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On surface fluxes at night – the virtual chamber approach.

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Abstract

Quantification of the emission rates of various gases from soils at night remains a challenge, confronting climate science (in the case of CO_2 and CH_4) and agriculture science (for NH_3 and N_2O, among others). In sufficiently stable conditions at night, concentrations of such emitted gases build up at the surface, with intermittent interruptions commonly attributed to the passage of packets of turbulence. The utility of conventional micrometeorological experimental methods in such circumstances is questionable, and chamber methods have been developed to meet the challenge. Here, a statistical approach is proposed, in which micrometeorological field data are used to replicate the likely characteristics of a chamber experiment, yielding estimates of surface fluxes at the surface itself rather than at some height above it. The methodology proposed is developmental at this time, with details intended to correspond to the use of both closed and vented chambers. Its application to three recent field studies is explored: (1) a study of nocturnal CO_2 emission from two test areas (one previously tilled and the other not) in Ohio in 2015; (2) a similar experiment conducted in Zimbabwe in 2013 (one area previously tilled and a second left fallow), and (3) an investigation of NH_3 effluxes from a crop previously treated with urea ammonium nitrate (UAN), in Illinois in 2014. There are few measurements with which to compare the results presented here, however the values obtained are within the range of available field data.

Keywords: Soil efflux, CO_2, CH_4, NH_3, nocturnal intermittency, Zimbabwe

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1. Introduction

Quantification of the emission rates of trace gases from soils in fields, wetlands and forests presents a problem that standard micrometeorological methods fail to solve (Skiba et al., 2009; Wilson et al., 2012). While eddy correlation techniques, in their various forms, have gained popularity, their requirement for sufficient fetch remains an obstacle that is difficult to overcome, especially at night (Aubinet, 2008). Bowen ratio methods are less susceptible to fetch limitations, because relevant measurements can be made at a lower height than for eddy correlation or flux/gradient calculations (Meyers et al., 1996).

Measurement of fluxes at night is especially demanding (Schneider et al., 2009; Darenova et al., 2014). While sensitivity to fetch limitations is reduced, the Bowen ratio methods remain fallible at night, when the inherent assumption that gradients and fluxes are closely associated is vulnerable. To address the matter of emissions from soils at night, field programs often rely on measurement methods of an entirely different kind – the use of chambers that confine emissions from the ground within closely-monitored volumes and thus eliminating the problems associated with fetch. In the case of carbon dioxide (CO_2), for example, the rate of increase in CO_2 concentrations within such a confined volume is an indication of the flux from the surface. However, it is recognized that the presence of any such chamber imposes an obstacle to the natural flow regime, with consequences that are hard to quantify. On the whole, there is no method that appears to satisfy the objections of all critics.

Comparisons among results obtained using chambers of different configurations have been revealing. Comparison of results from closed ('static', q.v. Edwards, 1982) chambers and alternative 'dynamic' approaches (Norman et al., 1992) has received particular attention. Field

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studies summarized by Nay et al. (1994) have indicated considerable differences, sufficient that laboratory tests were conducted of their performance involving the measurement of CO_2 efflux rates of known magnitude from test surfaces. The laboratory evaluations confirmed the level of uncertainty derived from the many field comparisons, with differences sometimes exceeding a factor of two. A more extensive examination was reported by Pumpanen et al. (2004), whose independent research allowed them to conclude that "Any use of the static-chamber method ought to be particularly scrutinized." Wang et al. (2004) compared results from closed and vented chambers, with results indicating differences in derived soil efflux rates (of ammonia (NH_3) in their tests) ranging up to a factor of five.

Here, a statistical approach is proposed, replicating the constraints associated with chamber methods in a way that leads to estimates of average fluxes rather than specific short-term situations. The present intent is to demonstrate the utility of the methodology, without proposing that it should replace other experimental methods but indicating the benefits of a statistical way of looking at the results of field studies.

The concept of a 'virtual chamber' analysis to derive flux information from nighttime concentration data (of trace gases like CO_2, methane (CH_4), nitrogen oxide (NO_x), and NH_3) arose in examination of data obtained in Zimbabwe, which illustrated the ramp structure at night considered due to dilution of CO_2 accumulation in the stratified layers of air near the surface by nocturnal intermittent turbulence (Hicks et al., 2015). The Zimbabwe dataset is of special interest, because it relates to a field site on the arid Zimbabwe plateau near Harare, at an altitude of more than 1400 m asl. The Zimbabwe dataset will be revisited below, as one of the three examples of the analysis methodology now proposed.

