WIND TUNNELS vs. FLUX CHAMBERS: AREA SOURCE EMISSION MEASUREMENTS AND THE NECESSITY FOR VOC AND ODOUR CORRECTION FACTORS

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Abstract

Wind tunnels and flux chambers have been used to measure fluxes of volatile organic compounds (VOC), odour, and ammonia (NH_3) with little regard to air velocity or sweep air flow rates. As a result, flux measurements have been highly variable and scientists have been in disagreement as to the better methodology. Over five years we have conducted a multitude of laboratory and field experiments to compare flux measurements at varying sweep air flow rates with a variety of chamber configurations including the 'USEPA' flux chamber, modified USEPA flux chamber, NCSU flux chamber, UNSW wind tunnel, and WTAMU mini wind tunnel. Flux of gas-film limited compounds increased with increasing airflow rate in all chamber configurations. Through mass balance studies, we have learned that chamber methods most often underestimate the true flux for gas-film limited compounds. Emissions of compounds commonly found at feedlots are positively correlated with measured evaporation rates. We show that wind speed and temperature adjustments corresponding to equivalent field evaporation rates are a justified method for making flux corrections to those gas-film limited compounds responsible for odour at feedlots. Post-measurement corrections show promise to correct chamber measurements to real-world emissions.

Keywords: flux chamber, emission, volatile organic compound, fatty acids, gas chromatography, two film model, Henry's law, ammonia

1. Introduction

Odour, volatile organic compounds (VOCs) and volatile inorganic compounds (VICs) are emitted from wastewater treatment plants, food processing plants, landfills, and feedlots. VOCs are produced from the degradation of amino acids and carbohydrates in the intestines of humans and animals and from incomplete anaerobic digestion. VOC emissions are important because many VOCs are malodorous. Ammonia is the primary VIC emitted from feedlots.

The quantification of VOC emissions from feedlots is important for estimation of emission factors from a regulatory standpoint. There are several approaches to estimating emission rates: 1) the mass balance approach, 2) indirect methods where ambient concentrations are measured and source emission rates are back-calculated using dispersion models, and 3) direct methods where emission rates are measured from the source using a wind tunnel or flux chamber. The mass balance approach is preferred, but instances are few, especially for VOC and odour emissions from large area sources, where the mass balance approach can be used in field conditions.

2. Literature Review

2.1. Wind Tunnels and Flux Chambers

There has been a long-standing debate about the appropriateness and accuracy of wind tunnels and flux chambers for quantifying area source emissions. Scientists have recognized that wind velocity across soil and water surfaces affects the flux of ammonia and some VOCs, as documented in a detailed literature review (Parker et al., 2008). Henry's law constant is a useful parameter for predicting the emission behaviour of individual VOCs (Hudson and Ayoko, 2008; USEPA, 1982). There have been several approaches to model the mass transfer of VOCs including the two-film model.

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2.2 The Two-Film Model

The conventional two-film volatilization model, once called the "stagnant film model," has been used for describing volatilization of a solvent-solute mixture. Much of the earlier research with the two-film model was related to estimating gas exchange over the ocean. The two-film model can be conceptually described by the diagram in Figure 1.

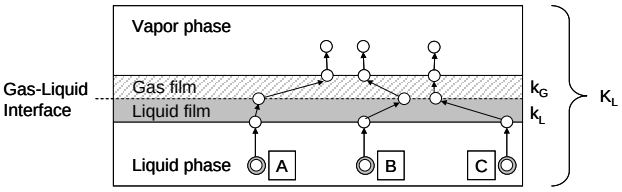

Figure 1. A conceptual diagram of the two-film model showing pathways for molecules that are gas-film controlled (A), liquid-film controlled (C), or both gas- and liquid-film controlled (B). The path length is indicative of the resistance to molecular movement (long path=high resistance).

As a molecule moves from the liquid phase to the vapour phase, it must pass through two films, the liquid film and the gas film. If a molecule is gas-film limited, then conceptually its path will follow that of molecule A in Figure 1, and if it is primarily liquid film limited it will follow the path of molecule C. Further discussion on this topic can be found in Hudson and Ayoko (2008) and USEPA (1982).

In the two-film model, the volatilization flux through these two films is defined as

$$J = k_L(C_L - C_L^*) = k_G(C_G^* - C_G) \qquad [1]$$

where J=flux (mass/area-time); k_L is the liquid-film transfer coefficient (length/time); k_G is the gas-film transfer coefficient (length/time), C_L is the VOC concentration in the liquid phase (mass/volume); C_G is the VOC concentration in the vapour phase; C_L^* is the VOC concentration at the liquid film-gas film interface and C_G^* is the VOC concentration at the gas film-vapour phase interface. Because C_L^* and C_G^* cannot be measured directly, Eq. 1 has been simplified assuming $C_G^* = H_{cc}\, C_L^*$ to obtain

$$J = K_L(C_L - C_G/H_{cc}) \qquad [2]$$

where K_L is the overall solute transfer coefficient and H_{cc} is the dimensionless Henry's constant discussed in more detail later. K_L is calculated using the equation:

$$K_L = \frac{k_L k_G H_{cc}}{k_L + k_G H_{cc}} \qquad [3]$$

where k_L and k_G are the liquid-film and gas-film transfer coefficients, respectively.

