



1 **Ammonia emissions from a grazed field estimated by**  
2 **miniDOAS measurements and inverse dispersion modelling**

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15



## 16 Abstract

17 Ammonia ( $\text{NH}_3$ ) fluxes were estimated from a field being grazed by dairy cattle during spring, by applying a  
18 backward-Lagrangian Stochastic model (bLS) model combined with horizontal concentration gradients  
19 measured across the field. Continuous concentration measurements at field boundaries were made by open-path  
20 miniDOAS (differential optical absorption spectroscopy) instruments, during the cattle's presence and for 6  
21 subsequent days. The deposition of emitted  $\text{NH}_3$  to 'clean' patches on the field was also simulated, allowing  
22 both 'net' and 'gross' emission estimates, where the dry deposition velocity ( $v_d$ ) was predicted by a canopy  
23 resistance ( $R_c$ ) model developed from local  $\text{NH}_3$  flux and meteorological measurements. Estimated emissions  
24 peaked during grazing and decreased after the cattle had left the field, while control on emissions was observed  
25 from covariance with temperature, wind speed and humidity/wetness measurements made on the field, revealing  
26 a diurnal emission profile. Large concentration differences were observed between downwind receptors, due to  
27 spatially heterogeneous emission patterns. This was caused by uneven cattle distribution and a low grazing  
28 density, where 'hotspots' of emissions would arise as the cattle grouped in certain areas, such as around the  
29 water trough. The spatial complexity was accounted for by separating the model source area into sub-sections,  
30 and optimising individual source area coefficients to measured concentrations. The background concentration  
31 was the greatest source of uncertainty, and based on a sensitivity/uncertainty analysis the overall uncertainty  
32 associated with derived emission factors from this study is at least 30-40%.

33 Emission factors can be expressed as  $6 \pm 2 \text{ g NH}_3 \text{ cow}^{-1} \text{ day}^{-1}$ , or  $9 \pm 3\%$  of excreted urine-N emitted as  $\text{NH}_3$ ,  
34 when deposition is not simulated, and  $7 \pm 2 \text{ g NH}_3 \text{ cow}^{-1} \text{ day}^{-1}$ , or  $10 \pm 3\%$  excreted urine-N emitted as  $\text{NH}_3$ ,  
35 when deposition is included in the gross emission model. The results suggest that around  $14 \pm 4\%$  of emitted  
36  $\text{NH}_3$  was deposited to patches within the field that were not affected by urine or dung.

## 37 1. Introduction

38 Over 90% of anthropogenic ammonia ( $\text{NH}_3$ ) emissions in Europe have agricultural sources (Erisman et al.,  
39 2008; Reidy et al., 2008; Hertel et al., 2011), 70-90% of which have been estimated to be produced by livestock  
40 (Pain et al., 1998; Hutchings et al., 2001). In addition to decreasing nitrogen efficiency for farming systems, the  
41 volatilisation of  $\text{NH}_3$  from agricultural areas is a principal factor in the formation of fine fraction secondary  
42 aerosols due to its reactions with nitric and sulphuric acids in the atmosphere, and upon deposition is linked to  
43 acidification and eutrophication of natural ecosystems (Stutton et al., 2011). Following the application of urine  
44 and dung to the soil surface by grazing livestock, urea is microbially converted to  $\text{NH}_3$  which is volatilised at  
45 rates which vary extensively depending on soil and canopy layer properties, weather, and culture conditions  
46 (Laubach et al., 2013a). It has been estimated that 75-90% of the N ingested by a grazing cow is metabolised  
47 inefficiently and returned by excreta to the grazing paddocks, of which over 70% is returned as urine  
48 (Whitehead, 1995; Zaman et al., 2009).  $\text{NH}_3$  emissions have been measured from cattle urine patches at the ratio  
49 of 7-25.7% of excreted urine nitrogen (N) for grazed pastures (Jarvis et al., 1989; Ryden et al., 1987; Laubach et  
50 al., 2012; 2013a), and measurements from sheep urine patches in summer-winter experiments have suggested  
51 emissions which represent 12.2–22.2% of excreted urine-N (Sherlock and Goh, 1984).

52 Methods for estimating emissions from grazed pastures include micrometeorological methods, where profiles of  
53 concentration and wind speed are measured at one or more points downwind from the source, allowing fluxes to



54 be calculated using the theory of turbulent transport in the atmospheric surface layer (Laubach et al., 2012).  
55 Dynamic chambers or movable wind tunnels may be used to estimate emissions from simulated grazing in the  
56 laboratory or the field (Sommer et al., 2001). However enclosure measurements may not always be  
57 representative of emissions at the field scale (Genermont and Cellier, 1997; Sintermann et al., 2012). The  
58 inverse dispersion method concerns the inferring of the atmospheric emission rate ( $Q$ ) of localised gas sources  
59 from the excess concentration ( $\Delta C$ ) they cause above background, by modelling the  $\Delta C/Q$  relationship for a  
60 given measurement setup under the existing meteorological state (Flesch et al., 2004; Flesch et al., 2014).

61 The local dry deposition of  $\text{NH}_3$  within the grazed field is an important consideration to make, as in contrast to  
62 other pollutants a significant proportion may be deposited locally (e.g. Loubet et al., 2009). The proportion of  
63 deposited  $\text{NH}_3$  is sensitive to multiple parameters, including the source height, wind speed, atmospheric  
64 stability, land cover type and the numerous specific surface parameters therein (e.g. Sutton et al. 1993). This  
65 leads to modelling results that vary widely, with local recapture ranging from 2% to 60% within 2km from the  
66 source (Loubet et al., 2006, Asman et al., 1998). Accordingly, the modelling of  $\text{NH}_3$  deposition can be a  
67 challenging undertaking, with models ranging from simple steady-state canopy resistance models to dynamic,  
68 bi-directional, multi-layer and multi-process chemical species schemes (Flechard et al., 2013). Local-scale  
69 deposition models may ignore the wet deposition process, as dry deposition is most likely the dominant  
70 deposition mechanism near sources (Loubet et al., 2009).

71 In this study, a bLS dispersion model with a coupled dry deposition scheme has been applied to estimate the  
72  $\text{NH}_3$  emissions from a field being grazed by dairy cows, using the horizontal concentration gradients measured  
73 across the field by three open-path miniDOAS instruments (Sintermann et al., 2016; Volten et al., 2012). The  
74 open-path measurement system is to considerable benefit, as most techniques to measure atmospheric  $\text{NH}_3$  are  
75 sampling techniques and therefore involve inlet contact with the highly adhesive  $\text{NH}_3$ , which may slow response  
76 times and lead to interaction with water molecules and interference by ammonium aerosols dissociating on tubes  
77 or filters (e.g. von Bobruzki et al., 2010). The miniDOAS system is a comparatively interference-free  
78 measurement technique, since it utilises the wavelength-dependent UV-light absorption of  $\text{NH}_3$  over an open  
79 light path. The system also has capacity for long-term fast response continuous measurements, and a broad  
80 measurement path which makes the miniDOAS well-suited concentration receptors for monitoring the  
81 fluctuations in  $\text{NH}_3$  concentrations across field boundaries.

82 The objectives of our study were: (1) to evaluate the  $\text{NH}_3$  emissions from cattle grazing using the bLS  
83 dispersion technique and contribute towards an emission factor, as there is a limited number of existing  
84 measurements, (2) to simulate the degree of re-deposition that occurs within the field, and (3) evaluate the  
85 application of the bLS technique and the miniDOAS measurement system to derive  $\text{NH}_3$  fluxes from  
86 agricultural diffuse sources such as grazing. The bLS model assumes a homogenous source area, therefore it  
87 was assumed that emission estimates would be insensitive to irregular cattle distribution and excretion patterns.  
88 The measurement of concentration gradients across grazed fields is challenging, as downwind concentration  
89 levels may not rise far above background as is the case with stronger sources, such as applied slurry. Therefore  
90 this is an exercise which requires precise and continuous measurements from two or more sensors to evaluate  
91 ( $\Delta C$ ). However the method is also nonintrusive and is not labour intensive, and can provide continuous emission  
92 estimates over long or short time periods if the conditions and experimental design are in agreement.



## 93 2. Methods

### 94 2.1 Site description and experimental design

95 The experiments were conducted from 18-29 May 2015, on a rectangular grazing pasture of about two hectares  
96 at the INRA-Méjusseume dairy research experimental farm in NW France (48.11°N, 1.79736°E). The site was  
97 flat and benefited from a lack of wind-disturbing elements within 100m of the field boundaries (e.g. trees,  
98 buildings or other protruding elements). The cattle were not given additional feed to supplement grazing (mixed  
99 grass sward rich in *Lolium perenne*). The field had been previously grazed one month prior (16-27 May 2015) to  
100 the beginning of the experiment, and mineral fertiliser had been applied on 31/03. During measurement Period  
101 1, 25 cows were allowed to graze within the southwestern section of the field (Area D, Figure 1) from 08:00  
102 18/05 - 15:00 20/05 UTC (28 hours grazing), with three sets of miniDOAS open-path sensors and placed along  
103 the northern, western and eastern boundaries. The miniDOAS sensors were placed to optimise the measurement  
104 of ( $\Delta C$ ) across the field after reviewing wind directions forecast for the week ahead. The miniDOAS sensors  
105 have been given the names S1, S2 and S3, where the S2 sensor was placed upwind of the grazed field while the  
106 S1 and S3 sensors were placed at downwind locations. During Period 2, the whole field (Areas A, B, C, D) was  
107 opened for 44 grazing cattle, with the cattle present on the field from 10:00 20/05 – 05:00 23/05 (60 hours  
108 grazing), while the miniDOAS sensors were left in place to measure residual emissions from 23-29/05. The  
109 cattle were removed from the field for milking during both periods for roughly one hour twice per day. As the  
110 field area during Period 2 was much larger, the S2 and S3 miniDOAS sensors were moved to the north-western  
111 and south-eastern field boundaries respectively, leaving the three miniDOAS paths in-line with a NW-SE  
112 transect of the field (Figure 1). The grazing densities during Periods 1 and 2 were 44 and 22 cattle ha<sup>-1</sup>,  
113 respectively.