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2. The virtual chamber

Consider the case of trace gas emission from a specific surface. At this point, there is no consideration of the conventional requirement for time stationarity and spatial uniformity. These issues will be considered later. In daytime convective (and unstable) situations, the measurement of the fluxes is typically considered as a standard micrometeorological exercise. At night, however, the constraints imposed by the necessary assumption that fluxes measured in the air at some convenient height above a surface of special interest are indeed representative of that particular surface presents substantial obstacles (Aubinet, 2008). It is the nocturnal stratified atmosphere in contact with the surface that will be considered here.

There are many published examples of nighttime time series of measurements of concentration of some gas (e.g. CO_2 or CH_4) in ground-level air that displays a saw-tooth pattern, with slowly increasing concentrations interrupted by sharp decreases (Wehr et al., 2013). These intermittent decreases are commonly attributed to bursts of turbulence interrupting an otherwise quiescent surface boundary layer. There are several possible causes of these turbulent events, such as the oscillations of a low-level jet or the generation of gravity waves by some upwind obstacle (Aubinet, 2008; Mahrt et al., 2019). It is possible that the phenomena are a basic feature of strongly stratified flow (Manneville and Pomeau, 1979; He and Basu, 2015), as a consequence of interactions among different processes (Lorenz, 1963). The related phenomena are almost invariably external to the classical micrometeorological framework, in which turbulence is associated with the characteristics of the local surface. The optimal time resolution is therefore not associated with conventional micrometeorological examinations of fluxes and gradients, but instead short enough to identify with clarity occasions of

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intermittency so that these can be excluded from the analysis now proposed -- intended to focus on the causes of increases in surface concentrations. Field experience indicates that a time resolution of the trace gas concentration record should best be such that events shorter than five minutes can be resolved.

Suppose a fast-response anemometer is deployed at some convenient height, providing three-dimensional velocity data (means and variances) every five minutes, or over some alternative averaging time deemed appropriate. Simultaneously, measurements of concentration (C) of some atmospheric trace constituent are made, at some point below the sonic installation. After data accumulation extending over many days, consider the statistical characteristics of ensembles of data generated after sorting according to time of day. A partial correlation examination of three variables is of present relevance:

$$X_1 = dC/dt \quad (1)$$

$$X_2 = u \quad (2)$$

$$X_3 = \sigma_w \quad (3)$$

where notation is conventional. In practice, the wind speed u is an output of the sonic anemometer, as is the standard deviation of the vertical wind component σ_w. The rate of change of concentration, dC/dt, is conveniently computed from the initial time sequence of measurement as:

$$dC/dt = (C_{n+1} - C_{n-1})/(t_{n+1} - t_{n-1}) \quad (4)$$

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A first-order partial correlation analysis (or multiple regressions) yields the best-fitting coefficients in a relationship of the kind:

$$X_1 = a_x + b_{x12} \cdot X_2 + b_{x13} \cdot X_3 \qquad (5)$$

The intercept a_x is therefore the value of X_1 (i.e. dC/dt) that would be expected in the case for which X_2 and X_3 were both zero; i.e., for when there is no effect of the wind (no advection) and no turbulent exchange in the vertical at the level of the anemometer (z_a). The situation then envisioned is that of a conventional closed-chamber experiment, but lacking the consequences of a physical presence that could influence the natural circumstances.

Figure 1 presents a schematic illustration of the construct now considered. Two configurations are illustrated. Consider, first, the closed-chamber option as discussed above and as illustrated to the left of the diagram. Clearly, the assumption that a positive value of dC/dt represents the accumulation of trace gas in the stable layer of relevance warrants examination. In concept, the quantity C would best represent the average within the virtual chamber so defined, of cross-sectional area of 1 m^2 and of height z_a. While this conceptual entity is defined in terms of specific measurable dimensions, its relevant characteristics are now based on the statistical extrapolation of other observations.

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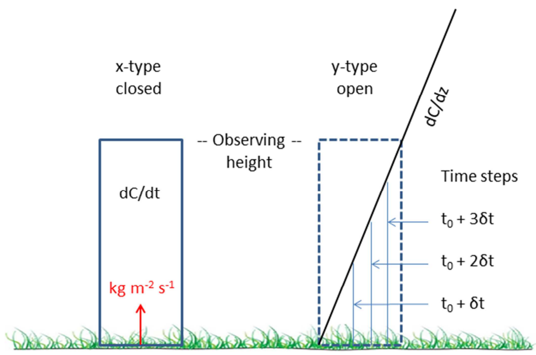

Figure 1. A schematic illustration of the concepts proposed. The x-type chamber simulation is represented to the left, leading to an approximation that the efflux at the surface can be derived from measurements of the rate of change of concentration with time. This is considered an extreme case for the limiting statistical analysis now proposed. An alternative y-type extreme is represented to the right, in which the depth of the layer of relevance is allowed to grow while maintaining the same concentration gradient.