If the VOC concentration in air (C_G) is low such that it does not inhibit the VOC flux, then Eq. 2 can be simplified to the following:

$$J = K_L(C_L - C_G/H_{cc}) \cong K_L(C_L) \qquad [4]$$

Note that the Eq. 4 approximation is only valid when $C_G/H_{cc} << C_L$. On the other extreme, the flux will be zero (suppressed by the elevated gas concentration) when $C_G = C_L\, H_{cc}$ which may be more typical of conditions within flux chambers when air flow rates are low.

Empirical correlations for estimating k_L and k_G have been proposed based on values for reference compounds:

$$k_L = k_L^R\left(\frac{M_R}{M}\right)^{1/2} \qquad [5]$$

$$k_G = k_G^R\left(\frac{M_R}{M}\right)^{1/2} \qquad [6]$$

Where k_L^R is the reference liquid-film transfer coefficient (i.e. oxygen) and k_G^R is the reference gas-film transfer coefficient (i.e. water vapour); MR and M are the respective molecular weights of the reference substance (oxygen=32 and water=18) and the solute or VOC. The k_L^R of oxygen (0.2 m/hr) and the k_G^R of water vapour (30 m/hr), are often used for estimating k_L and k_G of the solute.

2.3 Henry's Law Constants

Henry's law constants can be expressed in a variety of units as mass per volume per pressure (i.e. mg L^{-1} atm^{-1}). Henry's law constant is often presented in its dimensionless form H_{cc} as

$$H_{cc} = \frac{C_{air}}{C_{water}} \qquad [7]$$

where C_{air} is the concentration in air (mass/volume) and C_{water} is the concentration in water (mass/volume). In this form, Henry's law states that, at equilibrium, the VOC concentration in the air is directly proportional to the VOC concentration in the water. Henry's law constants are temperature dependent. Henry's law constants for several VOCs found at feedlots and industrial facilities are presented in graphical form in Figure 2.

2.4 Accounting for Wind Velocity or Sweep Air Flow Rate

Methods have subsequently been developed to account for wind velocity in the two-film model. These methods apply corrections to k_G using equations or empirically-derived turbulence factors (Parker et al., 2008; USEPA, 1982). As summarized by Bianchi and Varney (1997), the early stagnant film model (Liss and Slater, 1974) was recognized to significantly underestimate emission rates of some VOCs, primarily because of the failure to take into account wind velocity effects. Mills et al. (1985) and Delos et al. (1984) presented an equation for

estimating k_G which takes into account the effect of wind speed (V):

$$k_G = 170\left(\frac{18}{M}\right)^{1/4} V \qquad [8]$$

with k_G in m/d and V in m/s. Though the height of the wind speed is not always mentioned, most scientists have used either the 2 m or 10 m height (Wanninkhof, 1992). Lee et al. (2004) introduced the "β concept" for calculating k_G which includes an empirically determined turbulence factor based on the velocity in the wind tunnel:

$$k_G = \beta\left(\frac{RT}{2M_R\pi}\right)^{1/2} \qquad [9]$$

where β is an empirical factor determined through laboratory experiments with a small wind tunnel that accounts for the efficiency of vapour moving into air. Lee reported that β was almost the same for different VOCs.

Researchers have also used a power curve relationship for scaling odour emissions measured with wind tunnels:

$$E_V = E_1 V^b \qquad [10]$$

where E_V is the emission rate at average velocity V and E_1 is the standardised emission rate at velocity 1 m/s. Ormerod (1991) developed a first-order feedlot odour emissions model using an exponent of 0.63, based on European wind tunnel data on pig slurry and compost. Pollock (1997) detailed changing the exponent factor of 0.65 which was derived from studies on feedlot pads (Smith and Watts, 1994) to 0.5 for use on pond surfaces. Schmidt et al. (1999) found that the exponent for a lagoon surface was 0.89 for odour and 0.90 for hydrogen sulphide.

In a project conducted at EPA's Atmospheric Research and Exposure Assessment Laboratory, Gholson et al. (1989; 1991) evaluated the flux chamber method for measuring VOC emissions from quiescent liquid surfaces, and stated that "varying the sweep flow rate was found to have little effect on the measured emission rate between 2 L/min and 10 L/min". This has led some scientists to believe that flux chambers are appropriate for measuring all VOCs, including those at feedlots. However, it is important to note that the VOCs that Gholson tested were those typically found in landfills and other industrial facilities. As shown in Figure 2, industrial-type VOCs have much higher Henry's law constants (H_{cc}) than the VOCs typically found in feedlot operations. Most industrial VOCs have H_{cc} values that make them liquid-film controlled as opposed to the VOCs at feedlots which are gas-film controlled. When H_{cc} is greater than 1.0×10^{-3}, the VOCs are liquid-film controlled, and VOCs that are liquid-film controlled are not affected by wind velocity. Thus, while Gholson's conclusion was appropriate for the VOCs tested, his conclusions are not valid for most feedlot VOCs.

