Higher N2O emissions from organic compared to synthetic N fertilisers on sandy soils in a cool temperate climate

Petersen, Søren O.; Peixoto, Leanne E.k.; Sørensen, Helle; Tariq, Azeem; Brændholt, Andreas; Hansen, Line Vinther; Abalos, Diego; Christensen, Alice Thoft; Nielsen, Cecilie Skov; Pullens, Johannes W.m.; Bruun, Sander; Jensen, Lars Stoumann; Olesen, Jørgen E.

Published in:
Agriculture, Ecosystems and Environment

DOI:
10.1016/j.agee.2023.108718

Publication date:
2023

Document version
Publisher's PDF, also known as Version of record

Document license:
CC BY

Citation for published version (APA):
Higher N\textsubscript{2}O emissions from organic compared to synthetic N fertilisers on sandy soils in a cool temperate climate

Søren O. Petersen\textsuperscript{a,}\textsuperscript{*}, Leanne E.K. Peixoto\textsuperscript{a}, Helle Sørensen\textsuperscript{b}, Azeem Tariq\textsuperscript{c,1}, Andreas Brændholt\textsuperscript{a}, Line Vinther Hansen\textsuperscript{c}, Diego Abalos\textsuperscript{a}, Alice Thoft Christensen\textsuperscript{d}, Cecilie Skov Nielsen\textsuperscript{d}, Johannes W.M. Pullens\textsuperscript{a}, Sander Bruun\textsuperscript{c}, Lars Stoumann Jensen\textsuperscript{c}, Jørgen E. Olesen\textsuperscript{a}

\textsuperscript{a} Department of Agroecology, Aarhus University, Tjele, Denmark
\textsuperscript{b} Data Science Lab, Department of Mathematical Sciences, University of Copenhagen, København Ø, Denmark
\textsuperscript{c} Department of Plant and Environmental Sciences, University of Copenhagen, Frederiksberg C, Denmark
\textsuperscript{d} SEGES Innovation P/S, Aarhus N, Denmark

\* Corresponding author.
\textit{E-mail address: sop@agro.au.dk} (S.O. Petersen).
\textsuperscript{1} Present address: School of Environmental Sciences, University of Guelph, Canada

\textbf{A B S T R A C T}

The atmospheric increase in N\textsubscript{2}O is mainly derived from N fertilisation in agriculture, and improved emission estimates are needed for effective mitigation. This study presents first estimates of country-specific N\textsubscript{2}O emissions from synthetic and liquid organic fertilisers in Denmark. Representative crop rotations were established in four locations across Denmark to provide a realistic context for the estimation of N\textsubscript{2}O emissions, i.e., a dairy farm rotation in Western Denmark, dairy and pig farm rotations in Southwestern Denmark, and an arable rotation in Eastern Denmark. The four sites were light-textured and typical for Northern Europe, whereas rainfall varied considerably among sites and years. A randomised block design was used, and all crops were represented in triplicate each year with monitoring of N\textsubscript{2}O emissions between April 2020 and March 2022. Spring barley was part of all rotations, and here three synthetic fertilisers (NS, NPK and urea ammonium nitrate) and eight organic fertilisers (three cattle slurries, three pig slurries and two digestates) were applied in 1 m\textsuperscript{2} plots at either two or four sites in order to compare N\textsubscript{2}O emissions from the same N fertiliser materials under contrasting site conditions. Identical methodologies for management, fertiliser application, and N\textsubscript{2}O measurement and flux calculation, were used at all sites to ensure comparability. Manually operated chambers were used for N\textsubscript{2}O flux measurements. The continuous monitoring indicated a strong seasonal pattern across all four sites with the main part of N\textsubscript{2}O emissions during spring. The side-by-side comparison of several N sources at four sites in two years showed for synthetic fertilisers an average N\textsubscript{2}O emission factor for the spring period of 0.15\% (95\% C.I. –0.17 to 0.37\%, n = 16), and for liquid organic fertilisers (pig and cattle slurries, and digestates) an average of 1.02\% (95\% C.I. 0.75 – 1.30\%, n = 44). The higher N\textsubscript{2}O emissions from organic fertilisers, which was significant at each of the four sites, is in opposition to new N\textsubscript{2}O emission factors recently proposed in a refinement of the IPCC methodology for national inventories. The conflicting results are discussed with reference to region-specific site conditions and fertiliser types, and in particular the predominance of soils with a low clay content, and of liquid manure management, may explain the deviations from global estimates. A comparison of annual and spring N\textsubscript{2}O emissions indicated a difference in the order of 0.1 – 0.2\% of the N input (n = 8), and the feasibility of estimating N\textsubscript{2}O emission factors based on emissions during the growing season only is discussed.

\textbf{1. Introduction}

Agriculture contributed around 52\% to global anthropogenic emissions of nitrous oxide (N\textsubscript{2}O) during 2007–2016, and the annual emission, at 5.6 (3.6–8.7) Tg N yr\textsuperscript{-1} in the 1980s, currently increases at a rate of 0.6 ± 0.2 Tg N yr\textsuperscript{-1} per decade (Tian et al., 2020). Most of this...
increase originates from the use of synthetic fertilisers and recycling of livestock manure as organic fertiliser, and therefore N\textsubscript{2}O mitigation strategies are needed which address these sources.

The documentation of N\textsubscript{2}O mitigation requires rigorous estimates of current emissions, but the default (Tier 1) emission factors (EFs) for N\textsubscript{2}O recommended by the Intergovernmental Panel on Climate Change (IPCC), which most countries use for national inventories, have large uncertainty ranges (IPCC, 2006). A recent refinement of the Tier 1 N\textsubscript{2}O EFs (IPCC, 2019) recommends a distinction between wet and dry climates, where the EF is 0.016 (uncertainty range: 0.013–0.019) for synthetic and 0.006 (uncertainty range: 0.001–0.011) for organic N fertilisers (mainly livestock manure) in wet climates, and 0.005 (uncertainty range: 0.000–0.011) in dry climates irrespective of N source. However, the uncertainty ranges are still very wide, showing that factors other than climate contribute to the observed variation in N\textsubscript{2}O emissions. Accordingly, countries are recommended to adopt higher Tier methods that can better represent local conditions, i.e., country-specific N\textsubscript{2}O EFs (Tier 2) or a predictive model (Tier 3), both of which require experimental verification of N\textsubscript{2}O emissions.

The distinction between synthetic and organic N fertilisers is particularly challenging. There is high diversity in the composition of livestock manure depending on animal type, housing conditions, treatment and management, and even within Europe the proportions of liquid manure (slurry) and solid manure vary widely, i.e., for individual countries ranging between 0 and >90% liquid manure management (Leip et al., 2010). For Denmark the proportions given for dairy cattle and pigs were 87% and 92%, respectively. Organic fertilisers may constitute hotspots of microbial activity in the soil with high oxygen consumption rates. Since water restricts diffusion, the supply of oxygen will be particularly limited in hotspots of liquid manure, and as a consequence denitrification and N\textsubscript{2}O production occurs over a wider range of soil moisture conditions than if mineral fertilisers (Li et al., 2019; Baral et al., 2017) or solid manure (Charles et al., 2017; Thoman et al., 2020) is applied. To resolve the interactions between fertiliser type and site conditions, a factorial approach is needed where the same materials are applied under a variety of site conditions.

