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REVIEW ARTICLE

# Application of a high-temporal resolution method to estimate ammonia emissions from farmland

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**Abstract** A viable method—open-path tunable diode laser absorption spectroscopy (OPTDL) in conjunction with a backward Lagrangian stochastic (bLS) dispersion model—has been used for micrometeorological monitoring of ammonia fluxes. In this technique, the gas concentration measured with the OPTDL sensor is used to infer the surface emission rate with the aid of dispersion model calculations. On the basis of numerous assessment experiments and field trials, several beneficial strategies for using the OPTDL technique properly to monitor atmospheric $NH_3$ concentrations in the field have been summarized. Theoretically, the location of the concentration measurement can be anywhere in the emission plume, but in practice, the concentration measurement position must be carefully selected to avoid making measurements which are on the periphery of the downwind plume or are affected by obstructions. To obtain accurate estimates, periods with low friction velocity or extreme atmospheric stability, where Monin–Obukhov similarity theory-based relationships are invalid, or unrepresentative estimates due to unsuitable wind direction, should be excluded. A validation experiment showed that there was no significant difference between the ammonia emission rates obtained by the micrometeorological mass balance method and those obtained by the bLS model combined with the OPTDL technique. This study also indicated the potential of the bLS and OPTDL technique for investigation of diurnal emission patterns and environmental influences.

**Keywords** Backward Lagrangian stochastic dispersion model · Influencing factors · Installation and measurement · Open-path tunable diode laser absorption spectroscopy · Validation experiments

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## Introduction

In recent decades, various methods have been used to quantify $NH_3$ emissions from fertilized areas to atmosphere, including the mass-balance method, the chamber method, and the micrometeorological techniques (e.g., micrometeorological mass balance method, integrated horizontal flux method, eddy covariance method, flux gradient method). The mass-balance method is an indirect method which assumes that the ammonia emissions are equivalent to the difference between the total N supply and that accounted for by crop uptake, nitrate leaching losses, and residual soil nitrogen (Nommik 1973). Because this method requires estimation of many parameters, many of which are difficult to measure accurately, and neglects denitrification, the results often contain large errors. The chamber method has been widely used because of its simplicity and low cost. However, modification of the environment within the chamber introduces large uncertainty into $NH_3$ emissions estimates (Denmead and Raupach 1993; Fowler et al. 2001). In principle, micrometeorological techniques reflect actual ammonia emissions more accurately because they have minimal influence on the field environment being measured (Denmead et al. 1982). However, their requirements for complex instrumentation and strict environmental conditions may restrict their application.

Note that those methods that rely on capturing ammonia in an acid absorbent require a sampling time of hours (particularly for low concentrations of ammonia in air) to collect sufficient $NH_3$ for detection in the laboratory, which also necessitates much labor and laboratory analysis time after exposure. Moreover, $NH_3$ can easily absorb on the measurement equipment surfaces due to the active chemical property and highly soluble in water (Warland et al. 2001; Mosquera et al. 2005), and may cause significant error. Therefore, searching for alternative methods to meet the need for faster, more specific, and more precise measurements is worthwhile. Chemiluminescence detectors, in which ammonia is first oxidized to nitric oxide, provide a rapid way of measuring ammonia concentrations with a detection limit of 2 $\mu g \cdot m^{-3}$ and a response time of $<$1 min (Sutton et al. 1993). However, this technique requires measurement of the background concentrations of ammonia, nitric oxide, and nitrogen dioxide. Dias (1998) and Warland et al. (2001) reported a tunable diode laser trace gas analyzer system to monitor ammonia concentrations with great precision and rapid response. However, these techniques rely on pumping air, which may cause significant error due to adsorption of ammonia on the equipment walls (Warland et al. 2001).

Tunable diode laser absorption spectroscopy (TDLAS) in combination with long optical paths (i.e., open-path tunable diode laser absorption spectroscopy, or OPTDL) is a reliable and convenient tool with high precision, high sensitivity, high selectivity, and fast response time (Werle 1998) for making long-term, continuous, real-time, online, nonintrusive, and unattended measurements of small concentration fluctuations or gradients in the lower atmosphere and has been extensively used to detect atmospheric trace gases (e.g., $CH_4$, $NH_3$, $CO_2$, and NO) (Wagner-Riddle et al. 1997; Sharpe and Harper 1999). Besides, the OPTDL technique tackles the problem of $NH_3$ adsorption and rapid ammonia concentration measurement under field conditions. Recently, Flesch et al. (2004) used a backward Lagrangian stochastic (bLS) dispersion model to quantify gas emissions using open-path tunable diode lasers. This technique has several potential advantages over other measurement methods: insensitivity to the size or shape of the emission source, simplicity of field observation, and flexibility in location of the concentration measurement (Flesch et al. 2004). But the source configuration and the location of the concentration measurement relative to the source must be known. Many studies have demonstrated the accuracy of the bLS model together with the OPTDL technique in gas recovery experiments (Flesch et al. 2004, 2005b; McBain and Desjardins 2005; Gao et al. 2009a, b) and its applicability to determining ammonia (Flesch et al. 2007; Todd et al. 2008) or methane (Laubach and Kelliher 2005a; Gao et al. 2011) fluxes from feedlots.