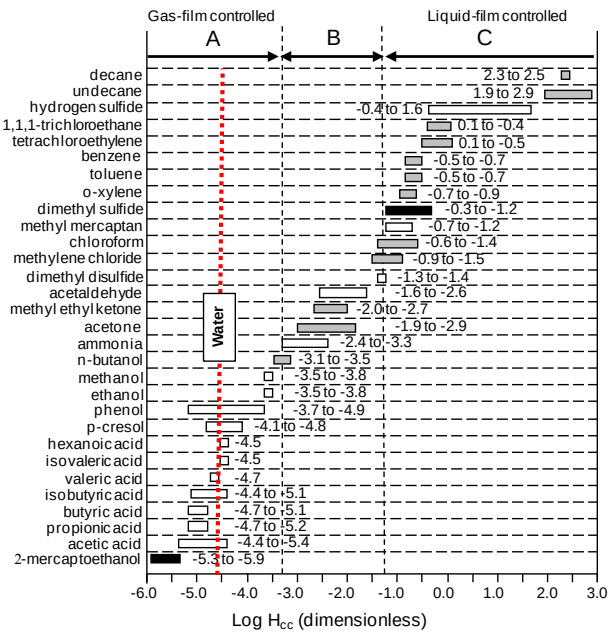

Figure 2. Ranges of published dimensionless (log) Henry's law constants. Open rectangles are feedlot compounds. Shaded rectangles are primarily industrial compounds. Dark rectangles are sulphur-containing VOCs evaluated in Experiment 1. VOCs are either gas-film controlled (A), liquid-film controlled (C), or partially both (B) (adapted from Sander, 1999; Hudson & Ayoko, 2008).

In contrast to Gholson's conclusions, a 1982 USEPA/University of Toronto study in which fluxes of a variety of compounds with varying Henry's constants were measured in a 6 m long wind tunnel, the following conclusion was made "It is concluded that function (i.e. wind) velocity is the primary determinant of mass transfer coefficient in gas and liquid phases" (USEPA, 1982).

While these two divergent hypotheses (i.e. wind velocity either does not or does influence flux rate) can be supported in part by their own literature, from a scientific standpoint neither is universally correct for all compounds of concern. The apparent inapplicability of the flux chamber method to emissions of compounds of concern from feedlots and other facilities has been the focus of numerous laboratory and field experiments conducted at West Texas A&M University aimed at improved methodologies for determining accurate emissions from feedlots.

2.5 Objectives

As part of ongoing research to quantify VOC, odour, and NH_3 emissions from feedlots, and in an attempt to increase the knowledge base concerning measurement of emissions with wind tunnels and

flux chambers, field and laboratory experiments have been conducted over the past few years to evaluate how air flow rate affects flux rates of gas-film limited compounds at feedlots.

The specific objectives were to 1) quantify the effect of varying sweep air flow rate on VOC and NH_3 flux, and 2) provide a methodology for conducting post-sampling corrections to simulate field emission rates.

3. Materials and Methods

3.1. Wind Tunnels and Flux Chambers

Flux measurements were collected using a variety of wind tunnels and flux chambers. The 'USEPA' flux chamber was dome-shaped with a 30 L volume and 0.13 m^2 footprint (Kienbusch, 1986). The modified USEPA flux chamber ($USEPA_{mod}$) had a similar dome shape, with 58 L volume and 0.19 m^2 footprint (Rhoades et al., 2005). The WTAMU mini wind tunnel had dimensions of 51 mm height, 305 mm length, and 152 mm width, with a surface area of 0.046 m^2 and cross-sectional area of 0.0062 m^2 (Parker et al., 2008). The UNSW wind tunnel had a footprint of 0.32 m^2. Flux density (i.e. emission rate) was calculated on a mass per unit area per unit time using Eq. 11:

$$E = \frac{CQ}{A} \qquad [11]$$

where E = flux rate for analyte (µg m^{-2} min^{-1}), C=concentration of component measured in the exit air (µg/L), Q = sweep air flow rate (L/min), and A = surface area enclosed by the chamber (m^2).

3.2. VOC Experiment

3.2.1. Experiment 1 – VOC Emissions vs. Wind Velocity

Experiment 1 was conducted using the WTAMU wind tunnel. Sweep air was passed through an activated carbon filter and rotameter, then into the wind tunnel. Sweep air flow rate ranged from 1.1 to 85 L/min, corresponding to average cross-sectional air velocities of 0.003 to 0.23 m/s and sweep air volumetric exchange rates of 0.6 to 44 exch./min. Exit air was sampled using a portable vacuum pump (200 mL/min) and stainless steel sorbent tubes (SKC Inc). Sampling time ranged from 5 to 15 min, with a target sampling volume of 1.0 to 3.0 L per sample. VOCs were analysed using recognized standard techniques (Parker et al., 2008).

Evaporation of water (evaporative flux) was measured as a function of wind velocity. The reference gas-film transfer coefficient k_G^R was back-calculated for each wind velocity using the two-film model and measured liquid evaporation rates as described in Parker et al. (2008).

3.3. NH_3 and Evaporation Experiments

3.3.1. Experiment 2 – Field Measurement of NH_3 Emissions at Varying Flowrates

The effect of sweep air flowrate on NH_3 emissions was evaluated at open-lot beef cattle feedlots and dairies. NH_3 concentrations were measured using a TEI 17C chemiluminescence NH_3 analyzer (Franklin, MA). Flux measurements were collected using the EPA_{mod} and NCSU flux chambers. (Rhoades et al., 2005).

3.3.2. Experiment 3 – Laboratory Evaluation of NH_3 Emissions in Simulated Retention Ponds and Feedlot Surfaces

Laboratory studies were conducted in 2007 to evaluate the effect of varying sweep air flow rate on NH_3 emissions. A buffered ammonium sulphate solution at two pH values and with or without cellulose was placed within small rectangular plastic chambers (Tupperware®) (205 x 205 x 120 mm). The solution was composed of the following: 15.22 g/L K_2HPO_4; 1.8 g/L KH_2PO_4; 1.88 g/L $(NH_4)_2SO_4$; 0.6 or 1.2 g/L NaOH corresponding to pH of 8.6 or 9.6, respectively, and initial N content of 400 mg/L.

