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Ammonia: Measurement Issues

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Ammonia (NH_3) is a colorless gas under standard conditions, whose pungent odor is easily discernible at concentrations above about 10 ppm, and to some persons, down to almost 1 ppm. It is the major basic neutralizing gas in the atmosphere so it has an important role in the neutralization of atmospheric acids generated by the oxidation of sulfur dioxide (SO_2) and nitrogen oxides (NO_x). As a result, the reaction product of NH_3 , ammonium (NH_4^+), forms an aerosol that is a major component of atmospheric aerosols and in precipitation (Asman et al., 1998). Other organic forms also exist, such as amines and organic N compounds (not currently studied), but the concentrations of these components are generally negligible by comparison (Van der Eerden, 1982).

Most NH_3 is emitted near the earth's surface and a large proportion of these sources are of anthropogenic origin (Bouwman et al., 1997). Land-based NH_3 emissions are mainly from agricultural production (Fig. 15–1.). These sources are numerous, have low source heights and are scattered both temporally and spatially. One anthropogenic component of Fig. 15–1 not included is NH_3 emissions from motor vehicles. Recent studies (Fraser & Cass, 1998) found that automobile emissions in the South Coast Air Basin (surrounding Los Angeles, CA) were comparable to livestock waste emissions with about 15% each of the total emissions inventory (Russell et al., 1988; Dickson, 1991). A comparison of vehicle emissions in North Carolina (McColloch, 2001, personal communication) with emissions from swine production [using Harper et al. (2004a) emission factors] suggested that automobile emissions were about 28% of that from swine production. A reevaluation of nationwide anthropogenic emissions is needed with the increase in three-way or dual-bed catalytic converters (Fraser & Cass, 1998) on vehicles, which are designed to reduce N oxides to the atmosphere.

There has been recognition of gas-phase NH_3 since the 19th century but the interest was focused largely on its effect as a fertilizer (Lawes & Gilbert, 1851). It was not until the mid 20th century that techniques were available to determine that plants emit and absorb NH_3 in relation to an NH_3 compensation point in plants (Meyer, 1973; Farquhar et al., 1983). Because of the ability of NH_3 to react with measurement equipment, many of the early studies were somewhat inaccurate; however, noninvasive techniques were developed and used to evaluate net

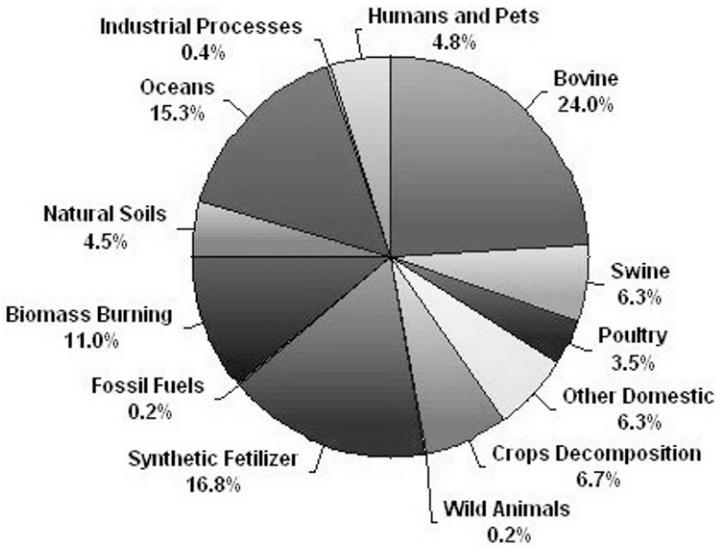


Fig. 15-1. Global ammonia emissions (after Bouwman et al., 1997) [Note: Ammonia emissions for vehicles are not included in this inventory.]

transport of NH_3 in cropping systems (Denmead et al., 1978; Harper et al., 1983, 1987) and using these techniques, it was found that significant amounts of NH_3 can be absorbed from the atmosphere under periods of diurnal and seasonal plant N stress.

The release of anthropogenic NH_3 into the atmosphere has increased in many regions of the world, which has led to deposition of N downwind from major sources (Asman, 1994). Areas of high deposition may show forest decline (Nihlgard, 1985) and some estimates have suggested that atmospheric deposition may contribute 35 to 60% of the total N loading to some coastal waters (Paerl, 1995). Although NH_3 is basic, it may still contribute toward acidification of ecosystems, as 1 mol of ammonium sulfate (NH_4SO_4) can result in the release of 4 mol of hydrogen ions (H^+) by nitrification (Van Breemen et al., 1982). Dry deposition of NH_3 also can result in the release of one proton by nitrification. These concepts are, however, a simplification and the net acidification from atmospheric $\text{NH}_3 + \text{NH}_4^+$ is complex and will vary with respect to the nutrient status of the soil. Indeed, Galloway (1995) has suggested that NH_3 emissions are, potentially, more acidifying than current emissions of SO_2 or NO_x depositions.

Ammonia volatilization is a complex physical and chemical process (Freney et al., 1983) and emissions are generally related to four factors: NH_4^+ concentration of the medium, temperature of the medium, pH (hydrogen ion concentration where $[\text{H}^+] = 1 \times 10^{-\text{pH}}$ of the solution) of the medium, and turbulent transport of the NH_3 from the medium. The chemical effect, the partial pressure of NH_3 at the solution surface, may be explained as a function of Henry's law and the dissociation relationship of $\text{NH}_3 = \text{NH}_4^+$, which can be expressed by the generalized relationship,

$$P_{(\text{NH}_3)} = RT \left(10^{n_1 - \frac{n_2}{T}} \right) \frac{[\text{NH}_4^+]}{\text{H}^+} \quad [1]$$

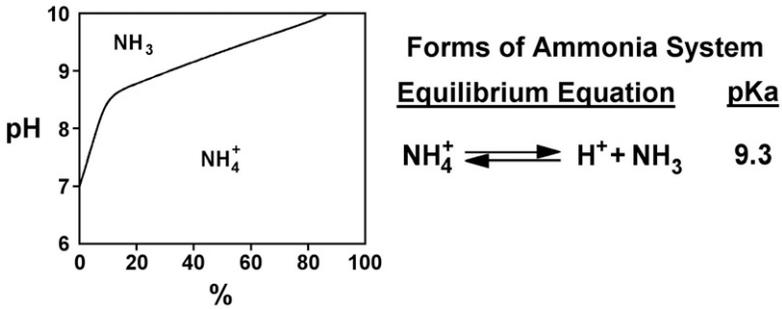


Fig. 15-2. Equilibrium relationship for ammoniacal N and resultant amount of NH_3 and NH_4^+ as affected by pH of a dilute solution (after Koelliker & Kissel, 1988).

where R is the gas constant and n_1 and n_2 are derived constants (Denmead et al., 1982; Zhang et al., 1994; Harper et al., 2004a). The equilibrium equation for this reaction is shown in Fig. 15-2, along with the percentage of ammoniacal N ([AN]) that exists as NH_4^+ and NH_3 for a dilute solution.

The physical effect is the ability of the wind turbulence to remove NH_3 from the water-surface-atmospheric-boundary layer. For a soluble gas, such as NH_3 , the rate-limiting boundary layer is the diffusive air boundary layer. Removal of NH_3 from this boundary layer is a function of the atmospheric turbulence (windspeed) and atmospheric stability [measured by Richardson's Number (Richardson, 1929)]. During seasonal studies when climatic conditions were reasonably constant, turbulence was found to account for as much as 75% of the variability in emissions over a swine lagoon (Harper & Sharpe, 1998, unpublished data). An example of the interrelationship of windspeed and animal waste lagoon temperature with NH_3 emissions is shown in Fig. 15-3. Variability in emissions among sources may be affected by the pH of the medium. As gaseous NH_3 escapes from the medium solution, NH_4^+ in the solution dissociates to NH_3 to maintain the partial pressure of gaseous NH_3 in the solution. Interestingly, as NH_3 is lost by volatilization, NH_4^+ ions dissociate to NH_3 and H^+ to maintain equilibrium in the solution (Koelliker & Kissel, 1988). The net result is that volatilization tends to decrease pH and reduce the volatilization rate. A number of emissions models have been developed, basing the inputs on these measured components (Denmead et al., 1982; Zhang et al, 1994; Harper et al., 2000b, 2001, 2004a,b; DeVisscher et al., 2002;). Characterization of the turbulent component is the most difficult of these parameters to determine.

Conclusive studies on NH_3 emissions from crops and animal production systems depend on reliable experimental and analytical techniques. The purpose of this chapter is to discuss field and analytical methods for measurement of NH_3 losses. Methods employed most frequently to measure gaseous loss include: enclosure methods, in which the flux density of the gas at the surface is calculated from changes in gas concentration in an enclosure placed over the surface; noninterference micrometeorological techniques, in which the vertical or horizontal flux density of the gas is measured in the free air above the soil, plant, or water surface; and release of known tracer gases for ratioing the known and unknown emissions.