At present, there are only a few reports in the literature of measurements of ammonia emissions from farmland-applied manure using a combination of the bLS model and OPTDL. Due to the relatively simple circumstances and low ammonia concentrations in crop fields, it is necessary to test the bLS model in conjunction with the OPTDL for estimating ammonia fluxes from farmland. The objective of this paper is to review the literature on the impacts of location of laser path, atmospheric stability, friction velocity, wind direction and obstruction on accuracy of the bLS model combined with OPTDL technique. The appropriate implementation of this technique in real farm situations is discussed. The results of an experiment to assess the applicability of the bLS technique together with OPTDL technique are also presented.

## Open-path TDLAS technique

### Underlying principles

According to Beer–Lambert's law, the intensity $I_0(v)$ of a laser beam at frequency $v$ transmitted through an absorption gas is given by (Kan et al. 2007):

$$I(v) = I_0(v)\exp[-S\varphi(v)CL], \quad (1)$$

where $I_0(v)$ and $I(v)$ are the initial and absorbed laser intensities, respectively, $v$ is the frequency of the laser beam, $C$ is the concentration of the absorption gas, $L$ is the optical path length, $S$ is the absorption strength of the line centered at frequency $v$, and $\varphi(v)$ is the normalized line-shape function. For harmonic detection, it is assumed that the value of $-S\varphi(v)L$ is confined to $-S\varphi(v)L \ll 0.05$. Then Eq. (1) must be modified to read:

$$I(v) = I_0(v)[1 - S\varphi(v)CL]. \quad (2)$$

At atmospheric pressure, the line-shape function can be described by a Lorentzian line-shape function. Then the second harmonic signal obtained by demodulation can be expressed as

$$I_{2f} \propto I_0\sigma_0 CL, \quad (3)$$

where $\sigma_0$ is the absorption coefficient. From this equation, the $2f$ signal is proportional to the gas concentration and the optical path length, which can be used to deduce the concentration.

## System components

The TDL system (provided by Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, China) comprises a tunable infrared diode laser, electronic elements, and optical elements. The electronic elements contain the temperature and current controllers, the photodiode detector, the lock-in amplifier and the signal control and processing electronics. The optical elements consist of the transmitter head, retro-reflector, reference cell and fiber-optic cable. With this system, the tunable infrared diode laser driven by the temperature and current controllers produces a collimated beam of light (a $NH_3$ absorption line centered at 1,544 nm) at the absorption frequency. The laser light is divided into two beams by beam splitter. A weaker laser light is then passed through the reference cell to provide a continuous calibration update. The other beam is transferred to a transmitter head via fiber-optic cable. The laser light emitted from the transmitter head propagates through the atmosphere to the retro-reflector and returns to the transmitter head, where it is focused onto the photodiode detector by a lens. The returned signal is then transmitted back to the control unit via coaxial cable and is analyzed to determine the gas concentration along the measurement path. Details of the TDL system, field data collection and analytical methods are summarized in Xia et al. (2008).

## BLS dispersion model

The bLS model calculates ground-to-air emissions by simulating the numerous upwind trajectories of gas particles in the downwind emission plume from a concentration measurement location to the source area (Flesch et al. 1995). The principle of the bLS model is introduced as follows, and detailed descriptions of the model are given in Flesch et al. (1995, 2004).

Monin–Obukhov similarity theory (MOST), which underlies the bLS model, posits that over short time intervals (e.g., 30 min), the statistical properties of the wind in a horizontally homogeneous atmospheric surface layer (height $z \leq 50$ m, but above a plant canopy) can be described by four key variables (Garratt 1992): the atmospheric friction velocity $u_*$, the Obukhov stability length $L$, the surface roughness length $z_0$ and the wind direction $\beta$. Consider an area source of known configuration emitting gas at a continuous but unknown rate $Q$ (kg $m^{-2}$ $s^{-1}$), with the time-average gas concentration $C_M$ measured at an arbitrary point $M$ (the location of $M$ relative to the source must be known) within the resultant plume. The bLS model predicts thousands of upwind diffusion trajectories based on MOST to calculate the ratio of the net concentration $C$ (concentration $C_M$ above the background) at $M$ to the emission rate $(C/Q)_{sim}$:

$$(C/Q)_{sim} = \frac{1}{N}\sum\left|\frac{2}{w_0}\right|, \quad (4)$$

where $N$ is the total number of particles released from $M$, $w_0$ is the vertical velocity at touchdown, and the summation covers only touchdowns within the emission source (Flesch et al. 1995, 2004). The emission rate, $Q$ can then be inferred as:

$$Q = \frac{(C_M - C_b)}{(C/Q)_{sim}}, \quad (5)$$

where $C_b$ is the background concentration.

