

AC0221 Annex 2

Review of nitrous oxide emissions

The current UK greenhouse gas (GHG) emissions inventory (MacCarthy *et al.*, 2010, inventory year 2008) estimates that 75% of nitrous oxide (N₂O) is produced from agriculture, amounting to 82,070 t N₂O (25,443,160 t CO₂e). Approximately 60% of the N₂O produced from agriculture is directly emitted from agricultural soils. Less than 10% of agricultural N₂O is emitted from manure management and c.30% is emitted indirectly from soils from two mechanisms, namely:

- i) following N loss via ammonia (NH₃) volatilisation/NO_x emission (c.20%),
- ii) nitrate (NO₃⁻) leaching (c.80%).

Nitrogen directly lost from agricultural soils, either by NO₃⁻ leaching or NH₃ emissions to the atmosphere, may subsequently become potentially available for loss as N₂O.

Overall, N₂O emissions from soils account for more than 50% of GHG emissions from UK agriculture, on a CO₂e basis. Of these, the most important N₂O emissions are from fertiliser N applications, grazing (urine) returns and manure applications to land.

Under the Kyoto Protocol, the UK is required to reduce its GHG emissions by 12.5% relative to 1990 levels by the period 2008-2012. Furthermore, GHG emission reductions are required from agriculture (in common with all other sectors) in order to meet the reduction targets set by the UK Climate Change Act 2008, as detailed in the Low Carbon Transition Plan recently published by DECC. Agriculture, therefore, has a significant role to play in helping to achieve these GHG emission reduction targets.

Agricultural N₂O mitigation methods based on changes in on-farm management practices (without the introduction of new technologies) could provide potentially lower cost alternative strategies that might be more readily taken up by the agricultural industry. One such example of a 'soft' mitigation strategy is strategic fertiliser nitrogen (N) application timing. A number of recent reviews of potential N₂O mitigation strategies for agriculture have placed a high priority on the need for assessment of fertiliser N timings under UK conditions.

For example:

- Defra project IF0175. *A Critical Review of Recent Policy-Relevant Research in Nitrogen Cycling* recommended that "Splitting applications of N deserves to be more fully investigated".
- Defra project AC0206. *A Review of Research to Identify Best Practice for Reducing Greenhouse Gases from Agriculture and Land Management*. "There is a need to develop improved mineral fertiliser N application timing policies that explicitly aim to reduce N₂O emissions" (Key Knowledge gap 7.1).
- Dairy Co project F08/019 (Crompton *et al.*, 2009). *A Desktop Review of Greenhouse Gas (GHG) Emissions*. Future Research Recommendations: "More tactical application timings of fertiliser N could result in reduced N₂O emissions."
- Defra project RMP4950. *UK Marginal Abatement Cost Curves for Agriculture and Land Use, Land-Use Change and Forestry Sectors out to 2022, with Qualitative Analysis of Options to 2050*. This project highlighted the benefits of improved timing of mineral fertiliser N application and based on 'expert judgement' estimated that such practices would result in small (3-5%) increases in yield through more efficient use of nutrients, but judged that there would be no reduction in N use (i.e. the applied N rate). The improved timing of mineral fertiliser N application was estimated to apply to 80% of the combinable crop area, 70% of the grassland/root crop area and 50% of other crop areas.
- Defra project RMP/5142. *Analysis of Policy Instruments for Reducing Greenhouse Gas Emissions from Agriculture, Forestry and Land Management*. This project was rather more

conservative in estimating the GHG reduction potential of mitigation methods identified in Defra project RMP4950 (see above) – estimating that abatement potential may be “around half of that suggested in RMP4950”. In terms of the improved timing of mineral fertiliser N applications this was estimated to be applicable to 10% of land and highlighted that there would be associated other water quality benefits, but more energy would be used in the need to apply more N applications.