For the pond simulation, 2 L of the buffer were added to plastic containers. For the feedlot surface simulation, 400 g of cellulose and 1 L of the buffer solution was added. The containers were weighed at the start, after 6 h, and again after 24 h and samples were analysed for total nitrogen. NH_3-N flux was determined from the loss of N from each chamber. Only the high pH data is presented herein. Further details on this experiment can be found in Cole et al. (2007).

3.3.3. Experiment 4 – Direct Comparison of NH_3-N and Evaporative Fluxes

Further experiments were conducted in June and July 2009 to assess the effect of air flow rate on NH_3-N and evaporative fluxes from ammonium sulfate solutions (solution as described in Exp. 3 with pH 8.6). Fluxes were measured side-by-side using the USEPA flux chamber and WTAMU mini wind tunnel. In Experiment 4a, the flux chamber and wind tunnel were placed in the laboratory, and compared to fluxes from open pans both in the laboratory and outside. The large and small pans were the same size as the USEPA flux chamber and WTAMU wind tunnel, respectively. The experiment was conducted over 48 hrs, during which the inside temperature was 21°C and the average outside 2m wind speed and temperature were 0.2 m/s (calm) and 26.7°C. In Experiment 4b, the chamber and wind tunnel were placed outside, and compared to fluxes in similar-sized open pans

also placed outside. Sweep air flow rates were 5 L/min in the USEPA chamber and 15 L/min in the WTAMU wind tunnel, equivalent to an average cross-sectional velocity of 0.032 m/s. The experiment was conducted over 24 hrs, during which the average 2m wind speed and temperature were 0.1 m/s (calm) a and 24.5°C. In both Exp. 4a and 4b, the pans were placed on the north side of the building, such that they were shielded from the sun until 1000 hrs. Experiment 4c was conducted on the roof of the building, in an area exposed to the sun and unprotected from wind. Evaporative fluxes were measured with the USEPA flux chamber (5 L/min) and WTAMU wind tunnel (15 L/min) every 2 hrs from 0800 to 2200, then once from 2200 to 0800. The average wind speed and temperature (measured 2 m above the flux chambers) during the 24 hr period were 2.9 m/s and 31.8°C.

4. Results and Discussion

4.1. Experimental Results

4.1.1. Experiment 1 – VOC Emissions vs. Wind Velocity

Evaporative flux was linearly correlated with wind velocity (Figure 3). Fluxes for all eleven VOCs found at feedlots increased with increasing wind velocity, with coefficients of determination typically in the 0.70 to 0.99 range (Figure 4). The linear relationship occurred for both liquid and solid samples. Of the sulphur-containing VOCs, 2-mercaptoethanol flux was linearly correlated with wind velocity (R^2=0.98, graph not shown), whereas dimethyl sulphide showed little dependence with wind velocity (R^2 = 0.123 and 0.0143). This follows the logic explained in Section 2, as 2-mercaptoethanol falls in the 'A range' of Figure 2, and dimethyl sulphide falls in the 'C range.'

The empirically-derived values of the reference gas-film transfer coefficient are presented in Table 1. When used in the two-film model, the predictions were very good (Figure 5).

4.1.2. Experiment 2 – Field Measurement of NH_3 Emissions at Varying Flowrates

Field-measured NH_3 emissions increased with increasing airflow rate in all instances except for very dry areas in the open-lot pens. These findings were typical for all chamber designs, at both the beef feedlot and the open-lot dairy, and for open-lot pens and lagoons. A typical graph of NH_3 emissions as a function of airflow rate for a wet urine spot at a dairy is shown in Figure 6. Additional results for this experiment can be found in Rhoades et al. (2005).

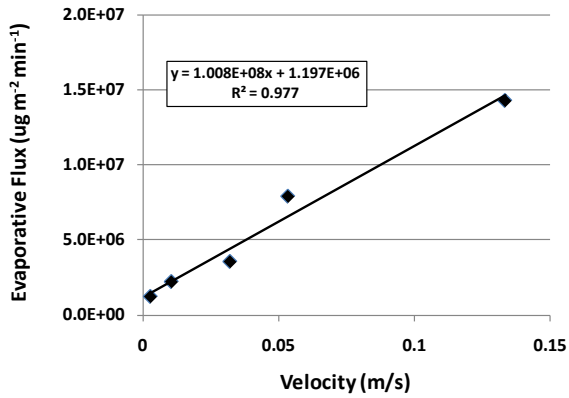

Figure 3. Evaporative fluxes in the WTAMU wind tunnel at varying air velocities.

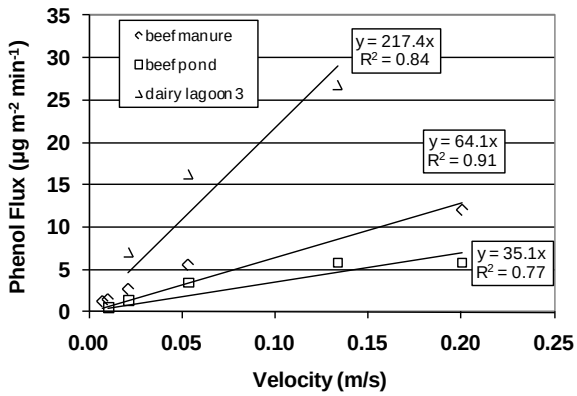

Figure 4. Graph showing the relationship between measured flux and wind velocity at 20 mm height for phenol as measured on three feedlot sources.

