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Atmospheric ammonia and nitrogen deposition on Irish Natura 2000 sites: Implications for Irish agriculture

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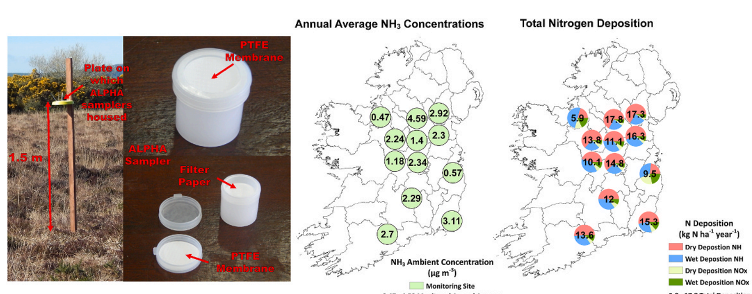
HIGHLIGHTS

- Ambient ammonia across twelve Natura 2000 sites was 0.47–4.59 μg NH_3 m^{-3}.
- Nitrogen deposition across twelve Natura 2000 sites was 5.93–17.78 kg N ha^{-1} yr^{-1}.
- Average nitrogen deposition comprised of 50.4% dry NH_3 & 31.7% wet NH_4.
- Average nitrogen deposition comprised of 7.5% dry NOx & 10.3% wet NOx.
- Agriculture is the primary source of biodiversity impacts from the more harmful NH_3.

GRAPHICAL ABSTRACT



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ABSTRACT

With growing global demand for food, the agriculture sector worldwide is under pressure to intensify and expand, risking acceleration of existing negative biodiversity impacts. Agriculture is the dominant source of ammonia (NH_3) emissions, which can impact biodiversity directly through dry deposition as NH_3 and by wet deposition following conversion to ammonium (NH_4) in the atmosphere. Nitrogen deposition is one of the leading causes of global decline in biodiversity alongside changing land use and climate. Natura 2000 sites which are intended to protect important habitats and species across Europe, require strict levels of protection to ensure designated features achieve favourable conservation status. Many of these sites are nitrogen-limited, and/or contain sensitive species such as lichens or mosses. This project carried out ambient NH_3 monitoring on selected Irish Natura 2000 sites, in order to establish potential impacts from agricultural NH_3. Monitoring on twelve Natura 2000 sites observed concentrations ranging from 0.47 to 4.59 μg NH_3 m^{-3}, from which dry deposition was calculated to be 1.22–11.92 kg N ha^{-1} yr^{-1}. European Monitoring and Evaluation Programme (EMEP) was used to quantify wet deposited NH_4 and nitrogen oxides (NOx), in addition to dry deposited NOx on monitored sites. Estimated total nitrogen deposition ranged between 5.93 and 17.78 kg N ha^{-1} yr^{-1}. On average across all monitored sites, deposition was comprised of 50.4%, 31.7%, 7.5%, and 10.3% dry NH_3, wet NH_4, dry NOx and wet NOx respectively. Implications for Irish agriculture are discussed in the light of both this monitoring and the European Commission Dutch Nitrogen Case (C 293/17 & C 294/17), highlighting a number of recommendations to aid compliance with the EU Habitats Directive (92/43/EEC).

