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Measurement and modelling of ammonia emissions from an anaerobic digestion plant.

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Michael Bell

THE UNIVERSITY OF EDINBURGH

ABSTRACT OF THESIS

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Abstract:

Anaerobic digestion (AD) is becoming increasingly popular for treating organic waste. The methane produced can be burned to generate electricity, and the digestate, which is rich in mineral nitrogen, can be used as a fertiliser. The storage and processing of large volumes of organic wastes through AD has been identified as a significant source of NH_3 emissions, however only one study has previously quantified the totality NH_3 emissions that arise in situ at an AD plant. In this study the emissions from an AD plant was estimated through the integration of supportive methodologies involving passive and continuous air NH_3 sampling, atmospheric dispersion modelling and the application of published emission factors (EFs) and empirical models within the literature. Two dispersion models (ADMS and a Lagrangian stochastic model) were applied to produce robust emission estimates. The Lagrangian stochastic model (Windtrax) was used for inverse dispersion modelling to back-calculate the total emission rate from the point of continuous measurement. Back-calculated emission rates and literature EFs were applied to the ADMS model to make predictions of air NH_3 concentrations. Predicted concentrations were verified against weekly passive (CEH ALPHA) NH_3 measurements, where measured concentrations were well described by the numerical model framework using the emission rate estimated by inverse dispersion modelling. EFs that were applied from the literature required adjustment to fit the measured concentrations, however after sensible adjustment an excellent match of observed and predicted concentrations was achieved. Total emissions from the AD plant was estimated to be 16.8 µg s-1 ± 1.8 mg s-1. This is significantly higher than the back-calculated estimate (10.3 ± 1.1 mgs-1), due to a more realistic treatment of the source area. The storage of solid digestate and the aerobic treatment of liquid effluents were the most significant sources of NH_3. The representativeness of the existing EF estimated for AD plants is evaluated through application to the present case study and comparing with NH3 measurements and estimated emission rates. The existing AD EF considerably overestimated observed concentrations by an average factor of 54. The applicability of calculated EFs to other AD plants is discussed.

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1. INTRODUCTION

1.1 ANAEROBIC DIGESTION AND AMMONIA EMISSIONS

Anaerobic Digestion (AD) is an organic waste treatment technology that is seen as a viable means to recover heat and electricity from organic waste streams such as animal slurry and food wastes (e.g. Wulf et al. 2006). The number of AD plants in the UK has increased from 68 to 140 between 2011 and 2014 (Defra 2013; biogas-info.co.uk); supported by national and international policy objectives (e.g. the European Landfill Directive and Renewable Energy Directive). AD is the microbially-mediated process of decomposition of organic matter in the absence of oxygen to recover biogas and a nutrient-rich digestate which is often used as an organic fertilizer (Pain et al. 1990). The biogas (a mixture of methane and carbon dioxide) produced can be sold as an energy fuel or combusted on-site to produce renewable heat and electricity.

Organic waste sources are highly distributed across the landscape at agricultural, commercial, and municipal activities – primarily originating from the food and drink production industries. Anaerobic Digestion plants are centralised locations where organic wastes are delivered, stored and processed in high volume. This presents a high risk of significant and often highly malodourous gaseous emissions associated with the decay of organic materials. The decay of organic materials and the presence of nitrogen compounds such as urea can lead to the release of ammonia (NH_3) into the air by the process of volatilisation. Organic wastes and NH_3 volatilisation from them may be concentrated to the extent that the deposition of ammoniacal nitrogen (NH_3 & NH_4) has led to deleterious effects on semi-natural ecosystems through excess nitrogen acidification and eutrophication (Bobbink et al. 2010; Nihlgard 1985; Draaijers et al. 1989). Emissions of ammonia also lead to the accumulation of formation fine particulate matter (PM2.5), which is recognised to have an adverse effect on respiratory and cardiovascular health (Lillyman et al. 2009).

Emissions of NH_3 in the UK are dominated by the contribution from the agricultural sector (e.g. Pain et al. 1998, NAEI). These emissions originate from surface application of agricultural wastes, livestock housings, slurry stores, fertilizer applications and grazing (Hill et al. 2008). AD plants could present a similar emission source to an intensive farming environment. The treatment of animal slurries or co-digestion of mixed substrates through AD has been investigated for its impact on gaseous emissions, where the NH_3 emissions from digested slurry have been measured to be twice as high as untreated slurry during a 140 day summer storage experiment (Clemens et al. 2006). Waste reception buildings at AD plants may emit NH_3 in a similar fugitive fashion to animal housing units, while numerous studies have measured the volitilisation of NH_3 following the application anaerobically digested livestock manures to agricultural fields (Clemens et al. 2006, Pain et al. 1990, Amon et al. 2006), although few have studied emissions from AD plants

Studies which quantify atmospheric emissions provide emission factors which are used to produce inventories of the total emissions, upscaling to national level. For NH_3, emissions inventories are important for several reasons including input into some chemical transport atmospheric models, assessment of the source sector contributions, geographic location of emissions and the development of abatement strategies for targeting reductions in NH_3 emissions to demonstrate compliance with international legislation on NH_3 emission ceilings (EC 2001). The accuracy of the emission estimates is determined by the quality of the emission factors that are applied (Hill et al. 2008). In order to capture real-world variability numerous emission factors for the variants of each source type may be required to be measured to ensure that emissions inventories are representative.

Anaerobic Digestion is not a new technology yet with the recent increase in numbers of AD plants further efforts should be made to quantify their gaseous emissions. Previous studies into gaseous emissions from AD plants have for the most part been carried out in the context of greenhouse gas (GHG) emissions, focussing on the abatement or release of methane (e.g. Moller et al. 2009; Flesch et al. 2011, Liebetrau et al. 2013). r *In situ* NH_3 emissions from the totality of AD plant sources has only been measured once previously (Cumby et al. 2005), thus the magnitude to which specific digester types emit NH_3 is not well defined. AD is classified as a known source of NH_3 however emissions are largely not quantified (Misselbrook et al 2011).

The current UK emission factor for AD plants was obtained from Cumby et al. (2005) who undertook a pilot Life Cycle Analysis (LCA) study at a large centralised AD plant processing mostly agricultural slurries near Holsworthy, Devon. NH_3 emissions from the site had increased +175 tonnes NH_3 per annum (pa) relative to previous manure management practices, caused by greater emissions from digestate storage and spreading. The pH of the digestate is higher than undigested slurry increasing NH_3 volatilisation. Fugitive emissions from the waste reception area at the plant were also significant. The authors identified two key areas of NH_3 emission: (a) the waste reception area where the organic waste substrates are delivered for processing; (b) the digestate storage area which holds the final product of the AD process (separated or unseparated) before further processing or use as biofertiliser. The degree to which these sources emit NH_3 will likely show significant variation between AD plants, as the rate of NH_3 volatilisation is governed by numerous environmental and substrate parameters, most importantly temperature, pH, ventilation and ammoniacal N concentration (e.g. Hansen et al. 2005). NH_3 emissions are also dependent on site practices concerning the handling, storage and treatment of organic wastes. For example, Whelan et al (2010) demonstrated in *ex-situ* experiments that despite a high propensity for NH_3 to volatilise from food waste digestate due to an elevated pH and NH_3:NH_4^+ ratio, emissions could be controlled by covering storage facilities and increasing the depth to surface ratio. Cumby et al. (2005) demonstrated that the concentration of NH_3 above a wet scrubber and biofilter was reduced by 87% relative to untreated air within the waste treatment area at the Holsworthy biogas plant.

1.2 LOCAL SCALE DISPERSION MODELS

Short-range atmospheric dispersion models are frequently used to estimate the concentration and/or deposition of NH_3 across a specified area or receptor within environmental impact assessments (Theobald et al. 2012). For example, Fowler et al (1998) quantified concentrations and deposition fluxes within 300m of a poultry farm in Scotland using concentration measurements and dispersion modelling, reporting a strong decrease in NH_3 concentrations with distance downwind from the source in the woodland environment. Hill et al. (2008) used short-range dispersion models and passive samplers to estimate the NH_3 emission fluxes from livestock slurry stores. Theobald et al. (2012) highlighted the importance of such integrated approaches with the measurement and modelling of NH_3 concentrations to determine emission fluxes, as the performance of models can vary significantly between sites and can often require calibration against verification measurements.

The dispersion of NH_3 emitted to the atmosphere can be investigated with the use of mathematical models such as ADMS (Carruthers et al. 1994), AERMOD (Cimorelli et al. 2002) and LADD (Dragosits et al. 2002). Such models are typically used to predict air concentrations (X_m, in g m^{-3}; Eq. 1) arising from known, or estimated, rates of emission (E, in g s^{-1}) and a modelled dispersion factor (D, in s m^{-3}, Equation 1). The dispersion factor is a function of the prevailing meteorological conditions (particularly wind speed, wind direction and atmospheric stability), the geometry of the source and dynamics of emission, and the potentially complex interactions with terrain, surface roughness and building effects.

$$X_m = DE \tag{1}$$

Predicting the air concentrations that arise from a known emission rate is known as a ‘forward-dispersion modelling’. As the downwind concentration of a pollutant is directly proportional to the source strength (Eq. 1), the accuracy of model predicted concentrations relative to atmospheric concentration measurements is heavily dependent on NH_3 emissions being accurately defined (Dragosits et al. 2002; Hellsten et al. 2008). Where the emission rate is not known, dispersion models can also be applied to back-calculate the emission rates from known air concentrations. Also known as ‘inverse-dispersion modelling’ – these techniques have been applied to determine emissions from single isolated sources, such as dairy farms (Flesch et al. 2009), agricultural AD plants (Flesch et al. 2011) and penguin colonies (Theobald et al. 2013).

Inverse dispersion modelling uses the clear relationship that exists between the downwind concentration measurement *C* and the gas emission rate *Q*, which depends on the size and shape of the emission source, wind conditions, and the *C* sensor location (Flesch et al. 2011). The inverse dispersion technique back-calculates the source strength using a micrometeorological method which predicts the downwind concentration (above background level) to the emission rate, $(C/Q)_{sim}$, so that:

$$Q = \frac{(C - C_b)}{(C/Q)sim} \tag{2}$$

Where C_b is the background gas concentration (Flesch et al. 2004).

A spread of field C measurements has been demonstrated to work in harmony with well-populated forward and inverse dispersion models as a tool for emissions and environmental impact assessment. Such systems do not require the time-consuming and expensive task of individual gaseous emission rate(s) being directly measured, which is of major benefit for a complex site such as an anaerobic digestion plant which has many possible emission points, such as liquid treatment tanks, waste reception and digestate storage buildings, surface water tanks etc. The inverse dispersion modelling technique may be applied where the totality of emissions is to be calculated or one or a group of emission sources lie directly upwind of a *C* sensor location. The effective use of the inverse dispersion has been demonstrated where the modelling scenario benefits from significant reductions in complexity due to well-defined sources, a lack of complex terrain and where concentration measurements are made sufficiently downwind from the source to negate any source complexity that is present (Flesh et al. 2011).

1.1 AIMS OF THIS STUDY

In this study the total of NH_3 emissions that arise *in situ* at a commercial food waste-processing anaerobic digestion plant in Cumbernauld, Scotland are modeled and compared against measurements. The Cumbernauld AD is of the ‘community’ variety - meaning that wastes are accepted from the surrounding catchment of municipal and commercial (predominantly food waste) collections. Of the 140 ADs in the UK, 38% are of the community-type (biogas-info.co.uk). The other two major AD types are: 1) agricultural – which use feedstock derived on-farm such as livestock slurries and crop residues; 2) industrial - plants which treat waste generated on-site such as brewery effluent or food waste processing residues.

The use of forward and inverse dispersion modelling methods may be applied in a supportive fashion in cases where the emission rate(s) are not known while air concentration measurements are made that allow for calibration and verification of estimated emission rates. This is the approach that was applied in this study, where concentration measurements were made in and around the anaerobic digestion plant using passive samplers and a continuous gas analyser. NH_3 concentrations were likely to arise from multiple sources within the plant depending on the direction of the prevailing wind and atmospheric stability conditions. Emission estimates were determined by several methodologies, using published emission factors within the literature, field measurements and plant specifications, inverse dispersion techniques and applying optimized scaling factors for emission rates that are determined by fitting the modelled air concentrations against measured concentrations in forward simulations.

The objective of this project was to quantify NH_3 emissions from the AD plant to add to the single existing UK AD NH_3 emission factor study. An assessment of the uncertainties involved and the applicability of this approach and others for future work is discussed.

2 MATERIALS AND METHODS

2.1 NH_3 MEASUREMENTS

2.1.1 Passive NH3 samplers

NH_3 concentration measurements were conducted using three methods: 1) time-integrated sampling with passive diffusion ALPHA (Adapted Low-cost Passive High Adsorption) samplers (Tang et al. 2001), 2) continuous on-line NH_3 analysis using a trace gas analyser and 3) instantaneous/snap measurements made with a portable NH_3 gas analyser. The high-sensitivity ALPHA samplers were deployed during each successive measurement period. Six ALPHA measurement periods in total were carried out at the site from the 15th of May to the 10th of July. The period of individual measurement campaigns ranged from 6 days to 2 weeks.

The open end of each sampler holds in place a PTFE membrane (27 mm diameter, 5 µm pore size) (Figure 1), this serves to limit the formation of a boundary layer in front of the sampler and ensure that a stable, turbulent-free path length is achieved behind the membrane. A citric acid-coated filter paper is held behind the membrane which absorbs atmospheric NH_3 which passes through the membrane. The samplers were placed out as triplicates at 20 locations in and around the AD plant (Figure 3). They were attached with velcro underneath shelters (upturned plant saucers) at sampling heights of around 1.5m above the ground (protocol used in the Defra National Ammonia Monitoring Network). Each saucer was fitted with bird spikes to prevent birds from perching and ammonia contamination. The samplers were stored in sealed plastic containers and were kept refrigerated before and after exposure. After each measurement period the samplers were extracted with 3 ml of deionised water, and analysed for NH_4^+ on the AMmonium Flow Injection Analysis system (AMFIA) (Wyers et al. 1993). The flow injection method is based on the selective dialysis of ammonium across a membrane at a high pH, followed by measurement of conductivity. Calibration of the extracted samples with prepared ammonium solutions of 0.1 ppm, 1 ppm and 10 ppm enabled the concentration of ammonium in the extracted samples to be determined. Laboratory blanks were subtracted from the samples. The air NH_3 concentration is estimated from the NH4 concentration within the extracted samples and the uptake rate calculated according to the principles of Fick's law. The theoretical uptake rate of a sampler is a function of the diffusion length, L (m), the cross sectional area, A (m^2) of the stationary layer within the sampler and the diffusion coefficient (D) $m^2\ s^{-1}$) of the gas being analysed. The effective volume of the gas air sampled (V, m3) is therefore given by:

$$V = \frac{DAt}{L} \tag{3}$$

Where: t = time of exposure (h), $D = 2.09 \times 10^{-5}$ m2/s at 10°C, $A = 3.4636 \times 10^{-4}$ m2, L = 0.006 m. Thus V (m^3) = 0.00434 m3 x t (h)

The air concentration of a pollutant (C $\mu g/m^3$) can then be calculated as:

$$C = (m_e - m_b)/\,V \tag{4}$$

Where: m_e = amount of NH3 collected on sample ($\mu g\ m^{-3}$)

m_b = amount of NH3 in blank sample ($\mu g\ m^{-3}$)

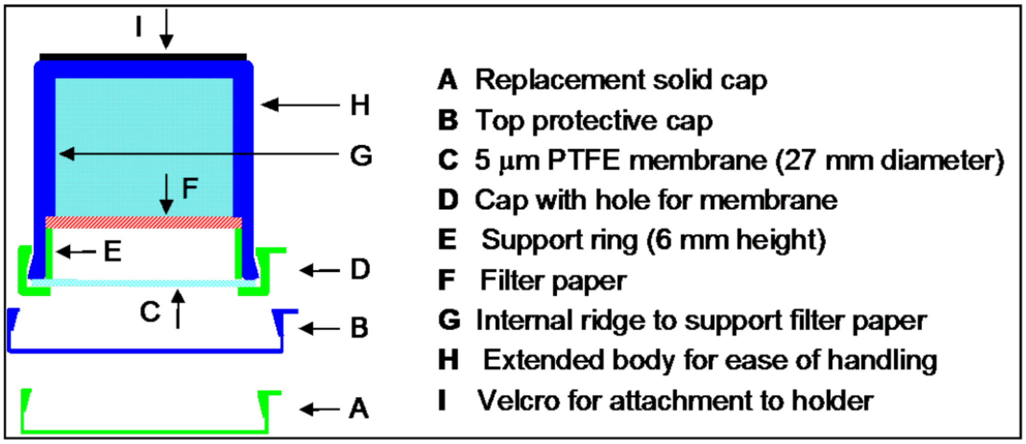


Figure 1: Outline Diagram of a single CEH ALPHA sampler

The ALPHA samplers are calibrated against a reference denuder method, DELTA (Sutton et al. 2001) to derive an effective field uptake rate, which was determined as : V (m^3) = 0.00324 m^3 x t (h).

The coefficient of variation (CV) was calculated from the difference between measured NH_4^+ between sample triplicates as an indicator for uncertainty. The analytical precision was also assessed by co-analysing the samples with four quality control solutions at concentrations of 0.2, 0.9, 2 and 9ppm. The analysis of the NH_4^+ content of the ALPHA samples was also checked against international quality standards from the laboratory intercomparison programme of the World Meteorological Organisation Global Atmospheric Watch, where the accuracy of the AMFIA analysis system was found to be within 5% of the provided standards.

2.1.2 Continuous NH3 analyser

On-line continuous NH_3 concentration measurements were made with an AiRRmonia gas analyser (Mechatronics, NL). The AiRRmonia was strategically deployed for two periods of measurement at two locations (Figure 3, 4). The first measurement campaign, (28th May – 26th June) was 100m northwest of the AD plant along the axis of the prevailing wind direction, while the second (27th June – 16th July) was within the inner courtyard at the plant, 20m from the entrance to the digestate store (Figure 4), which was assumed to be a key source of emissions for the plant (Figure 3, 4). The continuous sampler consists of a membrane sampler for quantitative sampling of gas-phase NH3. NH_3 within the air stream at the sampling inlet diffuses through a membrane where it is absorbed in a sampling solution which is pumped continuously (ECN, 2003). The aqueous sampling solution is mixed with a NaOH carrier solution of around pH 12 which converts all NH4+ to NH_3, at which point NH_3 is the only small molecule in solution that may readily diffuse through a 0.22 µm pore size teflon membrane. NH_3 which passes through the membrane is met with a counterflow of deonised water. At pH 7 the NH_3 converts back to NH_4 and is analysed by a conductivity detector. The AiRRmonia was housed within a weather-proof box (Figure 2) and sampled air at a rate of 1 l/m. Measurements were recorded every minute by the in-built datalogger, and the data was later averaged for 10, 30 and 60 minute periods for analysis. Calibration was carried out in the field every 6 days with 0, 50 and 500 ppb NH_4^+ solutions and showed good stability over the periods of measurement.

Figure 2: AiRRmonia gas analyser & ALPHA setup.

AiRRmonia air sampling inlet.

Upturned saucer with attached birdspikes and ALPHA triplicate held underneath.

AiRRmonia continuous gas analyser.

Laptop for data acquisition.

2.1.3 Portable gas analyser

The gas alert Micro 5 portable multi-gas analyser (www.calgarysense.com) was used to provide snap measurements of the concentration of NH_3 inside the central waste reception building at the site which was expected to be a key source NH_3. The portable gas analyser was only suited to the high concentrations within the waste reception building as the limit of detection for the device was 1 ppm (0.75 mg m^{-3}), which is two orders of magnitude higher than the background concentration determined for the area (1.5 µg m^{-3}). Snap measurements were made upon visits to the site every week in an attempt to characterise the observed NH_3 concentrations rather than provide long-term averages, as it was not possible to maintain continuous measurement due to a lack of power supply. The observed NH_3 concentrations from within the waste reception building were used to estimate fugitive emissions, making assumptions on the direct discharge rate from the findings of the fugitive emissions study by Cumby et al (2005).

2.2 ESTIMATION OF AMMONIA EMISSIONS

Multiple approaches were taken to estimate the emission rate for the plant as a whole and for the individual emission sources at the site. Windtrax and ADMS Urban were both used and methodologies are described below.

2.2.1 Windtrax

The Windtrax atmospheric dispersion model (Flesch et al. 2004) was used to calculate the totality of emissions from the AD plant. The Windtrax model (available at www.thunderbeachscientific.com) is of the backward Langrangian stochastic (bLS) dispersion type. Windtrax has the capability to operate in ‘forwards’ and ‘backwards’ mode, where in both cases fifty thousand “fluid particles” are released and from an emission source or concentration receptor. The trajectory of the particles are predicted through the equations of Lagrangian stochastic motion, which are used to simulate the transport of gases from an emission source to a receptor or the reverse if in backwards mode.