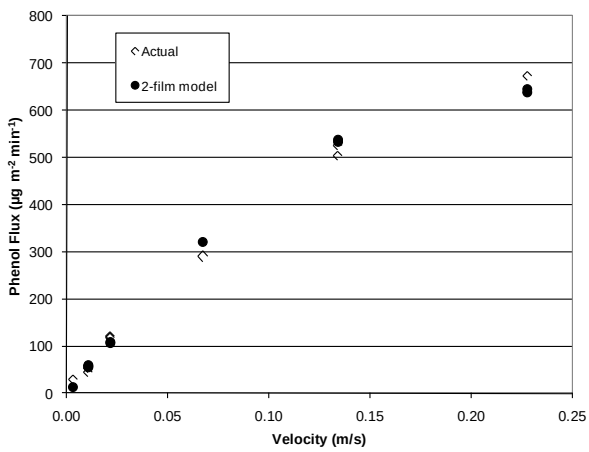

Figure 5. A comparison of actual phenol flux vs. two-film modelled flux using the empirically derived k_G^R and dimensionless Henry's law constant of 1.21E-05 at 21.1°C.

Table 1. Empirically-derived values of k_G^R for distilled water under tested wind velocity for the WTAMU mini wind tunnel.					
Wind velocity (m/s)*	0.003	0.010	0.032	0.053	0.133
Air Exchange Rate (exchanges/minute)	0.58	2.05	6.31	10.5	26.3
k_G^R (m/day)	79.8	142.0	226.0	500.0	903.0
*Average velocity at height of 20 mm above water surface.					

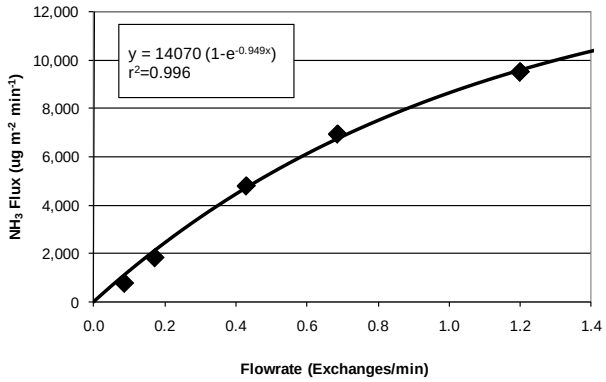

Fig. 6: Graph showing NH_3 flux from a urine spot in a dairy dry-lot pen at different sweep-air exchange rates as measured using the EPA_{mod} flux chamber (from Rhoades et al., 2005).

4.1.3. Experiment 3 – Laboratory Evaluation of NH_3 Flux in Simulated Retention Ponds and Feedlot Surfaces

Ammonia flux increased with increasing sweep air flow rate in both the free liquid and the wetted cellulose. Evaporative fluxes were smaller in the cellulose than the solution and the difference was more pronounced at the highest sweep air flow rate (Figure 7). There was a positive correlation between evaporative and NH_3-N fluxes for both the solution and cellulose (Figure 8).

4.1.4. Experiment 4 – Direct Comparison of NH_3-N and Evaporative Fluxes

The evaporative flux from the USEPA flux chamber was 57% of that from an open pan in the laboratory, while the NH_3-N flux was 82% (Figure 9). In separate side-by-side studies conducted in the laboratory (data not shown), the UNSW wind tunnel operating at a cross-sectional velocity of 0.5 m/s had an evaporative flux 2.7 times that of an open pan in the laboratory. These results show that the USEPA flux chamber is adequate for simulating 'calm, no-wind' conditions such as within buildings, while the UNSW wind tunnel would overestimate these same conditions. Evaporative and NH_3-N fluxes from the WTAMU wind tunnel were 4.1 and 1.3 times greater than the USEPA flux chamber, indicating that the air velocity should be reduced to simulate 'within building' emissions. There was a positive correlation between evaporative and NH_3-N fluxes (r=0.993) (Figure 10).

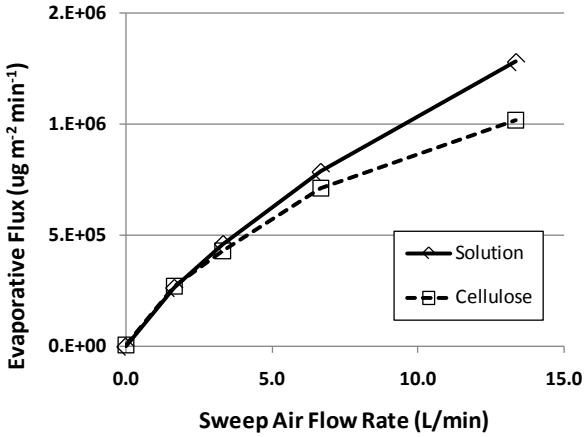

Figure 7: Evaporative fluxes as a function of sweep air flow rate for the simulated pond (solution) and feedlot surface (cellulose).

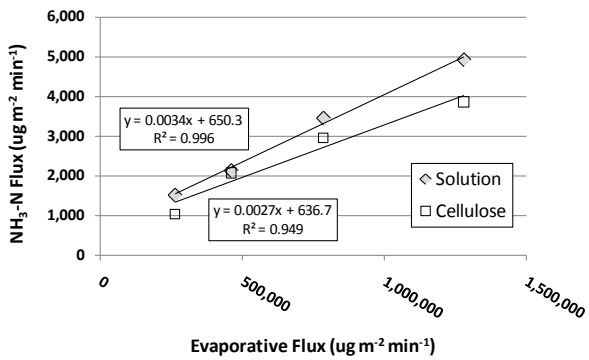

Figure 8. Comparison between NH_3-N and evaporative fluxes for simulated feedlot pond (solution) and moist feedlot surface (cellulose), with a starting solution pH of 9.6 (from Cole et al., 2007).