Nitrous oxide emissions from agricultural soil are predominately produced via the microbially mediated processes of nitrification and denitrification (Firestone and Davidson, 1989). The key factors which control the magnitude of N_2O emission include; soil mineral nitrogen content (particularly soil nitrate), soil temperature and soil moisture content (Dobbie & Smith, 2001; Dobbie & Smith, 2003).

The typical non-linear response of N_2O to moisture content as represented by water-filled pore space (WFPS) is shown by Davidson (1991) in Figure 1. This diagram indicates that there is an optimum production of N_2O , which occurs at a WFPS roughly equal to a transition point below which N_2O is predominantly emitted from the aerobic process of nitrification and above which N_2O is predominantly emitted from the anaerobic process of denitrification. Davidson suggests that this transition occurs at a WFPS of 60%. Other research, however, has shown that the position of the maximum emission can vary with soil type and conditions. Notably, UK studies have indicated that the maximum (i.e. largest) N_2O emissions frequently occur under more anaerobic conditions i.e. at a WFPS >60% (Dobbie *et al.* 1999; Dobbie & Smith, 2001; Dobbie & Smith, 2003). For example, in a laboratory study using arable soil, Dobbie & Smith (2001) measured an approximate 30 fold increase in N_2O emissions as the WFPS increased from 60 to 80%. These emissions are likely to be from denitrification and are commonly short-term episodic events that develop with the onset of the anaerobic soil conditions, as a result of the increase in soil WFPS.

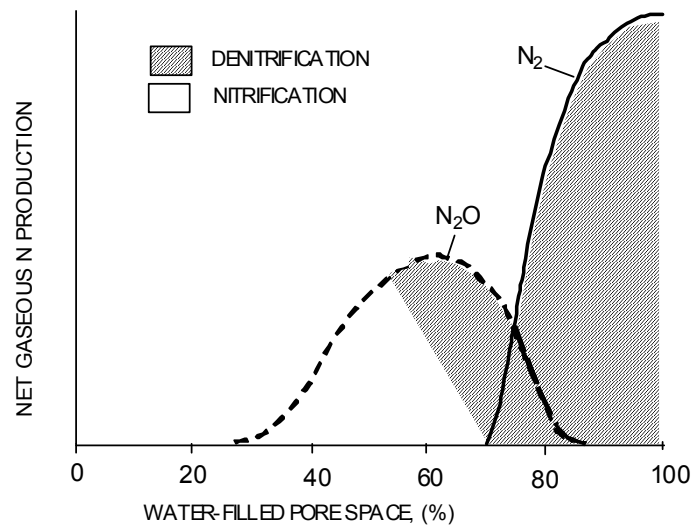


Figure 1. Schematic representation of the effect of water-filled pore space on emissions of N_2O and N_2 , by nitrification and denitrification (Source Davidson, 1991).

The WFPS of the soil is controlled by the water addition processes of rainfall and irrigation, and the water removal processes of evapotranspiration and drainage. Consequently, the amount and distribution of rainfall is frequently considered to be a strong driver of N_2O loss, particularly during the crop growing season. Following N fertiliser application N_2O emission from soil is unlikely to be limited by the mineral N content and, therefore, temperature and moisture are likely to be more critical in influencing the magnitude of loss.

Effect of N fertiliser application timing

To our knowledge there are no experiments that have been carried out in England specifically designed to examine the effect of N fertiliser application timing to arable (or grassland) crops on N₂O fluxes. Experiments have, however, been carried out to quantify the effect of contrasting slurry application timings on N₂O losses.

Results from Defra project ES0115 (OPTI-N), where direct and indirect N₂O losses were measured following the application of slurry to free draining arable land or grassland showed that generally the highest N₂O losses were associated with slurry applications in October, November and December, when temperatures were relatively warm, soils were moist and crop growth (and nitrogen uptake) was slow. The lowest N₂O losses ($\leq 0.20\%$ of total N applied) were generally associated with slurry applications during periods of active crop growth (i.e. spring and early autumn for oilseed rape), where crop N uptake reduced the soil mineral N pool potentially available for loss as N₂O and when the soil was either dry and/or relatively cold.

