Measurements of ammonia emissions from spreading of manure using gradient FTIR techniques

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Abstract

Emissions of biogenic trace gases from soils and plants often show strong spatial and temporal variation. Thus, there is a need for the development of area-integrating measurement techniques with good time resolution. The present paper describes area-integrated measurements of ammonia emissions after spreading of pig slurry on a wheat field, based on flux-gradient measurements using Fourier transform infrared (FTIR) spectroscopy. Two methods are described; the aerodynamic method where the flux is derived from measured micrometeorological parameters, and a tracer method where the flux is derived from simultaneous measurements of a tracer gas released over the area under study. Although not ideal in the actual measurement situation, this latter method has a potential for use on more local sources with less restrictions on micrometeorological conditions, and is thus included for validation. A code for modelling of the "footprint" of gradient measurements is also described, and is used to compare the results from the above-mentioned methods. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Emissions of biogenic trace gases to the atmosphere have environmental impacts which may be direct, e.g. \( \text{NH}_3 \), may affect global climate, e.g. \( \text{N}_2\text{O} \) and \( \text{CH}_4 \), or may arise via atmospheric chemistry, e.g. CO and \( \text{CH}_4 \) (Graedel and Crutzen, 1993). Due to their biogenic origin these emissions show high spatial and temporal variation (Folorunzo and Rolston, 1984; Ambus et al., 1993; Ryden, 1981; Priemé et al., 1996). In order to understand the processes leading to these emissions, and to be able to quantify the contributions from various ecosystems, methods for making area-integrated measurements of these gases need to be developed. Different approaches include statistical methods using large numbers of field chambers (Christensen et al., 1996; Priemé et al., 1996), use of large field chambers (Galle et al., 1994; Smith et al., 1994a) and micrometeorological techniques like eddy-correlation, flux-gradient and conditional sampling (Lenschow, 1995; Wienhold et al., 1994). These techniques have been employed in many configurations with different analysis instrumentation such as non-dispersive infra red spectroscopy (NDIR), tunable diode laser absorption spectroscopy (TDLAS), gas chromatography (GC) and long-path fourier transform infra red (LPFTIR) spectroscopy.

Manure application leads to a number of different environmental problems, as ammonia emission, nitrogen leaching and nitrous oxide emissions (IPCC, 1997). The environmental aspects are on local, regional and global scales. New methods for manure applications have to be developed in order to mitigate the problems. During the developing of these methods all the aspects have to be simultaneously investigated. This puts a large demand on
the experimental design and method selection. A number of different measurement techniques have been employed to study emissions of ammonia. These methods includes chamber techniques (Svensson and Ferm, 1993), mass balance techniques and time-integrating gradient techniques using denuders (Schjørring et al., 1992). These techniques all have their different limitations regarding time resolution and area integration.

The methods presented here are flux-gradient techniques based on FTIR spectroscopy combined with micrometeorological measurements or with the release of a tracer gas at a known rate over the area under study. Although more technically complicated than the abovementioned methods, these techniques offers good area integration and high time resolution. The aerodynamic method is suitable for measurements from large fields with good micrometeorological conditions, while the tracer method has a potential for measurements from more local sources and imposes less restrictions on the micrometeorological conditions.

2. Experimental techniques

2.1. FTIR-gradient system

In LPFTIR spectroscopy IR-light from a source is transmitted through a gas and then spectrally analysed in an FTIR spectrometer. Thus an absorption spectrum of the gas is obtained. Due to their different spectral signatures different gases may be simultaneously and uniquely determined. By the use of multiple reflection optics (e.g. White cells), a long optical path can be obtained through the gas to improve detection limits. In combination with powerful retrieval algorithms this results in high-precision quantitative analysis of a number of interesting compounds e.g. N₂O, CO, CO₂, CH₄, NH₃ and H₂O.

