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A Passive Sampler for the Determination of Airborne Ammonia Concentrations near Large-Scale Animal Facilities

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Few data are available on the ammonia emissions of large-scale outdoor animal facilities in arid climates such as those found in California's San Joaquin Valley. Passive samplers provide an ideal tool for studying such large and heterogeneous area sources, because they are inexpensive, portable, and fully self-contained. UC Davis passive ammonia samplers incorporate modifications on a previous design, the Willems Badge, for ease of analysis. Citric acid was chosen as a coating medium though it performed as well as oxalic, sulfuric, and tartaric acids. Zefluor PTFE prefilters were used instead of Teflo though both showed the same resistance to diffusion. Citric acid-coated filters were stable for up to 10 weeks, though more so if stored in Petri dishes rather than in the sampling cassettes themselves. The most effective sampler position was found to be in a face-down configuration fixed into the wind to avoid debris and sensitivity to wind shifts. A new method of rinsing the filters within the cassettes by dropwise elution proved highly effective, with 85% of the ammonium being removed in the first 3 mL of the 10-mL rinse volume. Application of the sampler at a dairy in the Joaquin Valley revealed large variations in concentrations at different locations along the downwind fenceline, which correlated with animal populations and activities directly upwind. In addition, large variations in ammonia concentrations were observed in relation to time of day and animal activity. Field blank loadings were of 1.40 μg NH_4-N/filter (SD = 0.74 μg NH_4-N/filter). Replicate passive samplers placed side-by-side during sampling episodes agreed with a slope of 1.010 (standard error = 0.028). Impingers were used as a reference method to obtain the correlation between filter loadings and air concentrations, yielding an "effective sampling rate" for the passive samplers of 6.18 L/h (error = 0.23 L/h). Using a theoretical calculation, that "effective flow rate" was calculated to be 6.29 L/h. The method's limit of detection was found to be 82.5 μg NH_4-N/ m^3. Wind speed was found to theoretically affect linearity of sampler response only for speeds less than 0.92 m/s.

Introduction

Ammonia (NH_3) plays an important role in atmospheric chemistry because it is highly water-soluble and it is the

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dominant alkaline gas in the atmosphere (*1*). Because of this, NH_3 plays a key role in atmospheric acid−base reactions and in the formation of secondary aerosols. Ammonia is generated by both natural and anthropogenic sources, but the predominant sources are animal wastes and fertilizers (*2*). In the United States, California is the leading state in agricultural production; dairy products, cattle, and calves are among its top five agricultural commodities. Much of the state's agricultural activity occurs in the arid and fertile San Joaquin Valley.

On January 8, 1993, the San Joaquin Valley was classified by the U.S. Environmental Protection Agency as a serious nonattainment area for particulate matter (*3*). This status defined a need to develop sampling methodology to evaluate possible sources of airborne particulate matter, including the contributions of ammonia to the formation of fine secondary particulate matter. California dairies and feedlots are typically very large operations in terms of both surface area and herd size and are always outdoors. About 60% of beef cattle are raised in operations of 1000 head or more (*4*), while 78% of dairy cows are housed in operations of 500 head or more (*5*). To determine ammonia concentrations in and around these large nonuniform area sources, a large sampling array is necessary which requires the use of an effective sampling device that is inexpensive and portable enough to deploy simultaneously in large numbers, is unrestricted by the availability of power, and is easy to analyze for ammonia content.

There are numerous technologies available for the sampling and analysis of ambient atmospheric ammonia, and several field comparisons of their analytical performance have been carried out (*6−9*). To sample at large-scale outdoor animal facilities, two main concerns are the number of samplers needed to form a representative array to characterize the entire surface area and the limited availability of electrical power, in what is otherwise an area in which high concentrations are expected. Passive filter packs such as the Willems badge developed in Holland (*10*) have demonstrated the ability to meet these requirements: they are inexpensive, compact, and rugged and operate on the principle of diffusion, without need for pumps. The UC Davis passive ammonia samplers were adapted from the Willems badge. They innovate on that design by incorporating caps in either end of the sampler, making analysis more rapid and efficient. Specially intended for outdoor conditions near the source, they do require wind speeds greater than 1 m/s and concentrations of ammonia gas significantly higher than background.

The results presented here correspond to the sum total of data from laboratory- and field-derived development as well as data from typical field sampling. Six full-scale field trials have been conducted using these samplers. Results from these have been used to compute emission factors, which are presented elsewhere in the literature: the first three field trials together (*11*), the fourth on its own (*12*), and the fifth and sixth later (*13*). Data collected in the fourth trial as well as some comparison data from the fifth which was conducted at the same facility are presented here to fully demonstrate the method and sampling regimen.