### 114 2.2 Ammonia measurements

115 The DOAS technique is based upon the wavelength dependent absorption of light over a specified light path.  
116 The miniDOAS instruments offer greater portability and a lower cost relative to prior DOAS instruments  
117 (Volten et al., 2012). The broadband and narrowband extinction of UV-light (=absorption + scattering) is  
118 measured across the light path, and the concentration of different trace gases is determined by their respective  
119 absorption spectra (details in Sintermann et al., 2016). In the wavelength range used by the miniDOAS (204 –  
120 230nm), narrowband-absorption is seen by NH<sub>3</sub>, sulphur dioxide (SO<sub>2</sub>), and nitrogen oxide (NO), while other  
121 absorbers with broader absorption features are eliminated by high-pass-filtering. The systems were calibrated  
122 using a flow-cell in the miniDOAS light path with a high-concentration NH<sub>3</sub> gas standard; in addition the cell's  
123 outlet-flow was checked by wet chemical impinger samples (two in a row) and photometric NH<sub>3</sub> determination.  
124 Details are presented by Sintermann et al., (2016). Reference spectra ( $I_{ref}$ , see Sintermann et al., 2016) were  
125 determined for each instrument during an inter-comparison phase at the field site one week prior to the grazing  
126 experiment, where the three miniDOAS systems were configured to measure in parallel (measuring  
127 concentrations across the same open-path). In order to provide the absolute concentration reference ( $c_{ref}$ , see  
128 Sintermann et al., 2016) for the miniDOAS, a transect of three sets of ALPHA passive sampler triplicates (Tang  
129 et al., 2001) were placed along the path length, giving a time-integrated  $c_{ref}$  measurement. The miniDOAS inter-  
130 comparison showed close agreement in the concentration levels between the three systems, where the coefficient



131 of variation was 3.4% (unpublished data). Revision of the calibration procedure applied by Sintermann et al.  
132 (2016) led to an increase in the slope by 16%, due to a gas standard correction in the conversion from ppm to  $\mu\text{g}$   
133  $\text{m}^{-3}$ .

134 To measure horizontal concentration gradients across the field, three miniDOAS instruments were placed  
135 strategically (based on the forecasted wind direction) at field boundaries at heights 1.4m above the ground, on  
136 stands drilled into the ground for stability. Retro-reflectors were set 37m away from each light source at the  
137 same height. A sensor placed upwind of the field would measure the background concentration ( $C_b$ ), which can  
138 be subtracted from the downwind concentration measurements ( $C$ ) to determine the horizontal concentration  
139 gradient or excess in concentration caused by emissions ( $\Delta C$ ). The miniDOAS concentration measurements  
140 were recorded at 1-minute averaging intervals, and later averaged to 30 minute intervals for analysis.

### 141 2.3 Micrometeorological measurements

142 A three-dimensional ultrasonic anemometer (Gill Windmaster, Gill Instruments Limited, Lymington, UK) was  
143 mounted on an instrument tower at 1.5m height above the ground within a fenced-off section in the centre of the  
144 field. The three orthogonal wind components ( $u, v, w$ ,  $\text{m s}^{-1}$ ) and a temperature measurement were logged at a  
145 frequency of 20 Hz. Later the eddy covariance measurements were processed over 30 minute averages, and the  
146 friction velocity ( $u^*$ ,  $\text{m s}^{-1}$ ), surface roughness ( $z_0$ , cm), Monin-Obukhov length ( $L$ , m), standard deviations of  
147 the rotated wind components ( $\sigma_u, \sigma_v, \sigma_w$ ), and resultant horizontal wind speed ( $u$ ,  $\text{m s}^{-1}$ ) and wind direction  
148 ( $wd$ ) were computed. Correction factors were applied to fix a ‘bug’ implicit within the Gill Windmaster  
149 instrument, as recommended by the manufacturer (Gill Instruments, 2016). The applied correction was a  
150 multiplication factor of 1.166 applied to positive vertical  $w$  wind axis measurements, and a factor of 1.289  
151 applied to negative  $w$  wind axis measurements.

152 Mounted on the instrument tower at 2m height was a HMP45C sensor (Campbell Scientific, Loughborough,  
153 UK) which provided temperature ( $T$ ,  $^{\circ}\text{C}$ ) and relative humidity ( $RH$ , %) measurements. Leaf wetness ( $LW$ , %  
154 time wet) at canopy level was measured by a specialised conductivity sensor (Campbell Scientific,  
155 Loughborough, UK) placed 10 cm above the ground.

### 156 2.4 Dispersion modelling

157 The backward Lagrangian Stochastic (bLS) type dispersion model is frequently applied for the computation of  
158 the inverse dispersion method (Flesch et al., 2004). Driven by measurements of the prevailing wind conditions,  
159 and with knowledge of the rise in concentration above background ( $\Delta C$ ) caused by an emitting source, the  
160 model can be applied to estimate the emission rate that best fits the measured concentration data. During bLS  
161 simulation the trajectories of thousands of fluid particles are calculated backwards in time from a reference point  
162 (concentration receptor) under the prevailing wind conditions. The locations where the trajectories intersect the  
163 ground (“touchdowns”) and proportion of these which fall within the source area ( $N_{source}$ ) are used to calculate  
164 ( $\Delta C/Q$ ), along with the associated vertical velocity ( $w_0$ ) of each touchdown (Flesch et al., 2005).

165 The bLS-R model (Häni, 2016), is an inverse dispersion model that is based upon the backward Lagrangian  
166 stochastic dispersion theory described by Flesch et al., (1995; 2004); however bLS-R has an additional function  
167 which computes the effect of dry deposition on gas concentrations. The bLS-R package provides functions to set  
168 up and execute the model within the R statistical software (R Core Team, 2015). The model calculates the



169 dispersion coefficient  $D$  ( $\text{s m}^{-1}$ ), used to derive the flux emitted from the source ( $Q$ ,  $\mu\text{g m}^{-2} \text{s}^{-1}$ ), by the measured  
170 rise in concentration above background ( $\Delta C$ ) (Eq. 1).

$$171 \quad Q = (\Delta C) * D^{-1} \quad (1)$$

172 where  $D$  is retrieved by the model from the number of source area interactions ( $N_{source}$ ) and the thousands of  
173 trajectories ( $N$ ) released backwards in time from the receptor locations (Eq. 2).

$$174 \quad D = \frac{1}{N} \sum_{N_{source}} \left| \frac{2}{w_0} \right| \quad (2)$$

175 The following input data were applied in the bLS-R model as 30 minute averages: wind direction, friction  
176 velocity ( $u^*$ ) the standard deviations of the rotated wind vector components ( $\sigma_u, \sigma_v, \sigma_d$ ) and surface roughness  
177 ( $z_0$ ). The spatial dimensions of the grazed field source area and the miniDOAS receptors were also specified.

178 Independent concentration measurements and emission estimates were derived using the two downwind  
179 miniDOAS receptors (S1 and S3), which are compared throughout the paper, e.g. CS1, CS3 and QS1, QS3. All  
180 concentrations and fluxes are expressed in units of  $\text{NH}_3$ , e.g.  $\mu\text{g NH}_3 \text{m}^{-3}$  and  $\mu\text{g NH}_3 \text{m}^{-2} \text{s}^{-1}$ .

## 181 2.5 Data filtering

182 The miniDOAS  $\text{NH}_3$  measurements were filtered to remove periods of high uncertainty, indicated by the  
183 standard error (SE) of the measurements. This filter only affected the S1 miniDOAS sensor, which was not  
184 fitted with an automatic alignment system to correct minor shifts in the light path between lamp and reflector.  
185 After applying this filter 92 out of 430 half hourly measurements were removed from the Period 2 S1  
186 measurements (Period 1 measurements were unaffected).

187 Previous studies (Flesch et al., 2004; Harper et al., 2011) have applied  $u^*$  and Monin-Obukhov length ( $L$ )  
188 filtering to remove emission estimates that do not meet given criteria ( $u^* > 0.15 \text{ ms}^{-1}$  and  $L > 10\text{m}$ ). These  
189 criteria were established on the basis of an observed reduction in the accuracy of model predictions as  $u^*$  and  $L$   
190 decrease (e.g., Flesch et al., 2004; Gao et al., 2009). However filtering out periods with low wind speeds and  
191 unstable stratification can be detrimental to emission estimates, often creating a bias to characterise certain  
192 sources under specific daytime or night-time conditions, whilst ignoring potentially valuable data that do not  
193 meet the criteria. This is a major limitation as we calculate average emissions from grazing cattle, where strong  
194 diurnal cycling is expected to occur (e.g. Laubach et al., 2013a). Flesch et al., (2014) developed alternate criteria  
195 for bLS data filtering, finding that (for their particular experiment) the  $u^*$  threshold could be reduced to  $0.05 \text{ m s}^{-1}$ ,  
196 and after finding no improvement after imposing a stability ( $L$ ) filter, introduced a supplementary vertical  
197 temperature gradient filter.

198 A filtering procedure was developed after assessing the standard error (SE) of emission estimates ( $\sigma_{Q/Q}$ ), which  
199 describes period-to-period fidelity and identifies “spiking” in model predictions caused by unsuitable input  
200 conditions, which do not confirm to an underlying assumption of a horizontally homogenous surface layer  
201 (Flesch et al., 2014). It was found that a  $u^*$  threshold of  $0.1 \text{ m s}^{-1}$  was sufficient to remove the significant  
202 outliers, while retaining acceptable data coverage, although this filter was at times limiting for nocturnal (low  
203 wind) periods. A wind direction filter was applied to remove periods where miniDOAS sensors S1 and S3 were  
204 not downwind of the field area. This filter only affected sensor S3 during Period 2, where estimates were  
205 ignored if  $wd > 30$  &  $wd < 270$ .



## 206 2.6 Modelling of dry deposition within the source area

207 Downwind from a source of  $\text{NH}_3$ , local recapture will remove a certain fraction of emitted  $\text{NH}_3$  from the air.  
208 Therefore the measured rise in concentration above background ( $\Delta C$ ) is a function of the source emission rate,  
209 atmospheric dispersion, and the fraction that has been deposited. Within a field being grazed by dairy cattle,  
210 emissions of  $\text{NH}_3$  are expected from urine and dung patches, while deposition will occur to clean surfaces  
211 within and beyond the field. Therefore, as we apply the bLS method to estimate emissions from the measure  
212 concentration gradient across the field ( $\Delta C$ ), we calculate the “net” flux constituting emissions from the field  
213 minus the fraction that has been deposited. However, if dry deposition is simulated in the dispersion model the  
214 lost fraction of emissions due to deposition can be quantified, providing an estimate for the “gross” emissions  
215 from excretions during grazing.