The gradient technique is a micrometeorological method for area-integrated surface flux measurements. In this method, the vertical concentration gradient of the gas under study is measured over the surface where exchange is occurring and effectively integrates over an area or “fetch” extending upwind of the measurement site. The flux $F_\gamma$ is related to the gradient via the diffusion constant $K$ in accordance with

$$ F_\gamma = - K_\gamma \frac{d \chi_g}{dz}, \quad (1) $$

where $K_\gamma$ is the vertical turbulent diffusion coefficient, $\chi_g$ is the gas concentration, and $z$ is the height above the effective surface. $K_\gamma$ can be derived from micrometeorological measurements directly or by measurement of the flux and gradient of a reference quantity controlled by the same process e.g. heat, CO₂ or H₂O. An alternative method, especially attractive with FTIR due to its multicomponent analysis capabilities, is to establish an area release of known flux $F_i$ of a tracer gas over the source area. If then the gradients of the tracer gas and the gas under study are simultaneously measured, $K$ can be cancelled in Eq. (1) and the unknown flux $F_\gamma$ can be derived from Eq. (2), where $\chi_g$ and $\chi_i$ are the concentrations of the studied gas and the tracer gas respectively,

$$ F_\gamma = F_i \frac{d \chi_g}{d \chi_i}. \quad (2) $$

The major advantage of the tracer gradient technique as compared to traditional tracer techniques (Lamb et al., 1986, 1995; Howard et al., 1992) is that it gives a more focused footprint and thus is less affected by interfering remote sources. A source outside the footprint does not influence the gradient measurement as the concentrations at the different heights are equally influenced, while concentration measurements in a traditional tracer experiment are affected.

The FTIR system as well as the measurement strategy employed are described in detail elsewhere (Griffith and Galle, 2000) and are only briefly described here. The measurement system consisted of a medium resolution (1 cm⁻¹) FTIR spectrometer specially configured for dual beam output (BOMEM, model MB100-2E), coupled to two nominally identical multiple reflection cells (Infrared Analysis Inc, supercell 100) yielding an optical pathlength of 96 m in 25 l volume each. Air was drawn into the two cells via two 25 m long 0.5” Teflon tubes at a rate of 25 l min⁻¹. The two cells could be connected to inlets at 3 heights on a mast, at 0.6, 1.2 and 1.8 m, via computer-controlled switching valves. In normal operation, simultaneous measurements from the lower two inlets were made, alternately with parallel measurements from the top inlet to quantify calibration offsets in the two cells and provide a third point for determination of the vertical gradient. In a typical gradient measurement the two inlets were first both switched to the high level. The detector then alternately collected spectra from the two cells at a rate considerably higher than the air exchange rate of the cells, thus providing an effectively simultaneous measurement of the same air in both cells. After thisough the cells were switched to 0.6 and 1.2 m, the cells were flushed and then the same measurement procedure was performed again completing one measurement cycle. Thus four spectra at three different levels were obtained typically every 10 min. In the evaluation the balance between the two cells was first checked, then the concentration differences between 0.6–1.8 and 1.2–1.8 m, respectively, were obtained by ratioing the low-level spectrum to the high-level spectrum for each cell. In this way instrumental spectral differences in the two cells were cancelled.

The spectra were analysed using classical least-squares (CLS) multiregression techniques (LabCalc, Galactic...
Fig. 1. Trace gas release system based on silicone tube permeation of SF$_6$.

Fig. 2. Plot showing the temperature dependence and reproducibility of SF$_6$ emission from the permeation system.

Industries). Calibration spectra for the fit were synthesised from the IR-database HITRAN using the software Multi Atmospheric Layer Transmission (MALT) (Griffith, 1996) except for SF$_6$ where the reference spectrum was obtained from a field calibration as described below.