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1. Introduction

1.1. Nitrogen emissions & deposition

Nitrogen deposition has been identified as the third greatest threat to global biodiversity, human activity constituting its primary source (Payne et al., 2017), being significantly linked with negative effects on biodiversity (Field et al., 2014; Stevens et al., 2004; Wilkins et al., 2016). Various forms of nitrogen contribute to these effects through a combination of dry and wet deposition. Dry deposition occurs when the gas is directly absorbed by the soil or vegetation, and wet deposition occurs when the gas combines with rainfall (Anderson et al., 2003). Dry deposition of ammonia (NH_3) is particularly harmful to biodiversity as, in addition to eutrophication and acidification, it also causes direct foliar damage (Dise et al., 2011). Wet deposition of ammonium (NH_4), formed when NH_3 reacts with other pollutants such as nitrogen oxides (NOx) or sulphur oxides (SO_x) (Sharma et al., 2007) travels greater distances as fine particulate matter below 2.5 μm ($PM_{2.5}$), before being deposited in rainfall (Warneck, 1999). $PM_{2.5}$ is also problematic for human health (Holst et al., 2018; Kim et al., 2015; Stokstad, 2014), with agricultural NH_3 being a significant precursor for its formation in urban areas (Hristov, 2011; Wu et al., 2016). Not only acting as a precursor for $PM_{2.5}$ production, NOx can also contribute directly to total nitrogen deposition resulting in biodiversity impacts (Bobbink and Hicks, 2009). Since the European agricultural and industrial revolutions, anthropogenic activities are estimated to have increased nitrogen emissions fourfold relative to background rates (Fowler et al., 2005). This increase is in part driven by growing global demand for food as the global population increases (Clay, 2011).

The National Emissions Ceilings (NEC) Directive (2016/2284/EU) (European Comission, 2016) and its predecessor (2001/81/EC) (European Comission, 2001) has set emission limits for all European Member States. These limits have country-specific reduction targets set for 2020 and 2030 relative to a 2005 baseline. Ireland (Republic of Ireland) has committed to reductions of 1% and 5% by 2020 and 2030 respectively. The primary source of NH_3 across Europe is from agriculture, where it accounts for between 80 and 90% of emissions (Webb et al., 2005),. Ireland has exceeded its NEC threshold since 2016 (99.1% of Ireland's emissions from agriculture), and though recent predictions estimate Ireland can meet its 2030 target, it will require widespread immediate adoption of emission reduction techniques (Buckley et al., 2020). Agriculture emits 32.4% of Ireland's NOx emissions, with the majority (40.6%) being emitted by traffic. The remaining NOx emissions come from industrial, power generation and commercial sectors. Despite emissions decreasing by 38.4% since 1990, Ireland predicts non-compliance with the NEC NOx threshold for 2020, however using the same estimates the threshold for 2030 can be met (Environmental Protection Agency, 2020).

1.2. Critical thresholds for nitrogen

Reduced N, in the form of NH_3 & NH_4 is considered a greater threat to biodiversity than NOx (Haddad et al., 2000; Paulissen et al., 2004; Pitcairn et al., 2003) and has been linked to damage on bryophyte species where NOx elicited no response (Verhoeven et al., 2011). This highlights the importance of these reduced forms of nitrogen for biodiversity impacts compared to oxidised nitrogen. Due to the importance of effects from NH_3 and its relative ease of ambient monitoring, Critical Levels (CLEs) have been set at concentrations beyond which adverse effects are expected (Posthumus, 1988). The United Nations Economic Commission for Europe (UNECE) currently recommend the use of annual critical levels of 1 and 3 μg NH_3 m^{-3}, for lichens/mosses and higher plants respectively (United Nations Economic Commission for Europe, 2007). The CLE of 3 μg NH_3 m^{-3} is based on a range of 2–4 μg NH_3 m^{-3}, where impacts on heather (*Calluna vulgaris*) were observed above 2 μg NH_3 m^{-3} (Sutton et al., 2008). NH_3 ambient concentration monitoring has been conducted twice in Ireland, once in 1999–2000 (de Kluizenaar and Farrell, 2000) and in 2013–2014 (Doyle et al., 2017). Doyle et al. (2017) carried out monitoring on 26 sites across Ireland and identified only 3 sites with a concentration below the CLE of 1 μg NH_3 m^{-3}, though none of the sites monitored exceeded the higher CLE of 3 μg NH_3 m^{-3}. The previous study by de Kluizenaar and Farrell (2000) monitored concentrations across 40 sites, with a greater range of observed concentrations: 0.18–3.21 μg NH_3 m^{-3}. Both studies selected sites at least 2 km from intensive sources of NH_3.