Principally, five pairs of measurements following cattle slurry applications on grassland soils showed that direct N₂O losses were greater ($P < 0.05$) from autumn/winter slurry applications (1.10% total-N applied) than from spring (0.51% total-N applied) applications (Thorman *et al.*, 2007). This difference was attributed to slurry being applied in close relation to crop demand and during a period when the soil was relatively cool and drying out in spring, compared with the late autumn/winter period when there was little crop demand for N and soils were relatively warm and wet.

Two pairs of measurements following slurry application on arable land (one winter wheat, one winter oilseed rape) showed that there was no consistent effect of slurry application timing on direct N₂O emissions, probably as a result of complex interactions primarily between soil moisture, soil temperature and crop uptake on the pattern of N₂O loss. For example, in February following pig slurry application to oilseed rape, emissions continued at a low rate over the first 40 days, probably because the 'cold' weather (mean air temperature of 2.5°C over 28 d after application) during February and early March restricted soil microbial activity. Towards the end of the c.2.5 month monitoring period N₂O emissions increased concurrently with a rise in temperature and substantial rainfall resulting in an increasing net cumulative N₂O emission.

In order to fully account for total N₂O emissions following fertiliser/manure application it is necessary to not only consider direct losses of N₂O, but to also include losses that occur indirectly following application as a result of nitrate leaching and as ammonia volatilisation. The importance of including losses of ammonia- and nitrate-N, which may be subsequently converted to N₂O in the wider environment, is shown in figure 2.

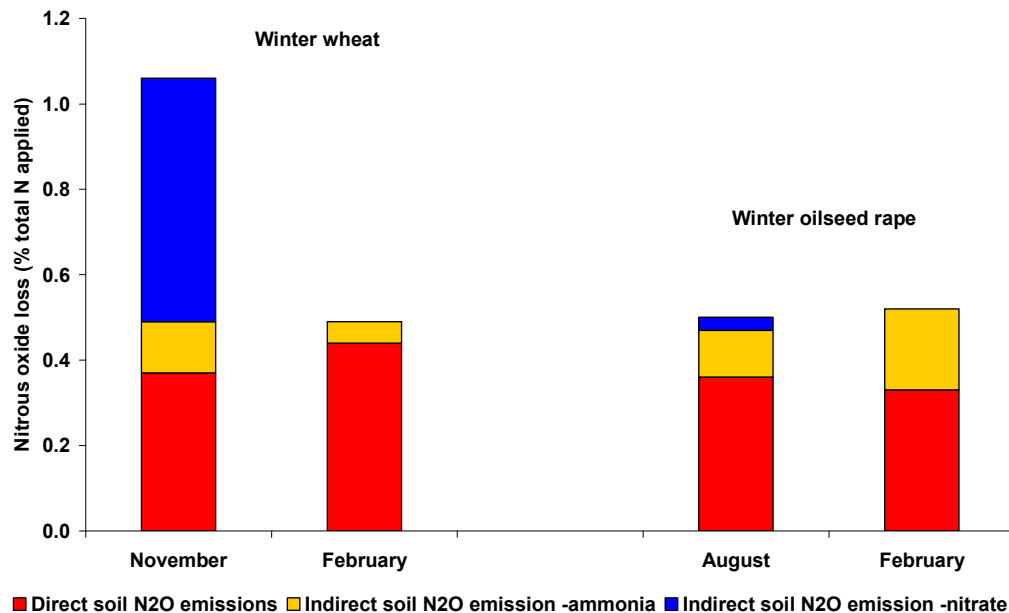


Figure 2. Total nitrous oxide emissions following the application of slurry to arable land

On arable land, the elevated nitrate leaching losses (20% of total N applied) and ammonia losses (11% of total N applied) following a November cattle slurry application to winter wheat gave estimated indirect N₂O emissions equivalent to 0.69% of total N applied, which was c.2-fold greater than the direct emissions following application at 0.37% of total N applied. In contrast, indirect N₂O emissions following pig slurry application in August to oilseed rape were estimated at equivalent to only 0.14% of total N applied reflecting the low nitrate leaching losses (1% of total N applied) and ammonia losses (10% of total N applied) following application. Indirect emissions following slurry applications in February to oil seed rape and to winter wheat were low at 0.19 and 0.05 % of total N applied, respectively, reflecting the lack of nitrate leaching losses and low ammonia volatilisation losses (7-13% of total N applied) following application.

