing concentrations and as used is an exact interpolator. Many interpolators plot values at sampled locations that differ from the known sampled values. An exact interpolator plots the actual value at each sampled location.

### *PSD Description*

The Ogawa® Passive Sampler is a small polymer device with a cylindrical shape. It is 3 cm in length and 2 cm in diameter (Figure 5). It holds two collection filters, one on each side. The collection filters are held between two stainless steel screens. The screens and filters are held in place with an endcap. The caps have 25 holes to allow ammonia to diffuse through to the filters (Figure 5). The PSD is placed in a plastic holder that is then placed in a rain shelter (Figure 6). The rain shelters are standard 4” PVC pipe endcaps.

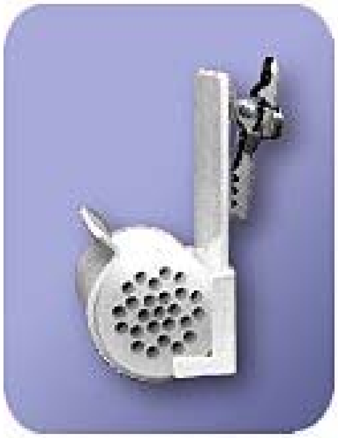
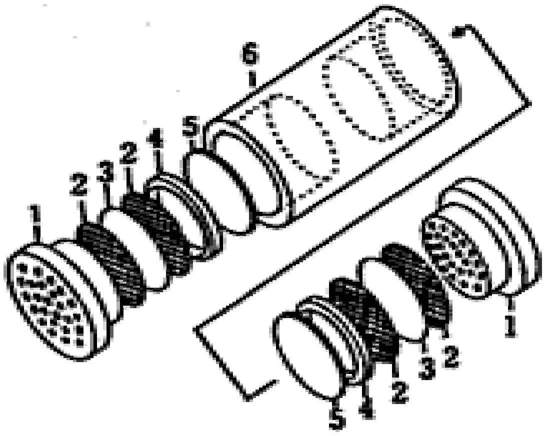


**Figure 5. PSD and Clip**(Ogawa, 1999)

**Figure 6. PSD and Rain Cap**(Ogawa, 1999)



1. End Cap
2. Stainless Steel Screen
3. Pre-Coated Collection Filter
4. Retainer Ring
5. Inner Base Pad
6. Sampler Body

**Figure 7. PSD Schematic**(Ogawa, 1999)

### *Sampling Rate*

The sampling rate was calculated from the diffusivity of ammonia and the diffusion area and length. Table 4 lists the diffusion coefficient of ammonia, and the area and length of the endcaps and the screens.

**Table 4. Sampling Rate Parameters**

| | | |
|---|---|---|
| D | Diffusion coefficient of ammonia | 0.249 $cm^2/s$ |
| A | Cross sectional area of diffusion channel openings | 0.785 $cm^2$ endcap ($A_1$)<br>0.152 $cm^2$ screen ($A_2$)[3] |
| L | Length of diffusion channel | 0.6 cm endcap ($l_1$)<br>0.02 cm screen ($l_2$) |

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[3] The area used in these calculations is different than the area later provided by Ogawa® of 0.371 $cm^2$, see appendix IV.

Equation 10 and Equation 11 below show the calculations for the sampling rate of the endcap ($r_1$) and the sampling rate for the screen ($r_2$). Equation 12 and Equation 13 show the combining of the two sampling rates ($r_1$, $r_2$) into one sampling rate $r_s$.

$$r_1 = \frac{DA_1}{l_1} = \frac{0.249cm^2}{s}\frac{0.785cm^2}{0.6cm}\frac{60s}{\min} = \frac{19.55cm^3}{\min}$$

**Equation 10**

$$r_2 = \frac{DA_2}{l_2}\frac{0.249cm^2}{s}\frac{0.152cm^2}{0.02cm}\frac{60s}{\min} = \frac{113.5cm^3}{\min}$$

**Equation 11**

$$\frac{1}{r_s} = \frac{1}{r_1} + \frac{1}{r_2} = \frac{\min}{19.55cm^3} + \frac{\min}{113.5cm^3} = \frac{0.05999\min}{cm^3}$$

**Equation 12**

$$r_s = \frac{16.67cm^3}{\min \cdot filter}$$

**Equation 13**

Sampling rate $r_s$ is for one side of the sampler. Each sampler has two sides each with a filter. Since the filters for each side are extracted and analyzed together, this rate must be multiplied by 2 to give $r_t$ of 33.28 $cm^3$/min

Equation 14 shows a sample calculation using 2 μg of ammonia collected for a two-week deployment (336 hr.) using the above-calculated sampling rate (after converting the rate to $m^3$/hr).

$$c = \frac{Q}{rT} = \frac{2\mu g \cdot hr}{0.001997m^3 \cdot 336hr} = \frac{2.99\mu g}{m^3}$$

**Equation 14**

Ogawa® recently provided a sampling rate for ammonia of 38.8 $cm^3$/min. Equation 15 shows a sample calculation using 2 μg of ammonia collected for a two-week deployment (336 hr) using the Ogawa® sampling rate (after converting the sampling rate to $m^3$/hr).

$$c = \frac{Q}{rT} = \frac{2\mu g \cdot hr}{0.002328m^3 \cdot 336hr} = \frac{2.56\mu g}{m^3}$$

**Equation 15**

### *Blanks*

Mean blank values were subtracted from exposed PSD values, and the standard deviation of the blanks was used to determine the Sampling Detection Limit (SDL). From earlier experiments, it was clear that the blank values had a high degree of variability and values close to the values of exposed PSDs (at ambient levels). Because the blank values did vary, one concern was that a small set of blank values for any one experiment would be abnormally high or low. To avoid this, blanks were tracked over many experiments.

In "Principles of Environment Sampling," Keith describes a formula for developing a control chart. A control chart allows assessment of blanks over time instead of using the values for each sampling event as an independent set (Keith, 1996). Keith recommends the use of the control charts to help determine if values begin to show variation outside the average thereby showing a problem. However, this method can be applied to determine an accurate mean and standard deviation. The mean value subtracted from exposed samplers was calculated using blank values acquired over many experiments.

Because the blanks were high and variable, a new cleaning procedure was utilized for the Tampa sampling event. Blank values and variability were lowered significantly. A paired *t*-test showed that the mean of the blanks prior to the Tampa experiment was different from the mean for that experiment. Because the values were different, the blank values subtracted from exposed samplers was one value for the Tampa and Gandy deployments and a different (higher) value for all other deployments.

The new cleaning procedures did lower the blank values for the Tampa sampling; however, after the Tampa sampling event, a set of seven blanks were analyzed independently of any sampling event using the new cleaning and coating procedures. Those seven were not lower than the earlier values, and shows that the blank “problem” was not fully resolved.

### *Detection Levels*

For this research, two detection levels (DL) were needed. First, a detection level for the analytical equipment and second a detection level for the entire sampling method.

The analytical instrument used was a Dionex® ion chromatograph (IC). IUPAC defines minimum detectability for chromatography as: “The concentration or mass flow of a sample component in the mobile phase that gives a detector signal equal to twice the noise level”(IUPAC, 1993). Using this method yielded a detection limit of 0.06 ppb for $NH_4$. Another approach used was to inject a low-level standard seven times and multiply the standard deviation of the seven replicates by a t-value of 3.14 (6 degrees of freedom at 99% confidence level)[4](Clesceri et al., 1998). The detection level using this method was 5 ppb. This latter approach utilizes the variability of an instrument’s response and ensures that the detection limit is set at a reproducible value. However, the detection level of the instrument is not what determined the overall sampling method detection limit (SDL) for this research.

Both of the above instrument detection limits were well below the concentrations of the PSD blanks. The PSD blanks (Tampa experiment) had a mean of 0.12 ppm (aqueous extract concentration of $NH_4$). The value of 0.12 ppm is 2000 times higher than 0.06 ppb

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[4] For this to be valid, “The replicate measurements should be in the range of one to five times the calculated MDL” Clesceri, L. S., Greenberg, A. E. and Eaton, A. D. "Standard Methods for the Examination of Water and Wastewater", 20th ed. American Public Health Association, DC (1998)..

and 24 times higher than 5 ppb. Because of this, the detection limit of the instrument was not the determining factor in defining an SDL.

To determine an SDL IUPAC was again consulted:

> *Detection limit, lower*: The minimum concentration of a compound in an air sample that can be determined by an analytical method with a given statistical probability. Usually the lower detection limit is defined as three-times the standard deviation of the noise of an analytical method under the assumption that its distribution is Gaussian. In this case a concentration can be detected with a probability of 99.7%. This is sometimes referred to as the absolute detection limit (IUPAC, 2000).

The noise for the sampling method was the variability of the blanks. Two different SDLs were computed. One using the standard deviation of the blanks prior to new cleaning procedures and one after the new procedures were implemented.

The two graphs below represent the time of deployment versus the SDL. The longer a sampler is deployed the lower the detection limit. Figure 8 represents the SDL before the new cleaning procedures and Figure 9 represents the SDL afterwards.

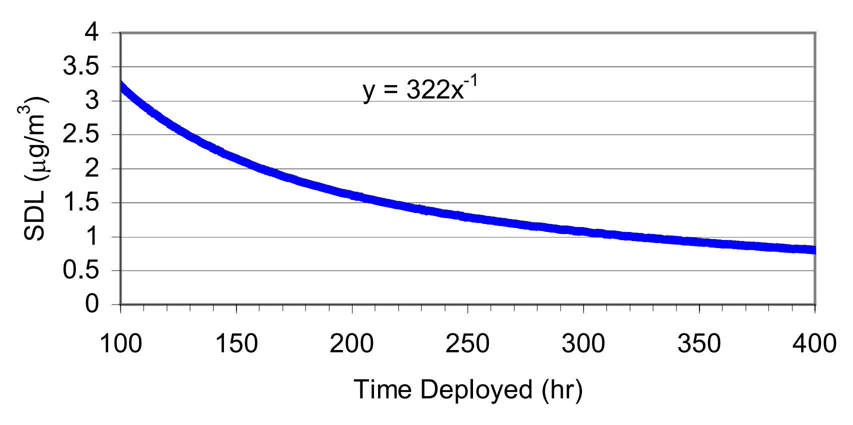

**Figure 8. Sampling Detection Level**

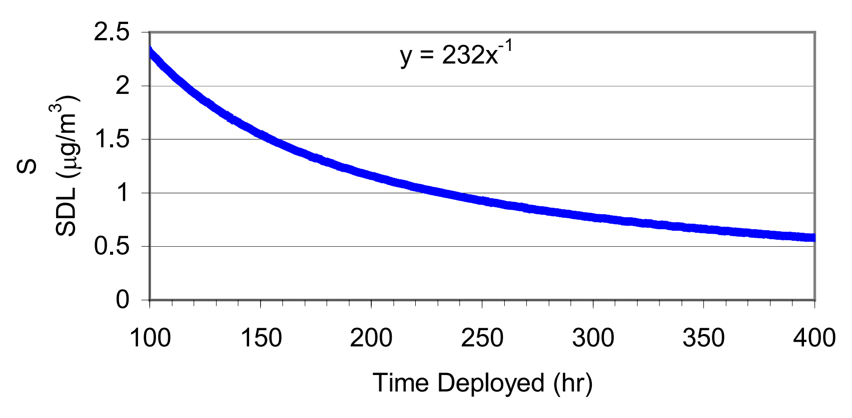

**Figure 9. Sampling Detection Level**

For the Oldsmar 1, 2 and the Tampa deployment the SDLs were 2.0, 1.3 and 0.7 $\mu g/m^3$ respectively. For Oldsmar 1, only one value was above the SDL. For Oldsmar 2 all readings were above the SDL. For the Tampa deployment, 11 values fell below the SDL. All values, whether above or below the SDL, are reported in Appendix IV—Tables of

Data. For computing the means, standard deviations, and determining elevated values, all non-outlier values were used.

### *Deployment Strategy*

The deployment strategy included determination of placement of samplers to determine "hot spots" of ammonia, sufficient deployment time, proper height above the ground, placement to avoid being tampered with, and ease of locating raincaps.

### *Placement in a Grid Pattern*

To determine hot spots of a particular size the samplers were placed in a grid pattern. To determine the type and size of the grid pattern, the program HotSpot-Calc®(Keith et al.) was used. HotSpot-Calc®[5] is a program designed to help with determining the number of samplers and the required grid spacing needed to determine a hot spot. Table 5 shows the input and output values used in HotSpot-Calc®. The equations HotSpot-Calc® uses are discussed in Appendix I – Specifics on HotSpot-Calc®.

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[5] HotSpot-Calc is a subprogram within DqoPro and is available from an American Chemical Society affiliated website at: http://www.acs-envchem.duq.edu/dqopro.htm

**Table 5. Inputs and Outputs of HotSpot-Calc®**

| **Input description** | **Input Value** |
|---|---|
| Type of grid | Triangular |
| Size of hot spot (radius) | 0.75 km |
| Shape of hot spot | Circular |
| Size of area to be sampled | 180 $km^2$ |
| Chance of missing hot spot | 5% |
| | |
| **Output description** | **Output Value** |
| Required grid spacing | 1.5 km |
| Number of samplers needed | 91 |

The first HotSpot-Calc® parameter entered was the shape of the hot spot. Because the deployment period would be for at least 10 days, it was decided that the winds would vary enough over the 10-day period to make any hot spot circular. Next, 5% was selected as the chance of missing a hot spot. Three grid patterns are listed in the program, triangular, square, and rectangular. A triangular pattern was used because it required fewer samplers than a square or rectangular pattern. The area under consideration for sampling was measured and determined to be approximately 180 $km^2$. With these parameters set, an iterative process helped decide the grid spacing. Knowing that 91 samplers were available for deployment, a grid spacing that would utilize only 91 locations was established. A value of 0.25 km was entered for the hot spot radius. The output for this size hot spot was 1021 sample locations at 0.42 km spacing. This was clearly well above the 91 samplers available, so a hot spot size of 0.5 km was used. This process was repeated until the hot spots size of 0.75 km yielded a result of 91 sample locations with 1.5 km spacing.

The theoretical number of samples needed was 91. The number actually used was 94. The extra three were needed because the samplers could not always be placed on the nodes of the grid pattern. When the node could not be sampled, the nearest available spot was used. Once the 91 points were plotted, 3 additional samplers were added to fill in "holes" in the grid pattern. Using a map to calculate the sampled area yields an area of 187 $km^2$. This value is very close to the one used in HotSpot-Calc® of 180 $km^2$. The plotted sampling area is slightly smaller—153 $km^2$. The plotted sampling area does not take into account the area circumventing the sampled area. The samplers located on the edge of a sampled area are theoretically sampling a 0.75 km band outside the grid pattern; however, in practice this extra band is not plotted.

In addition to the 94 samplers, 14 duplicates and 9 trip blanks were used. Those equaled approximately 15% and 10% of the total 94, respectively. Choosing a higher percentage for duplicates and blanks than the more traditional 10% and 5% respectively was based on the high variability and high blank values of previous sampling experiments[6].

### *Length of Deployment*

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[6] The above values refer to the Tampa Deployment a similar process was used for the Oldsmar studies.

Deployment length was determined based on the method detection limit. A 10-day deployment had a detection limit of 1.3 μg/m$^3$. During the Oldsmar sampling periods, both 7- and 10-day deployments were used because a detection limit had not yet been established. The Tampa deployment was for two weeks. A 14-day deployment ensured a sampling detection limit (0.95 μg/m$^3$)[7] lower than typical ambient levels (1-4 μg/m$^3$) and better fit into the schedule of many of the people helping with the deployment.

### *Deployment Height*

The samplers were deployed between 1.5 and 2.0 meters above the ground. This height was selected for two reasons: one, the raincap had to be within reach of those deploying; and two, the caps needed to be above $z_o$. The term $z_0$ refers to the height above the ground where the wind velocity reaches zero. $Z_o$ is affected by surface roughness, the rougher the terrain the higher the value of $z_0$ (Arya, 2001). Figure 10 shows $z_0$ values for various types of terrain. To determine the minimum height, the category titled "Centers of large towns, cities" on Figure 10 was used. The $z_o$ value for this category is 0.6-1 m. All terrain types for the Tampa sampling area would yield a lower value, hence 1.5 meters was a sufficient height to consistently be above $z_o$.

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[7] This sampling detection limit SDL is different than the one later reported because it was based on the blank values obtained prior to the Tampa sampling.