Materials and Methods

Passive Sampler. Because ammonia gas is basic, acid-coated cellulose filters can be used to trap it. A Teflon prefilter is placed above the coated filter to establish a layer of undisturbed air between the filters and to exclude particulate matter. An additional boundary layer at the opening is created
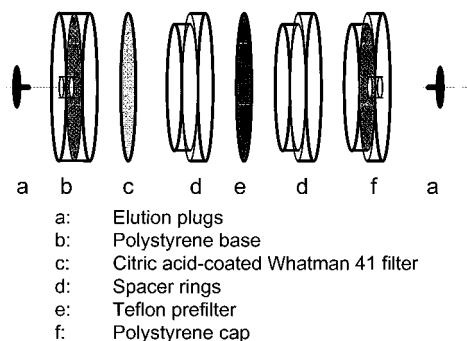
FIGURE 1. Schematic of the UC Davis passive ammonia sampler.

a: Elution plugs
b: Polystyrene base
c: Citric acid-coated Whatman 41 filter
d: Spacer rings
e: Teflon prefilter
f: Polystyrene cap

by the flow of wind, without which the sampler response to air concentration becomes nonlinear (14). As a whole, badge-type passive samplers have compared well in performance tests against more sophisticated and demanding devices when these conditions are met (8). Previous passive sampler designs require that the acid-coated filters be removed from the cassettes after exposure and submerged in water to dissolve the collected ammonia, drawing off the resulting solution for colorimetric determination. This technique proved time-consuming and was resolved by elution of the filter in the cassette itself.

The UC Davis passive ammonia samplers consist of 37-mm air sampling cassettes (37-mm styrene acrylonitrile filter holders, Gelman 01−038) originally intended for particulate sampling using vacuum filtration. They include a cap and filter-holding base, each having center inlets with plugs (see Figure 1) and two center spacer rings (37-mm monitor rings, Micron Separation Inc. DM 0000RING) to hold the filters in place during exposure. The distance between the filter and prefilter within the first spacer ring (d) is 1.03 cm, with a diameter of 3.29 cm. After the prefilter, in the second spacer ring, the opening consists of a cylinder 3.30 cm in diameter and 1.02 cm long, which then widens to a diameter of 3.78 cm for a length of 0.64 cm.

The acid-coated filters were prepared by dipping 80-filter batches of 37-mm diameter Whatman-41 chromatography paper disks individually in coating solution of 0.16 M citric acid in 1:5 ethanol:diethyl ether (prepared by dissolving 1.921 g of citric acid in 60 mL of the organic solvent combination). Organic solvents were chosen for their short drying time. After coating, filters were placed on a Teflon block to dry for approximately 10 s and then stored in sterile Petri dishes. Gelman 37-mm 2 micron pore Zefluor filters (Fisher 09-730-298) were used as prefilters, which are 1.52×10^{-4} m thick with a porosity of 60.5%. Filters were coated and cassettes assembled in a laminar-flow hood equipped with activated charcoal filter, covering the air intakes with citric acid-coated paper to prevent contamination. Field and laboratory blanks were set aside from each 80-filter batch.

During the development phase for the samplers, oxalic, tartaric, citric, and sulfuric acids were tested for use in the coating solution. In three separate experiments, three filter packs were prepared from each acid and exposed to ammonia gas of concentrations varying from 0 to 2000 μg NH$_4$−N/m^3 in a small gas chamber. In another series of chamber experiments to determine the capacity of the filters, triple replicates of the passive sampler were exposed to ammonia for 2 h at gaseous concentrations ranging from 0 to 4000 μg NH$_4$−N/m^3, more than four times the expected airborne concentrations found by Willems et al. (10). The chamber used in these experiments consisted of an acrylic tank 0.38 m deep, 1.02 m long, and 0.38 m high, equipped with a small muffin fan to achieve higher-than-threshold air flow inside. Aqueous solutions of ammonium chloride were acidified to release ammonia gas at desired concentrations.

Reference Methodology. In the field, active samplers were placed at various locations alongside the passive samplers as a reference method. An impinger (15−17) with a total of 40 mL of 3% H$_3$BO$_3$ was used as the reference method. The samplers consisted of two 60 mL glass vials with Teflon lined rubber septa connected in tandem by 1/8 in. Teflon tubing with plastic diffusion stones on the submerged end and a Teflon filter in a polypropylene holder at the inlet. Air flow rates were kept constant between 1.5 and 3 L/min and were recorded at the start and end of sampling. The resulting solutions were analyzed conductometrically for NH$_4$−N concentration by the UC Davis Division of Agriculture and Natural Resources (DANR) laboratory, and air concentrations were calculated by dividing the sample mass by the air volume.