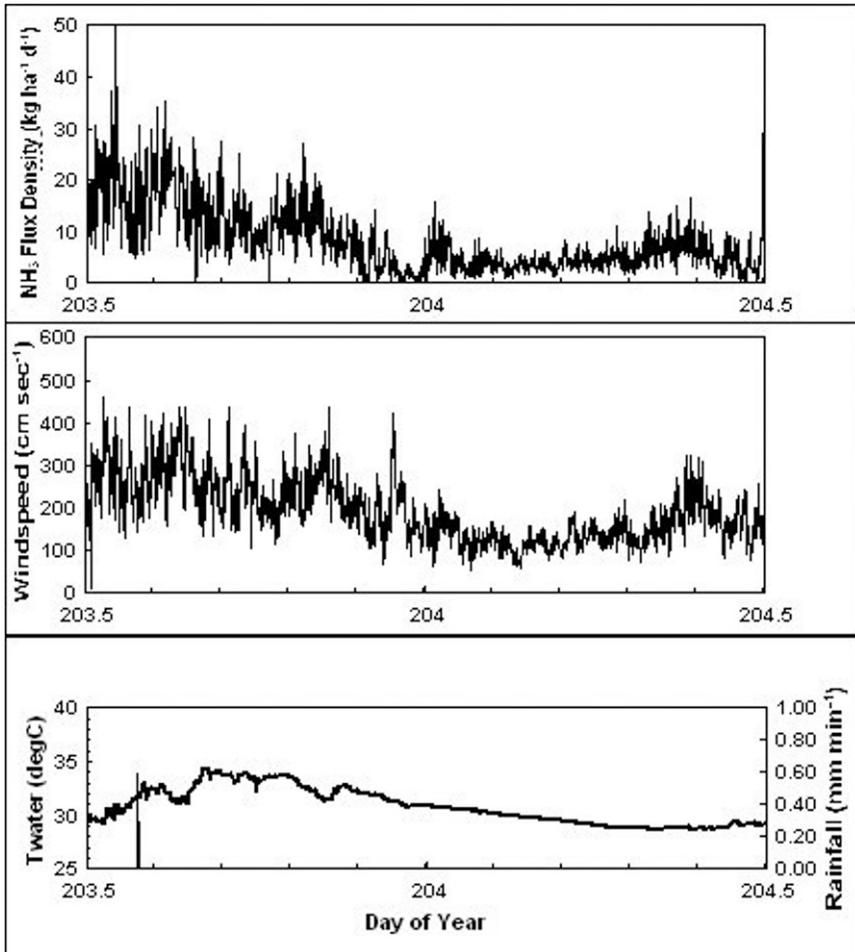


Fig. 15-3. Ammonia flux density variation compared with windspeed and lagoon water temperature over a swine lagoon (after Harper et al., 2001, 2004a).

METHODS FOR MEASURING AMMONIA CONCENTRATION

Historically, there has been a lack of reliable, fast-responding, and sensitive sensors for the measurement of NH₃. There are several sensors becoming available and this review will not try to characterize available sensors because technologies are rapidly changing. There are, however, several classes of sensors for NH₃ measurement.

Gas-Washing

This technique has been used as a standard for many years. Much of the early work on atmospheric transport was accomplished, by necessity, using this

technique. The technique employs absorption of the atmospheric gaseous NH_3 into an acid, such as sulfuric or phosphoric, where the air-flow rate through the acid and the length of time are known or measured. Both NH_3 and volatile amines are “scrubbed” from the air sample but the total mass of volatile amines is normally quite small (Hutchinson et al., 1982). The NH_3 average concentration is then calculated across the sample period from the solution NH_4^+ concentration and the known flow rate. If the air is dusty or hazy, the incoming air sample should be filtered to avoid particulate contamination. With considerable sampling and chemical analysis care, during a period of 2 to 4 h a sensitivity of 0.5 to $1.0 \mu\text{g m}^{-3}$ can be obtained (Weier et al., 1980). In situations with considerable dust, the air should be filtered to remove aerosol dust particles that may contain NH_4^+ . Additionally, gaseous amines will be absorbed but even in areas of high NH_3 emissions the levels of amines will be rather small (Hutchinson et al., 1982). With background atmospheric concentrations ranging from 5 to $15 \mu\text{g m}^{-3}$, this technique has been used extensively and continues to be used where fast-sampling is not necessary and high-sensitivity is required. The technique is, however, very labor intensive and prone to sample-contamination. Consequently considerable quality assurance and control is required.

Annular Denuders

The principle of this technique is to pull air through glass tubes coated with either basic solution (such as sodium carbonate) for collection of acid gases or an acid solution (such as citric acid) to absorb basic gases. The denuder is a high surface area glass collection device designed to exclude particles from the collection surface allowing it to separate the vapor phase (NH_3) and particulate phase (NH_4) in ammoniacal air samples. In air, molecules diffuse more quickly than particles and gas-phase NH_3 diffuses from the laminar flow to the coated wall while particles pass through the tube. Because of the much higher diffusivity of gases as they pass through the denuder, they have a higher probability of being collected by the coating, whereas the fine particles have a lower probability of collection, thus residence time in the denuder tube should be as short as possible (approximately a few seconds) to avoid the interference of NH_3 evaporated from particles and gas-particle and particle-particle reactions. There are problems that must be addressed in these systems (McColloch & Shendrikar, 2000) as comparisons to other measurement methods have shown that citric acid denuders consistently collect approximately 80% of the NH_3 measured by a chemiluminescence analyzer. The relatively low precision found by McColloch and Shendrikar may suggest a random fluctuation in the dissociation of the citric acid/ NH_3 complex, perhaps due to environmental variables. The use of phosphoric acid for coating may reduce this problem (Perrino & Gherardi, 1999). If desired, the particles also can be collected by placing a filter pack at the end of the denuder. McCulloch et al. (1998) described a situation where hydrogen chloride, nitrous acid, nitric acid, sulfur dioxide, NH_3 , and fine aerosols of chloride, nitrate, sulfate, and NH_4 particle measurement were made at each sampling using a series of two sets of denuders with filters appropriately placed between the denuders. The tubes may be configured as a single tube (Zhu et al., 2000), as concentric tubes (McCulloch et al., 1998), or a series of tubes, and air going through the tubes must be estab-

lished as laminar flow. When using a denuder system to trap acid or basic gases, it is important to know when the denuder tube begins to lose its sorption efficiency (breakthrough) after a large volume of air has been sampled. Residence time of the air in tubing also should be known. Passive denuder samplers will collect both NH_3 and NH_4 at times of very low natural windspeeds; however, laminar flow rates may not be developed by low natural windspeeds. Another potential problem is the deposition of particles by gravitation on the tube wall at low windspeeds. This problem may be minimized by placing the tubes vertically; however, this configuration cannot be used for passive samplers (Schjorring et al., 1992) and "shuttles" (Denmead, 1983). It should be acknowledged that passive denuder samplers contain large approximation and empiricism (Sutton et al., 2000) but the technique has generated interest since it provides a much cheaper means of estimating long-term fluxes than the classical approaches.

Another type of denuder system is the continuous annular denuder systems such as the AMANDA (ammonia measurement by annular denuder sampling with on-line analysis; Wyers et al., 1993), batch rotating wet denuders (Keuken et al., 1988), and WEDD (wet effluent diffusion denuders; Neftel et al., 1998). These systems incorporate on-line chemical analysis and logging of the sampled NH_3 and have been used successfully with both flux-gradient and relaxed eddy accumulation techniques (Sutton et al., 1997, 2000, 2001).

Spectrometers

There are several types of instrumentation that fall generally into this class. Closed-path spectrometers include chemiluminescence (McCulloch et al., 2001) and closed-path tunable diode laser spectrometers (Diaz et al., 1996; Warland et al., 2001). These instruments can be quite sensitive with proper sample handling and sequencing procedures. Open-path tunable diode laser spectrometers (Bauer et al., 1999) and open-path Fourier transform infrared spectrometers (OP-FTIR) provide a technique not requiring the gas sample to be transported to the laser source/detector site (Todd et al., 2001).

Chemiluminescence detectors use quantitative measurements of the optical emission from energized chemical species to determine analyte concentration and can take place in either the solution or gas phase. Tunable diode lasers can be adjusted to specific wavelengths to take advantage of gases that absorb light in a unique absorption signature or spectrum made up of a large number of individual absorption lines. Tunable diode lasers can be tuned to select a single absorption line of a target gas that does not overlap with absorption lines from any other gases, giving a capability of being very selective and not suffering interference from other gases. Open-path Fourier transform infrared spectrometers pass a single beam of light through the atmosphere that develops an absorbance spectrum. This absorbance spectrum is analyzed using a Classical Least Squares fitting program and calibrated reference spectra, since each spectrum exhibits a distinct pattern that varies predictably in relative intensity, line width, and line position. This capability allows for simultaneous measurement of a number of different interested gas species; however, uncertainty in results caused by spectral overlap has been a matter of concern. Similarly, any open-

path (and closed-path where the sample is not dried) system may have concentration effects due to the presence of water vapor when the gas is in high concentrations. In the case of NH_3 , background concentrations need not be corrected since the ambient concentrations are quite small and the error is negligible (Denmead, 1983). This is fortunate since it is difficult to dry air without removing the NH_3 as well. Further information on the use of spectrometers may be found in Wagner-Riddle et al. (2005, this volume).

FLUX MEASUREMENTS

In general, there are two types of measurements, those which interfere with the transport processes and those that are designed to minimize the interference of transport processes. These techniques fall into three classes of measurements that have generally been used—enclosure, micrometeorological, and tracer techniques.