The assumption that dC/dt is the appropriate revealing quantity in the present closed-chamber context requires further attention. It is considered here to represent an extreme circumstance controlling the statistics that follow. An alternative extreme might well simulate an open chamber, in which the depth of the affected layer increases with time, according to the flux from the surface, but maintaining a constant gradient in the air. In this alternative hypothetical case, the concentration observed at some height at or below z_a will increase as the square root of elapsed time (as is illustrated in Figure 1), rather than linearly as required by the closed-

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chamber approach. Hence, the conceptual virtual chamber can be considered in two ways, representing extremes. The first ('x-type') makes use of dC/dt as a key variable, with conceptual association with the operation of a closed but stirred chamber. The second ('y-type') is intended to simulate the characteristics of an open chamber, by substituting $Y_1 = (dC/dt)^2$ for $X_1 = dC/dt$ in the discussion above (specifically in Equation (1)). In this second case, the eventual relationship sought is

$$Y_1 = a_y + b_{y12} \cdot X_2 + b_{y13} \cdot X_3 \qquad (6)$$

which replicates Equation (5). The two separate estimates of the ensemble-mean average fluxes are then

$$F_x = z_a \cdot a_x. \qquad (7)$$

and $$F_y = z_a . a_y^{0.5}/2 \qquad (8)$$

where the divisor arises from the consideration of a right-triangular conceptual configuration in the second case (as is evident in Figure 1), rather than the rectangular figure that contains it in the former.

Regardless of the assumption adopted, a measure of the depth of the layer of relevance is a central requirement. Here, this depth is assumed to be the level at which the loss vertically is indicated to trend to zero – the height of measurement of σ_w or of some other convenient indicator of minimal vertical turbulent exchange. Virtual temperature gradients or TKE could be used equivalently. (Note, however, that the intent to consider the limit as transfer to air above trends to zero requires that the temperature gradient variable of relevance should be the

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inverse of the virtual potential temperature gradient, i.e. determining the limit as δTv tends to infinity.) The inclusion of wind speed is in recognition of the desire to eliminate advection as a major causative property, even though if the site in question is sufficiently uniform the wind speed contribution would be expected to become negligible. If fetch is limited and if the flux of interest can be associated solely with that fetch, then u/X_f becomes an attractive variable, where X_f is the upwind fetch.

In the analysis to follow, two distinct methodologies are proposed. The x-analysis as outlined above assumes that changes in concentration in air near the surface can be considered as being proportional to changes in the surface fluxes. The corresponding y-analysis replaces X_1 by $Y_1 = X_1^2$ (q.v. Figure 1) and assumes that changes in concentration measured at some specific height are determined by changes in the depth of the surface stable layer, such that the concentration gradient remains the same.

In practice, the requisite analysis employs standard statistical methods, adapted from textbook examples (in which matrix algebra is commonly employed) for the present simple case by evaluating the correlation coefficients of relevance (R_{12} is the correlation coefficient between variables X_1 and X_2) and the resulting partial correlations ($R_{12.3}$ is the partial correlation between variable X_1 and X_2 when the influence of variable X_3 is accounted for). Of considerable relevance in analyses like that presented here are the consequent quantities

$$R_{1.23}^{\ 2} = R_{12.3}^{\ 2}(1 - R_{13}^{\ 2}) + R_{13}^{\ 2} \quad (9)$$

$$R_{1.32}^{\ 2} = R_{31.2}^{\ 2}(1 - R_{12}^{\ 2}) + R_{12}^{\ 2} \quad (10)$$

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which quantify the proportion of the variance in variable X_1 that can be explained by the combination of variables X_2 and X_3. Finding the equality evident in the two ways of deriving this quantity is a confidence-building exercise of some considerable satisfaction.

Standard statistical relationships lead immediately to the quantification of the variables a_x and a_y in Eqs. (5) and (6). Estimates of the effluxes then derive immediately, assuming that the height of measurement determines the average height used to define the conceptual chamber of relevance. This is a statistical matter that invites further examination.

In neither the closed-chamber or the open-chamber approximation can the results be considered actual measurements of the surface efflux rates. They are no more than statistical estimates of these fluxes, based on numerically quantified heurism. Conventional experimental campaigns typically provide bodies of suitable data. In the following, three examples of recent application of the virtual chamber approach will be described. The first of these relates to a study of the consequences of tilling on the emissions of CO_2 from an agricultural surface in central Ohio (O'Dell et al., 2018). The measurement program was based on standard Bowen Ratio Energy Balance protocols. The second repeats the analysis, using similar data derived from an earlier study conducted in Zimbabwe (Hicks et al, 2015, O'Dell et al, 2015). The third is based on a study of ammonia emissions from an area previously treated with urea-ammonium nitrate (UAN) as a nitrogenous fertilizer in central Illinois (Nelson et al., 2017, 2019). These examples were selected for present attention because the dimensions of the subject areas are sufficiently small that conventional nighttime micrometeorological methods are not likely to be productive.