Sample Analysis. Following exposure, cassettes were returned to the laminar-flow hood, and the two spacer rings were removed along with the prefilter, which was discarded. After removing the elution plugs, Teflon capillary tubes were connected to the center inlets. The samples were eluted using 10 mL of distilled water dispensed dropwise from a syringe through the cassette and into a sample vial, using gravity flow followed by compressed nitrogen gas to apply constant pressure to the eluant. Using an eight-channel manifold constructed for this purpose, eight cassettes were eluted simultaneously in about five minutes, allowing for high-throughput. After elution, sample solutions were analyzed by the UC Davis DANR laboratory using an established conductometric method (18). In this technique, the sample solution is injected into a continuous-flow sodium hydroxide solution, which carries the released ammonia gas to silicone rubber hollow tubes through which the gas diffuses to reach a second stream of deionized water; this solution then flows through an electrical conductivity cell that responds to ammonium in solution.

To assess whether pH might affect the accuracy of the conductometric analytical method, aqueous solutions of ammonium chloride were acidified to various pH levels and sent for blind analysis by DANR laboratory.

Data Analysis. Because the passive filters do not sample a well-defined volume of air, an "effective sampling rate" must be determined by comparison to a collocated reference sampler. Units are consistently presented in terms of μg NH$_4$−N in order to avoid confusion when switching between ammonia and ammonium forms. Reference air ammonia concentrations were calculated from measurements by the active boric acid bubblers using the mass of ammonia collected and the volume of air sampled. Ammonia mass measured on the passive filters was corrected for artifacts by subtraction of the average mass measured on field blanks. Corrected masses falling below double the standard deviation in the field blanks were considered "not detectable". Mass of ammonia collected per sampling hour was calculated from this corrected value.

The ratio of passive NH$_3$ mass/time to active concentration (mass/volume) provides the effective sample "flow rate" for the passive sampler, termed "F" and calculated in L/h, from which the air concentration can be determined

$$F = \frac{m_{filter}/t}{m_{bubbler}/vol} \qquad (1)$$

in which m_{filter} is the mass of ammonium nitrogen collected on passive sampler filters (in μg NH$_4$−N/filter), t is the exposure time (in hours), $m_{bubbler}$ is the mass of ammonium nitrogen collected in bubbler solutions (in μg NH$_4$−N/reference sample), and vol is the volume of air drawn through the bubbler (in L). Thus the slope of the linear correlation between the time-corrected NH$_4$−N passive filter mass and the NH$_4$−N concentration in air determined by the collocated
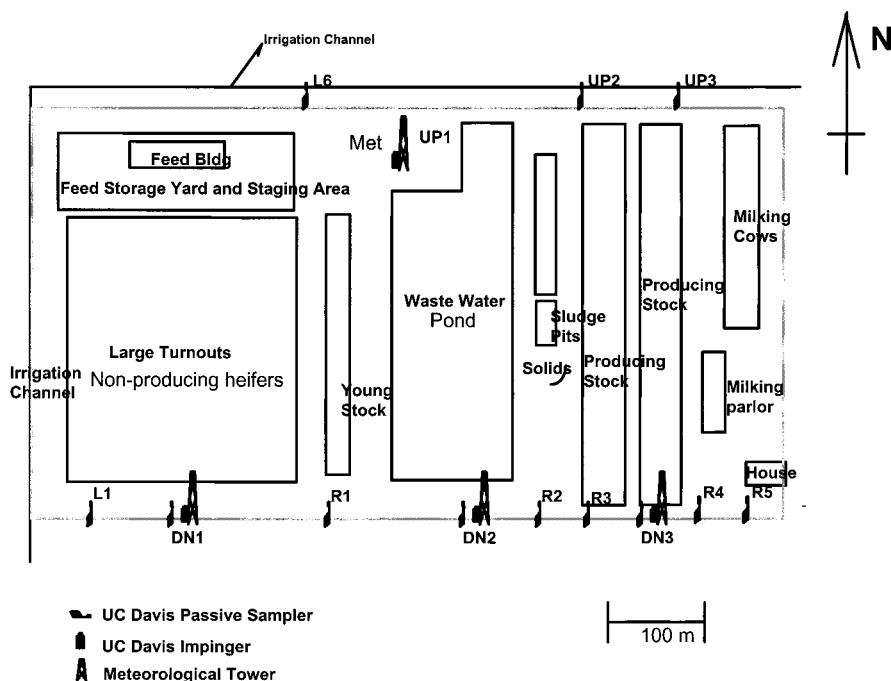
FIGURE 2. Layout of the dairy, with ammonia and meteorological monitoring locations.

active samplers provided estimates of the F-value, with the standard error of that slope as a measure of uncertainty.