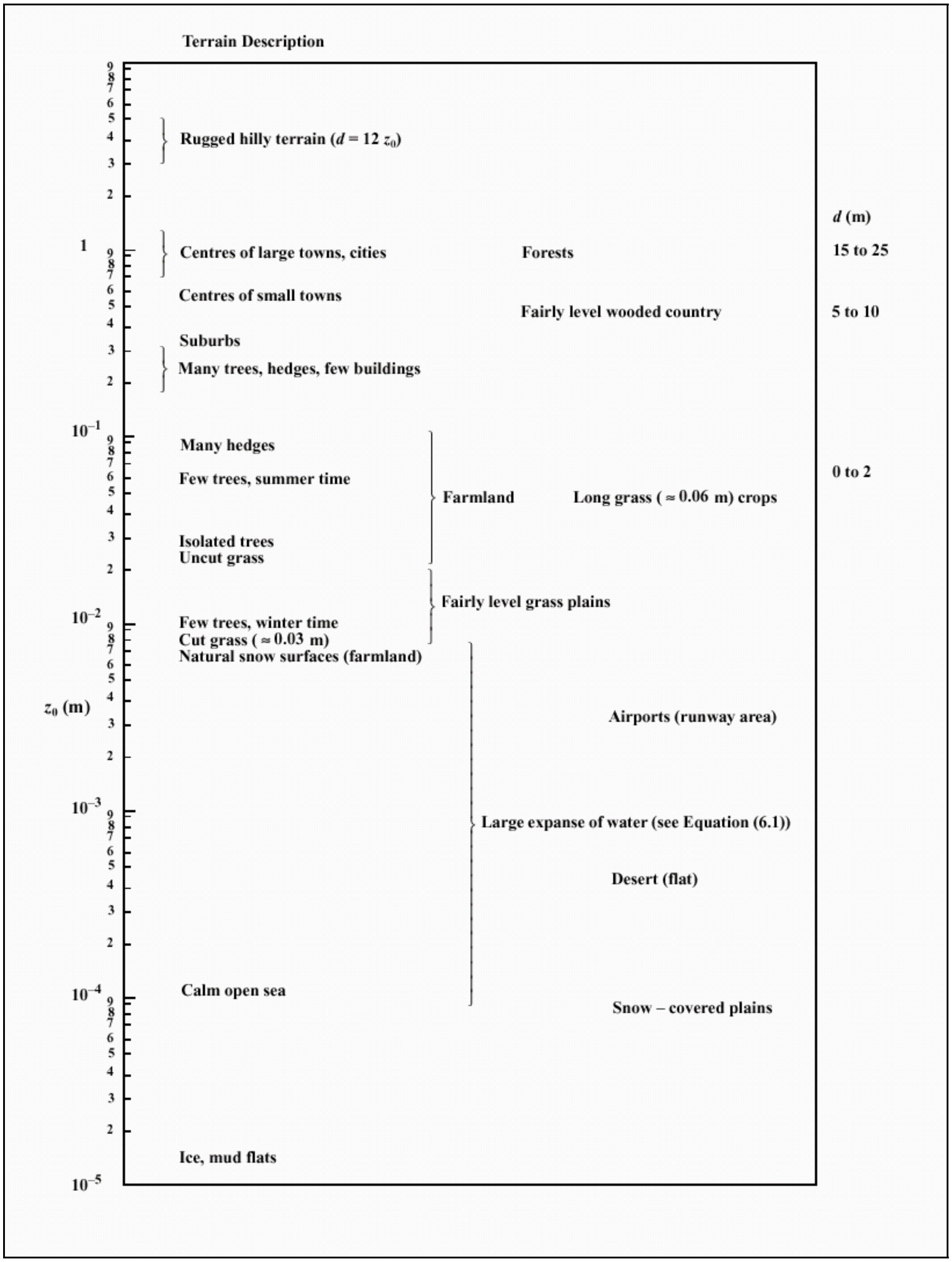

**Figure 10. Values for $z_o$ (Reprinted with permission from ESDU: Strong Winds in the Atmospheric Boundary Layer. Part I: mean-hourly wind speeds ESDU Data Item No. 82026, Issued September 1982, (With Amendments A to D, April 1993).**

### *Tampering*

During the Oldsmar study, three (15% of the total) of the post, raincaps and PSDs were completely removed. A resident living near one of the missing posts said young teenagers "roam" the neighborhood vandalizing property. With this in mind, the raincaps for the Tampa deployment were placed in inconspicuous locations. Instead of placing the raincaps on freestanding posts, it was decided to place the raincaps on existing objects, such as fences, signs, and telephone poles. In addition, to cut down on tampering, the following note was written on the caps or on labels placed on the caps: "Student Research. For Information Please Contact Paul Tate at 813-974-8226," Both the written messages and the labels faded or were washed off, leaving many raincaps unmarked. This may have led to three missing samplers (3% of the total). Future deployment will need a better method for labeling the raincaps. In addition, fliers should be made and handed to the residents living near raincap locations.

### *Ease of Locating Each Deployment Site*

Deployment consisted of 10 people helping to deploy and retrieve the samplers. During the initial deployment, only one person knew where all the raincaps were located. The rest had to follow directions. Because of this, the raincaps were attached to easy to locate objects, such as street signs. There was a necessary trade off between competing factors:

proximity to the desired location, how easily it could be found and accessed, and whether it would be vandalized. In addition, a concern was placing a sampler too close to a very busy intersection. Cars emit small amounts of ammonia and a sampler too close to a heavily traveled intersection could have an elevated ammonia level that is not indicative of the surrounding area. A previous sampling event next to a busy street showed that idling cars at a busy intersection caused elevated ammonia concentrations that drop off dramatically within 20 meters. A similar study showed the values are not as elevated next to a busy road when monitored well away from an intersection[8]. Because of this, when a sampler needed to go near a busy intersection there was an attempt to locate that sampler more than 20 meters away from the intersection. This was not a concern if the sampler was on a busy road but not near an intersection. One sampler that was located only 10 meters away from a busy intersection showed a slightly elevated value of 3.6 $\mu g/m^3$ compared to a an overall mean of 2.0 $\mu g/m^3$.

### *Deployment Method*

The goal was to deploy all the samplers in the 180-$km^2$ Tampa area within two hours. From the Oldsmar deployment, it was estimated that one person could deploy one sampler every 10 minutes. Assigning a maximum of ten samplers per person ensured that all samplers would be deployed in less than two hours. For the Tampa deployment, the

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[8] Sampling performed prior to the Port of Tampa deployment but not discussed in this thesis.

time was only 5 minutes per sampler. The difference in deployment times between the Oldsmar and Tampa deployments can be attributed to the well written directions. Each person was given a packet that contained one sheet per raincap location. Each sheet included at least one picture of the raincap and written directions. The directions were checked prior to deployment by having someone else (other than the person who wrote the directions) drive to each spot using only the directions and pictures. This person then gave suggestions on how the directions could be improved. This approach improved the directions significantly and led to the shorter deployment times.

### *PSD Cleaning*

The washing procedure evolved from earlier experiments. The original cleaning procedure was simply to rinse the PSDs with copious amounts of DI water. High blank values were problematic and other cleaning methods were tried. The method adopted for the Tampa sampling included removing the inner retaining ring and the inner base pad then soaking all components in a 0.1% w/w potassium hydroxide solution for 24 hours.

It was realized that the coating solution from previous deployments could be trapped beneath the inner base pad. This trapped acid could not be easily removed with rinsing only. Not only could the trapped acid contain ammonium from previous experiments, but it could also continue to collect ammonia while sitting in the lab between deployments.

This contamination probably led to ammonia carryover from previous experiments causing high blank values, variability, and poor accuracy.

In addition to the removal of the inner pad, all components were soaked for 24 hours in 0.1% KOH (w/v) (.026M). The pH of the solution was >12. The $pK_a$ of ammonium is 9.25. With the pH well above the $pK_a$ the ammonium should be converted to ammonia and driven off or rinsed away.

### *PSD Coating Procedure*

The PSDs were coated in a glove box. The glove box was filled with bench top air that was bubbled through two flasks in series. Each flask contained 800 ml of 6% v/v sulfuric acid solution and 1 ml of 1% (w/v) phenolphthalein in deionized water. The acid removed the ammonia and the phenolphthalein was added to indicate if all of the acid was neutralized. The air was then filtered through Drierite®. The Drierite® removed moisture from the air but more importantly, it removed any volatilized sulfuric acid. All PSDs and necessary equipment were loaded into the glove box, and the glove box was sealed.

The PSD inner pad, retaining ring, one screen, and a filter were inserted into the one end of the PSD. Coating solution (100 μl) was pipetted directly onto the filter. The coating solution was 1% (w/w) phosphoric acid in deionized water. The PSD endcap was then snapped into place and the process was repeated on the other side. The assembled PSD was then put into a holder. After that, the entire assembly was placed in a small resealable plastic bag and then enclosed in a plastic vial. The samplers were stored at room temperature until deployment.

### *PSD Extraction*

After retrieval, the PSD vials and all necessary equipment were placed in a glove bag filled with ammonia-free air. The PSDs were disassembled and the filters and screens from each PSD were place in a 50-ml centrifuge tube. Three milliliters of deionized water were added and the tube closed. The tubes were placed in a sonication bath and sonicated for 30 minutes. After sonication, the tubes were placed back in the glove box and the extract was transferred to a 10-ml syringe and filtered through a 0.45-µm syringe-tip filter directly into an IC autosampler vial.

### *Denuder Coating and Extraction*

Denuders[9] were coated with a solution of either 1% w/v phosphoric acid or citric acid, 80% v/v methanol and 20% v/v water (phosphoric acid was used in all experiments except the Gandy comparison).

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[9] Denuders are URG brand, part number URG-2000-30X242-3CSS

The denuders were rinsed with a steady stream of deionized water for one minute each. Then approximately 5 ml of coating solution was added and the denuder was shaken for 10 seconds. The 5 ml was drained and the denuder was filled with coating solution so that the glass on the flow-straightening end was covered. The denuder was shaken, drained, and then dried using filtered air. Bench top air was filtered through silica gel, activated charcoal and then glass beads. The glass beads had been washed using the same coating solution and then dried, leaving an acid coating. The acid coating on the glass beads should have captured any ammonia in the bench top air prior to it entering the denuders.

The analytes were removed by adding 10 ml of deionized water and shaking the denuder for 1 minute, then decanting the extract into an autosampler vial. The extract was then analyzed using ion chromatography.

### *Analysis*

Analysis of the extract was done using a Dionex 600 Ion Chromatograph. The columns used were the Dionex CG12A 4-mm x 50-mm guard column and the CS12A 4-mm x 250-mm analytical column. The suppressor was the Dionex CSRS (cation self-regenerating suppressor) set at 50 mV. The detector was a Dionex CD25A conductivity detector. The eluent was methanesulfonic acid (MSA). The gradient step elution used was as follows:

**Table 6. Gradient Elution Parameters**

| Time | MSA concentration mN | Flow ml/min |
|---|---|---|
| 0-10 | 4 | 1 |
| 10-15 | 4-6 (linear ramp) | 1 |
| 15-20 | 6-30 (linear ramp) | 1 |
| 20-25 | 30 | 1.5 |
| 25-26 | 4 | 1 |

The sample extracts contained large amounts of sodium. Using an isocratic separation the sodium overwhelmed the ammonium (Figure 11). The gradient elution listed in Figure 12 was developed to separate small amounts of ammonium from large amounts of sodium. As can be seen in Figure 12 baseline separation was achieved. However, the overall analysis time was increased. The isocratic separation took 15 minutes and the gradient 26.

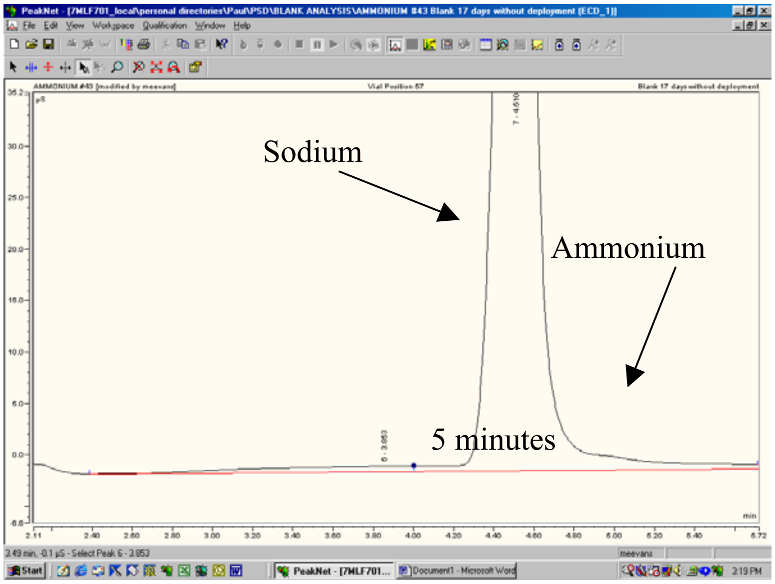


**Figure 11. Traditional Isocratic Separation of Sodium and Ammonium by IC**

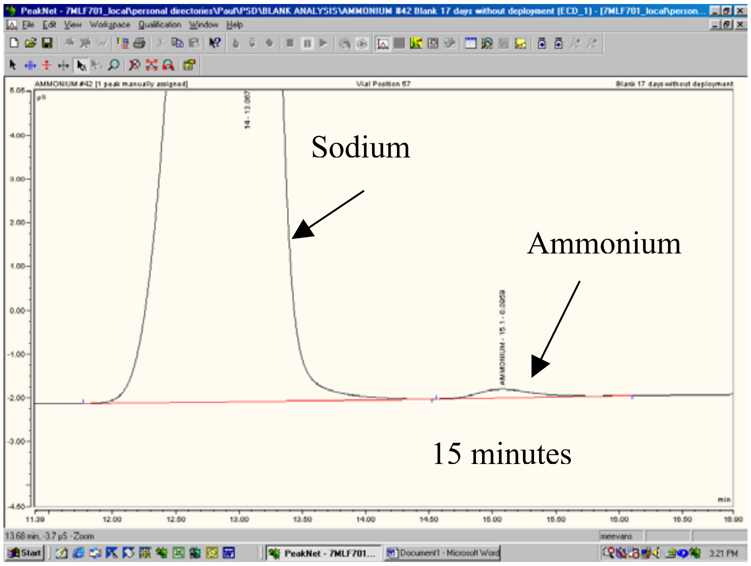


**Figure 12. Gradient Elution of Cations by IC**

# Chapter IV Results And Discussions

## *Port of Tampa Deployment*

One of the preliminary deployments for this research was at the Port of Tampa (Figure 13). Four locations were picked. Two locations were approximately 50 and 75 meters from an ammonia unloading dock; they are referred to as Dock and Fence, respectively. A third location called Railroad was approximately 50 meters south of a facility where railroad cars are loaded with ammonia. The fourth location called Sludge was located 20 meters east of sludge drying beds located at the Tampa wastewater treatment plant. Each location had four PSDs. Two of the four PSDs were left in place for the entire month. The other two were changed weekly.

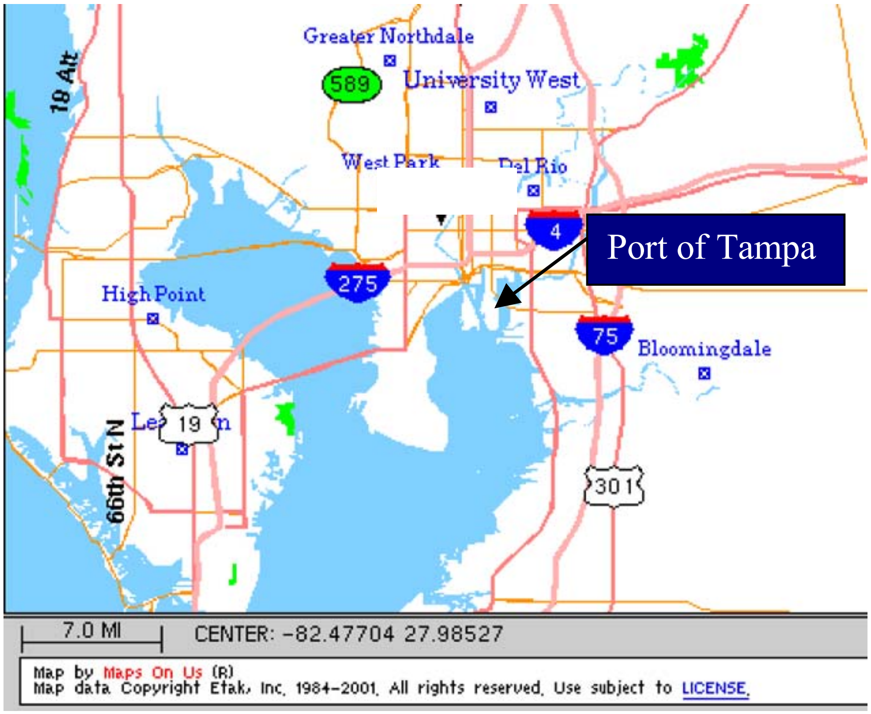
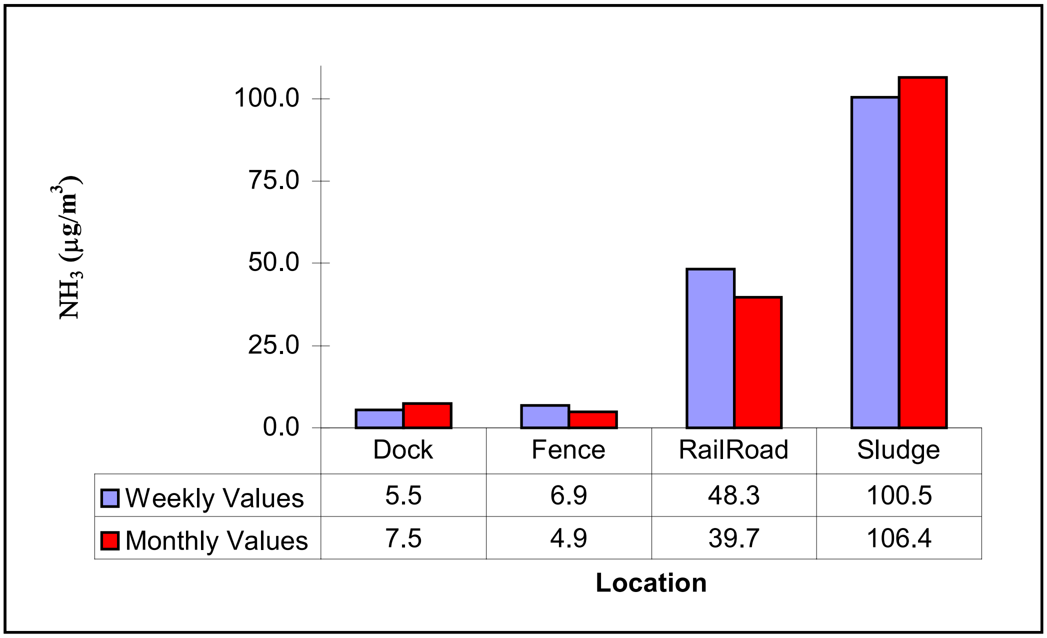


**Figure 13. Deployment Sites at the Port of Tampa**

The weekly ammonia concentrations obtained were averaged together and compared to the monthly value (Figure 13). The weekly values and the monthly values had a strong correlation (Figure 14). When forced through zero, the equation for the regression line was $y = 0.98x$ with an $R^2$ value of .98 (Figure 15). These were very encouraging results. They demonstrated that results from shorter weekly deployments correlate well with the results from the longer deployments.



| | Dock | Fence | RailRoad | Sludge |
|---|---|---|---|---|
| 🟦 Weekly Values | 5.5 | 6.9 | 48.3 | 100.5 |
| 🟥 Monthly Values | 7.5 | 4.9 | 39.7 | 106.4 |

Figure 14. Port of Tampa Monthly Readings and Averaged Weekly

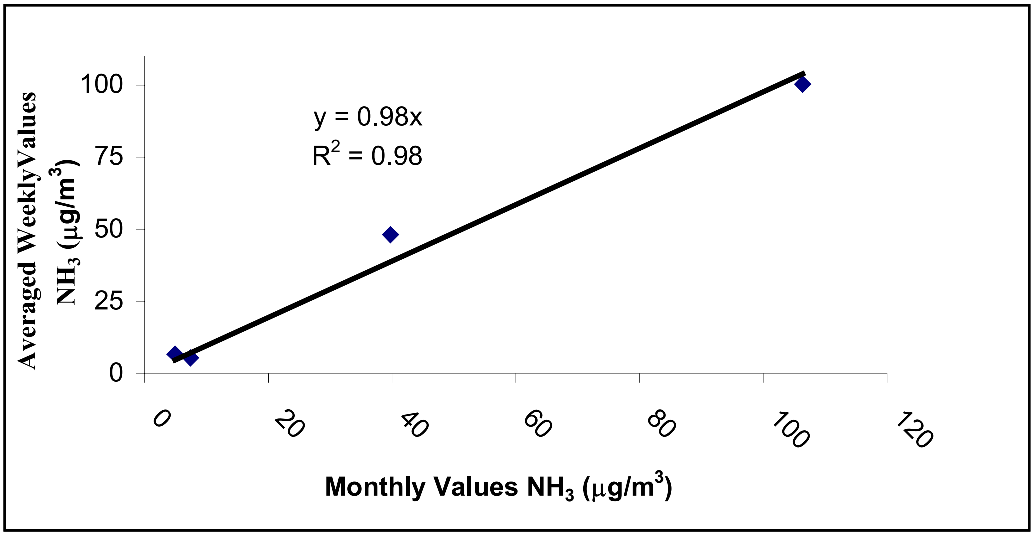


Figure 15. Monthly vs. Weekly PSD Deployments at the Port of Tampa

On Figure 16, the y-axis contains the relative percent difference between the monthly and weekly values. The x-axis contains the monthly ammonia concentrations at each location. This chart demonstrates that the precision increases with increasing concentrations.