Continuous NH3 concentration data from the AiRRmonia measurements was averaged over 10 minute or 1 hour periods for various functions and combined with meteorological data which was provided by a local weather station in Cumbernauld (www.cumbernauldweather.co.uk), located 1.6km to the northeast of Deerdykes. Note *in situ* meteorological measurements were attempted but the newly bought meteorological station had a fault. Cumbernauldweather.co.uk provided a high resolution anemometer that allowed the comparison of NH_3 concentration data from different wind sectors. This was better suited than the met. data which was made available from the on-site weather station, as wind direction data from the on-site anemometer is given in sectors of 22.5° which reduces the resolution of model output. The AiRRmonia data was filtered to select only measurements taken where the AD plant was directly upwind of the AiRRmonia gas analyser (chosen to be 220 - 230°). The AiRRmonia NH_3 concentration data was also filtered to remove calibration periods and where wind speed (u) was less than 0.1 m/s. The mean, median, 75th, 95th and 99th percentiles where then calculated from the filtered AiRRmonia data over the first measurement period (28th May – 26th June).

The data input to Windtrax was filtered averages of the following parameters: NH_3 concentration at 2m height (X_m µg/m^3), background concentration (X_b µg/m^3), wind speed (u, m/s), wind direction (WD, °), temperature, (T, °C), and an atmospheric stability parameter. As the long-term average concentration was used across the 220 - 230°C wind sector, the mean temperature (15 °C) for that period was used in the model. ALPHA measurements from locations that had little influence from the Deerdykes AD plant or other sources of NH_3 suggested that the local background concentration was around 1.5 µg m^{-3}, which was set as the background concentration in the Windtrax model. This was later affirmed in forward dispersion modelling scenarios, where the ability of the model to accurately predict concentrations at ALPHA receptors was significantly improved when using this background concentration value.

Without a sonic anemometer measuring atmospheric stability, it was assumed that a neutrally stratified surface layer would best represent the averaged stability throughout the measurement period. This assumption seemed to be valid as the predicted concentrations given from the Windrax model in forwards mode fared better with long-term concentration measurements than unstable or neutral surface layer conditions. Therefore the atmospheric stability parameter was given in general terms, specified as neutral or Pasquill-Gifford stability class D.

The Deerdykes AD facility presents complications for inverse dispersion calculations. Buildings and structures generate complex wind movements, and the intensity and precise locations of all the emission sources is unknown. However studies using the inverse dispersion method have demonstrated insensitivity to these complications if X_m is measured far enough downwind (Flesch et al. 2005, McGinn et al. 2006, Flesch et al. 2011). It is suggested by Flesch et al. (2008) that the downwind distance of the concentration sensor should be a minimum of ten times the height of the largest wind obstacle, and roughly two times the maximum distance between potential sources. The largest obstacle is the waste reception building at 6.4m tall, as the AIRRmonia gas analyser is 70m from the nearest obstacle, the sequencing batch reactor (SBR), and 100m from the waste reception building this criterion is met. However Flesch et al (2008) also recommend that the concentration sensor should be roughly two times the maximum distance between potential sources, in this case the distance between the surface water balancing tank (SWBT) is greater than the distance to the concentration sensor. Furthermore, the Windtrax model assumes a spatially uniform surface area source, which is not a realistic treatment as emissions will not be evenly distributed over the ground area. Therefore the Windtrax model is not expected to accurately reproduce near-source NH_3 concentration characteristics, however it was hoped that this tool will provide a reasonable estimate of the totality of emissions that occur at the site.

A conceptual model for NH_3 emission and dispersion was created for the site after consultation with the operators of the plant and obtaining knowledge of the storage conditions of waste being delivered to the site and of the digestate produced by the digestion process. The waste reception building (containing the digestate store), and the sequencing batch reactor were identified as likely being the most significant source of NH_3 (Figure 4). Early NH_3 measurements quickly identified the surface water balancing tanks as another major source at the plant. These were the three source definitions within the Windtrax model where each was given as an area source spatially proportional to their plan which is shown in Figure 4. Each of the three area sources defined in the model were assigned identical emission rates per unit area.

ADMS Urban

Source strengths may be determined by assigning an arbitrary emission rate and fitting the modelled concentrations to the measured values (above background) by applying a correction factor (e.g. Hill et al. 2008; Faukner et al. 2007; Theobald et al. 2013). This technique was applied with the Atmospheric Dispersion Modelling System (ADMS) (Carruthers et al. 1994). ADMS is an “advanced generation” Gaussian-type model that uses the Gaussian Plume equation to provide a statistical approximation of the complex nonlinear equations that control the dispersion of gases in the atmosphere. ADMS incorporates several features which makes it a strong choice for simulating the emissions from a complex source such the Deerdykes AD plant: ADMS includes a building effects module which allows for the streamline deflections and enhanced turbulence that occur downwind of structures at the site such as the waste reception building and the various tall tanks present at the site, ADMS can compute dispersion across an x-y field where the roughness length varies to simulate the effects of complex terrain such as woodland, agricultural land and built-up areas within the model domain, and also a realistic treatment of the atmospheric boundary layer, using Monin-Obukhov scaling, to describe the vertical variation in wind speed and turbulence in the atmosphere. Without direct measurements of atmospheric stability taken at the site, ADMS features a meteorological pre-processor that can provide an estimate of the Monin-Obukhov scaling using cloud cover, wind data and air temperature to estimate the surface-sensible heat flux and provide a reciprocal of the Monin-Obikhov length. Cloud cover data was obtained from the Met Office MIDAS Land Surface Station dataset. The nearest synoptic surface station was the Glasgow Bishopon station (55°54'0N, -4°31'58.8W"). As this station is 30km west of the Deerdykes facility it may not capture local variations in cloud cover data that can be observed over the site, but it was assumed that the cloud cover data would be representative of the study area.

The ADMS model was configured with the following input data:

- Meteorological data for each measurement period provided by cumbernauldweather.com and the Deerdykes site meteorological station, including wind speed and wind direction, rain intensity, air temperature and relative humidity.
- Cloud cover data from the Glasgow Bishopton surface observation station.
- Source location and dimensions for the major points of NH_3 emission at the site, including the biofilter stack, the entrances to the waste reception area and digestate store, the surface water balancing tank (SWBT) and the sequencing batch reactor (SBR) (Figure 4).
- A building configuration for the site; specifying location, width, length, height and shape.
- Estimates of the surface roughness length for the structures at the site and the surrounding landscape, given as surface roughness file containing a matrix of around 1700 surface roughness definitions across the model domain.
- The positions of the ALPHA monitoring points.
- Dry deposition rate ($m\ s^{-1}$).
- Washout coefficient.

Gaseous NH3, being chemically reactive and highly soluble, has a short residence time in the atmosphere. Losses of NH3 from the atmosphere occur due to dry and wet deposition and chemical reactions to form particulate NH^{4+}. As a result the concentration of NH_3 within an emission plume will become depleted with distance downwind than pollutants that are conserved in the gaseous phase. ADMS describes the rate of dry deposition by the dry deposition rate which is given as a constant settling velocity across the model domain. The recommended UK Environment Agency deposition velocity value for NH_3 ($0.02\ ms^{-1}$, short grass) was adopted for the model. Wet deposition is described by the washout coefficient, which is defined as a constant value as a function of the precipitation rate for a particular pollutant. The washout coefficient for NH_3 was given as $9\ x10^{-6}\ s^{-1}$ (CLAG 1994).

A number of scenarios were set up to investigate the emissions of NH_3 from the Deerdykes AD. Firstly the back-calculated emission rate for the totality of the emissions from the plant was applied and measured concentrations were compared with predictions to evaluate the Windtrax estimate. The subsequent scenarios involved model differentiation into multiple sources, using the all of the available information including: published emission factors within the literature, on-site measurements using a the portable Gas Alert Micro 5 portable gas analyser (www.calgarysense.com), indications from ALPHA and AiRRmonia measurements and site parameters such as chemical analysis of solid digestate and liquid effluents obtained from the AD plant. Emission factors were adjusted to fit the modelled concentrations with time-integrated measurements from the ALPHA samplers. The available information concerning the composition of organic materials and practices at the site was referenced against published emissions factors and literature examples to develop a model with source descriptions that are as realistic as possible. Discretion was used when adjusting these emission factors to fit the ALPHA measurements. Finally, the current APIS (Air Pollution Information System) emission factor for NH_3 emissions from anaerobic digesters was then applied to this area source to investigate whether the findings of Cumby et al. (2005) are representative for the Deerdykes food waste anaerobic digester. All of the scenarios predicted the long-term average concentrations across a 900x700m model domain at a 10x10m resolution. Each scenario used the available meteorological data and ALPHA NH_3 concentration measurements corresponding to ALPHA periods 2-5 (28th May – 26th June). Dispersion modelling could not be conducted for July as total cloud cover data from the Met Office Glasgow/Bishopton surface station had not been released. Thus without a proxy for atmospheric stability it was not possible to run ADMS.

Uncertainty in dispersion modelling generally can be due to: 1) variability due to random turbulence, 2) input data errors, and 3) errors and uncertainties in model physics (Fox 1994). Dispersion is primarily controlled by turbulence in the atmospheric boundary layer, which is random by nature and thus cannot be accurately predicted. As a result, the concentration of a pollutant in the atmosphere will vary significantly in space and time over an observed field (Chang and Hanna 2004). In order to describe turbulence in a meaningful way, dispersion parameters are defined to elicit turbulence as a time averaged mean value, in the case of ADMS the dispersion parameters correspond to the hourly averaged input run through the meteorological pre-processor. However variation around this mean value is not considered (Fox 1994), which neglects uncertainty in the estimated concentration of a pollutant for a particular modelling scenario. Decades of experience and numerous validation studies has led many authors to adopt a rule-of-thumb confidence limit of ± 'a factor of 2' for a given time and location (Pasquill, 1974, Smith, 1984, Chang and Hanna 2004). Here, the ALPHA measurements provide means to assess the performance of the ADMS dispersion models to predict the air concentration over space and time across the study field. Therefore because the predicted concentrations can be verified against the observed concentrations at ALPHA sites, uncertainties in dispersion modelling are considerably reduced. However as the model is verified by and calibrated with the ALPHA measurements any error associated with the passive ALPHA sampling or NH_4^+ analysis techniques will directly influence the validity of the model and any emission rates deduced therein. Furthermore, after adjustment to fit observed concentrations the two datasets are no longer independent which is a key assumption of statistical tests (Chang and Hanna 2004). Therefore there must be a qualitative element to the discussion of uncertainties after the models are fitted to measurements in this manner.

2.3 MODEL PERFORMANCE EVALUATION

Evaluation of model performance requires a statistical comparison of predictions (C_p) with observed values (C_o). For the evaluation of ADMS predictions against ALPHA measurements, the five performance measures suggested by Chang and Hanna (2004) are used:

Fractional bias : FB = $\frac{2(\overline{C_o}-\overline{C_p})}{(\overline{C_o}+\overline{C_p})}$; (5)

Geometric mean bias : MG = $\exp\left(\overline{\ln C_o} - \overline{\ln C_p}\right)$; (6)

Normalised mean square error: NMSE = $\frac{\overline{(C_o - C_p)}^{\,2}}{\overline{C_o C_p}}$ (7)

Geometric variance : VG = $\exp[\overline{(\ln C_o - ln C_p)^2}]$ (8)

and the fraction of model predictions that are within a factor of two within the observations

FAC2 = fraction of data that satisfy : $0.5 \le \frac{Cp}{Co} \le 2$

Overbars denote the mean of each dataset. The NMSE, VG and FAC2 are composite measures that take into account the both bias and scatter in the predicted values relative to the observations, while the FB and MG are measures of model bias and describe the tendency of the model to over or under-predict observed concentrations. Chang and Hanna have suggested ranges for the five performance indices that indicate acceptable model performance. The ranges suggested are: FB < 0.3, 0.7 < MG < 1.3, NMSE <1.5, VG < 4 and FAC2 > 50%. The correlation coefficient (R^2) was also calculated and used an index for model performance. The model suitability was assessed by comparing the performance measures to these criteria for the mean atmospheric concentration at each ALPHA receptor. Later studies have recognized that due to stochastic and turbulent processes, even an acceptable model may not be able to meet all the acceptability criteria for all the experiments (Hanna and Chang 2010; Theobald et al. 2012). As a result, it has been proposed that an acceptable model is one which meets at least half of the performance tests. This approach was adopted in defining the ‘acceptability’ of the models developed, however in determining the source strength the emission rates of individual sources were sensibly iterated to closely match the ALPHA. Thus the objective was to develop a model that performs well in statistical tests but also finds a balance with the conceptual model of emissions from the AD and the published findings within the literature.

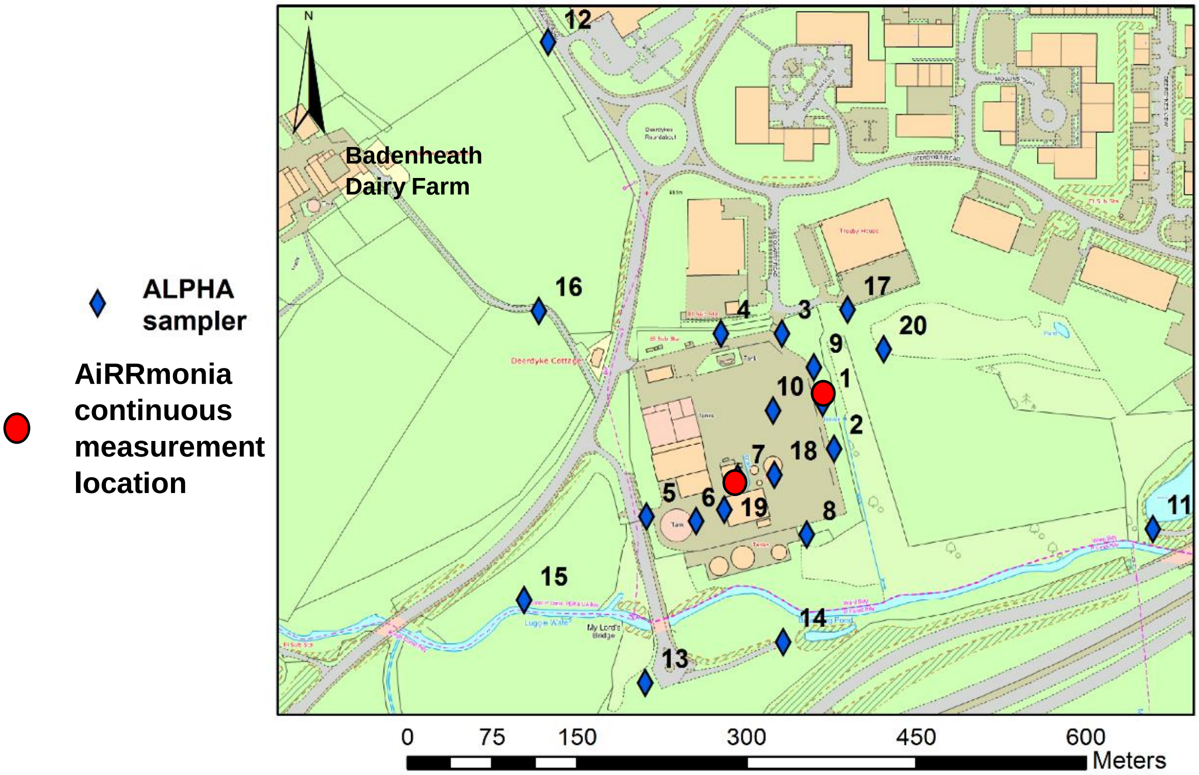


Figure 3: Location of passive ALPHA and continuous AiRRmonia NH_3 monitoring sites. Samplers were predominantly aligned to the SW – NE axis of the site, in line with the prevailing wind direction.

Figure 4: Site plan of the Deerdykes anaerobic digestion plant.

The inner site is mostly concrete courtyard with tall buildings and tanks that are associated with the AD process or the posting facility that was in place prior to 2011. The AD plant is surrounded by tall trees, hedges and a screening bund

Suspected sources of NH3 at the site are marked in red, which may be grouped as the sources in and around the Waste Reception Building (biofilter, waste reception area, pre-processing area and digestate store); the sequencing batch reactor (SBR) which aerobically treats the separated liquid effluents; the open Surface Water Balancing Tank (SWBT), which collects surface drainage from the plant and is hence contaminated by spillages; and the subterranean sludge reception tank which stores deliveries of liquid substrates to the site.

The location of passive NH3 ALPHA samplers placed at the site are marked with green circles, while the AiRRmonia continuous gas analyser locations for both AiRRmonia measurement periods are marked as blue circles.

3. DEERDYKES ANAEROBIC DIGESTER/LITERATURE REVIEW OF EMISSIONS

2.4 SITE OPERATION

The Deerdykes combined heat and power (CHP) biogas AD plant is located to the south of the Westfield Industrial Estate and approximately 250m North of Mollinsburn, Cumbernauld (55°55’28N, 4°03’24W). Constructed in 2010, the plant processes about 30,000 tonnes of materials per year, comprising a mixture co-mingled green/catering wastes from municipal collections, biodegradable industrial sludges and category 3 animal by-products. The wastes to be digested arrive both in liquid and solid form, the solid wastes being delivered to the floor of the waste reception hall, where it is transferred to equipment that will shred and decontaminate the waste before it is fed into the process by screw conveyors (See Figure 6 for a schematic diagram). Liquids and sludges are offloaded to a separate subterranean tank, before being pumped into the anaerobic digestion process via a small buffer tank. Various waste inputs are combined with recycled, anaerobically treated and diluted process liquor to form a 15% slurry using high energy mixers. This slurry is screened to remove packaging and oversized materials, before passing into a buffer tank to even out its composition before going forward for anaerobic digestion, whilst allowing time for the hydrolysis of suspended solids into soluble components and the formation of short chain fatty acids in advance of anaerobic digestion. Following pasteurisation at 70°C for one hour to destroy pathogens, the slurry is transferred into the anaerobic digester which operates at mesophilic temperature (37°C), which operates on a semi-continuous basis. The biogas released during anaerobic digestion (primarily methane and carbon dioxide) is withdrawn from the digester headspace into a dedicated biogas holder adjacent to the digester and buffer tank. The biogas is combusted by one or two spark ignition gas engines to produce electricity and heat, although some or all biogas may be combusted by a flare in the event of excess biogas production or vented to air via release valves if biogas pressure rises too high.

The digested sludge (digestate) displaced from the bioreactor is dewatered and separated into liquid and solid fractions, where the solids are stored temporarily on-site before being sold as biofertiliser. The liquor expressed from the sludge that isn’t recycled to the pumping stage is sent to a large sequencing batch reactor where the aerobic treatment process will convert ammoniacal nitrogen to nitrite and nitrate, while the residual BOD in the effluent is be further reduced. Treated effluent that cannot be recycled to the start of the process is discharged to sewer.

Figure 5: Aerial photograph of the Deerdykes Anaerobic Digestion Plant looking northwards. From the bottom, the biogas holder, digester and buffer tank can be seen from left to right. The primary emission sources are labeled as follows: 1) Biofilter; 2) Waste reception hall door; 3) Digestate store; 4) SBR; 5) Surface Water Balancing Tank; 6) Sludge reception tank.

Due to the high volume of malodourous of wastes present at the plant, odour control technologies are employed to limit the release of odorous emissions. The solid waste reception zone of the plant takes place within a dedicated waste reception building that is fitted with an air extraction system. The air extraction system captures contaminated air within the waste reception and preprocessing areas of the waste reception building, which vents to the atmosphere *via* a downflow biofilter and ultimately a 3m discharge stack. Room air is extracted from the waste reception building at a rate of 9000 m^3/hour, passing through a humidified biofilter with sufficient residence time to provide a minimum deodourising efficiency of 75%. The solid digestate is stored within a separate compartment of the waste reception building which does not feature any odour control measures. This may increase the likelihood of release NH3 from room air within the store into the atmosphere, most likely as the digestate store opened to allow the loading of digestate onto biofertiliser delivery trucks, which occurs roughly three times per week. A portion of the liquid digestate is aerobically treated within an open sequencing batch reactor tank, which causes the potential for further emissions from the tank surface. The subterranean sludge reception tank is fitted with an activated carbon drum to scrub any gases from the tank that are vented to the atmosphere. The gaseous emissions from this tank should be generally the air that is displaced when the tank is filled with sludges and liquids, as breathing losses should be minimal. The emissions from this tank have not been quantified in terms of volume or NH_3 concentration, and it is not known the extent to which the tank emits to the atmosphere nor the effectiveness of the activated carbon drum or the concentration of NH3 in the air within the tank.