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3. The Ohio study of tilling

Figure 2 (a) shows the layout of the field site of the Ohio study (O'Dell et al., 2015). Measurements were made of the concentration of CO_2 in the air, the air temperature and vapor pressure at two levels close to the surface, wind speed, and the surface temperature as reported by downward looking infrared thermometers. The central question related to whether previous tilling of the surface exacerbated CO_2 emissions from the soil at night. The experimental program involved the collection of data from two adjacent areas (as seen in Figure 2), each about 200 m x 200m in size. One of these test areas was tilled (#1), and the other not tilled (#2) before maize (*Zea mays* L.) was planted. The data were collected in November 2015, during the immediate post-harvest period. Observations used here were obtained centrally within each of the study areas, with a time resolution of five minutes. Experimental constraints caused this resolution to be adjusted, so that the data used here represent ten-minute intervals.

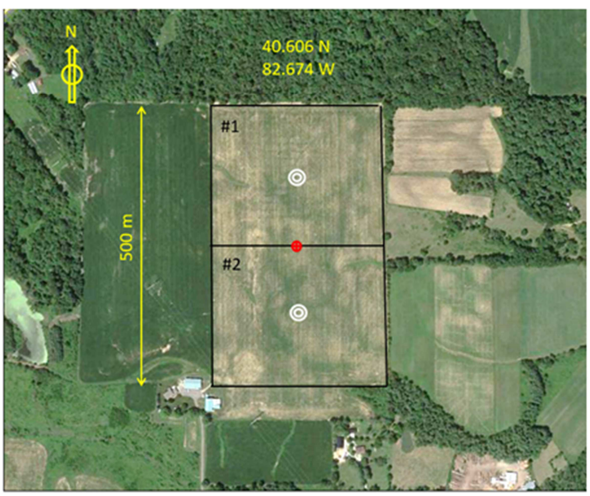

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Figure 2. The surface layout of the test areas of the Ohio (2015) field study. Stars indicate the locations of measurement systems. The image is derived from copyright © Google Earth.

The selection of data for use in the present study has been based on the requirements of the concepts involved. First, nighttime data must be considered. Hence, data records with reported positive net radiation have been excluded. Further, the intent was to interpret the increases in concentration observed near the surface in stable conditions. To this end, situations in which dC/dt < 0 have been rejected (since such situations are likely the consequence of nocturnal turbulence intermittency, another controlling mechanism to be considered elsewhere). In the absence of sonic anemometer data, measurements of the virtual temperature gradient derived from the conventional Bowen ratio energy balance (BREB) methodology have been used. To quantify the limit as vertical mixing approaches zero, X_2 has been taken to be $(\delta\theta_v)^{-1}$, where $\delta\theta_v$ is the difference between levels z_1 and z_2 (above the ground) of the measured virtual potential temperature. In the present case, z_1 is about 0.3 m and z_2 about 1.8 m, so that the effective height to be used in the estimation of fluxes from the evaluations of a_x and a_y is about 1 m.

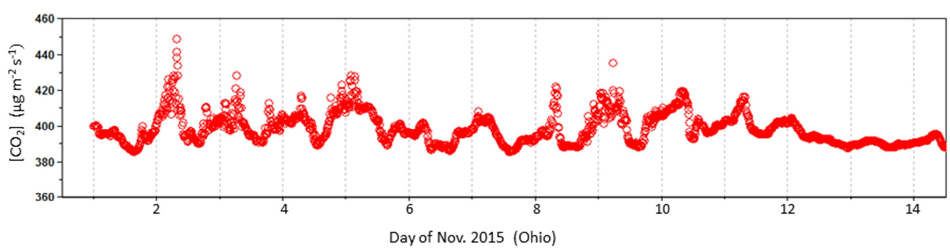

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Figure 3. Time trends of CO_2 concentration at a height of about 1 m above a recently harvested maize field in Ohio.

Figure 3 presents a sample time record of CO_2 concentrations from the Ohio experiment, obtained above the untilled field. The characteristic nighttime concentration build-ups are obvious, as are the consequences of intermittent turbulence. The mid-American farmlands (within which the present Ohio field site was located) are notorious homes of frequent nocturnal jets, with consequences that include the generation of irregular bursts of turbulence (q.v. Blackadar, 1957; Banta, 2008). It is assumed here that it is such irregular bursts of turbulence that curtail the otherwise steady accumulation of CO_2 in the atmospheric boundary layer adjacent to the surface. The present intent is not to investigate these bursts of turbulence, but instead to accept them as features of the nighttime atmospheric environment and then to examine the trends with time when they are not dominant factors.