Using the point measurement increases sensitivity to wind direction (i.e., increases the probability of the plume bypassing the sensor caused by the wind). One may sidestep this problem by employing line sensors due to the great likelihood of the sensor intercepting the emitted plume (Crenna et al. 2008). Furthermore, Flesch et al. (2004) and Laubach and Kelliher (2005a) argued that using line-average concentration measurements can reduce error in bLS model. Hence, it is encouraging to pursue bLS combined with line-average gas sensors. When using a line-averaged concentration ($C_L$), $C_L$ is assumed to be the average of $P$ point concentrations spaced evenly along the laser path, with particle trajectories being calculated from each of these points. Then Eqs. (4) and (5) must be modified as follows (Flesch et al. 2004):

$$(C_L/Q)_{sim} = \frac{1}{P}\sum_{i=1}^{P}\left(\frac{1}{N}\sum\left|\frac{2}{w_0}\right|\right), \qquad (6)$$

$$Q = \frac{(C_L - C_b)}{(C_L/Q)_{sim}}, \qquad (7)$$

where $N$ is the number of particles released at each point, $P$ is the number of specified release points along the laser path and the inner summation refers only to touchdowns within the source.

In the present research, gas-emission calculations were carried out using the freely available WindTrax2.0 software (Thunder Beach Scientific, Halifax, NS, Canada).

## Installation and measurement

The gas emitted from the source will spread laterally and vertically with the wind and will generate the downwind plume. Generally, gas concentrations and fluxes in or near the center of the plume are less fluctuating and less variable than those at the plume margin. As argued in Flesch et al. (2007), a concentration measurement location at or near the edge of the plume has several disadvantages. First, the bLS model cannot accurately predict $(C_L/Q)_{sim}$ at the plume edge, where the gas trajectories are too extreme to accurately model. Second, the margin of the plume, which is associated with emissions only from the source edge, may inadequately represent overall emissions. Third, slight errors in wind measurements (especially wind direction) can cause dramatic errors in $(C_L/Q)_{sim}$ at the plume margin. Finally, the concentration at the edge of the emitted plume is too close in concentration to the background to detect accurately. To avoid making concentration measurements on the periphery of the downwind plume, an appropriate and strategic position for the concentration sensor must be carefully selected.

The following discussion generalizes how to use open-path TDLAS to monitor atmospheric $NH_3$ concentrations in real applications.

### Optical path length

The optical path is two times the length of the laser path (the separation between the transmitter head and the retro-reflector). The detection sensitivity of the laser system depends on the optical path length and the gas species. The longer the path length, the lower will be the detection limit of the laser system (Table 1). The sensitivity of the TDL system is 5 ppm-m for $NH_3$ (i.e., over a 10-m optical path length measurement, the detection limit is 0.5 ppm for $NH_3$). The maximum path length for the instrument used is up to 1,000 m for $NH_3$ detection systems. The poor detection limit for short path lengths is inadequate to meet the requirements of $NH_3$ concentration measurements. Moreover, the likelihood of the sensor crossing the emitted plume decreases as the path length is reduced. However, the authors are unwilling to recommend a long optical path as a measurement strategy to enhance detection sensitivity and maximize the number of usable wind directions. For one thing, the alignment of the optical path is not always stable (i.e., the transmitter head becomes misaligned with the retro-reflector) over long paths in on-farm situations, which decreases data yield from the laser system (Laubach and Kelliher 2005b). Moreover, a single wind observation cannot sufficiently represent the winds along a very long path for dispersion calculations because the fluctuations in wind speed over the laser path are likely to be very different from the wind-speed fluctuations at a single location. According to the authors' experience, for $NH_3$ detection, an open-path TDLAS with an optical path length of 200–400 m is recommended, corresponding to a detection limit of 0.0125–0.025 ppm.