Characterising the variability of N\textsubscript{2}O emissions is a significant challenge, and trade-offs are necessary in the allocation of resources (Charteris et al., 2020). One choice is the length of monitoring to estimate N\textsubscript{2}O EFs, where the period should include the entire emissions envelope (i.e., emissions must have returned to the background level), and the increase in N\textsubscript{2}O emission over an unfertilised control plot is then related to the total N applied. The duration may depend on N source and season, with spring application having the shortest duration (Charteris et al., 2020). Thus, arable crops show an N\textsubscript{2}O emission envelope after N fertilisation events, and emissions typically return to the background level after several weeks when crop uptake of soil mineral N is complete (e.g., Velthof and Mosquera, 2011). However, the higher N level of fertilised soil may increase N turnover and N\textsubscript{2}O emissions relative to an unfertilised control beyond this period, and therefore it is often recommended to document net N\textsubscript{2}O emissions during a full year (Shang et al., 2020). Notably, the studies used to derive N\textsubscript{2}O EFs for the recent 2019 IPCC refinement ranged from <120 d to >300 d, and statistical analysis could not show an effect of the length of monitoring (IPCC, 2019). It indicates that documenting minor increases against a variable background may be difficult and increase overall uncertainty, and it is important to discuss what is the most effective balance between accuracy and precision when estimating N\textsubscript{2}O EFs for N fertilisers in agriculture.

An important challenge for robust documentation of N\textsubscript{2}O emissions is to understand the legacy of the cropping history of monitoring sites. The previous crop in a rotation, like fertilisation, may influence N\textsubscript{2}O emissions by changing the availability of reactive soil N (and C in the case of organic fertilisers), and hence both the previous crop and cover crops may interact with N fertilisation and affect N\textsubscript{2}O emissions (Charles et al., 2017). This can occur if, for example, the decomposition of crop residues changes soil oxygen status (Miller et al., 2008) or leads to microbial immobilisation of fertiliser N (Jensen et al., 2005). It follows that N\textsubscript{2}O EFs for synthetic and organic N fertilisers are best determined in realistic crop rotations.

Based on these various considerations, a multi-site field study was planned to provide a first estimate of annual N\textsubscript{2}O emissions from synthetic and organic fertilisers for Denmark, one of the most intensively farmed regions in the world (Dalgaard et al., 2014). Crop rotations were established at four sites representing soil types typical for Denmark and Northern Europe, and climatic conditions typical for Denmark which, in the IPCC terminology, is predominantly wet; all crops of the rotation were represented each year. For this study, we determined annual N\textsubscript{2}O emissions from field plots with spring barley during two years, as well as emissions during spring in both years from a range of synthetic and liquid organic N fertilisers. We hypothesized that N\textsubscript{2}O emissions from liquid manure would be higher than predicted by the global average N\textsubscript{2}O EF for organic fertilisers recently proposed by the IPCC, and that N\textsubscript{2}O emission levels would be higher at sites or years with more abundant rainfall during spring.

## 2. Materials and methods

### 2.1. Experimental sites

Four sites, Taastup (55°40 N, 12°18 E), Foulum (56°29 N, 9°34 E), Askov (55°28 N, 9°06 E) and Vejen (55°26 N, 9°08 E), were selected for this study representing different soil types in the Danish classification system, with textural compositions ranging from coarse sand to sandy clay loam.

| Site       | Geographical coordinates | Annual rainfall a | Annual temperature a | Rainfall during spring b | Temperature during spring b | Soil type | Textures          | Clay (g 100 g\textsuperscript{-1}) | Silt (g 100 g\textsuperscript{-1}) | Fine sand (g 100 g\textsuperscript{-1}) | Coarse sand (g 100 g\textsuperscript{-1}) | Organic matter (g 100 g\textsuperscript{-1}) | Total C (g 100 g\textsuperscript{-1}) | Bulk density (Mg m\textsuperscript{-3}) | pH (1 M KCl) |
|------------|--------------------------|-------------------|----------------------|--------------------------|-----------------------------|----------|------------------|-------------------------------|--------------------------------|------------------------------------------|----------------------------------------|----------------------------------|-------------------------------|
| Foulum     | 56°29 N, 9°34 E          | 803               | 8.6                  | 177                      | 10.9                       | Sandy    | Clay              | 7.0 (0.03)                   | 27.7                          | 32.2                                      | 30.2                                      | 3.8 (0.09)                   | 1.9 (0.05)                   | 1.25                          | 5.30                          |
| Vejen      | 55°26 N, 9°08 E          | 933               | 9.0                  | 165                      | 11.3                       | Sandy    | Silt              | (0.00)                       | (0.08)                        | (0.65)                                    | (0.76)                                    | (0.58)                         |                   | 1.53                          | (0.14)                        |
| Askov      | 55°28 N, 9°06 E          | 933               | 9.0                  | 165                      | 11.3                       | Sandy    | Fine sand         | (0.28)                       | (0.49)                        | (0.27)                                    | (0.58)                                    |                   |                   | 27.3                          | (0.27)                        |
| Taastup    | 55°40 N, 12°18 E         | 646               | 9.3                  | 139                      | 11.7                       | Sandy    | Coarse sand       | 10.5 (0.23)                  | 22.4                          | 32.0 (0.72)                               | 35.7                                      |                   | 3.6                            | (0.11)                        |

| aAverage for the period 2011–2019. | bDay of fertilisation of individual campaigns in Table S2; final sampling c. 1 July.
loam soil. Foulum and Vejen sites were relatively sandy, and Askov and Taastrup more clayey (Table 1, Fig. 1A). Annual average temperatures were comparable at the four sites, ranging between 8.6 and 9.3 °C. Annual average precipitation during 2011–2019 ranged from 646 to 933 mm, and rainfall during spring (April, May and June) from 139 to 177 mm. Foulum and Taastrup sites represented a drier, and Askov and Vejen sites a wetter climate as indicated by mean annual precipitation (Fig. 1B). The ratios between average precipitation and average evapotranspiration in the period 1981–2010 were, respectively, 1.04 (Taastrup), 1.31 (Foulum) and 1.53 (Askov, Vejen) (S. Gyldenkærne, personal communication), and following the terminology of the IPCC, all sites could be defined as having a cool wet temperate climate.

Experimental crop rotations were established that represented major agricultural production systems in the respective areas, including dairy production (Foulum, Vejen), pig production (Askov), and stockless farming with only cash crops (Taastrup). All crops were included in each of three randomised blocks each year. Detailed crop sequences are shown in Table S1. Briefly, Foulum and Vejen sites had identical crop rotations representing dairy farms with two years of spring barley, maize, and grass-clover, whereas Askov and Taastrup sites had cereal-based crop rotations representing pig or arable farms (but differing in fertiliser type) with two years of spring barley, winter oilseed rape, and winter wheat. Non-leguminous cover crops (see Table S1) were grown outside the main cropping season (autumn-winter) in accordance with current legal regulations. The two crop rotations at Foulum and Taastrup were initiated in spring 2019, and Askov and Vejen in spring 2020. Only N₂O emissions from spring barley are presented here to serve as reference for the screening of N₂O emissions from a wide range of fertiliser materials in spring campaigns.