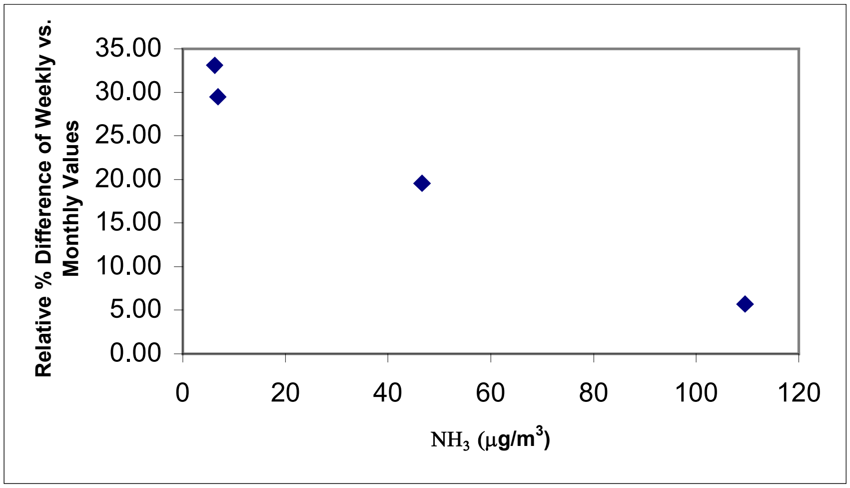


**Figure 16. Ammonia Concentrations at the Port of Tampa vs. the RPD of Weekly vs. Monthly Values**

### *Oldsmar Trial 1 and 2 Results*

Before the larger area around Tampa was sampled, a smaller area (Figure 17) in Oldsmar was sampled to "practice" the process. The sampling area contained residential areas, a protected wetland and a small wastewater (1.6 million gallons per day) treatment plant. It was hoped that the data analysis would show the plant as a hot spot without having a sampler directly next to the source.

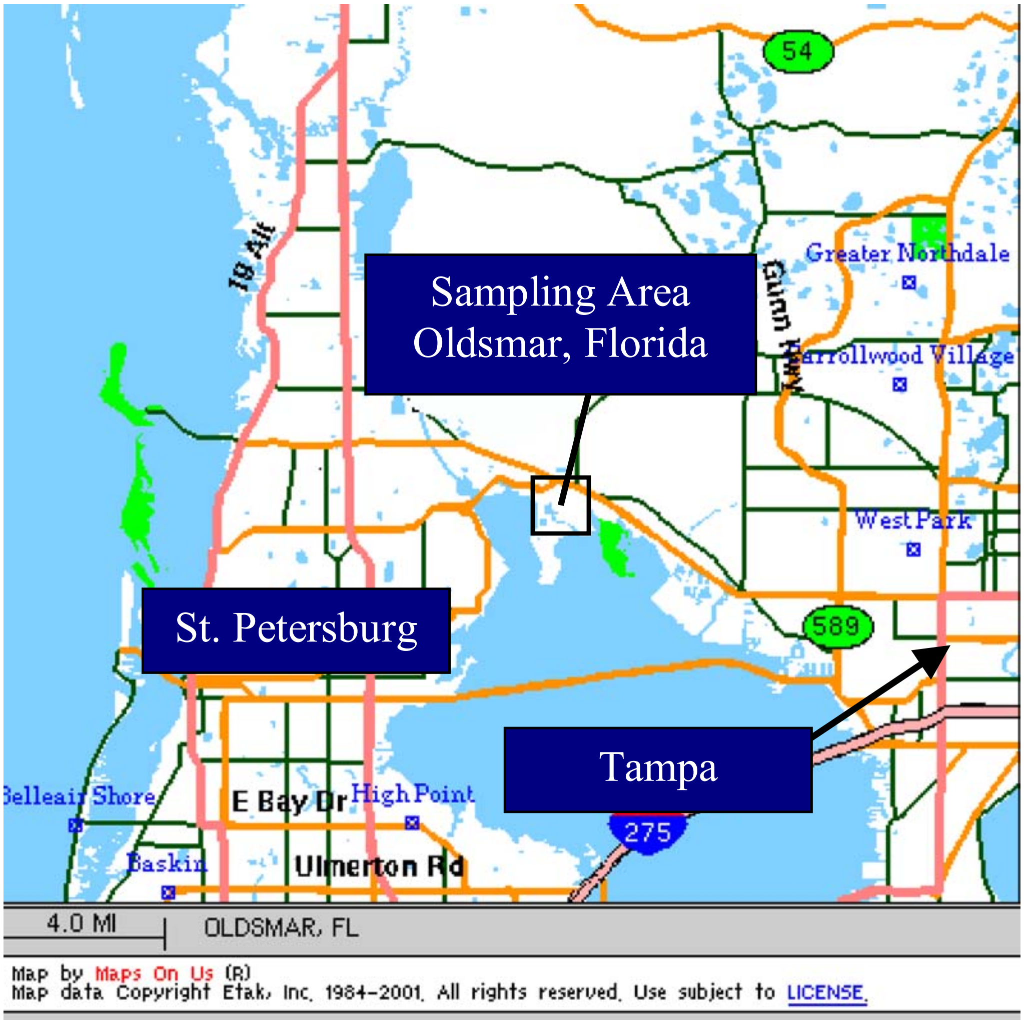


**Figure 17. Oldsmar Sampling Area**

A 2 km by 2 km area was picked with the wastewater plant located near the middle. The 4-km$^2$ area was sampled using a triangular grid pattern and a spacing of 0.5 km. Hot spot-Calc® was used to determine grid spacing and the number of sample locations needed

(Table 7)[10]. HotSpot-Calc® calculated the need for 19 samplers. To make the sampling area symmetric, however, 20 sample locations (5 rows of 4 samplers) were planned. Sampling was performed with one less location than planned because point 19 (Figure 18) was located in a swampy area that and was unreachable.

**Table 7. HotSpot-Calc Parameters for Oldsmar Sampling**

| **Input description** | **Input Value** |
|---|---|
| Type of grid | Triangular |
| Size of hot spot (radius) | 0.25 km |
| Shape of hot spot | Circular |
| Size of area to be sampled | 4 $km^2$ |
| Chance of missing hot spot | 5% |
| | |
| **Output description** | **Output** |
| Required grid spacing | 0.5 km |
| Number of samplers needed | 19 |

The area was sampled twice. The first sampling period was for seven days between May 21, 2001, and May 28, 2001. The second deployment was for 10 days between May 28, 2001, and June 7, 2001. The second deployment used 20 locations because one location was added. The added location (point 21) was on the property of the wastewater treatment plant directly outside the sludge processing building. This is the strongest source for ammonia in the entire plant and it was hoped that the closely-placed sampler would pick up

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[10] See sections titled Deployment Strategy and Appendix I – Specifics on HotSpot-Calc® for more information about using Hotspot-Calc®

the higher concentration. For the first deployment, the post, raincap, and two collocated samples were stolen from location 12. The second sampling period was increased to ten days to determine if the additional mass collected would lower the variability of the duplicates and ensure a sampling detection below measured values.

The graphical results for the first sampling period are shown in Figure 18. The mean and mode were 1.2 $\mu g/m^3$ and 1.2 $\mu g/m^3$. The highest and lowest readings were 2.2 and 0.4 $\mu g/m^3$. The sampling detection limit was 1.9 $\mu g/m^3$.

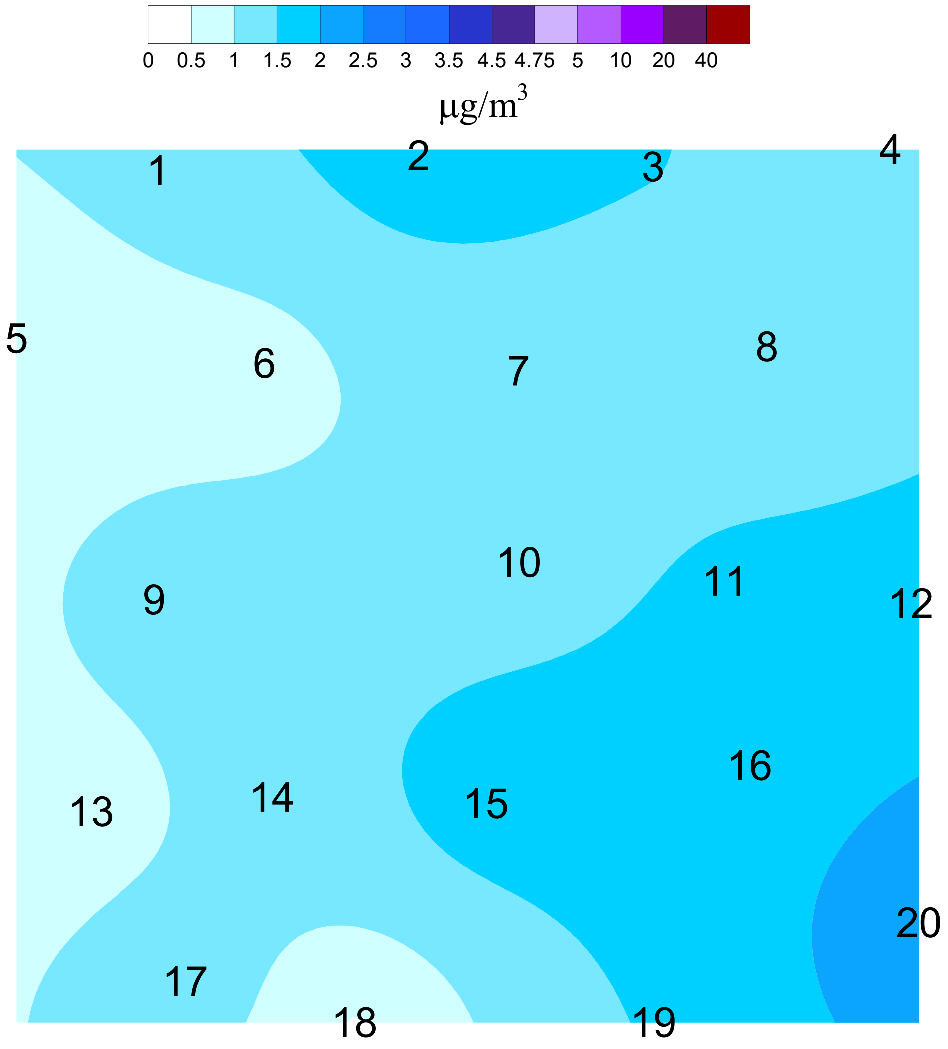

**Figure 18. Oldsmar Sampling—Week One**

The second deployment was analyzed in two ways, one including (Figure 19) and one excluding point 21 (Figure 20), which was located within 10 meters of the sludge-processing building of the wastewater treatment plant. The sludge goes through a process called lime stabilization. Calcium oxide is added to the sludge to raise the pH and kill any pathogens. The rise in pH causes ammonium in the sludge to be released as ammonia.