216 The bLS-R model has a post-processing routine to take into account the effect of the dry deposition of  $\text{NH}_3$  on  
217 flux predictions. The exchange or deposition velocity ( $v_d$ ) is based upon a uni-directional resistance model  
218 approach, defined as the inverse of a sum of a series of resistances to deposition (Eq. 3, left side).

$$219 \quad v_d = \frac{1}{R_a + R_b + R_c} = \frac{-F}{C} \quad (3)$$

220 where  $R_a$  is the aerodynamic resistance to transfer through the turbulent surface layer for a certain reference  
221 height,  $R_b$  is the boundary layer resistance associated with the viscous quasi-laminar sublayer adjacent to the  
222 deposited surface, and  $R_c$  is the canopy resistance representing the combined surface resistance accounting for  
223 stomatal and non-stomatal pathways to deposition (Flechard et al. 2013). It should be noted that  $R_a$  is implicit  
224 within the bLS-R calculations and does not need to be input to the model as a variable.


225 The resistances to deposition  $R_a$  and  $R_b$  can be calculated using ultrasonic anemometer measurements and well-  
226 established models (Asman, 1998), while  $R_c$  is a composite term representing numerous physical barriers to  
227 deposition at the surface. To obtain local, field-scale estimates of  $R_c$ , Two COTAG systems (conditional time-  
228 averaged gradient systems, Famulari et al., 2010) were operated at the centre of the grazed field for 1.5 years,  
229 allowing  $R_c$  to be estimated from calculations of  $R_a$  and  $R_b$  and time-integrated measurements of  $\text{NH}_3$   
230 concentration ( $C$ ), flux ( $-F$ ) and  $v_d$  (Eq. 3). The COTAG measurements were filtered to remove grazing  
231 periods and periods up to two weeks after grazing had ended, to ensure ‘clean’ background conditions. Clear  
232 correlation was then observed between the time-integrated  $R_c$  estimates with the variables  $T$  and  $RH$ , thus a  
233 double exponential equation was parameterised as follows to fit the data (Eq. 4, Figure 2), with similar form to  
234 Flechard et al., (2010):

$$235 \quad R_c = R_{c, \min} \times \exp^{\alpha \times (100 - RH)} \times \exp^{\beta \times Abs(T)} \quad (4)$$

236 A curve fitting procedure provided estimates of the parameters  $\alpha$ ,  $\beta$  and  $R_{c, \min}$  as 0.013 and 0.  and  $10 \text{ s m}^{-1}$ ,  
237 respectively.

238 The deposition component of bLS-R operates on the assumption that the whole grazed field is acting as a  
239 homogenous surface for deposition, however in reality urine and dung patches on the field are obviously  
240 hotspots of emissions, and not  $\text{NH}_3$  sinks. The ratio of ‘clean canopy’ where deposition may occur to ‘soiled  
241 canopy’ is not known, thus it is difficult to provide a true emission estimate including the effect of deposition.  
242 We can expect that the emission estimate without deposition ( $Q$ ) represents a ‘net’ emission rate from the field,  
243 while if we assume that the whole field behaves as homogenous sink, the emission rate including deposition will



244 represent an upper limit of the gross emission estimate. The actual emission rate for a soiled field can be  
245 expected to fall somewhere in between the net and upper gross estimates.  
246 A means of addressing this issue with the heterogeneous canopy surface may be found in reviewing the  $R_c$   
247 timeseries derived from the time-integrated COTAG concentration and flux measurements on the field, as  $v_d$   
248 acts on the local vertical concentration gradient between surface and reference height, i.e. the flux is  
249 concentration-gradient driven. At certain periods over the course of the year cattle were brought onto the field  
250 for grazing, and shortly after the grazing periods had ended the  $\text{NH}_3$  flux would return back to the negative  
251 (deposition), and therefore  $R_c$  could be calculated. Averaging all of the COTAG  $R_c$  calculations within one  
252 month following each grazing period gives an  $R_c$  value of  $260 \text{ s m}^{-1}$ , and comparing this value with the average  
253  $R_c$  where there had been no grazing on the field for at least one month ( $130 \text{ s m}^{-1}$ ). Therefore fertilisation of the  
254 field surface through grazing appears to have caused an increase in  $R_c$  of  $130 \text{ s m}^{-1}$ . This measured increase  
255 caused by excreted N to the field surface has been applied as an offset to the modelled  $R_c$  estimated by Eq. 4,  
256 and has been input to bLS-R. The bLS emission estimates without including deposition are referred to as  $Q$ ,  
257 while the estimates including deposition and the  $R_c$  offset are referred to as  $Q_{dep}$ . Emission estimates including  
258 deposition but without the  $R_c$  offset are referred to as  $Q_{depmax}$  

## 259 2.7 N excretion model

260 To contribute towards an emission factor for cattle grazing and to compare with literature values, it was  
261 necessary to express the emission estimates as a fraction of excreted N or urine-N. A nitrogen excretion model  
262 based on the Swiss feeding recommendations for dairy cows (Menzi et al. 2015; Muenger personal  
263 communication) was applied to quantify the total N and urine-N excreted to the field during both grazing  
264 periods, from the following set of inputs: (1) milk yield, (2) animal numbers, average weight and date after  
265 calving, (3) the net energy for lactation (NEL) and crude protein (CP) content of the grass, (4) the number of  
266 animals grazed and the duration of grazing on the experimental plot. The excretions per day were calculated as  
267 consumption minus retention in milk and animal growth. The share of N excreted in faeces and urine was  
268 calculated using regressions of fecal N digestibility derived from N balance studies (Bracher et al. 2011, 2012).

## 269 3. Results

### 270 3.1 Period 1 (18-20/05): grazing on SW paddock only

#### 271 3.1.1 Concentration measurements

272 The wind direction during Period 1 was consistently W-WSW (Figure 3). Therefore DOAS S2 was located  
273 upwind of the grazed SW paddock while S1 and S3 were situated downwind to the eastern and northeastern  
274 boundaries of the field respectively. Concentrations across the S2 path length would be expected to be low and  
275 near background, except during periods of very low wind speed, while any rise in concentration measured by S1  
276 and S3 above S2 would show the influence of emissions from the field.

277 The upwind S2 concentration measurements reveal background concentrations of  $2\text{-}3 \mu\text{g m}^{-3}$  during times of  
278 steady W/SW winds, increasing slightly when wind speed was low. Concentration polar plots (Figure 3) show  
279 the average concentrations measured as a function of wind speed and direction, where the influence of emissions





280 from the grazed field is illustrated by the increase in measured concentrations at downwind receptors S1 and S3  
281 relative to S2 ( $C_b$ ).

282 Power failure led to a partial loss of measurements from miniDOAS S2, which are required to specify  $C_b$  for  
283 estimating emissions through bLS modelling. A significant linear regression was found between the measured  
284 background S2 concentration and wind speed ( $u$ ), temperature ( $T$ ) and relative humidity ( $RH$ ):

$$285 \quad C_b = 4.26 - 0.59u + 0.06T - 0.017RH, r^2 = 0 \quad (5)$$

286 The wind direction remained consistent after the S2 power failed on 19/05, therefore the empirical relationship  
287 (Eq. 5) was found to be suitable and was applied to estimate and extend S2 concentrations, as a proxy for  $C_b$ .

288 The predicted S2 concentrations follow the measured S2 concentrations closely until the point of data loss on  
289 19/05 (Figure 4, panel). This lends confidence to the rest of the  $C_b$  predictions used to fill the gap in the  
290 measurements, even though there is increased uncertainty associated with the last 15 hours of emission  
291 estimates calculated from the predicted  $C_b$ , relative to periods where  $C_b$  was measured by the S2 sensor.

### 292 3.1.2 Field-scale emissions estimates

293 Overall there is very good agreement between the emission calculations from both downwind concentration  
294 datasets. The average emission rate calculated by bLS-R for the S3 measurements ( $Q_{S3}$ ) is  $0.29 \mu\text{g m}^{-2} \text{s}^{-1}$ ,  
295 while the QS1 average is  $0.27 \mu\text{g m}^{-2} \text{s}^{-1}$ . The modelled emission of  $\text{NH}_3$  is low (generally below  $0.2 \mu\text{g m}^{-2} \text{s}^{-1}$ )  
296 during the first 24 hours, as the measured concentration gradient across the field was less than  $1 \mu\text{g m}^{-3}$ . As the  
297 cattle were introduced to the field on the first morning (18/05) it likely took some time for  $\text{NH}_3$  to ‘build up’  
298 from hydrolysis of excreted urea before significant emissions occurred. Downwind concentrations ( $CS1$  and  
299  $CS3$ ) peaked during the next day (19/05), with peak emissions occurring at midday when there was a  $5\text{--}6 \mu\text{g m}^{-3}$   
300 horizontal concentration gradient ( $\Delta C$ ) measured between the upwind and downwind receptors. The peak  
301 emission rate at this time was around  $1.1 \mu\text{g m}^{-2} \text{s}^{-1}$  for both downwind receptors. A decrease in the measured  
302 downwind concentrations occurred at 15:00, and an associated decrease in emissions is logically estimated for  
303 this time period. The decline in emissions follows 4.4 mm of rain during the day of 19/08, where the rainfall  
304 intensity peaked shortly after midday. In addition, the cattle were removed from the field at 15:00; therefore the  
305 suspension of excretions to the field and the wet conditions are most likely the dominant factors driving the  
306 declining emissions. The  $LW$  sensor indicated that the canopy was wet (conductivity reading above baseline) for  
307 84% of Period 1 (Table 2).

308 Coinciding with the daytime peak in emissions and downwind concentrations were peaks in  $T$  and  $u$ , while  $RH$   
309 reached a minimum (Figure 4). During the night emissions decreased to near 0, where  $RH$  reaches a maximum  
310 and  $T$  and  $u$  reach a minimum. The average  $Q_{dep}$  gross emission estimates are greater than the  $Q$  net emission  
311 estimates by 13–16%.