Enclosure Methods

Noninterfering techniques are preferred for measuring NH_3 gas fluxes because they do not disturb the sample area or its microclimate; however, enclosure or chamber methods are often used because they are simple, suitable for pot experiments and for small field plots, and may have a lower sensitivity requirement for measuring gas concentrations. They can enclose one or more plants and can allow separation of growth medium and plant, making it theoretically possible to determine the amount of NH_3 (or other gases) that have been emitted directly and exclusively from the aboveground parts of plants. The air can be passed over a condenser and returned to the leaf. Reduced and oxidized compounds can be separated; however, N_2O , NO , and N_2 are not detected in this process since they are not very soluble. Researchers using this technique report higher losses from plant systems than that of other methods (Holtan-Hartwig & Bockman, 1994) possibly due to the condensation of CO_2 and NH_3 , leading to enhanced photorespiration, larger stomatal aperture, and an enhanced difference in partial pressure of NH_3 from inside to outside of the leaf. Although some chambers have no circulation of air (Recous et al., 1988), NH_3 volatilization rates will be sensitive to air circulation speed. Marshall and Debell (1980) compared sealed enclosures with and without circulation and found 31% greater NH_3 loss from the enclosures with circulation. Also, it is very difficult to maintain gas concentrations at about ambient concentrations in the enclosure and to avoid pressure changes. In some experiments, air supplied to the chamber is scrubbed free of NH_3 (Morgan & Parton, 1989; Aneja et al., 1999), which may give more NH_3 volatilization than under natural conditions, particularly if there are plants in the measurement system. Parton et al. (1988) obtained comparable results in a growth chamber simulating specific conditions in the field and obtained similar results by allowing long periods of equilibration before measurement began. Large errors have been found (Hoff et al., 1981) using enclosures and field losses estimated by this technique must be regarded as questionable, since the enclosure

cannot closely duplicate soil, water-surface, and environmental aspects (McInnes et al., 1986).

An enclosure system developed by Kissel et al. (1977) was designed to minimize alteration of soil and environmental factors by removing the enclosure covers except for only short periods during measurement. Although removing the cover allowed normal environmental conditions to exist during the remainder of the time, Hargrove et al. (1987) expressed concern about extrapolating losses measured with the enclosure technique to field losses. They found that measurements inside the chambers indicated that windspeed at 1 cm from the soil surface were not representative of windspeeds in the field a significant percentage of the time. These differences were of particular concern when mulch or other roughness elements were used. This type of system, however, provides a useful means by which *relative* differences between treatments can be tested.

In further attempts to minimize differences between enclosures and the field, Vallis et al. (1982) and Lockyer (1984) developed "wind tunnel" enclosures whereby emphasis was placed on the requirement that the natural conditions of the plant community measured would be influenced as little as possible. The systems were designed so that airflow through the tunnel enclosure could be controlled within the range normally encountered in the field. This type of system requires treatments with N above background or the surrounding area since the gas concentrations between entrance and exit or between treatment and control enclosures are measured. Care must be taken in the design of these enclosures to avoid countergradient flux from the tunnel opening (Vallis & Harper, 1982, unpublished data) and condensation on the inner surfaces (Vallis et al., 1982; Lockyer, 1984). Little effect was found on plant, air, or soil temperature and soil water content when air velocity through the tunnel was matched to the ambient windspeed (Vallis et al., 1982; Ryden & Lockyer, 1985). Another consideration with the wind tunnel enclosure is that of rainfall, which can reduce NH_3 loss (Fox et al., 1996). Relocating wind tunnels after rainfall events enables the effects of rainfall to be included (Ryden & Lockyer, 1985); however, tunnel relocation may be impractical where the objective is comparative data (Thompson & Meisinger, 2001, unpublished data) between treatments. When wind tunnels are used at fixed windspeeds, and there is an appreciable difference between the tunnel windspeed and ambient windspeed, there is probably an error in the estimate of loss rates (Thompson & Meisinger, 2001, unpublished data). Additionally, the presence of canopies may restrict surface gas exchange by reducing the development of turbulent eddies that transport air from the soil in open field conditions (Harper, 1988). Nevertheless, wind tunnel chamber systems qualitatively track NH_3 loss and enable replicated comparisons of different treatments.

There are a number of other problems associated with using enclosures to measure NH_3 flux. These problems are associated with the chemistry of the gas and the strong effect that environmental conditions have on the volatilization processes (Denmead, 1983). Factors such as radiation, energy balance, evaporation rate, temperature, windspeed, and dew formation all have important influences and the effects of these factors are difficult to mimic in enclosures. Ammonia is highly reactive and readily soluble in water and thus is likely to adsorb and desorb from the measurement enclosure and tubing walls. [Consider-

able effort has been expended to determine the best materials to be used in NH_3 measurement systems. Experience (Thurtell & Harper, 2000, unpublished data) has suggested the following materials from better to worse: clear, low-density polyethylene > Teflon > glass > stainless steel > nylon. Previous studies (Hutchinson, 1987, unpublished data) used oxidized nickel tubing to minimize NH_3 absorption.]

Generally, the surface area enclosed by chambers is relatively small, often $<1 \text{ m}^2$, whereas the point-to-point variability of NH_3 and other gas emissions from soils, plants, and water systems may be quite large (Denmead & Raupach, 1993). Soil emission rates may vary 2 to 10 times within a few meters (e.g., Matthias et al., 1980; Galbally et al., 1985) creating highly variable results from chamber measurements. For example, Folorunso and Rolston (1984) found coefficients of variation of 282 and 379% in chamber measurements of N_2O emissions and calculated that as many as 350 measurements would be necessary to estimate the true mean flux within $\pm 10\%$ on a $3 \times 36 \text{ m}$ experimental plot. Plant systems may be even more variable although variations in water systems may be somewhat less variable (Harper & Sharpe, 2002, unpublished data). To circumvent the large spatial variability of chambers, multi-chamber and large-chamber systems have been developed. A system of 16 chambers was constructed (Schultz & Seiler, 1989) where each enclosed an area of 1 m^2 with lids closing periodically under computer control. Methane emission rates were determined eight times per day and the system remained in place for the growing season. Very large chambers have been constructed of light-weight plastic. One of these systems (Galle et al., 1994) enclosed an area of 64 m^2 and used a long-path Fourier Transform Infrared (FTIR) Spectrometer to measure changes in the concentrations of CH_4 and N_2O . Another system (M. Poach and P. Hunt, 2001, personal correspondence) was used to cover the width of a constructed wetland for processing animal wastes. The chamber fit the cross-section of the constructed wetland and was tall enough to include the wetland vegetation. This system was developed for use in areas where turbulence was too erratic for microclimate measurements. Gas washing techniques were used for NH_3 concentration determination.

Because of the unique properties of NH_3 , there is a pressing need for nondisturbing measurements of this trace gas flux that integrate across larger areas and longer time scales. Micrometeorological techniques offer more promise in these respects.

Micrometeorological Methods

Micrometeorological methods are noninterference methods and are preferred in principle over interference methods such as chambers (Denmead, 1983; Ferguson et al., 1988; Harper, 1988) because (i) they do not disturb the soil, plant, water system, or environmental processes that influence NH_3 exchange; (ii) they allow continuous measurement, facilitating the investigation of environmental effects on the production and transport of emissions; and (iii) they provide average emissions across an area, minimizing the sampling problem of point-to-point variation found using enclosure techniques; however, their successful application requires relatively large experimental areas (causing problems of practical

replication) and emissions are often small, requiring very sensitive equipment and careful attention to measurement protocol. Micrometeorological techniques assume sources and sinks of energy and mass are evenly distributed and may require a considerable amount of data processing before data analysis. Several types of micrometeorological methods have been applied to NH_3 measurements. Meyers and Baldocchi (2005, this volume) review a broad range of micrometeorological methods for trace gases, many of which have been used for NH_3 . They include:

1. Eddy Covariance. The basic concept of gas transport is that the mass of gases is transported by the eddy motion of the atmosphere and the instantaneous vertical flux density of a gas is the product of the vertical windspeed, ω , and its density, ρ_g , described by the equation,

$$F = \overline{\omega\rho_g} + \overline{\omega'\rho'_g} \quad [2]$$

where bars denote average across a period and primes, the fluctuations about the means (Denmead, 1983). Meyers and Baldocchi (2005, this volume) describe the assumptions underlying eddy covariance.

Fast response sensors are required (and a number of sensors for NH_3 have been developed) but fluxes will be underestimated if the sensor responds too slowly, so to keep the necessary correction small (Hicks, 1972), sensor deployment should be no less than two response lengths above the measurement surface [see LeClerc and Thurtell (1990) for a discussion of fetch/height ratios]. Consequently, a large fetch is needed for the assumption of no flux divergence to be met in practice. Additionally, simultaneous measurement of heat and water vapor for correctional measurements is required. For most gases, pre-conditioning of the air streams to remove H_2O vapor precludes the need for water vapor correction; however, for NH_3 , drying is not yet practical. In most situations, the NH_3 concentrations are small enough that errors associated with corrections for density fluctuations are small and corrections are not necessary.