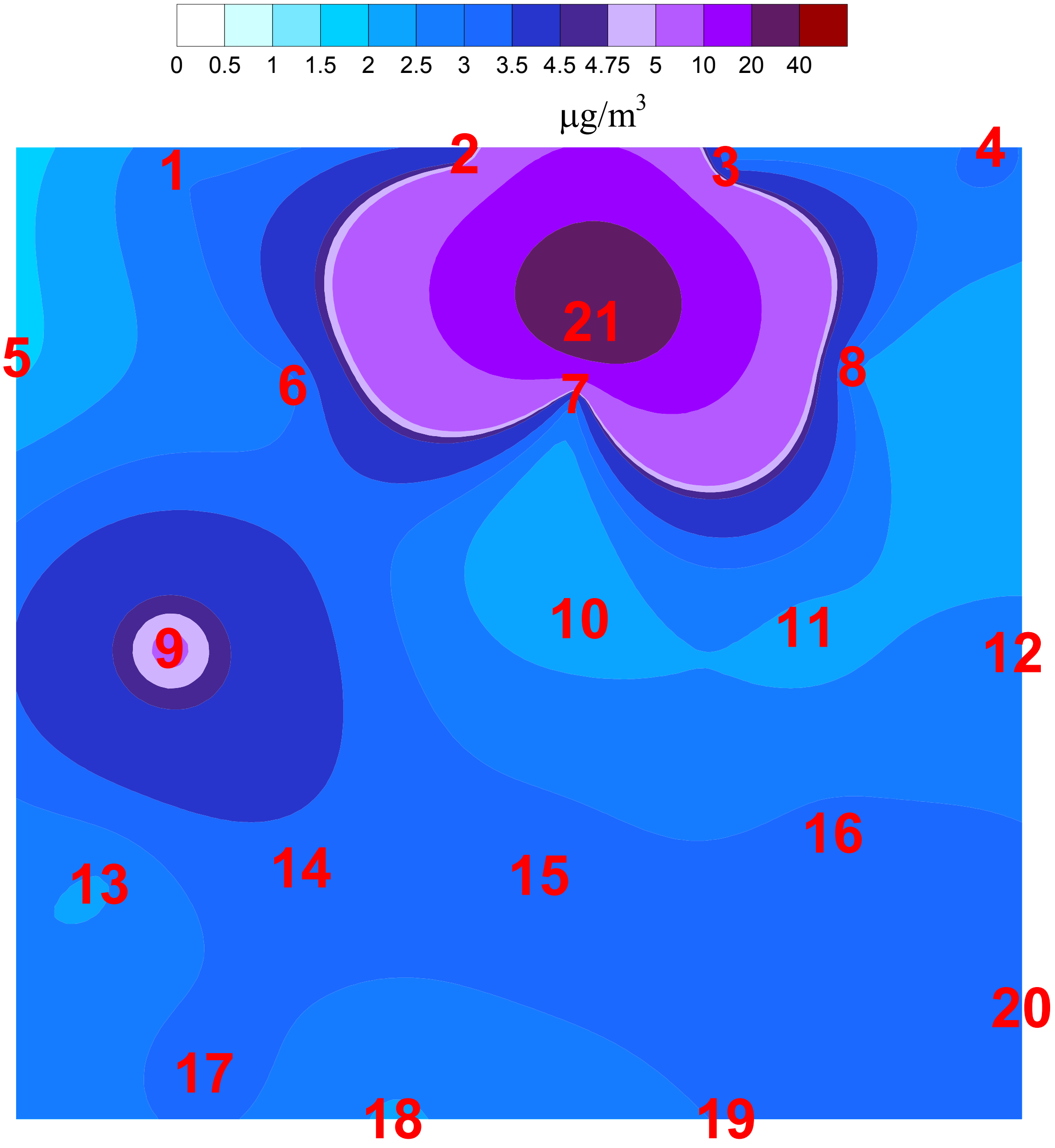

Figure 19. Oldsmar Week Two with Point 21

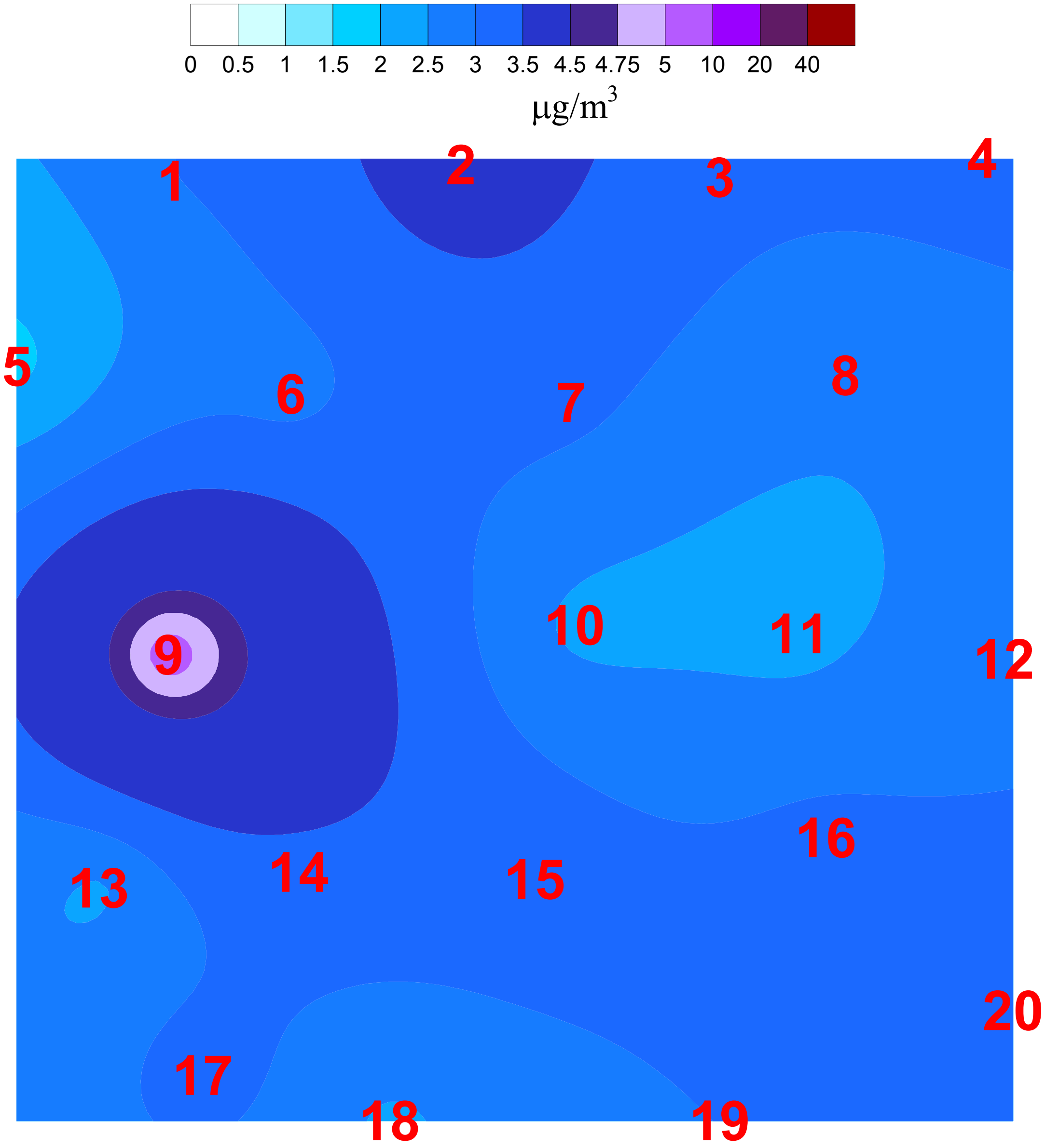

**Figure 20. Oldsmar Week Two without Point 21**

With the value for point 21 included, the mean value was 4.6 μg/m$^3$. The highest and lowest readings were 37 and 1.7 μg/m$^3$. The median was 3.0 μg/m$^3$. Without the value for point 21, the mean value was 2.9 μg/$m^3$. The highest and lowest values were 5.0 and 1.7 μg/$m^3$. The median was 3.0 μg/$m^3$. The sampling detection level was 1.3 μg/$m^3$.

Without the value for point 21, the mean values for the first and second deployment were 1.2 μg/$m^3$ and 2.9 μg/$m^3$ respectively. The elevated mean value for the second week was probably due to differences in rainfall. During the first deployment, there was no precipitation; however, during the second deployment, it rained frequently. The increased rainfall may have led to higher ammonia levels due to increased biological activity.

Using the criteria that any measurements above the 90th percentile are elevated, locations 20, and 2 are high for deployment 1. For deployment 2, locations 21 and 9 are high. Tables are located in Appendix IV—Tables of Data that list the ammonia concentration at each location and if a value was considered elevated.

Locations 20 and 15 were in very swampy areas, which may account for their higher values during deployment 1. Location 2 was elevated for both sampling periods. It was located on an undeveloped lot within a residential neighborhood. Other than the lot being overgrown with vegetation, there was no clear reason for the elevated values. It was located due north of the wastewater treatment plant. However, given the dominant land/sea breeze (east and west) during both sampling periods, it seems unlikely that an ammonia plume from the wastewater plant traveled north.

Excluding location 21, the nearest sample location to the sludge building was deployment site number 7, which was located only 135 meters south-southwest of the building and did not show an elevated ammonia concentration. With the easterly and westerly winds, the samplers most likely to have picked up the ammonia from the wastewater treatment plant were points 6 and 8. However, they were 0.5 km away from either side of the sludge building. The only point to indicate the sludge building as a hot spot was point 21. Missing this source (without point 21) can be attributed to two possibilities. The plume was much smaller than the 0.5-km diameter plume that the grid pattern was designed to find or the plume was elliptical. As a plume narrows, the necessary spacing of the sample locations goes down and the number of sample locations needed dramatically increases. This makes looking for a narrow plume very impractical.

Every sample location for the Oldsmar deployments had collocated samplers. This was done to assess the variability of the samplers. The variability is discussed in Chapter III. Most duplicates showed similar values except for two sets used in the first Oldsmar deployment. The values for Point 5 were 18.5 and 0.6 $\mu g/m^3$, and the values for point 9 were 31.6 and 1.3 $\mu g/m^3$. The first step was to determine if the variability of the two samples were significantly different from the variability of the rest of the duplicates. The Z-Scores for the relative percent difference (RPD) for point 5 and point 9 were 2.6 and

2.7, respectively. The critical Z-Score at 95 % confidence level is 1.64. Using this criteria, the variabilities of the two points were considered outliers. Once this was determined, the next step was to determine which of the duplicates could be considered the value for that location. Z-scores were calculated for all 34 samplers (17 locations, 2 at each location). The highest reading for both locations 5 and 9 were outside the critical Z-score of 1.64 and were rejected. The lower values had Z-scores well below the critical Z-score and were retained.

### *Tampa Results*

The Tampa sampling area consisted of approximately 180-km$^2$ area surrounding the northern part of the bay (Figure 21). The sampling area included residential areas to the west and north, and industrial areas to the east. Ninety four sample locations were used. The locations were spaced 1.5 km apart using a triangular grid pattern. The diameter of the smallest hot spot that could be located using this spacing was 1.5 km. The chance of missing a 1.5 km hot spot was 5%. The spacing was determined using HotSpot-Calc®[11]. The PSDs were deployed for 14 days starting on September 28, 2001, and were retrieved October 12, 2001. Of the 94 samplers originally deployed, three points 34, 43 and 48 were missing at the time of retrieval.

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[11] For details on Hotspot-Calc® see the sections titled, Placement in a Grid Pattern and Appendix I – Specifics on HotSpot-Calc®.

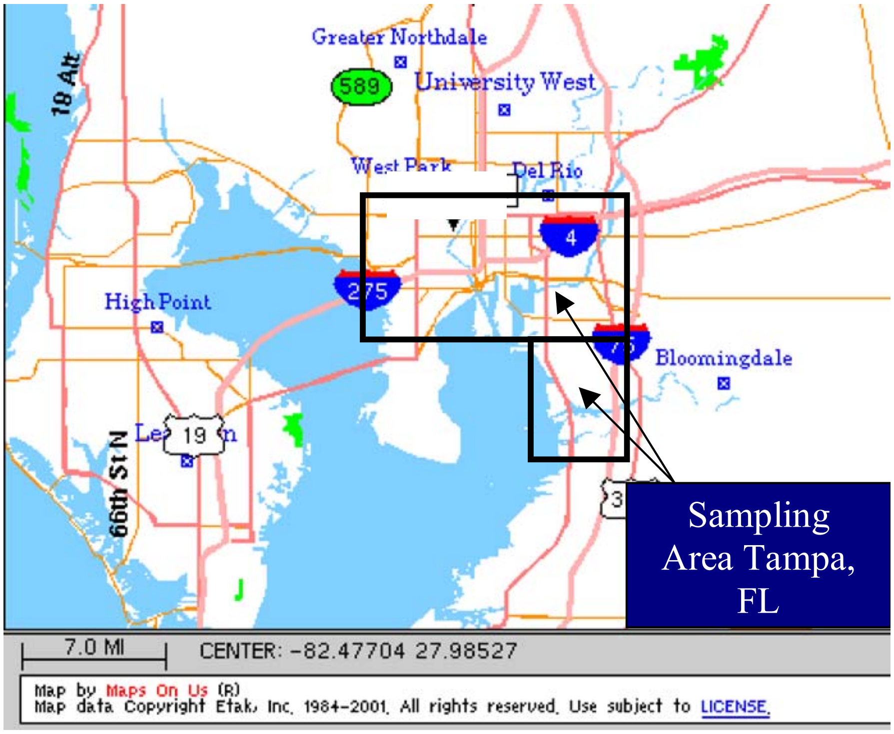


**Figure 21. Tampa Sampling Area**

The mean of all the samples was 2.0 µg/m$^3$ with a high of 15, a low of 0.07 a median of 1.45. The 90th percentile was 3.4 µg/m$^3$ and was used as the demarcation between ambient concentrations and values considered elevated. The 90th percentile was used because hot spots can skew the data (see section titled Statistical Methods Used in Chapter III). The Tampa results are graphically shown in Figure 22. The readings were graphed by first grouping the values into 0.5 µg/m$^3$ increments and then graphing the frequency of values in each group. The graph shows a Gaussian trend towards the lower values and clearly shows that some values are well away from the rest. When the values considered “elevated” (the highest 8) are removed the mean and median become 1.39

μg/m$^3$ and 1.36 μg/m$^3$, demonstrating that approximately 1.4 μg/m$^3$ best reflects the "averaged" value.

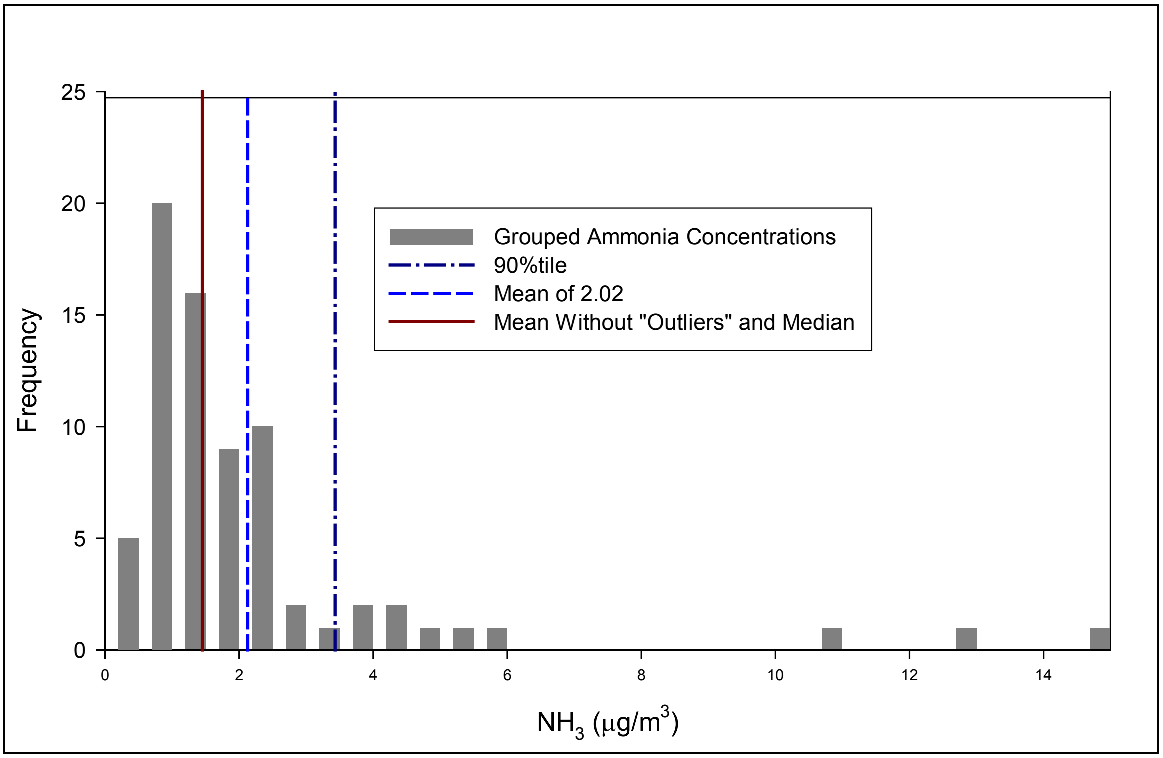


**Figure 22. Frequency Distribution of Tampa Samplers**

Figure 23 is a contour map of the Tampa deployment, interpolated using kriging. The map clearly shows an area of elevated values. This map also has the area's sources and strengths graphically represented. The sources and their strengths were taken from an ammonia inventory done by Connie Mizak (2001) at the University of South Florida (Table 9). The high concentration of sources correlated with the elevated values shown on the contour map. All of the points in the hot spots shown on the contour map are located above the 90th percentile, meaning that they meet the criteria established for considering a value as elevated.

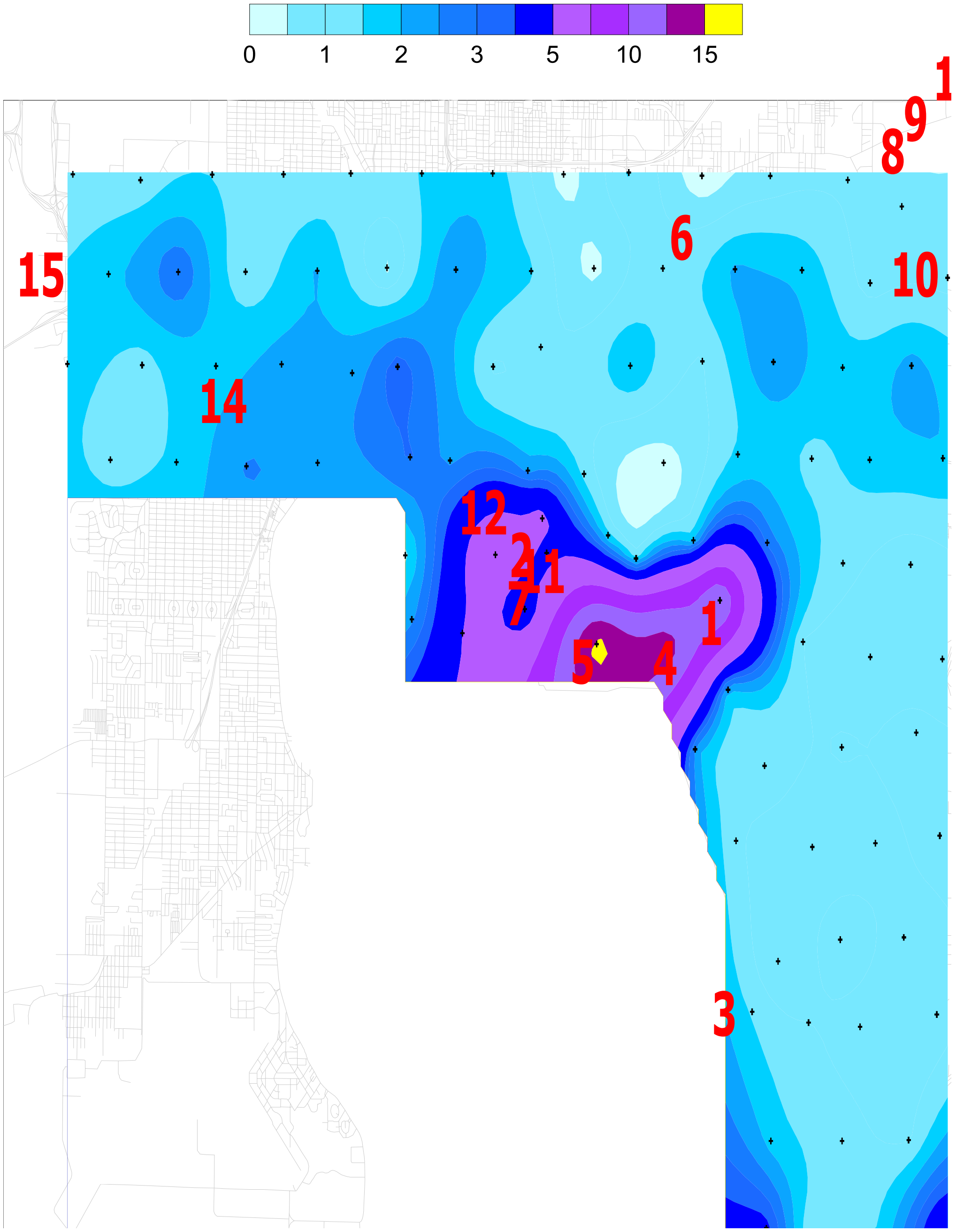


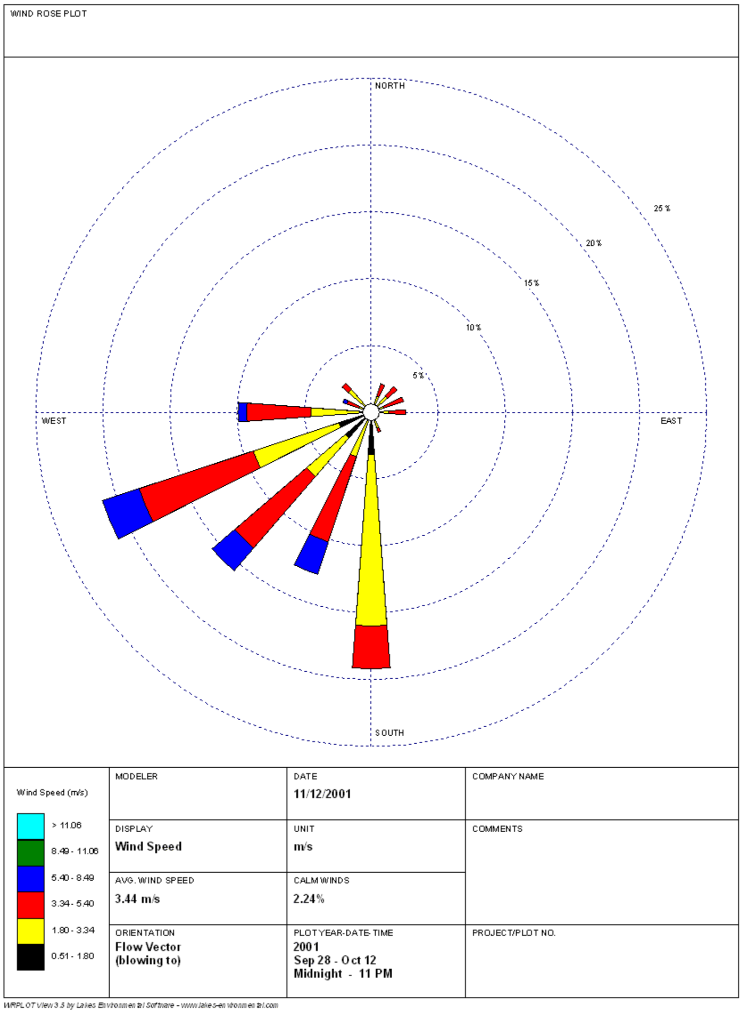
Figure 23. Tampa Sampling Contour Map of Ammonia Concentrations