**Table 1** Sensitivity of the open-path TDLAS system for ammonia

| Optical path length (m) | 1 | 10 | 100 | 200 | 400 | 1,000 |
|---|---|---|---|---|---|---|
| Sensitivity (ppm) | 5 | 0.5 | 0.05 | 0.025 | 0.0125 | 0.005 |

### Laser path height

The laser path height is defined as the average of the path center height and the transmitter head/reflector height in the bLS simulations. Wilson et al. (1982) and Denmead (1983) assumed that there was one particular height (called the ZINST) at the center of the circular plot at which the concentration was most insensitive to atmospheric stability and $C/Q$ was nominally independent of stability. Generally, the ZINST will not exist for other source geometries (i.e., a non-circular plot). However, there are heights at which the influence of atmospheric stability on $C/Q$ is minimized, which can be regarded as the optimum measurement positions for the bLS technique (McBain and Desjardins 2005). McBain and Desjardins (2005) showed how the accuracy of the bLS method is affected by measurement height. Their finding that values of $Q_{\mathrm{bLS}}/Q$ (the ratio of emissions estimated using the bLS model to actual emissions) were related to sampling height indicates that an ideal measurement height ZINST exists and is estimated to be 1.35 m. They also found that using average values of $Q_{\mathrm{bLS}}$ from heights of 1.0 and 1.5 m provided a better estimate of $Q$ than data from ZINST or from either of these heights. It is therefore suggested that the use of two (or possibly more) measurement heights selected around ZINST is more advantageous than use of a single optimal height.

From the results of Wilson et al. (1982) that the ZINST changed in different sized circular plots, it can be inferred that the optimum heights for other source geometries vary with fetch. Flesch et al. (2004) suggested that for a homogenous surface layer, concentration measurements should be made at a maximum height of $0.1X$ ($X$ being the available fetch) to avoid detecting concentrations at the plume edge. It is further hypothesized that the accuracy of the model at heights >2 m improves as the fetch increases. McBain and Desjardins (2005) found that results at height >2 m improved slightly as the fetch exceeded 20× height, but that accuracy and precision were still poor, which was likely attributable to $C_{\mathrm{L}}$ being measured near the plume margin. They also studied the accuracy of the bLS model at various fetches and stabilities and suggested that the error in $Q_{\mathrm{bLS}}$ for other measurement heights might be due to inaccuracies in simulating stability influences in WindTrax software (Thunder Beach Scientific, Halifax, NS, Canada).

The ideal concentration measurement height is also affected by the plant canopy, the presence of obstructions, and other factors which will be discussed in the following sections.

### Fetch

The fetch (the distance between the source and the laser path) depends on the location of the source relative to the measurement path and on the wind direction.

Flesch et al. (2007) suggested that locating the concentration measurement in the emission source or at the edge of the source has the following advantages: relatively high concentrations, which reduce measurement uncertainty and sensitivity to background concentration in the bLS emission calculations; the likelihood of modeling emissions for almost all wind directions and of acquiring more complete emission time series due to the excellent possibility of the sensor across the plume. However, monitoring concentrations in the source or at the source edge may increase dispersion modeling errors on account of high source variability (particularly the strong inhomogeneity in emissions) (Flesch et al. 2004, 2005a, 2007). If a line sensor is placed downwind of the source, the accuracy of the bLS model becomes less susceptible to any spatial inhomogeneity of the source and to wind disturbances caused by the plant canopy, obstructions, or other factors (Flesch et al. 2005a, 2007). Nevertheless, moving the sensor further from the source may create other problems: it increases the likelihood that the emission plume misses the laser path and yields a much sparser record of emissions compared with positioning in or near the source; it adds considerable uncertainty to the measurements because the resulting concentrations are close to background level at times (Flesch et al. 2004, 2007). Most notably, the reduction in ammonia concentration due to chemical transformation and deposition during long transport processes, because $NH_3$ is readily soluble in water, very reactive, and of low extent of migration, may introduce a bias in the emission calculations. McBain and Desjardins (2005) obtained good estimates ($Q_{\mathrm{bLS}}/Q$ close to one) from an artificial $3 \times 3\ \mathrm{m}^2$ area source with fetch values averaging 22 m (path height = 1 m), but poor results for fetch values ≥32.5 m. Loh et al. (2009) also found the standard errors for fetch = 30 m were greater than for fetch = 10 m because the concentration rise above the background level decreases with increasing fetch as the downwind plume disperses into an increasingly large volume. Mosquera et al. (2005) argued that, far from the source (>25–50 m), the plume is rapidly dispersed and lower concentrations are monitored, which increases the measurement uncertainty. From these results, it can be argued that a line sensor should be placed in a location as close to the source as possible, where the accuracy of the bLS model is much less sensitive to any inhomogeneity in the source, to reduce measurement uncertainty, and to reduce the probability of the plume missing the sensor.