In turn, this F-value was used to obtain the air concentrations of ammonium nitrogen at all other passive sampler locations, for which passive filter loadings per hour were simply divided by the F-value to obtain air concentration, while incorporating a conversion from L to m^3.

Site Description. The sampling array applied in the field study described here was developed to be fully representative of the downwind fenceline emissions while still allowing rapid sample changes at all locations at the beginning and end of sampling episodes. The dairy described in this work is located in the southern San Joaquin Valley; this study took place in February, 1999. It measures 840 m on the east–west axis by 375 m on the north–south axis and housed approximately 2200 milking cows at the time of the trial. There were also approximately 3850 nonproducing heifers on the property, but none under 2 months of age. Figure 2 shows the layout of the dairy with locations of ammonia and meteorology measurement devices.

The milking cows were located on the east side of the dairy, the nonproducing heifers were on the west side, and the waste management systems, including the wastewater lagoon, were located in the center. This freestall dairy uses a flush system to wash manure from concrete pads, where it is deposited by the milking stock, to the lagoon. The concrete pads covered 100% of the area accessible to milkers and about 10% of the area in heifer pens during the sample collection periods reported. The nonproducing heifers were penned in large turnouts in which only the feeding lanes (concrete areas) were flushed. The manure was flushed three times per day using water recycled from the lagoon. Before passing into the lagoon, the solids were separated from the waste stream in settling basins and pumped through a solids separator. The solids were trucked off-site approximately monthly for drying and then returned to the dairy to be used as bedding. No data have been collected at the drying site.

Sampling Array Description. An upwind-downwind sampling scheme was used to measure ammonia concentrations, with towers for meteorological monitoring and vertical profiling at three locations. The prevailing wind direction was from the northwest, and the south side of the

TABLE 1. Comparison of Sampler Collection Efficiencies Using Different Acids for Filter Coating[a]

acid	regression slope	regression intercept	R^2
citric	1.11×10^{-2} (1.9×10^{-3})	0.13 (3.09)	0.97
forced through 0	1.11×10^{-2} (0.7×10^{-3})	N/A	0.97
oxalic	1.30×10^{-2} (0.5×10^{-3})	0.04 (0.78)	1.00
forced through 0	1.30×10^{-2} (0.2×10^{-3})	N/A	1.00
sulfuric	1.24×10^{-2} (1.0×10^{-3})	0.08 (1.65)	0.99
forced through 0	1.24×10^{-2} (0.4×10^{-3})	N/A	0.99
tartaric	1.29×10^{-2} (0.8×10^{-3})	−0.01 (1.30)	1.00
forced through 0	1.29×10^{-2} (0.3×10^{-3})	N/A	1.00

[a] Regressions are between passive sampler ammonium-nitrogen loadings for the different coating acids (in μg NH_4-N/filter·h) and set chamber concentrations of ammonia-nitrogen (in μg NH_4-N/m^3).

dairy was defined as the downwind side under these conditions. Nine passive sampler stations were placed along the south side of the dairy and three along the north side. Replicate passive samplers and reference active samplers were used at four locations, termed DN1, DN2, DN3, and UP1 (Figure 2). Sampling duration was based on meteorology, with a minimum of approximately 2 h to collect sufficient ammonia on the passive filter, based on prior experience.

Passive samplers were placed 2 m above the ground; active samplers had inlets at 2, 4, and 10 m above ground. To expose passive samplers, caps were removed and samplers were oriented in a "face down" configuration (with the Zefluor filter facing down) so that the flow of wind traversed the open face of the cassette. To hold the sampler, an aluminum prong was designed to fit atop a six-foot steel fencepost. This holder design positions the sampler away from the post and into the wind, to avoid eddy and turbulence effects. The sampler is kept face-down to avoid dust and dew deposition.

Results and Discussion

Sampler Development. In comparing various acids for coating, no significant difference in response or performance consistency was found between the four acids (see Table 1). Citric acid was ultimately chosen because of its ease of handling and dissolution during the coating step. Recent
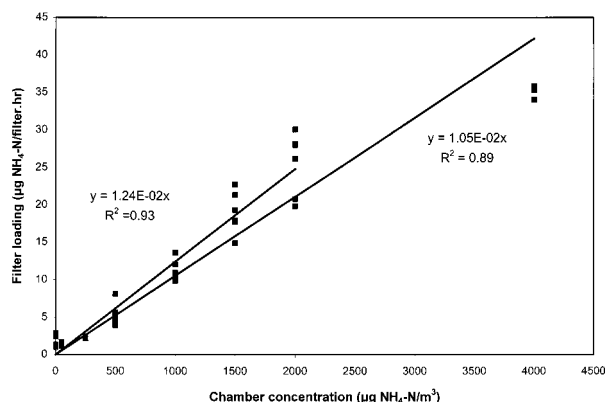
FIGURE 3. Sampler response to set ammonia concentrations in chamber experiments, showing the regression with and without points for 4000 μg NH$_4$−N/m^3.