**Table 8. List of Business That Emit Ammonia in the Tampa Sampling Area (Mizak, 2001)**

| # | Name | Emissions $NH_3$ 1000 kg/yr |
|---|---|---|
| 1 | NITRAM | 161 |
| 2 | HOWARD CURRAN WASTEWATER TREATMENT PLANT | 153 |
| 3 | CARGILL FERTILIZER - RIVERVIEW OPERATIONS | 50 |
| 4 | IMC AGRICO - PORT SUTTON TERMINAL | 17 |
| 5 | FARMLAND HYDRO L P - AMMONIA TERMINAL | 17 |
| 6 | AMERICOLD - TAMPA | 14 |
| 7 | C F INDUSTRIES - AMMONIA TERMINAL | 13 |
| 8 | REDDY ICE - TAMPA | 3.9 |
| 9 | COCA COLA BOTTLING - TAMPA | 3.5 |
| 10 | TRADEMARK NITROGEN | 2.0 |
| 11 | HARBORSIDE REFRIGERATED SERVICES | 1.9 |
| 12 | AMERICOLD - PORT | 0.91 |
| 13 | UNIROYAL OPTOELECTRONICS | 0.68 |
| 14 | RAPID BLUEPRINT | 0.43 |
| 15 | BAY REPROGRAPHICS | 0.41 |

Cargill fertilizer plant (Location 3 on Figure 23) is a large source of ammonia and yet it did not show up as a hot spot during the sampled period. The windrose graph (Figure 24) shows south and southwesterly winds dominated during the two-week sampling period. Cargill is located very near the east side of the bay. An ammonia plume from Cargill would have been in part pushed over the bay. No samplers were located on the bay and this may be one reason an ammonia plume from Cargill was not detected.

Another explanation for “missing” the ammonia plume is that ammonia emitted from Cargill may react with other plant-emitted constituents and byproducts. Sulfur dioxide is emitted at the rate of 0.04 kg/Mg of product during the manufacturing of ammonium sulfate fertilizer (EPA, 1995). Once emitted sulfur dioxide can be oxidized to sulfuric acid by reacting with water, the sulfuric acid can then react with ammonia to form ammonium sulfate, thereby removing the ammonia from the air. Another possible removal mechanism is by reaction with gypsum-stack pond water. The gypsum stack water is used during the manufacturing process and becomes highly acid (< 3 pH). The acidic water can behave as a sink for ammonia. Given the active gypsum stack at Cargill is approximately 1.0 km by 0.6 km this removal mechanism is not trivial. East-northeast of Cargill, where the gypsum stack is located, the ammonia concentrations were low and homogenous (Figure 23). This area looks distinctly different from areas near the northern part of the sampled area where concentrations are near ambient but are heterogeneous.



MODELER

DATE
11/12/2001

COMPANY NAME

DISPLAY
Wind Speed

UNIT
m/s

COMMENTS

AVG. WIND SPEED
3.44 m/s

CALM WINDS
2.24%

ORIENTATION
Flow Vector
(blowing to)

PLOT YEAR-DATE-TIME
2001
Sep 28 - Oct 12
Midnight - 11 PM

PROJECT/PLOT NO.

**Figure 24. Windrose for TIA Data** (The, et al., 2000)

There appears to be elevated areas south and southwest of the four sources located in and above the northeastern corner of the sampling area. However, the concentrations in these elevated areas did not meet the criteria used to determine hot spots (90th percentile or above).

The Port of Tampa was sampled during the "Port of Tampa" deployment and the Tampa deployment. Some values were very different during the two deployments and should be compared. Point 55B was located at the same site as the location referred to as "Sludge" during the Port of Tampa deployment. It was located 20 meters east of sludge drying beds located at the Tampa wastewater treatment plant. The concentrations there were 106 μg/m$^3$ during the Port of Tampa deployment and 5.3 μg/m$^3$ during the Tampa deployment[12]. This dramatic difference in concentrations from the same location can be attributed to the fact that during the first week of the Port of Tampa deployment the drying beds were filled with freshly processed sludge. The first week the concentration was 82 μg/m$^3$. The second week it was 125 μg/m$^3$. It reached a maximum during the third week of 174 μg/m$^3$, and then dropped off to 22 μg/m$^3$ for the fourth week. By the fourth week, the sludge was very dry. During the Tampa deployment, the sludge drying beds were completely empty and this may have led to lower ammonia values when compared to the previous sampling at that location.

Location 54 of the Tampa deployment was 400 meters west of the "Railroad" site used during the Port of Tampa deployment. Again, the concentrations were very different. The Railroad had a concentration of 40 μg/m$^3$ and location 54 had a concentration of 6.8 μg/m$^3$. The Railroad location was approximately 50 meters south of a facility where

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[12] The concentration report here and any subsequent concentrations in the follow paragraphs for the Port of Tampa results are the Monthly integrated values and not the weekly averaged values unless otherwise noted.

railroad cars are loaded with ammonia and 800 meters from the sludge drying beds at the wastewater treatment plant. The weekly values at the Railroad site show a similar trend as the Sludge site, peaking in the third week and then dropping off. It was originally believed that the elevated values at the Railroad site were due to loss during the loading of railroad cars. It is now believed that the elevated values at the Railroad location were due to the close proximity to the sludge drying beds.

Locations “Dock” and “Fence” for the Port of Tampa deployment were approximately 400 meters north of point 54 of the Tampa deployment and have very similar concentrations. Dock and Fence were 7.5 and 4.9 $\mu g/m^3$ and point 54 was 6.8 $\mu g/m^3$.

### *Accuracy and Precision of the PSD*

#### *Accuracy*

Six experiments were performed comparing annular denuder system (ADS) values with PSD values. The ADS was used as the reference method and for the this comparison the ADS values were considered the “true” values. One of these experiments was performed in the hallway in the College of Public Health building at USF, one at a site located near the eastern side of the Gandy Bridge[13] and the other four at the Oldsmar wastewater

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[13] The Gandy Bridge spans the northern part of Tampa Bay.

treatment plant (WWTP). Three of the six experiments were below the detection limit and were not used for this comparison. Using the Ogawa® calculated sampling rate of 38.8 ml/min, the relationship of the PSD values to ADS values is represented by the equation: $y = 1.24x$ with an $R^2$ of 0.98 Figure 25. The trendline was forced through zero.

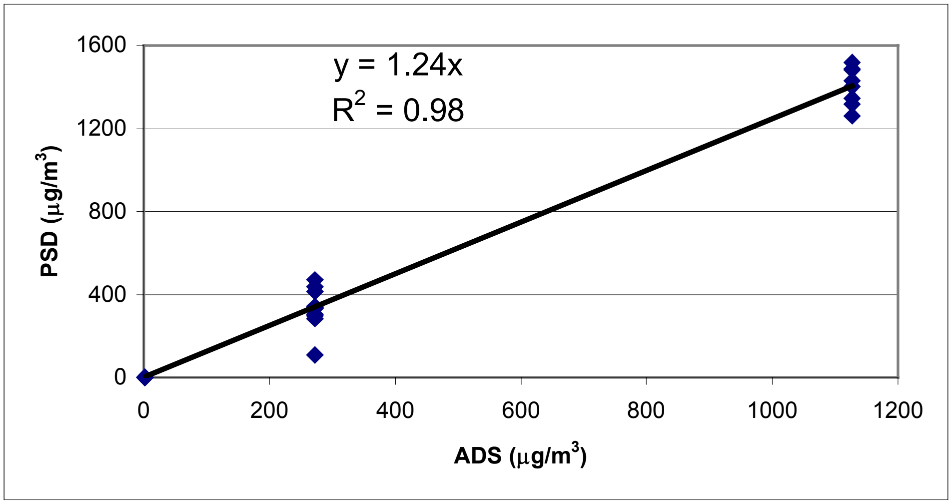

**Figure 25. ADS vs. PSD Using the Calculated Rate**

This equation demonstrates that the PSD values were on average 1.25 times the ADS values, representing a positive bias. This bias could represent ammonia breakthrough on the ADS. All experiments at the Oldsmar WWTP were run using two 242-mm acid-coated denuders[14] in series. For two of the four experiments, ammonia broke through the first denuder. It appears, for at least one experiment, that ammonia broke through both denuders causing ammonia loss. Additional comparisons by Captain Scott Mower (2002)

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[14] Denuders are URG brand, part number URG-2000-30X242-3CSS.

demonstrated this same bias. It is possible that at extremely high concentrations denuders under estimate ammonia. In an attempted to confirm this Mower sampled simultaneously with an impinger a PSD and a denuder. The PSD and impinger results were similar yet the denuder values were considerably lower.

Another way of approaching this comparison is to look at the relationship of only one data set. Most of these experiments had very high variability with outliers. The most recent comparison at the Gandy site was done after new procedures were implemented to reduce the variability seen in blank values. This experiment had a variability of only 18%, and the samplers were located at ambient level. Looking at only this one data set yields an equation of: $y = 0.70x$. Looking at two other one-point calibrations (that were at levels well above ambient) yielded slopes of 1.12 and 1.22.

At first, the wide range of slope values was discouraging. This discouragement led to the assessment of the ADS as a sampling method. Was the ADS accurate? How well do other methods compare? Table 9 shows many side-by-side comparisons of ammonia sampling methods and their results. The information in this table shows that most methods of measuring ammonia do not agree at or near ambient levels. The highlighted row is of particular interest. This row shows the linear regression statistics for two collocated denuders that were integrated for 24 hours every six days for four years in Tampa, FL, and were coated, extracted and analyzed by the same lab (TBADS, 2001). From this comparison, it appears one denuder was biased by 5 % and the $R^2$ value was only 0.70. When one looks at the range of slope values and poor $R^2$ values for other methods and even for the ADS compared to itself, one determines the ± 30 % accuracy of the PSDs relative to the ADS is very reasonable.

**Table 9. Comparisons of Collocated Ammonia Detection Method**

| Reference Instrument | Instrument 2 | Slope | $R^2$ | Prec. % | Notes | Reference |
|---|---|---|---|---|---|---|
| ADS | PSD<br>Ogawa® | 0.7 | | 18 | Below Detection Limit | Tate |
| ADS | PSD<br>Ogawa® | 1.12 | 0.99 | 5-30 | Outliers Removed<br>1-1100 μg/m$^3$ | Tate |
| ADS | ADS (HoneyComb) | 1.15 | 0.75 | | | (Sioutas et al., 1996) |
| ADS | ADS | | | 16 | 0.10-0.57 | (Vossler et al., 1988) |
| ADS | ADS | 0.95 | 0.70 | 17 | | (TBADS, 2001) |
| Continuous | Photoacoustic monitor | 1.09 | 0.92 | | Outliers Removed | (Mennen et al., 1996) |
| ADS | PSD (Tube Type) | 1.02 | 0.99 | 8-20 | 7 μg/m$^3$-Lab Mean Used | (Frenzel et al., 1995) |
| Continuous | $V_2O_5$ 1 l/min Thermodenuder | 1.02 | 0.96 | | Outliers Removed | (Mennen et al., 1996) |
| Continuous | DOAS | 1.02 | 0.94 | | Outliers Removed | (Mennen et al., 1996) |
| ADS | Impinger | 1.01 | 0.99 | 8-20 | 7 μg/m$^3$-Lab Mean Used | (Frenzel et al., 1995) |
| ADS | Filter Pack | 0.988 | 0.78<br>95 | | 0.18-1.1 μg/m$^3$ | (Luke et al., 2000) |
| ADS | Diffusion Tube | 0.92 | 0.86 | 4 | 6-35 μg/m$^3$ | (Thijsse et al., 1998) |
| Filter Pack | Impinger | .91 | .97 | | $NH_3$ + $NH_4$ | (Luke et al., 2000) |
| Continuous | $V_2O_5$ 10 l/min Thermodenuder | 0.87 | 0.94 | | Outliers Removed | (Mennen et al., 1996) |
| Chemiluminescence | ADS | 0.82 | 0.92 | 19-100<br>18-3 □g/m$^3$ | | (McCulloch et al., 2000) |
| ADS | Filter Pack | 0.82 | 0.84 | | | (Luke et al., 2000) |
| Continuous | $WO_3$ Thermodenuder | 0.63 | 0.97 | | Outliers Removed | (Mennen et al., 1996) |
| ADS | Filter Pack | 1.06-1.11 | | 10 | | (Pakkanen et al., 1999) |
| ADS | Willems PSD | 0.065-1.2 | | | 23 Hours | (Luke et al., 2000) |

| | | | | | | |
|---|---|---|---|---|---|---|
| ADS | Ogawa® PSD | 0.97-2.32 | | | 23 Hours | (Luke et al., 2000) |
| Impinger | Semiconductor | | 0.68 | | 4-75 µg/m$^3$ | (Kawashima and Yonemura, 2001) |

### *Precision*

The precision was determined by analyzing the variability of collocated PSDs. Each experiment comparing the ADS values to PSD values included 8-10 collocated PSDs. The Port of Tampa and Oldsmar deployments included duplicates at each location. The Tampa area deployment included 14 sets of collocated PSDs.

The variabilities for each deployment are shown in Table 10. The first seven experiments listed involved the collocation of 8-10 PSDs and the reported variabilities are the relative standard deviations (RSD) of the group. The last four experiments listed involved the placement of many collocated pairs. The reported variabilities are the mean of the relative percent differences (RPD) of the pairs.

**Table 10. Variability of Duplicates**

| Location | Variability RSD/RPD[15] | Number of Duplicates |
|---|---|---|
| Hallway | 70[a] | 10 |
| Inside Oldsmar Sludge Building 1 | 106[a] | 10 |
| Inside Oldsmar Sludge Building 2 | 178[a] | 9 |
| Inside Oldsmar Sludge Building 3 | 31 | 10 |
| Inside Oldsmar Sludge Building 4 | 32 | 10 |
| Outside Oldsmar Sludge Building | 5 | 10 |
| Gandy Site | 18 | 8 |
| Port of Tampa | 17 | 20 pairs |
| Oldsmar Study 1 | 21 | 18 pairs |
| Oldsmar Study 2 | 24 | 20 pairs |
| Tampa | 16 | 14 pairs |

[a] Measured concentrations were below MDL

The variability of the PSDs during the PSDs versus ADS experiments inside the Oldsmar sludge building may not be valid for longer deployments. For those experiments, three sets were deployed for two hours and one set for six hours. In addition, the PSDs were exposed to levels 25 to 500 times above ambient levels and were placed very near an

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[15] The RSDs (relative standard deviations) and RPDs (relative percent differences) reported are after outliers had been removed.

ammonia source. These two factors may have led to a heterogeneous concentration within the sampling area. The Oldsmar, Port of Tampa, Gandy and Tampa area studies represent longer deployments and are more representative of the amount of variability that one can expect from longer deployments at or near ambient levels.

The Port of Tampa, Tampa area, and the Gandy deployments showed a much lower variability. The lower variability for the Port of Tampa deployment is attributed to the elevated concentrations found there. The lower variability for the Tampa and Gandy deployments was attributed to a change in cleaning the PSDs. For a description of cleaning procedures, see section titled PSD Cleaning.

Figures 26, 27 and 28 show the amount of ammonium collected on the x-axis and the RPD on the y-axis. Figure 26 shows all values while Figure 27 shows only the duplicates that collected 12 µg or less of ammonium. Figure 28 graphs only the duplicates from the Tampa and Gandy deployments. By looking at the first two graphs, one can see that above 10 µg the RPD settles down to less than 15%. Ten µg of $NH_3$ collected during a 2-week deployment would be equal to 13 µg/$m^3$, a concentration well above ambient levels. Figure 28 shows the values for the Tampa and Gandy deployments. These data demonstrate that any value above 0.6 µg has an RPD of 5 or less, 0.6 µg collected during a two-week deployment corresponds to 0.76 µg/$m^3$, which is below ambient levels. This value is very close to the sampling method detection level of 0.7 µg/$m^3$.