## 312 3.2 Period 2 (20-29/05): grazing on whole field

### 313 3.2.1 Concentration measurements

314 Concentration measurements during Period 2 (20-29/05) revealed considerable differences between downwind  
315 receptors, where the average  $CS1$  at the center of the field was much greater than the average  $CS3$  at the SE  
316 corner (Figure 5), with period averages of  $5.6 \mu\text{g m}^{-3}$  and  $3.9 \mu\text{g m}^{-3}$ , respectively. This may be partially



317 explained by the location of the receptors relative to the grazed field under the prevailing wind conditions.  
318 Sensor S1 was located in the center of the field, with an upwind fetch of grazed field across a wider band of  
319 wind directions. Sensor S3 on the other hand is located at the SE field boundary, and was more limited as a  
320 receptor for emissions under the prevailing northerly wind conditions. However, during NW wind directions  
321 where all sensors in-line across a diagonal fetch of the field one would expect the S3 sensor to be measuring  
322 similar or higher concentrations relative to S1 at the center (assuming homogenous emissions across the field),  
323 which is not the case. It is also important to note that the grazing density was about 50% lower during Period 2  
324 as the field was much larger.  
325 Power failure led to significant data gaps from the S2 sensor and hence a loss of  $C_b$  measurements (Figure 6).  
326 To fill the gaps a linear regression applied between the measured S2 concentration and temperature ( $T$ ), wind  
327 speed ( $u$ ) and relative humidity ( $RH$ ), however there was considerable scatter in the data and the  $C_b$  prediction  
328 was much more uncertain than during Period 1.

$$329 \quad C_b = 2.5 - 0.1u + 0.01T - 0.02RH, r^2 = 0 \quad (6)$$

### 330 3.2.2 Field-scale emissions estimates

331 The average net emission rate ( $Q$ ) from the grazed field estimated using the S1 measurements was  $0.27 \mu\text{g m}^{-2} \text{s}^{-1}$   
332 while much lower emissions were estimated from the S3 measurements ( $0.12 \mu\text{g m}^{-2} \text{s}^{-1}$ ). Both estimates show  
333 a generally diurnal trend of peak emissions during the afternoon, similar to the trend observed during Period 1.  
334 However there are gaps in QS1 and QS3 overnight due to data filtering as  $u$  drops below the defined threshold  
335 ( $0.1 \text{ m s}^{-1}$ ). Peak emissions occurred on 22/05 when the maximum concentration difference between upwind and  
336 downwind receptors was measured. Grazing of the field ended and the cattle left the field at 15:00 GMT on  
337 23/05. After this point a generally decreasing trend in emissions is derived from the decreasing concentrations  
338 measured by S1 and S3. There is greater uncertainty attributed to the periods without active  $C_b$  measurements  
339 marked on Figure 6.

340 Emission estimates from the bLS-R model were initially made on the assumption that emissions from the grazed  
341 field are spread equally (thus randomly) across a homogeneous field. However a herd of cattle can be expected  
342 to move and disperse across the field in a generally non – random way, grouping together as they graze across  
343 the field rather than acting individually. Systematic effects of uneven cattle distribution within grazed pastures  
344 have been reported previously, impacting on bLS-derived mean gaseous emissions from grazing cattle (Laubach  
345 et al., 2013b). Our measurements during Period 2 certainly support spatial heterogeneity in emissions, with  
346 higher concentrations at the centre of the field (CS1) than at the SE corner (CS3) during periods where the wind  
347 direction was from the NW. Had emissions from the field been homogenous, an increase in  $\text{NH}_3$  concentration  
348 would have been measured across the NW - SE transect of the field.

349 A second set of emission estimates (Figure 6 Panel 3) were produced after optimising the emission rates from 4  
350 separate areas (A, B, C & D, Figure 1) within the field to reproduce the observed concentrations at S1 and S3 on  
351 each measurement day. An excellent fit between QS1 and QS3 was achieved after running a numerical solver to  
352 minimise the squared error ( $e^2$ ) between them. The coefficients given in Table 1 are the result of the solver,  
353 describing the spatial changes in relative emission strength over time. The solver was executed with the  
354 following conditions: (1) the sum of the area coefficients must equal 1; and (2) no area coefficient can be below  
355 0.075. The minimum value for any area coefficient ( $AC_{min}$ ) is a parameter which describes the heterogeneity of



356 emissions, where in this case it was assumed that each source area must contribute at least 30% of the original  
357 (homogenous) value.

358 Henceforth the initial emission estimates calculated without applying emission area coefficients are referred to  
359 as Scenario 1 estimates, while the calculations involving heterogeneous emission area coefficients are referred  
360 to as Scenario 2 estimates. It is important to note that there can be more than one combination of coefficients to  
361 reconcile the  $QS1$  and  $QS3$  estimates, thus these coefficients should not be taken as definite emission strengths  
362 for each area of the field. However they do offer a rough guide to which sections had greater emissions relative  
363 to the others, and confirm that emissions from the field were certainly not homogeneous over the course of the  
364 grazing period. The large difference in Scenario 1  $QS1$  and  $QS3$  estimates may therefore be attributed to strong  
365 emissions in areas A and D, relative to C and B (Figure 1, Table 1), which explains the high measured  
366 concentrations at sensor S1 relative to S3. Emission area D represents the SW field which was grazed during  
367 Period 1, thus high emissions from this area may have been a legacy effect left by continuing emissions from  
368 cattle excretions during Period 1. Emission area D also contained a water trough which was only 15-20m away  
369 from the S1 receptor, where cattle grouping was observed. Due to the combined effects of prior grazing within  
370 the SW field and grouping around the water trough, we can expect enhanced emissions within area D. The  
371 Scenario 2 (optimised)  $QS1$  and  $QS3$  estimates are similar ( $0.19$  and  $0.16 \mu\text{g m}^{-2} \text{s}^{-1}$  respectively), and are  
372 believed to give a more realistic estimate of the true field-scale emission rates after accounting for spatial  
373 complexity. The data coverage for  $QS3$  (64%) is greater than the  $QS1$  data coverage (59%), hence some  
374 differences between  $QS1$  and  $QS3$  can be expected even with perfect agreement. The  $Q$  estimates can be  
375 regarded as net emission rates for the grazed field, made without consideration of deposition to clean patches  
376 within the source area. The  $Q_{dep}$  estimates including the effect of deposition are 16% higher ( $0.22$  and  $0.19 \mu\text{g}$   
377  $\text{m}^{-2} \text{s}^{-1}$  for the Scenario 2 S1 and S3 estimates respectively).

### 378 3.3 Derived emission factors

379 Grazing Period 1 took place within a SW section of the field with a smaller area ( $5600 \text{ m}^2$ ) than the whole field  
380 opened up for grazing Period 2 ( $19800 \text{ m}^2$ ). Although there were fewer cattle grazing during Period 1 (25) the  
381 grazing density was twice as high relative to Period 2. Therefore the higher grazing density during Period 1 is  
382 consistent with the stronger emission estimates per unit area (Table 2). Emission factors (EFs) are given in  
383 Table 3 for Periods 1 and 2. For both measurement periods, the S3 sensor had greater data coverage than the S1  
384 sensor. Therefore, the S3 emission estimates are more representative and are selected to derive EFs. Both  
385 grazing periods have produced similar emission factors of the order of  $6\text{-}7 \text{ g NH}_3 \text{ cow}^{-1} \text{ d}^{-1}$ , though there are  
386 considerable differences between the two periods in terms of weather conditions and grazing timeline. Period 1  
387 was shorter in length, and was characterised by steady SW/W winds, lower temperatures and wetter conditions  
388 relative to Period 2 (Table 2). Therefore, the lower temperatures and wetter conditions likely limited emissions  
389 (e.g. Flechard et al., 1999; Laubach et al., 2012; Mórning et al., 2016).

390 The duration of Period 1 was too short to fully capture tailing emissions, while excretions to the field during  
391 Period 1 will have continued to emit  $\text{NH}_3$  during Period 2. Flux estimates are continued for 6 days after the  
392 cattle had left the field during Period 2, capturing residual emissions after grazing. The combined influences of  
393 weather conditions and experimental design and duration may therefore explain why a smaller fraction of  
394 excreted N and urine-N was emitted as  $\text{NH}_3$  during Period 1 relative to Period 2. The EFs derived from Period 2



395 fluxes may for these reasons be considered to be more representative of the total emissions from grazing, where  
396 emissions are estimated to be 6 and 7 g NH<sub>3</sub> cow<sup>-1</sup> d<sup>-1</sup>, and 9 and 10% excreted urine-N emitted as NH<sub>3</sub> for the  $Q$   
397 and  $Q_{dep}$  scenarios respectively. However, the greater uncertainty in Period 2 associated with missing  $C_b$   
398 measurements and heterogeneous emission patterns should be considered.

## 399 4. Discussion

### 400 4.1 Experimental design

401 Previous experiments to deduce surface-air fluxes by the bLS method have deployed sufficient measurement  
402 systems so that the problem to determine  $C$  and  $C_b$  was mathematically over-determined, and the experiment  
403 was not dependent on a specific range of wind directions (e.g. Flesch et al., 2014). The configuration of the  
404 three miniDOAS sensors and the grazed field during Period 2 led to certain wind directions being unsuitable for  
405 emission estimates, while additional miniDOAS sensors placed at field boundaries would have been beneficial.  
406 However, the configuration of the miniDOAS sensors was optimised by using the weather forecast to predict the  
407 wind direction prior to the grazing experiment and placing the miniDOAS sensors accordingly.

408 It was originally hypothesised that the model could treat the field area as a spatially homogenous source, where  
409 emission estimates would show insensitivity to cattle grouping and excretion patterns within the field. This  
410 assumption seemed valid for the Period 1 emission estimates, where very good agreement was achieved in  $C$   
411 and  $Q$  between the downwind receptors. The SW field grazed during Period 1 was smaller than the whole field  
412 grazed during Period 2, and the wind direction was more consistent. This allowed the downwind and upwind  
413 receptors to capture the inflow and outflow concentrations and produce reliable emission estimates, while the  
414 grazing density was higher. During Period 2 the field was larger and the grazing density was 50% lower, which  
415 led to some spatial and temporal emission ‘hotspots’ caused by cattle grouping and/or excretions within certain  
416 areas, such as around the water trough. The S1 sensor was located very close to a particular ‘hotspot’ of  
417 emissions at the centre and SW section of the field, while the S3 sensor was located next to an area (SE corner)  
418 which appears to have seen relatively little emissions. Because of this the model could not treat the field as a  
419 homogenous source area and reconcile emission estimates between downwind receptors, and source-area  
420 differentiation (Table 1) was required. Therefore there is a limitation in the application of the standard bLS  
421 method to estimate emissions from area sources which may not be treated as homogenous, such as pastures with  
422 a low grazing density. However as the Period 2/Scenario 2 emission estimates demonstrate it may also be  
423 possible to account for this heterogeneity if more than one downwind concentration receptor is used and they are  
424 suitably located. Insensitivity to heterogeneous emissions has been demonstrated if concentration measurements  
425 are made at least twice as far downwind as the maximum distance between potential sources (Flesch et al.,  
426 2005). Therefore had the miniDOAS sensors been placed differently to satisfy this criterion it is possible that no  
427 source area optimisation would have been necessary to reconcile bLS emission estimates. However, as  
428 emissions from excretions to the grazed pasture were relatively weak, at a greater distance downwind from the  
429 field the concentration rise above background may not be significant enough to evaluate the emissions.