pH	regression slope	regression intercept	R^2
1.00	0.99 (3.8×10^{-3})	0.11 (2.9×10^{-2})	1.00
	1.00 (4.5×10^{-3})	N/A	1.00
2.00	0.99 (7.0×10^{-3})	0.14 (5.4×10^{-2})	1.00
	1.00 (6.9×10^{-3})	N/A	1.00
3.00	1.00 (5.6×10^{-3})	0.04 (4.2×10^{-2})	1.00
	1.00 (4.4×10^{-3})	N/A	1.00
4.00	0.99 (11.3×10^{-3})	−0.09 (8.5×10^{-2})	1.00
	0.98 (8.8×10^{-3})	N/A	1.00
5.00	0.98 (5.6×10^{-3})	−0.05 (4.2×10^{-2})	1.00
	0.98 (4.4×10^{-3})	N/A	1.00
6.02 (unacidified)	0.98 (5.6×10^{-3})	0.18 (20.9×10^{-2})	0.99
	0.99 (21.7×10^{-3})	N/A	0.99

[a] Regressions are between known ammonium-nitrogen concentrations in solutions at different pH's (in ppm) and instrument-detected ammonium-nitrogen concentrations (in ppm).
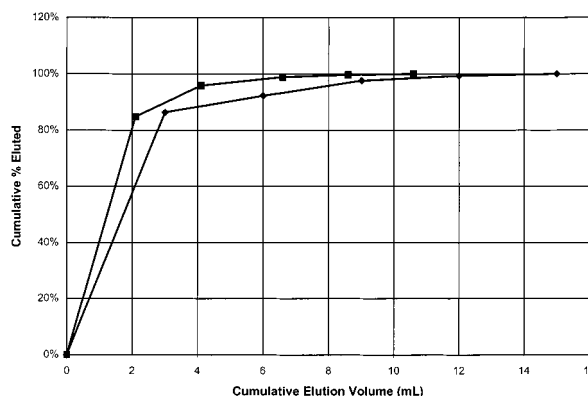

FIGURE 4. Elution profile for the passive sampler for two replicate runs.

research has indicated that citric acid volatility may have compromised the data collected during these studies *(19)*. While this had been found to be true for citric acid-coated glass annular denuders, data do not seem to support that this effect is significant in this sampler, since sampler response remains fairly stable from one field application to the next. It may, however, participate in the error, and further study should be made to investigate this.

In testing the linear range of the sampler response, cassettes were exposed to concentrations from 0 to 4000 μg NH$_4$−N/m^3 in a small chamber. Figure 3 shows the operating range of the samplers as determined in the chamber experiments. A linear response is found to 2000 μg NH$_4$−N/m^3, which seems to taper off between 2000 and 4000 μg NH$_4$−N/m^3, presumably due to saturation; that range of concentrations was significantly higher than those encountered in the field.

Experiments were also conducted to study the effect of the prefilter on collection efficiency. PTFE membranes were chosen because of their hydrophobicity and low reactivity. Two such membrane disk filters were compared, Gelman Zefluor and Teflo 37-mm filters, both with 2-micron pores. Four samplers of each type were exposed for 2 h at a local dairy. Analysis of ammonia loadings showed an average 5.76 μg NH$_4$−N/filter for the cassettes equipped with Teflo prefilters with a standard deviation of 1.12 μg NH$_4$−N/filter, whereas those with Zefluor prefilters had loadings of 5.22 μg NH$_4$−N/filter with a standard deviation of 0.90 μg NH$_4$−N/ filter. Since no significant difference in performance was found, Zefluor prefilters were chosen due to cost considerations.

In addition, experiments were carried out to determine the storage stability of both unexposed cassettes and eluted samples. No increase was seen in NH$_3$ artifact on coated filters when weekly measurements were conducted over a period of 10 weeks. There was, however, a larger artifact measured on filters stored in the cassettes (average = 2.63 (1.01) μg NH$_4$−N/filter, $n = 40$) than on filters stored in Petri dishes (average = 1.07 (0.34) μg NH$_4$−N/filter, $n = 40$). The pH of samples post-elution with distilled deionized unacidified water was approximately 1.0, likely due to the dissolved citric acid coating removed from the cassettes during elution. This low pH protected the sample from degradation when analysis could not be performed immediately after elution. Reanalyses conducted after up to 13 weeks in storage at room temperature showed an average decrease in NH$_4$−N concentration of 8% (standard deviation = 10%, $n = 4$). The acidity of the samples was found to have no effect on the accuracy of the conductometric analysis, as shown in Table 2.