Figure 4 summarizes results obtained from application of the virtual chamber analysis methodology outlined above. In Figure 4 (a), plots are shown of the proportion of the variance in X_1 and likewise in Y_1 that can be accounted for by consideration of variables X_2 and X_3 (following Eqs. (9) and (10)). If this proportion is close to unity, then the data constitute a sound basis for examination in the way now suggested. However, such high values are not often encountered in the surface boundary layer atmosphere. For example, the relationship between wind speed and the surface stress is usually quantified by a correlation coefficient of the order of 0.4, so that less than 20% of the variance in stress is accounted for by changes in the wind speed. In this light, the values plotted in Figure 4 (a) are somewhat reassuring, ranging from

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about 20% to 40%. It is noticeable, however, that the values associated with the open chamber (y-type) assumption are lower than those of the closed chamber kind (x-type).

Figure 4 (b) presents the estimates of surface effluxes derived from the present analysis. There being no obvious reason to prefer one of the two kinds of analysis rather than the other, it is presently preferred to accept both and to view them as extremes. It could be argued that Figure 4 (a) indicates that x-type must be preferred to y-type, but a conclusion of this kind would require multiple tests and is certainly premature at present. The best estimate of the average surface emission rate is therefore likely to be the average of all of the values plotted: For the tilled surface, 1.70 ± 0.31 µg m^{-2} s^{-1}, and for the untilled, 1.33 ± 0.08 µg m^{-2} s^{-1}. The most likely averages of CO_2 nocturnal emissions from Ohio agricultural soils are therefore indicated to be about 2 µg m^{-2} s^{-1} for the conditions of the current test, regardless of whether the surface was previously tilled.

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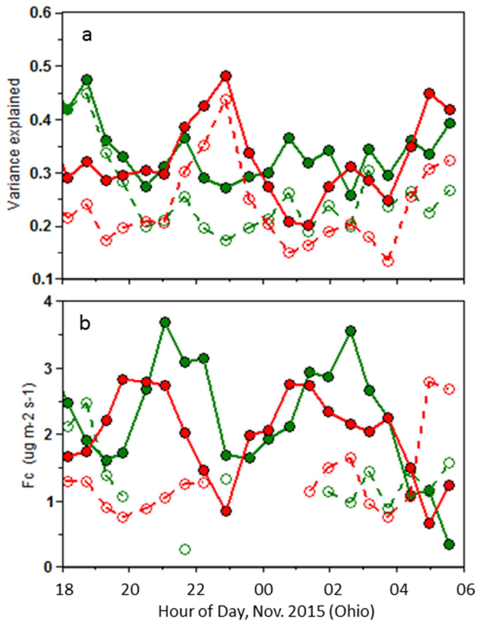

Figure 4. (a) The variation with time of the proportion of variance in dC/dt (= X1; 'closed chamber') and (dC/dt)^2 (= Y1; 'open chamber') that can be accounted for by statistical consideration of the virtual temperature gradient (employed as its inverse, 1/δTv) and wind speed (u), for the two areas of present interest – one tilled before seeding (green) and the other not tilled (red). (b) the estimates of surface effluxes derived from the same analysis. As elsewhere, solid points indicate results obtained using the closed-chamber approximation described here, open points represent vented chamber approximations.

4. The Zimbabwe plateau data

A field examination of the comparative benefits of various agricultural practices was conducted in Zimbabwe, starting in 2013 (O'Dell et al., 2015, Hicks et al., 2015). Identical BREB instrumentation was set up centrally in four neighboring experimental areas, of which two will be considered here (identified as #1 and #2 in the site depiction in Figure 5).

Figure 5. The field site of the Zimbabwe study, showing the two test areas, 1 and 2, considered in the present analysis. At the time of the analysis to follow, area 1 was fallow and area 2 was plated with maize. The inset locates to field site within the African continent (31.021E, 17.722S). Both images derive from copyright © Google Earth.

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An earlier analysis focused on the nocturnal data obtained, with a time resolution of five minutes so that occurrences of intermittent turbulence were readily apparent (Hicks et al., 2015). In the lack of major upwind surface irregularities, these occurrences were attributed to the gravity wave phenomenon considered in detail by Blackadar (1957) but Mahrt et al. (2019) show that there are several alternative causative mechanisms. The key point of the Zimbabwe finding was that the site in question was at an altitude of more than 1400 m asl, and the occurrence of the turbulence intermittency phenomenon at this altitude is a revealing indication of the ubiquity of the mechanism. The data collection protocols used in the Zimbabwe study were the same as were used in the Ohio experiment, discussed above. The analysis now considered for the Zimbabwe dataset mirrors that discussed above for Ohio.