The handling and application issues of slurry gives rise to autumn and winter slurry application timings. Cereals, however, do not have a requirement for nitrogen in the autumn/winter period and recent work has suggested that neither does winter oil seed rape. Consequently, the need for applications of manufactured N fertiliser in autumn/winter is minimal. It is, therefore, unlikely that the results from Defra project ES0115 comparing autumn/winter and spring application timings will directly translate to the application of manufactured N fertiliser. The results do, however, give an indication of the importance of application timing and, despite the lack of strong individual relationships between N₂O loss and environmental factors, highlight the complex nature of N₂O emission and the interaction between environmental controls (particularly temperature and the pattern and quantity of rainfall) and crop uptake.

To our knowledge, although no experiments in England have been specifically designed to examine the effect of manufactured N fertiliser application timings on N₂O losses, it has been possible to analyse data from previous studies, which may provide some limited evidence to develop N fertiliser application timing recommendations aimed at minimising direct N₂O emissions.

Nitrous oxide emission factors (EFs) were collated in a database containing the results of field studies where manufactured N fertiliser was applied to winter cereals in England. Experimental data had to satisfy certain criteria e.g. a full measurement period of c.12 months (IPCC compliant) before they were included in the data set. Data were also deemed

acceptable, even if the measurement period was <12 months, but >6 months, and if significant N₂O emissions were no longer likely e.g. due to the presence of an actively growing crop. Selection criteria resulted in the inclusion of data from a total of 2 experiments (Defra-funded projects NT2605 and AC0101) resulting in 92 N₂O measurements at a range of sites in England. In order to minimise confounding factors the database was further refined. Data from the two experiments were only included in the dataset if the fertiliser applied was ammonium nitrate and if the fertiliser application rate followed recommended practice (Anon, 2000). This resulted in a database containing 23 N₂O measurements (Appendix 1.) and is summarised in table 1.

As is common practice, the fertiliser was applied in 3 splits, although on one occasion only 2 splits were applied. Emission factors expressed as the % of total N applied lost as N₂O were calculated for each of the fertiliser application splits. Assuming that 3 splits were applied, the measurement period (mean 30 days) for the first 2 splits ended immediately before the next split was applied. For the last fertiliser split, in order to compare results on a similar basis to those from the first two splits, EFs were calculated over a measurement period which was as close as possible to the mean measurement period from the first 2 splits i.e. c.30 d. It is acknowledged that the length of the measurement periods did vary (16 to 63 days) and this may have influenced the amount of N₂O emitted following fertiliser application. Indeed, this is clearly demonstrated with the two mean EFs calculated following the 3rd fertiliser application split (Table 1). The mean EF calculated from application until the end of the full measurement period (c.285 days) was more than double that calculated over the c.30 d period following application, indicating that significant N₂O loss was measured after c.30 days.

Table 1 Summary of N₂O-N emission factors (EF) following the application of ammonium nitrate fertiliser to winter cereals in England

	1 st fertiliser split	2 nd fertiliser split	3 rd fertiliser split	3 rd fertiliser split
Application date	Early to mid March	Early to mid April	End April to mid May	End April to mid May
Mean measurement period (days)	34	25	30	286
Mean EF (% of total N applied)	0.21	0.13	0.62	1.44
Standard error of the mean	0.08	0.04	0.14	0.24
Median EF (% of total N applied)	0.14	0.10	0.63	1.62
Maximum EF (% of total N applied)	0.71	0.31	1.19	2.22
Minimum EF (% of total N applied)	0.00	0.04	0.05	0.38
Number of measurements	8	7	8	8