The basic experimental design applied at each of the field sites is shown in Fig. S1. There were minor differences between field sites in the layout of field plots, but all contained the elements described below. Each field plot (6 m × 12 m or greater) was split into two subplots. One subplot was used for long-term monitoring of N₂O emissions, soil sampling and determination of harvest yield (called harvest plots). Here, the N application rates were set for the individual crops in the rotation according to the statutory N norm (legal limits for max. available N application rate to individual crops and soil types), corrected for pre-crop effects (including cover crops), and for the prescribed availability of manure N (70% for cattle slurry, 75% for pig slurry and digestate). Besides N fertilisation, spring barley received 21, 59 and 15 kg ha⁻¹ P, K and S, respectively. The second subplot of each field plot was used for measurement of N₂O emissions during spring from several synthetic and organic fertilisers in a number of pre-defined mini-plots (1 m²) separated by 0.5 m strips that were also fertilised. The N fertilisation rate in these plots followed the N-norm for spring barley, and any pre-crop effects on N availability were disregarded since priority was given to application of the same rates of fertiliser N at all sites. The subplot with mini-plots also contained an area (2 m × 2 m or greater) without N fertilisation (“Zero N”) for year-round determination of background N₂O emissions.

### 2.2. Fertiliser treatments

In total, eight organic fertilisers were investigated in the mini-plot trials, i.e., three cattle slurries (CS1–3), three pig slurries (PS1–3), and two digestates from full-scale reactors processing a mixture of cattle and pig slurry co-digested with biomasses from the food industry (DS1) or with a mixture of maize and grass silage, deep litter and glycerol (DS2). Selected properties are shown in Table 2. The organic fertilisers CS1, PS1 and DS1 were applied at all four sites, whereas CS2, CS3, PS2, PS3 and DS2 were applied at Foulum and Taastrup only. Three synthetic N fertilisers (SN) were represented in the mini-plot trials, i.e., NS26–13 (SN1), NPK (SN2) and urea ammonium nitrate (UAN; SN3) as shown in Table 2. SN1 was applied at four rates corresponding to 0.5, 1, 1.5 and 2 times the recommended dose.

### 2.3. Field management

Management of crop rotations at the four experimental sites aimed to follow local practices with respect to the timing of field operations (such as tillage, fertilisation, pest management, seeding, and harvest) and was carried out with machinery for practical farming. Fertilisation in mini-plots in 2020 took place between 20 and 22 April at Foulum, Vejen and Taastrup, but two weeks earlier at Askov for logistical reasons (Table S2). In 2021 the time of fertilisation was comparable to 2020 at all sites except Vejen, where the mini-plots were fertilised in late March. Cattle or pig slurry was injected to c. 8 cm depth in ploughed and harrowed soil, followed by seedbed preparation and seeding. Synthetic N fertiliser was surface-applied. There was no traffic in the harvest plots.
as either field operations were carried out using a tractor with 3 m distance between the wheels, or field plots were distributed to allow driving between field plots (Taastrup).

In the mini-plot area of spring barley crops, the area surrounding mini-plots always received NS26–13 fertiliser after first covering the mini-plots and zero-N plots to prevent N additions. The injection of slurries and digestates was simulated by establishing injection slits to 8 cm depth in the pre-selected mini-plots, followed by manual application and immediate covering of the slits. Synthetic N fertilisers SN1 and SN3 were surface-applied, while the liquid SN2 was applied in a 25 cm × 25 cm grid to c. 8 cm depth and covered.

2.4. Nitrous oxide flux measurements

Long-term monitoring of N2O emissions in harvest plots were carried out with two-part static chambers of dimensions 75 cm × 75 cm × 20 cm (l × w × h) and 40 cm intersections when needed due to crop height. The chamber units were made of white PVC equipped with an open-cell rubber profile around the perimeter of the chambers and intersections. The chambers had a septum for gas sampling and were equipped with a battery-operated fan for mixing the headspace during measurements. Finally, chambers were equipped with straps fixed to the frame or secured with clamps during measurements (Taastrup). Supporting frames of stainless steel were permanently installed to c. 10 cm depth and only removed if necessary due to field operations. A 30-mm wide flange was attached 30 mm below the upper rim of frames and intersections to support the chambers while creating a wind break.

For the 1 m² mini-plots, smaller two-part static chambers of 27 cm × 37 cm × 20 cm (l × w × h) were used for the spring campaigns with several fertiliser materials. These chambers were made of gray polypropylene and equipped with an outer layer of Aluthermo Quattro (Addflex ApS, Odense, Denmark) for insulation and reflection of solar radiation. These chambers had an open-cell rubber profile or rubber seal (Taastrup) resting on a flange below the upper rim of supporting stainless steel frames (25 cm × 35 cm × 15 cm; l × w × h), and a septum for gas sampling. No fan was used with these smaller chambers, and instead the headspace was mixed with the syringe prior to sampling.

The two different chamber systems used in harvest plots and mini-plots, respectively, are depicted in Fig. S1.

The measurement procedure was the same for both chamber types. Four 10-ml (Taastrup: 5-ml) gas samples were taken with a plastic syringe and hypodermic needle during 1–1.5 h and stored in 6-ml (Taastrup: 3-ml) pre-evacuated Exetainer vials (Labco Ltd., Ceredigion, UK). Three N2O flux measurement campaigns were completed during the first week after fertilisation (see dates in Table S2), followed by weekly campaigns for 8–10 weeks until the end of June or early July. For long-term monitoring, biweekly campaigns were carried out during the rest of the year, with extra campaigns after fertilisation events such as a starter N application for winter oilseed rape in September at sites in Taastrup and Askov.

Above-ground plant biomass inside frames were taken at the time of the last gas sampling for determination of total N; unfortunately, plant cuts taken at the Foulum site by the end of monitoring in 2021 were lost.

2.5. Analytical methods

Concentrations of N2O and CO2 in samples from Foulum, Askov and Vejen sites were determined using a Model 7890 gas chromatography system with dual-inlet injection (Agilent; Nærum, Denmark) configured as previously described (Petersen et al., 2012). Samples collected at the Taastrup site were analysed on a Bruker 450-GC 2011 gas chromatograph as described in Tariq et al. (2022). Detection limits were 0.042 and 61 μL L⁻¹ or better for N2O and CO2, respectively.

The moisture content of soil and organic fertilizers were measured by drying at 105 °C for 24 h, and the volatile solids (VS) of organic fertilizers after an additional 6 h at 500 °C. The pH and electrical conductivity were measured by a MeterLab CDM210 (Hach; Loveland, Colorado, USA) in a 1:1 (w/v) soil:water slurry. For analysis of NH4 and NO3 in soil samples, about 10 g fresh wt. soil was extracted in 40 ml 1 M KCl; the mixture was rotated end-over-end for 30 min and centrifuged at 1500 rpm for 5 min. The supernatant was then filtered through a microfiber filter (Filter 691, VWR Europe) and measured colorimetrically by continuous flow analysis using an Autoanalyzer III (Bran+Luebbe, Germany) for the samples at Foulum, Vejen and Askov, and a Foss FLiStar Analyser 5000 for the samples from Taastrup.