In Experiment 4b, which was conducted outside, the evaporative flux from the USEPA flux chamber was 31.6% of that from an open pan, while the NH_3-N flux was 49% (Figure 11). The evaporative flux from the WTAMU wind tunnel was 88.7% of that from an open pan, while the NH_3-N flux was 72.4%. Given that the average 2m wind speed was only 0.1 m/s over the 24-hr period, this data would be representative of relatively calm outside conditions. In areas of higher wind velocity, such as an open feedlot, the discrepancy between the chambers and open pan would be greater. The USEPA flux

chamber consistently under-measured actual fluxes during the entire 24-hr period, though the spread was greater during the day. The WTAMU wind tunnel also under-measured actual fluxes though to a smaller extent. Given the goal of accurately predicting field-based emission rates, then in this case both are in need of post-measurement correction factors.

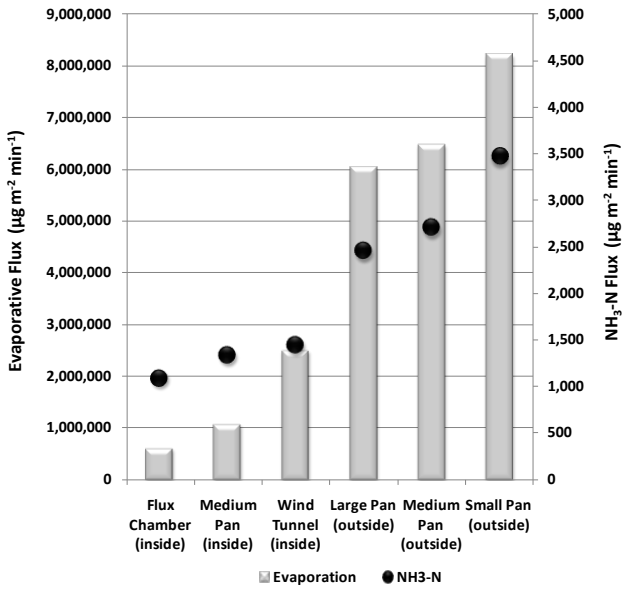

Figure 9. Evaporative and NH_3-N fluxes for the USEPA flux chamber and WTAMU wind tunnel (Experiment 4a).

In Experiment 4c, which was conducted on the unprotected rooftop, the 24-hr average evaporative flux from the USEPA flux chamber was 33.7% of that from a similar-sized open pan (Figure 12) while the WTAMU wind tunnel was 47.8%. The USEPA flux chamber performed best during the early afternoon (with ratios approaching 45%), and worst at night (21% ratio). This suggests that the solar loading (i.e. 'greenhouse effect') to the flux chamber increased the relative evaporative flux during the day, and contributed to a slightly more accurate flux measurement. Ratios for the WTAMU wind tunnel ranged from 30.2% at night to 71.2% in early afternoon.

4.2. Post-Sampling Correction Factors

As demonstrated in this research, wind velocity and temperature have a great impact on emission rates of VOCs found at feedlots. Thus, correct handling of wind velocity and temperature is critical for estimating accurate and representative field-based emission rates for emission factor calculations.

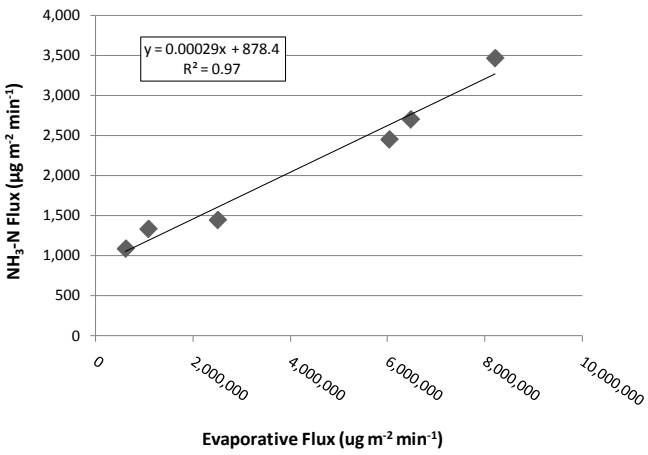

Figure 10. Comparison between NH_3-N and evaporative fluxes for Experiment 4a.