One metric for evaluating the gas-measurement position is the ratio of sensor height to fetch ($z/r$), with smaller values being desirable. Laubach and Kelliher (2005a) obtained the best agreement between the bLS technique and the IHF method when $z/r$ was as small as possible, which was in line with the suggestion of Flesch et al. (2004) to select $z/r < 0.1$. Wilson et al. (2001a) pointed out that despite ignoring wind complexity, they could still estimate emissions with error <15 % using $z/r = 0.028$. However, McBain and Desjardins (2005) found that at height >2 m and fetch ~22 m (i.e., $z/r < 0.1$), both the accuracy and precision of the bLS dispersion model were very poor, probably due to the measurement location, which was close to the top of the gas plume rather than at its center; this appears to conflict with the results previously described. The plant canopy also has an effect on the calculation of emissions using the inverse dispersion model. Given that the laser path is far above vegetation and at a distance from the source that far exceeds the canopy depth, the effect of a plant canopy on the transport of gas can be considered negligible (Wilson et al. 2001b).

A universal measurement fetch will not generally exist for any sources. The proper fetch should vary with size, inhomogeneity and ambient environment of the source. The recommendation here is therefore to use in-source or near-source concentration measurements, assuming that the experiment site is a horizontally homogeneous source with large upwind dimensions. Given an inhomogeneous site (especially with varying spatial distribution of emissions) or a small source, downwind measurements to reduce sensitivity of emission accuracy to inhomogeneity in source are necessary, but should be as close as possible to the source reduce concentration measurement uncertainty.

### Meteorological observations

The bLS model requires that at least four parameters be known: friction velocity, $u_*$; Monin–Obukhov length $L$, surface roughness length $z_o$, and wind direction $\beta$. These parameters can be determined from 3-D sonic anemometer measurements or from wind speed and temperature profile measurements. Traditionally, surface layer properties were determined by measuring temperature and wind-speed profiles (at least four measurements at different heights), usually on a tower 3–10 m in height. WindTrax estimates $u_*$, $L$, and $z_o$ by fitting a curve through profile measurements using a least-squares method. More recently, the 3-D sonic anemometer seems to have become an increasingly common tool to provide all the required model parameters directly and has been found to improve results over the profile system. Flesch et al. (2004) found that the estimated emissions from profile-system descriptions were inferior to sonic anemometer-based estimates because the values of $u_*$ derived from profile measurements were too high. Consequently, it is proposed here to measure the wind field using a 3-D sonic anemometer to improve the accuracy of the inverse dispersion model.

### Sampling interval

Monin–Obukhov similarity theory assumes that over a reasonable interval (e.g., 15–60 min), the lower atmosphere is in an equilibrium state which can be simulated accurately by MOST. All measurement data used in WindTrax must be values averaged into a representative period which is commonly 15–30 min. Values obtained using a shorter averaging time are less likely to be representative of the atmospheric state. Conversely, longer periods might enhance the difficulty and uncertainty of defining atmospheric stability because of gradual diurnal variations in the surface layer, especially during times of rapid transition (e.g., near sunrise and sunset).

What sampling interval should be used with the bLS model and OPTDL? Flesch et al. (2004) applied the bLS technique over 15, 30, and 120 min to investigate the influence of averaging time on the accuracy of the inverse dispersion model and found that the accuracy decreased with increasing averaging interval. Conversely, Gao et al. (2009a) reported that extending the sampling interval from 15 to 120 min slightly improved the accuracy and precision of the bLS method. However, after excluding periods when MOST-based relationships were inaccurate (i.e., extreme stabilities or light winds), there was not much difference between the recovery using 15-min intervals and the values for 120 min. Accordingly, it would be ideal to use shorter sampling intervals (say, 15–30 min), which agree with the traditional MOST description, to satisfy the assumption of stationarity and to improve the temporal resolution of the modeled emissions.

## Influencing factors on accuracy

### Atmospheric stability

Accurate estimation of emissions using the bLS model depends on the accuracy of the MOST-based atmospheric description. However, MOST-based relationships are invalid during periods of rapid atmospheric change (e.g., sunrise and sunset transitions) or extreme stability, which make inference of $Q$ unreliable (Flesch et al. 2004) due to the dramatic influence of atmospheric stability on the effectiveness of atmospheric transport and consequently on the value of $(C/Q)_{\mathrm{sim}}$. Flesch et al. (2004) found that the accuracy of the bLS technique varied with stability: underprediction under extremely unstable conditions and overprediction under extremely stable conditions. Gao et al. (2009a) also reported an underestimation of 31 % for extreme instability and an overestimation of 56 % for extremely stable stratification. McBain and Desjardins (2005) showed a trend toward decreasing accuracy as the atmosphere became more stable. Loh et al. (2009) obtained greater spread in the results with increasing stability, but no significant deterioration in accuracy.

How can a user distinguish periods of MOST invalidity due to extreme stability and ignore the predicted emission rates during these times? A conservative view considers $|z/L| < 1$ ($z$ being the meteorological observation height) as a threshold for the legitimacy of a MOST-based atmospheric description. Flesch et al. (2004) excluded periods with $|z/L| > 1$, which dramatically dropped the recovery from 127 to 102 %. The Obukhov stability length ($L$) is commonly used as an indicator for identifying periods of extreme atmospheric stability and is defined as follows: extremely unstable when $-10 < L < 0$ m and extremely stable when $0 < L < 10$ m. Flesch et al. (2005a) argued that the rejection criterion of $z > |L|$ was insufficient for large emission sources. After increasing the threshold from $|L| \leq 2$ to $|L| \leq 10$ m, less variable results were obtained.