2. Gradient and Aerodynamic Techniques. These techniques are based on an analogy between turbulent transport and molecular diffusion, assuming both processes transport a gas along its mean concentration gradient. Application of these methods is limited to measurements above crops or other systems where there is adequate profile development of windspeed, temperature, and gas concentrations. An additional assumption is that horizontal concentration gradients are negligible in relation to vertical gradients. If these requirements are met, the vertical flux density of the gas in question will be constant with height in the air layers close to the measurement surface and a one-dimensional (vertical) analysis can be made (Denmead & Raupach, 1993). This method has been widely used and measurement of gas transport between soils, plants, water systems, and the atmosphere has been reported by a number of researchers [Harper et al., 1973, 1976, 1983, 1987, 1996, 2000a, 2000b, 2001, 2004a;

Harper & Sharpe, 1995, 1998; Sharpe & Harper, 1997, 1999; Lemon & Van Houtte, 1980; Hutchinson et al., 1982; Denmead et al., 1974, 1976; Freney et al., 1981; Bussink et al., 1996; Sutton et al., 1997, 2000].

The usual form of the gradient diffusion relationship is

$$F_{FG} = -K_g(\partial\rho_g/\partial z) \quad [4]$$

where ρ_g is the density of the gas in question with respect to height z and K_g is the eddy diffusivity or transport coefficient of the gas. Prueger and Kustas (2005, this volume) discuss the method in detail, including methods to estimate K_g from wind profile data and approaches to correct for atmospheric stability.

Energy Balance Method

The energy balance method is an alternative approach to determining the flux-gradient eddy diffusivity. In this technique, all radiative and turbulent energy components are balanced as in Eq. [5],

$$R_n + G + \int_{z_1}^{z_2} \beta(z) dz + \ell k_{E(z)} \frac{\partial e}{\partial z} + c_p \rho k_{H(z)} \frac{\partial T}{\partial z} + \lambda k_{c(z)} \frac{\partial c}{\partial z} + M = 0 \quad [5]$$

where R_n is net radiation, G soil energy flux, ℓ latent heat of evaporation, e absolute humidity of air, c carbon dioxide concentration, c_p the heat capacity of air, the plant energy flux (heat), λ the energy conversion for fixation of CO_2 , and M a residual term associated with energy storage. Equality of the diffusivity coefficients is assumed (Lemon, 1967; Denmead & Raupach, 1993) and the equation is rearranged to solve for the transport coefficient. The Bowen ratio method for measuring evaporation is an extension of the energy balance technique and is described by Fritschen and Fritschen (2005, this volume). The technique assumes equality of transport coefficients for heat, water vapor, and NH_3 , so that measurements of each at two heights is sufficient to determine the fluxes of all three. A disadvantage of the energy balance method is that in early morning, late evening, and nighttime, R_n and G become small or approach the same value, which means that since the accuracy of the flux density estimate is proportional to the accuracy of the R_n and G measurements, the error may become large. Further, as these values approach zero, the error becomes infinite. Also at night, condensation on the instrumentation can cause erroneous measurements. Since many of the measurements are common to both techniques, both the momentum and energy balance methods should be used in conjunction giving a comparison in diffusivity coefficients during periods when the energy balance technique may be used.

Energy and mass do not transport identically under all conditions and the use of energy to determine mass transport coefficients will require corrections to the transport coefficient. Recent studies suggest that while the eddy diffusivity for momentum (K_m) in the atmosphere is reasonably well known, the eddy diffusivity for mass (K_c) is more uncertain. This uncertainty can be conveniently

expressed as uncertainty in the turbulent Schmidt number (Sc) [Flesch et al., 2002]:

$$Sc = \frac{K_m}{K_c}. \quad [6]$$

Most flux-gradient (classical) relationships assume that Sc value is 1.0; however, some authors have observed this possible underestimation of flux-gradient emissions and have scaled their estimates of emissions by 30% (Simpson et al., 1995; Wagner-Riddle et al., 1996; Flesch et al., 2002) who justified this adjustment as giving better agreement with energy balance observations and the derivation of the energy balance eddy diffusivity, K_{eb} .

MASS BALANCE METHODS

Integrated Horizontal Flux Method

The eddy covariance and gradient methods require extensive and uniform surface areas for sufficient profile development. One mass balance technique, commonly called the integrated horizontal flux (IHF) method, overcomes this limitation. Flux densities are determined from the differences in the quantity of gas carried by the wind across the upwind and downwind boundaries of an experimental area (Denmead et al., 1974; Denmead, 1983). Instrumentation is relatively simple, requiring only windspeed and gas concentration profiles and wind direction. The concept is relatively simple and physically correct with no requirement for stability corrections. Flux density is given by

$$F_{IHF} = \frac{1}{x} \int_{z_0}^{z_p} \overline{(u\rho_g + u'\rho'_g)} dz \quad [7]$$

where x is the fetch (which must be known precisely) between the measurement boundaries, z is the height with z_0 denoting the height at which the windspeed goes to zero, z_p the height of the limit of the modified profile, and $\overline{u\rho_g}$ (where $\overline{\rho_g}$ denotes gas density in excess of background) the time-average horizontal flux density at any particular level in the vertical plane. All planes are integrated (summed) vertically to get the total flux density. The $\overline{u\rho_g}$ is the flux due to horizontal convection while the $\overline{u'\rho'_g}$ is the flux due to horizontal diffusion (counter-gradient flux that occurs in the direction opposite to that of the wind). Raupach and Legg (1984) suggest that the diffusion term is usually <10% and can be omitted. Footprint analysis (Wilson et al., 1982; LeClerc & Thurtell, 1990) has shown that more than 90% of the emitted gas will be contained within a gas cloud that will extend vertically to a height, z , which is about 1/10 of the fetch (upwind turbulent characteristics). Practical experience (Denmead, 1983) suggested that for small fetches, a good working approximation is that $z_p \cong 0.1x$. Vertical measurement heights must take into account the influence of stability on the shape of profiles of the trace gas (Fig. 15-4). Five measurement levels should be used for a

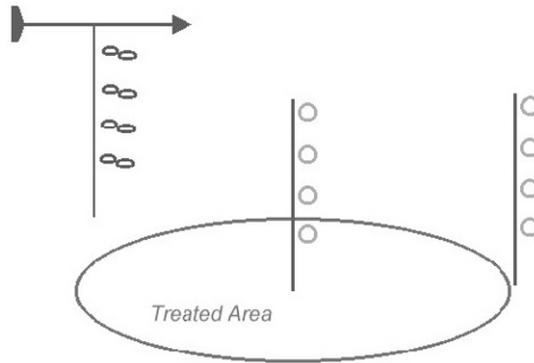


Fig 15-4. Conceptual schematic of the IHF technique.

well-defined profile situation in a short crop but more measurements may be needed if irregular profiles are obtained.

A simplification (experimentally) of the IHF method was proposed by Philip (1959) and Wilson et al. (1982), based on the assumption of a particular height within the modified layer where the normalized horizontal flux (i.e., $\overline{u\rho_g}/F$) has about the same value in all stability conditions. If the appropriate value of the normalized horizontal flux at that height is known, then measurements of \bar{u} and $\bar{\rho}_g$ only at that height are necessary to determine F . Denmead (1983) and McInnes et al. (1985, 1986) and Meissinger (2000, personal communication) discuss the method and indicate that the fluxes agreed well with the IHF method. The method by Philip showed less variation but slightly overestimated the IHF method, while the Wilson et al. method showed larger variation but slightly underestimated the IHF method. A further simplification was developed by Denmead (1983) and Leuning et al. (1985) using an isokinetic gas sampler with an air intake of area (A) that trapped a mass of gas (Mg) during time (t). The Mg/At is then $\propto \overline{u\rho_g}$, and a single determination Mg at the end of the study (perhaps lasting several days) will provide a measure of the total gas loss from the area.

Micrometeorological Mass Difference Method

Large test areas required for application of conventional micrometeorological approaches and spatial variability in horizontally spatial emissions rates present problems in many situations where measurements of trace gas exchange are required. Some examples include emissions of gases from small, treated plots or contaminated sites where lateral dimensions are 10s rather than 100s of meters and the source distribution is not uniform. In a landfill, Czepiel et al. (1996) reported a coefficient of variation of 326% for 139 point measurements of methane emissions. In this circumstance, the measurement problem becomes two- or three-dimensional and conventional micrometeorological methods are not appropriate. Similarly, gas may be produced from scattered point sources that

may even vary temporally in location horizontally and vertically, such as grazing animals. Certainly, this measurement situation becomes a three dimensional problem. To resolve this problem, Harper et al. (1999) developed a micrometeorological mass difference method (MMD) that is an extension of the IHF method (Fig. 15-5).