Several sampling positions were tested in field conditions over the course of development, including holding the sampler face up, sideways, and placing them on rotating windvanes. Face-up sampling resulted in the deposition of particulate matter and debris onto the exposed cassette and fouled the prefilter, while sideways sampling caused sensitivity to even mild changes in wind direction, evidenced by decreased precision in replicates. Rotating windvane holders did not provide any added benefits but were impractical for field use and impeded the side-by-side exposure of replicate samplers. As a result, a simple prong was chosen to hold the passive sampler face-down into the wind 8 in. from a steel fencepost.

In terms of sample handling and analysis, the use of syringes to elute exposed filters in situ proved an effective method: elution profiles show that 85% of the collected ammonia is actually eluted in the first 3 mL of the 10-mL rinse solution (see Figure 4). Prior work has shown that while water can be distilled to remove all ammonia and thus decrease its contribution to overall laboratory contamination, high laboratory air ammonia concentrations can rapidly lead to new water contamination *(20)*. Thus the ability to keep the filters as well as the wash solution in an environment separate from laboratory air represents a significant decrease in the risk of contamination.

Blank and Replicate Samples. For each lot of 80 filters coated, prepared, and packed into sampling cassettes, four were set aside as blanks. Of these, two were left at the laboratory and two were taken to the field under the same conditions as other samplers but were never exposed. These blanks were used to monitor the quality of individual lots of
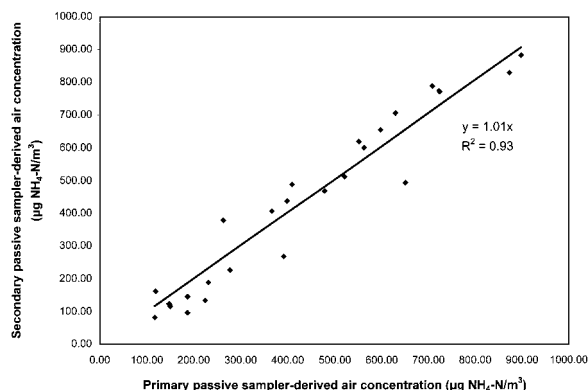
FIGURE 5. Correlation between passive sampler replicate pairs placed less than a foot apart.
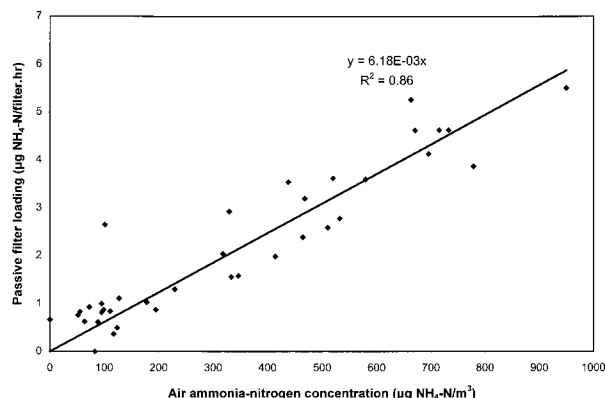

FIGURE 6. Correlation between passive sampler loadings and collocated active sampler air ammonia concentrations for all locations in the specified site.

samplers as well as to calculate the limits of detection and error for the passive samplers. In this field trial, laboratory blanks had an average loading of 1.15 μg NH_4-N/filter (standard deviation = 0.81, $n = 15$), while field blanks had an average loading of 1.40 μg NH_4-N/filter (standard deviation = 0.74, $n = 16$). Uncoated filter paper had an average mass of 1.85 μg NH_4-N/filter (standard deviation = 1.99, $n = 32$), establishing the primary source of NH_3 artifact on blank filters to be the cellulose itself. The limit of detection for the samplers, being double the variability in the field blanks, was calculated to be 1.48 μg/filter. Hence blank-subtracted samples with loadings below this level were reported as "not detectable".

Replicate samples were collected by placing passive samplers side by side, which were then submitted to the same exposure times and analytical methods. As shown in Figure 5 agreement between replicate samples was good, with a slope of 1.01 (2.8×10^{-2}), with intercept set to zero. Without the intercept set to zero, the least-squares regression reveals a slope of 1.08 (5.4×10^{-2}), with an intercept of -0.24 (0.16). From this plot, a clear limit appears in the lower concentrations, below which samples typically fall below the variability in the blanks, establishing the limit of detection for the method at 82.5 μg NH_4-N/m³.