2.6. Data analyses

As the first step in data processing, CO2 concentration-time series were inspected. In contrast to N2O emissions, there is measurable soil respiration during most of the year, and the trend in CO2 accumulation was therefore used to check the quality of gas samplings. Fluxes of N2O were calculated using the flux estimation software HMR (Pedersen, 2022) as an add-on package in R (R Core Team, 2022). New functions available were used to constrain flux estimates to avoid the outliers sometimes obtained with a nonlinear model when the signal-to-noise ratio is low (Pullens et al., 2023). The analytical error was defined by a prefitering parameter, pfvar, of 0.0001 μg N₂O L⁻¹, corresponding to a C.V. of 3%, and the significance level α of the prefitering test, pfalpha, was 0.05. Two other parameters, SatPct and SatTimeMin with values of 90 (unit: %) and 2 (unit: hours), respectively, together limit the curvilinearity of nonlinear fluxes. The cumulative N2O...
emissions during spring were calculated by linear interpolation between daily fluxes, with spring being defined as the period between the date of N fertilisation (Table S2) and the last flux measurement which was always close to 1 July.

Emission factors were calculated as:

$$\frac{\sum N_2O_{\text{meas}} - \sum N_2O_{\text{model}}}{N_{\text{applied}}} \times 100\%,$$

where cumulative N\(_2\)O emissions from fertilised and unfertilised plots are expressed as kg N\(_2\)O N ha\(^{-1}\) and N applied as kg N ha\(^{-1}\). A single unfertilised Control (0 N) plot from Foulum had a negative cumulative N\(_2\)O emission and was not used for the analysis. The remaining cumulative N\(_2\)O emissions were log-transformed and analysed with linear mixed models (LMMs); log-transformation ensured variance homogeneity and normally distributed residuals. Location and Year effects were assessed in a LMM with Location, Year, their interaction, and Treatment as fixed factors (L \(\times\) Y \(\times\) T) using data from all 15 treatments. Treatment effects were assessed in LMMs with Location, Year, Treatment, and all their interactions (L \(\times\) Y \(\times\) T) using data from the relevant treatments. In all analyses Block, nested within Location, was included as a random factor (12 levels in total). Hypothesis tests were carried out on marginal means in the full above-mentioned LMMs, i.e., averaging over factors occurring in interactions with the factor in question for the hypothesis, using F-tests with the Satterthwaite approximation. We used 0.05 for significance. P-values for pairwise comparisons of locations or treatments were adjusted with Tukey’s method. As a supplement to inform about factors driving N\(_2\)O emissions, an alternative LMM was used in which the fixed factors were replaced by the following numerical covariates: manure dry matter, manure total ammoniacal nitrogen, soil bulk density (BD, determined at block level), above-ground N in the crop at the last gas sampling, average air temperature and cumulative precipitation during the monitoring period. We used R packages lmerTest and emmeans for the analyses (Kuznetsova et al., 2017; Lenth, 2022).

3. Results

3.1. Site conditions

The experimental sites had clay contents ranging from 3% to 16% of the dry weight and hence they were all light-textured. In 2020 the spring monitoring period was characterised by dry conditions at all sites with rainfall in the range 102–122 mm, which was 58–83% of the average rainfall in the period 2011–2019 (Table 1). This was different in 2021 where rainfall was 10% above average at the Foulum site with 196 mm, and 62–73% above average at the sites in Askov and Vejen with > 250 mm. In contrast, rainfall in 2021 at the Taastrup site receiving 95 mm during the spring monitoring period was again low at 68% of the average.

Fertilisation in mini-plots occurred within a week of the fertilisation of harvest plots used for long-term monitoring of N\(_2\)O emissions with two exceptions, where the deviations were 13 and 25 d, respectively (Table S2). However, when comparing the times of fertilisation in experiments with the timing of synthetic and organic N fertiliser application on commercial farms, the experimental fertilisation was always within the recorded periods (Fig. S2).

3.2. N\(_2\)O emissions from synthetic and organic N fertilisers

The emissions of N\(_2\)O from synthetic fertilisers SN1-SN3, and from organic fertilisers CS1-CS3, PS1-PS3 and DS1–2, during spring 2020 and 2021 are compiled in Figs. 2 and 3, respectively; all treatments corresponding to the recommended rate are included, as well as the unfertilised control. Cumulative N\(_2\)O emissions during spring, and EFs for these periods, are shown in Table 3.

In 2020, across all four sites, N\(_2\)O emissions from synthetic N fertilisers corresponded to a loss of 0.05–0.69% of N applied, whereas emissions from organic N fertilisers corresponded to 0.22–1.98% (Foulum), 0.65–2.49% (Vejen), 0.17–0.38% (Askov) and –0.01–0.39% (Taastrup). At Taastrup, spring emissions of N\(_2\)O from organic fertilisers were only marginally higher than those from synthetic fertilisers. The higher rainfall during spring 2021 compared to 2020, except at Taastrup (Table 1), was accompanied by higher N\(_2\)O emissions from synthetic fertilisers at Foulum and Askov, and marginally higher emissions at Vejen and Taastrup (Fig. 3). Across sites, cumulative N\(_2\)O emissions from synthetic N fertilisers corresponded to < 0–1.18% of the N applied, and emissions from organic N fertilisers from 0.01% to 2.47% of the N applied. There was again a consistent trend for lower N\(_2\)O emissions at the Taastrup site.

On average, across the four locations and two years, the EFs for N\(_2\)O emissions for the spring period were 1.02% (95% C.I. 0.75–1.30) for organic N fertilisers, and 0.15% (95% C.I. –0.17 to 0.37%) for synthetic N fertilisers.

There were a number of pair-wise differences in N\(_2\)O emission levels between experimental sites in both years, but only the difference
Table 3

\[
\begin{array}{ccccccc}
\text{Treatment} & \text{Year} & \text{Origin} & \text{Source} & \text{Concentration} & \text{Enrichment} & \text{Error} \\
\hline
\text{Pig slurry} & 2020 & \text{NPS} & \text{DS1} & 0.62 & 0.45 & 0.05 \\
\text{Cattle slurry} & 2020 & \text{NPK} & \text{PS1} & 1.23 & 1.09 & 0.38 \\
\text{Synthetic N fertiliser} & 2020 & \text{SN1 (UAN)} & \text{SN2} & 0.72 & 0.50 & 0.04 \\
\text{Background 0} & 2020 & - & - & - & - & - \\
\text{Background 200%} & 2020 & - & - & - & - & - \\
\text{Background 150%} & 2020 & - & - & - & - & - \\
\text{Background 100%} & 2020 & - & - & - & - & - \\
\text{Cattle slurry} & 2021 & \text{NPK} & \text{CS1} & 0.51 & 0.04 & 0.00 \\
\text{Synthetic N fertiliser} & 2021 & \text{SN1 (UAN)} & \text{SN2} & 0.22 & 0.00 & 0.00 \\
\text{Background 0} & 2021 & - & - & - & - & - \\
\text{Background 200%} & 2021 & - & - & - & - & - \\
\text{Background 150%} & 2021 & - & - & - & - & - \\
\text{Background 100%} & 2021 & - & - & - & - & - \\
\end{array}
\]
Table 4
Analysis of cumulated N\textsubscript{2}O-N emissions in spring campaigns. Location and year effects are based on the model \(L \times Y + T\) and estimated marginal means across all 15 treatments listed in Table 3. Treatment effects are based on the model \(L \times Y \times T\) and estimated marginal means across year and location.