430 Felber et al., (2015) applied corralling of grazing cattle into paddocks over a rotational grazing cycle to increase  
431 grazing density, and placed GPS trackers on individual cattle to attribute eddy covariance methane fluxes using  
432 a footprint model. The Period 1 emission estimates demonstrate that a smaller paddock and higher grazing



433 density can be a solution to the heterogeneous emissions problem, however  $\text{NH}_3$  emissions from grazing cattle  
434 arise from excretions to the field surface and are not enteric, hence GPS trackers on cattle may not track the  $\text{NH}_3$   
435 emissions directly as they do for methane. In order to accurately attribute fluxes from grazed pastures there is  
436 call to develop a method to track excretions spatially and temporally across a grazed field, potentially using  
437 visual observations or cameras and animal detection software. We did carry out visual observations of urination  
438 events during Period 1 (day time only), which described a fairly homogenous distribution (data not shown, Andi  
439 Móring, personal communication). However observations were not carried out during Period 2.

#### 440 **4.2 Uncertainty in field-scale emission estimates**

##### 441 **4.2.1 Uncertainty in miniDOAS concentration measurements and dispersion model**

442 The instrumental uncertainty associated with the miniDOAS concentration measurements was evaluated during  
443 the initial inter-comparison phase, where the systems were configured to measure in parallel. Very good  
444 agreement was observed between the analysers, with a slope of one and an intercept close to zero. Deviations  
445 between the S1, S2 and S3 analysers were minor, and the coefficient of variation between them was determined  
446 to be 3.4% (unpublished data). Sintermann et al. (2016) have described this inter-comparison phase and the  
447 miniDOAS performance in detail.

448 Since the input data had been filtered to remove conditions which do not meet the established criteria ( $u * < 0.1$   
449  $\text{m s}^{-1}$ ), and instrumental uncertainty associated with the concentration measurements is very low, the principal  
450 uncertainties are associated with the modelled results, principally the input variables which could not be  
451 measured directly, such as  $R_c$ , and the predicted background concentration  $C_b$  used for gap-filling.

452 The bLS dispersion model theory has been well validated in past experiments (e.g. Flesch et al., 2004; McGinn  
453 et al. 2009), however we can assume a general overall uncertainty based on evaluated performance by an  
454 ensemble of published trace gas release experiments. A review of 24 bLS tracer release assessments (Häni et al.,  
455 2016) found that the uncertainty is generally between 10 and 20% for the bLS method.

##### 456 **4.2.2 Uncertainty in background concentration**

457 The background concentration ( $C_b$ ) had to be predicted to “fill in” the gaps in the  $C_b$  measurements upwind of  
458 the field measured by miniDOAS sensor S2. Multiple regression equations (Eq. 5; 6) were based on previous  
459 observations that background  $\text{NH}_3$  is dependent on wind speed, temperature and relative humidity (Flechard and  
460 Fowler, 1998), but nonetheless error is introduced due to differences between the predicted  $C_b$  and the actual  $C_b$ .  
461 The mean absolute error (MAE) between the measured and predicted  $C_b$  for Periods 1 and 2 have been applied  
462 to offset to the predicted  $C_b$  timeseries input to the model, to determine the limits (upper and lower) of emission  
463 estimates caused by this uncertainty. The MAE between the observed and predicted background concentrations  
464 during Period 1 was  $0.33 \mu\text{g m}^{-3}$ , while the percentage of data coverage (observed  $C_b$  measurements) was 67%.  
465 Measurement Period 2 had a greater MAE between observed and predicted  $C_b$  ( $0.56 \mu\text{g m}^{-3}$ ) (Table 4), as the  
466 multiple regression equation used to fill ( $C_b$ ) measurement gaps did not give very accurate predictions (Eq. 6).  
467 Furthermore, the upwind sensor S2 was only active during 44% of the measurement period; therefore the Period  
468 2 emission estimates are more sensitive to this uncertainty. The % change in  $Q_{dep}$  to predicted  $C_b \pm \text{MAE}$  was  
469 much greater during Period 2 ( $\pm 31\%$ ) than Period 1 ( $\pm 5\%$ ).



#### 470 4.2.3 Uncertainty in local dry deposition of field-emitted NH<sub>3</sub>

471 The inclusion of dry deposition within the bLS-R model is intended to simulate the deposition of NH<sub>3</sub> to the  
472 surface of ‘clean’ grass patches within the grazed field. This process is described by a resistance model, and  
473 while the  $R_a$  and  $R_b$  components may be derived directly from eddy covariance measurements, as well as well-  
474 established models, the  $R_c$  component is empirical. In this case, the empirical  $R_c$  model (Eq. 4) was derived  
475 from a curve fitting exercise of time-integrated COTAG flux measurement to meteorological variables  $T$  and  
476  $RH$ . The  $R_c$  model is based on a long (1.5 years) series of measurements taken from the field (deposition periods  
477 only), while the effect of soiled grass areas on  $R_c$  during grazing is also approximated using the  $130 \text{ s m}^{-1}$   $R_c$   
478 offset within the  $Q_{dep}$  scenario. It is conceivable that there is significant error (up to 50%) in estimating  $R_c$  by  
479 this method. The sensitivity of the bLS-R model to potential uncertainty within the  $R_c$  estimates has been  
480 evaluated, where the  $R_c$  timeseries has been varied by factors of plus and minus 50%. The results of this  
481 sensitivity test are given in Table 4. The % change in  $Q_{dep}$  after varying  $R_c$  by  $\pm 50\%$  was -4% and +12% for  
482 Period 1 and  $\pm 5\%$  for Period 2.

483 While impact of this uncertainty on the absolute value for  $Q_{dep}$  is not very large, the change in  $Q_{dep}$  relative to  
484  $Q$  is significant. The Period 2  $Q_{dep}$  uncertainty due to predicted  $R_c$  is  $\pm 5\%$ ; therefore including deposition in the  
485 model has increased  $Q_{dep}$  above  $Q$  by  $16 \pm 6\%$ . Alternatively, we can say that  $14 \pm 4\%$  of NH<sub>3</sub> emitted from  
486 excretions had been re-deposited to clean patches on the field.

#### 487 4.2.4 Uncertainty associated with heterogeneous emission patterns

488 To address the resulting disparity between emission estimates from the downwind concentration receptors  
489 during Period 2, the emission area coefficients (Table 1) were applied to reconcile the independent emission  
490 estimates. This is a valid approach to describe emissions from the field as a whole, as sensor S1 was placed at  
491 the center of the field near the strongest area of emissions, causing emissions to be overestimated as a whole,  
492 while the field area around sensor S3 at the SE corner seems to have contributing very little emissions, hence  
493 causing an underestimation. However, as mentioned previously there are multiple configurations of source area  
494 coefficients which can reconcile  $QS1$  and  $QS3$ . Therefore a sensitivity test has been carried out to evaluate the  
495 potential error in this method. The numerical solver which derives the source area coefficients contains a  
496 parameter assuming the maximum degree of heterogeneity for the field, where each source area cannot  
497 contribute less than a defined percentage to the overall emissions. This parameter ( $AC_{min}$ ) was varied to provide  
498 differing sets of source area coefficients, yet still reconciling the  $QS1$  and  $QS3$  emission estimates which was a  
499 necessary precondition for the sensitivity test.  $AC_{min}$  was initially assumed be 0.075, 30% of the value for a  
500 homogenous field (0.25), and this value was varied by  $\pm 67\%$  (to 50% and 10% of the homogenous value). The  
501 results of this sensitivity test are given in Table 4, where the percentage change in  $Q_{dep}$  after varying the  
502 parameter by +67% and -67% was 9 and 1, respectively. The percentage change is greater after increasing  
503  $AC_{min}$  because  $QS1$  and  $QS3$  cannot be reconciled as closely, whereas decreasing  $AC_{min}$  from 0.075 leads to  
504 very little change as the numerical solver can find very close agreement. This suggests that emissions from  
505 excretions to the field are too heterogeneous to assume an  $AC_{min}$  value of 0.125 (50% of homogeneous value),  
506 and that the 1% change in  $Q_{dep}$  after reducing  $AC_{min}$  to 0.025 (10% of homogeneous value) is more indicative  
507 of the uncertainty in the source area optimisation method.



508 The % change in emission estimates was much more sensitive to uncertainty in predicted  $C_b$  than to uncertainty  
509 in  $R_c$  or  $AC_{min}$ . Therefore we expect predicted  $C_b$  to be the greatest source of error in derived fluxes from the  
510 grazed field.

#### 511 4.3 Temporal variability in estimated emissions

512 The estimated emissions show significant temporal variability during both measurement periods, typically with  
513 peak emissions occurring during the day with little emissions occurring overnight. Similar diurnal profiles have  
514 been observed in  $\text{NH}_3$  emissions from cattle urine and dung patches (Laubach et al., 2012; 2013a), and from  
515 urine patch emission models (Móring et al., 2016). Mechanisms which limit nocturnal emissions can be  
516 summarised as: (1) low wind speeds and stable conditions, which increases the aerodynamic transfer resistances  
517 between the soil/canopy layer and the atmosphere, (2) low temperatures which limit the hydrolysis of urea, and  
518 affect  $\text{NH}_3/\text{NH}_4^+$  partitioning in solutions, (3) dew formation on leaf surfaces which act as sinks for  $\text{NH}_3$ .

519 A longer temporal trend in emissions is observed during Period 1; with very little emissions occurring on the  
520 first day the cattle were introduced to the field, and peak emissions occurring during the afternoon of the second  
521 day. After 44 cattle had begun to graze the whole field during Period 2, peak emission rates occurred from 22-  
522 23/05, 2-3 days after the cattle had been introduced. A decreasing trend in emissions occurred after the cattle  
523 were removed from the field on 23/05 until the end of the measurement period. This is in-line with the reported  
524 emissions from urine and dung patches by Laubach et al., (2013a), where emissions peaked during the third and  
525 fourth days after grazing had begun, and a following decreasing trend in emissions after the cattle had been  
526 removed from the field on the third day.