When gas is released from the ground into the atmosphere, it is convected horizontally by the wind while diffusing laterally and vertically (Denmead et al., 1998a). In unstable conditions, the height of the gas cloud will be greater and in stable conditions, smaller. If the source is above the soil surface, such as from animals (Harper et al., 1999), the height above the soil surface must be accounted for in the vertical measurement heights. The effect of a canopy, if present, is negligible as long as there is no unmeasured horizontal flux divergence above the uppermost measurement height. The horizontal convective flux density at a point in the atmosphere is then given by the product of horizontal windspeed, u , and the gas density, ρ_g . If emissions are within a defined space, the flux from the source can be calculated from the difference between the total gas fluxes across the upwind and downwind boundaries for the space. If the emissions are released within the confines of a square field of side x , such as in Fig. 15-6, then its mean emission rate, \bar{F} , can be given by

$$\bar{F}_{MMD} = \int_0^z \int_0^x \left[\bar{U}_z (\bar{\rho}_{g_{4,z}} - \bar{\rho}_{g_{2,z}}) + \bar{V}_z (\bar{\rho}_{g_{3,z}} - \bar{\rho}_{g_{1,z}}) \right] dx dz \tag{8}$$

where horizontal distance is x with boundary numbers n and \bar{U} and \bar{V} are the wind vectors perpendicular to each other. Time averages are denoted by an overbar. By

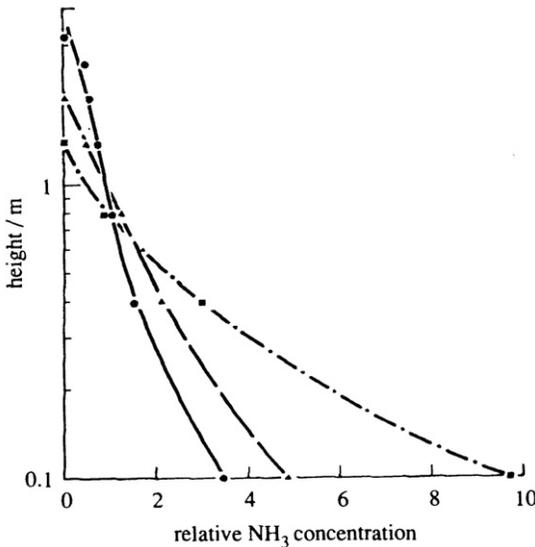


Fig 15-5. Influence of stability on shape of profiles of atmospheric ammonia across a urea-treated plot. Unstable, solid line; neutral, dashed line; stable, dash-dot line (after Denmead, 1983).

fixing the horizontal distance as in Fig. 15–6, the relationship in Eq. [7] reduces to

$$\bar{F}_{MMD} = \int_0^z \left[\bar{U}_z \left(\langle \bar{\rho}_{g_{4,z}} \rangle - \langle \bar{\rho}_{g_{2,z}} \rangle \right) + \bar{V}_z \left(\langle \bar{\rho}_{g_{3,z}} \rangle - \langle \bar{\rho}_{g_{1,z}} \rangle \right) \right] dz \quad [9]$$

where the angular brackets denote spatial averages. Equation [8] can be evaluated numerically using the trapezoidal rule.

The net horizontal flux density of gas, q , is the time mean of the product of the instantaneous windspeed and gas density, $q = \overline{u\rho_g}$. If u and ρ_g are the sums of the time means and deviations from those means are denoted by primes, then $q = u\bar{\rho}_g + u'\rho'_g$. The first term on the right side of the preceding equation is the convective flux. The last term represents the turbulent, diffusive flux in the upwind direction along the concentration gradient. Field tests by Leuning et al. (1985) suggests that the apparent horizontal flux overestimates the true flux by about 15%. With measurements in fetches using the IHF technique, where emissions are uniform and emissions are from the soil surface, a good working approximation for $z = 0.1x$; however, when emissions are not at the soil surface (such as from animal breaths), z must be increased to account for this height (Harper et al., 1999).

This technique has been used for measuring enteric CH_4 emissions from grazing and feedlot animals (Harper et al., 1999; Denmead et al., 1998b; Harper et al., 2001), N_2O emissions from grazed pastures (Leuning et al., 1998; Denmead et al., 2000b, 2000c), and CH_4 and N_2O from landfills (Denmead et al., 1998a). This technique may not be used for reactive gases such as NH_3 emissions because of the problem of absorption–desorption of the gases on the sampling tubing; however, with the advent of multiple-sensor, open-path laser spectrome-

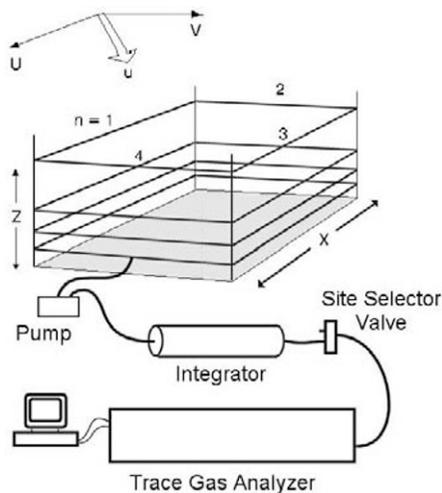


Fig. 15–6. Measurement scheme for the micrometeorological mass difference technique (after Harper et al., 1999).

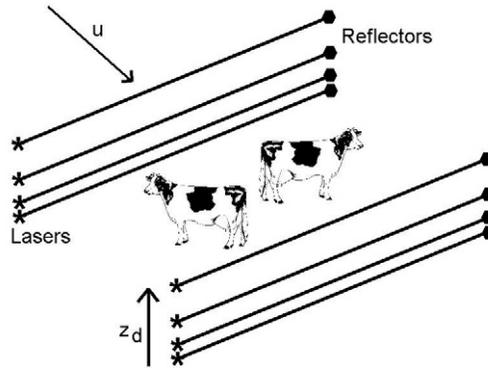


Fig. 15-7. Measurement setup for a noninterference modified mass balance technique to measure trace-gas emissions from crops and animal systems (after Harper, 2001, unpublished data).

ters for NH_3 , this technique may become useful to measure source emissions that are horizontally, vertically, and temporally variable. Harper (2001, unpublished data) developed a modified mass balance technique of the same principle as the MMD technique to be used with vertically-arrayed open-path lasers (Fig. 15-7). This technique, currently under development, would be useful for variable sources (spatially and vertically) and would have minimal interference and/or stress on crops or animals. Since only upwind and downwind measurements are made, this technique must be used in a general cross-wind direction. The first trials Denmead et al. (2003) of 23 release studies with an exclusion angle (the angle between the source and the ends of the laser line) of 10° , regression of recovered versus released gas emissions gave a mean recovery of 105% (r^2 of 0.91) with a 4% standard error. Allowing for the 5% overestimation of recovery, the system could detect a 9% change in emission rate with a probability of 5%.

Normalized Horizontal Flux Method

A further extension to the IHF concept is that both theory and experiment indicate that (in certain situations), it is possible to infer the surface flux from measurements of the horizontal flux at just one height above the measurement plot center. Three requirements must be met, however, (i) although the treated plots may be relatively small, the treated area in which the plots are located must be large and uniform enough so that the wind profiles are equilibrium profiles, (ii) the treated area should have no vegetative cover (at least a very short cover) so that virtually all of the horizontal flux occurs in the unobstructed air layer above the surface, and (iii) the surface emission should be driven by processes in the soil and/or vegetation rather than by the atmospheric gas concentration (i.e., there should be a constant flux rather than a constant concentration boundary condition at the surface). The profile of horizontal flux density has theoretically predictable shape that is determined by surface roughness, plot geometry, and atmospheric stability (Philip, 1959; Mulhearn, 1977, Wilson et al., 1982). From analysis of the influence of stability on profile shape, Wilson et al. (1982) pre-

dicted the existence of a particular height within the plot boundary layer at which the normalized horizontal flux, $\overline{u\rho_g}/F$ has almost the same value in all stability situations. This height is denoted z_{inst} and if the appropriate value of $\overline{u\rho_g}/F$ at z_{inst} is known, measurements of \bar{u} and $\bar{\rho}_g$ at only that height are sufficient to determine F_g (Wilson et al., 1982, 1983; Denmead, 1983). Freney et al. (1992) have used an extension of this concept with a passive sampler to measure the horizontal flux of NH_3 at the z_{inst} . Denmead (1983) and McInnes et al. (1985, 1986) and Meissinger (2000, personal communication) discuss the method and indicate that the fluxes agreed well with the IHF method. A further simplification was developed by Denmead (1983) and Leuning et al. (1985) using an isokinetic gas sampler with an air intake of area (A) that trapped a mass of gas (Mg) during time (t). The Mg/At is then $\propto \bar{u\rho}_g$, and a single determination of Mg at the end of the study (perhaps lasting several days) will provide a measure of the total gas loss from the area.

LAGRANGIAN METHODS

Lagrangian Dispersion Analysis

Flux-gradient techniques have been used extensively to describe NH_3 transfer between the atmosphere and crop surfaces (Denmead, 1983; Harper, 1988), but theoretical difficulties limit the use of flux-gradient techniques within plant canopies, particularly where there are vertically distributed sources and sinks. The Lagrangian dispersion theory developed by Raupach (1989) enables a prediction of the gas concentration profile, which he designated as $C(z)$ from knowledge of the source strength, $S(z)$. The inverse Lagrangian method described by Raupach (1989) builds on that work to allow the inference of $S(z)$ from $C(z)$. Flesch and Wilson (2005, this volume), gives a complete discussion of the technique. This technique has been used (Raupach et al., 1992; Denmead et al., 2000a) to deduce source and sink strengths for H_2O vapor, heat, and CO_2 exchange in crop canopies, showing interesting emissions and adsorption/absorption sites. Harper et al. (2000a) extended the analysis to identify sources and sinks of NH_3 in a canopy following sprinkler application of dairy effluent. The technique allowed an examination of the processes of loss within the canopy showing small but not insignificant NH_3 losses from the soil, while showing unexpectedly large losses occurring from the foliage in the top half of the canopy.