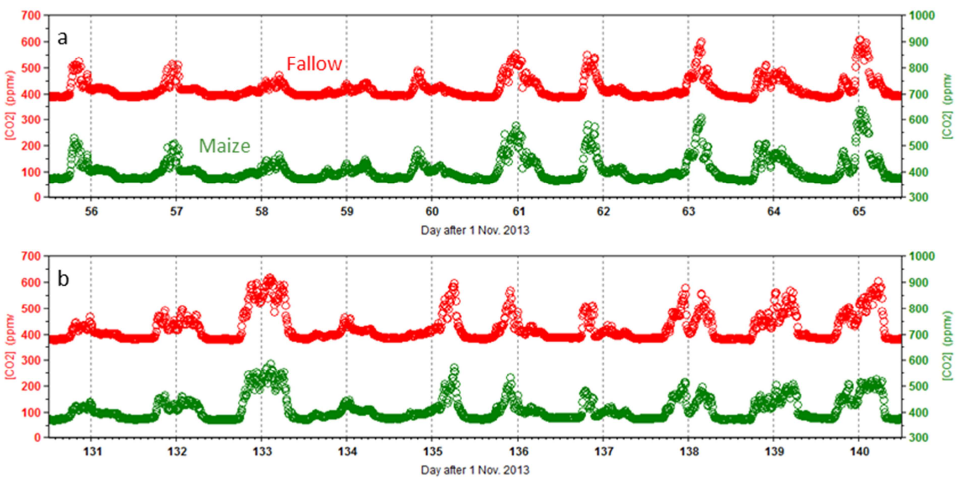

Figure 6. Data from the Zimbabwe field site, illustrating the repeated occurrence of a nighttime saw-tooth pattern for two widely-separated periods (selected at random from the overall six-month data record). Values plotted represent ten-minute average CO_2

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concentrations. Red represents data for the fallow field (#1 in Figure 1), and green the adjacent field (#2) carrying a growing crop of maize. No data have been omitted.

Figure 6 presents two sequences of CO_2 concentration measurements, obtained above the two fields of current interest at an average height of about 1 m above the vegetation or soil. The periods selected for presentation here were selected at random, but are intended to show the similarity in the overall behavior of the growing maize and the fallow field. Note, however, that the fallow field carried a coverage of flourishing native weeds, so that any difference could well have been obscured.

Figure 7 replicates Figure 4 using the Zimbabwe data. In Figure 7 (a) it is seen that the proportion of variance explained is generally low, except for a peak centered on midnight. The interpretation of this is that the efflux conclusions based on the two-hour window around midnight are the most robust. In Figure 7 (b) it is clear that the flux estimates are well behaved for this period, with an average of about 20 $\mu g\ m^{-2}\ s^{-1}$ of CO_2 emission. As before, there is no convincing reason to prefer the y-type results over the x-type, even though the negative results (x-type) indicated in the diagram are disturbing. If all of the results are averaged (as was the case in consideration of the Ohio dataset), the resulting estimate of the CO_2 efflux for the Zimbabwe November data is $11.1 \pm 1.3\ \mu g\ m^{-2}\ s^{-1}$ for the area sown with maize, and $10.3 \pm 1.5\ \mu g\ m^{-2}\ s^{-1}$ for the fallow. At the time of these measurements, the maize had not yet fully emerged and the fallow field was poorly vegetated (with weeds). Concentration and virtual temperature data refer (as before) to a height of about 1 m above ground level.

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The test areas used in the Zimbabwe study were smaller than those of Ohio: 80 m on side in comparison to 200 m. It must be expected that this difference in size will have an effect on the conclusions derived from the present analyses, although the procedure is designed to be based on extrapolation of observations to a situation in which the wind speed is zero, at which point fetch considerations become meaningless.

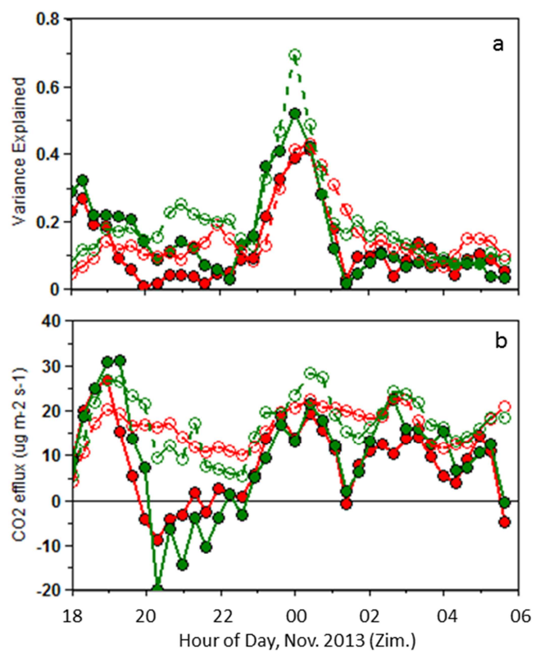

Figure 7. As in Figure 3, with red points relating to a fallow field and green to an adjoining area recently planted with maize (on 8 November, 2013). The dataset development in this case differs, with fewer points making up each ensemble and with consequent increased scatter in the results. The period represented here is the entire

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month of November. Solid points indicate results obtained using the closed-chamber approximation described here, open points represent vented-chamber approximations.