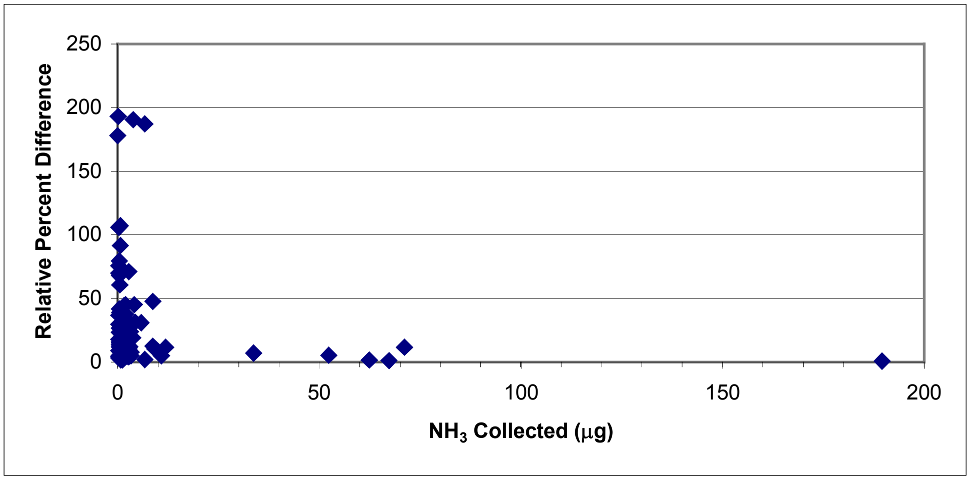

Figure 26. $NH_3$ vs. RPD of all Duplicates

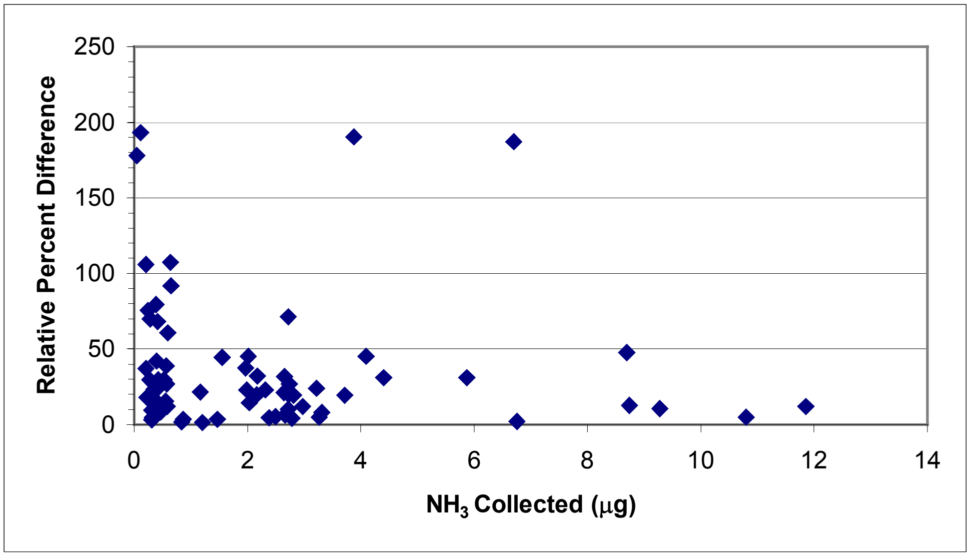

Figure 27. $NH_3$ Collected vs. RPD for Values Less Than 12

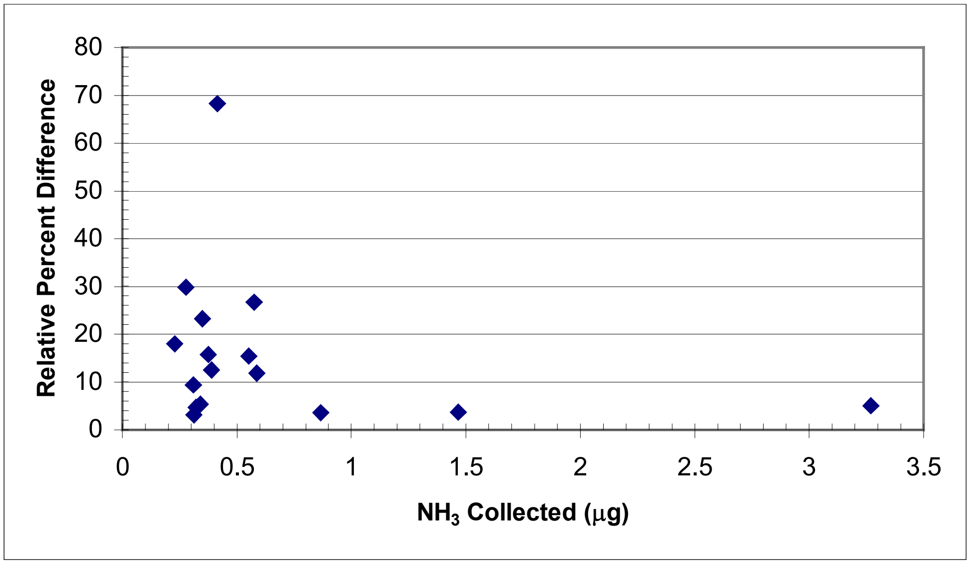

**Figure 28. $NH_3$ Collected vs. RPD for Tampa and Gandy Deployments**

### *Outliers*

Outliers continued to be problematic. Both blank values and duplicates contained outliers. It was hoped that the outlier problem would be solved when new cleaning and coating procedures were implemented. The variability of the duplicates became lower after the new procedures were implemented; however, the blank values continued to have outliers. Outliers were determined using Grubb's outlier test (see section titled Statistical Methods Used in Chapter III)

# Chapter VI Conclusions

Using the Ogawa® PSD for ammonia sampling has some strengths and some drawbacks. Its strengths are its ease of deployment, retrieval and analysis, low cost, and reasonable reproducibility. Its drawbacks are unexplainable outliers in both blanks and duplicates, long deployment times and the possibility of a sampling rate affected by concentration or other factors.

The ability to deploy, retrieve and analyze many samplers over a large network allows for the drawing of contour maps. This type of deployment would be cost prohibitive and labor intensive using active sampling systems. These make the passive sampler an excellent tool for this type of task. The reproducibility of the PSDs for the Tampa and Gandy deployments were at reasonably low levels of 16% and 18%. These two deployments were performed after new steps were implemented to eliminate contamination, a major source of variability.

The new steps helped bring down the contamination of the blanks overall; however, the blanks continued to have outliers, which was very disconcerting. When deployed, a single PSD with a high reading is assessed as a hot spot, not as an outlier. This could lead to false identification of a hot spot. One way to avoid this problem is to use three samplers at each location. While this approach would help to determine outliers it would lead to greater expense and effort.

The Ogawa® PSD is an excellent tool for determining hot spots qualitatively. The Ogawa® sampler's ability to quantitatively determine $NH_3$ was within ± 30 % of the reference method, making its quantitative ability an asset as well. The mean PSD values (2.0 $\mu g/m^3$) and median (1.4 $\mu g/m^3$) were compared to the average of four years of ADS values (1.7 $\mu g/m^3$) taken at a location within Tampa (the Gandy Site). This comparison showed that the mean of PSD values were within ±18 % of the mean of the ADS values. This is further evidence that the PSDs are in agreement with the reference method. The biggest concerns for using the Ogawa® PSDs for sampling ammonia are the outliers and the length of deployment.

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Appendices

## Appendix I – Specifics on HotSpot-Calc®

DQO-PRO is a software package written by Dr. Lawrence Keith author of *Principles of Environmental Sampling* and President and CEO of Instant Reference Sources, Inc., an environmental consulting firm. DQR-PRO is available for free download from an American Chemical Society affiliated website: http://www.acs-envchem.duq.edu/dqopro.htm

HotSpot-Calc is a specific program built into DQO-PRO that is used to determine the grid spacing and number of samples needed for a given set of parameters.

Grid spacing is calculated by using Equation 16.

$$G = L/X$$

**Equation 16**

G = required grid spacing

L = length of radius of the circular hot spot

X= is a value taken from a chart originally published in “Statistical Methods for Environmental Pollution Monitoring” (Gilbert, 1987). Dr. Gilbert developed charts that have β, the chance of missing a hot spot, on the Y-axis and L/G, length of hot spot divide by the grid spacing, on the x-axis. The value of β is chosen by the researcher and then the chart is used to find the corresponding value of X.

The number of samples is computed using Equation 17.

$$n = A / 0.886 (G)$$

**Equation 17**

$n$ = number of samples,

$A$ = area to be sampled, using the same units as $G$, and

$G$ = grid spacing

0.0886 = conversion factor, used for triangular grids (for square grids the factor is 1)

## *Appendix II – Tampa Sampler Locations*

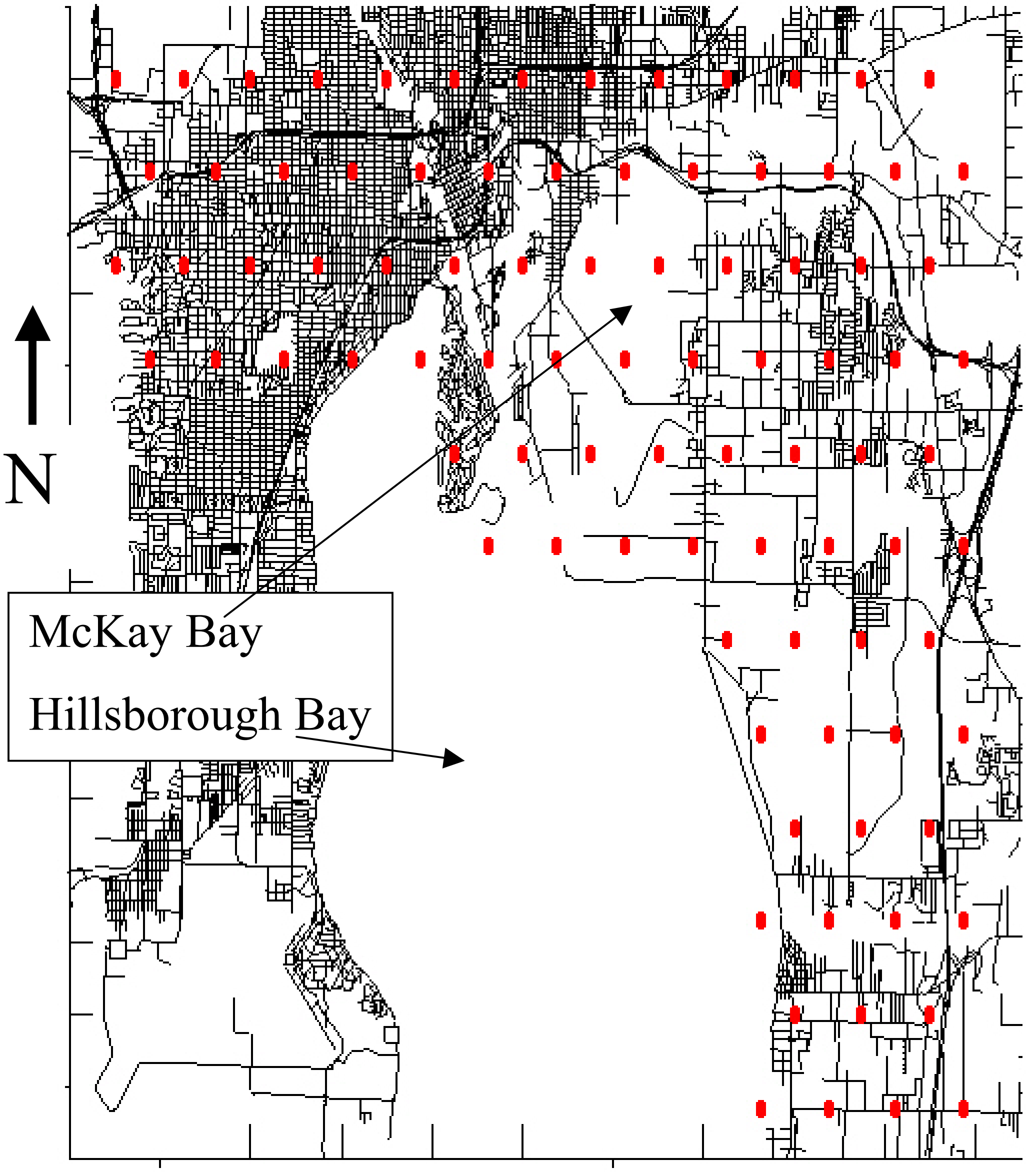

**Figure 29. Proposed Tampa Sample Locations**

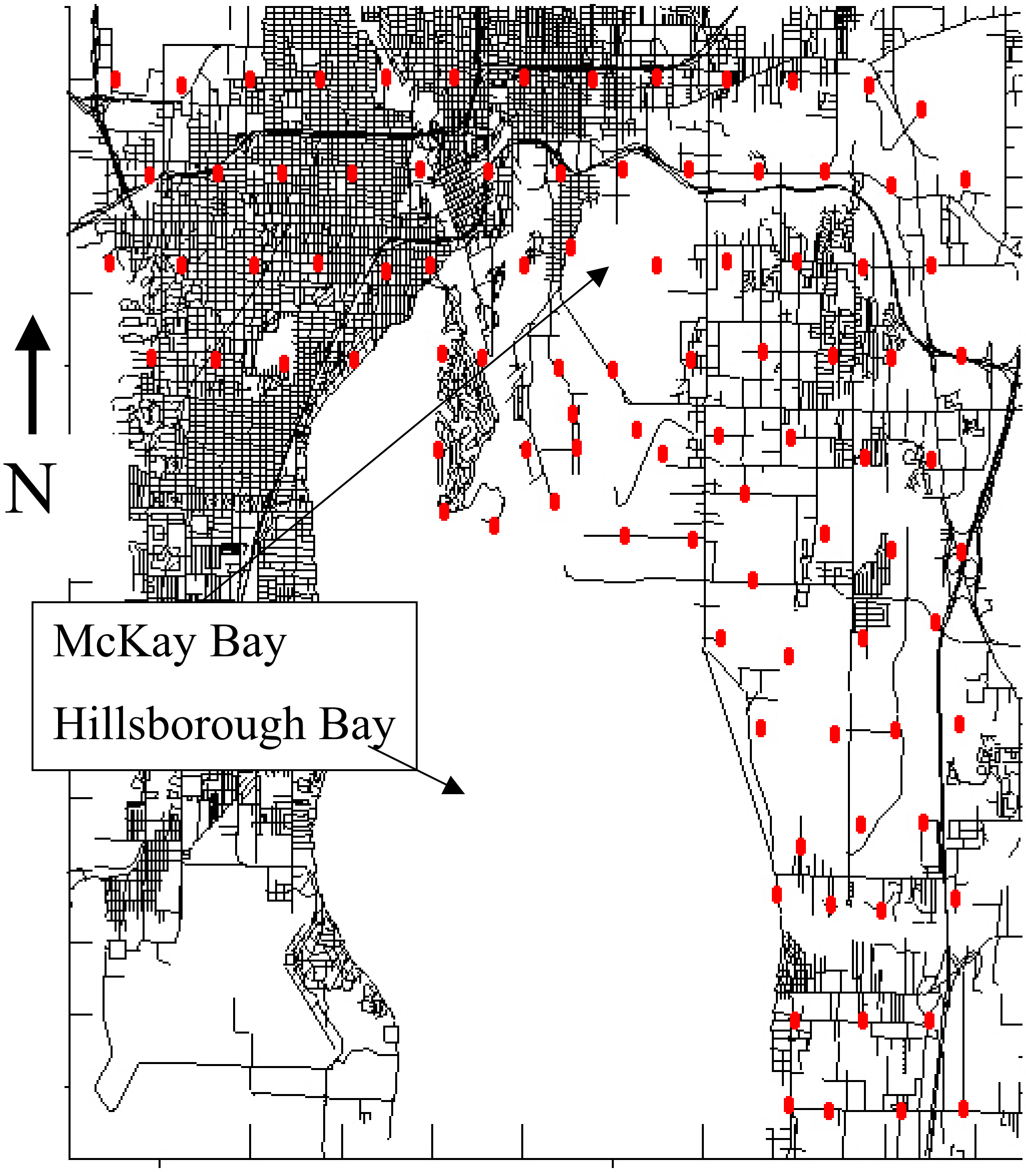

**Figure 30. Actual Sampling Locations**

## *Appendix III--Problems Corrected during Method Development*

### Filter Problems\Sodium and Ammonium Overlap

The filters that were used for early experiments were too small for the PSD and came with ammonia and sodium contamination. The sodium concentration was problematic. During analysis, using ion chromatography (IC), the sodium peak was overwhelming the ammonium peak (Figure 11).

Much effort went into finding a filter of the right size that was either free of contamination or could be cleaned. Most filters purchased had contamination and fell apart when cleaned. Dr. Scudlark of the University of Maryland, who also uses the Ogawa® PSD, suggested using Schleicher and Scheull brand filters. The new filters contained no ammonium; however, they had even more sodium than the previously used filters. A washing procedure was devised to remove the sodium, which unfortunately added ammonium.

This problem was resolved when the lab obtained a new IC with gradient elution capabilities. The gradient elution allowed for the baseline (complete) separation of ammonium from sodium (see section titled Analysis). Because the sodium was no longer a problem, the filters no longer needed to be washed thereby eliminating one source of ammonium contamination.

# Appendix III--Problems Corrected during Method Development (Continued)

## High Blank Values

The PSD blank values on average where high relative to the amount collected at ambient levels and were highly variable. Contamination of the blanks was narrowed down to three factors: contamination during washing to remove sodium, contamination during the coating of the PSDs, and carryover from the body of the PSD from previous experiments. These problems were resolved as follows.

### Contamination during Washing

When the PSDs were first being used, the filters had to be washed before coating to remove excess sodium. The sodium was interfering with the analysis; however, the washing was adding ammonium contamination. Removal of excess sodium was no longer necessary after the lab obtained a new ion chromatograph that has gradient elution capabilities (see section titled Analysis).

### Contamination during Coating and Extraction of the PSD

It was determined that some contamination was taking place during the coating and extraction of the PSDs. This problem was reduced by coating and extracting the PSDs in an ammonia free glove bag and by using a repeat pipettor. The repeat pipettor holds 5 ml of coating solution within a syringe-like tip thereby eliminating the opportunity for the acidic solution to be exposed to ambient ammonia during the coating process.