527 The peak in emissions which occurred during grazing can be attributed to the hydrolysis of urea within the urine  
528 patches, which leads to a rapid rise in pH and the formation of  $\text{NH}_4^+$ , and a high rate of  $\text{NH}_3$  volatilisation  
529 (Sherlock and Goh 1985). As volatilisation proceeds, a subsequent chemical reduction in surface pH occurs  
530 with an accompanying release of a proton to the transformation of  $\text{NH}_4^+$  to  $\text{NH}_3$  (Laubach et al., 2012; Sherlock  
531 and Goh, 1985, Móring, et al. 2016), which prevents further volatilisation and can explain the declining  
532 emission rate after the cattle had left the field on 23/05.

#### 533 4.4 Emission factors from the grazing experiment

534 Emission factors from the grazing experiment have been evaluated as  $6 \pm 2$  and  $7 \pm 2$  g  $\text{NH}_3$  cow<sup>-1</sup> d<sup>-1</sup>, and  $9 \pm$   
535  $3\%$  and  $10 \pm 3\%$  of excreted urine-N emitted as  $\text{NH}_3$  for the  $Q$  and  $Q_{dep}$  scenarios respectively (average  
536 emission factor  $\pm$  predicted  $C_b$  uncertainty). These emission factors were taken from the Period 2/Scenario 2  
537 estimates as Period 1 was not long enough to fully capture emissions from excretions to the field. Previous  
538 experiments have measured  $\text{NH}_3$  emissions from cattle urine patches at ratios of 7-25.7% of excreted urine-N to  
539 grazed pastures (Jarvis et al., 1989; Ryden et al., 1987; Laubach et al., 2012; 2013a). Our estimates for  
540 emissions from grazing are towards the lower end of the range of published emission factors. Differences  
541 between reported emission factors may be related to differing weather conditions affecting the hydrolysis of  
542 urea, or differences in soil properties, where emissions can be limited due to urine percolation into porous soil  
543 (Móring et al., 2016). It is also possible that significant emissions occurred after the miniDOAS instruments had  
544 been removed from the field, which would lead to an underestimation of the proportion of excreted N or urine-N  
545 emitted as  $\text{NH}_3$ . The period of significant emissions from urine patches generally lasts 4-8 days after urine



546 deposition (Sherlock and Goh, 1985; Laubach et al., 2012). However, a rainfall event after a dry period can lead  
547 to a delayed onset of  $\text{NH}_3$  emissions by restarting urea hydrolysis (Móring et al., 2016). On the other hand, the  
548 Period 2 emission factors are also influenced to some degree by emissions from excretions during Period 1 on  
549 the SW field, which could cause an overestimation of emissions. Emission factors derived from Period 2 are  
550 also affected by  $u^*$  filtering, which may slightly increase estimates due to a measurement bias towards  
551 turbulent daytime periods.

552 The emission estimates presented here show that the ‘gross’ emissions from the field ( $Q_{dep}$  scenario) are around  
553  $16 \pm 6\%$  higher than the ‘net’ emissions ( $Q$  scenario). Both of these estimates are potentially useful to contribute  
554 towards an emission factor for livestock grazing. For example, regional-scale atmospheric dispersion models  
555 may require source inputs as ‘gross’ emission factors due to deposition simulations implicit within the regional-  
556 scale model.

## 557 5. Conclusion

558 Fluxes of  $\text{NH}_3$  were estimated through measurement of atmospheric concentrations upwind and downwind of a  
559 grazed field, and applying a bLS dispersion model to simulate the emission rate on a half hourly basis from the  
560 observed horizontal concentration gradient and wind/turbulence measurements. The miniDOAS systems were  
561 well-suited to the task, providing continuous high-time resolution concentration measurements at field  
562 boundaries across the field. Horizontal concentration gradients of  $\sim 0\text{--}9 \mu\text{g m}^{-3}$  were measured between upwind  
563 and downwind receptors. Control on emissions was observed from covariance with temperature, wind speed and  
564 humidity/wetness measurements made on the field, revealing a diurnal emission profile. Two separate  
565 experiments to evaluate emissions were carried out; a Period 1 experiment (2 days) which took place on a small  
566 field with a grazing density of  $44 \text{ cows ha}^{-1}$ , and a Period 2 experiment (10 days) on a larger field with a  
567 grazing density of  $22 \text{ cows ha}^{-1}$ . Spatial heterogeneity in emissions across the field was apparent during Period  
568 2, as a result of uneven cattle distribution and a low grazing density, adversely affecting the accuracy of the bLS  
569 model estimates. However, after treating the larger field as a grid of discrete source areas the spatial  
570 heterogeneity of emissions was accounted for, by optimising source area coefficients to the measured  
571 concentrations and reconciling emission estimates between downwind receptors.

572 Data gaps in the  $C_b$  measurements were filled by applying linear regression equations with  $u$ ,  $T$  and  $RH$ , which  
573 introduced significant uncertainty into the emission estimates. The evaluated uncertainty in derived emissions  
574 due to  $C_b$  gap-filling was 5% during Period 1 and 31% during Period 2.

575 In contrast to the standard bLS approach, we simulated the effect of re-deposition to unsoiled field patches,  
576 where the canopy resistance ( $R_c$ ) component was estimated by an empirical model derived from local flux and  
577  $R_c$  measurements with  $T$  and  $RH$ . Including deposition in the model increased emissions by  $16 \pm 6\%$ . The  
578 results present both ‘gross’ and ‘net’ emissions from the field, and show that deposition of  $\text{NH}_3$  is an important  
579 consideration when deriving  $\text{NH}_3$  emission factors.

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#### 587 **Competing interests**

588 The authors declare that they have no conflict of interest.

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733 **Tables**

734 **Table 1: Series of emission coefficients obtained by numerical solving of the difference between QS1 and QS3,**  
 735 **applied to individual emission areas to fit the bLS-R model to concentration measurements on each day. For a grazed**  
 736 **field with homogeneous emissions the emission coefficients for each area would be 0.25. Therefore the emission**  
 737 **coefficients offset the bias in emission estimates between the sensors S1 and S3 by adjusting to the heterogeneity in**  
 738 **emissions across the field area.**

Emission area	20/05	21/05	22/05	23/05	24/05	25/05	26/05	27/05	28/05	29/05
A	0.56	0.31	0.28	0.56	0.36	0.42	0.26	0.21	0.25	0.17
B	0.08	0.14	0.13	0.17	0.18	0.17	0.25	0.25	0.23	0.25
C	0.07	0.07	0.20	0.09	0.19	0.11	0.23	0.28	0.21	0.27
D	0.29	0.47	0.40	0.18	0.26	0.30	0.27	0.26	0.31	0.31

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**Table 2: Summary table of measurement and modelling results.**

	Period 1			Period 2		
	Scenario <sup>1</sup>	S1	S3	Scenario	S1	S3
$C - C_b$ ( $\mu\text{g NH}_3 \text{ m}^{-3}$ )		1.4	2.1		2.9	1.2
$Q$ ( $\mu\text{g NH}_3 \text{ m}^{-2} \text{ s}^{-1}$ )		0.27	0.29	1 2	0.27 0.19	0.12 0.16
$Q_{dep}$ ( $\mu\text{g NH}_3 \text{ m}^{-2} \text{ s}^{-1}$ )		0.31	0.34	1 2	0.31 0.22	0.14 0.19
$Q_{depmax}$ ( $\mu\text{g NH}_3 \text{ m}^{-2} \text{ s}^{-1}$ )		0.33	0.38	1 2	0.33 0.24	0.14 0.2
$T$ ( $^{\circ}\text{C}$ )		10			14	
$u$ ( $\text{m s}^{-1}$ )		2			1.2	
$RH$ (%)		77			76	
Total Rain (mm)		4.4			0	
$LW$ (% time wet)		84			40	
$R_c$ ( $\text{s m}^{-1}$ )	$Q_{depmax}$	145		$Q_{depmax}$	208	
	$Q_{dep}$	275		$Q_{dep}$	338	
$v_d$ ( $\text{mm s}^{-1}$ )	$Q_{depmax}$	4.4		$Q_{depmax}$	3.2	
	$Q_{dep}$	2.8		$Q_{dep}$	2.2	

<sup>1</sup>Description of model scenarios:  $Q_{dep}$  is the bLS-R emission estimate including dry deposition, with an offset of  $130 \text{ s m}^{-1}$  applied to the  $R_c$  timeseries to account for the limiting of excreted  $\text{NH}_3$  to deposition.  $Q_{depmax}$  is the emission estimate without the offset applied to the  $R_c$  timeseries, and is hence a maximum prediction of the gross emissions from the field. Period 2 emission estimates contain both the original Scenario 1 emission estimates assuming a homogenous field, and the optimised Scenario 2 emission estimates using the area coefficients given in Table 1.

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**Table 3: N excretion model inputs, results, and derived emission factors**

Model Input	Value		Model Output or Emission Factor <sup>1</sup>	Scenario <sup>2</sup>	Value	
	Period 1	Period 2			Period 1	Period 2
Animal Numbers	25	44	N excretion total (kg)		11	40
Animal weight (kg)	650	650	N excretion urine (kg)		8	28
Days since calving	180	183	N excretion faeces (kg)		3	12
Milk yield (kg cow <sup>-1</sup> day <sup>-1</sup> )	21	22	EF (% total excreted N emitted as NH <sub>3</sub> )	<i>Q</i>	2.5	5.2
				<i>Q<sub>dep</sub></i>	2.9	6
Grass sward: net energy for lactation (MJ kg DM <sup>-1</sup> )	6.4	6.4	EF (% total excreted urine-N emitted as NH <sub>3</sub> )	<i>Q</i>	2.9	8.9
				<i>Q<sub>dep</sub></i>	4.2	10.4
Grass sward: crude protein content (g kg DM <sup>-1</sup> )	168	168	EF (g NH <sub>3</sub> cow <sup>-1</sup> d <sup>-1</sup> )	<i>Q</i>	5.7	6.2
				<i>Q<sub>dep</sub></i>	6.5	7.2

<sup>1</sup>N excretion calculations are given as the herd total for each measurement period.  
<sup>2</sup>*Q* is the net emission rate derived without including deposition in the bLS-R simulation, *Q<sub>dep</sub>* is the gross bLS-R emission estimate including dry deposition, with an *R<sub>c</sub>* offset of 130 s m<sup>-1</sup>. EFs are derived from the S3 flux estimates due to better data coverage during both measurement periods, and Period 2 fluxes are derived from Scenario 2 estimates.