Analysis of the database shows that over a c.30 day measurement period following ammonium nitrate application significantly greater ($P<0.01$) emissions of N₂O occurred after the 3rd split (0.62% total N applied) than from the 1st (0.21% total N applied) or 2nd (0.13% total N applied) splits. The database also contains information collected in the experiments on environmental variables which are known to strongly control N₂O emissions e.g. rainfall, temperature etc. Emission factors were plotted against these variables in order to try to understand the processes driving the larger emissions measured after the 3rd fertiliser application split. There were no significant individual relationships between N₂O loss and air temperature, rainfall or WFPS. Plotting N₂O loss vs both temperature and rainfall or WFPS

did, however, improve our understanding of the controlling variables. Emission factors were plotted against total rainfall and the mean air temperature calculated over the week before application and 3 weeks after. This 4 week period was chosen because it produced the most significant relationship and best fit between N₂O emission and rainfall in earlier studies following fertiliser application to grassland in Scotland (Dobbie *et al.*, 1999) and to grassland in the UK (Dobbie & Smith, 2003). A better relationship was, however, observed with our data when the N₂O EFs were plotted against mean air temperature calculated over the week before application and 3 weeks after, and either total rainfall calculated over 7 days after application ($R^2 = 0.60$; $P < 0.01$) (Figure 3) or WFPS calculated over the week before application and 3 weeks after ($R^2 = 0.49$; $P < 0.01$) (Figure 4).

Figures 3 and 4 show that threshold levels of rainfall and temperature exist where clearly the greatest emissions occurred when the soils were both warm and wet, conditions which frequently occurred after the 3rd split application. Even with heavy rainfall, if the temperature was $< 10^\circ\text{C}$, generally large emissions did not occur, which was a combination routinely observed following the first 2 split applications. Similarly, even with temperatures $> 10^\circ\text{C}$, if the total rainfall was $< c.20$ mm large emissions also were not generally measured. Clayton *et al.* (1997), also reported the existence of threshold levels of soil temperature and WFPS following the application of N fertiliser to grassland in Scotland. With mesh plots showing a similar relationship to ours, they reported a steep rise in N₂O emissions with temperature where WFPS or mineral N values were not limiting.

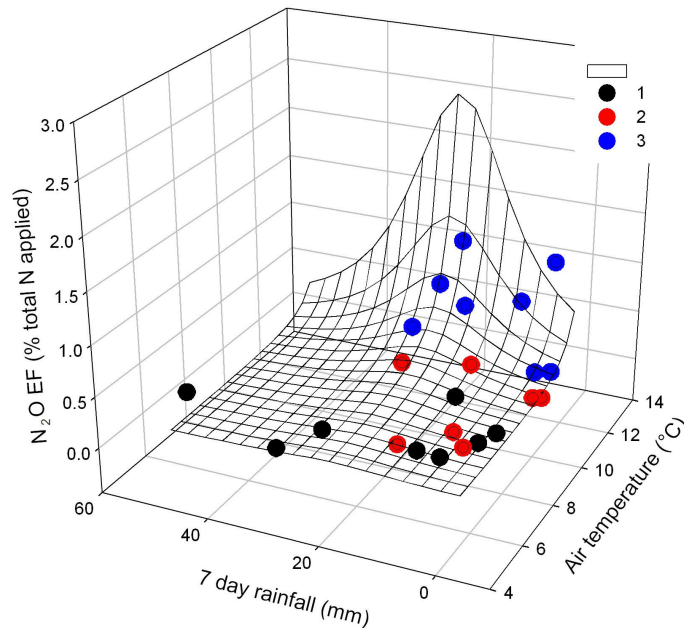


Figure 3. Relationship between N₂O emission factors (EF) (% of total N applied) calculated over c.30 d following the application of ammonium nitrate fertiliser to winter cereals and, mean air temperature calculated over a 4-week period from 1 week before fertiliser application to 3 weeks after and cumulative rainfall calculated over 7 days after application. Black dots represent data from the 1st fertiliser split; Red dots represent data from the 2nd fertiliser split; Blue dots represent data from the 3rd fertiliser split.