## Contamination from Carryover

The PSD bodies were determined to be a source of contamination. They held on to ammonium, which could be released into a newly coated filter. This was a source of high blank values, outliers, and variability for both blanks and exposed PSDs. Determining an effective cleaning method reduced this problem. The PSDs were originally washed in only DI water. The washing procedure adopted for the Tampa sampling included removing the inner retaining ring and the inner base pad then soaking all components in a 0.1% w/w potassium hydroxide solution for 24 hours. This reduced the overall contamination of the blanks, however, the blank values continued to contain outliers.

## Ammonia Collected on the Screens

The original extraction method did not include the screens. Extraction of just screens demonstrated that ammonia was being collected by the screens and therefore should be extracted with the filters. An interesting note: Ogawa’s protocol for ozone does not include extraction of the screens but the recently released protocol for ammonia does.

**Table 11. Data and Statistics for Oldsmar Deployment 1**

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ | Z-Scores | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile |
|---|---|---|---|---|---|---|---|---|---|---|
| 20 | 337.96 | 3100.353 | 2.2 | 2.20 | No | x | x |  | x | x |
| 2 | 336.946 | 3101.907 | 1.7 | 1.15 | Elevated |  |  |  | x |  |
| 15 | 337.081 | 3100.594 | 1.7 | 1.09 | Values |  |  |  | x |  |
| 16 | 337.616 | 3100.671 | 1.6 | 0.85 |  |  |  |  |  |  |
| 11 | 337.566 | 3101.045 | 1.5 | 0.72 |  |  |  |  |  |  |
| 3 | 337.421 | 3101.884 | 1.4 | 0.51 |  | x = values statistically above the mean using different confidence levels and methods.<br>SDL = 1.9 µg/m$^3$ $NH_3$<br>Mean 1.2 µg/m$^3$ $NH_3$<br>Median 1.2 µg/m$^3$ $NH_3$ |  |  |  |  |
| 17 | 336.472 | 3100.234 | 1.3 | 0.16 |  |  |  |  |  |  |
| 9 | 336.409 | 3101.007 | 1.2 | 0.02 |  |  |  |  |  |  |
| 1 | 336.416 | 3101.877 | 1.2 | 0.09 |  |  |  |  |  |  |
| 14 | 336.648 | 3100.607 | 1.2 | 0.12 |  |  |  |  |  |  |
| 10 | 337.148 | 3101.083 | 1.1 | 0.17 |  |  |  |  |  |  |
| 7 | 337.148 | 3101.471 | 1.1 | 0.22 |  |  |  |  |  |  |

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ | Z-Scores | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile |
|---|---|---|---|---|---|---|---|---|---|---|
| 4 | 337.903 | 3101.919 | 1.1 | 0.27 | | | | | | |
| 8 | 337.652 | 3101.52 | 1.1 | 0.28 | | | | | | |
| 6 | 336.633 | 3101.486 | 0.8 | 1.07 | | | | | | |
| 13 | 336.281 | 3100.578 | 0.7 | 1.26 | | | | | | |
| 5 | 336.13 | 3101.537 | 0.6 | 1.38 | | | | | | |
| 18 | 336.815 | 3100.151 | 0.4 | 1.80 | | | | | | |

**Table 12. Data and Statistics for Oldsmar Deployment 2**

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ | Z-Score with Point 21 | Z-Score without Point21 | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 21 | 337.18 | 3101.602 | 36.8 | 4.23 | 49.86 | x | x | x | x | x | x | x=with 21 |
| 9 | 337.148 | 3101.083 | 5.0 | 0.05 | 3.08 | x | o | o | o | x | o | o= without 21 |
| 2 | 336.946 | 3101.907 | 3.6 | 0.12 | 1.11 | x and o = values statistically above the mean using different confidence levels and methods for data including 21 and excluding | | | | | | |
| 15 | 337.081 | 3100.594 | 3.2 | 0.18 | 0.45 | | | | | | | |

Appendix IV—Tables of Data—Sorted by Descending Ammonia Concentrations (Continued)

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ | Z-Score with Point 21 | Z-Score without Point21 | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 14 | 336.648 | 3100.607 | 3.1 | 0.19 | 0.40 | confidence levels and methods for data including 21 and excluding 21, respectively.<br>SDL = 1.3 µg/m$^3$ NH$_3$<br>With Point 21<br>Mean 2.9 µg/m$^3$ NH$_3$<br>Median 3.0 µg/m$^3$ NH$_3$<br>Without Point 21<br>Mean 4.6 µg/m$^3$ NH$_3$<br>Median 3.0 µg/m$^3$ NH$_3$ | | | | | | |
| 20 | 337.96 | 3100.353 | 3.1 | 0.19 | 0.32 | | | | | | | |
| 17 | 336.472 | 3100.234 | 3.1 | 0.20 | 0.30 | | | | | | | |
| 4 | 337.903 | 3101.919 | 3.1 | 0.20 | 0.29 | | | | | | | |
| 3 | 337.421 | 3101.884 | 3.0 | 0.20 | 0.20 | | | | | | | |
| 16 | 337.616 | 3100.671 | 3.0 | 0.21 | 0.19 | | | | | | | |
| 7 | 337.148 | 3101.471 | 3.0 | 0.21 | 0.18 | | | | | | | |
| 1 | 336.416 | 3101.877 | 2.8 | 0.23 | 0.07 | | | | | | | |
| 6 | 336.633 | 3101.486 | 2.7 | 0.25 | 0.25 | | | | | | | |
| 12 | 337.943 | 3100.999 | 2.6 | 0.25 | 0.36 | | | | | | | |
| 8 | 337.652 | 3101.52 | 2.4 | 0.28 | 0.62 | | | | | | | |
| 13 | 336.281 | 3100.578 | 2.3 | 0.30 | 0.85 | | | | | | | |
| 18 | 336.815 | 3100.151 | 2.3 | 0.30 | 0.88 | | | | | | | |
| 10 | 337.155 | 3101.061 | 2.2 | 0.30 | 0.92 | | | | | | | |
| 11 | 337.566 | 3101.045 | 2.2 | 0.31 | 0.95 | | | | | | | |
| 5 | 336.13 | 3101.537 | 1.7 | 0.37 | 1.64 | | | | | | | |

**Table 13. Data and Statistics for Tampa**

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ | Z-Score | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile |
|---|---|---|---|---|---|---|---|---|---|---|
| 63 | 360.258 | 3087.642 | 15.12 | 9.01 | x | x | x | x | x | x |
| 64 | 361.75 | 3087.607 | 13.20 | 7.69 | x | x | x | x | x | x |
| 65 | 362.906 | 3088.233 | 11.85 | 6.76 | x | x | x | x | x | x |
| 54 | 358.084 | 3088.853 | 6.78 | 3.28 | x | x | x | x | x | x |
| 55B | 359.088 | 3089.342 | 5.30 | 2.26 | x | x | x |  | x | x |
| 61 | 357.373 | 3087.789 | 4.78 | 1.90 | x | x | x |  | x |  |
| 90 | 367.732 | 3079.696 | 4.47 | 1.69 | x | x | x |  | x |  |
| 55 | 359.183 | 3088.876 | 4.29 | 1.56 | x | x |  |  | x |  |
| 87 | 363.902 | 3079.745 | 3.61 | 1.09 |  |  |  |  | x |  |
| 62 | 358.712 | 3088.114 | 3.42 | 0.96 |  |  |  |  |  |  |
| 32 | 355.98 | 3091.393 | 3.13 | 0.76 | Highlighted points equal samplers within the hot spot. |  |  |  |  |  |
| 44 | 356.249 | 3090.171 | 2.90 | 0.61 |  |  |  |  |  |  |

## Appendix IV—Tables of Data—Sorted by Descending Ammonia Concentrations (Continued)

| Location # | UTM EW | UTM NS | $\mu g/m^{-3}$ | Z-Score | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile |
|---|---|---|---|---|---|---|---|---|---|---|
| 15 | 351.262 | 3092.675 | 2.85 | 0.57 | | | | | | |
| 58 | 363.926 | 3089.014 | 2.68 | 0.46 | | | | | | |
| 42 | 352.731 | 3090.049 | 2.41 | 0.27 | | | | | | |
| 37 | 364.057 | 3091.458 | 2.37 | 0.24 | | | | | | |
| 19 | 357.232 | 3092.707 | 2.35 | 0.22 | | | | | | |
| 45 | 357.106 | 3090.125 | 2.22 | 0.14 | | | | | | |
| 46 | 358.777 | 3089.989 | 2.18 | 0.11 | | | | | | |
| 69 | 362.378 | 3086.22 | 2.13 | 0.08 | | | | | | |
| 30 | 353.484 | 3091.429 | 2.11 | 0.06 | | | | | | |
| 31 | 355.002 | 3091.309 | 2.09 | 0.05 | | | | | | |
| 39 | 367.025 | 3091.406 | 2.08 | 0.04 | | | | | | |
| 23 | 363.234 | 3092.712 | 2.00 | -0.01 | | | | | | |
| 35 | 360.982 | 3091.406 | 1.98 | -0.03 | | | | | | |
| 17 | 354.255 | 3092.692 | 1.94 | -0.06 | | | | | | |
| 52 | 367.699 | 3090.157 | 1.86 | -0.11 | | | | | | |
| 14 | 349.765 | 3092.647 | 1.82 | -0.14 | | | | | | |

x = values statistically above the mean using different confidence levels and methods.

SDL = 0.7 $\mu g/m^3$ $NH_3$
Mean 2.0 $\mu g/m^3$ $NH_3$
Median 1.5 $\mu g/m^3$ $NH_3$

Appendix IV—Tables of Data—Sorted by Descending Ammonia Concentrations (Continued)

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ | Z-Score | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile |
|---|---|---|---|---|---|---|---|---|---|---|
| 53 | 356.148 | 3088.844 | 1.76 | -0.18 | | | | | | |
| 24 | 364.67 | 3092.7 | 1.74 | -0.19 | | | | | | |
| 64B | 363.083 | 3087.025 | 1.72 | -0.20 | | | | | | |
| 84 | 364.004 | 3080.921 | 1.70 | -0.22 | | | | | | |
| 29 | 352.075 | 3091.403 | 1.70 | -0.22 | | | | | | |
| 51 | 366.125 | 3090.134 | 1.69 | -0.23 | | | | | | |
| 7 | 358.023 | 3094.007 | 1.67 | -0.24 | | | | | | |
| 57 | 362.335 | 3089.046 | 1.59 | -0.30 | | | | | | |
| 27 | 348.885 | 3091.432 | 1.57 | -0.31 | | | | | | |
| 38 | 365.544 | 3091.382 | 1.54 | -0.33 | | | | | | |
| 9 | 360.95 | 3094.021 | 1.50 | -0.36 | | | | | | |
| 49 | 363.293 | 3090.209 | 1.50 | -0.36 | | | | | | |
| 89 | 366.362 | 3079.665 | 1.49 | -0.37 | | | | | | |
| 20 | 358.852 | 3092.688 | 1.49 | -0.37 | | | | | | |
| 41 | 351.228 | 3090.104 | 1.49 | -0.37 | | | | | | |
| 56B | 360.503 | 3089.114 | 1.46 | -0.38 | | | | | | |

Appendix IV—Tables of Data—Sorted by Descending Ammonia Concentrations (Continued)

| Location # | UTM EW | UTM NS | μg/m$^{-3}$ | Z-Score | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile |
|---|---|---|---|---|---|---|---|---|---|---|
| 6 | 356.501 | 3094.007 | 1.46 | -0.39 | | | | | | |
| 70 | 363.869 | 3085.996 | 1.45 | -0.39 | | | | | | |
| 3 | 351.995 | 3093.992 | 1.41 | -0.42 | | | | | | |
| 80 | 363.6 | 3082.671 | 1.37 | -0.45 | | | | | | |
| 5 | 354.974 | 3094.007 | 1.36 | -0.45 | | | | | | |
| 78 | 365.492 | 3083.644 | 1.36 | -0.45 | | | | | | |
| 40 | 349.805 | 3090.133 | 1.34 | -0.47 | | | | | | |
| 85 | 365.532 | 3080.921 | 1.28 | -0.51 | | | | | | |
| 47 | 359.985 | 3089.944 | 1.27 | -0.52 | | | | | | |
| 50 | 364.878 | 3090.151 | 1.26 | -0.52 | | | | | | |
| 56 | 361.106 | 3088.801 | 1.23 | -0.54 | | | | | | |
| 22 | 361.681 | 3092.725 | 1.18 | -0.58 | | | | | | |
| 28 | 350.488 | 3091.416 | 1.17 | -0.59 | | | | | | |
| 59 | 365.552 | 3088.735 | 1.16 | -0.59 | | | | | | |
| 72 | 367.126 | 3086.445 | 1.14 | -0.61 | | | | | | |
| 88 | 364.79 | 3079.679 | 1.13 | -0.61 | | | | | | |

Appendix IV—Tables of Data—Sorted by Descending Ammonia Concentrations (Continued)

| Location # | UTM EW | UTM NS | $\mu g/m^{-3}$ | Z-Score | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile |
|---|---|---|---|---|---|---|---|---|---|---|
| 76 | 367.632 | 3085.051 | 1.12 | -0.62 | | | | | | |
| 73 | 363.253 | 3084.984 | 1.05 | -0.67 | | | | | | |
| 4 | 353.528 | 3093.995 | 1.01 | -0.69 | | | | | | |
| 2 | 350.455 | 3093.918 | 1.01 | -0.70 | | | | | | |
| 71 | 365.526 | 3086.245 | 1.00 | -0.70 | | | | | | |
| 16 | 352.708 | 3092.678 | 0.95 | -0.73 | | | | | | |
| 81 | 364.813 | 3082.523 | 0.95 | -0.74 | | | | | | |
| 1 | 349 | 3093.997 | 0.93 | -0.75 | | | | | | |
| 66 | 364.695 | 3087.672 | 0.90 | -0.77 | | | | | | |
| 36 | 362.529 | 3091.466 | 0.88 | -0.78 | | | | | | |
| 86 | 366.964 | 3080.935 | 0.87 | -0.79 | | | | | | |
| 12 | 365.656 | 3093.919 | 0.86 | -0.80 | | | | | | |
| 33 | 358.033 | 3091.397 | 0.85 | -0.81 | | | | | | |
| 79 | 366.859 | 3083.675 | 0.79 | -0.85 | | | | | | |
| 75 | 366.251 | 3084.949 | 0.78 | -0.85 | | | | | | |
| 82 | 365.92 | 3082.466 | 0.77 | -0.86 | | | | | | |

Appendix IV—Tables of Data—Sorted by Descending Ammonia Concentrations (Continued)

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ | Z-Score | Grubbs 95% Conf. | 90% Conf. | 95% Conf. | 99% Conf. | 90%tile | 95%tile |
|---|---|---|---|---|---|---|---|---|---|---|
| 26 | 367.801 | 3092.597 | 0.76 | -0.87 | | | | | | |
| 67 | 366.14 | 3087.468 | 0.75 | -0.87 | | | | | | |
| 25 | 366.135 | 3092.527 | 0.74 | -0.88 | | | | | | |
| 11 | 363.988 | 3093.974 | 0.65 | -0.94 | | | | | | |
| 83 | 367.568 | 3082.632 | 0.61 | -0.97 | | | | | | |
| 60 | 367.007 | 3088.718 | 0.56 | -1.00 | | | | | | |
| 13 | 366.817 | 3093.561 | 0.55 | -1.01 | | | | | | |
| 68 | 367.688 | 3087.439 | 0.52 | -1.03 | | | | | | |
| 74 | 364.892 | 3084.898 | 0.50 | -1.04 | | | | | | |
| 77 | 364.158 | 3083.352 | 0.48 | -1.06 | | | | | | |
| 18 | 355.753 | 3092.733 | 0.32 | -1.17 | | | | | | |
| 21 | 360.199 | 3092.723 | 0.28 | -1.20 | | | | | | |
| 8 | 359.549 | 3093.996 | 0.25 | -1.22 | | | | | | |
| 10 | 362.521 | 3093.978 | 0.06 | -1.35 | | | | | | |

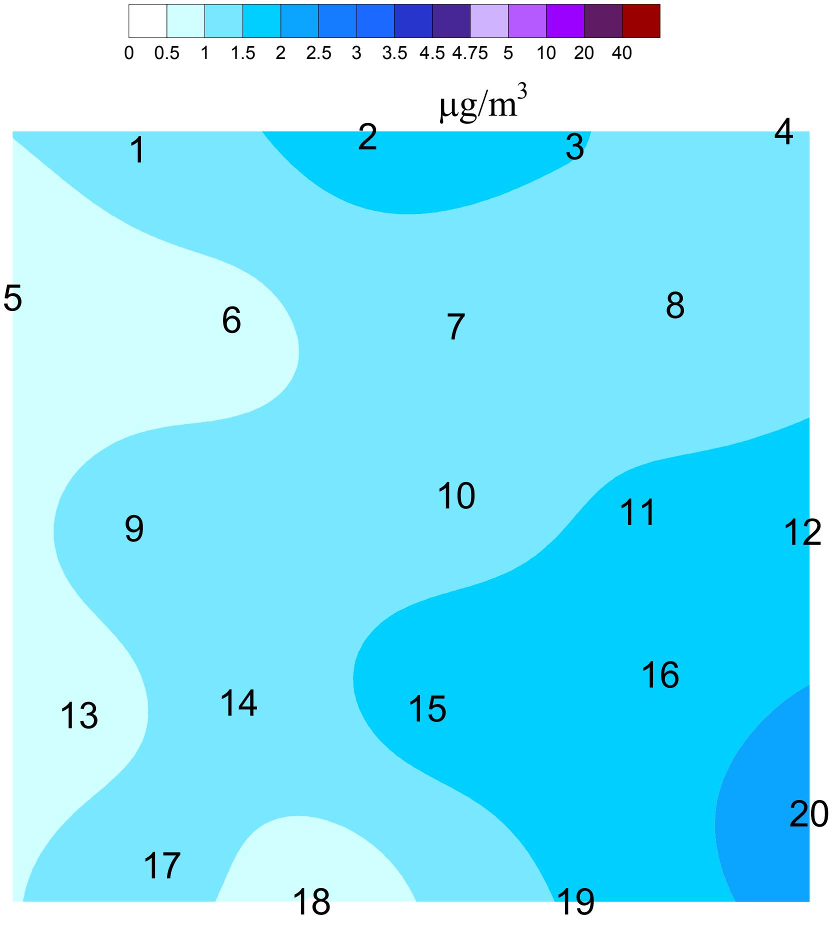

**Figure 31. Oldsmar Receptor Locations Week One**

**Table 14. Oldsmar Deployment 1 Data Sorted by Location Number**

| Location # | UTM EW | UTM NS | μg/m$^{-3}$ |
|---|---|---|---|
| 1 | 336.416 | 3101.877 | 1.2 |
| 2 | 336.946 | 3101.907 | 1.7 |
| 3 | 337.421 | 3101.884 | 1.4 |
| 4 | 337.903 | 3101.919 | 1.1 |
| 5 | 336.13 | 3101.537 | 0.6 |
| 6 | 336.633 | 3101.486 | 0.8 |
| 7 | 337.148 | 3101.471 | 1.1 |
| 8 | 337.652 | 3101.52 | 1.1 |
| 9 | 336.409 | 3101.007 | 1.2 |
| 10 | 337.148 | 3101.083 | 1.1 |
| 11 | 337.566 | 3101.045 | 1.5 |
| 13 | 336.281 | 3100.578 | 0.7 |
| 14 | 336.648 | 3100.607 | 1.2 |
| 15 | 337.081 | 3100.594 | 1.7 |
| 16 | 337.616 | 3100.671 | 1.6 |
| 17 | 336.472 | 3100.234 | 1.3 |
| 18 | 336.815 | 3100.151 | 0.4 |
| 20 | 337.96 | 3100.353 | 2.2 |