2.2. Trace gas release system

To obtain a quantitatively known emission of the tracer gas, a large permeation system was developed. A schematic view of the trace gas release system is shown in Fig. 1. The system consists of 1 km silicone tubing (outer diameter 16 mm, inner diameter 14 mm). The tube was laid out upwind of the mast covering approximately 40 × 50 m, then filled with pure SF$_6$ at atmospheric pressure, a small purging through a waterlock at the outlet ensuring that the system remained filled. Due to its solubility in silicone, SF$_6$ slowly permeates the walls of the tube at a reproducible but temperature-dependent rate. The permeation rate was measured by passing a 2 m section of the tube through a box of 24 l volume and monitoring the concentration buildup in the box after the lid was closed. Samples were taken from the box 5, 10 and 15 min after closure of the lid using a 5 ml syringe and analysed by injecting into the FTIR cell. The permeation rate of the tube can be expressed directly in absorbance units and no absolute measurement of the SF$_6$ is necessary for quantitative analysis. This procedure also provided the reference spectra of SF$_6$ to be used in the evaluation algorithms. For convenience, an estimate of absolute SF$_6$ concentrations and permeation rates from the tubing can be obtained by comparing the measured spectra to a library SF$_6$ spectrum (QAsoft, IRanalysis Inc.). This gives a typical emission of 13.6 μg m$^{-1}$ s$^{-1}$ at 10°C, corresponding to a flux of 5.68 kg ha$^{-1}$ d$^{-1}$ over the area covered by the tubing.

The reproducibility of the SF$_6$ emission along the tube, as well as its temperature dependence was investigated by making a total of 26 measurements at eight different locations along the tube, with temperatures ranging from 5 to 12°C. A plot of these measurements is shown in Fig. 2. A linear fit to the data of Fig. 2 (rate = 0.52t ($^\circ$C) + 7.94 μg m$^{-1}$ s$^{-1}$) was then used to correct...
calculated emission rates for temperature, using ambient air temperature.

2.3. Gradient “footprint” modelling

In the present application the trace gas release system did not cover the whole area that contributed to the gradient. This had the effect that the measured SF$_6$ gradient became lower than would be the case if the whole fetch would have been covered, and thus the flux of ammonia was overestimated. In order to account for this effect, as well as making it possible to model the actual contribution from different areas under different meteorological conditions, a model was developed. The model calculates the “footprint” of the measurement given the heights of the gradient measurement and the meteorological conditions.

The model is based on a 200 x 200 m grid comprising 40,000 point sources upwind of the mast. The model assumes a Gaussian plume spreading from each point source in accordance with Eq. (3) below. The Gaussian plume vertical and horizontal diffusion is controlled by eddy diffusion and is empirically determined by the prevailing micrometeorological conditions. Based on Eq. (3), the individual contributions from each point to the gradient are calculated (Pasquill and Smith, 1983; Hanna et al., 1982).

$$\chi_b = \frac{q}{2\pi x K} \exp \left( -\frac{u}{4x} \left( \frac{y^2}{K_y} + \frac{z_b^2}{K_z} \right) \right),$$

where $\chi_b$ is the gas concentration, $q$ the source strength, $K = \sqrt{K_x K_z}$, $K_x = k u_z z$ the vertical coefficient of diffusion, $K_z = c K_x$ the horizontal coefficient of diffusion, $c$ the empirical parameter, $k = 0.4$ the von Karmans constant, $u_z = ku(z_h)/\ln(z_h - d)/z_0$ the surface friction velocity, $u$ the mean wind speed at $z_h$, $d$ the zero plane displacement of ground vegetation $\approx 0.75h$, $z_h$ the height of measurement point, $z_0$ the aerodynamic roughness length ($\approx 0.1h$), $h$ the canopy height and $x$ the distance from source to measurement point along an axis parallel to the wind direction.

In addition to the approximation of the Gaussian plume formula itself, the application in this context requires two further approximations (1) the formulation where the vertical wind speed $\sigma_z$ of the plume is assumed to be $\sigma_z = \sqrt{2K_z t}$, $t = x/u$ being the diffusion time, is only valid in the far field where $\sigma_z$ has become much larger than the scale of the turbulence (same argument for $\sigma_y$). However, this is never fully obtained for a ground level source, and (2) the formula assumes that the surface roughness length and the displacement height of the canopy are negligible compared to $\sigma_z$ as well as to $z_h$. With a surface cover of 40 cm high wheat this is not quite realized (for $x = 50$ cm, $\sigma_z \approx 3$ m). Despite the above, we feel that the use of Eq. (3) for interpretation of the measured gradients is sufficiently justified.