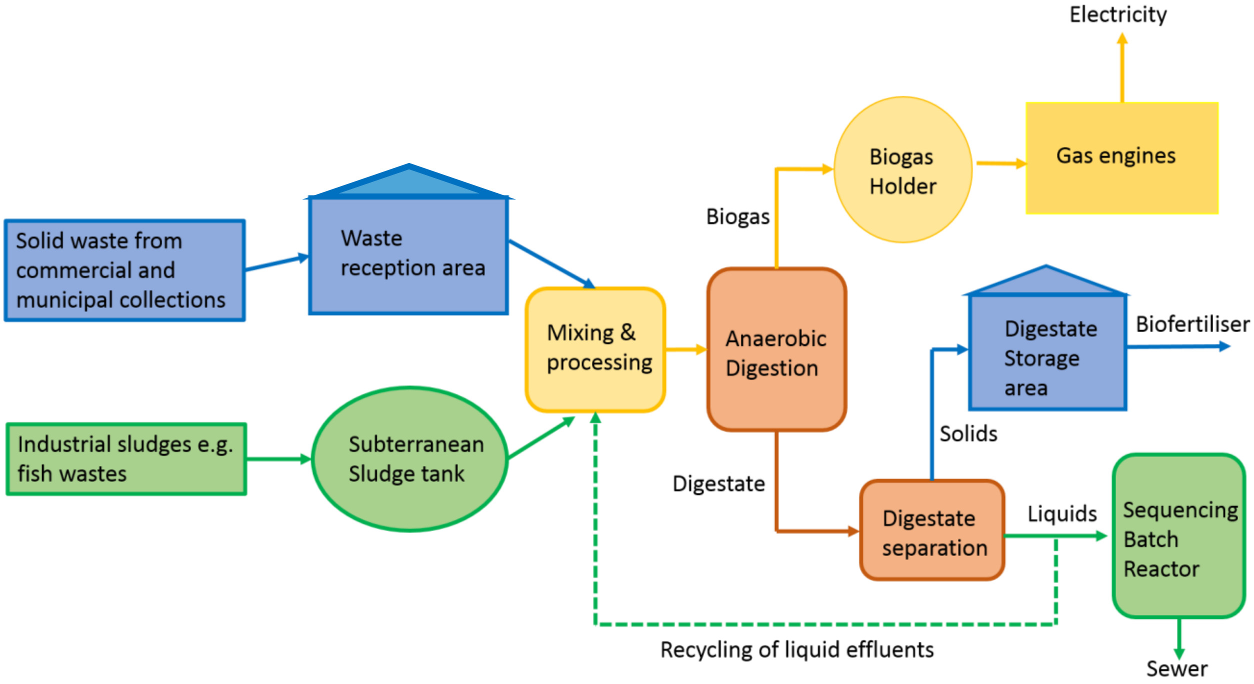


Figure 6: Schematic model of the pathways of wastes through the Deerdykes AD plant.

2.5 EMISSIONS FROM SOLID DIGESTATE

The anaerobic digestion process is for the most part a closed system, which limits the contact of process matters with the atmosphere and hence the potential for fugitive emissions of NH_3. Odour control measures further constrict potential pollution pathways for NH_3, however the storage and treatment of substrates and effluents in liquid and solid form are key parts of the anaerobic digestion system where emissions of NH_3 can occur. If the effluents are separated, the heaps of solid digestate are similar to farmyard manure heaps and contain aerobic and anaerobic micro-sites (Sommer and Moller 2000), readily degradable carbon and a nitrifiable nitrogen source (Asmus et al. 1988; Reinold et al. 1990, moisture (Chadwick et al. 1999) and heat (Clemens and Ahlgrimm 2001). During digestion, dry matter is partially degraded (Koriath et al. 1985), which reduces the total effluent volume while increasing the concentration of nutrients. Anaerobic digestion effluents have a reduced biological oxygen demand, a higher ammonium (NH4+)/total nitrogen (N) ratio, a smaller C/N ration and an elevated pH than the digestion substrates (Asmus et al. 1988; Moller et al. 2008). The culmination of these effluent properties is to produce favorable conditions for gaseous NH_3 emissions and the production of nitrous oxide (N_20) via denitrification.

Previous studies that have set out to measure or estimate the emissions of ammonia from manure and slurry stores through mathematical models have done so through the use of simple empirical relationships (e.g. Jarvis 1993; Ross et al. 2002), to the development of models for the detailed mechanistic descriptions of the physical characteristics of mass transfer (See Ni 1999, for a review). The similarities between digestate and agricultural slurries and manure heaps has led some authors to assume a comparable rate of NH3 loss. Concerning NH_3 emissions from solid and liquid effluents only, applying the default IPCC emission factors for gaseous N loss during manure storage (30% for dairy cow manure, and 45% for swine manure (IPCC 2006), Moller et al. (2010) reported that 30 – 40% and around 1% of the total N contained within solid and liquid effluents respectively were released as NH_3 emissions during the storage of digestate from two biogas digestion plants in Germany. The primary substrate was dedicated energy crops, where after digestion the effluents were separated into liquid and solid fractions which were stored on-site. The greater loss of NH_3 assumed from the solid fraction was due to storage practices, where the solid fraction was piled in open heaps within a warehouse, while the liquid fraction that is not recycled through the process was stored in closed tanks. Cumby et al (2005) reported that the total nitrogen content of the digestate from the Holsworthy agricultural anaerobic digester was 64% higher than cattle slurry, 33% higher than pig slurry, and 43% lower than poultry layer slurry. Cumby et al. (2006) also noted an elevated pH of 8.2, relative to the undigested slurry of enrolled farms to the centralised anaerobic digestion system (pH 7.5). The elevated pH was estimated to increase NH_3 volatilisation during storage by a factor of 1 and 4, where a 2.6 fold increase in ammonia emissions was observed between slurries with a pH 7.5 and 8.

Clemens et al (2006) measured NH_3 and GHG emissions from the storage of digested and undigested cattle slurry in summer (140 days) and winter (100 days) experiments, finding comparable NH_3 emissions during winter. However emissions from digested slurry during summer were twice as high as undigested slurry. The effect of temperature on NH_3 losses from agricultural slurries is well documented in the literature. Denmead et al. (1982) developed a regression equation that estimates NH_3 losses from NH_4-N content, temperature, and pH following the furrow irrigation of maize. They demonstrated an increase in NH_3 emissions with temperature, especially if slurry NH_4-N and pH are high.

The effect of covering slurry and manure heaps on NH_3 emissions relative to leaving uncovered has been shown to significantly reduce emissions of NH_3 by maintaining a high concentration of NH_3 at the surface, limiting volatilisation and physically preventing emission to the atmosphere (Cumby et al. 1995). Clemens et al (2006) showed a 65% decrease in NH_3 emissions from digestate stored with a wooden cover relative to uncovered digestate. Another experiment in the same study demonstrated that emissions from digestate covered with a layer of chopped straw were nearly as high as uncovered slurry, highlighting the need for effective storage facilities (Table 1).

Whelan et al. (2010) conducted an experimental study to evaluate the volatilisation of NH_3 from food waste anaerobic digestate whilst developing a mathematical model to describe the process. This is of particular relevance to the Deerdykes project as it is the only study in the literature to specifically target NH_3 emissions from anaerobically digested food waste. The authors reported that the rate of NH_3 loss is inversely proportional to the depth of the digestate storage container, thus deep containment facilities have relatively low emission rates. Secondly, storage facilities with a poorly ventilated headspace (i.e. closed) will also have relatively low emission rates. The presence of a cover can limit the losses of ammonia by allowing the concentration of NH_3 above the digestate to approach a thermodynamic equilibrium with the free ammonia in the liquid, thereby minimizing the net flux. Cumby et al. (1995) investigated the release kinetics of NH_3 within an odour and emissions chamber (OEC), finding that the equilibrium concentration between free NH_3 in the manure the air NH_3 above it occurred as the air concentration reached 300 – 400ppm. The rate of ventilation of digestate containers also affects the rate of turbulent diffusion across the liquid interface, where a reduction in the ventilation rate (α) suppresses the convective mass transfer of NH_3 between the interface and the free air, thus limiting emissions of NH3 (Whelan et al. 2010).

Empirical relationships based upon the regression of NH3 emissions against influencing parameters such as temperature, NH_4-N content, pH and air ventilation rates can give valuable predictions of NH3 emission rates when limited parameters are available for calculation (e.g. Jarvis 1993; Ross et al. 2002). The model of Borka et al. (2000) describes the emissions of NH_3 (E, $mg\,m^{-2}\,h^{-1}$) from manure in livestock buildings, and was developed from the regression of substrate temperature (TS, °C), air exchange rate (LD, $m^3\,h^{-1}\,m^{-2}$), and NH_4-N content (TAN, $g\,N\,kg^{-1}$) (Eq 4), in controlled experiments within respiration chambers.

The correlation of each experiment was highly significant, and from each regression a simple multi-factorial emission model was developed:

$$\mathbf{E = 17.254 * 1.060^{TS} * LD^{0.274} * TAN} \tag{9}$$

2.6 APPLICATION OF BORKA MODEL TO STUDY AD PLANT

Table 1 presents a comparison of the chemical properties and calculated NH_3 emission rates of the solid fraction of the Deerdykes digestate against the properties of digestate in published articles. The Deerdykes digestate has a substantially higher Total Kjeidjahl Nitrogen (TKN) and NH_4-N content than any of the published studies on the composition of digestate. This in theory allows more free NH_3 available for volatilisation by moving the equilibrium towards the composition of free NH_3 in thermodynamic equilibrium within the digestate, as described by the dissociation constant K_d. The Deerdykes digestate shares a similar food waste digestion substrate with the digestate that was analysed in the study of Whelan et al (2010). The composition also features a better fit to the Deerdykes digestate than the digestate livestock slurries that were analysed and reported by Clemens et al. (2006) and Cumby et al. (2006). Solid digestate at Deerdykes is stored in shallow, sprawling heaps within the digestate storage area, the average depth (z) of which is less than 1m (Figure 7). Thus for comparison the NH3 equivalent flux rate (J_{NH3}) in the experiments and model scenarios of Whelan et al. (2010) for ventilation rates (α) of 0.1, 1 and 10 air changes per hour are given, where z = 1m. The Deerdykes digestate store is not well ventilated which helps to limit odourous emissions. However it is by no means a secured storage vessel, thus the air exchange rate (α) was assumed to be between 0.5 and 1.5, typical values for buildings of tight and loose insulation respectively. However around three times per week the large digestate store door is opened for several minutes in order to extract the digestate for sale as biofertiliser. The large door is fully opened (Figure 7), while a JCB loader transfers the digestate into a storage container for haulage off the site where the end-use is application to agricultural land. This ventilates the digestate storage area and is an intense NH3 emission event at the site, and may shift the ventilation rate towards the higher end of estimates. Due to the uncertainty around this parameter, the emission rate for air change rates of 0.5, 1 and 0.5 were calculated for use in dispersion modelling (Table 1). The equivalent flux rates calculated using equation 1 correspond well to the literature values given. However, equivalent flux rates calculated using Eq. 4 are less sensitive to changes ventilation rate than model of Whelan et al. (2010) would suggest.

In the AD plant studied, the digestate pile typically covers the floor of the storage area, which is 60m^2 (Figure 7). However the surface of the digestate is not smooth, i.e. has a high roughness factor, which was estimated to increase the surface area available for volatilisation by between a factor of between 5 and 10. These roughness factors were applied to the source area in ADMS. The temperature was recorded from inside the digestate store between the 27th of June and the 7th of July using a Tiny Tag data logger (www.geminidataloggers.com). The temperature within the digestate store displayed strong diurnal variations, with temperatures ranging from 25°C during the day to 10°C during the night. The average temperature over this period was 16.4°C. The average air temperature (16.4 °C) was taken as the temperature of the surface of the manure for calculations of emission rates using the empirical model of Borka et al. (2000), Eq. 9.

Table 1: Intercomparison of the Deerdykes digestate chemical composition and NH3 emission rates from the storage of different digestates reported in the literature.

Parameter	Deerdykes (Food Waste) (16.4 °C)			Cumby et al. 2006 (Livestock Slurry)	Clemens et al. 2006 (Cattle Slurry, Summer Experiment, 140 days)					Whelan et al. 2006 (Food Waste) (25°C)		
	Digestate			Digestate	Cattle Slurry		Digestate			Digestate		
TKN (mg/l)	62600			6583	2170		2280			-		
NH_4-N (mg/l)	25000			5040	1190		1510			5775		
pH	8			8.2	7.4		7.8			8.28		
DM (g/kg)	120			-	32.9		22.9			37.2		
J_{NH3} (g NH_3 m^{-2} d^{-1})	Borka et al. (2000) model[1]			-	uncovered	covered	uncovered	straw cover	covered	α = 0.1	α = 1	α = 10
	α = 0.5*	α = 1.0	α = 1.5		0.73	0.43	1.59	0.9	0.56	2.06	14	38.9
	1.24	1.5	1.68									
EF_{NH3} (kg N as NH_3, % TKN/year)				21.78	-		-			-		

The Total Kjeidjahl Nitrogen (TKN), NH_4 concentration (NH_4-N), pH and Dry Matter (DM) are given. NH_3 emission rates are given as the equivalent flux rate (J_{NH3}) and the yearly emission factor (EF_{NH3}). *α is the ventilation rate (air changes per hour).

[1] Deerdykes equivalent fluxes calculated from the empirical model of Borka et al. (2000), Eq. 9. Where: TS = 16.4, LD = 0.5,1.0,1.5, TAN = 20.516

Figure 7: Top; photograph of digestate taken from inside the digestate store at Deerdykes. Bottom; photograph of digestate being loaded into a container for haulage off site, note the opening of the large door which will induce ventilation.

2.7 LIQUID FRACTION OF EFFLUENTS

The liquid fraction of the separated digestate that is not recycled through the digestion process is sent to an aerobic treatment tank on site. During the batch process, organic material is converted mainly to carbon dioxide and water through biological activity. The aerobic treatment of liquid digestate at the plant is facilitated through a sequencing batch reactor system. This occurs within an open single treatment tank with a volume of 1000m^3 and a liquid surface area of 200m^2. Liquid digestate is fed into the into the aeration tank, in the period following the addition of slurry, NH_3 is nitrified to nitrite and/or nitrate and then denitrified to nitrogen gas (N_2) with the breakdown of degradable organic substances. Ammonia emissions can be expected when nitrification and denitrification of rich process liquors occurs in open tanks. Burton et al. (1993) reported a loss of 2% of total N as $_{NH3}$ emissions when pig slurry was aerated under nitrifying/denitrifying conditions.

After the aeration cycle is stopped, remaining solids are allowed to settle while the top layer of the supernatant was discharged as wastewater to the local sewage system. SBR systems typically operate in 24 hour cycles, Willers et al. (1995) monitored the emissions of NH3 during the cycling of a SBR system which processes large volumes of veal slurry in the Netherlands, reporting ammonia emission rates of 0.7% of total Kjeldahl nitrogen per day during the aeration cycle of the batch process. A mean emission rate of 220mg m^{-2} h^{-1} was observed during the first 10 hours of the aeration cycle, while no emissions were detected during the remaining 10 hours of the cycle nor the sludge settling or effluent discharge phases of the 24 hour batch process. Without directly measuring emissions from the SBR, the NH4+ concentration and pH of the liquid fraction of the Deerdykes digestate was compared with the composition of the veal slurry in the study of Willers et al. (1995) (Table 2). Upon comparing the composition of both liquids the valididity of the published emission factor of 220 mg^{-1} m^{-2} h^{-1} for 10 hours out of 24 was assessed and found to be acceptable for the estimation of emissions from the Deerdykes Anaerobic Digestion plant.

Table 2: Chemical comparison of liquid effluents within the Deerdykes SBR tank against the properties of the SBR experiment of Willers et al. (1995).

SBR	Ammonium content (mg/l)	pH
Willers et al. 1996	150	8.5 – 8.7
Deerdykes	mean 104 max 438	7.7 – 8.7

2.8 FUGITIVE EMISSIONS FROM THE WASTE RECEPTION AREA

The waste reception and pre-processing areas at Deerdykes are fitted with an air extraction and humidified biofilter system. The degree to which the biofilter scrubs NH_3 from extracted room air is not known, however due to the reactive properties of NH_3 a high percentage can be expected to be removed. Cumby et al (2005) reported an 87% reduction in NH_3 concentrations above the biofilter of the Holsworthy anaerobic digestion plant relative to the waste reception area. However in monitoring the concentration of a non-reactive trace gas (SF_6) released into the waste reception area over time, the authors reported that around 50% of the room air within the waste reception area escaped through discrete sources such as openings within the building, primarily as the reception doors were opened for deliveries of wastes to the site. Therefore only half of the contaminated room air was treated by the biofilter system. As a result 95% of NH_3 emissions from the waste reception area occurred from discrete fugitive sources, while the remaining 5% was released from the biofilter stack (Table 3). The Deerdykes biofilter system achieves an air flow through rate of 1.6 room changes/hr, which is similar to that of the Holsworthy system (1.2 air exchanges/hr). Both setups share the same design principle where the waste reception door will open only where a delivery vehicle approaches and will quickly close after the vehicle is fully inside the building to reduce fugitive emissions. Yet Cumby et al (2005) reported that significant emissions can occur despite these prevention measures; while the large doors were opened for loading/unloading or where spillages occurred. Due to the similarities between the two waste reception systems the discrete emission rate of 50% and biofilter NH_3 scrubbing efficiency of 87% were adopted as emission factors for the waste reception area at Deerdykes.

Concentration measurements from within the waste reception building at Deerdykes using the Gas Alert Micro 5 multi gas detector showed distinct concentration profiles between the three sections within the waste reception building (waste reception area, pre-processing area and digestate store). The highest concentration measurements were taken from inside the digestate storage compartment of the waste reception building (Figure 7, Table 3), where concentrations measurements ranged from 7 – 60ppm as recorded episodically on visits to the site. The most commonly recorded concentration measurement which was thought to be the most representative of the digestate store was around 20ppm which was recorded on several occasions. The digestate store is not connected to the biofilter system and this area of the building is largely isolated, except where the store is opened and digestate is manually removed for sale as biofertiliser which occurs roughly three times per week. The air extraction and biofilter system serves the waste reception and pre-processing area: measurements with the portable gas detector indicated a higher concentration of NH_3 within the pre-processing area (2-3 ppm) than within the waste reception area (≤ 1).

This is in striking contrast to the concentrations found within the Holsworthy biogas plant, where a mean concentration of 50 ppm was recorded within the waste reception area (Table 3). This is likely a result of the difference in digestion substrates between the two plants, where the Holsworthy biogas plant predominantly processed livestock slurries from surrounding farms, while the waste reception area at the Deerdykes plant receives solid food wastes from municipal collections and industrial collections, while sludges are held separately in a subterranean tank. As a result, NH_3 emissions from the Deerdykes waste reception area are expected to be significantly lower (See Table 3 for the calculated biofilter and fugitive emission rates for the waste reception area and biofilter). As the outside entrances to the pre-processing area are small personnel doors, the assumed fugitive emission rate of 50% would likely be too high in this case. Scenarios were therefore created for 0 and 25% discrete direct discharge rates from this source. It was assumed for Deerdykes that the room air flow rate through the biofilter was directly proportional to the volume of each source (waste reception and pre-processing areas), thus maintaining a constant air exchange rate of 1.63 room changes/hour throughout.

Table 3: Estimation of biofilter and fugitive emission rates for the Deerdykes waste reception and pre-processing areas.

Measurement	NH3 Concentration (ppm)		
Measured NH3 Concentrations (ppm)	Waste Reception	Preprocessing Room	Digestate Store
15/05/2014		2	7-8
12/06/2014	3-4	7-8	7-8
18/06/2014	1-2	3 (3 hrs)	15-16
23/06/2014			58
26/06/2014			18 (3 hrs)
04/07/2014	0 (2 hrs)		22 (4 hrs)
10/07/2014	8 (2 hrs)	2 (1 hr)	40 (1 hr)
16/07/2014	2	6-7	18 (2 hrs)
Best Estimate	**≤ 1**	**2-3**	**20 (mode)**
(Cumbernauld)		-	-
Holsworthy mean	50		

Holsworthy Physical Characteristics	
Reception Hall volume:	3600 m3
Air flow rate through biofilter:	1.2 air changes/h
Biofilter discharge rate:	4320 m3/h
Direct discharge:	4320 m3/h

Deerdykes Physical Characteristics	
Waste Reception Area volume:	2997 m3
Preprocessing Area volume:	2511 m3
Total building volume:	5508 m3
Air flow rate through biofilter:	1.63 air changes/h
Biofilter discharge rate:	9000 m3/h
Direct discharge rate:	4900 – 6050 m3/h

Holsworthy Biofilter & Fugitive NH3 Emissions	
Waste Reception Area concentration:	37.5 mg/m3 (50 ppm)
Biofilter NH3 scrubbing efficiency:	87%
Biofilter discharge rate:	4320 m3/h
Bioflter NH3 emission rate:	**5.8 mg/s**
Waste Reception leakage rate:	50%
% total emissions from discrete sources:	95%
Direct discharge:	4320 m3/h
Fugitive emission rate:	**28 mg/s**

Deerdykes Biofilter & Fugitive NH3 Emissions	
Waste Reception Area concentration:	0.75 mg/m3 (1 ppm)
Preprocessing Area concentration:	2.25 mg/m3 (3ppm)
Combined concentration:	1.43 mg/m3 (1.91 ppm)
Biofilter emission rate:	**0.465 mg/s**
Waste Reception Area direct discharge:	4900 m3/h
Waste Reception Area fugitive emission rate:	**1.02 mg/s**
Preprocessing Area direct discharge:	0 – 2050m3/h
Pre-processing Area fugitive emission rate:	**0 – 1.285 mg/s**

Emission rates were estimated on the basis of the experiments and findings at the Holsworthy digester (Cumby et al. 2005); where 50% of room air was discharged via the biofilter, which achieved an NH3 scrubbing efficiency of 87%, while the remaining 50% escaped via fugitive pathways (direct discharge).