<table>
<thead>
<tr>
<th>Factors</th>
<th>Effects</th>
<th>(p) value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location (both years, all treatments)</td>
<td></td>
<td>0.0005</td>
</tr>
<tr>
<td>Foulum - Taastrup</td>
<td></td>
<td>&lt; 0.01</td>
</tr>
<tr>
<td>Foulum - Askov</td>
<td>0.008</td>
<td></td>
</tr>
<tr>
<td>Foulum - Vejen</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>Tastrup - Askov</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Tastrup - Vejen</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Askov - Vejen</td>
<td>0.154</td>
<td></td>
</tr>
<tr>
<td>Year (all treatments)</td>
<td>2020 &lt; 2021</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Foulum</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Tastrup</td>
<td>NS</td>
<td>0.1089</td>
</tr>
<tr>
<td>Askov</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Vejen</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>L x Y</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Treatments (synthetic N vs. organic N)</td>
<td>MIN &lt; MAN</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Foulum</td>
<td>MIN &lt; MAN</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Tastrup</td>
<td>MIN &lt; MAN</td>
<td>&lt; 0.0001</td>
</tr>
<tr>
<td>Askov</td>
<td>0.0213</td>
<td></td>
</tr>
<tr>
<td>Vejen</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>L x Y x T</td>
<td>NS</td>
<td>0.1400</td>
</tr>
<tr>
<td>Y x T</td>
<td>NS</td>
<td>0.1000</td>
</tr>
<tr>
<td>L x T</td>
<td>0.0949</td>
<td></td>
</tr>
<tr>
<td>Treatments, organic (DS vs. CS vs. PS)</td>
<td>NS</td>
<td>0.0062</td>
</tr>
<tr>
<td>CS — DS</td>
<td>NS</td>
<td>0.5793</td>
</tr>
<tr>
<td>CS — PS</td>
<td>NS</td>
<td>0.3580</td>
</tr>
<tr>
<td>DS — PS</td>
<td>0.0559</td>
<td></td>
</tr>
<tr>
<td>L x Y x T</td>
<td>NS</td>
<td>0.6167</td>
</tr>
<tr>
<td>Y x T</td>
<td>NS</td>
<td>0.1332</td>
</tr>
<tr>
<td>L x T</td>
<td>0.9476</td>
<td></td>
</tr>
<tr>
<td>Treatments, synthetic (SN1 vs. SN2 vs. SN3)</td>
<td>NS</td>
<td>0.0098</td>
</tr>
<tr>
<td>SN1 — SN2</td>
<td>0.0283</td>
<td></td>
</tr>
<tr>
<td>SN1 — SN3</td>
<td>0.0297</td>
<td></td>
</tr>
<tr>
<td>SN2 — SN3</td>
<td>0.9997</td>
<td></td>
</tr>
<tr>
<td>Tastrup:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SN1 — SN2</td>
<td>NS</td>
<td>0.2900</td>
</tr>
<tr>
<td>SN1 — SN3</td>
<td>NS</td>
<td>0.6301</td>
</tr>
<tr>
<td>SN2 — SN3</td>
<td>NS</td>
<td>0.6883</td>
</tr>
<tr>
<td>L x Y x T</td>
<td>NS</td>
<td>0.3894</td>
</tr>
<tr>
<td>Y x T</td>
<td>NS</td>
<td>0.2764</td>
</tr>
<tr>
<td>L x T</td>
<td>0.4367</td>
<td></td>
</tr>
<tr>
<td>Treatments (50 vs. 100 vs. 150 vs. 200% of norm)</td>
<td></td>
<td>0.0077</td>
</tr>
<tr>
<td>Foulum</td>
<td>50 &lt; 150 &lt; 200 &lt; 100</td>
<td>0.2791</td>
</tr>
<tr>
<td>Tastrup</td>
<td>0.0087</td>
<td></td>
</tr>
<tr>
<td>Askov</td>
<td>0.0605</td>
<td></td>
</tr>
<tr>
<td>Vejen</td>
<td>0.3886</td>
<td></td>
</tr>
<tr>
<td>L x Y x T</td>
<td>NS</td>
<td>0.1863</td>
</tr>
<tr>
<td>Y x T</td>
<td>NS</td>
<td>0.9372</td>
</tr>
<tr>
<td>L x T</td>
<td>0.1341</td>
<td></td>
</tr>
</tbody>
</table>

between Foulum and Tastrup was significant in both years (Table 4). Across sites and all 11 fertiliser types, the level of N\textsubscript{2}O emissions was significantly higher in the wet spring of 2021 compared to 2020 \((p < 0.0001)\). Notably, there were higher N\textsubscript{2}O emissions from organic fertilisers than from synthetic fertilisers \((p < 0.0001)\), and this was also true for each individual site. There was a significant interaction between location and treatment. Among the three types of organic fertilisers there was only one non-significant trend (DS vs. PS), and hence variation within each fertiliser category was generally as high as between categories. For synthetic fertilisers, SN1 (NS26–13) resulted in higher N\textsubscript{2}O emissions than SN2 (NPK) and SN3 (UAN) at Foulum, but no differences were seen at the other sites which showed a generally low level of N\textsubscript{2}O emissions (Table 4).

Since there were significant location-year and location-treatment interactions, an additional analysis only including organic fertilisers was conducted to investigate the relative importance of N source and site conditions (soil, climate) for N\textsubscript{2}O emissions. The independent variables were manure dry matter (DM) and manure total ammoniacal nitrogen (TAN), soil BD, and above-ground N in the crop at the last gas sampling, as well as average air temperature and cumulative precipitation during the monitoring period. Although there was a significant positive \((p < 0.05)\) effect of manure TAN, and a negative effect of soil BD \((p = 0.01)\), on N\textsubscript{2}O emissions across sites and years, these effects were not significant without the results from the Foulum site in 2021, which had relatively high N\textsubscript{2}O emissions and the lowest soil BD, and hence the relationships may not be robust. In contrast, there were strong and consistent positive effects of air temperature \((p < 0.0001)\) and precipitation \((p < 0.0001)\) on N\textsubscript{2}O emissions.