From Eq. (3) the contribution from each gridpoint to the concentration gradient at the measurement mast is calculated. By adding the contributions from all gridpoints together the total gradient from the area is obtained. Ratoing the individual contribution from each gridpoint to the total gradient gives an individual weighting factor for each gridpoint representing the “footprint” of the gradient measurement under the actual conditions. If the gridpoints are taken in order of decreasing contribution, a plot of the area responsible for e.g. 20, 40, 60 and 80% of the gradient can be made. Such a plot is shown in Fig. 3.

3. Results

The gradient system has been used in three field experiments: emission of N$_2$O from fertilised grassland in

Fig. 3. View of the measurement site, trace gas release system and “footprint” at noon day 2 (29 May).
Scotland (Smith et al., 1994b; Hargreaves et al., 1994), emission of \( \text{N}_2\text{O} \) from an organic soil in Denmark (Christensen et al., 1996; Griffith and Galle, 2000) and emission of \( \text{N}_2\text{O} \) and \( \text{NH}_3 \) from spreading of manure in Sweden, (this work). During the Swedish field campaign the trace gas release system and the model were tested on measurements of ammonia, while the model was used in Denmark to compare gradient/FTIR flux of nitrous oxide with field chamber/GC (Hargreaves et al., 1996).

3.1. Gradient flux measurement of \( \text{NH}_3 \)

In this experiment liquid pig manure was spread in a wheatfield at the research farm Lanna (58°21’N, 13°08’E) in southern Sweden. The soil at the site has a clay content of 40% in the topsoil with an organic matter content between 3 and 6%. The landscape was flat agricultural land and the fetch in the prevailing wind direction (SE) was more than 300 m. An amount of 60 kg N ha\(^{-1}\) was spread by broadcasting in growing crops of 40 cm height starting at 11 am on 28 May (day 1). Weather conditions were unfavourable for micrometeorological measurements, with low variable winds and sunshine. On the following day the conditions were good with overcast sky and a stable wind from SE of 3–7 m s\(^{-1}\).

Fig. 3 presents a map over the area showing the field, the locations of the meteorological mast, the gradient mast and the caravan housing the FTIR, the trace gas release system and the calculated footprint at noon day 2 (29 May) obtained from the above-mentioned model with the parameter \( c \) in Eq. (3) set to 10. The choice of this value is made by assuming \( K_y/K_z \) proportional to the ratio of the turbulence intensities of the lateral and vertical velocity components in the near neutral surface layer.

The inlets to the FTIR were positioned at the mast at 0.6, 1.2 and 1.8 m height above ground respectively. The \( \text{SF}_6 \) trace gas release tubing were laid out during the afternoon on the day of spreading (28 May). To investigate the potential loss of \( \text{NH}_3 \) in the sampling system, a plug of \( \text{NH}_3 \) (10 ml of headspace gas from aqueous \( \text{NH}_3 \) solution) was injected into one inlet at the mast, the system was immediately closed by connecting the outlet of the pump to the mast inlet and the gas was circulated through the system. Under these conditions the \( \text{NH}_3 \) concentration decayed exponentially with an initial time constant of 140 s, compared to the residence time of the air in the sampling system of 60 s at the flow rate used. The decay is presumed to be due to wall losses in the tubing, White cell and pump. However, since the gradient measurements were made under slowly varying steady conditions we expect the sampling system to be close to equilibrium with respect to the gas-phase exchange of \( \text{NH}_3 \) with the walls, and we have therefore ignored possible losses of \( \text{NH}_3 \) in the sampling system.

Fig. 4 shows the concentration of \( \text{NH}_3 \) at the three different heights during the day following the spreading (29 May).

A clear vertical gradient can be seen, as well as a gradual decay on all levels due to the evaporation and consumption of \( \text{NH}_3 \).