Concentration measurements with a (n hrs) denote averaged concentrations over n hours. Non-marked measurements are spot measurements.

2.9 SURFACE WATER BALANCING TANK

The surface water balancing tank (SWBT) receives most of the runoff and from the central area of the site where spillages are most likely. The yard and vehicles are also regularly washed with power-hoses around this area, thus this tank receives a significant amount of organic wastes and is highly contaminated (Figure 8). This tank was found to be a significant source of NH_3 after the measured concentration at the edge of it was consistently the highest or among the highest in the ALPHA surveys. It was therefore concluded that a significant amount of NH_3 was volatilising from its surface which should be included within local dispersion models. As no samples were taken from the SWBT its emission strength was inferred by fitting modelled air concentrations to ALPHA data from the same period. The SWBT may be comparable to waste water ponds at a dairy farm containing parlour wash and feeding lot runoff in wet seasons, as a body of water that is highly contaminated by organic wastes. Emission rates were taken from studies which measured the emission rates from waste water ponds through inverse dispersion methods. Flesch et al. (2009) and Leytem et al. (2010) published emission rates of 3.5 and 2.02 g m^{-2} d^{-1} respectively. These emission factors were initially used for modelling the emissions from the tank, which has a surface area of $200m^2$.

Figure 8: The contaminated Surface Water Balancing Tank and ALPHA sampler saucer located at its edge.

3 Results

3.1 AiRRmonia Period 1/Windtrax Emission Estimates

The AIRRmonia continuous air NH_3 measurements was found to fluctuate with changes in wind direction, where the highest concentrations were measured when the AiRRmonia was directly downwind of the AD plant (Figure 9, 10). The mean air NH_3 concentration between the 28th of May and the 26th of June was 3.96 µg m-3. Filtering the AiRRmonia data measurements to where the wind direction is between 214 and 236° and wind speed is greater than or equal to 0.1 m s^{-1} corresponds to periods where the AiRRmonia sensor was directly downwind of the central area of the AD plant, including key sources such as the SBR, waste reception building and the SWBT. After filtering the data to meet these conditions the average air NH_3 concentration measurements was 7.42 µg m-3. Further filtering the data to the wind sector between 220 and 230° produced the highest mean concentration within the AiRRmonia data at 7.87 µg m^{-3}, as the footprint of the key sources are more exclusively sampled at this narrower wind sector. The data pertaining to the 220 - 230° wind sector was taken as the input data for inverse dispersion modelling, where the mean, median, 75th and 95th percentile of the NH_3 concentration measurements was run in a model which represented the spatial distribution of the AD plant relative to the AiRRmonia sensor. It was assumed that all of the emissions originated from the waste reception building, the SBR and the SWBT. A bearing from the AiRRmonia sector at 225° intersects these sources at a distance of 100m at the nearest point. The source strength was then calculated for the mean and each percentile of the data. The calculated source strength ranged from 2.93 µg m^{-3} using the median NH_3 concentration and 16.27 µg m^{-3} using the 99th percentile of the data (Table 4).

Figure 9: Time series of AiRRmonia continuous air NH_3 measurements against wind direction, AiRRmonia Period 1 (28th May – 26th June). Sections that are shaded in blue correspond to periods where the AiRRmonia NH3 sensor is approximately downwind of the AD plant (wind direction 200 - 250°), during these periods the highest measured NH3 concentrations occurred.

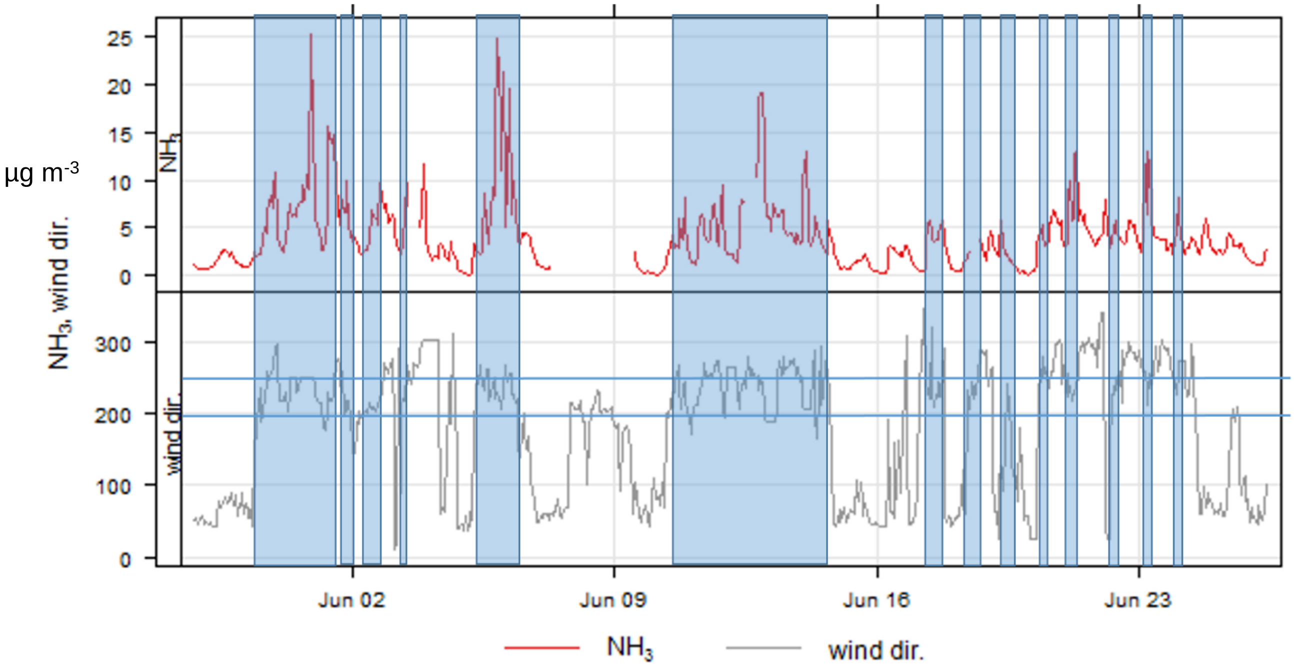


Table 4: Mean, median and percentiles of AiRRmonia NH_3 concentration data from AiRRmonia Period 1 (28th May – 26th June) and Windtrax source strength calculations

	AiRRmonia averaged NH_3 concentration per wind sector (µg m^{-3})			Windtrax-Calculated Source Strength 220 - 230° (µg m^{-2} s^{-1})	Area-Integrated Source Strength (2231m^2) (mg s^{-1})
	All wind sectors	214-236°	220-230°		
Mean	3.96	7.42	7.87	4.04	10.21
Median	3.13	5.95	6.13	2.93	7.42
75th	5.11	8.96	9.51	5.07	13.24
95th	10.61	18.90	19.39	11.33	29.58
99th	18.61	26.0	27.19	16.27	42.47

The source strength using the Windtrax model was back calculated from NH_3 concentrations captured when directly downwind from the AD plant (220 - 230° wind sector). The background NH_3 concentration in each simulation was 1.5 µg m^{-3}.

Plotting the AiRRmonia Period 1 (28th May – 26th June) NH_3 concentration data against wind speed and wind direction as a concentration polar plot using the OpenAir package (Carslaw 2012) illustrates the influence of the AD plant and wind direction on the air NH_3 concentration at the AiRRmonia receptor (Figure 10). Air originating from the easterly half of the windrose has a much lower average NH_3 concentration (1.76 µg m^{-3}), than southwesterly winds (220 - 230°, 7.89 µg m^{-3}) while the northwesterly wind sector (290 - 330°) had higher mean concentration (4.49 µg m^{-3}). This suggests a possible influence of the Dairy Farm which is located 500m northwest (280 - 300°) of the measurement point. Assuming that all of the emissions originate from the yard and animal housing area at the farm (9000m^2), the Windtrax calculated source strength for the Farm was 1.54 µg m^2 s^{-1}.

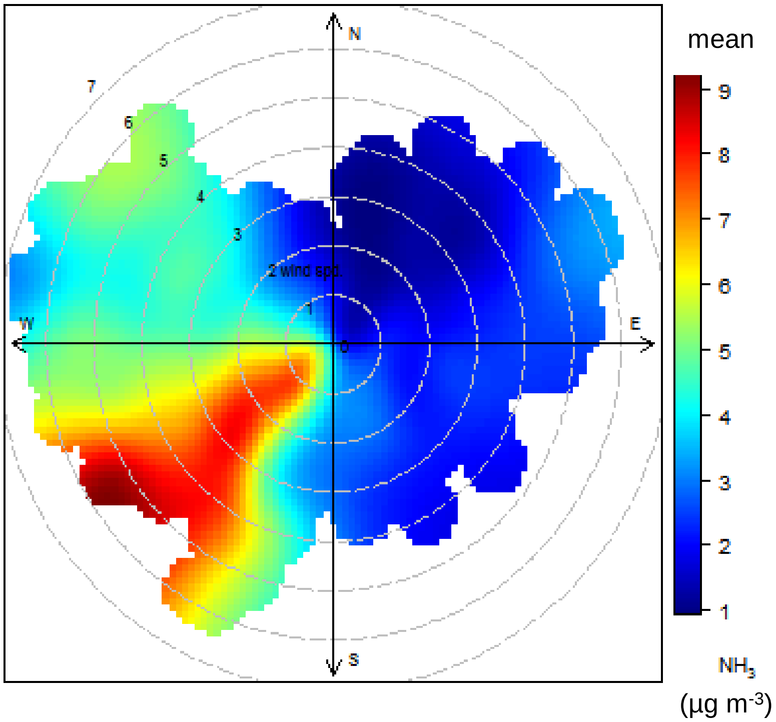


Figure 10: Polarplot of AiRRmonia data with wind speed and direction for AiRRmonia Period 1, (28th May – 26th June). Averaging period is 10 minutes.

Met. data supplied by www.cumbernauldweather.com, plotted using the OpenAir package.

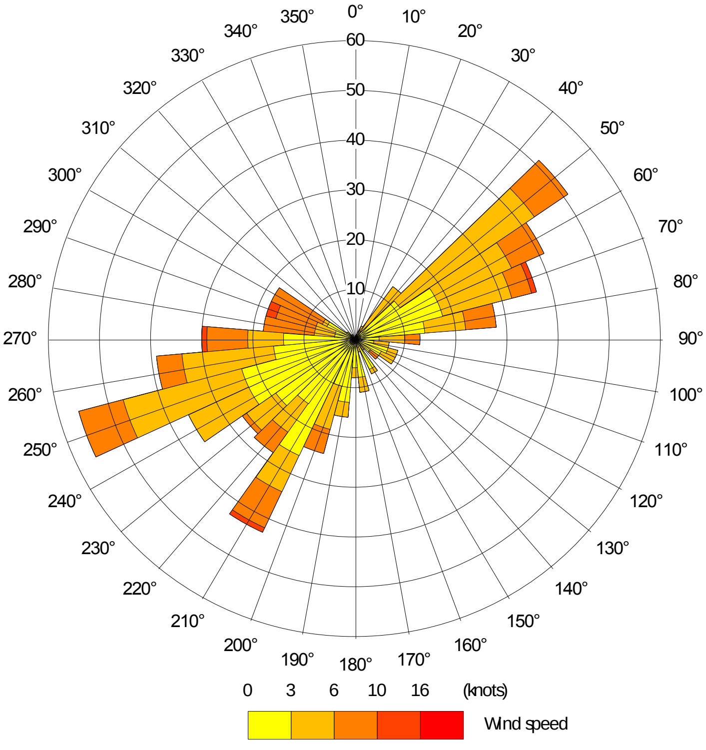


Figure 11: Windrose of meteorological data from the 28th May to the 26th June. Averaging period is 1 hour.

Met. data supplied by www.cumbernauldweather.com. Plotted using the ADMS met. data processor.

A wind rose pertaining to AiRRmonia Period 1 (Figure 11) reveals that the prevailing wind at the site is polarised in the NE and SW wind directions. Therefore receptors in these bearings from the plant will be more strongly influenced by emissions from the plant than those to the south, southwest or north of the plant. This also indicates that passive NH_3 samplers around the site are not likely to be significantly influenced by NH_3 emissions originating from the Dairy Farm.

3.2 ALPHA MEASUREMENTS

Table 5: ALPHA sampler NH_3 measurements at Deerdykes.

Site	OSX	OSY	Distance* (m)	NH_3 Concentration ($\mu g\ m^{-3}$)						
				Period 1 15/05-27/05/2014	Period 2 27/05-03/06/2014	Period 3 03/06-12/06/2014	Period 4 12/06-18/06/2014	Period 5 18/06-26/06/2014	Period 6 26/06-10/07/2014	Period 2-5 Average
1	271700	672155	115	2.30	2.31	3.31	2.99	2.95	4.15	2.92
2	271679	672113	93	2.22	2.82	3.71	2.95	3.63	3.94	3.33
3	271634	672215	158	1.79	1.68	3.68	1.97	2.31	2.72	2.53
4	271579	672215	157	1.76	1.80	4.06	2.05	2.56	2.54	2.76
5	271515	672054	83	2.85	2.50	4.05	3.58	3.53	9.25	3.46
6	271557	672049	45	7.39	10.52	23.10	18.49	11.71	42.18	16.20
7	271595	672088	26	9.90	9.69	10.23	18.90	14.62	17.15	13.01
8	271656	672038	58	1.58	1.26	2.21	2.36	3.38	2.72	2.33
9	271662	672186	142	1.90	2.01	2.78	2.14	2.24	3.20	2.34
10	271626	672148	88	4.09	3.48	4.60	3.51	2.99	5.43	3.70
11	271960	672043	364		1.50	1.42	1.75	1.52	1.80	1.53
12	271427	672475	446		3.71	3.69	3.26	3.45	3.38	3.55
13	271512	671907	177		1.31	1.29	1.64	1.18	1.91	1.34
14	271634	672194	122		1.79	1.63	2.08	1.74	2.05	1.78
15	271406	671974	212		1.47	1.76	1.88	1.53	2.62	1.66
16	271417	672238	252		2.71	8.14	3.22	3.18	4.14	4.56
17	271692	672237	200			2.24	2.59	2.97	2.90	2.59
18	281627	672096	38				12.53	13.49	9.03	12.34
19	271583	672060	16				13.73	8.45	27.50	9.95
20	271723	672203	186					1.50	1.47	1.50

*Distance is given as the distance from the center of the waste reception building to the sampler.

In general, the samplers that were placed in the central area of the AD plant (site 6, 7, 18, 19) showed the highest measured concentrations. However the concentration at these sites was also the most variable, suggesting that NH_3 emissions from the plant can vary from week to week – this is either due to variability in emissions or other factors such as temperature, rainfall or site management. Site 6 at the

SWBT showed the highest degree of variation (7.39 – 42.18 µg m^{-3}), while sites 5 (2.50 – 9.25 µg m^{-3}) and 19 (8.45 – 27.5) which are nearby also vary to a degree in response to changes in emissions from the SWBT. Site 16 (which is near the Dairy Farm) also shows a higher degree of variation and measured concentrations are typically higher than other samplers which are a similar distance from the AD. NH_3 emissions from farm activities and grazing livestock are likely to influence concentrations at this site. ALPHA site 12 is far north of the site and closer to the farm, therefore the relatively high NH_3 concentration measurements may be influenced by the farm or the main road which it is sited near. The lowest concentrations were generally measured at sites furthest from the plant, where concentrations of around 1.5 µg m^{-3} were common. Therefore 1.5 µg m^{-3} was taken as the background concentration for dispersion modelling. The regression of measured versus predicted concentration using dispersion modelling also showed the best fit when this value is used. The average of ALPHA periods 2-5 is given in Table 5 and Figure 12 as this period corresponds 1st period of AiRRmonia measurement, the data from which was used to back-calculate the source strength using Windtrax and make predictions of average concentration of NH_3 in the area using ADMS dispersion model.

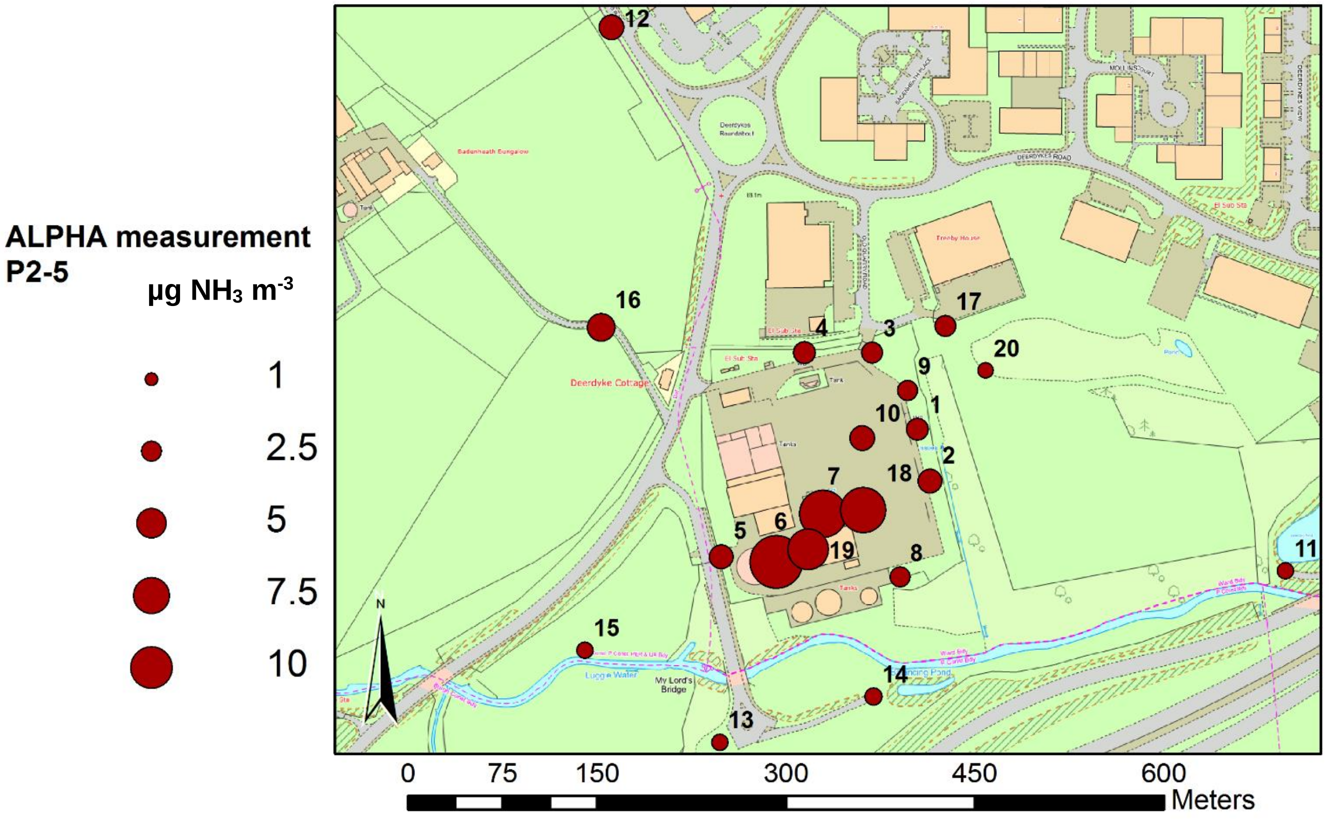


Figure 12: Map showing the location and average NH_3 concentration at ALPHA receptors (Period 2-5, 28th May – 26th June) through proportional symbols.

Figure plotted using ArcMap software.