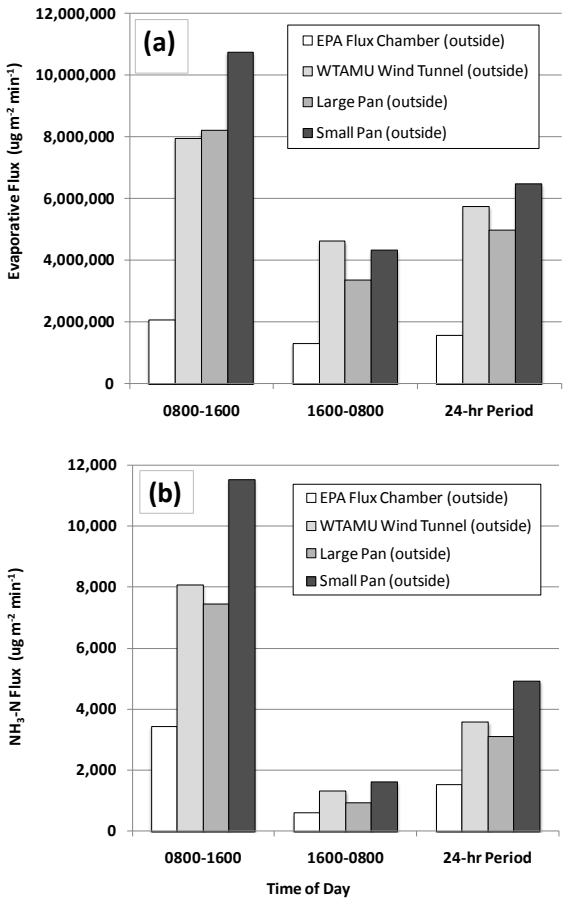

Figure 11. A comparison of evaporative (a) and NH_3-N (b) fluxes over a 24-hr period for two chamber types and two open pans placed side-by-side outdoors in a wind-protected area (Experiment 4b).

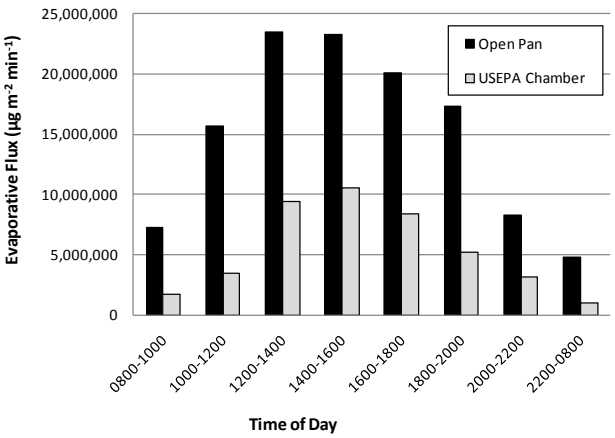

Figure 12. Evaporative fluxes at varying times of day (Experiment 4c).

A post-sampling correction factor that follows the logic proposed by Vlek and Stumpe (1978) is suggested. It would be difficult and cumbersome to quantify volatilization of VOCs in small containers in the field. But because the volatilization of feedlot compounds is correlated to evaporation (Figures 8 and 10), Class A pan evaporation data could be used for correcting previously measured field-based fluxes. A similar evaporation analogy was proposed by Ormerod (1990). This method requires knowing the evaporation vs. wind speed and temperature relationship for the specific chamber being used. Flux rates are not just a function of air flow rate, but also turbulence. Laboratory testing of chamber evaporation as a function of air flow rate provides a direct measure of emissions as affected by velocity and turbulence.

A step by step example of how the local pan evaporation data and the evaporation vs. air flow rate relationship for the WTAMU wind tunnel could be used to correct the field-measured flux data is provided in the following steps. The data from Experiment 4b is used for this example.

Step 1 – The average annual Class A pan evaporation rate and temperature for the site is determined from historic weather records (7.1 mm/day and 14°C annual average for Amarillo, Texas, USA).

Step 2 – The air flow rate that gives this evaporation rate at the given average annual temperature is determined in the laboratory (25 L/min, see Figure 13 which was derived from data for the WTAMU wind tunnel).

Step 3 – The field-measured flux is adjusted to the average annual temperature. Because the relationship between flux and temperature is approximately linear between 10 and 40°C (Parker et al., 2008), the ratio of average annual temperature to sampling temperature is used for the temperature correction factor. The temperature at time of sampling was 24.5°C, and the average annual temperature was 14°C. The temperature correction factor is 14/24.5 or 0.57.

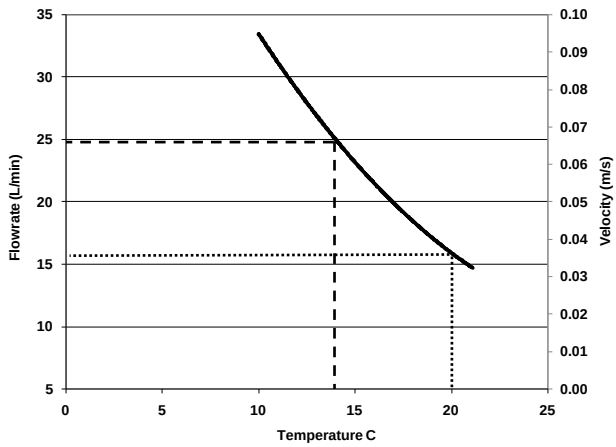

Figure 13. Graph showing the required sweep air flow rate and corresponding wind velocity to obtain the average annual pan evaporation rate of 7.1 mm/day for Amarillo, Texas USA at various temperatures for the WTAMU wind tunnel. A flow rate of 25 L/min is required at the average annual temperature of 14°C (heavy dashed line).

Step 4 – Because the air flow rate used in the field is different from that determined in Step 2 above, an air flow rate correction is necessary. A flow rate of 25 L/min is required to simulate the average annual evaporative flux at the average annual temperature of 14°C, and the field measured flow rate was 15 L/min, thus a flow rate correction of 25/15 or 1.67 is required.

Step 5 – The combined temperature-wind speed correction factor is obtained by multiplying the two correction factors (0.57x1.67=0.95). Thus, for this example, the field-measured flux at 24.5°C and 15 L/min would be corrected to average annual weather conditions by multiplying by 0.95.