Fig. 5 shows the difference of \( \text{NH}_3 \) and \( \text{SF}_6 \) concentrations between 0.6 and 1.2 m, for the same period.
The variation in the NH$_3$ gradient is due to variation in flux as well as in meteorological conditions, whereas the variations in SF$_6$ gradient is attributed mainly to meteorology with a small dependence on ground temperature.

From the measured SF$_6$ gradient we can calculate a SF$_6$ flux using measured micrometeorological parameters from the expression

$$\text{Flux}_{SF_6} = k^2 \frac{\Delta u}{\Delta \ln(z - d)} \frac{\Delta \gamma_{SF_6}}{\Delta \ln(z - d)}.$$  (4)

This expression is obtained from Eq. (1) using the neutral stability estimate of $K_z$ given in Eq. (3) and $u$ determined from the logarithmic law for the wind profile (also defined in Eq. (3)). The flux obtained in this way assumes an infinitely large source area.

As the true SF$_6$ flux is known, the SF$_6$ flux obtained from Eq. (4) gives an opportunity to validate the source model. The model was run for the average meteorological conditions prevailing between 08:00 and 20:00 on day 2, and the obtained footprint is shown in Fig. 3. By integrating the obtained weighting factors over the area covered by the SF$_6$ trace gas release-tubing it was found that this area corresponded to 47% of the footprint area.

Thus one expects that the flux obtained from Eq. (4) if applied to SF$_6$ will only give 47% of the flux we would have obtained if the release tubing had covered an infinite area. The ratio of calculated to known SF$_6$ flux is given in Fig. 6, and is seen to be in good agreement with the source model.

The deviation from 0.47 in both ends of the experimentally determined curve is due to violation of the theoretical assumptions about neutral stability. During night the stratification is stable which leads to larger mean concentration gradients for the same magnitude of flux.

We now have two possibilities to calculate the NH$_3$ flux. One is to use micrometeorology in accordance with Eq. (4) (assuming that the emission fetch is longer than the footprint), the other is to use the SF$_6$ gradient and the known SF$_6$ emission in accordance with Eq. (2) and allowing for the footprint correction of 0.47. In Fig. 7 the ammonia emissions measured by the aerodynamic method for days 2 and 3 after spreading, as well as the emission derived from the tracer measurements for day 2 are shown. Also shown is air temperature and windspeed 1.5 m above ground. As can be seen the agreement between the two methods are good as long as the meteorological conditions are favourable. The emission shows a strong diurnal pattern which is likely to depend on both windspeed and temperature. The average emission during daytime (10:00–20:00) was found to be 2.63 kg NH$_3$-N ha$^{-1}$ d$^{-1}$ for day 2 and 1.44 kg NH$_3$-N ha$^{-1}$ d$^{-1}$ for day 3 after spreading. This decay is reasonably consistent with an emission of 3.6 and 4.3 kg NH$_3$-N ha$^{-1}$ d$^{-1}$ measured at the same site, on the day of emission, with integrating gradient and chamber techniques, respectively (Ferm et al., 2000).

4. Discussion

The gradient FTIR method has proven to be a valuable method for measurement of ammonia emissions.
from wide area sources, although the detection limits of the present system limits its use to relatively high emissions. Improvements in the system can be expected to increase the system sensitivity and operability. Major advantages of this technique as compared to many other methods (Ferm et al., 2000) are its area integrating capability and high time resolution.

The tracer gradient method has been validated against the aerodynamic gradient method. Because the tracer release system did not cover the whole footprint of the
gradient measurement, a direct comparison could not be made. However, by means of the footprint model this difference in release area could be accounted for, and after this correction the two methods showed good agreement. Thus, the tracer method has a potential to be used for emission measurements in suitable situations. Examples of such situations are studies of area sources of limited extent, where the whole emitting area can be covered uniformly by the tracer release system, i.e. NH$_3$ emission from manure heaps or CH$_4$ emissions from ponds. Under such conditions measurements can also be made under less stringent micrometeorological restrictions as compared to the aerodynamic methods.

The model has proven to be a valuable tool both in order to understand and visualise the actual footprint area measured with the gradient technique under different conditions, and in order to make corrections when comparing methods with different footprint areas.

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