3.3. Spring vs. annual N\textsubscript{2}O emissions

The side-by-side comparison of several N fertiliser materials during spring was supplemented by monitoring of N\textsubscript{2}O emissions in the four crop rotations throughout the two-year period as a contribution to constrain estimates of annual N\textsubscript{2}O EFs. In crop rotations, fertilisation was determined by the nutrient management plans of the respective crop rotations, which followed recommended farming practices and the current statutory N-norms. Table 5 shows the statutory N norms for spring barley, as well as pre-crop effects and the effective (i.e., plant available) N applied. The deficit in N applied at the Vejen site in 2020 was due to the fact that only weeds and volunteers (growth from spilled grain and weeds), and not an established grass-clover sward, were present in this first experimental year. This contrasted with the identical crop rotation at Foulum, which had been initiated the year before for a pilot study. The moderate amount of N applied for spring barley in the dairy rotations at Foulum and Vejen was synthetic N and not cattle slurry, which was reserved for maize and grass-clover. At Askov a combination of pig slurry and synthetic N was applied, and at Tastrup synthetic N only, and hence the long-term monitoring differed from the screening campaigns in several ways and did not allow a direct comparison between the EFs estimated from spring campaigns and the long-term monitoring. Instead, the emissions during spring (defined as the period from 1 April to c. 30 June) in the long-term monitoring were compared with annual emissions in the same experimental plots.

The annual emissions of N\textsubscript{2}O between spring fertilisation and the 31 March in the following year are shown for all four sites and both years in Fig. 4, while cumulative emissions and EFs for the full year and spring period are shown in Table 5. There were substantial differences between sites and years with respect to N\textsubscript{2}O emission dynamics, and at the sandy sites (Foulum and Vejen) the emission was low throughout the year. Starter N was given in the autumn for winter oilseed rape, and this enhanced N\textsubscript{2}O emissions at Askov, but not at Tastrup. At Vejen there was high N\textsubscript{2}O emission during spring in 2021 in both fertilised and non-fertilised plots following the termination of grass-clover, while the stimulation of background emissions at Foulum was much less. With few exceptions, higher N\textsubscript{2}O emissions occurred during spring in both years (Fig. 4), and this was also true for the other crops in the rotations (data not shown). An extremely high level of N\textsubscript{2}O emissions was observed at Askov in 2021 in the harvest plots receiving a combination of pig slurry and synthetic N, but this combination was also applied in 2020 without a substantial increase in N\textsubscript{2}O emissions. The two years differed in two respects, firstly, in 2021 a winter cover crop was ploughed in prior to fertilisation, in contrast to the first project year where only volunteers and weeds were present in the plots, and secondly, the level of rainfall during spring was much greater in 2021 compared to 2020 (Table 1).

4. Discussion

This field study aimed to determine the level of N\textsubscript{2}O emissions from typical N fertilisers under conditions representing arable farming in
Denmark. Monitoring in crop rotations throughout the year served as a reference for the screening of N₂O emissions from several N fertiliser materials during spring (60 treatment combinations in total) where, under Danish regulations, most N application takes place. In the allocation of resources, priority was given to include soil types, climatic conditions, crop rotations, N fertiliser types, and application rates and timing typical for Denmark, albeit at the expense of high sampling intensity in the individual trials.

### 4.1. Representativeness of experimental sites

The four soil types represented in this study together cover 69% of the total land area in Denmark (Greve et al., 2007). The textural composition, with clay contents between 3% and 16%, and sand content of 60–90%, is typical for mineral soil in Northern Europe including Scandinavia (Ballabio et al., 2016), but distinctly different from the rest of Europe. Considering the importance of soil texture for water retention characteristics and gas exchange and, as a consequence, for N₂O emissions, there may be a need for region-specific N₂O emission estimates within Europe.

Denmark is dominated by a cool wet temperate climate categorised as Atlantic North or Continental (minor parts of Northern and Eastern Denmark) according to the typology of Metzger et al. (2005). In this two-year study, the spring period was relatively dry in 2020 at all four sites, whereas in 2021 conditions during spring were very variable and with an East-West gradient in rainfall (Table 1 and Fig. 1). Together, the four sites and two experimental years covered a wide range of soil and climatic conditions that may occur in Denmark.

### 4.2. Representativeness of fertiliser treatments

All three synthetic N fertilisers contained reduced as well as oxidised forms of N (Table 2). This can have synergistic effects on crop growth compared to either ammonium or nitrate alone, one reason being that nitrate is more mobile in the soil than ammonium and hence more readily available to an emerging crop (Britto and Kronzucker, 2002). At national level, nitrate-N constitutes 40% of the total N input in synthetic N fertilisers (Birkmose, 2022).

The organic fertilisers, including dairy cattle slurry, finishing pig slurry and digestates, showed some variation between farms, and in some cases between years within a single farm (Table 2). Compared to Danish manure standard values of 6.1–6.6% (Bursting and Hellwin, 2021), the dry matter content of the pig slurries used in this study was lower, whereas total and ammoniacal N contents were comparable to the standard values of 4.4–4.7 and 3.3–3.5 kg N Mg⁻¹, respectively. Similarly, for cattle slurry the dry matter contents were lower than the corresponding standard of 8.0%, and this was also the case for total and ammoniacal N where standard values are 4.6 and 2.8 kg N Mg⁻¹, respectively (Bursting and Hellwin, 2021). Digestate DS1 from a centralised biogas facility (LinkoGas in Ribe, Denmark) had contents of total and ammoniacal N that were close to those announced on the company website for 2022, while no reference values were available for DS2 from a biogas plant at Aarhus University near the Foulum site. Limited use of bedding material could have contributed to the lower DM values of pig and cattle slurry in experiments described above, but overall the N sources used in this study were probably representative of liquid manure, including digestates, which is the predominant form of organic fertilisers recycled for crop production in Denmark.

The timing of N fertilisation in spring depends on site conditions such as weather and soil type, the termination of any cover crops ahead of seedbed preparation, and fertiliser type (synthetic or organic). The timing of fertilisation was compared with on-farm registrations collected by SEGES Innovation during 2020 on 20 cattle farms, 18 pig farms and 19 arable farms distributed across the country (Christensen et al., 2022). Hence, field operations could be related to soil type, crop and fertiliser type (Fig. S2). The timing of N fertilisation for spring barley in the experiments presented was always within the range observed on commercial farms, indicating that fertiliser management in the trials was realistic. The farm data were not available at the time of conducting the field trials in this study, but such information could be a valuable reference for the planning of future studies.

The four experimental crop rotations represented dairy production (Foulum, Vejen), pig production (Askov) and cash crops (Taastrup).

Dairy farms occupy an area of 464,000 ha in Denmark that receives on average 170 kg N ha⁻¹ in cattle slurry, while pig farms occupy 570,000 ha and receive on average 140 kg N ha⁻¹ in pig slurry. Stockless farms occupy 855,000 ha with little or no manure application (I.S. Kristensen, personal communication). The average manure N application in the experimental crop rotations was 84 kg N ha⁻¹, which is close to the national average manure application rate of 90 kg N ha⁻¹.