The above example is for correcting to average annual flux, a technique that would be appropriate for determination of annual emission factors. The logic presented in this paper could also be used to develop evaporation-based correction factors for shorter time periods that are more appropriate for odour flux prediction. A field-based, time-of-sampling evaporation method could also be used, where evaporation from a small pan placed inside the flux chamber or wind tunnel is compared to a small pan placed on the area source a few metres away. Given the accuracy of portable electronic mass balances, it is feasible that field-based, short term (i.e. 15-30 minute) evaporation measurements could be conducted simultaneously with area source measurements.

5. Conclusions

Theory and experimental data show that temperature and air velocity are the primary factors affecting flux of gas-film controlled compounds. There is evidence that low-flow flux chambers and wind tunnels bias the actual flux, generating the need for a post-sampling correction factor. Because evaporation is correlated with flux of gas-film limited compounds, a correction factor that relies on field-measured evaporation data is proposed.

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References

Bianchi, A. P. and Varney M. S. 1997. 'Volatilisation processes in wastewater treatment plants as a source of potential exposure to VOCs'. *Ann. Occup. Hyg.* **41**:437-454.

Cole, N. A., Todd R. W., Parker D. B. and Rhoades M. B.. 2007. 'Challenges in using flux chambers to measure ammonia emissions from simulated feedlot pen surfaces and retention ponds'. *Proc. Int. Symp. on Air Quality and Waste Management for Agriculture*. September 16-19, 2007.

Delos, C. G., Richardson W. L., DePinto J. V., Ambrose R., Rodgers P., Rygwelski K., St. John J., Shaughnessy W., Fana T., and Christie W. 1984. 'Technical guidance manual for performing waste load allocations, Book II Streams and rivers, Chapter 3 Toxic substances.' EPA-440/4-84-022. United States EPA.

Gholson, A., Albritton J. and Jayanty R. 1989. 'Evaluation of the flux chamber method for measuring volatile organic emissions from surface impoundments'. EPA/600/3-89/008, U.S. Environmental Protection Agency.

Gholson, A. R., Albritton J. R. and Jayanty R. K. M. 1991. 'Evaluation of an enclosure method for measuring emissions of volatile organic compounds from quiescent liquid surfaces'. *Environ. Sci. Technol.* **25**:519-524.

Hudson, N. and Ayoko G. A. 2008. 'Odour sampling 1: Physical chemistry considerations'. *Bioresource Technology* **99**:3988-3992.

Kienbusch, M. R. 1986. 'Measurement of gaseous emission rates from land surfaces using an emission isolation flux chamber'. User's Guide. EPA Contract No. 68-02-3889.

Lee, J-F, Chao H-P, Chiou C. T. and Manes M. 2004. 'Turbulence effects on volatilization rates of liquids and solutes.' *Environ. Sci. Technol.* **38**:4327-4333.

Liss, P. S. and Slater P. G. 1974. 'Flux of gases across the air-sea interface.' *Nature* **247**:181-184.

Mills, W. B., Porcella D. B., Ungs M. J., Gherini S. A., Summers K. V., Mok L., Rupp G. L., Bowie G. L., Haith D. A. 1985. 'Water quality assessment: A screening procedure for toxic and conventional pollutants in surface and ground water.' EPA-600/6-85-002a. U.S. EPA.

Ormerod, R. 1990. 'Odours from cattle feedlots: A review of Australian experience'. Proceedings of International Clean Air Conference, Auckland New Zealand, CASANZ, pp 39-42.

Ormerod, R. J. 1991. 'Modelling emissions and dispersion of feedlot odour: A case study'. Proc. of a Workshop on Agricultural Odours, Queensland Dept. of Primary Industries Report No. DAQ64/7.

Parker, D. B., Caraway E. A., Rhoades M. B., Cole N. A., Todd R. W., Casey K. D., Donnell C. D., Spears J. P.. 2008. 'Effect of wind tunnel air velocity on VOC flux rates from CAFO manure and wastewater'. ASABE Paper No. 08-3897.

Pollock T. J. 1997. Dispersion Modelling to Predict off-site Impact of Odour Sources, Proceedings of the National Workshop on Odour Measurement Standardisation, UNSW.

Rhoades, M. B., Parker D. B., Cole N. A., DeOtte R., Auvermann B. W. and Buser Z. L. 2005. 'Factors affecting ammonia emission measurements with surface isolation flux chambers'. ASABE Paper No. 05-4026.

Sander, R. 1999. 'Compilation of Henry's Law constants for inorganic and organic species'. Available at: http://www.mpch-mainz.mpg.de/~sander/res/henry.html.

Schmidt D. R., Bicudo J. R. And Janni K.A. 2002. 'Determinng odor emissions from manure surfaces using a wind tunnel'. ASABE Paper No. 99-4033.

Smith R. J. and Watts P. J. 1994. 'Determination of odour emission rates from cattle feedlots: Part 1, A Review.' *J. Agric. Engr. Res.* **57**:145-155.

USEPA. 1982. 'Volatilization of organic pollutants from water'. Contract No. R805150010. University of Toronto. EPA 600/3-82-019. USEPA. Athens, Georgia. 213 pp.

Vlek, P. L. G. and Stumpe J. M. 1978. 'Effects of solution chemistry and environmental conditions on ammonia volatilization losses from aqueous systems'. *Soil Sci. Soc. Am. J.* **42**:416-421.

Wanninkhof, R. 1992. 'Relationship between wind speed and gas exchange over the ocean.' *J. Geophysical Research* **97**:7373-7382.