Comparisons between Lagrangian and “conventional” micrometeorological methods have shown generally excellent agreement and comparable to the mutual agreement *among* the conventional methods of eddy covariance, energy balance, and momentum balance.

Backward Lagrangian Stochastic Analysis

The usual and most obvious meaning of a theory of atmospheric dispersion is that it defines a forward “source–receptor relationship” from a source field, and on the basis of some assumptions about the turbulent flow, it gives expression for

a resultant mean concentration field (Wilson et al., 2001). An important point is that it is possible to exploit a given source-receptor relationship to infer flux density from a measured concentration—given some “supporting” information defining the flow. Flesch et al. (1995) introduced the “backward Lagrangian stochastic” (bLS) source-receptor method, applicable to a source of any geometry, and is described in detail elsewhere in this volume (Flesch and Wilson, 2005, this volume).

In this technique, one measures the gas concentration at a single point, C_p , and the variables defining the state of the surface layer (At least minimally a single windspeed, u_{ref} , and wind direction is required. For improved accuracy, atmospheric stability, L , is needed.). The model is applied by generating an ensemble of N trajectories, such as NH_3 , from a point, P , backward in space and time (Fig. 15–8), and where any trajectory touches the ground, the point (x,y,z) is recorded and the particle’s touchdown position and vertical velocity, F_{bLS} , is inferred from those touchdowns as

$$F_{bLS} = \frac{u_{ref} C_p}{N} \sum \left(\frac{w}{U_{ref}} \right)^{-1} \quad [10]$$

where the summation runs over all touchdowns on the source (Wilson et al., 2001).

To illustrate the potential magnitude of errors, Wilson et al. (2001) added conservation equations for a tracer gas to a “local advection” model (Rao et al., 1974) to simulate emissions from a lagoon with a spatially uniform emission rate, Q . They generated spatial distributions of windspeed, temperature, and tracer concentration above and downwind of the lagoon. These simulated data provided the basis for a synthetic experiment where several micrometeorological estimates of the emission rate were compared with the prescribed Q . They compared these estimates of synthetic data and found that the fluxes in the synthetic data set estimated by the IHF compared well with the known Q but not as well with flux-gradient estimates by the momentum balance method.

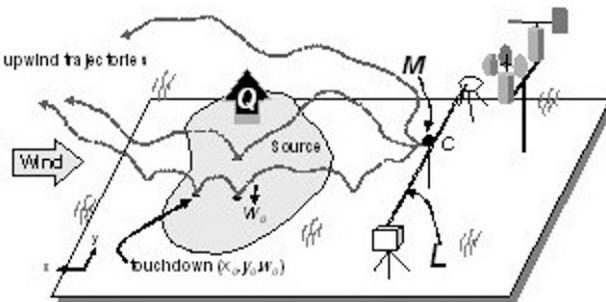


Fig. 15–8. Illustration of the bLS technique for estimating tracer emission rate (Q). Average concentration C is measured at point M or line L downwind of the source. The ratio $(C/Q)_{sim}$ is calculated from upwind trajectory “touchdowns” inside the source (w_0 is the vertical velocity at touchdown; after Flesch et al., 2003).

Further comparisons using CH_4 and NH_3 as tracer gases were made and the estimates of prediction in uniform flow across a field release surface area were quite good. Studies by Flesch et al. (2004) considered the bLS method as applied to an ideal case: estimating emissions from a synthetic source (a square grid of gas emissions of known rate) located in an open landscape where the Monin-Obukhov similarity theory (MOST) is likely to be upheld. They found the diagnosed emission rates (Q_{bLS}) were satisfactory when MOST gave a good description of the surface-layer, but poor during periods of extreme atmospheric stability and transition periods in stratification. With such periods eliminated, the average Q_{bLS} over-predicted the true Q by only 2%; however, individual 15-min predictions exhibited sizeable variability. In the best case where MOST gave a good description, the variability in Q_{bLS} was approximately 20% of Q .

OTHER MICROMETEOROLOGICAL METHODS

Relaxed Eddy-Accumulation

An alternative to enclosure and techniques based on atmospheric turbulence, the relaxed eddy-accumulation (REA) technique is a relatively new method for measuring trace gas fluxes. It involves the partitioning of the gases traveling vertically (up and down) into two separate reservoirs, based on whether a real-time wind-measuring system (normally sonic anemometer) that senses ascending or descending air movement. The separate samples can be absorbed into gas washing reservoirs that can later be analyzed, be sampled by continuous denuder technology (Businger & Oncley, 1990), or be analyzed instantaneously by tunable diode laser spectroscopy (Diaz et al., 1996). Originally, Desjardins (1972) and Desjardins et al. (1984) developed the technique to sample the air at a rate proportional to the magnitude of the vertical wind velocity, w . Businger (1990) suggested a relaxation of this method in which the valves split the flow strictly on the basis of the sign of w without the proportional sampling. The conceptual simplicity of this technique is appealing because the vertical flux estimate, F , for a trace gas is a simple function of the standard deviation of the vertical wind velocity, σ_w , the difference of the mean concentrations between the ascending air (c^+) and descending air (c^-), and an empirical coefficient A ,

$$F_{\text{REA}} = A\sigma_w \left(\overline{c^+} - \overline{c^-} \right) \quad [11]$$

Field experiments have indicated that the REA works quite well as an alternative measurement technique for nonreactive gases such as CO_2 , volatile organic compounds, and pesticides (Majewski et al., 1993; Pattey et al., 1993; Zhu et al., 1999); however, because of the reactivity, stickiness, and ability to convert to NH_4^+ , NH_3 sampling using REA requires careful sample handling and/or measurement. The annular denuder system (ADS) is a suitable trap for this purpose (Zhu et al., 2000) to avoid the interference of NH_4^+ in particulate phase with the collection of gas-phase NH_3 —if (i) there is need to separate the constituents and (ii) the NH_4^+ constituent is sufficiently high compared with NH_3 .

Gaussian Plume–Puff Dispersion Model

Gaussian plume and puff models have become a standard for modeling atmospheric dispersion for two reasons: simplicity and flexibility. They are attractive because of the large degree of flexibility in handling arbitrary source characteristics (continuous line source, moving source, etc.), effluent characteristics (buoyancy, stack downwash, etc), and varying meteorological conditions. They are promoted as having a modeling range of 10s of meters to 1000s of kilometers.

Despite its apparent sophistication, the Gaussian framework is rather primitive. While the derivation of these models starts with the rigorous mass-conservation equation, often a host of unrealistic assumptions are then employed: homogeneous wind field (conditions of steady, uniform wind-flow, spatially-independent turbulence), a gradient-diffusion hypothesis of turbulent transport, and mass diffusivities independent of position (Arya, 1999). The result is a deceptively simple relationship for the concentration field downwind of an emission source. The key model parameters are the plume “sigmas,” the standard deviation of plume–puff spread in each direction downwind of the source (σ_x , σ_y , σ_z). However, because the underlying Gaussian model assumptions are not generally realistic, these models are essentially empirical, and the sigma functions are determined by fitting experimental data. The Gaussian modeler must assume that the sigma functions derived from another particular experiment will be valid in their situation (McColloch, 1999); however, since the Gaussian framework does not describe the atmosphere, these sigma relationships are not universal. They vary with weather conditions, local terrain, source geometry, concentration observation locations, etc., and to be successfully employed, the Gaussian model requires the user to find an experimental value for the sigmas in a situation as close to theirs as possible. In many agricultural and environmental applications, accurate models of dispersion near the ground ($z < 100$ m) and across short ranges ($x < 1000$ m) are required. These conditions are where Gaussian models are most unreliable. Near the ground, the average wind and turbulence levels change dramatically with height, invalidating the foundation of Gaussian models (Flesch, 2001, personal communication). In these cases, Gaussian models should be used with a great deal of caution. Different experiments will yield different sigma relationships.

In a comparative study of several techniques in eastern North Carolina, Gaussian model results in summer (McColloch, 1999) showed emissions 2.3 times larger than emissions determined by flux-gradient (Harper et al., 2001). During winter, the Gaussian model gave emissions 2.6 times higher. On an annual basis (summer winter, and spring emissions) the average emissions were 2.7 times higher than the flux-gradient emissions determined on the same lagoon.

It should be noted that at the present time there is no exact model of turbulent dispersion in the atmospheric boundary layer. Dispersion models exist that are more rigorous than Gaussian models, but they require a much more extensive description of the wind field, and in the case of nonuniform terrain or non-stationary conditions, even the more sophisticated models are subject to unknown and probably large errors. Gaussian models are a compromise requiring minimal input data and consuming minimal computer time.

ISOTOPE AND OTHER TRACER METHODS

Tracers have been used extensively to increase our understanding of N cycling in soil–plant systems and for use in evaluating emissions from soil, plant, or aqueous systems. Caution must be used for NH₃ transport studies because of intimate linkages among its various forms. Nitrogen in agricultural production is particularly sensitive to biological and chemical transformations.