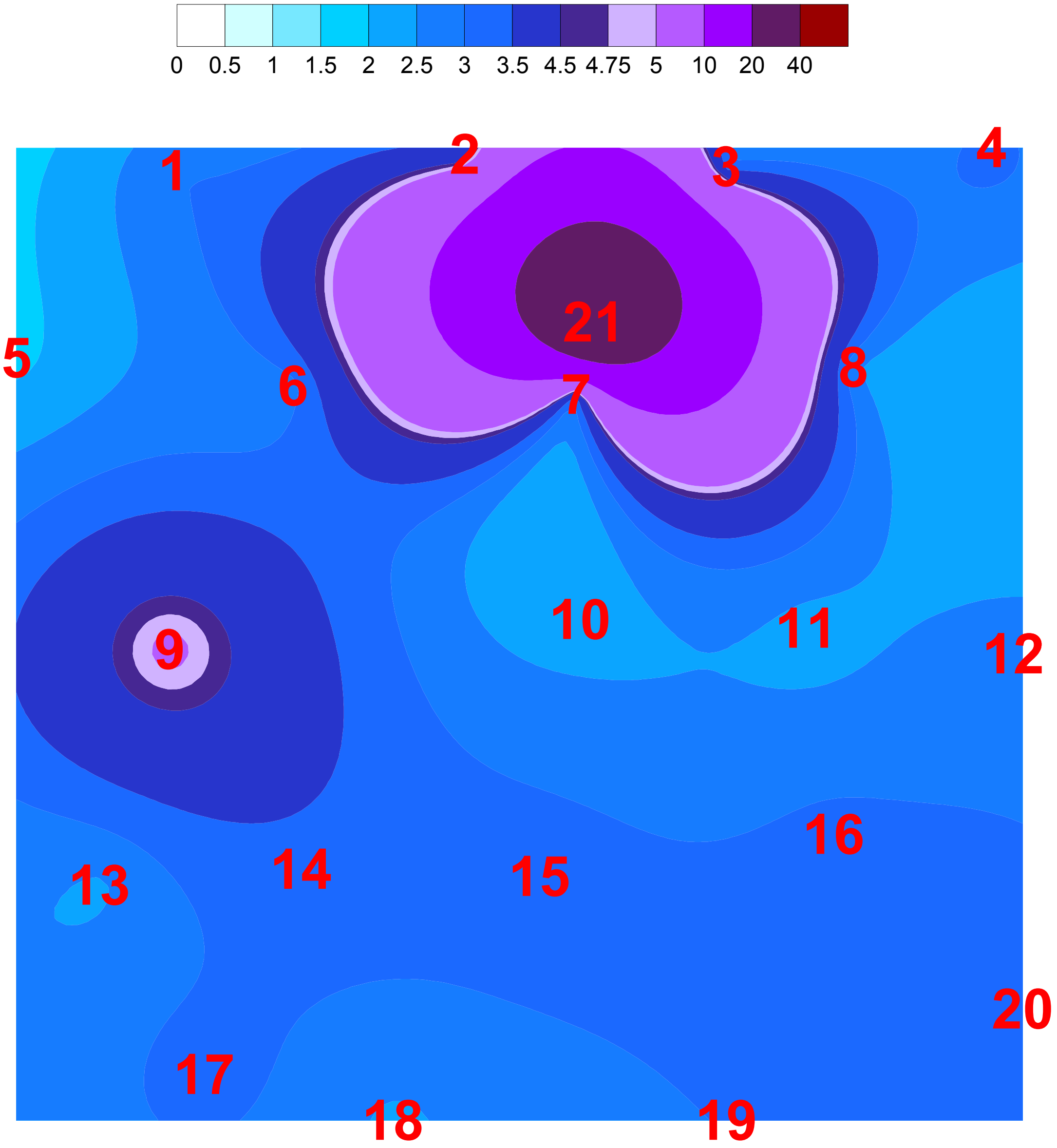

**Figure 32. Oldsmar Receptor Locations Week Two with Point 21**

**Table 15. Oldsmar Deployment 2 Data Sorted by Location Number**

| Location. # | UTM EW | UTM NS | µg/m$^{-3}$ |
|---|---|---|---|
| 1 | 336.416 | 3101.877 | 2.8 |
| 2 | 336.946 | 3101.907 | 3.6 |
| 3 | 337.421 | 3101.884 | 3.0 |
| 4 | 337.903 | 3101.919 | 3.1 |
| 5 | 336.13 | 3101.537 | 1.7 |
| 6 | 336.633 | 3101.486 | 2.7 |
| 7 | 337.148 | 3101.471 | 3.0 |
| 8 | 337.652 | 3101.52 | 2.4 |
| 9 | 337.148 | 3101.083 | 5.0 |
| 10 | 337.155 | 3101.061 | 2.2 |
| 11 | 337.566 | 3101.045 | 2.2 |
| 12 | 337.943 | 3100.999 | 2.6 |
| 13 | 336.281 | 3100.578 | 2.3 |
| 14 | 336.648 | 3100.607 | 3.1 |
| 15 | 337.081 | 3100.594 | 3.2 |
| 16 | 337.616 | 3100.671 | 3.0 |
| 17 | 336.472 | 3100.234 | 3.1 |
| 18 | 336.815 | 3100.151 | 2.3 |
| 20 | 337.96 | 3100.353 | 3.1 |
| 21 | 337.18 | 3101.602 | 36.8 |

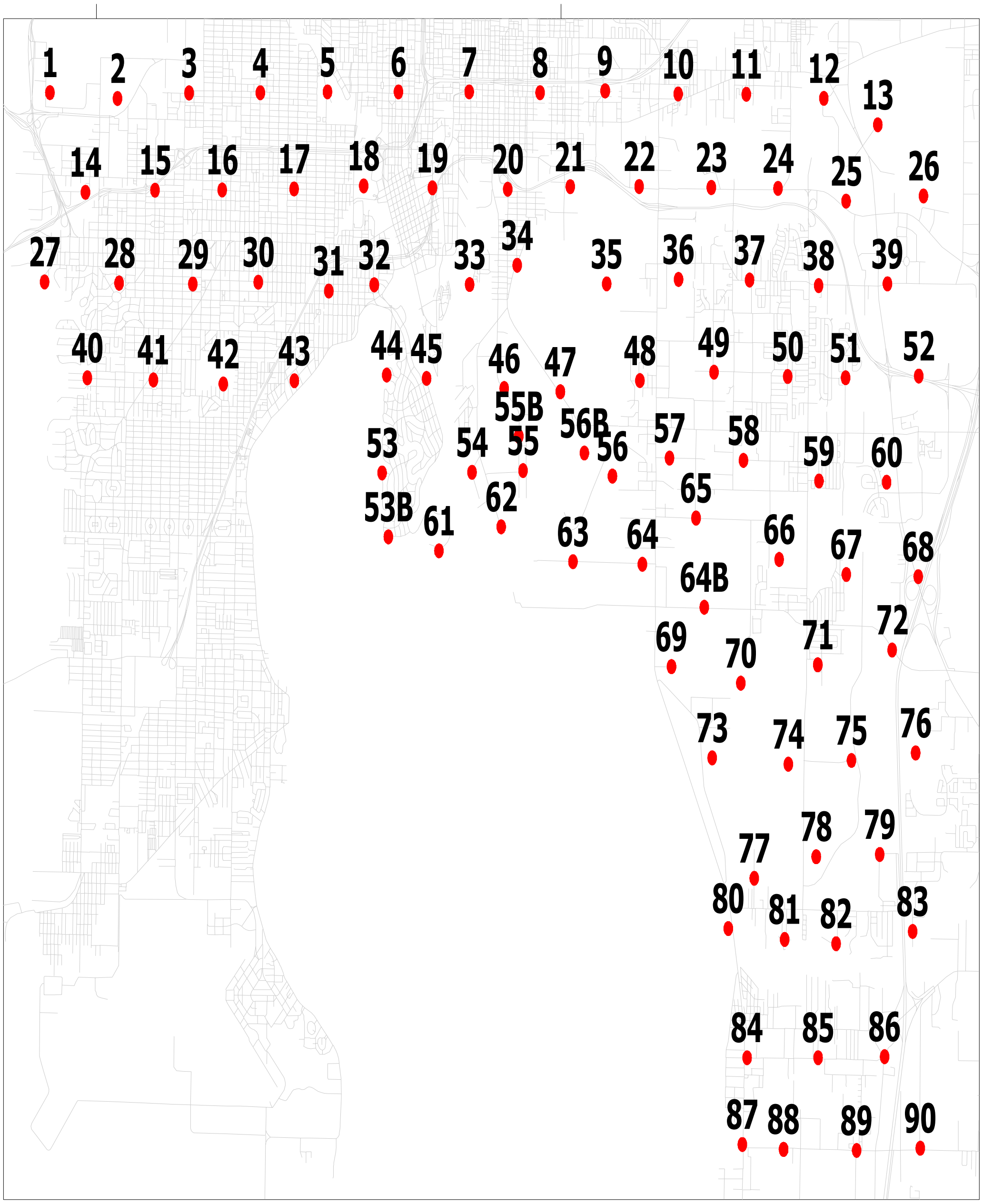

Figure 33. Tampa Receptor Locations

**Table 16. Tampa Deployment Data Sorted by Location Number**

The numbers are links to pictures and directions for each sampled location.

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ |
|---|---|---|---|
| 1 | 349 | 3093.997 | 0.93 |
| 2 | 350.455 | 3093.918 | 1.01 |
| 3 | 351.995 | 3093.992 | 1.41 |
| 4 | 353.528 | 3093.995 | 1.01 |
| 5 | 354.974 | 3094.007 | 1.36 |
| 6 | 356.501 | 3094.007 | 1.46 |
| 7 | 358.023 | 3094.007 | 1.67 |
| 8 | 359.549 | 3093.996 | 0.25 |
| 9 | 360.95 | 3094.021 | 1.50 |
| 10 | 362.521 | 3093.978 | 0.06 |
| 11 | 363.988 | 3093.974 | 0.65 |
| 12 | 365.656 | 3093.919 | 0.86 |
| 13 | 366.817 | 3093.561 | 0.55 |
| 14 | 349.765 | 3092.647 | 1.82 |
| 15 | 351.262 | 3092.675 | 2.85 |
| 16 | 352.708 | 3092.678 | 0.95 |
| 17 | 354.255 | 3092.692 | 1.94 |
| 18 | 355.753 | 3092.733 | 0.32 |
| 19 | 357.232 | 3092.707 | 2.35 |
| 20 | 358.852 | 3092.688 | 1.49 |
| 21 | 360.199 | 3092.723 | 0.28 |
| 22 | 361.681 | 3092.725 | 1.18 |
| 23 | 363.234 | 3092.712 | 2.00 |
| 24 | 364.67 | 3092.7 | 1.74 |
| 25 | 366.135 | 3092.527 | 0.74 |
| 26 | 367.801 | 3092.597 | 0.76 |
| 27 | 348.885 | 3091.432 | 1.57 |
| 28 | 350.488 | 3091.416 | 1.17 |
| 29 | 352.075 | 3091.403 | 1.70 |
| 30 | 353.484 | 3091.429 | 2.11 |
| 31 | 355.002 | 3091.309 | 2.09 |
| 32 | 355.98 | 3091.393 | 3.13 |
| 33 | 358.033 | 3091.397 | 0.85 |
| 35 | 360.982 | 3091.406 | 1.98 |
| 36 | 362.529 | 3091.466 | 0.88 |
| 37 | 364.057 | 3091.458 | 2.37 |
| 38 | 365.544 | 3091.382 | 1.54 |
| 39 | 367.025 | 3091.406 | 2.08 |
| 40 | 349.805 | 3090.133 | 1.34 |
| 41 | 351.228 | 3090.104 | 1.49 |
| 42 | 352.731 | 3090.049 | 2.41 |
| 44 | 356.249 | 3090.171 | 2.90 |
| 45 | 357.106 | 3090.125 | 2.22 |
| 46 | 358.777 | 3089.989 | 2.18 |
| 47 | 359.985 | 3089.944 | 1.27 |
| 49 | 363.293 | 3090.209 | 1.50 |
| 50 | 364.878 | 3090.151 | 1.26 |
| 51 | 366.125 | 3090.134 | 1.69 |

# Appendix V—Tables of Data Sorted by Location Number (Continued)

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ |
|---|---|---|---|
| 52 | 367.699 | 3090.157 | 1.86 |
| 53 | 356.148 | 3088.844 | 1.76 |
| 54 | 358.084 | 3088.853 | 6.78 |
| 55B | 359.088 | 3089.342 | 5.30 |
| 55 | 359.183 | 3088.876 | 4.29 |
| 56B | 360.503 | 3089.114 | 1.46 |
| 56 | 361.106 | 3088.801 | 1.23 |
| 57 | 362.335 | 3089.046 | 1.59 |
| 58 | 363.926 | 3089.014 | 2.68 |
| 59 | 365.552 | 3088.735 | 1.16 |
| 60 | 367.007 | 3088.718 | 0.56 |
| 61 | 357.373 | 3087.789 | 4.78 |
| 62 | 358.712 | 3088.114 | 3.42 |
| 63 | 360.258 | 3087.642 | 15.12 |
| 64 | 361.75 | 3087.607 | 13.20 |
| 64B | 363.083 | 3087.025 | 1.72 |
| 65 | 362.906 | 3088.233 | 11.85 |
| 66 | 364.695 | 3087.672 | 0.90 |
| 67 | 366.14 | 3087.468 | 0.75 |
| 68 | 367.688 | 3087.439 | 0.52 |
| 69 | 362.378 | 3086.22 | 2.13 |
| 70 | 363.869 | 3085.996 | 1.45 |

| Location # | UTM EW | UTM NS | µg/m$^{-3}$ |
|---|---|---|---|
| 71 | 365.526 | 3086.245 | 1.00 |
| 72 | 367.126 | 3086.445 | 1.14 |
| 73 | 363.253 | 3084.984 | 1.05 |
| 74 | 364.892 | 3084.898 | 0.50 |
| 75 | 366.251 | 3084.949 | 0.78 |
| 76 | 367.632 | 3085.051 | 1.12 |
| 77 | 364.158 | 3083.352 | 0.48 |
| 78 | 365.492 | 3083.644 | 1.36 |
| 79 | 366.859 | 3083.675 | 0.79 |
| 80 | 363.6 | 3082.671 | 1.37 |
| 81 | 364.813 | 3082.523 | 0.95 |
| 82 | 365.92 | 3082.466 | 0.77 |
| 83 | 367.568 | 3082.632 | 0.61 |
| 84 | 364.004 | 3080.921 | 1.70 |
| 85 | 365.532 | 3080.921 | 1.28 |
| 86 | 366.964 | 3080.935 | 0.87 |
| 87 | 363.902 | 3079.745 | 3.61 |
| 88 | 364.79 | 3079.679 | 1.13 |
| 89 | 366.362 | 3079.665 | 1.49 |
| 90 | 367.732 | 3079.696 | 4.47 |

## *Appendix VI—Further discussion of Ogawa®'s sampling rate*

A few changes in the rate calculations should be discussed. An attempt was made to determine if the Ogawa® supplied rate was determine empirically or calculated. Since those who could answer this question are in Japan and do not speak English clarifying this was no small feat. The first email reply listed two sampling rates that were calculated using two different diffusion coefficients and a third rate was given with no explanation. All three rates were different (32.3, 30.4 ml/min calculated, and 19.4 ml/min). It was understood why the first two calculated rates were different (they used different diffusion coefficients both of which were different than the diffusion coefficient used for this research) but it was not clear why the third rate was different. A request was made to clear up why the third rate was different. The response did not directly address this difference but offered a fourth recommended rate of 35.8 ml/min, which was described as the observed rate.

While reviewing the documents provided by Ogawa® it was noticed that the area of the screens listed in Table 4 (and used is subsequent rate calculations) and the area Ogawa® used for rate calculations was different. The area used was 0.152 $cm^2$ and the value given by Ogawa® was 0.371 $cm^2$. The sampling rate was recalculated using the area provided by Ogawa® and the average ammonia diffusion coefficient found in the literature of 0.249 $cm^2/s$. This yielded a sampling rate of 36.44 $cm^3/min$. Given this is within two percent of the recommended rate provided by Ogawa® either one could be used. However, for future research the 36.44 $cm^3/min$ rate is recommended by this author.