Table 6 presents an intercomparison of measured NH_3 concentrations with the ALPHA samplers and AiRRmonia instrument (continuous data averaged to ALPHA periods). The AiRRmonia measured mean concentrations appear to exceed the ALPHA measured concentrations from ALPHA periods 2 – 5 (ALPHA site 1), while the ALPHA measurements were greater than the AiRRmonia measurements for ALPHA periods 6 and 7 after the AiRRmonia was moved to a central location within the plant (ALPHA site 7), opposite of the entrance to the digestate store. At location 1, the AIRRmonia was operated from inside a small weighbridge cabin where there was access to mains power, sampling via a short (<1.5 m) insulated polyethylene inlet line. This building is next to a weighbridge where passing HGVs containing volatilising wastes may have influenced the AIRRmonia sampler more than the ALPHA location which was 6 meters east of the AiRRmonia. An alternative explanation may involve emissions of amines which are likely to be emitted from the AD plant but at much lower concentrations than NH_3 therefore they may be a positive interferent close to the source. The CV between the triplicates of ALPHA samplers were typically less than 5%, confirming good precision in the measurements (Table 10, Appendix 1).

Table 6: Intercomparison of co-located ALPHA and AiRRmonia NH_3 samplers at Deerdykes.

ALPHA Period*	Start GMT	End GMT	ALPHA (µg m^{-3})	AiRRmonia (µg m^{-3})	% AiRRmonia coverage
2	27/05/2014 11:00	03/06/2014 11:30	2.31	4.89	100
3	03/06/2014 11:30	12/06/2014 11:10	3.31	3.83	72
4	12/06/2014 11:10	18/06/2014 11:20	2.99	3.48	96
5	18/06/2014 11:20	26/06/2014 12:00	2.95	3.49	97
6	26/06/2014 14:00	10/07/2014 12:00	14.62	10.82	87
7	10/07/2014 12:00	16/07/2014 13:00	7.88	6.15	100

*The AiRRmonia was located 10m west of the location of ALPHA site 1 during ALPHA period 2-5. It was then moved to the location of ALPHA site 7 for the final ALPHA periods 6 and 7.

3.3 MODELLING OF NH$_3$ CONCENTRATIONS

Each of the Windtrax back-calculated emission rates given in Table 4 was entered into ADMS, where the model assumes a constant emission rate per m^2 at the three sources identified in the model: the waste reception building (1369 m^2), the SWBT (661 m^2) and the SBR (201 m^2) using met. data corresponding to the time period for which the emission strength was back-calculated (28th May – 26th June). The emission rate back-calculated from the mean of the filtered AiRRmonia concentration data (7.9 µg m^{-3}) best fit the measurements around the site. The predicted concentrations around Deerdykes can be seen in Figure 13. The ALPHA measurements for this period are set over the predicted concentration contour plot with the same scale on the colour axis to allow comparison. Measured concentrations from ALPHA samplers 17-20 which were set in place later and don’t cover the measurement period are included. The concentration is heavily influenced by the SE – NW prevailing wind directions and by buildings and tanks (5 – 10 m in height) to the north and south of the central area source, which limits dispersion in these directions.

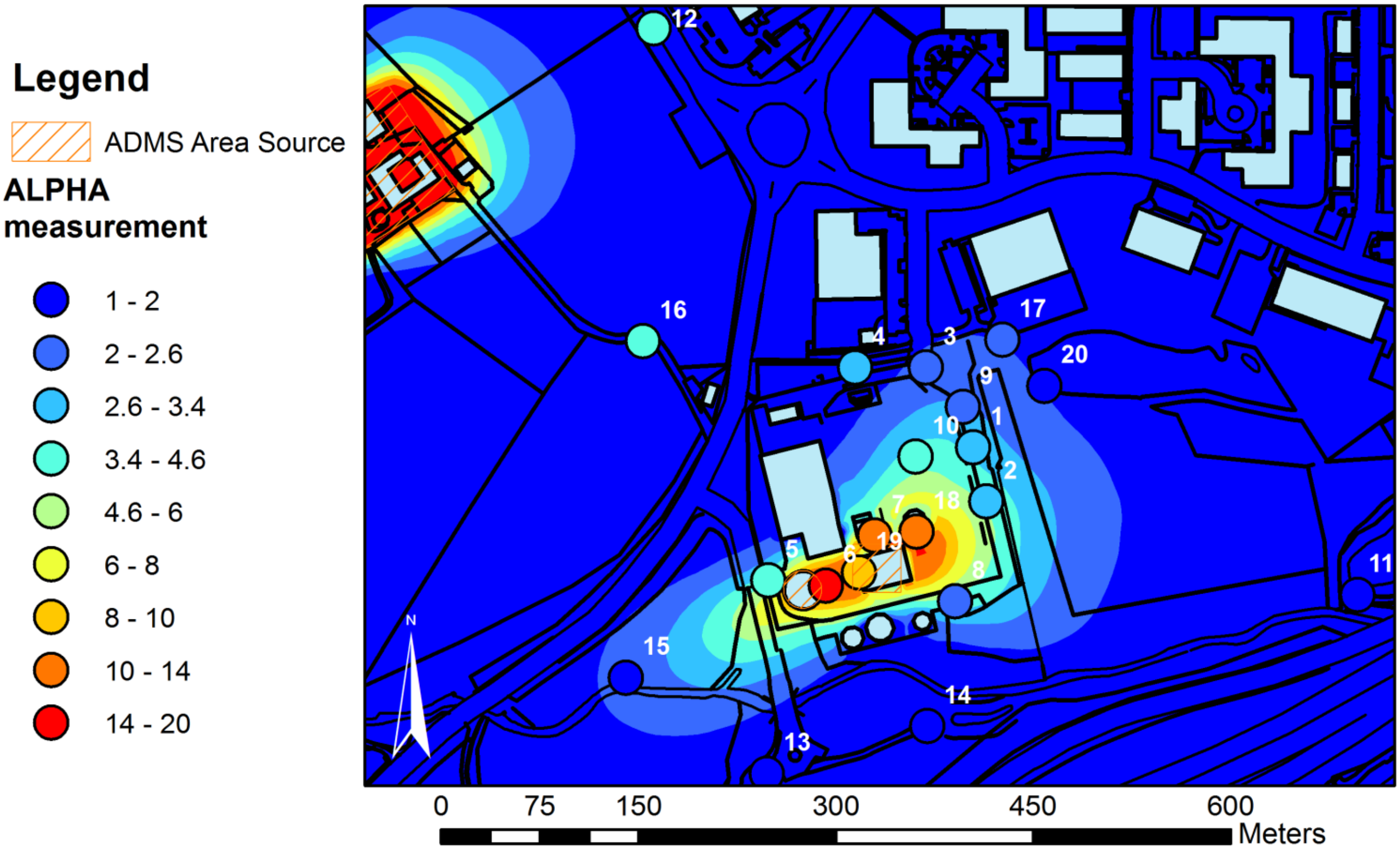
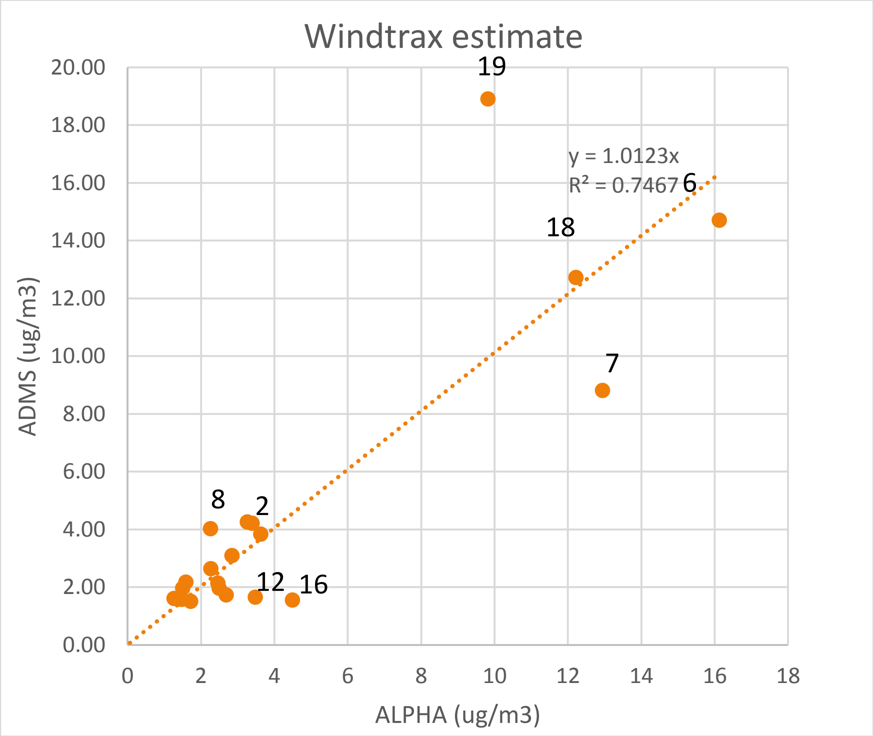


Figure 13: Contour map of the ADMS predicted long-term average concentrations (28th May – 26th June). ALPHA measurements are plotted over the ADMS predicted concentration background using the same colour axis. Plotted using the ADMS-ArcGIS extension. The emission factor (4.035 µg m^{-2} s^{-1}) is backcalculated from the mean of the filtered 220° - 230° wind sector AiRRmonia NH$_3$ concentration data (7.87 µg m^{-3}). All emissions in this model are emitted from the waste reception building, the SBR and the SWBT.

The regression of the modelled concentration at the ALPHA receptors shows a near 1:1 ratio which suggests that the magnitudes of the modelled and measured data are roughly proportional to one another (Figure 14). However there is a poorer fit near to the central area sources where concentrations are highest. The predicted concentration at ALPHA receptor 19 is over twice the measured concentration. Windtrax assumes that emissions are homogeneously distributed at the source, which produces an equal emission rate at the boundary of the central area source when run in ADMS. As NH_3 emissions at the plant arise from distinct locations at varying strengths, this treatment will not accurately capture the measured distribution. For example, receptor 19 is sited a few meters from the western wall of the waste reception building which is assumed to be emitting NH_3 at the same rate as the door of the digestate store, thus the concentration at receptor 19 is increased relative to site 7. The predicted concentration at receptor 2 and 8 are increased relative to measurements as the waste reception building is closed from the south and east ends. Therefore low emissions are expected to occur in these areas while the area source assumes equal emissions from all surfaces surrounding the waste reception building.

ALPHA measurements at sites 12 and 16 are significantly higher than model predictions. It is likely that the proximity of these sites to the dairy farm is increasing the air NH_3 which is not well simulated by the model. The Windtrax-calculated emission rate of the Dairy Farm was 1.54 µg m^{-3} s^{-1}, where it was assumed that all of the emissions are produced at the farmyard and animal housing area. The model suggests that this emission rate has little influence on the receptors at ALPHA site 12 and 16. However cattle were observed grazing in fields near to these receptors and emissions from fields was not included in the source definitions within the model. As the predicted influence of the AD plant on these receptors is very low these points can be removed when assessing the regression of measured vs modelled concentrations to remove this source of error.

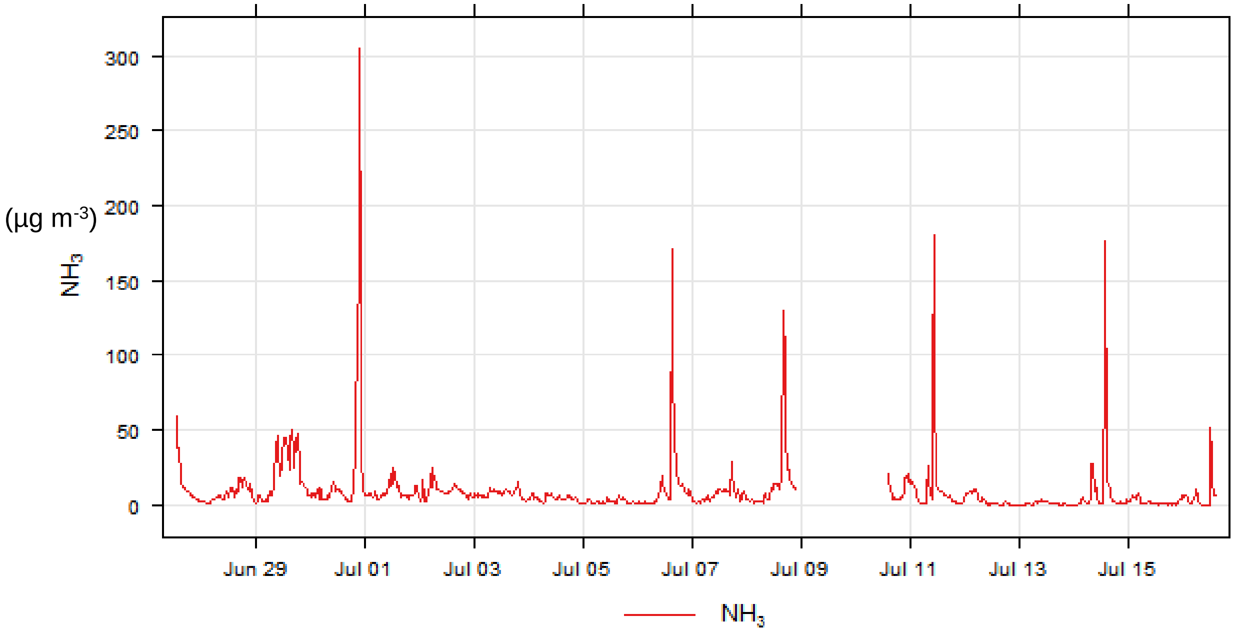


<u>Figure 14: Scatterplot of measured versus ADMS-predicted NH_3 concentrations from the Windtrax-calculated area sources (4.035 µg m^{-2} s^{-1}, 2231m^2). The three sources included are the waste reception building the SBR and the SWBT.</u>

3.4 AIRRMONIA PERIOD 2

During the second period of AiRRmonia continuous air NH_3 concentration monitoring, the AiRRmonia was placed to the north of the waste reception building at ALPHA site 7, 20m from the entrance to the digestate store. The NH_3 concentration time series during this period (27th June – 16th July) is characterised by a relatively low baseline with high-concentration events occurring every 2 – 6 days, where air concentration would rise up to 300 µg m^{-3} and return back to a low baseline (<10 µg m^{-3}) within a few hours from (Figure 15). Emissions from the digestate store are expected to be episodic as high concentrations accumulate within the digestate store and are released as the store is opened and the digestate is extracted. This is said to occur roughly three times per week (days/times were not recorded by the AD plant), which is consistent with the number of emission events that occurred over the monitoring period. Therefore the digestate store door is a dominating point source at this location which should be differentiated in source definitions within the dispersion model.

Figure 15: Timeseries of AiRRmonia-measured NH_3 concentrations



3.5 DIFFERENTIATION OF MODEL INTO MULTIPLE SOURCES

In order to accurately reproduce the measured concentrations near the source it was necessary to individually define each significant source within the model (Figure 16). While the flux rate from these sources was not directly measured, NH_3 concentration measurements from ALPHA, AiRRmonia, and handheld multi-gas detector sensors were able to identify the most significant sources at the plant. A literature review allowed an estimate of the emission rate for each source to be produced, which are listed in Table 7.

Table 7: NH$_3$ Emission factors for differentiated sources at Deerdykes

Source Name	Type	Emission Factor	Intensity	Area-Integrated Emission Rate (µg s^{-1})	Rationale/Reference
Digestate store	Point	17.4 µg m^{-2} s^{-1}	60 m^2 x 5 roughness factor	5208	Calculated using the empirical model of Borka et al. (2000), Eq. 4. The assumed ventilation rate is 1.0 air changes per hour. Surface roughness factor is estimated to be 5.
Biofilter	Point	465 µg s^{-1}	1	465	Calculated from the mean of the measurements of NH3 concentration within the waste reception area, air flow rate is 9000 m^3 h^{-1}. Biofilter NH$_3$ scrubbing efficiency is assumed to 87% (Cumby et al. 2006) (Table 3).
Waste reception area door	Point	1020 µg s^{-1}	1	1020	Based on the assumption that 50% of air exchange occurs through direct discharge (Cumby et al. 2006), and that the large door to the waste reception area on the west side of the building is the only outlet (Table 3). Measured inside concentration: 0.75 mg m^{-3}.
Pre-processing area	Line	41.5 µg m^{-1} s^{-1}	31 m	1285	Assumed 25% direct discharge (Table 3) from the pre-processing area which features two small personnel doors on the north side of the building. Emissions assumed to occur evenly across this surface. Measured inside concentration: 2.25 mg m^{-3}.
SBR	Point	61.1 µg m^{-2} s^{-1}	200 m^2 x (10/24)	5091	The emission factor of 220 mg^{-1} m^{-2} h^{-1} for SBR aerobic treatment of veal slurry (Willers et al. 1995), which was found to be suitable after comparing to chemical analysis of Deerdykes SBR liquid. The authors reported that this was the average emission for the first 10 hours of the 24 hour cycle, with no emissions occurring after.
SWBT	Area	23.4 µg m^{-2} s^{-1}	616 m^2	14409	Flesch et al. (2009) and Leytem et al. (2010) published emission rates from dairy farm wastewater lagoons in the U.S., the lower estimate of the two (2.02 g m^{-2} d^{-1}, Leytem et al. 2010) was selected for the SWBT at Deerdykes.

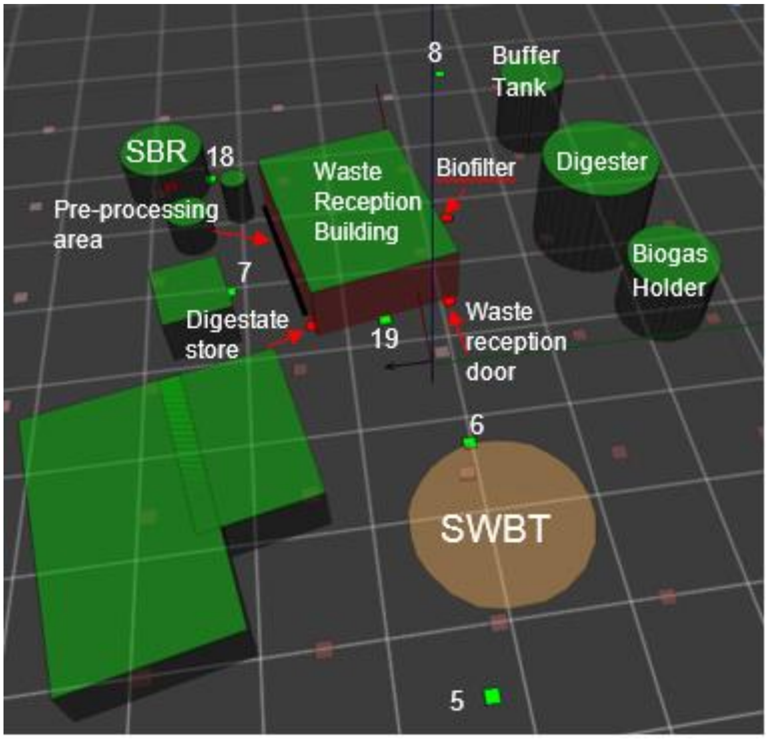


Figure 16: ADMS source and building configuration at Deerdykes.

Red circles are point sources, orange shaded areas are area sources, black lines are line sources and green squares are ALPHA receptors.

SBR: Sequencing batch reactor

SWBT: Surface water balancing tank.

Annotated screenshot taken from the ADMS 3D Mapper utility.

After applying the emission factors listed in Table 7, predicted concentrations at the ALPHA receptors exceeded ALPHA measurements by a factor of around 2.4 (Figure 17, 18). In particular, the predicted concentrations around the SWBT were much higher than the ALPHA measurements, with concentrations at site 5, 6 and 19 all exceeding measured concentrations by factors of around 3.2. Therefore as the SWBT emission rate in the model is much higher than reality, a model optimisation factor must be added to produce a realistic emission rate for this source. It was found that an optimisation factor of 2/9 best replicated the long-term average concentration of the ALPHA samplers around the SWBT for periods 2-5. Further optimisation factors were applied to the digestate store (increase), the water reception hall door (decrease), and the pre-processing area line source (decrease) to fit the predicted concentrations against the ALPHA measurements. The final optimisation factors after a series of iterations are shown in Table 8 along with the resulting emission rates for each source. The predicted concentrations around the site relative to ALPHA measurements are shown in Figures 19 and 20, where a near-perfect linear regression can be seen between measured and predicted concentrations.