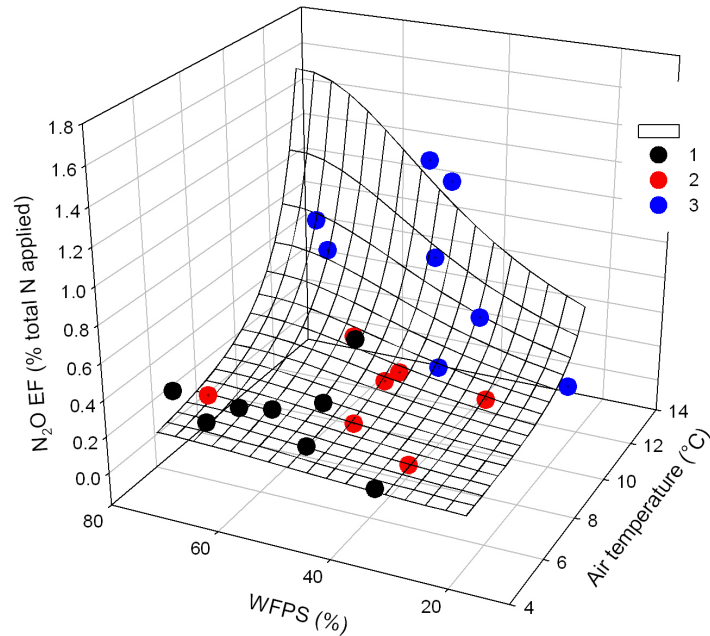


Figure 4. Relationship between N₂O emission factors (EF) (% of total N applied lost as N₂O) calculated over c.30 d following the application of ammonium nitrate fertiliser to winter cereals and, mean air temperature and WFPS both calculated over a 4-week period from 1 week before fertiliser application to 3 weeks after. Black dots represent data from the 1st fertiliser split; Red dots represent data from the 2nd fertiliser split; Blue dots represent data from the 3rd fertiliser split.

Our mesh plots suggest, therefore, that the larger emissions measured following the 3rd split fertiliser application may be related to the increased risk of the coincidence of both wet and relatively warm soils at this time of year i.e. late spring. Indeed runs of the model UK-DNDC showed that delaying each of three split fertiliser applications by one month generated a large increase in emission concurrent with an increase in temperature (Brown *et al.*, 2002). In a laboratory study using soil cores taken from arable fields in Scotland, Dobbie & Smith (2001) also demonstrated the importance of soil temperature in controlling N₂O emissions. They reported that, “temperature had a profound effect on the size of the mean N₂O emissions, particularly over the 5-12°C range”, i.e. a similar range to that which our data spans.

The two experiments which produced the measurements in the database were not, however, specifically designed to examine the effects of fertiliser application timing on N₂O emissions. Consequently, it was impossible to determine the contribution of each fertiliser application to each split EF. Residual fertiliser N remaining in the soil from the first two split fertiliser applications may also have contributed to the greater emissions measured following the 3rd split fertiliser application. Fertiliser N from the first two application splits may have remained in the soil until soil conditions developed which were suitable for substantial N₂O loss, a phenomenon described above which occurred following pig slurry application to oilseed rape in early spring. Nonetheless, the limited evidence would suggest that in order to minimise N₂O emissions following the application of manufactured N fertiliser, early to mid spring applications may be preferable compared with applications in late spring when temperature is less likely to be the limiting factor to N₂O loss.