Nitrogen Isotopes

Early studies on fertilizer efficiency and predictions of NH₃ loss from fertilizers were determined using stable N isotopes (¹⁵N). Although NH₃ emissions have been found in cropping systems to be significant in many circumstances, net N loss as NH₃ has been found to be smaller than losses using isotopic techniques (Harper & Sharpe, 1998). Schjorring et al. (1989) and Francis et al. (1993) showed a decline of labeled N in the aerial parts of plants during the growing season but Catchpoole et al. (1983) showed that NH₃ volatilized from surface-applied urea fertilizer could be directly absorbed by the surrounding grass (*Setaria sphacelata* Nandi) canopy. In this study, isotope plots were fertilized at the same rate and time as the surrounding pasture. They found that the largest recovery of ¹⁵NH₃ by the surrounding grass occurred when the tropical grass activity was highest (in summer and spring). They also found that the highest *apparent* loss of fertilizer, compared with micrometeorological methods where *net emissions* were measured, occurred during periods of highest plant activity (2.4 times higher apparent losses than net losses). They found that when the grass sward was dormant, NH₃ losses estimated from ¹⁵N mass balance (45% loss) were not significantly different from losses (42% loss) measured using micrometeorological techniques (Harper et al., 1983). Thus, in studies similar to these, the use of *only* ¹⁵N to measure N-use and NH₃ volatilization would indicate erroneously large losses of fertilizer N and much lower plant N-use efficiency.

In another study, N cycling in wheat (*Triticum aestivum* L.) showed that NH₃ can be absorbed and emitted from the same crop during the same year (Sharpe et al., 1988). They found that during a period of maximum vegetative production, soil mineral N dropped to very low concentrations resulting in a crop N use higher than soil mineralization and fertilizer N release rates. Micrometeorological measurements showed an NH₃ absorption flux from the atmosphere to the plants at about the same rate as the difference in plant use and soil N availability rates (Harper et al., 1987). In other studies, Francis (1995, personal communication) observed simultaneous NH₃ emission from the ear leaf of corn (*Zea mays* L.) while absorption occurred in the upper leaves. Because NH₃ can be both absorbed and emitted, ¹⁵NH₃ in a growing plant will be lost and substituted for ¹⁴NH₃, even if the net flux is zero. Francis and collaborators (1994, personal communication), using ¹⁵N in a similarly managed cornfield adjacent to a study by Harper and Sharpe (1995), suggested about 23 kg N ha⁻¹ was lost as volatile NH₃ during the maturation phase of the corn canopy. Overall for the growing season, using micrometeorological techniques, they found a *net* loss of 3.6 kg N ha⁻¹, about one-sixth of the NH₃ emissions estimated by the iso-

tope techniques. Legumes have been found (Harper & Sharpe, 1998) not to emit NH_3 from the foliage as long as there is any plant activity. They found (Harper et al., 1989) using both $^{15}\text{N}_2$ gas for fixation measurement in soybeans [*Glycine max* (Merr.) L.] and micrometeorological techniques for NH_3 flux measurements that 6 to 9% of the total estimated N 'fixation' was actually absorbed atmospheric NH_3 . In a greenhouse study, Sharpe and Harper (1997) found that about 27% of the $^{15}\text{NH}_3$ emitted from treated plants was absorbed by control plants not treated with ^{15}N .

Consequently, use of N isotopes to estimate NH_3 loss may be permissible if there is no plant activity for absorption and desorption. If there is plant activity, micrometeorological techniques must be concurrently used to evaluate the isotope substitution and fractionation.

Tracer-Gases

A ratioing technique is often used for comparing known tracer-gas emission rates with unknown gas emissions rates (Eklund & LaCrosse, 1995; Todd et al., 2001). The limitations and assumptions inherent in this measurement approach must be recognized when using this technique. They include the following: (i) The tracer gas must adequately simulate the emission source [Note: a potential error is introduced due to the assumption that the point or area release of the tracer gas, which may be lighter or heavier than air, mimics the area NH_3 emissions, which is itself lighter or heavier than air (McColloch, 1999)], (ii) The vertical distribution of the tracer gas emissions must not be different from that of the unknown emission plume from the measurement area (Eklund & LaCrosse, 1995), and (iii) The horizontal distribution of the tracer is not different from that of the unknown emission plume. This technique does not use plume dispersion models nor other meteorological measurements such as stability corrections. Other uses of tracer techniques have been to release and evaluate known amounts of the gas to be determined prior to the measurements themselves. Denmead et al. (1998a) found that using CH_4 as a tracer released to simulate emissions from a point source (such as from a cow) that under windspeeds of less than one to 1.5 m sec^{-1} , much of the released CH_4 was lost to the atmosphere above the measurement height (see discussion of MMD technique). This problem had the effect of biasing the rates low. For gases such as commonly-used sulfur hexafluoride (SF_6) and carbon tetrafluoride (CF_4), which are heavier than air, if the tracer gas plume tended to remain closer to the ground than the source plume, the measured tracer gas concentrations would be relatively lower and the calculated source emission rates would be biased high (Eklund & LaCrosse, 1995). Results using these tracers have tended to be higher than comparable measurements or reasonable results. Ammonia emissions determined on a lagoon in Texas (Eklund & LaCrosse, 1995) were larger than the amount of N fed to the animals. In a transport technology comparison study NH_3 emissions determined using tracers in a North Carolina lagoon (Todd et al., 2001) gave results about 2.3 times higher than chamber studies (Aneja et al., 1999) and 3.6 times higher than flux-gradient studies (Harper et al., 2001).

EMISSIONS

Emissions Measurements

Emission factors have been used to calculate NH_3 emissions from animal husbandry in Europe (Asman, 1992) and the USA (Battye et al., 1994). Table 15-1 presents a list of USA and European emission factors based on a "per animal per year" basis. The factors are quite variable because there are not clear-cut links between countries and their studies (Battye et al., 1994), between measurement technologies, components included (housing, storage, application), and animal categories. Consequently, emission factors must be used with caution because of variability induced by geography and meteorology, methodology for measurement (Denmead & Raupach, 1993; Harper, 1988), type and weight of animals (Harper et al., 1998), N content of feedstuffs, housing and management, and other factors. Asman (1992) developed a composite factor for Europe of 4.4 $\text{kg NH}_3\text{-N animal}^{-1} \text{ year}^{-1}$. Later evaluations by van der Hoek and Couling (1995) separated animals into classes and gave slightly higher emissions for farrow-to-finishing (FF) animals of 5.3, and considerably higher factor of 13.5 for farrow-to-wean (FW) animals. Battye et al. (1994), using emissions from Europe and USDA Agricultural Statistics Service animal classifications, developed a similar composite factor to that of Asman (1992) for the USA of 9.2 $\text{kg NH}_3\text{-N animal}^{-1} \text{ year}^{-1}$ which is considerably higher than the European factors or the earlier

Table 15-1. USA and Europe swine production emission factors.

Source	Emission factor $\text{kg NH}_3\text{-N animal}^{-1} \text{ yr}^{-1}$	Region
Asman, 1992	4.4	Europe
Buijsman et al., 1987	1.9	Europe
Cass et al., 1982	3.7	Europe
Jarvis & Pain, 1990	3.6	Europe
Kruse et al., 1989	2.9	Europe
van der Hoek & Couling, 1995		
Farrow to Finish	0.7	Europe (composite)
Farrow to Wean	1.8 [†]	Europe (composite)
Farrow to Finish	5.3	Europe (composite)
Farrow to Wean	13.5	Europe (composite)
Aneja et al., 1999		
Farrow to Finish	1.8 [†]	USA (NC10-chambers)
Battye et al., 1994	9.2	USA (composite)
Eklund & LaCrosse, 1995	517.6	USA (TX-tracer studies)
Harper et al., 2000		(microclimate techniques)
Farrow to Finish		
Primary lagoon	1.3 [†]	USA (GA1)
Four-stage lagoons	2.1 [†]	USA (GA)
Voorburg & Monteny, 1991	3.0 [‡]	Netherlands
Warn et al., 1990	1.3	USA
Harper & Sharpe, 2004a		
Farrow to Finish	0.8 [†]	USA (NC10)
Farrow to Wean	1.2 [†]	USA (NC20)

[†] Storage only.

[‡] Per fattening place.

NAPAP factors (Warn et al., 1990) [There is some question that the Northern European emission factors (Asman, 1992) were used improperly and the U.S. factors developed may be too large by about a factor of two (Asman & Harper, 2000, personal communication)]. Comparison of lagoon emission factors for FF management systems were similar for van der Hoek and Couling (1995) in Europe, for Harper et al. (2000b) in Georgia (the primary lagoon only, GA1), and for Harper et al. (2001) in North Carolina. Even emission factors determined from the same lagoon using different technologies have shown considerable variation (Table 15–2). On a highly-studied farm in the Coastal Plains of North Carolina (designated NC10), several studies of NH_3 emissions were compared. Aneja et al. (1999), using floating chambers obtained an estimate of lagoon annual emissions of 2.7 times larger than those of Harper et al. (2001) using microclimate techniques for the same lagoon.

McColloch (1999), using a Gaussian model, determined annual emissions of 2.3 times higher than Harper et al. (2001) whereas Todd et al. (2001), using tracer techniques, obtained annual emissions 4.7 times that of Harper et al. (2001). For that farm, a total N balance of individually-measured components (Fig. 15–9) accounted for about 95% of the input N as feed (Harper et al., 2004a).