### Friction velocity

It is known that the assumptions of stationarity and horizontal homogeneity (which underlie MOST) become increasingly invalid and meteorological measurement errors increase as $u_*$ decreases (which is often linked to stable conditions). Using friction velocity as a criterion for filtering micrometeorological inferences is not unusual (e.g., Black et al. 2000; Massman and Lee 2002). Flesch et al. (2004) and McBain and Desjardins (2005) found that the accuracy of the bLS technique deteriorates as $u_*$ decreases. Flesch et al. (2004) reported that ignoring data with $u_* \leq 0.15$ m s$^{-1}$ results in an average $Q_{\mathrm{bLS}}/Q$ of 0.97 and viewed $u_* \leq 0.15$ m s$^{-1}$ as the best indicator of inaccurately estimated emissions. After removing periods with $u_* \leq 0.19$ m s$^{-1}$ from the results of McBain and Desjardins (2005), the influence of atmospheric stability on the accuracy of the bLS model became more evident.

Inaccuracy in the bLS model is primarily correlated with extreme stability, low $u_*$, or both. Excluding periods with $u_* \leq 0.15$ m s$^{-1}$ or $|L| < 10$ m (or $|z/L| > 1$) has been a common data-quality filtering process. Loh et al. (2009) showed that a rejection criterion of $u_* \leq 0.15$ m s$^{-1}$ or $|z/L| > 1$ had little effect on accuracy ($Q_{\mathrm{bLS}}/Q$ dropped from 0.98 to 0.96), but caused a significant decline in the standard deviation (a decrease from 1.63 to 0.28). Gao et al. (2009a, b) found that application of the selection criteria ($u_* > 0.15$ m s$^{-1}$ and $|L| \geq 10$ m) led to satisfactory recovery rates ranging from 103 to 109 %. The proposed rejection criteria of $u_* \leq 0.15$ m s$^{-1}$ or $|L| < 10$ m have also been successfully used for data screening of ammonia or methane flux measurements at the feedlot by Flesch et al. (2005a, 2007) and Gao et al. (2011).

### Wind direction

As argued earlier, concentration measurements on the periphery of the emitted plume can introduce dramatic errors into emission inference. Variability in wind direction might lead the plume simply to “glance over” the laser path, which necessitates a wind-direction filtering criterion for eliminating unsuitable wind directions to ensure data quality. Desjardins et al. (2004) and Loh et al. (2009) thought that data should be deleted when the wind direction was outside certain angles of the normal to the rectilinear source area and selected the angle along the line between the center of the source and the transmitter/reflector as a suitable exclusion threshold, as illustrated in Fig. 1. However, this critical exclusion threshold is likely to reject some data during favorable wind directions, and is impractical for sources with irregular shapes. When running the backward model to estimate emissions, the WindTrax software computes the percentage of touchdowns covering the emission source. Touchdown area is an alternative reasonable selection criterion which may increase the proportion of acceptable observations. Flesch et al. (2007) suggested that the user remove periods in which the portion of the source area covered by the footprint of the laser path located at the source is <5 %, but 10 % for a sensor downwind of the source, to avoid unrepresentative estimates.

## Obstructions

A MOST-based atmospheric description applies mainly to horizontally homogeneous terrain. However, in the real world, there exist a variety of structures (buildings, trees, etc.), which can create wind disturbances that entail a risk of error in the emission inference. At some distance (the threshold distance) downwind of the obstruction, where the wind promptly returns to the ambient state (i.e., where MOST can be expected to be valid), the effect of the wind perturbation on the trace dispersion is essentially negligible, that is, is insignificant in predicting $(C/Q)_{\mathrm{sim}}$. Consequently, the best strategy is to make observations beyond this threshold distance. The threshold distance is dependent on atmospheric stability (Seginer 1975; Wilson 2004), obstacle configuration (Sakamoto and Arie 1982), and obstacle porosity (McNaughton 1989), and is greatly affected by the obstruction height $h$ (Flesch et al. 2005a). Heisler and Dewalle (1988) postulated that the effect of a windbreak on downwind flow is proportional to the windbreak height. Tokairin and Kitada (2004) studied the influence of fences on downwind gas dispersion and found that a fence increased the concentration by approximately 40 % right beside the fence (2.4$h$ from the fence) compared to the value without the surrounding fence, but only caused a slight difference beyond 10$h$ downwind of the fence. A similar result can be seen in a field trial with a synthetic area source surrounded by a windbreak fence (1.25 m tall) performed by Flesch et al. (2005b), which showed that the bLS model with concentrations measured near the fence overestimated actual emissions by an average of 50 %, but that eliminating these near-fence predictions reduced these systematic errors to only about 2 %. Therefore, these researchers speculated that the threshold distance for ignoring wind complexity was about 10$h$ from the fence. Results obtained by McBain and Desjardins (2005) suggested that the presence of obstacles has little impact on the model provided that concentration and wind measurements are made beyond 25$h$ downwind of the obstruction; these results agree with the thinking of Tokairin and Kitada (2004) and Flesch et al. (2005b). From these results, it can be concluded that by careful selection of a measurement location (beyond about 10$h$ from the obstruction), a MOST-based bLS technique can be applied with reasonable confidence to a disturbed wind field.