Standardization with Active Samplers. The passive samplers were calibrated using the air ammonia concentrations measured by reference active samplers collocated with passive samplers. The empirical relationship between passive loadings and air concentrations is shown in Figure 6. As shown in the relationship described in eq 1, the F-value or "effective sampling rate" for the passive sampler was calculated to be approximately 6.03 L/h with a standard error of 0.18 L/h. At a different site in winter of the same year, the
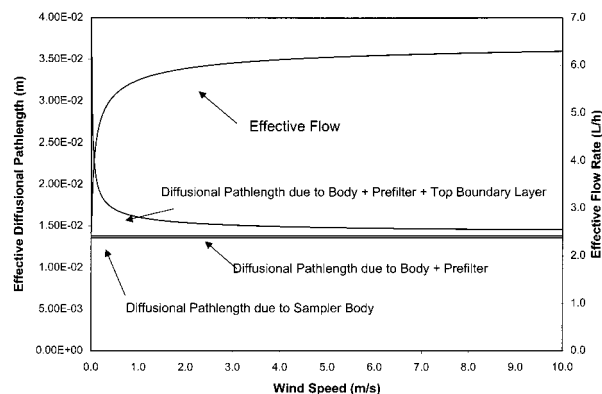

FIGURE 7. Effect of wind speed on the diffusional path length and effective flow rate through the sampler.

F-value was calculated to be 7.22 L/h with a standard error of 0.37 L/h.

The effective flow rate for the sampler can also be determined mathematically according to the theory described by Kasper and Puxbaum *(14)*, which is based on the sum of individual sampler components' contributions to the diffusional resistance of the different air layers in and above the sampler. If all four layers of air (the air layer between the filter and the prefilter, the air layer within the prefilter, the air layer within the open recess above the prefilter and the boundary layer above the open recess due to the flow of wind) are taken into account and assumed to be calm as described in theory for the Kasper sampler, then the calculations yield a flow rate one-third that which was observed. However, if the air layer within the open recess is neglected, the theoretical effective flow rate reaches a value of 6.29 L/h, which closely approximates the effective flow rates observed (see Figure 7). Because the open recess is very wide and shallow, it is unlikely it would create a calm layer of air. The empirical value seems to remain relatively stable for all ambient sampling conditions encountered and lends support to the theoretical basis for passive samplers' mechanism of action. For comparison, the original Willems badge was reported to have badge deposition rates between 174 and 278 s/m, which convert to values between 6.9 and 11.0 L/h *(10)*.

Using the same theoretical approach, the effect of wind speed on effective flow rate can also be calculated. These calculations suggest that the effective flow rate remains stable and approximately constant for all wind speeds above 0.92 m/s with a maximum error of 10%. Wind speeds observed during the sampling episodes averaged 2.145 m/s (SD = 1.414), and they exceeded the 1 m/s threshold 84% of the time. Attempts were made to verify this relationship experimentally using a wind tunnel, but low wind speeds and constant low concentrations of ammonia were difficult to achieve, so the experiments were unsuccessful and results inconclusive.

As shown in Figure 6, concentrations encountered in the field were high, considering the typical range of concentrations from remote areas and severe air pollution episodes in urban areas have been observed to range between less than 0.02 ppb to 100 ppb (or 11.4×10^{-3} to 57.3 μg NH_4-N/m³) *(1)*. Clearly this method is specifically useful only for areas of high concentrations.