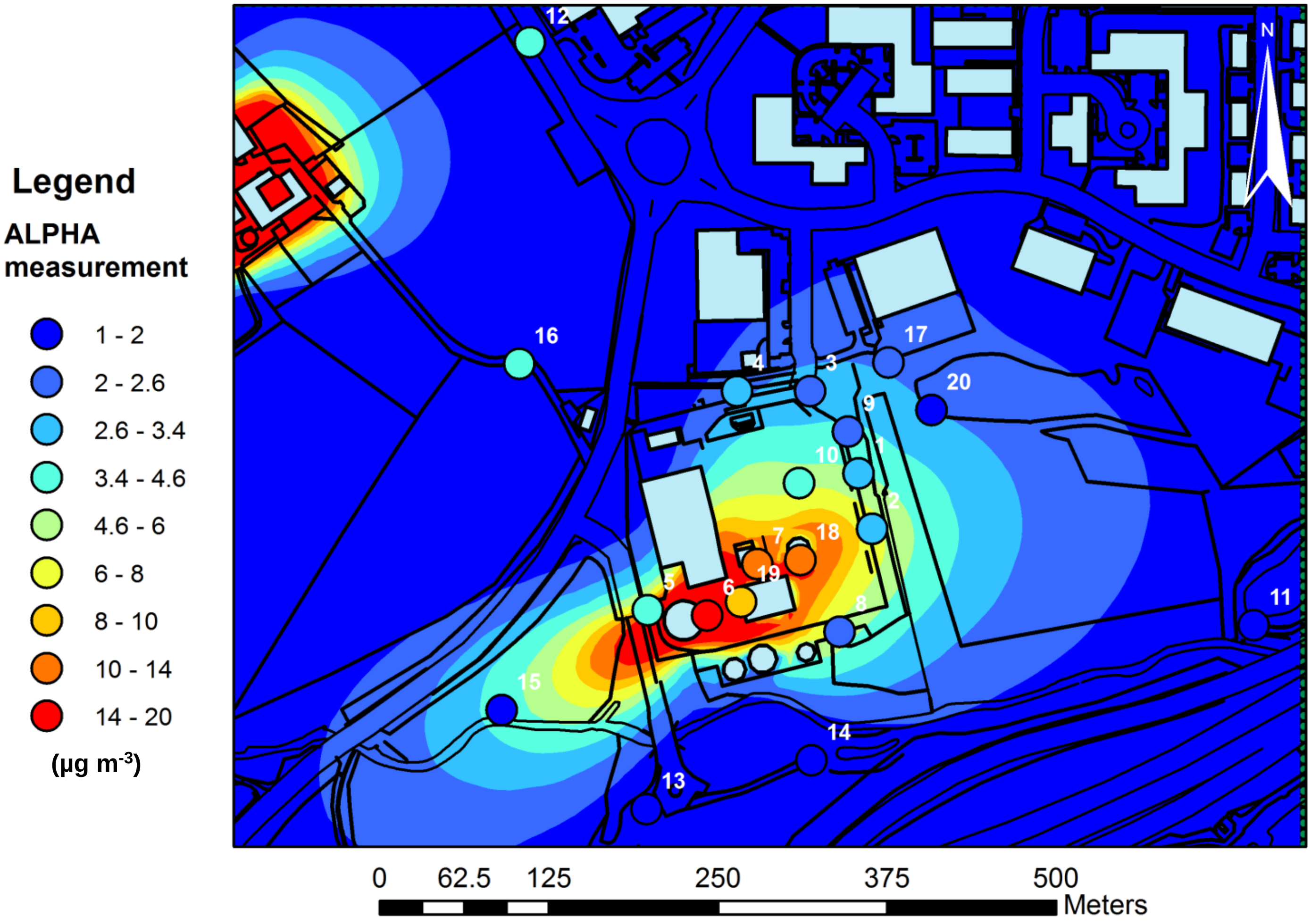


Figure 17: Contour map of the ADMS predicted concentrations using the source definitions listed in Table 7.

Note the high concentrations around the SWBT and ALPHA site 6 associated with an elevated SWBT emission rate relative to observed concentrations.

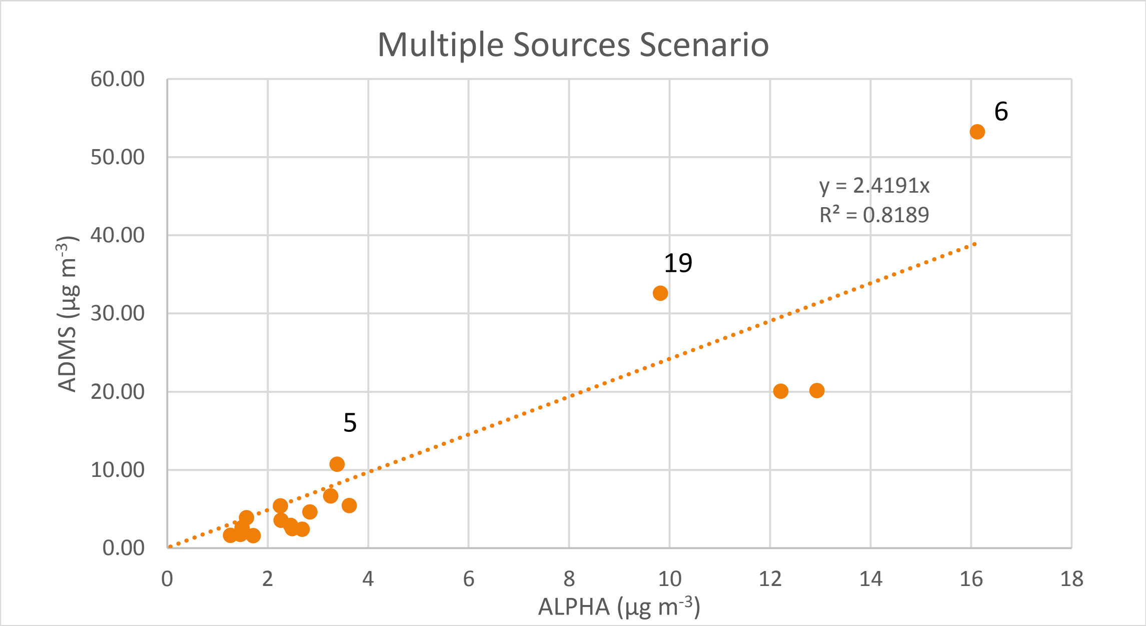


Figure 18: Scatterplot of modelled concentrations calculated using the source definitions listed in Table 7 versus modelled concentrations.

Table 8: Optimised emission factors for NH$_3$ sources at Deerdykes

Source Name	Type	Emission Factor	Area-Integrated Emission Rate (µg s^{-1})	Optimisation Factor	**Optimised Emission Factor**	**Optimised Emission Rate (µg s^{-1})**	Description
Digestate store	Point	17.4 µg m^{-2} s^{-1}	5208	60 m^2 x **7** roughness factor	**17.4 µg m^{-2} s^{-1}**	**7290**	Same emission factor but assuming a higher surface roughness factor (7) which scales the total emissions.
Biofilter	Point	465 µg s^{-1}	465	-	**465 µg s^{-1}**	**465**	No change.
Waste reception area Door	Point	1020 µg s^{-1}	1020	1/16	**63.8 µg s^{-1}**	**64**	Emissions reduced by a factor of 16.
Pre-processing area	Line	41.5 µg m^{-1} s^{-1}	1285	1/2	**20.8 µg m^{-1} s^{-1}**	**643**	Now assuming a 12.5% direct discharge rate along the northern boundary of the waste reception building.
SBR	Point	61.1 µg m^{-2} s^{-1}	5091	-	**61.1 µg m^{-2} s^{-1}**	**5091**	No change.
SWBT	Area	23.4 µg m^{-2} s^{-1}	14409	2/9	**5.2 µg m^{-2} s^{-1}**	**3202**	Emissions reduced by a factor of 2/9.
		Total (mg s^{-1}):	**27.5**		**Total (mg s^{-1}):**	**16.8**	

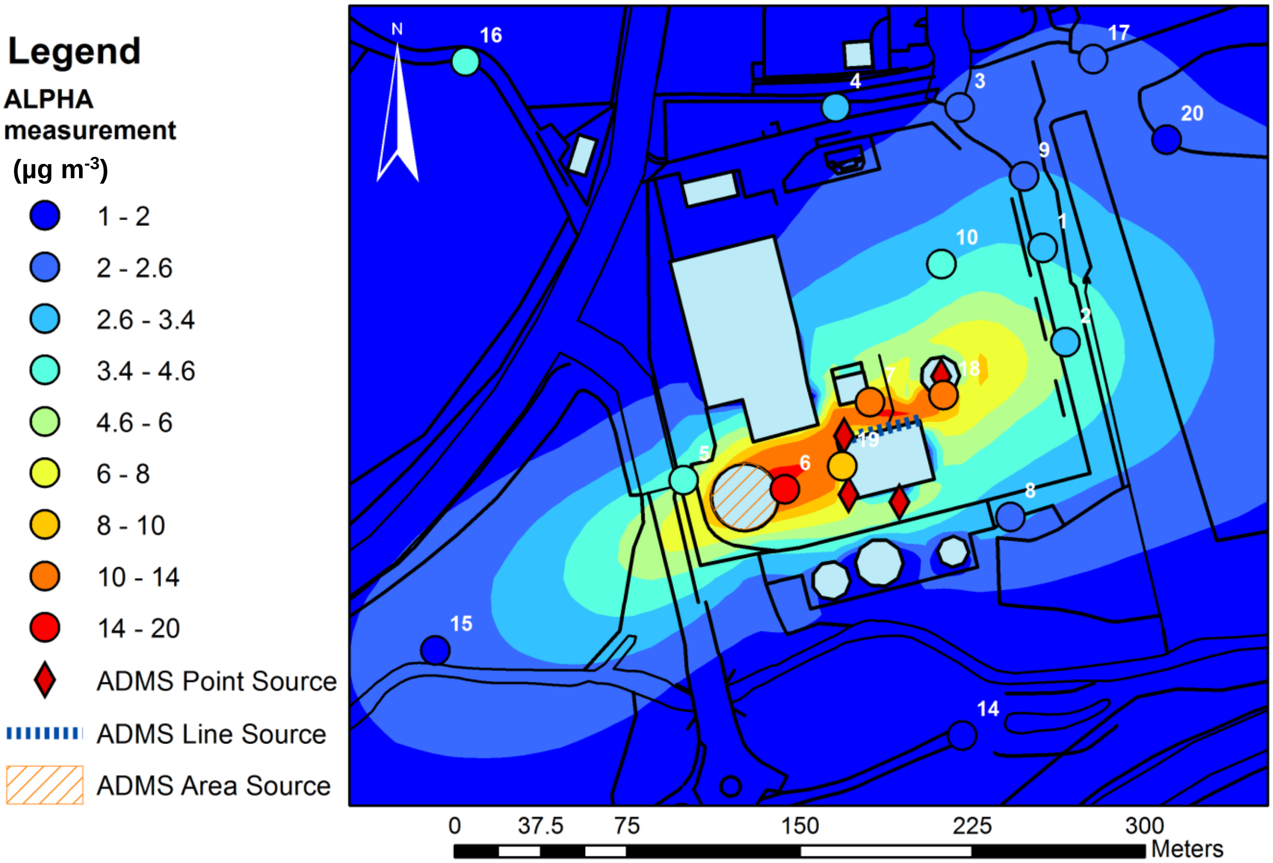


Figure 19: Contour map of predicted concentrations after applying optimisation factors to the sources that required adjustment. This model shows an excellent fit to the ALPHA measurements and provides the best estimate of the magnitude and distribution of emissions of NH_3 at Deerdykes.

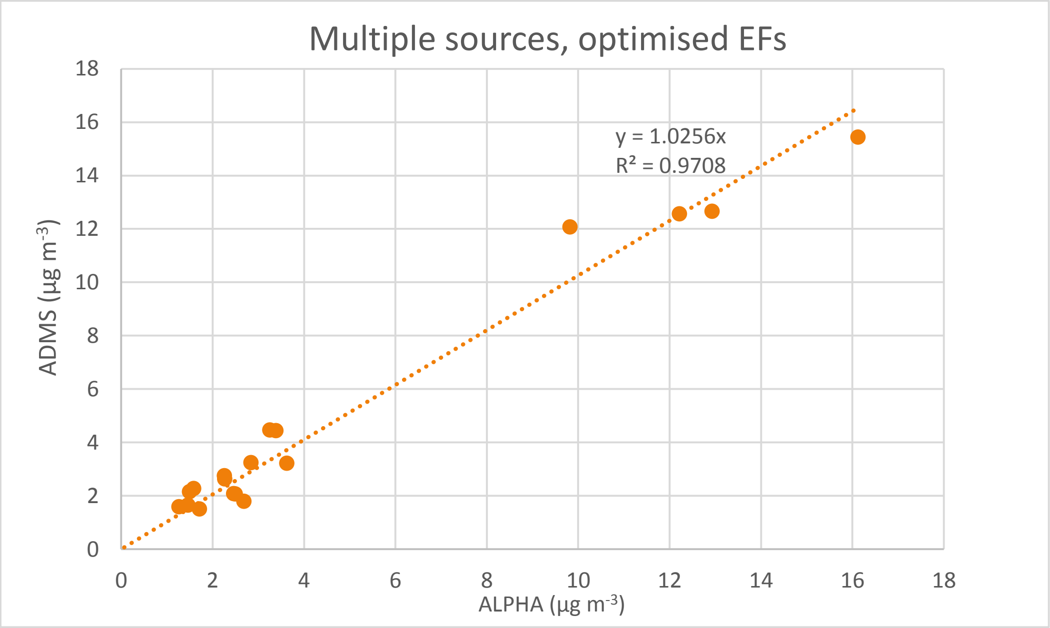


Figure 20: Scatterplot of measured and predicted concentrations of NH_3 after applying optimisation factors (Table 8).

3.6 EVALUATION OF EXISTING AD EMISSION FACTOR

An intercomparison of the Windtrax and source-differentiated emission factors and total emission rates are given in Table 9. The existing EF is a factor of 56 and 34 higher than the Windtrax and optimsed multiple source estimates respectively (Table 9). This generates predicted concentrations that exceed the ALPHA concentration measurements on average by a factor of 54 (Figure 21 & 22). This EF is clearly is not representative of the Deerdykes anaerobic digester, thus the emission factor given for the total of the differentiated sources is recommended.

Table 9: Comparison of the existing EF against calculated emission rates for Deerdykes. The existing emission factor appears to exceed the Windtrax-calculated EF by a factor of 34 - 56. Total annual fresh waste input to Deerdykes is the listed capacity of 30,000 tonnes per year

	Existing emission factor	Windtrax – calculated emission factor	Optimised emission factor for total of multiple sources scenario
Emission Factor (% Total FW input volatalised as NH_3 (t NH_3 / t input FW) Annual input = 30,000 t FW	0.0599636*	0.00106666	0.00176602
Annual emissions (t NH_3) (Applied to Deerdykes)	18.0	0.32	0.53
Total Emission rate (mg s^{-1}) (Applied to Deerdykes)	570.5	10.3	16.8
* Existing emission factor taken from Dragosits et al. 2013.			

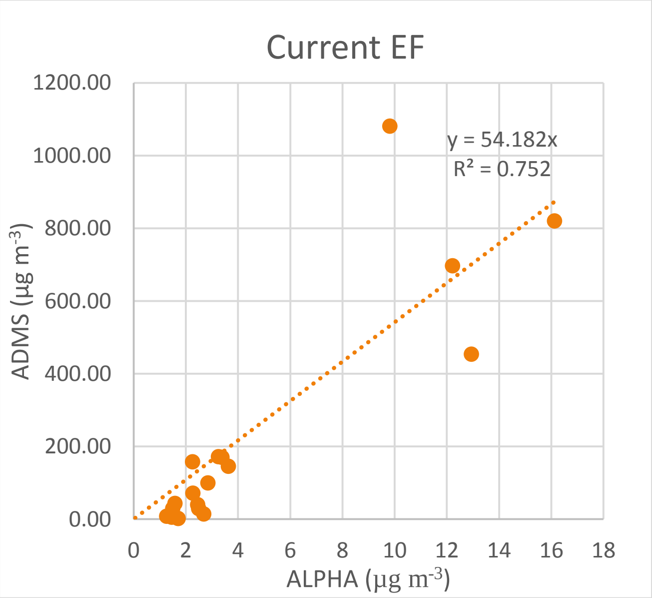


Figure 21: Scatterplot of measured concentrations against modelled concentrations calculated using the current emission factor for AD plants (0.06% Total FW input volatalised as NH_3).

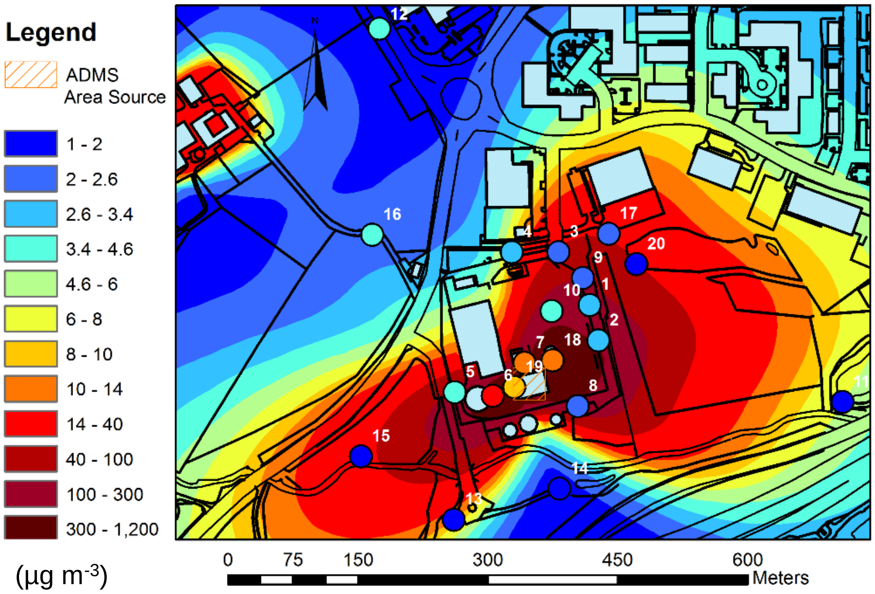


Figure 22: Contour map of the ADMS predicted concentrations using the current AD EF (0.06 % Total FW input volatalised as NH_3).

The difference between the total emission rate of the Windtrax-calculated emission factor and the total of the differentiated sources is likely caused by the positioning of individual sources relative to the ALPHA receptors, the bias of the sampling locations at the site which are predominantly towards the northeast of the site along the axis of the prevailing wind direction, and the interaction of emission plumes with buildings at the site. In assuming equal emissions at the boundary of the emission source, treating the waste reception area as a single area source introduces higher emissions at the eastern boundary of the waste reception area where there is a high concentration of ALPHA samplers. Thus it is possible to achieve a similar regression with ALPHA measurements with a lower total emission rate. The SWBT and digestate store are two of the greatest sources of emissions at the plant, emissions from which are obstructed by tanks and buildings along the axis of the prevailing wind direction reducing the impact on concentrations downwind. The emissions from the SBR occur at a height of 5m which increases dispersion and dilution with the ambient air which will reduce concentrations relative to an area source at ground level.

3.7 EVALUATION OF MODEL PERFORMANCE

The model performance criteria of Chang and Hanna (2004) suggests that three of the four models presented can be considered ‘acceptable’, with the model run using the existing EF for AD plants performing very poorly compared to the measured values (Table 10). A perfect model would have MG, VG, R^2 and FAC2 = 1.0; and FB and NMSE = 0.0. The multiple source model with optimised emission factors performs exceptionally well, with each performance criterion approaching ideal values. The model run with the Windtrax-calculated source strength also fares well and is within the acceptability range for all of the Chang and Hanna performance measures. The initial multiple source passes more than half of the performance criteria and can be considered ‘acceptable’, although the model considerably over-estimates the observed concentrations and as a result does not pass the fractional bias and geometric mean bias criteria.

Table 10: Statistical performance criteria for model evaluation

Performance measure	NMSE	VG	FB	MG	FAC2	R^2	Pass/Fail
Chang and Hanna (2004) acceptability criteria	< 1.5	< 4	< 0.3	0.7 < MG <1.3	> 50%	-	-
Windtrax source strength	0.003	1.21	0.09	0.91	100%	0.76	Pass
Multiple source scenario (initial)	0.07	1.01	0.74	0.46	80%	-	Pass
Multiple source scenario (optimised)	0.007	1.18	0.06	0.95	100%	0.97	Pass
Current EF	9.00	17.12	1.92	0.021	5%	-	Fail

NMSE : normalized mean squared error ;VG : geometric variance; MG : geometric mean bias; FB : fractional bias; R^2 : correlation; FAC2 : fraction of model predictions within a factor of two of observations.
Measured and predicted concentrations at ALPHA receptors 12 and 16 are excluded.