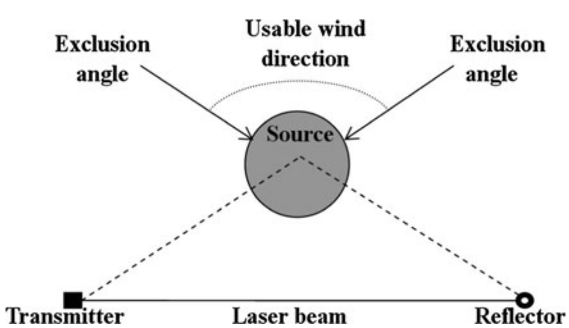


**Fig. 1** Schematic representation of the criteria to exclude unsuitable data due to unfavorable wind direction

## Validation of the method

A validation experiment was conducted on farmers' fields beside the Fengqiu State Key Agro-Ecological Experimental Station of the Chinese Academy of Sciences in Fengqiu County, Henan Province, China (114°24′E, 35°00′N) after maize harvest and before wheat sowing in October 2010. The site was essentially flat with no significant obstructions for several hundred meters north (the prevailing wind direction during the experiment) of the experimental area and only a row of about 10-m tall trees within about 200 m south of it. One circular plot (diameter 40 m) was selected as the ammonia emission source. The commercial granular urea (total N $\geq$ 46.4 %, 1–3 mm in particle diameter) was evenly broadcasted by hand over the soil surface at the rate of 348 kg N $ha^{-1}$ between 6:30 and 7:00 a.m. on October 2, 2010. Three open-path lasers (provided by Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, China) were used to monitor ammonia concentrations simultaneously. Two lasers were placed 24 m south and east of the center of the plot in anticipation of dominant northwest winds. The third laser was situated approximately 100 m upwind of the source to detect background concentration. The lasers were all set 1.0 m above the ground with laser path length (separation between transmitter and reflector) of 80 m. The data were processed to give 30-min means and used to estimate ammonia emissions by the bLS model. Ammonia fluxes were also measured by the micrometeorological mass balance technique (MMB, as reference method; Leuning et al. 1985) with 12-h sampling intervals from 7:00 a.m. on October 2 to 7:00 a.m. on October 7. According to Flesch et al. (2004), periods with $u_* \leq 0.15$ m $s^{-1}$, $|z/L| > 1$ or when $C_L$ was unrepresentative due to unfavorable wind direction were eliminated to avoid failure of the MOST-based model. For all 240 half-hour periods, 77 half-hour periods were eliminated due to low $u_*$ and extreme stability, of which 26 observations were at daytime and 51 observations were at night. There were no data associated with poor touchdown coverage.

As Fig. 2 illustrates, there were strong diurnal variations in the ammonia emission pattern. The diurnal pattern in $NH_3$ emission, characterized by a peak between 14:00 and 15:00 and a minimum during the night, was modulated by meteorological condition. The emission rate and variability in emission rates was much greater during the daytime than over the nighttime. The fluctuations in rate were similar to fluctuations in wind speed (Fig. 2a) and air temperature (Fig. 2b), indicating that the variations in $NH_3$ emission were attributed to the changes in air temperature and wind speed. Due to low wind speed and extreme stability, nighttime measurements yielded a much sparser data than the daytime. Only daytime measurement periods were selected to analysis the effect of the wind speed and air temperature on $NH_3$ volatilization. Correlation analysis showed