5. The Illinois NH_3 study

Nelson et al (2017) reported a study of NH_3 fluxes from an area previously treated with UAN as a nitrogenous fertilizer. Such treatment is a common practice within the agricultural community particularly in the Midwestern US. The site is illustrated in Figure 8.

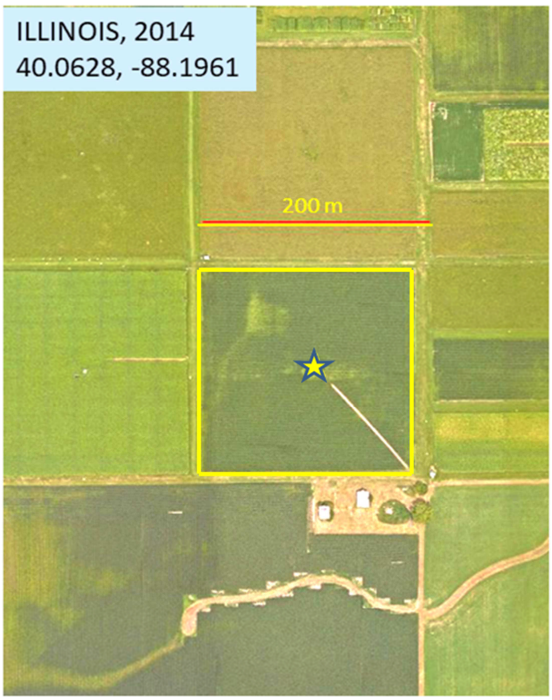

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Figure 8. As derived from copyright © Google Earth, a map of the 4-ha field site used in the Illinois (2014) study of ammonia fluxes following fertilization using urea ammonium nitrate.

Classical investigations of this issue have relied on gross measurements of changes in soil nitrogen content, typically over periods of weeks. The results of such measurements are highly influenced by external factors, especially rainfall. The Illinois study of interest here was intended to explore the micrometeorological use of new fast-response ammonia sensors. In the process, time series of NH_3 concentrations near the ground were derived, illustrated in Figure 9, which constitute a basis for exploration using the virtual chamber methods now proposed. Like the Ohio experimental area considered above, the Illinois site is within the mid-American farmlands and is subject to characteristic nocturnal jets and consequent bursts of turbulence occurring at night (as have been investigated in detail by Banta, 2008, for example). Ammonia gas measurements made at the Illinois site in 2014 reveal precisely the cyclical pattern expected to result from such turbulence intermittency, as is seen in Figure 9. The opportunity exists, therefore, to make use of the analytical methods suggested here in order to derive information regarding the rate of emanation of ammonia gas from the previously fertilized area, so as to derive flux data not influenced by rainfall itself but such that the influence of factors like soil moisture content and temperature could perhaps be assessed.

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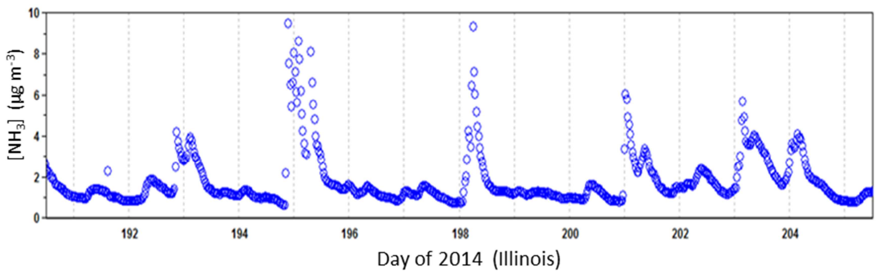

Figure 9. A time sequence of NH_3 concentration measurements obtained in the 2014 Illinois field study.