Ireland has participated in the critical loads mapping programme under the Convention on Long-range Transboundary Air Pollution (LRTAP) since 1990 (Aherne et al., 2017). A Critical Load (CL) refers to a deposition rate below which significant harmful effects do not occur "according to present knowledge" (Posthumus, 1988). Empirical CLs for total nitrogen deposition are habitat-specific, and typically present a range based on site-specific conditions. For example, raised and blanket bogs have a CL of 5–10 kg N ha^{-1} $year^{-1}$. The high end of this range is intended to represent bogs in areas with high precipitation or a high water table (Bobbink and Hettelingh, 2011). This approach, however, presumes the bog is in favourable conservation status, whereas guidance from the Air Pollution Information System (APIS) in the United Kingdom recommends the lower limit if the bog is not in favourable condition (Air Pollution Information System, 2016). Ireland's most recent Article 17 reporting under the Habitats Directive (92/43/EEC) (European Economic Committee, 1992) highlighted that the conditions of bogs in Ireland are declining and no site was deemed to have favourable conservation status (National Parks and Wildlife Service, 2019) highlighting that the lower range should be applied to all bog sites in Ireland.

1.3. Protecting Natura 2000 sites

The Habitats Directive (92/43/EEC) protects internationally important habitats and species across Europe through a designated network of Natura (2000) sites. These sites require a strict staged environmental assessment protocol termed Appropriate Assessment (AA), where it must be proven beyond reasonable doubt that any proposed plan or project does not negatively affect the conservation objectives of that Natura 2000 site. This typically requires four stages of assessment, where the first screens out plans or projects unlikely to have a significant effect upon a designated site's conservation objectives. The term "significant effect" can refer to any loss of designated habitat, impacts on its conservation objectives (e.g. habitat area, vegetation quality, typical species, etc.), or exceedance of a predefined threshold (Möckel, 2014). Critical levels and loads are commonly used as thresholds to assess the potential negative effects on Natura 2000 sites from atmospheric ammonia and nitrogen deposition (Hicks et al., 2011).

There is, however, some question over what contribution to concentration or deposition is required to move from stage 1 screening to stage 2 assessment. Past EU guidance recommended 0.3 kg N ha^{-1} $year^{-1}$ as *de minimis* contributions from an intensive source, where it stated contributions to deposition below this could not be attributable to a single source (IMPEL, 2017). However, the recent Dutch Nitrogen Case (C 293/17 & C 294/17) (CJEU, 2019) has clarified that even contributions as low as 0.0014 kg N ha^{-1} $year^{-1}$ may require a full AA. This judgement states that, even if contributions are below 0.0014 kg kg N ha^{-1} $year^{-1}$, a stage 2 assessment is required if the critical loads are already exceeded for that Natura 2000 site. This assessment must show that the additional contribution from the new development, in combination with existing deposition, will not negatively affect the site (Anker et al., 2019). Hence, before an assessment can be considered adequate, the baseline concentration and deposition on a Natura 2000 site must be understood. As a requirement of the Habitats Directive (92/43/EEC) the cumulative effects from multiple sources must be considered; where contributions from hotspot sources such as livestock housing or slurry/fertiliser spreading, may not be represented in national models and should be considered as part of baseline concentrations (Vogt et al., 2013).