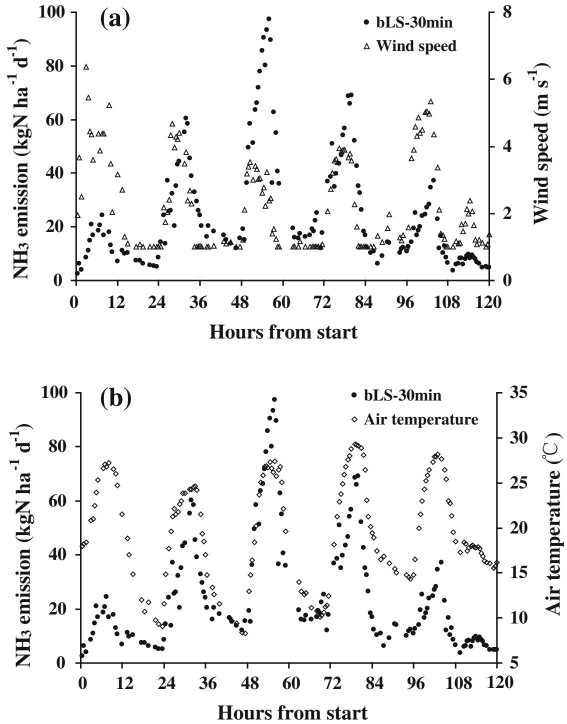


**Fig. 2** Dynamic of ammonia emission and wind speed (**a**), air temperature (**b**)

significantly positive correlation ($p < 0.01$) between ammonia emissions and air temperature with $r$ values of 0.867, 0.774, 0.814, 0.810 and 0.787 for 0.5–12, 24.5–36, 48.5–60, 72.5–84 and 96.5–108 h after fertilization, respectively. The Pearson correlation coefficient between ammonia emissions and wind speed was 0.418 ($P > 0.05$), 0.387 ($P > 0.05$), 0.431 ($P < 0.05$), 0.741 ($P < 0.01$) and 0.810 ($P < 0.01$) on the 5 daytime measurement periods. In the present study, the dominant relationship was between ammonia emissions and air temperature in this study.

Only daytime data were used to analyze because the MMB method was invalid due to low wind speed at night. The ammonia emissions estimated by the bLS model were averaged into 12-h values to compare with that obtained with the MMB method. The MMB method is considered the standard technique when validating new methods for estimating $NH_3$ emissions from field-applied animal manure or fertilizers (Wilson et al. 1983; McInnes et al. 1985; Sherlock et al. 1989). The scatter plot of $NH_3$ emissions of $Q_{bLS}$ versus $Q_{MMB}$ (Fig. 3) shows that the two methods gave similar $NH_3$ emission estimates. The quantitative

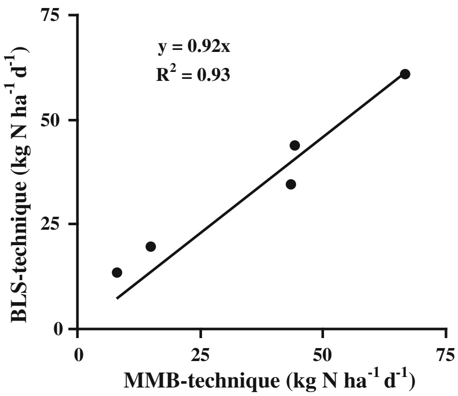


**Fig. 3** Ammonia fluxes estimated using the TDLAS–bLS technique versus emission rates determined by the micrometeorological mass balance technique

agreement between the two estimates was evaluated using the linear regression slope and the squared correlation coefficient. The regression fit of the paired data points (Fig. 3) gave the slope of the linear fit line as 0.92, indicating that $Q_{bLS}$ was lower on average than the mean $Q_{MMB}$ by only 7 %. There was a strong linear relationship between the ammonia fluxes obtained by the two methods, as indicated by the squared correlation coefficient of 0.93. A paired Student's $t$ test was also performed, and the result showed that there was no significant difference at the 95 % level between the emissions observed by the MMB method and those obtained by the bLS technique. Gao et al. (2009b) also found that the bLS model combined with OPTDL and the micrometeorological mass difference method together with OPTDL provided equally accurate measurements of emissions, but that the latter had smaller variability. However, compared to the MMD technique, the bLS technique is practical and preferable because it requires concentration and wind measurements from only one height and therefore less instrumentation.

## Conclusions

The OPTDL in combination with the bLS technique has become increasingly useful and viable for estimating ammonia emissions from agricultural sources. Numerous assessment experiments and field trials have provided many valuable experiences and beneficial recommendations. With proper positioning of the laser sensor to avoid taking concentration measurements within the plume margin and a good selection of sampling interval, the bLS technique can be accurately used for continuous measurements of ammonia fluxes. Note that the concentrations and the meteorological observations should be performed well away from obstructions to reduce the effect of the resulting wind disturbances. The user should also exclude periods of MOST inaccuracy (low friction velocity or extreme atmospheric stability) and unrepresentative estimates due to unsuitable wind direction to improve the accuracy of the bLS model. The results presented here, combined with those of Gao et al. (2009b), indicate that the inverse dispersion technique is preferable to the micrometeorological mass balance technique and can be used to estimate ammonia emissions from agricultural sources accurately.

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