The application of slurries and digestates for spring barley was by simulated injection prior to seeding. An alternative strategy would have been simulation of trail hose application followed by incorporation, which is mandatory for spring-seeded crops in Denmark. Spring fertilisation of autumn-seeded crops, in contrast, leaves N at the soil surface with an elevated risk for NH₃ volatilisation which is an indirect source of N₂O (PCC, 2019). Based on balances from a three-year field study, Velthof and Mosquera (2011) reported a trade-off between direct and...
indirect N\textsubscript{2}O emissions when comparing surface-applied and injected slurry, and hence the level of N\textsubscript{2}O emissions observed in the present study may be realistic when considering both direct and indirect sources.

4.3. \textit{N}_{2}\textit{O} EFs and environmental controls

Several significant effects on N\textsubscript{2}O emissions were observed in the multi-site comparison of synthetic and organic N fertiliser materials. Here, the most notable result was that N\textsubscript{2}O emissions were significantly higher from organic compared to synthetic fertilisers at all four sites with EFs of 1.02\% (with 95\% confidence interval 0.75 – 1.3\%) and 0.15\% (with 95\% confidence interval –0.07 to 0.37\%), respectively. Velthof and Mosquera (2011) found a similar difference between synthetic N fertiliser (calcium ammonium nitrate, CAN) and organic N fertilisers (pig and cattle slurry) applied to maize on sandy soil, on average 0.1\% (CAN), 0.9\% (cattle slurry) and 3.6\% (pig slurry). In their study, the EF for pig slurry was dominated by one extreme value of 7.0\% in a wet year, which paralleled the observed N\textsubscript{2}O EF of c. 8\% observed for pig slurry at Askov in 2021 (Fig. 5). These observations contrast with the recent refinement of N\textsubscript{2}O EFs proposed by the IPCC (2019) for wet climates, suggesting that there were deviations from the global analysis behind IPCC estimates of importance to N\textsubscript{2}O emissions.

The potential for N\textsubscript{2}O emissions from synthetic N fertilisers depends mainly on soil conditions during the period after field application. The soil types of this study, typical for Denmark and large parts of Northern
Europe (Ballabio et al., 2016), were all light-textured with a maximum of 16% clay. In a survey of N₂O emissions across the United Kingdom, Bell et al. (2015) reported EFs for a synthetic N fertiliser (ammonium nitrate) of 0.20% and 0.33% for two arable sites with low rainfall and 11–21% clay, and an EF of 1.07% for a wet site with 13% clay. In accordance with this result, the largest individual N₂O EF observed in the present study for synthetic N was 1.13% at Askov under near-saturated soil conditions in 2021 (Table 3). Similarly, for Germany, a national average N₂O EF for synthetic N fertilisers of 0.55% was recently reported (Mathivanan et al., 2021). On the other hand, a global meta-analysis by Charles et al. (2017) reported an average EF for synthetic fertilisers of 1.34% supporting the most recent IPCC recommendation. Results from the present and other studies cited above indicate that rainfall is a key driver of N₂O emissions, but also that for Northern Europe the N₂O EF for synthetic fertilisers will in many cases be much lower than 1%. Several field trials and meta-analyses, as summarised by Takeda et al. (2021), have reported a non-linear response of N₂O emissions with fertiliser N application rate when exceeding crop N requirement. Although spring barley is poorly represented in these studies, a similar pattern was expected in the present study. While a significant positive response to the N rate was seen (Table 4), we did not find support for a non-linear increase in N₂O emissions from SN1 in this study (Table 3), possibly due to the generally low level of emissions with synthetic N in this study.

The organic fertilisers used in the present study were all liquid. The meta-analysis by Charles et al. (2017) showed that weighted N₂O EFs were significantly lower for solid manure (0.35%) compared to liquid manure (1.12%), the latter value being close to the value of 1.02% found in the present study for N₂O emissions during spring. Thorman et al. (2020) reported EFs of 0.93% and 1.05% for spring-applied cattle slurry on two arable sandy loam soils in the UK. Solid organic fertilisers will normally have a higher C:N ratio, and a lower water content compared to liquid organic fertilisers, and both factors can reduce the availability of fertiliser N for soil microorganisms due to net N immobilisation and constraints on solute diffusivity. The national N₂O EF for organic fertilisers recently reported for Germany was lower at 0.56% (Mathivanan et al., 2021), but around 30% of the N applied in organic fertilisers in Germany is straw-based manure or deep litter (Umweltbundesamt, 2022). Further, the recent refinement of the IPCC default EF recommendation of 0.6% for organic fertilisers in wet climates was based on an analysis of datasets that included 56% liquid and 46% solid manure (Hergoualc’h et al., 2021). The results discussed above suggest that the accuracy of N₂O emission inventories can be improved by distinguishing between solid and liquid organic fertilisers.

The apparent regional differences in N₂O EFs suggest that drivers of N₂O emissions differ between pedoclimatic zones. Synthetic N fertilisers depend on rainfall to develop oxygen-limited conditions that will sustain N₂O production (Charles et al., 2017), and wet soil conditions are short-lived in light-textured and well-drained soils. At the other extreme, liquid organic fertilisers may create anoxic hotspots at cm-dm scale that are temporarily stable and permit the development of coupled nitrification-denitrification (see Wagner-Riddle et al., 2020 and references therein), and sustained N₂O emissions can be seen even in well-drained soil. Thus, oxygen microsensor (Petersen et al., 1996) and oxygen optode measurements (Kravchenko et al., 2017) showed soil oxygen concentrations near ambient levels in light-textured soil except around organic hotspots with intense decomposer activity. The balance between the supply and demand of oxygen in soil (Thomsen et al., 2010) may be key to understanding the effect of pedoclimatic conditions on N₂O emissions. In light-textured and well-structured soil, rainfall is likely to enhance N₂O emissions by increasing the tortuosity for oxygen transport to sites of nitrification and potential denitrification, whereas in more fine-textured soil, where oxygen transport is already restricted, rainfall could inhibit nitrification activity and promote complete denitrification (Peixoto and Petersen, 2023). The tipping point will be different for organic fertilisers with a high oxygen sink capacity. In accordance with this interpretation, Vethof and Mosquera (2011) found greater N₂O emissions from liquid manure compared to CAN on a sandy soil, but the opposite effect on a clay soil.

4.4. Spring vs. annual N₂O emissions

The monitoring of N₂O emissions from synthetic and organic fertilisers only took place during spring. When comparing the annual emissions of N₂O from spring barley crops in the four rotations (Fig. 5), the determination of N₂O emissions during spring was vital, but for the EFs at the lower end of the range there was a contribution outside the spring period in the order of 0.1–0.2% of the N input (Fig. 5). In a meta-analysis, Shang et al. (2020) compared N₂O emissions during the growing season with those from a full year for different crop categories, and for cereals, maize and leguminous crops the net increase in N₂O emissions during the post-harvest period corresponded to 0.05–0.1% of the N input, which is consistent with the observations in the present study. Previous studies on sandy loam soil in Eastern Canada (Pelster et al., 2012), the Netherlands (Vethof and Mosquera, 2011), Germany (Herr et al., 2020) and Denmark (Brozyna et al., 2013) also found that annual N₂O emissions occurred mainly in the period between fertilisation and 1 July. Winter crops may require fertilisation in the autumn, as was the case in the present study for winter oilseed rape at Askov and Taastrup sites; autumn fertilisation can be included in the annual fertiliser N input depending on the objective of the study.