Table 11: Intercomparison of measured and modelled concentrations

ALPHA Data			ADMS Predictions			
ALPHA Receptor	**Measured concentration ($\mu g\ m^{-3}$) P2-5**	**Coefficient of Variation between ALPHA triplicates P2-5 (%)**	**WIndtrax-calculated emission rate ($\mu g\ m^{-3}$)**	**Multiple sources (inital) ($\mu g\ m^{-3}$)**	**Multiple sources (optimised) ($\mu g\ m^{-3}$)**	**ADMS predicted from current AD EF ($\mu g\ m^{-3}$)**
1	2.92	10.7	3.10	4.61	3.25	99.97
2	3.33	2.4	4.27	6.65	4.47	172.42
3	2.53	3.9	2.14	2.90	2.09	40.25
4	2.76	3.5	1.73	2.39	1.80	14.50
5	3.46	5.7	4.22	10.72	4.45	169.98
6	16.2	10.9	14.71	53.25	15.44	820.16
7	13.01	4.6	8.81	20.13	12.67	454.19
8	2.33	5.3	4.03	5.38	2.76	157.93
9	2.34	3.2	2.64	3.57	2.63	71.35
10	3.7	2.5	3.84	5.43	3.23	145.98
11	1.53	6.8	1.58	1.74	1.66	5.97
12	3.55	6.7	1.66	1.66	1.66	1.83
13	1.34	4.9	1.61	1.65	1.60	8.34
14	1.78	4.0	1.52	1.57	1.52	2.36
15	1.66	3.2	2.18	3.87	2.28	43.77
16	4.56	1.9	1.56	1.58	1.56	2.22
17	2.59	4.4	1.97	2.49	2.08	29.68
18	12.34	3.0	12.73	20.06	12.57	696.79
19	9.95	5.9	18.91	32.60	12.08	1080.47
20	1.5	3.2	1.97	2.62	2.16	29.70

4 DISCUSSION

4.1 MEASUREMENT/MODELLING APPROACH

The aim of this project was to estimate the emissions of NH_3 from the Deerdykes AD plant. No direct measurements of emissions were made, rather the source strength was inferred using three techniques: 1) back-calculating the emission rate for the totality of emissions at the plant using a backward Lagrangian stochastic (bLS) dispersion model and in-line continuous NH_3 concentration measurements with integrated meteorological information; 2) estimation of emission rate using published emission factors for similar sources, information relating to the composition of digestate at the plant, and measurements taken of the NH_3 concentration within key sources; 3) applying optimization factors to the emission rate of sources within the ADMS dispersion model to fit the predicted and observed concentrations at ALPHA receptors.

Ultimately, three dispersion models were produced using these methods which met the Chang and Hanna (2004) model performance criteria. The first treated the emissions from the AD plant as three area sources that are marked by the boundaries of the waste reception building, sequencing batch reactor and surface water balancing tank, which were identified as likely to be the main sources. The emission rate was determined by back-calculating (Windtrax) from the average concentration that was measured from the filtered 220-230° wind sector of the period 1 (28th May – 26th June) AiRRmonia continuous NH_3 measurements. Considering the simplifications made in assuming homogenous area sources, the ADMS predicted concentrations of this model performed very well in satisfying all of the criteria for model acceptability listed in Table 11. This was an economical means of estimating the source strength which required only the spatial arrangement of the AD plant relative to the concentration receptor, a continuous gas analyser and rudimental met. data. A lack of atmospheric stability measurements was a limiting factor in the use of Windtrax to estimate the source strength. However the stout assumption that the averaged atmospheric stability would correspond to neutrally stratified atmospheric conditions seemed to be supported by the observed NH_3 concentration profile across the site. Although the Windtrax estimates showed very good statistical performance relative to passive measurements, predictions were less reliable at the source area and the total emission rate is likely underestimated by around 40% (relative to the optimised multiple source model). This is attributed to the complexity of the source area at Deerdykes, which was better described after differentiating the source area into discrete sources.

The second model differentiated the source area into six discrete sources. Emission rates for each source was estimated after a review of emission factors for comparable sources published in the literature, which were applied to the information that was available regarding plant specifications, composition of digestate and measurements of NH_3 concentrations within the waste reception building. The predictions made by this model could be considered at the borderline ‘acceptable’ according to the Chang and Hanna (2004) criteria as more than half of the performance measures were met, however there was considerable bias to overestimate the observed concentrations and as a result the fractional bias (FB) and geometric mean bias (MG) criteria was failed. This positive bias was due to an applied emission factor to the SWBT being too high, this was not unexpected as the SWBT was the source at the site with the least available information as no samples were taken and thus it was difficult to estimate the extent to which it will emit NH_3. The third dispersion model was developed after numerous iterations of optimisation factors applied to the estimated emission rates of the multiple source scenario. The key changes were to decrease the emissions from the SWBT by a factor of 2/9, decrease fugitive emissions from the waste reception area door by a factor of 16, decrease fugitive emissions from the pre-processing area by a factor of 2 and increase emissions from the digestate store by around 1/3 (Table 8). Often when estimating the emissions from an unknown source in this way the starting point is an arbitrary value, yet presented here is an initial condition where the emission rate has been estimated purely from published emission factors and the information on the plant that was available. The model source area was defined by these initial conditions without consulting the ALPHA or AiRRmonia measurements and a model was produced that could be considered acceptable according to the established performance criteria. The initial estimates were found to be particularly robust as the final model with the greatest statistical performance differed in total emissions from the initial source condition by less than 40%, with the great majority of this difference attributed to the SWBT.

4.2 KEY SOURCES OF EMISSIONS

The optimised model with six discrete source performed well in reproducing the observed concentrations at the ALPHA receptors. The largest source of NH_3 at the plant was found to be the digestate store (7290 µg s^{-1}). Continuous AiRRmonia measurements taken over a period of 3 weeks from 20m outside of the digestate store revealed that concentrations were dominated by high-magnitude events during which the air concentration would rise up to 300 µg m^{-3} and return back to a low baseline (<10 µg m^{-3}) within a few hours (Figure 13). This is consistent with the conceptual model of intense emission events occurring as the digestate store is opened, inducing ventilation and release of the NH_3 within the room air of the digestate store, measurements of which were as high as 60 ppm (45 mg m^{-3}). Fugitive emissions from the waste reception and pre-processing area were much lower than the agricultural AD emissions study carried out by Cumby et al (2005). The indoor measured concentrations at Deerdykes seemed to be around 26 times lower than the Holsworthy agricultural AD plant (Table 3). The difference may also be due to a lower direct discharge rate from the Deerdykes waste reception building - the initial emission rates for the waste reception area door and pre-processing area at Deerdykes were reduced by factors of 16 and 2 respectively to match the measured concentrations at these areas. However determining the average concentration within a compartmentalised space with such a large volume proved difficult, especially as measurements could only be taken intermittently upon visits to the site and as measured concentrations showed significant variation. The waste reception area door at Deerdykes is located far from the solid waste depositing region and de-packaging equipment which are sources of NH_3. NH_3 measurements using the portable multi-gas analyser at the entrance were below the detection limit (1 ppm, 0.75 mg m^{-3}) for the device. Therefore it is also likely that the average NH_3 concentration assumed for emissions from this area (1 ppm) is too high, which is supported by the fact that emissions from the waste reception area door had to be reduced by a factor of 16 to fit to the measurements at ALPHA site 19 which is very close to this source. The SBR was the second greatest source of NH_3 at the plant (5091 µg s^{-1}) , a source which required no correction to fit the observed NH_3 concentrations around it from the initial emission factor (220 mg m^{-2} h^{-1}) adopted from the findings of Willers et al. (1996).

When the existing emission factor derived from the Holsworthy biogas plant was applied to Deerdykes, the total emission rate was 56 and 34 times higher than the Windtrax back-calculated estimate and the optimised multiple source estimate respectively. It is clear that this emission factor is unsuitable in this case, therefore it is also likely that the current emission factor also considerably overestimates the emissions from other food waste ADs. The current AD EF was derived from a pilot study into the overall environmental impact from a centralised AD which processed mostly livestock slurries. The most significant difference between the Holsworthy AD plant and Deerdykes was the emissions from the waste reception area, which were much greater at the Holsworthy biogas plant, likely due to greater volitilisation of NH_3 from livestock slurries relative to the solid commercial and municipal collections that are delivered to Deerdykes. The Holsworthy waste reception area receives digestion substrates as a slurry, whereas at Deerdykes solid and liquid substrates are delivered separately, with the liquids (sludge) sent to a subterranean storage tank and solids to the waste reception area. It assumed that the sludge tank was not a source of NH_3, as there was no indication from passive air NH_3 measurements near to this area that there should be a source at that location it was not included in the model. Therefore separating liquid and solid substrates in this way is likely to significantly reduce emissions of NH_3, assuming that the liquid fraction is stored securely underground and odour-abatement technologies such as activated carbons are in place to scrub any fugitive emissions – as is the case at Deerdykes.

4.3 UNCERTAINTY IN PREDICTIONS

The averaged CV between ALPHA triplicates for measurement periods 2-5 ranged from 1.9 to 10.9%, with the average being 4.5% (Table 12). As the downwind air concentration of a pollutant can be assumed to be directly proportional to the source strength (Eq 1), a maximum error of 10.9% may be applied to emission rates that have been deduced by fitting predicted concentrations to those observed at the ALPHA sites. This is considerably reduced relative to the rule-of-thumb of 'plus or minus a factor of two' that has often been adopted to describe the quality of predictions from atmospheric dispersion models (Pasquill, 1974, Smith, 1984, Chang and Hanna 2004). Taking the best performing model produced and the maximum error observed in the ALPHA measurements, this gives an emission rate for the totality of sources at the AD plant of 16.8 ± 1.8 mg s^{-1}. The emission rates for the Windtrax and initial multiple source models were 10.3 ± 1.2 mg s^{-1} and 27.5 ± mg s^{-1} respectively.

In optimising emission factors to fit the measured concentrations, the two data sets no longer become independent. The Chang and Hanna (2006) statistic tests assume independence which lessens the significance of the positive outcome of the tests. With six discrete sources grouped in a small area determining individual emission rates by optimising to fit measurements is challenging, as there may be multiple source strength configurations to arrive at the 'correct' predictions. Fortunately at Deerdykes buildings and structures add complexity which can isolate certain sources, and ADMS has the capability to provide accurate predictions where there are building effects (Hill et al. 2001). There is a distinct relationship in the measured concentrations between the ALPHA sites surrounding the SWBT (6, 5 & 19) that adds confidence to the emission rate estimated at this source. It is also clear that there must be very little influence from the waste reception area entrance. The digestate store and pre-processing area are difficult to separate as they are directly adjacent to each other. However the AiRRmonia measurements for period are clearly dominated by a high-magnitude intermittent source which can only be the digestate store. There is likely some contribution from fugitive emissions escaping from the pre-processing area, however there is expected to be significant error in the estimate of 643 µg s^{-1} (assuming 12.5% direct discharge rate). The digestate store is the largest source of the two (7290 µg s^{-1}), thus the uncertainty associated with the preprocessing area has less of an effect on this estimate. The emission rates from the biofilter and SBR were both derived from emission factors reported in the literature. Emissions from the biofilter is estimated to be relatively small (465 µg s^{-1}) while the SBR was the second largest source (5091 µg s^{-1}). Emissions from the SBR are released at a height of 5m which increases dispersion downwind creating a less distinct concentration profile. Therefore the confidence in this estimate is attributed to the suitability of the SBR emission factor produced by Willers et al. (1995), which was found to match the available parameters for the Deerdykes SBR which is a positive indication. Without any measurements for verification, emission factors reported in the literature and their applicability to Deerdykes (chemical composition etc.) are the only other means of assessing the quality of estimated emission rates. In this case relatively robust initial estimates reduces the uncertainties associated with model predictions, in qualitative terms.

The measurement period at Deerdykes was relatively short and is only representative of summer weather and climate. The volatilisation of NH_3 is strongly influenced by temperature, where emissions can be expected to be higher during summer than the rest of the year. The average air temperature over the measurement & modelling period was 16.4°C, while the multi-year average air temperature from 2011 – 2013 was 9.2°C. After applying the temperature regression equation from the Borka (2000) model (Eq 4) to the total estimated emissions from the plant, a 34% reduction can be expected for the annual emission factor with this temperature decrease. This gives an annual emission factor of 11.1 ± 1.2 µg m^{-3} when using the optimized multiple sources emission rate. However this is an extra source of error as ideally measurement would occur throughout the year to capture seasonal variability caused by weather, climate and variations in emissions and site management.

It may be advantageous to remove the contribution of the SWBT from the total emissions at the plant if applying the estimated emission factor from Deerdykes to other ADs of the food waste variety. Emissions from the SWBT were found to show the greatest variation throughout the measurement campaign, where although the available July meteorological data was not sufficient to run ADMS, the ALPHA data shows that NH_3 concentrations around the SWBT were nearly twice as high from the 26th June – 10th July as any other period, with samplers 5, 6 and 19 (around the SWBT) showing substantially elevated concentrations of up to 42 µg m^{-3}. Emissions from the SWBT will vary over time with temperature, rainfall and activities at the site. Spillages are drained directly into the SWBT, while all surface runoff during rainfall events is directed to the SWBT which will carry organic wastes into the tank but may also cause dilution and mixing. Excluding the emissions from the SWBT a total emission rate of 13.6 ± 1.5 mg s^{-1} was estimated (optimised multiple source model).

4.4 APPLICABILITY OF EMISSION FACTORS

Before broadly applying the Deerdykes emission factor it is important to determine whether the Deerdykes AD is representative of other food waste-processing facilities. The best performing model suggested that the most significant emissions from Deerdykes originated from the solid and liquid fractions of the separated digestate. At Deerdykes the digestate is dewatered and separated into solid and liquid fractions, where solids are stored on-site in a warehouse-type area with no odour control measures which is periodically opened to extract the digestate for sale as biofertiliser. A fraction of the liquids are recycled and mixed with fresh substrates while the remainder is aerobically treated within in an open sequencing batch reactor before being discharged to sewer. Digestate is continuously produced at an anaerobic digestion plant, which can cause issues with management and oversupply. When the digestate is extracted from the digestion tank (wet digestion) it is typically around 95% water (KTBL 2005). Therefore it is often necessary to reduce the water content of digestate to cut transport costs for field application and to make on-site storage more feasible. Digestate can be separated into solid and liquid fractions by a number of existing technologies (Rehl et al. 2011). The separated liquid fractions are often concentrated liquors of high NH_4^+ content, which may not be suitable for land application due to controls on the spreading of liquid fertiliser, and will require nitrogen removal before discharge to sewer (Scaglione et al. 2013). Therefore treatment liquid effluents within an on-site waste water treatment plant such as an SBR is sometimes featured at larger community AD plants where it is the most economical solution.

In the UK, it is a requirement of the Anaerobic Digestate Quality Protocol (ADQP) that on-site storage of digestate is covered, however this regulation does not apply to offsite storage (WRAP/EA 2009). Due to the yearly fertiliser spreading schedule and government regulation, it is often necessary to store the solid fraction of digestate for a few to several months before end use, either at the plant itself or at satellite storage tanks e.g. on farms (Paavola and Rintala 2008). At Deerdykes, the solid digestate retention time before sale to end-users is around 2-4 days, and the capacity of the digestate store is not sufficient for long periods of time. Therefore emissions may be lower than an AD plant which uses similar separation practices but retains a greater volume of solid digestate on-site before sale. However, although the solid digestate at Deerdykes is covered, the depth of the digestate heap is typically around 1m while there is an extra 5m of headspace above it. A cover directly over the heap will raise NH_3 concentrations within the headspace air and allow a thermodynamic equilibrium between the gaseous-phase NH_3 within the digestate and overlying air to be reached, limiting further volatilisation. The measured air NH_3 concentration range within the Deerdykes digestate store was 7 – 60 ppm, which is far from the air equilibrium range suggested by Cumby et al. (1995) of 300 – 400 ppm. The Deerdykes digestate store also features a large entrance, which causes ventilation of the headspace air and release of NH_3 whenever it is opened. Therefore an AD plant which utilizes a comparatively sealed storage system will reduce NH3 emissions in this respect. Other AD plants have packaged digestate in plastic bags for sale in the landscaping/horticultural sector, or delivered unseparated digestate directly from sealed storage vessels to agricultural tankers *via* an umbilical system (WRAP 2013). These systems limit exposure of digestate to the air and hence the opportunity for NH_3 volatilisation. The majority of digestate is used by the agricultural sector, where geography is a key factor determining the distribution strategy. If there is sufficient demand, the most cost-effective model is for the sale of unseparated digestate for land spreading. However if there is insufficient demand from nearby farms it may be more economical to invest in dewatering technologies for the significant savings that can be made in storage, transport and application. Dewatering of digestate typically produces liquids and solids and the ratio of 9:1 by volume (WRAP 2013), thus with the addition of waste water treatment infrastructure the volume of material to be handled is substantially reduced.

The digestate store and SBR were the greatest sources of NH_3 were identified as the greatest sources of NH_3 at Deerdykes. The emission factor of the best-performing model (0.0018 % Total FW input volatalised as NH_3) is likely to be representative AD plants where the digestate is separated into liquid and solid effluents, the liquid effluents being aerobically treated on-site while solids are stored for a short period of time in a warehouse-type storage unit with no emission control. Ultimately the management of digestate is an economic choice that is up to the operator, ranging from treating as a waste product and discharging to sewer to marketing as a high-value horticultural soil. The UK market for digestate is immature and the distribution is largely driven by local circumstances, where spreading of unseparated digestate to agricultural land is the most common end-use (WRAP 2013). Therefore this emission factor is not likely to be representative of the majority of cases. However, the estimated emissions from substrate storage and processing at the plant may well be representative of other community ADs that process source-segregated municipal and industrial wastes. There is a significant niche for emission from the aerobic treatment of liquid effluents and storage of separated solids to which the calculated emission factors could be applied. Emissions from substrate storage (waste reception area, pre-processing area & biofilter) contributed just 7% to the total emission rate for the Deerdykes plant, with biofilter emission rates around 12 times lower than the Holsworthy AD (Cumby et al. 2005) and fugitive emission rates around 30 times lower. Based on this evidence the EF for community ADs should be adjusted accordingly to incorporate lower substrate emissions for the 53 community ADs in operation within the UK (biogas-info.co.uk).

4.5 APPLICABILITY OF APPROACH FOR FUTURE STUDIES

This study has demonstrated an economical methodology for the estimation of NH_3 emissions from complex source. Predictions from forward and inverse dispersion models were the proxy for the estimation of emission rates without direct flux measurements. Passive NH_3 measurements at multiple locations around the site was an essential component in verifying emission estimates and also in producing them by matching predicted and observed concentrations. The continuous measurement and inverse dispersion modelling technique is best suited to sites which benefit from significantly reduced complexity and can be treated as a single isolated source. As the digestate store at Deerdykes was identified as the largest source of NH_3 but is not likely to be representative of the majority of ADs, applying the inverse dispersion technique to estimate the emissions from isolated or ‘satellite’ digestate storage tanks would be a valuable exercise.

The project could be simplified and uncertainties could be reduced by: 1) selecting a single emission source, 2) incorporating atmospheric stability measurements with a sonic anemometer and 3) selecting a site with little complex terrain. A small number of passive samplers would be needed for verification of estimated emission rates through forwards modelling, whilst the methodology regarding the integration of continuous NH_3 measurements and meteorological measurements would be much the same. It is also very important to compile information regarding the quantity, composition and management practices of the digestate in order for results to be interpreted and accurate emission factors to be calculated. Whilst further studies which measure the totality of emissions at an AD plant would certainly be beneficial, the presence of multiple sources in close proximity makes segregation of individual emission rates difficult. Digestate storage has been targeted as the key unquantified source of NH_3 emissions from AD which should be a focus of future investigations in this field. The compiling of NH_3 emissions inventories census would be benefit from a census of UK digestate management practices. This would significantly reduce error by ensuring that emission factors are applied in the correct proportion once sufficient emissions studies into the storage of digestate are available.

5 CONCLUSION

A multifaceted methodology was applied to estimate the totality of NH_3 emissions from an anaerobic digestion plant using passive and continuous NH3 sampling methods, forward and inverse atmospheric dispersion models, and existing emission factors and empirical models published in the literature. Four dispersion models were run with emission rates derived from a range of sources and methodologies and predictions were compared against the observed NH_3 concentration profile recorded across the site by ALPHA passive samplers. The totality of emissions was backcalculated from measurements at the continuous AiRRmonia NH_3 gas sensor using the Windtrax inverse dispersion model. The total emission rate estimated by Windtrax (10.3 mg s^{-1}) showed good agreement between predicted and observed concentrations in ADMS simulations, satisfying all of the Chang and Hanna (2004) model acceptability criteria. While this is a useful tool for estimating the totality of emissions, observations at near-source receptors were less accurately predicted. Due to simplifications of the source area within this model it was unsuitable for estimating the emission rate from individual sources. The second model differentiated the source area into six discrete sources. Emission rates for each source was estimated after a review of emission factors for comparable sources published in the literature, which were applied to the information that was available regarding plant specifications, composition of digestate and measurements of NH_3 concentrations within the waste reception building. The predictions made by this model could be considered at the borderline statistically ‘acceptable’ however there was considerable bias to overestimate the observed concentrations due to the emission factor adopted form dairy farm wastewater ponds for the SWBT being too high.