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**Table 4: Sensitivity analysis of the percentage change of the bLS-R gross emission estimates (*Q<sub>dep</sub>*) to variation in predicted *C<sub>b</sub>* and *R<sub>c</sub>*, and the source area coefficient parameter *AC<sub>min</sub>*.**

	Period 1	Period 2
<i>C<sub>b</sub></i> data coverage (%)	67	44
<i>C<sub>b</sub></i> MAE (µg m <sup>-3</sup> )	0.33	0.56
% Change <i>C<sub>b</sub></i> ± MAE <sup>1</sup>	-5% +5%	-31% +31%
% Change <i>R<sub>c</sub></i> ± 20%	-2% +3%	-3% +3%
% Change <i>R<sub>c</sub></i> ± 50%	-4% +12%	-5% +5%
% Change <i>AC<sub>min</sub></i> ± 67% <sup>2</sup>	-	-9% -1%

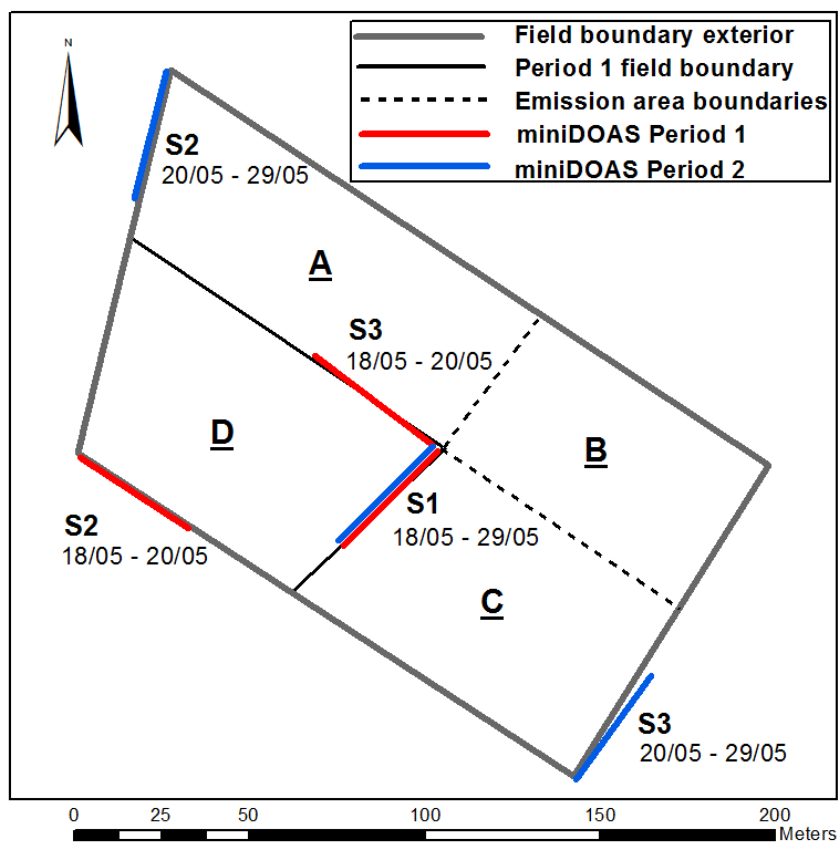
<sup>1</sup>The predicted *C<sub>b</sub>* timeseries input to the bLS-R model is varied by the Mean Absolute Error (MAE) between the measured and predicted *C<sub>b</sub>*. The first value in all cases the % change + variation and the second the % change – variation.  
<sup>2</sup> The percentage change in *Q<sub>dep</sub>* is given after varying the source area coefficient parameter *AC<sub>min</sub>* by 67% (0.075 ± 0.05).

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785 **Figures**



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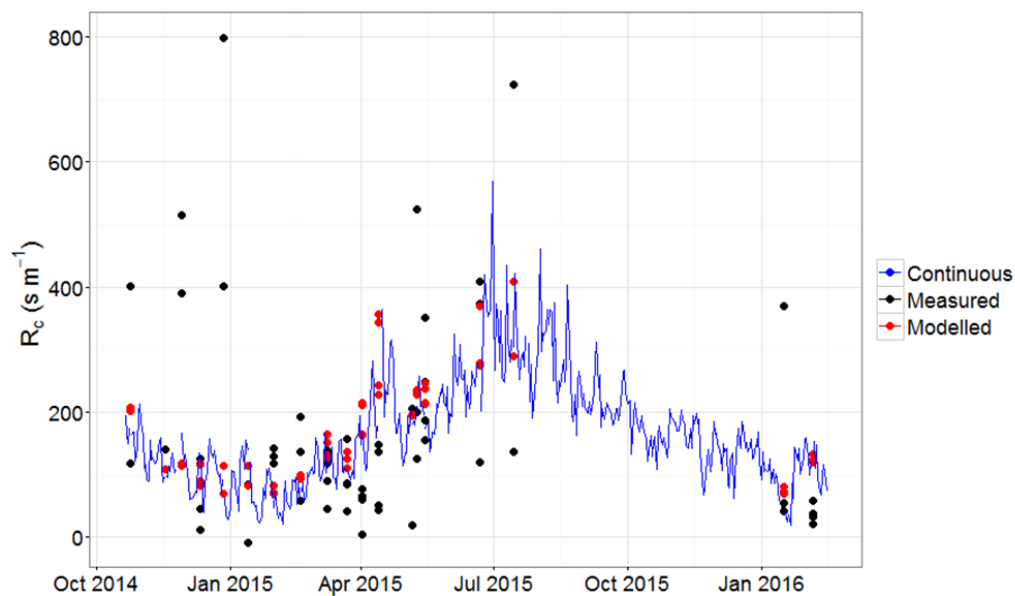
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**Figure 1:** Map of the grazed field showing positions of the three miniDOAS open-path measurement systems. During Period 1 (18-20/05) 25 cattle were fenced within the SW field section (area D). During Period 2 (20-29/05) the internal field boundaries were removed so that the cattle could graze the whole field. Later, for the attribution of emissions across the field, emission area quadrants have been allocated, marked A-D. There were no physical barriers between the emission areas during Period 2.





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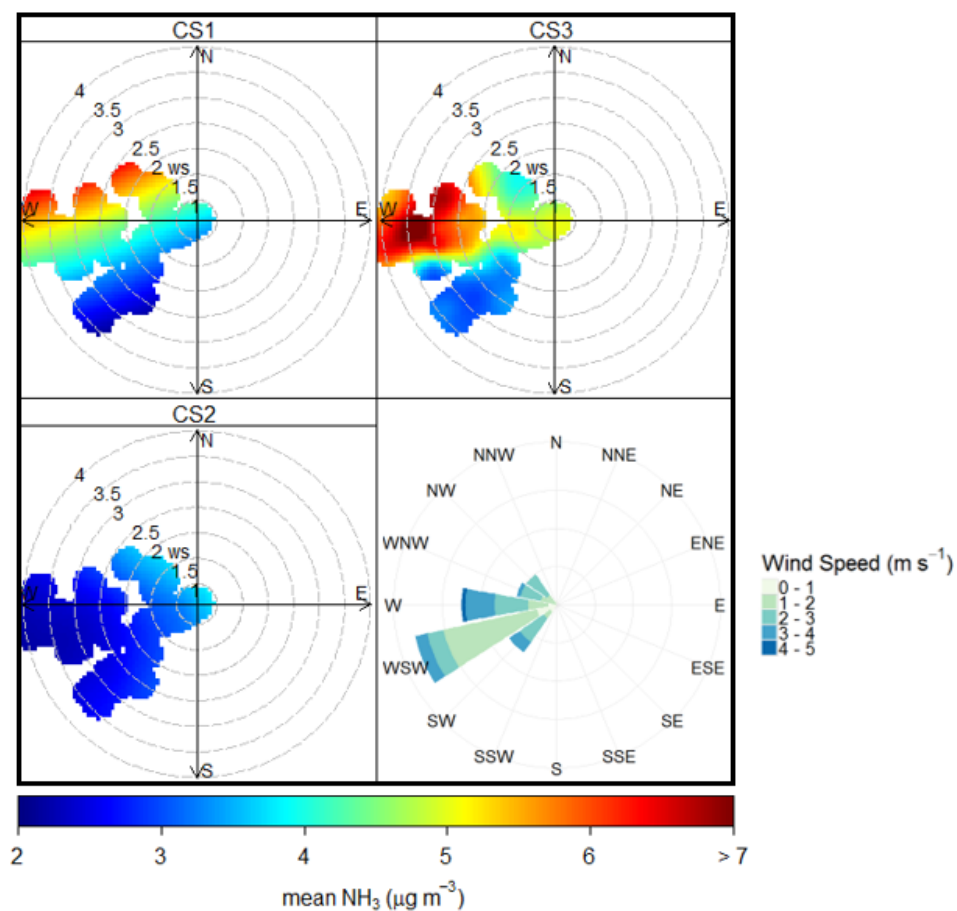
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Figure 2: Timeseries of time-integrated COTAG  $R_c$  measurements and Equation 4  $R_c$  estimates. The blue line represents continuous  $R_c$  estimates calculated from the daily mean  $T$  and  $RH$  measurements at the field site. Black points are the measured  $R_c$  values from the COTAG systems, and the red points are the modelled  $R_c$  from the same time-integrated data.



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801 Figure 3: Polar plots showing averaged  $\text{NH}_3$  concentrations (colour axis) as a function of wind speed (radial axis) and  
802 wind direction (cardinal direction) for each miniDOAS system, and a windrose showing the prevailing wind  
803 direction, Period 1 (18-20/05). The concentration Polar plots were produced using the OpenAir R package (Carslaw  
804 et al., 2014).