The determination of N₂O EFs for N fertilisers is based on the calculation of the net increase in N₂O emissions due to the amendment, which assumes that the contribution from other sources can be corrected by the inclusion of an unamended reference. Alternative sources of N₂O in arable crop rotations include crop residues after harvest and residues from winter cover crops (Abalos et al., 2022). Also, cultivation and fertilisation may enhance the decomposition of soil organic matter (positive priming effects, Azam, 2002). Nitrogen in crop residues (CR) and soil organic matter (SOM) is represented by FCR and FOM in the IPCC methodology (IPCC, 2019), and N₂O emissions are estimated as a proportion of the N content in these organic pools. Therefore, any emissions from these sources should be fully deducted to avoid double-counting.
Hansson et al. (1987) found that roots of spring barley at anthesis did not always show a difference (Chirinda et al., 2012; Cordoba et al., 2018), and the meta-analysis of Kim et al. (2013) found no difference in background emissions between arable systems and natural land. It is therefore at present unclear if differences in crop residue N between fertilised and unfertilised treatments are a source of error in the estimation of \( \text{N}_2\text{O} \) EFs for fertilisers.

Freeze-thaw effects on \( \text{N}_2\text{O} \) emissions are important in cold regions (Wagner-Riddle et al., 2017), as are drying-rewetting effects in dry soil following rainfall (Kröchels et al., 2022). Pelster et al. (2023) analysed Canadian data on non-growing season \( \text{N}_2\text{O} \) emissions, but here 22 of 34 studies with manure as fertiliser involved autumn application which increases the relative importance of post-growing season \( \text{N}_2\text{O} \) emissions (Pelster et al., 2023). In Denmark, fertilisation in the autumn is restricted by regulations to perennial grass and winter oilseed rape, and at country level only around 10% of cattle manure and 15% of pig manure is applied in August or later. There was little evidence for freeze-thaw effects on \( \text{N}_2\text{O} \) emissions during winter (Fig. 4), in contrast to significant off-season peaks observed in the autumn especially in Askov 2020/2021 and Taastrup 2021/2022, but transient emissions after thawing could have been missed in the absence of intense sampling and should be a topic of future investigations. Notably, in one case a net negative flux occurring after a freeze-thaw event in late January (Fig. 4) was suspected to be related to this. Freeze-thaw events should induce similar responses in fertilised and unfertilised plots, but apparently this was not the case here, possibly because of heterogeneity in the distribution of N in residues or soil properties. In accordance with this, Pelster et al. (2012) found that an unfertilised control had relatively low N emissions after harvest compared to fertilised treatments in one year, but the following year the emissions were far higher than from any fertilised treatments. These sources of experimental “noise” are difficult to avoid, but highlight the trade-off between accuracy (i.e., intent to measure all fertiliser-derived emissions during the year) and precision when selecting the length of monitoring periods, and following harvest there is a potential for confounding effects of other N inputs.

4.5. Implications for \( \text{N}_2\text{O} \) monitoring and mitigation

As mentioned above, there is evidence that with N fertilisation of the main crop in early spring, the emission of \( \text{N}_2\text{O} \) occurs mainly during spring and early summer (Charteris et al., 2020). For some management practices, such as the amendment of nitrification or urease inhibitors, any direct effects cease within a few weeks at soil temperatures above 10 °C due to biodegradation of the active compounds (Subbarao et al., 2006). For such measures, an estimate of \( \text{N}_2\text{O} \) mitigation can probably be obtained with a monitoring period of less than a year with little loss of accuracy. The same may be true for the effects of manure treatment technologies since most reactive organic C in manure is metabolised within 2–3 months (Thomsen et al., 2013).

Other mitigation strategies aim at modifying soil physical, chemical and biological properties that influence controls of \( \text{N}_2\text{O} \) emissions (Thangarajan et al., 2013). Such effects can potentially modify \( \text{N}_2\text{O} \) emissions throughout the year via effects on, e.g., soil structure, pH and soil gas diffusivity (Chirinda et al., 2010; Graham et al., 2017), which calls for monitoring around the year. Further, as outside the growing season the sources of \( \text{N}_2\text{O} \) are dominated by N released from crop residues and SOM, which are accounted for separately, it can be argued that the most consistent approach to estimate direct \( \text{N}_2\text{O} \) emissions from synthetic and organic N fertilisers, and EFs, would be to focus on emissions during the growing season before plant uptake, and to use empirical or more complex models to calculate the contributions from crop residues and SOM as modified by fertilisation. This would allow for a different allocation of research resources, for example to determine more site-specific \( \text{N}_2\text{O} \) EFs and with a wider range of synthetic and organic N fertilisers to support the development of country- or region-specific EFs, and verifiable GHG mitigation strategies.

Stricter regulations for the use of N fertiliser and manure for crop production have been introduced in many countries in Northern Europe (van Grinsven et al., 2012). In Denmark, increased manure storage capacity has become mandatory in order to promote field application in spring as a fertiliser for growing crops, and this implies that in the past more of the manure was land-applied in the autumn. To account for temporal trends in \( \text{N}_2\text{O} \) emissions it would be necessary to obtain documentation for \( \text{N}_2\text{O} \) emissions from autumn application of N fertilisers, even if this is no longer a common practice.

5. Conclusions

The multi-site and multi-year approach used in this study, with a combination of annual monitoring and spring campaigns to enable the inclusion of a wider range of organic and inorganic fertiliser sources, proved useful for this first investigation of country-specific EFs. The concurrent side-by-side comparison of several N sources at different sites allowed for a detailed and rigorous statistical analysis of effects and interactions. The \( \text{N}_2\text{O} \) EFs calculated for the spring period in the four arable crop rotations were, for both synthetic and organic fertilisers, comparable to annual EFs defined elsewhere under similar pedoclimatic conditions. Across the four locations and two years there was a strong relationship between spring and annual \( \text{N}_2\text{O} \) emissions from N applied to spring barley, and net increases in \( \text{N}_2\text{O} \) emissions in fertilised soil outside the spring period could partly be linked with other sources than fertiliser application. The results indicated that the stimulation of \( \text{N}_2\text{O} \) emissions occurring until crop N uptake was complete was a useful proxy for whole-year emissions on the light-textured soils investigated here. This study provided, for both synthetic and liquid organic fertilisers, support for country- or region-specific \( \text{N}_2\text{O} \) EFs that are, respectively, lower and higher than the global default EFs currently recommended.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Acknowledgements

This study was only possible with the dedicated support from numerous technicians including Arne Grud, Bodil Stensgaard, Camilla Kaskholt, Fritz Detlefsen, Henrik Norgaard, Jakob Engstrøm Nielsen, Jane S. Jakobsen, Jens B. Kjeldsen, Jonas Rasmussen, Lene Skovmose, Margit Paulsen, Mette S. Haferbier, Pia J. Andersen and Kathrine Østergaard. We also thank the farmers providing us with manure and digestate for experiments. This study was part of the Climate Research Program of the Ministry of Food, Agriculture and Fisheries (33010-NIFA-19-719).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agee.2023.108718.
References