Despite previous recommendations, there is no continuous NH_3 monitoring network in Ireland to date (Doyle et al., 2017), and NH_3 monitoring has never been carried out on Irish Natura 2000 sites. Ireland has, in the past, used kriged concentrations from the monitoring carried out in 1999–2000 (de Kluizenaar and Farrell, 2000) and 2013–2014 (Doyle et al., 2017) as representative baseline concentrations in the online screening tool SCAIL-Agriculture (Hill et al., 2014). Interpolating a limited number of monitoring points is not sufficient to represent the high spatial variability of NH_3 emissions (Singles et al., 1998). Other countries have adopted a modelling approach supported by a network of monitoring sites, such as FRAME (Fine Resolution AMmonia Exchange) in the UK (Singles et al., 1998), DAMOS (Danish Ammonia Modelling System) in Denmark (Geels et al., 2012) and OPS (Operational Priority Substances) in the Netherlands (Wichink Kruit et al., 2012). The MARSH (Mapping Ammonia Risk on Sensitive Habitats) model in Ireland estimated that 80.1, 34.3 and 5.9% of Natura (2000) sites potentially exceed NH_3 concentrations of 1, 2 and 3 μg m^{-3} respectively (Kelleghan et al., 2019). This work also highlighted the importance of developing a detailed source apportioned concentration model for Ireland. Even with such a map available, caution must be applied in its interpretation, as it has been shown that such models do not represent NH_3 concentrations at a local level, and more detailed modelling (particularly for intensive sources) is required to better predict baseline concentrations (Vogt et al., 2013). In reality, the spatial variability of emissions near, and concentration/deposition on, Natura 2000 sites is much more variable than the 1 km grids upon which such national maps are typically produced (Hallsworth et al., 2010; Plejdrup et al., 2018).

The updated NEC Directive (2016/2284/EU) recognises the importance of air pollution on sensitive habitats and, in addition to national ceilings, recommends a habitat-specific air pollution monitoring network. This network aims to establish long-term monitoring of air pollution, including NH_3 concentration and nitrogen deposition on sensitive sites such as bogs, heathland or semi natural grasslands. Linking this monitoring network with the Natura 2000 network of sensitive habitats will allow for continuous monitoring informing baseline concentration and deposition rates on selected sites. This monitoring could be used to validate any future national modelling programmes, required to carry out appropriate assessment on Irish Natura 2000 sites. This study aimed to monitor NH_3 concentration on 12 potentially sensitive Natura 2000 sites in order to calculate both CLE and CL exceedance on each Natura 2000 site, acting as a first assessment of monitored nitrogen impacts on Irish Natura 2000 sites. The implications for Irish agriculture as a result of both this monitoring, and the findings of the Dutch Nitrogen Case (C 293/17 & C 294/17)(CJEU, 2019), will be discussed.

2. Material and methods

2.1. Site selection and instrumentation

A stakeholder workshop was held with volunteers from within the National Parks and Wildlife Service (NPWS) and the Living Bog Project (Department of Culture, Heritage, and the Gaeltacht, 2020) in order to rank Natura 2000 sites at risk of impacts from NH_3 and hence a priority for monitoring. Emphasis was placed on identifying sites which had designation features sensitive to atmospheric NH_3 and nitrogen deposition. The process of selecting a suitable location identified twelve Natura 2000 sites to be included within a monitoring network, including seven Special Areas of Conservation (SAC) designated to protect bogs (Active raised bogs* [Annex I Habitat Code 7110], blanket bogs (active) * [Annex I Habitat Code 7130] and transition mires and quaking bogs [Annex I Habitat Code 7140]). Additionally, two sites were selected for containing semi-natural dry grasslands and scrubland facies on calcareous substrates (*Festuco-Brometalia*) (*important orchid sites) [Annex I Habitat Code 6210] and two for containing old sessile oak woods with *Ilex* and *Blechnum* in the British Isles [Annex I Habitat Code 91A0]. Asterisks indicate the listing of a habitat as priority for conservation under Annex I of the Habitats Directive (92/43/EEC). The remaining site Lough Lene SAC (Site K) was included both due to anecdotal accounts of slurry spreading onsite and the low critical load for oligotrophic waterbodies. A brief description of the selected Natura 2000 sites is provided in Table 1 below.

At each designated site, a 2.5 m stake was driven into the ground to which a plate was attached at a height of 1.5 m (See Fig. 1). Three ALPHA (Adapted Low-cost Passive High Absorption) samplers were attached to the underside of this plate using Velcro every 30 days by volunteers from the NPWS. The plate acted as a cover from rain and wind, with anti-bird spikes affixed to its top surface (Tang et al., 2017). Following protocols of the UK National Ammonia Monitoring Network, ALPHA samplers in triplicate were co-located beside Lough Navar's DELTA (DEnuder for Long-Term Atmospheric sampling) allowing the inherent bias in the ALPHA samplers to be assessed. The DELTA sampler is a low-volume denuder for long-term sampling of ambient ammonia and ammonium and is used in the UK network to provide ongoing calibration and assessment of the wider ALPHA network. This provided a reference method with which monitored concentrations were compared, as recent work has highlighted ALPHA samplers potentially underestimate concentrations compared to DELTA samplers (Pan et al., 2020).