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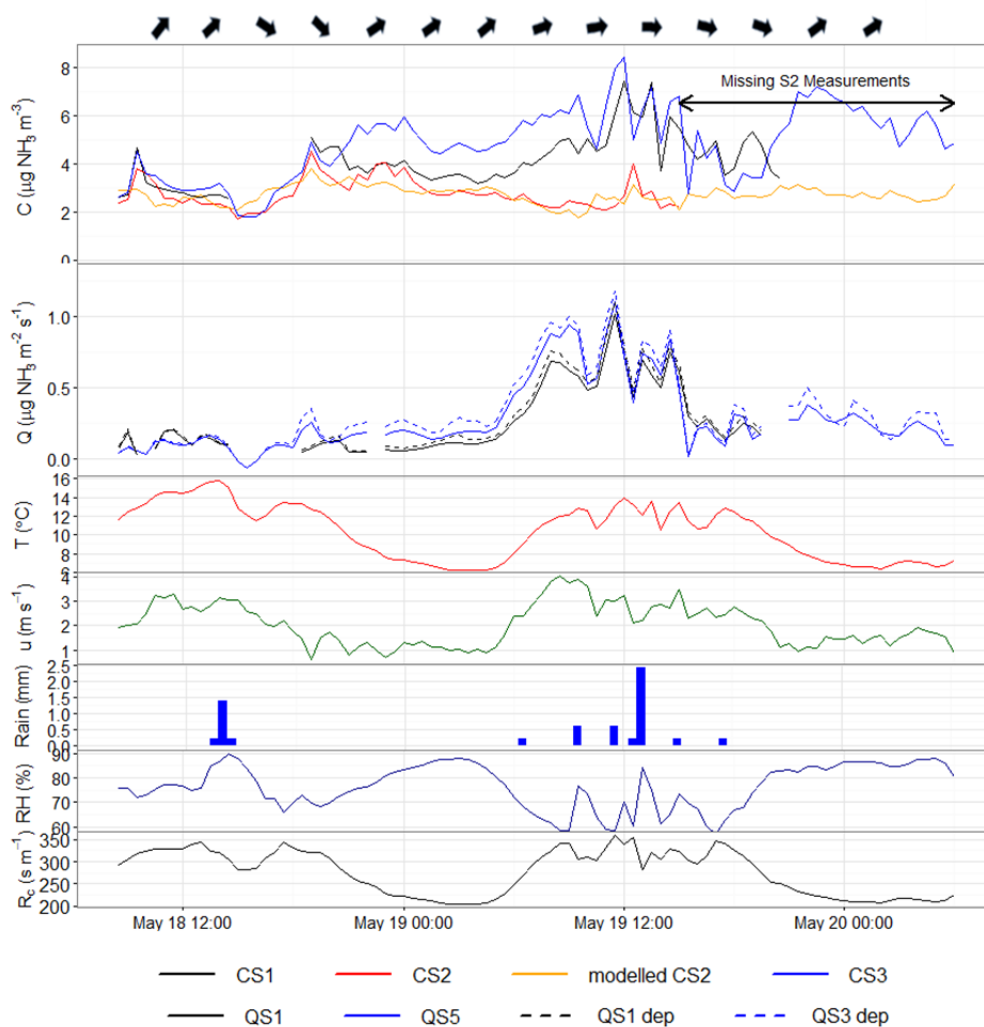
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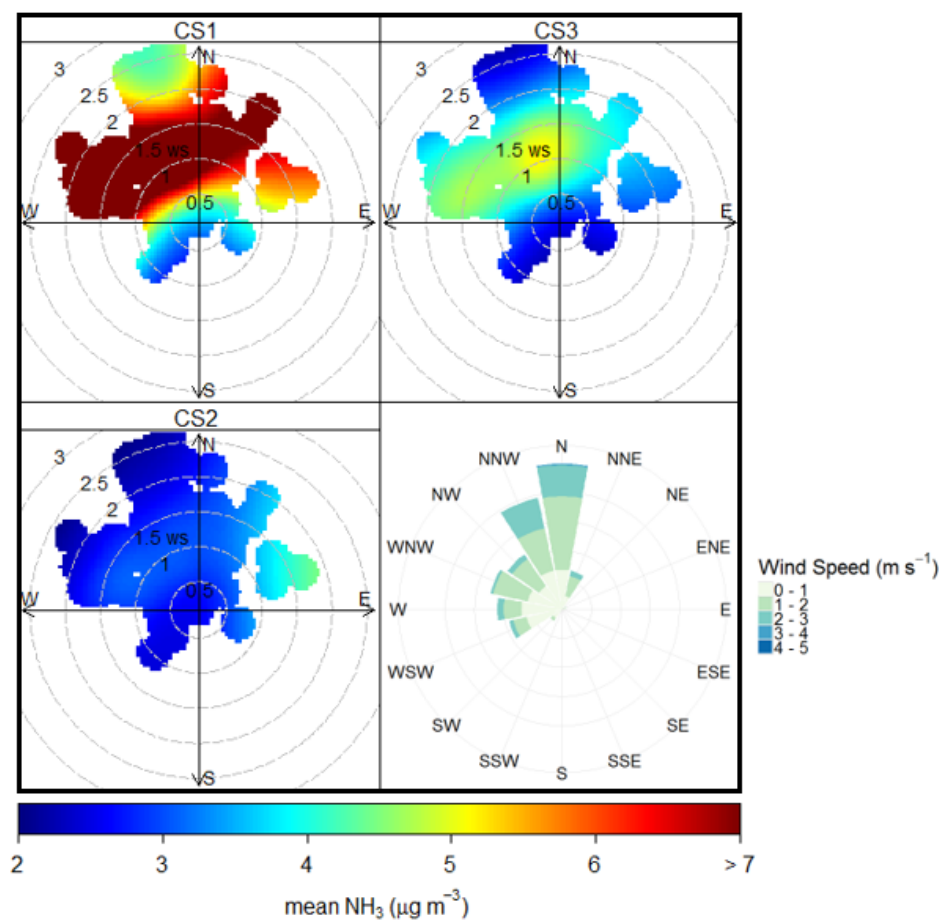
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816 **Figure 4:** Timeseries of Period 1 DOAS concentration measurements (CS1, CS2, CS3, and modelled CS2 using  
 817 Equation 6, top panel) and bLS-R emission estimates ( $Q$  and  $Q_{dep}$  scenarios, second panel), with  $T$ ,  $u$ , Rain,  $RH$ , and  
 818 modelled  $R_c$  using Equation 5 shown in the panels below. Wind direction arrows are set above the top panel to  
 819 visualise changes over time.

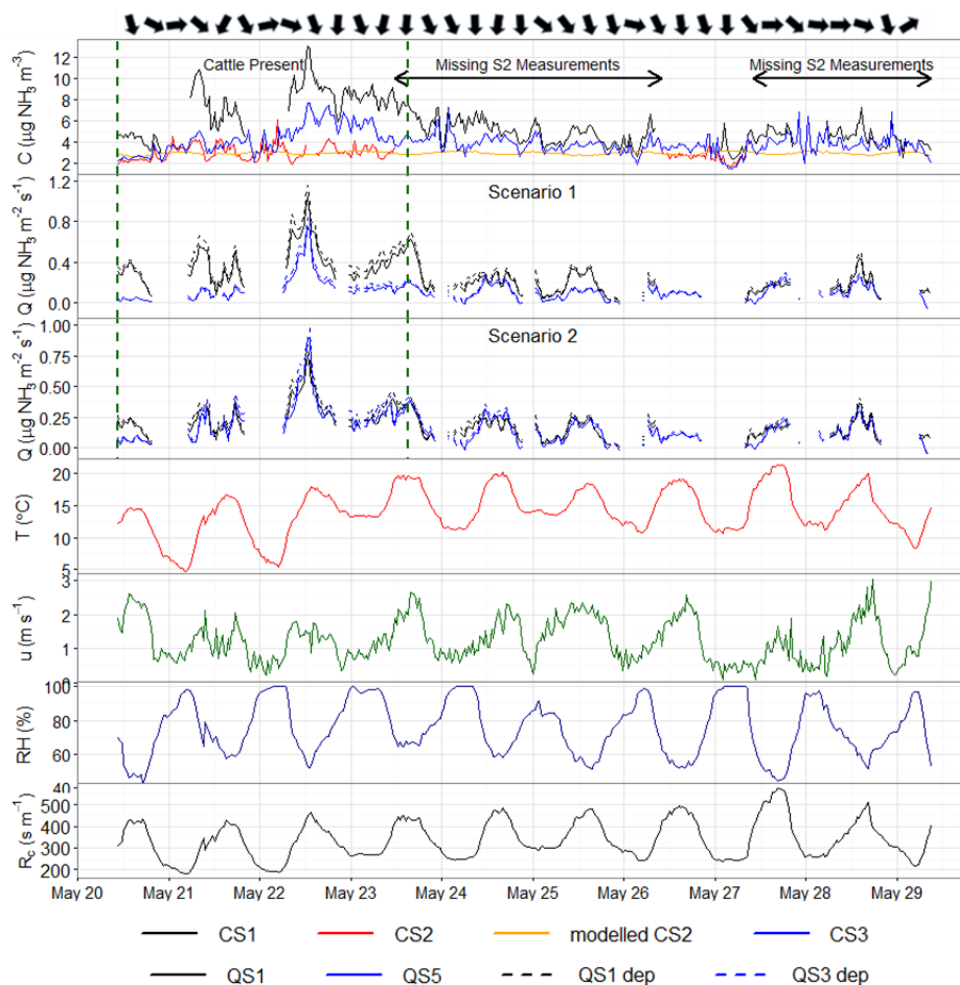


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Figure 5: Polar plots showing averaged NH<sub>3</sub> concentrations with wind speed and direction for each DOAS system, with a windrose showing the prevailing wind directions, Period 2 (20-29/05).



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824 **Figure 6:** Timeseries of Period 2 DOAS concentration measurements (top panel) and bLS-R emission estimates  
 825 (second and third panels, showing the  $Q$  (solid lines) and  $Q_{dep}$  (dashed lines) scenarios); with  $T$ ,  $u$ ,  $RH$ , and  $R_c$  (with  
 826  $130 \text{ s m}^{-1}$  offset) shown in the panels below. The second panel shows the Scenario 1 (homogenous field) emission  
 827 estimates, while the third panel contains the optimised Scenario 2 estimates using the heterogeneous source area  
 828 coefficients given in Table 1. Periods with missing S2 background concentration measurements are annotated on the  
 829 top panel to highlight the higher uncertainty of these periods for emission estimates. Wind direction arrows are set  
 830 above the top panel to visualise changes over time. The dashed green lines on the top panels mark the 3-day time  
 831 period where the cattle were grazing the field.

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