Measurement of emissions from animal housing also show some variability. Harris and Thompson (1998) determined barn annual average emissions on the NC10 farm (using FTIR and estimates of fan flow rates) of $3.7 \text{ kg NH}_3 \text{ an}^{-1} \text{ yr}^{-1}$. Direct fan flow-rate measurements and TDL spectroscopy by Harper et al. (2004b) gave emissions of $2.7 \text{ kg NH}_3 \text{ an}^{-1} \text{ yr}^{-1}$ on the same swine houses. Estimates by van der Hoek (1998) gave remarkably similar emissions (to that of Harper et al., 2004b) of $2.9 \text{ kg NH}_3 \text{ an}^{-1} \text{ yr}^{-1}$ from swine houses in Europe. It should be noted, however, that emissions may be very different for different animal types and seasons. Harper et al. (2004b) showed about twice as high NH_3 emissions from housing in summer than in winter but also showed considerable difference between animal types. They found that finishing pigs emitted about eight times as much NH_3 per animal as farrowing sows (including nursing

Table 15–2. Comparison of lagoon emissions determined by different techniques on a swine production farm in North Carolina.

Method	Season	Lagoon emissions $\text{kg NH}_3\text{-N ha}^{-1} \text{ yr}^{-1}$	Housing emissions $\text{kg NH}_3\text{-N animal}^{-1} \text{ yr}^{-1}$	Reference
Chambers	Summer	57.8		Aneja et al., 1999
Flux-gradient	Summer	18.7		Harper et al., 2001
Gaussian model	Summer	42.3		McCulloch, 1999
Tracers	Summer	96		Todd et al., 2001
Chambers	Winter	12.2		Aneja et al., 1999
Flux-gradient	Winter	7.6		Harper et al., 2001
Gaussian model	Winter	19.4		McCulloch, 1999
Tracers	Winter	27.5		Todd et al., 2001
Mass balance (direct fan measurements)	Annual		2.7	Harper et al., 2001
Mass balance (estimated fan flow)	Annual		3.7	Harris & Thompson, 1998

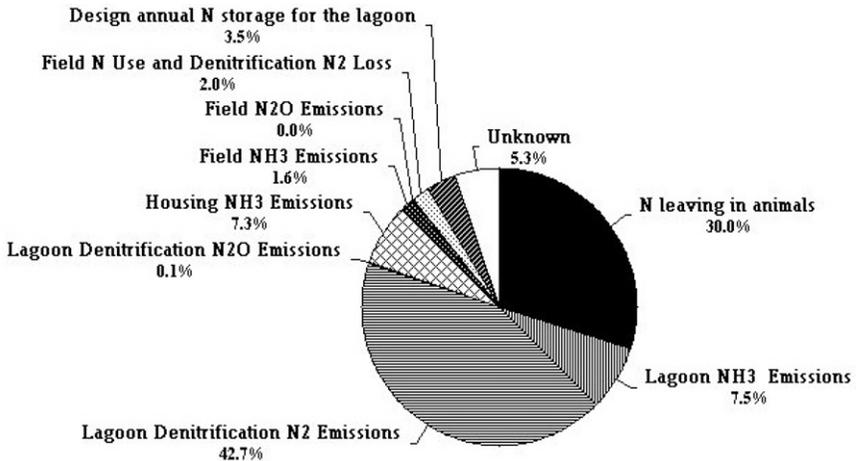


Fig. 15-9. Mass-balance of individually-measured N components in a North Carolina (NC 10) swine farm (after Harper et al., 2004a).

piglets), but on a per kilogram weight basis, finishers produced about 1.8 times as much NH_3 from houses as did farrowing sows and piglets. Similar differences and variabilities in emissions have been found for emissions from crops using different measuring methods, different crop species, and different crop growth stages (see Appendix, Holtan-Hartwig & Bockman, 1994).

General emission factors are requested by planners, designers, and regulators to estimate NH_3 and other trace gas emissions and these comparisons show the inherent dangers of basing emissions on animal numbers and not accounting for climatic, animal class, or management considerations. Other differences in published emissions factors can be explained, based on technologies of measurement.

COMPARISON OF TECHNIQUES

Table 15-3 gives a comparison of many of the techniques found in the literature. More complete discussions of accuracies, problems, and strengths of the techniques may be found in individual discussions (see Methods of Measurement). The IHF is generally considered to be the most physically-correct technique and may be considered to be a standard for making comparisons where possible. Another technique, stable N isotopes, using short-term measurements in the absence of plant activity also may be used as a good comparison. Flux-gradient techniques have been used extensively and successfully in many agricultural situations but a study (Harper et al., 1973) using CO_2 as a tracer, showed the necessity for a thermal stability correction using the momentum balance technique for determination of the transfer coefficient. A relatively-new technique, bLS, looks promising and further research should indicate its value and utility in trace-gas research and evaluation. Recent studies (L.A. Harper et al., 2005,

Table 15-3. Comparison of reported accuracies of microclimate, enclosure, and tracer methods.

Reference	F_{mb}	F_{ch}	F_{IHF}	F_{MMD}	F_{zint}	F_{hLS}	$F_{chamber}$	$F_{isotopes}$	$F_{tracers}$
Harper et al., 1973	-55 ± 19% †	-41 ± 26%							
Harper et al., 1976	14% > F_{ch}	14% < F_{mb}							
Field measurement comparison									
Craswell & Vlek, 1983									
Wind tunnel comparison									
Hoff et al., 1981	15% < F_{IHF}		15% > F_{ch}						
Comparison of ammoniacal N loss from plastic sheets							-52%		
Harper et al., 1983									
Field measurement comparison	7% $^{15}N ‡$							7% $F_{mb} ‡$	
Ferguson et al., 1988									
Comparison over bare soil									
Ferguson et al., 1988			37% > $F_{chamber}$				37% < F_{IHF}		
Comparison over wheat residue									
Denmead et al., 1998a			91% > $F_{chamber}$				91% < F_{IHF}		
Field measurement comparison for CH_4 emissions	2% < F_{MMD}								
Denmead et al., 1998a									
Field measurement comparison for CO_2 emissions	10% > F_{hLS}								10% < F_{mb}
Denmead et al., 1998a									
Field measurement comparison for tracer emissions	23% > F_{MMD}								23% < F_{MMD}

unpublished data) have shown no significant difference between flux-gradient (using momentum balance with Schmidt corrections) and bLS NH_3 emissions in a large beef feedlot of 50 000 animals. While closed-chamber techniques are useful for making *relative comparisons* of nonreactive gases, because of the nature of reactive and diffusive gases and the effect of turbulence on their transport processes, such as NH_3 and HF, the use of closed chambers are not appropriate. The use of wind tunnel type chambers is an improvement compared with closed-chamber techniques and are quite useful for making treatment comparisons, but they are still not appropriate for determination of absolute emissions. Table 15–1 compares the variabilities in measurements of NH_3 emissions in swine production systems among researchers, part of which is due to different measurement techniques. Table 15–2 exemplifies problems associated with obtaining accurate emissions using different technologies on the same lagoon. Consequently, the research, regulatory, or monitoring organization must be cautious of NH_3 emissions obtained where possible inappropriate methodologies and sensors have been used.

SUMMARY

Because of its chemical properties, NH_3 is a difficult gas to measure without disturbing its transport characteristics. Ammonia is a highly reactive, absorptive, and sticky gas requiring great care in sampling. Its chemical properties dictate the use of transport technologies that do not interfere with the source temperature, concentration, pH, and turbulent or diffusive transport. Its chemical measurement necessitates precautions since it may adsorb and desorb with most surfaces and with the sensors themselves. The purpose of this chapter has been to review available atmospheric-exchange and transport technology and discuss strengths and weaknesses of the methodologies.

Measurement of NH_3 transport with closed chamber systems is generally not recommended unless the systems are specifically defined and the information will be used only for comparative differences. If used, during the measurement process careful attention must be given to equilibration before measurement is begun. Ambient transport conditions can be approached using wind-tunnel chambers and this technique is useful in obtaining relative comparisons. Absolute emissions should be evaluated using non-interference techniques if at all possible.

There are a number of micrometeorological techniques and all have their strengths and weaknesses. The flux-gradient, eddy covariance, and relaxed eddy accumulation techniques are noninterfering and integrate large spatial source areas but have relatively large fetch requirements of at least 100:1 upwind distance to measurement height. Mass-balance techniques are more physically correct and are useful for relatively small source areas of less than a hectare. The Lagrangian dispersion analysis technique has been useful in evaluating source and sink strengths and absolute emissions have been shown to be comparable to other micrometeorological techniques. The backward Lagrangian stochastic analysis technique shows promise as a noninterference evaluation technology but is currently not proven except in the simplest atmospheric transport (or disturbance) situation.

The contribution of N compounds to the total deposition of pollutants is becoming more important. Nitrogen is difficult to abate because of the intimate linkages among its various forms and among agriculture, industry, and transportation emissions. Within agriculture, reducing NH_3 emissions may increase N_2O and NO_3 and in transportation, reducing NO_x emissions is leading to increased NH_3 and N_2O emissions. The global population is expected to grow continuously while the agricultural area used for food production cannot increase indefinitely. Therefore, the use of N to increase agricultural production is expected to grow considerably. The prospects for emissions reduction may consequently be limited. Therefore, correct and accurate measurements of NH_3 emissions are needed to address linkages in the environment.

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