With the third model applied optimisation factors to emission rates for the six discrete sources in order to fit the predicted concentrations. The outcome was a model which fit the measured concentrations very well and performed excellently in the model acceptability criteria. This was the best-performing model which suggested that the storage of solid digestate had the greatest contribution to total NH_3 emissions from the site, with the SBR and SWBT as the 2nd and 3rd most significant sources. The total averaged emission rate for the 4 week measurement and modelling period was 16.8 ± 1.8 mg s^{-1}. The storage and treatment of solid and liquid fractions of the separated digestate comprised 74% of total emissions, while the emissions associated with substrates from the biofilter, waste reception area and pre-processing area contributed 8%. The final model applied the existing emission factor for NH_3 emissions from AD plants, producing a total emission rate equivalent to 570 mg s^{-1}. Predictions from this model exceeded passive sampler measurements by an average factor of 54. Emissions from substrate storage and handling at Deerdykes was significantly reduced relative to the agricultural AD from which the current EF was calculated. Therefore it is suggested that the emission factor for community ADs should be reduced in order to reflect this finding. The emission factors associated with the storage and treatment of separated solid and liquid digestates are less applicable to the majority of ADs, as in most cases digestate is kept unseparated in sealed tanks on-site prior to transport and application to agricultural fields. Therefore it is recommended that focusing future emission studies on digestate storage tanks whilst taking precautions to isolate the emission source (e.g. by selecting particular wind sectors for continuous measurement) should be the immediate focus for future investigations.

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7 APPENDIX 1: ALPHA MEASUREMENTS

Period 1

							ppm NH_4^+ in 3 ml extract										
							sampler 1		Sampler 2		sampler 3				BLANK	Extracted	Calibrated
ALPHA	DATE OUT	TIME OUT	DATE IN	TIME IN	Time (Hrs)	Vol (m^3)	1	1 (rpt)	2	2 (rpt)	3	3 (rpt)	mean	% CV	ppm NH_4^+	Vol (ml)	NH_3 (µg m^{-3})
D1	15/05/14	14:12	27/05/2014	11:53	285.7	1.24	0.801	0.807	0.774	0.793	0.803	0.817	**0.799**	1.8	0.047	3.0	**2.30**
D2	15/05/14	14:45	27/05/2014	12:10	285.4	1.24	0.785		0.765		0.765		**0.772**	1.5	0.047	3.0	**2.22**
D3	15/05/14	14:49	27/05/2014	15:30	288.7	1.25	0.655		0.628		0.628		**0.637**	2.4	0.047	3.0	**1.79**
D4	15/05/14	14:54	27/05/2014	15:35	288.7	1.25	0.648		0.626		0.606		**0.627**	3.4	0.047	3.0	**1.76**
D5	15/05/14	15:10	27/05/2014	12:37	285.5	1.24	1.014		0.939		0.982		**0.978**	3.8	0.047	3.0	**2.85**
D6	15/05/14	15:17	27/05/2014	12:32	285.3	1.24	2.530		2.391		2.456		**2.459**	2.8	0.047	3.0	**7.39**
D7	15/05/14	15:25	27/05/2014	12:24	285.0	1.24	3.208	3.223	3.402	3.410	3.196	3.202	**3.274**	3.1	0.047	3.0	**9.90**
D8	15/05/14	15:35	27/05/2014	12:17	284.7	1.24	0.564		0.580		0.539		**0.561**	3.6	0.047	3.0	**1.58**
D9	15/05/14	15:50	27/05/2014	15:24	287.6	1.25	0.673		0.669		0.677		**0.673**	0.6	0.047	3.0	**1.90**
D10	15/05/14	16:08	27/05/2014	15:20	287.2	1.25	1.035		1.078		1.053		**1.055**	2.1	0.047	4.0	**4.09**

Period 2

							ppm NH_4^+ in 3 ml extract								BLANK	Extracted	Calibrated
							sampler 1		sampler 2		sampler 3						
Sample ID	**DATE OUT**	**TIME OUT**	**DATE IN**	**TIME IN**	**Time (Hrs)**	**Vol (m^3)**	**1**	**1 (rpt)**	**2**	**2 (rpt)**	**3**	**3 (rpt)**	**mean**	**% CV**	**ppm NH_4^+**	**Vol (ml)**	**NH_3 (µg m^{-3})**
D1	27/05/14	11:57	03/06/14	12:27	168.5	0.73	0.490		0.489		0.501		**0.493**	1.4	0.048	3.0	**2.31**
D2	27/05/14	12:12	03/06/14	12:32	168.3	0.73	0.590		0.589		0.593		**0.591**	0.3	0.048	3.0	**2.82**
D3	28/05/14	13:48	03/06/14	13:22	143.6	0.62	0.319		0.324		0.330		**0.324**	1.6	0.048	3.0	**1.68**
D4	28/05/14	13:50	03/06/14	13:19	143.5	0.62	0.348		0.349		0.332		**0.343**	2.9	0.048	3.0	**1.80**
D5	27/05/14	12:39	03/06/14	13:05	168.4	0.73	0.520		0.552		0.519		**0.531**	3.6	0.048	3.0	**2.50**
D6	27/05/14	12:34	03/06/14	12:56	168.4	0.73	2.050		2.099				**2.074**	1.7	0.048	3.0	**10.52**
D7	27/05/14	12:26	03/06/14	12:42	168.3	0.73	1.926	1.936	1.933	1.962	1.846	1.881	**1.914**	2.2	0.048	3.0	**9.69**
D8	27/05/14	12:19	03/06/14	12:36	168.3	0.73	0.291		0.296		0.286		**0.291**	1.7	0.048	3.0	**1.26**
D9	28/05/14	14:40	03/06/14	12:29	141.8	0.62	0.360		0.368		0.393		**0.374**	4.5	0.048	3.0	**2.01**
D10	28/05/14	13:45	03/06/14	13:13	143.5	0.62	0.636		0.611		0.609		**0.619**	2.4	0.048	3.0	**3.48**
D11	27/05/14	13:15	03/06/14	16:46	171.5	0.74	0.344		0.333		0.352		**0.343**	2.8	0.048	3.0	**1.50**
D12	27/05/14	13:48	03/06/14	15:52	170.1	0.74	0.708		0.832				**0.770**	11.4	0.048	3.0	**3.71**
D13	27/05/14	14:09	03/06/14	16:23	170.2	0.74	0.303		0.298		0.311		**0.304**	2.1	0.048	3.0	**1.31**
D14	27/05/14	14:20	03/06/14	16:28	170.1	0.74	0.414		0.377				**0.395**	6.5	0.048	3.0	**1.79**
D15	27/05/14	14:44	03/06/14	16:14	169.5	0.74	0.311		0.358		0.329		**0.333**	7.0	0.048	3.0	**1.47**
D16	27/05/14	15:04	03/06/14	16:05	169.0	0.73	0.592		0.565		0.559		**0.572**	3.1	0.048	3.0	**2.71**

Period 3

							ppm NH_4^+ in 3 ml extract							BLANK	Extracted	Calibrated
							sampler 1		sampler 2		sampler 3					
Site name	DATE OUT	TIME OUT	DATE IN	TIME IN	Time (Hrs)	Vol (m^3)	1	1 (rpt)	2	2 (rpt)	3	mean	% CV	ppm NH_4^+	Vol (ml)	NH_3 (µg m^{-3})
D1	03/06/14	12:27	12/06/14	12:12	215.8	0.94	0.828		0.818		0.802	**0.816**	1.6	0.059	3.0	**3.07**
D2	03/06/14	12:32	12/06/14	12:20	215.8	0.94	0.917		0.911		0.918	**0.915**	0.4	0.059	3.0	**3.47**
D3	03/06/14	13:22	12/06/14	13:20	216.0	0.94	0.883		0.896		0.947	**0.909**	3.7	0.059	3.0	**3.44**
D4	03/06/14	13:19	12/06/14	13:17	216.0	0.94	0.968		1.013		1.027	**1.003**	3.1	0.059	3.0	**3.82**
D5	03/06/14	13:05	12/06/14	14:48	217.7	0.95	1.014		1.010		1.002	**1.008**	0.6	0.059	3.0	**3.81**
D6	03/06/14	12:56	12/06/14	13:04	216.1	0.94	4.678		6.745			**5.712**	25.6	0.059	3.0	**22.86**
D7	03/06/14	12:42	12/06/14	13:02	216.3	0.94	2.497	2.607	2.329		2.525	**2.532**	5.5	0.059	3.0	**9.99**
D8	03/06/14	12:36	12/06/14	12:26	215.8	0.94	0.560		0.566		0.513	**0.546**	5.3	0.059	3.0	**1.97**
D9	03/06/14	12:29	12/06/14	13:55	217.4	0.94	0.664		0.692		0.721	**0.692**	4.1	0.059	3.0	**2.55**
D10	03/06/14	13:13	12/06/14	13:12	216.0	0.94	1.136		1.163		1.114	**1.138**	2.1	0.059	3.0	**4.37**
D11	03/06/14	16:46	12/06/14	14:22	213.6	0.93	0.390		0.348		0.303	**0.347**	12.6	0.059	3.0	**1.18**
D12	03/06/14	15:52	12/06/14	14:33	214.7	0.93	0.923		0.834		0.963	**0.907**	7.3	0.059	3.0	**3.45**
D13	03/06/14	16:23	12/06/14	15:02	214.7	0.93	0.302		0.354		0.290	**0.315**	10.8	0.059	3.0	**1.04**
D14	03/06/14	16:28	12/06/14	15:10	214.7	0.93	0.392		0.388		0.418	**0.399**	4.1	0.059	3.0	**1.39**
D15	03/06/14	16:14	12/06/14	15:07	214.9	0.93	0.428		0.438		0.432	**0.433**	1.3	0.059	3.0	**1.52**
D16	03/06/14	16:05	12/06/14	14:42	214.6	0.93	2.025		1.972			**1.999**	1.9	0.059	3.0	**7.90**
D17	03/06/14	15:34	12/06/14	14:06	214.5	0.93	0.533		0.518		0.601	**0.551**	8.1	0.059	3.0	**2.00**
D18	09/06/14	13:24	12/06/14	12:54	71.5	0.31	0.666	0.703	0.764	0.761	0.645	**0.725**	8.9	0.059	3.0	**8.15**
D19	09/06/14	13:32	12/06/14	13:00	71.5	0.31	0.535		0.509			**0.522**	3.5	0.059	3.0	**5.67**

Period 4

							ppm NH$_4^+$ in 3 ml extract							BLANK	Extracted	Calibrated
							sampler 1		sampler 2		sampler 3					
Sample ID	**DATE OUT**	**TIME OUT**	**DATE IN**	**TIME IN**	**Time (Hrs)**	**Vol (m^3)**	**1**	**1 (rpt)**	**2**	**2 (rpt)**	**3**	**mean**	**% CV**	**ppm NH$_4^+$**	**Vol (ml)**	**NH$_3$ (µg m^{-3})**
D1	12/06/14	12:12	18/06/14	12:23	144.2	0.63	0.821		0.404		0.390	**0.538**	45.5	0.045	3.0	**2.99**
D2	12/06/14	12:20	18/06/14	12:29	144.2	0.63	0.556		0.485		0.551	**0.531**	7.5	0.045	3.0	**2.95**
D3	12/06/14	13:20	18/06/14	13:52	144.5	0.63	0.374		0.361		0.375	**0.370**	2.2	0.045	3.0	**1.97**
D4	12/06/14	13:17	18/06/14	13:59	144.7	0.63	0.381		0.398		0.376	**0.385**	3.0	0.045	3.0	**2.05**
D5	12/06/14	14:48	18/06/14	16:08	145.3	0.63	0.624		0.644		0.653	**0.640**	2.3	0.045	3.0	**3.58**
D6	12/06/14	13:04	18/06/14	12:48	143.7	0.62	2.985		3.108		3.163	**3.085**	3.0	0.045	3.0	**18.49**
D7	12/06/14	13:02	18/06/14	12:41	143.7	0.62	3.041		3.251		3.159	**3.150**	3.3	0.045	3.0	**18.90**
D8	12/06/14	12:26	18/06/14	12:33	144.1	0.63	0.425		0.423		0.455	**0.434**	4.2	0.045	3.0	**2.36**
D9	12/06/14	13:55	18/06/14	13:48	143.9	0.62	0.401		0.400		0.393	**0.398**	1.2	0.045	3.0	**2.14**
D10	12/06/14	13:12	18/06/14	12:53	143.7	0.62	0.603		0.620		0.642	**0.622**	3.2	0.045	3.0	**3.51**
D11	12/06/14	14:22	18/06/14	14:53	144.5	0.63	0.331		0.322		0.348	**0.334**	3.9	0.045	3.0	**1.75**
D12	12/06/14	14:33	18/06/14	15:46	145.2	0.63	0.591		0.602		0.566	**0.586**	3.2	0.045	3.0	**3.26**
D13	12/06/14	15:02	18/06/14	16:13	145.2	0.63	0.306		0.332		0.314	**0.317**	4.2	0.045	3.0	**1.64**
D14	12/06/14	15:10	18/06/14	16:18	145.1	0.63	0.383		0.391		0.399	**0.391**	2.0	0.045	3.0	**2.08**
D15	12/06/14	15:07	18/06/14	16:04	145.0	0.63	0.362		0.351		0.359	**0.357**	1.7	0.045	3.0	**1.88**
D16	12/06/14	14:42	18/06/14	15:52	145.2	0.63	0.584		0.583		0.570	**0.579**	1.4	0.045	3.0	**3.22**
D17	12/06/14	14:06	18/06/14	14:35	144.5	0.63	0.455		0.483		0.481	**0.473**	3.4	0.045	3.0	**2.59**
D18	12/06/14	12:54	18/06/14	12:37	143.7	0.62	2.092		2.047		2.176	**2.105**	3.1	0.045	3.0	**12.53**
D19	12/06/14	13:00	18/06/14	12:44	143.7	0.62	2.627	2.075	2.365	2.041	2.552	**2.302**	10.9	0.045	3.0	**13.73**

Period 5

							ppm NH_4^+ in 3 ml extract								BLANK	Extracted	Calibrated
							sampler 1		sampler 2		sampler 3						
Sample ID	DATE OUT	TIME OUT	DATE IN	TIME IN	Time (Hrs)	Vol (m^3)	1	1 (rpt)	2	2 (rpt)	3	3 (rpt)	mean	% CV	ppm NH_4^+	Vol (ml)	NH_3 (µg m^{-3})
D1	18/06/14	12:23	26/06/14	15:02	194.7	0.85	0.774		0.743		0.790		**0.769**	3.1	0.112	3.0	**2.95**
D2	18/06/14	12:29	26/06/14	12:45	192.3	0.84	0.937		0.898		0.897		**0.911**	2.5	0.112	3.0	**3.63**
D3	18/06/14	13:52	26/06/14	12:22	190.5	0.83	0.646		0.583				**0.614**	7.3	0.112	3.0	**2.31**
D4	18/06/14	13:59	26/06/14	12:24	190.4	0.83	0.647		0.705		0.655		**0.669**	4.7	0.112	3.0	**2.56**
D5	18/06/14	16:08	26/06/14	14:39	190.5	0.83	0.845		1.038		0.761		**0.881**	16.1	0.112	3.0	**3.53**
D6	18/06/14	12:48	26/06/14	13:32	192.7	0.84	2.292	2.642	2.687	2.946	2.807	2.789	**2.694**	8.3	0.112	3.0	**11.71**
D7	18/06/14	12:41	26/06/14	13:25	192.7	0.84	3.330		3.122		3.556		**3.336**	6.5	0.112	3.0	**14.62**
D8	18/06/14	12:33	26/06/14	13:04	192.5	0.84	0.932		0.774		0.859		**0.855**	9.3	0.112	3.0	**3.38**
D9	18/06/14	13:48	26/06/14	12:19	190.5	0.83	0.586		0.618		0.595		**0.600**	2.8	0.112	3.0	**2.24**
D10	18/06/14	12:53	26/06/14	12:33	191.7	0.83	0.780		0.778		0.747		**0.768**	2.4	0.112	3.0	**2.99**
D11	18/06/14	14:53	26/06/14	14:00	191.1	0.83	0.413		0.463		0.455		**0.443**	6.1	0.112	3.0	**1.52**
D12	18/06/14	15:46	26/06/14	14:12	190.4	0.83	0.868		0.824		0.901		**0.864**	4.5	0.112	3.0	**3.45**
D13	18/06/14	16:13	26/06/14	14:44	190.5	0.83			0.373		0.366		**0.370**	1.3	0.112	3.0	**1.18**
D14	18/06/14	16:18	26/06/14	14:48	190.5	0.83	0.488		0.507		0.477		**0.491**	3.0	0.112	3.0	**1.74**
D15	18/06/14	16:04	26/06/14	14:35	190.5	0.83	0.458		0.450		0.429		**0.446**	3.3	0.112	3.0	**1.53**
D16	18/06/14	15:52	26/06/14	14:26	190.6	0.83			0.799		0.812		**0.805**	1.2	0.112	3.0	**3.18**
D17	18/06/14	14:35	26/06/14	13:50	191.3	0.83	0.759		0.757		0.772		**0.763**	1.0	0.112	3.0	**2.97**
D18	18/06/14	12:37	26/06/14	13:22	192.8	0.84	3.092		3.102		3.065		**3.087**	0.6	0.112	3.0	**13.49**
D19	18/06/14	12:44	26/06/14	13:30	192.8	0.84	1.983		2.032		1.910		**1.975**	3.1	0.112	3.0	**8.45**
D20	18/06/14	14:40	26/06/14	13:53	191.2	0.83	0.367		0.345		0.359		**0.357**	3.2	0.112	4.0	**1.50**

Period 6

							ppm NH_4^+ in 3 ml extract							BLANK	Extracted	Calibrated
							sampler 1		sampler 2		sampler 3					
Sample ID	DATE OUT	TIME OUT	DATE IN	TIME IN	Time (Hrs)	Vol (m^3)	1	1 (rpt)	2	2 (rpt)	3	mean	% CV	ppm NH_4^+	Vol (ml)	NH_3 (µg m^{-3})
D1	26/06/14	15:02	10/07/2014	13:08	334.1	1.45	1.773		1.622			**1.697**	6.3	0.111	3.0	**4.15**
D2	26/06/14	12:45	10/07/2014	13:33	336.8	1.46	1.619		1.596		1.667	**1.627**	2.2	0.111	3.0	**3.94**
D3	26/06/14	12:22	10/07/2014	13:47	337.4	1.47	1.142		1.180		1.160	**1.161**	1.6	0.111	3.0	**2.72**
D4	26/06/14	12:24	10/07/2014	13:47	337.4	1.47	1.141		1.045			**1.093**	6.2	0.111	3.0	**2.54**
D5	26/06/14	14:39	10/07/2014	16:00	337.4	1.47	3.786		3.700		3.552	**3.679**	3.2	0.111	3.0	**9.25**
D6	26/06/14	13:32	10/07/2014	12:32	335.0	1.46	16.291		16.354		16.187	**16.277**	0.5	0.111	3.0	**42.18**
D7	26/06/14	13:25	10/07/2014	12:20	334.9	1.45	6.528		6.818		6.700	**6.682**	2.2	0.111	3.0	**17.15**
D8	26/06/14	13:04	10/07/2014	14:15	337.2	1.46	1.152		1.146		1.187	**1.162**	1.9	0.111	3.0	**2.72**
D9	26/06/14	12:19	10/07/2014	13:39	337.3	1.47	1.380		1.308		1.350	**1.346**	2.7	0.111	3.0	**3.20**
D10	26/06/14	12:33	10/07/2014	13:04	336.5	1.46	2.266		2.137		2.206	**2.203**	2.9	0.111	3.0	**5.43**
D11	26/06/14	14:00	10/07/2014	15:15	337.3	1.46	0.801		0.822		0.792	**0.805**	1.9	0.111	3.0	**1.80**
D12	26/06/14	14:12	10/07/2014	15:30	337.3	1.47	1.379		1.452			**1.416**	3.6	0.111	3.0	**3.38**
D13	26/06/14	14:44	10/07/2014	16:02	337.3	1.47	0.857		0.853		0.829	**0.846**	1.8	0.111	3.0	**1.91**
D14	26/06/14	14:48	10/07/2014	14:10	335.4	1.46	0.907		0.884		0.896	**0.896**	1.3	0.111	3.0	**2.05**
D15	26/06/14	14:35	10/07/2014	15:55	337.3	1.47	1.107		1.076		1.178	**1.120**	4.7	0.111	3.0	**2.62**
D16	26/06/14	14:26	10/07/2014	15:30	337.1	1.46	1.698		1.732		1.697	**1.709**	1.2	0.111	3.0	**4.14**
D17	26/06/14	13:50	10/07/2014	14:37	336.8	1.46	1.244		1.207		1.229	**1.227**	1.5	0.111	3.0	**2.90**
D18	26/06/14	13:22	10/07/2014	12:25	335.1	1.46	3.603		3.417		3.699	**3.573**	4.0	0.111	3.0	**9.03**
D19	26/06/14	13:30	10/07/2014	12:30	335.0	1.46	10.489		10.822		10.640	**10.650**	1.6	0.111	3.0	**27.50**
D20	26/06/14	13:53	10/07/2014	14:55	337.0	1.46	0.708		0.674		0.647	**0.676**	4.5	0.111	3.0	**1.47**