Effect of altering N fertiliser application timing and quantity

Previous work has shown that under certain conditions there is a good relationship between soil mineral N surpluses at the field (and farm) level and N₂O emissions (Schils *et al.*, 2008; van Groenigen *et al.*, 2008). Applications of fertiliser N in excess of crop requirement will lead

to increased N₂O emissions, particularly, as discussed above, if applied under conditions conducive to elevated emissions i.e. 'wet' and warm soil conditions (e.g. Chantigny et al., 1998). Potentially avoiding applications under such conditions would reduce high emissions, but other than generally minimising late spring applications, such a strategy relies on being able to accurately forecast weather conditions up to a month after application (i.e. during the period after application when emissions are likely to be at their peak) and to be able to travel on soils when required, which is not always possible on the heavy soils that predominate in England. More frequent applications of smaller amounts of fertiliser N in close synchrony with crop requirements would minimise soil mineral N levels at risk from elevated N₂O losses at any point in time, including those when conditions are conducive to high N₂O emissions. Modelling studies predict that such a strategy would increase crop yields and N recovery and decrease gaseous N and leaching losses (e.g. del Grosso et al., 2002; del Prado et al., 2004). However, no UK data exists to validate these predictions and very few literature data exist from elsewhere; Sithaphanit et al. (2009) reported that increasing the number of split fertiliser N applications increased N use efficiency in maize (Thailand) and Burton et al. (2008) showed that split N application timings could reduce N₂O emissions from potatoes (Canada), but this was not consistent over all years. Experiments currently being carried out within Defra project AC0213 will, however, assess the potential for optimising fertiliser N application timings (i.e. "little and often" policies) to reduce N₂O emissions from cereal crops and grassland under UK conditions.

Effect of fertiliser type

Taking all the full-season EFs for AN and urea from both the NT2603 and NT2605 results together (12 experiments; and including CAN for the Hillsborough site in 2003 with the AN values, as AN could not be used there), the overall mean EFs are 2.02% for AN and 1.51% for urea. Correcting for the actual amount of AN entering the soil, the effective EF becomes $(1/0.975) \times 2.02 = 2.07\%$, while the corresponding value for urea is $(1/0.75) \times 1.51 = 2.01\%$. If one then applies the IPCC default value of 1% of the volatilised/redeposited N being converted to N₂O and combines this value with that for the direct emission, this will increase the overall "effective EF" for AN to 2.1%; there is a larger increase for urea because of the greater proportion volatilised, giving an effective EF of 2.26%. The difference between these "effective EFs" for the two N forms was not significant. Brentrup and Palliere (2008) estimated that the GHG emissions upon application were 9.33 kg CO₂e per kg N for urea and 5.62 kg CO₂ per kg of N for ammonium nitrate. When the manufacturing costs were included the GHG costs were 10.91 kg CO₂e per kg N for urea and 11.82 kg CO₂ per kg of N for ammonium nitrate.

Appendix 1 N₂O-N emission factors following the application of ammonium nitrate fertiliser to winter cereals in England

Defra project	Soil type	1 st fertiliser split			2 nd fertiliser split			3 rd fertiliser split		
		Date applied	EF (% of total N applied)	Measurement period (days)	Date applied	EF (% of total N applied)	Measurement period (days)	Date applied	EF (% of total N applied)	Measurement period (days)
NT2605	Silty clay loam	02/03/2004	0.34	35	05/04/2004	0.31	33	07/05/2004	0.61	29
NT2605	Clay loam	09/03/2005	0.17	41	19/04/2005	0.11	23	11/05/2005	0.05	27
AC0101	Clay loam	12/03/2007	0.12	22	02/04/2007	0.04	29	30/04/2007	1.04	30
AC0101	Loamy sand	05/03/2007	0.71	29	02/04/2007	0.10	22	23/04/2007	0.09	25
AC0101	Sandy loam	14/03/2007	0.02	63	-	-	-	15/05/2007	0.64	31
AC0101	Clay loam	13/03/2008	0.00	26	07/04/2008	0.09	22	28/04/2008	1.19	30
AC0101	Loamy sand	11/03/2008	0.05	28	07/04/2008	0.04	16	22/04/2008	0.54	37
AC0101	Sandy loam	04/03/2008	0.25	29	01/04/2008	0.22	28	28/04/2008	0.78	30