2.2. ALPHA sampler preparation and sample analysis

ALPHA samplers were prepared in University College Dublin laboratories and posted to NPWS staff every 30 days. The previous month's samples were collected and returned. Any features in the surrounding environment that could influence NH_3 readings, including, slurry spreading, proximal livestock, lost samples, etc were noted. Due to the secluded nature of monitoring sites, it was only possible to record activity while changing ALPHA samplers on site. All sampler preparation was carried out in accordance with UKCEH standard protocols (Tang et al., 2017) Samples were posted to volunteering NPWS staff in a sealed plastic bag, alongside gloves, a cool pack, a comment sheet, and a return envelope. A fourth sampler intended to be unexposed was posted to each volunteer to be returned, which acted as a field blank for each sampler set. Four laboratory blanks were also prepared for each batch of samplers. Monitoring was conducted every 30 days from August 2017 – to July 2018 resulting in 11 samples for each of the 12 sites, though site accessibility introduced slight variations in exposure times which were accounted for in sample analysis. Analysis of ALPHA samplers followed Willis et al. (1996). A calibration curve of 10, 1, 0.1 and 0 ppm ammonium chloride (NH_4CL) was prepared in order to calibrate absorbance readings to known concentrations.

2.3. Nitrogen deposition estimation

The monitored concentrations were used to calculate the dry deposition of NH_3 based on deposition flux and NH_3 dry deposition velocity. The equation below was used, where V_d is the deposition velocity in m s^{-1}, and C is the concentration in μm^{-3}. F is the deposition flux in μg NH_3 m^{-2} s^{-1}, which is converted to kg N ha^{-1} $year^{-1}$ by multiplying by a factor of 259.7 (e.g. Natural Resources Wales, 2019).

$$V_{d} \times C = F$$

The habitat-specific deposition velocity was obtained from a review across different habitat types (de Kluizenaar and Farrell, 2000), where 0.015 m s^{-1} was applied to bogs and 0.01 m s^{-1} to other habitats due to low vegetation where monitoring was conducted. Concentration and deposition models are compiled annually for all of Europe, under the European Monitoring and Evaluation Programme (EMEP). The most recent data was produced on a grid of 0.1 ° × 0.1 ° longitude – latitude

Table 1
Monitored Natura 2000 site summaries.