Concentrations. The typical field experiments described here included sampling during as much of the day and night as was feasible. Because the passive samplers are inexpensive and portable, they could be placed ubiquitously in and around area sources. Results from such extensive application show that the NH_3 concentration downwind of a dairy responds
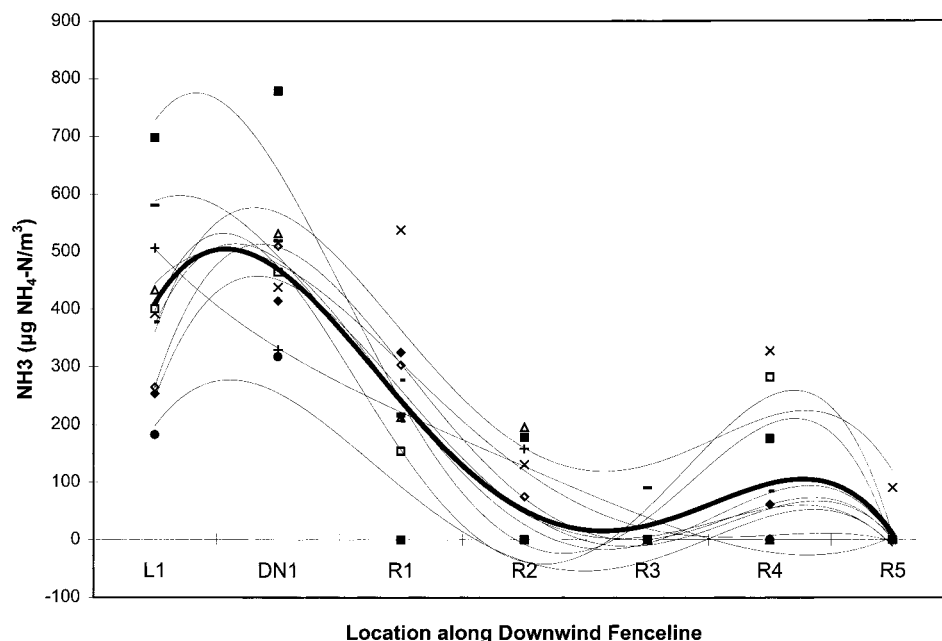
FIGURE 8. Ammonia concentrations along downwind fenceline according to position, each line representing one sampling period, with the heavy line marking the average of all lines.

strongly to several variables, including position along the downwind edge, time of day and related animal activity, and weather.

Figure 8 shows the variation in ammonia concentration along the downwind fenceline, from west to east. While there is a large variation between individual sampling periods, all follow the same general trend. The concentration profiles correspond well with the animal populations directly upwind, with a surprising minimum downwind of the wastewater storage pond. While this contradicted assumptions that the storage pond would constitute an ammonia emission "hot-spot", it can be explained in terms of the rapidity with which ammonia volatilizes from manure after excretion, peaking in less than 5 h and completing within 24 h in undisturbed systems (*21*). Figure 8 also shows higher concentrations downwind of the nonmilking stock to the west than the milkers to the east. There were about twice as many heifers as cows at the dairy, but this observation may also be related to the differences in waste management strategies for the two populations (see Methods). In addition, there is considerable evidence that the physiological, nutritional, and metabolic differences between the two populations could produce differences in the amounts of NH_3 volatilized from the excreta (*13, 22−24*).

Both active and passive samplers deployed in vertical profiles up to 12 m provided sufficient resolution of $NH_4−N$ concentration gradients for flux calculation, which are presented elsewhere (*11−13*). The gradients at these points were used to estimate fluxes from concentrations measured at all other locations along the fenceline (Figure 2) and were then integrated to compute emission factors for the dairy that accounted for the heterogeneity of the source more completely than could have been realized without the passive samplers.

Figure 9 shows the diurnal variations in ammonia concentrations during this study and during one performed 2 years prior at the same site. Though both the 1997 and 1999 studies were performed during the cold season under remarkably similar meteorological conditions (average temperatures = 13 and 12 °C, standard deviations 4 and 3 °C, respectively), with high relative humidity (average = 72% both years, standard deviations 13 and 15%, respectively), a difference in concentrations was measured between years.
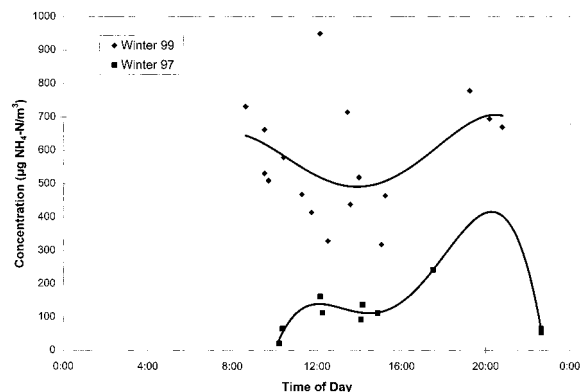

FIGURE 9. Ammonia concentrations at the DN1 position (see Figure 2) during different times of day in 1997 and 1999.

This correlates with a 60% increase in the number of heifers on the dairy from 1997 to 1999 (*12*). The variability in ammonia concentrations due to time of day is evident in both years. Diurnal and seasonal variations are a result of temperature, humidity, and wind speed fluctuations as well as differences in animal activity and feeding schedules. The finding is fully consistent with previously observed trends (*25*) which were attributed primarily to wind speed and temperature inversions. The diurnal variation observed in ammonia concentrations, however, gets corrected for in calculations of emission rates (*13*).

The large variations in concentrations observed in relation to sampling location along the downwind edge, time of day, season, and meteorological conditions demonstrate that sampling for ammonia at large area-sources requires a sampling strategy capable of taking all these variables into account.

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