Using a two-week period of data (of which Figure 9 is representative), results obtained using the virtual chamber approach are as indicated in Figure 10. A key distinction between the present ammonia case and the CO_2 examples considered above is that the NH_3 concentrations are available as 30-min averages, instead of the 10-min averages used for the Ohio and Zimbabwe datasets. The consequences of this are apparent in Figure 10 (a), where the total proportion of variance explained in the rate of change of NH_3 concentration with time is lower than that derived for the CO_2 cases. It is clear that the methods considered here require finer time resolution than is common for conventional micrometeorological studies, since the overall intent is now to detect and omit situations in which intermittent bursts of turbulence affect the buildup of concentrations in the layer of stratified air in immediate contact with the surface. Reliance on data that fail to permit fine distinction between periods of turbulence bursting and the quiescent periods between successive intermittent bursts occurrences certainly obscures

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the statistical correlations on which the present techniques are based, and will result in an underestimation of the efflux in question.

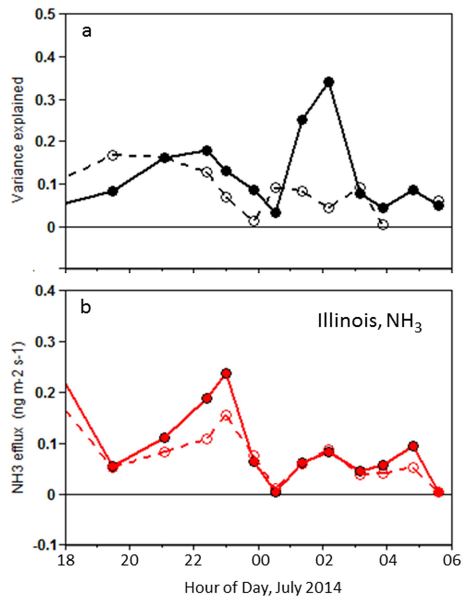

Figure 10. Results derived from measurements of NH_3 above a field previously fertilized with treatment of UAN, in Illinois in 2014. As in the similar presentations above, (a) represents the total proportion of variance explained in dC/dt by the combined influences of wind speed and turbulent mixing, from interpretation of which (b) indicates how derived NH_3 effluxes vary through the night. As before, solid points indicate results obtained using the closed-chamber approximation described here, open points represent vented chamber approximations.

6. Discussion

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The present intent has been to make use of several different datasets to illustrate the potential utility of the virtual chamber analytical methodology and not to focus on results from any specific location in detail. Nevertheless, it is clear from the analyses above that the CO_2 efflux from the Zimbabwe site exceeded that from the Ohio location by about an order of magnitude. The reason is not clear, but several obvious considerations are worthy of attention. For example, differences in soil temperatures could explain the difference: about 7.5 C for the Ohio dataset and 24.0 C for the Zimbabwe. Differences in soil moisture are to be expected, and would likely contribute to the difference. The Ohio surface was covered with the detritus of recent harvesting, whereas the Zimbabwe surface had been recently planted. All in all, the situation is complicated and requires more attention than is presently appropriate.

Irrespective of the negative consequences imposed by the half-hour sampling associated with the Illinois dataset, Figure 10 (b) provides a convincing indication that the rate of NH_3 emission from the ground was about 0.1 ng m^{-2} s^{-1}. Wang et al. (2004) report results that indicate that the rate of volatilization of ammonia from an area bearing a maize crop depended almost linearly on the amount of urea previously broadcast. The maximum NH_3 emission rate was about two days following application of the fertilizer, but at an average rate of from 0.1 to 0.8 kg ha^{-1} d^{-1}, corresponding to about 0.1 to 0.8 μg m^{-2} s^{-1}. The efflux estimate derived from the present analysis is three orders of magnitude lower. In all comparisons of this kind, it should be remembered that the classical chamber study results are typically presented as whole-day averages, whereas the virtual chamber results bow being considered represent only those times of the day when the air in contact with the surface is stratified – usually, at night. Once again, the difference invites investigation.

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7. Conclusions

The methodology presented here diverges substantially from familiar micrometeorological strategies. First, it is focused on the ground itself (or the vegetation above it), and does not rely on the assumption that measurements made above the ground are indicative of the local surface. Second, the reliance on statistical methods to drive the analysis towards situations in which the prevailing stability is high but the wind speed is zero reduces (if not eliminates) the conventional requirement regarding large fetches. Third, the method requires measurements with a sufficient time resolution (less than 5 min) such that the effects of intermittent bursts of turbulence can be identified and eliminated. This is in direct contrast to standard micrometeorological practice, which requires a sampling duration long enough that a statistically significant sampling of these same bursts of turbulence can be obtained.

However, the methods now presented do not result in a defensibly deterministic quantification of the relevant surface fluxes. It is assumed that the two alternative methods presented and discussed above represent extremes, so that the exchange rates of actual relevance lie between the corresponding bounds. A similar line of thinking was proposed by Wang et al. (2004), who report on results obtained from field studies over the North China Plain using both closed and vented chambers. These two experimental methods yielded flux estimates that differed by as much as an order of magnitude. Hence, the differences found in the studies now considered appear reasonable, although clearly requiring additional research.

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