Site Code	Site name	Site Description
Site A	Wicklow Mountains SAC	Wicklow Mountains SAC is an upland site featuring many sensitive habitats including blanket bog, heathlands, semi-natural grasslands and oak woodlands. These habitats are represented within the sites qualifying interests.
Site B	Blackwater River (Cork/ Waterford) SAC	Blackwater River SAC is a wide ranging riverine SAC, which follows the Blackwater River through Cork and Waterford. In addition to sustaining freshwater pearl mussel *Margaritifera margaritifera*, White-clawed Crayfish *Austropotamobius pallipes* and Salmon *Salmo salar* amongst other riverine species, it is designated for woodlands along its banks. These include both oak woodlands and alluvial forests.
Site C	Killyconny Bog (Cloghbally) SAC	Killyconny Bog SAC is a midlands raised bog, a priority Annex I habitat under the Habitats Directive (92/43/EEC) as it contains active raised bog.
Site D	Slaney River Valley SAC/ Wexford Harbour and Slobs SPA	Slaney River Valley SAC and Wexford Harbour and Slobs SPA are two Natura 2000 sites that overlap at Wexford Harbour. Slaney River Valley SAC is designated for a number of riverine species and habitats, including oak and alluvial woodlands along its banks. Wexford Harbour SPA is designated for a range of wetlands and waterbirds, but also hen harrier.
Site E	Raheenmore Bog SAC	Raheenmore Bog SAC is a midlands raised bog, a priority Annex I habitat under the Habitats Directive (92/43/EEC) as it contains active raised bog.
Site F	Spahill and Clomantagh Hill SAC	Spahill and Clomantagh Hill SAC is a semi-natural grasslands SAC, where it is solely designated for calcareous grasslands.
Site G	Bricklieve Mountains and Keishcorran SAC	Bricklieve Mountains and Keishcorran SAC is an uplands SAC containing a number of potentially sensitive grassland habitats, including calcareous grasslands and lowland hay meadows.
Site H	Ardagullion Bog SAC	Ardagullion Bog SAC is a midlands raised bog, a priority Annex I habitat under the Habitats Directive (92/43/EEC) as it contains active raised bog.
Site I	Brown Bog SAC	Brown Bog SAC is a midlands raised bog, a priority Annex I habitat under the Habitats Directive (92/43/EEC) as it contains active raised bog.
Site J	Garriskil Bog SAC	Garriskil Bog SAC is a midlands raised bog, a priority Annex I habitat under the Habitats Directive (92/43/EEC) as it contains active raised bog.
Site K	Lough Lene SAC	Lough Lene SAC is designated for oligo-mesotrophic waters and white clawed crayfish *Austropotamobius pallipes*.
Site L	Scragh Bog SAC	Scragh Bog SAC is designated for containing transition mires, quaking bogs and alkaline fens.

(8.3 km^2) this data was used to identify wet deposition of NH_4 and NOx, and dry deposition of NOx on the monitored sites (including particulates) (European Monitoring and Evaluation Programme, 2018). All forms of nitrogen deposition were converted to kg N ha^{-1} $year^{-1}$ and summed to estimate total nitrogen deposition at each monitoring location. The relative contribution of each form to total deposition was then calculated.

Fig. 1. ALPHA sampler on stake at Natura 2000 site.

2.4. Statistical analysis

ArcGIS was used to create 2 km buffers around each monitoring site, within which CORINE Landcover data was analysed. This was used to identify the proportion of agricultural land directly proximal to the ambient monitoring locations. Both the proportion of habitats “Pasture” and “Non-irrigated arable land” were summed and compared with monitored concentrations in an X, Y scatterplot. The average monthly mean temperatures for the sampling period were collected from 27 synoptic Met Éireann meteorological stations across Ireland (Met Éireann, 2020). These monthly mean temperatures were compared with monthly mean NH_3 concentrations from across all sites, as both a proxy for seasonal variation and the influence of temperature. Pearson correlations were tested to compare both land use and temperature on NH_3 concentrations in the monitored network.

Microsoft Excel was used to create a single factor ANOVA to calculate the significance of the difference between monitoring period and between sites and to produce Box and Whisker plots to further summarise monitoring data comparing concentrations between monitoring period and sites. Uncertainty was applied to monitored concentrations using previously published literature (Martin et al., 2019).

3. Results

3.1. Co-location DELTA

ALPHA samplers were co-located in triplicate with the DELTA sampler in Lough Navar, Northern Ireland; where the annual average for ALPHA samplers was 0.04 μg m^{-3} higher than that of the DELTA sampler. This difference was used to adjust both annual averages and monthly samples of concentrations for other sites. .

3.2. Temporal variation

Average NH_3 concentrations were calculated approximately every 30 days for all sites. Exceptions occurred where samplers were not returned or were lost. The seasonal trends of NH_3 concentration on every Natura 2000 site monitored is presented in Fig. 2 below. Though concentrations vary from site to site, a trend is visible across all sites with a slight increase in concentrations in spring (February–April), followed by a large peak in the summer (May–July) and a slight increase towards the end of the year. This trend was less pronounced for both the Wicklow Mountains (Site A) and Bricklieve Mountains & Keishcorran SAC (Site G) where NH_3 concentrations were consistently lower than all other sites. The highest concentration across any site was seen on Lough Lene SAC

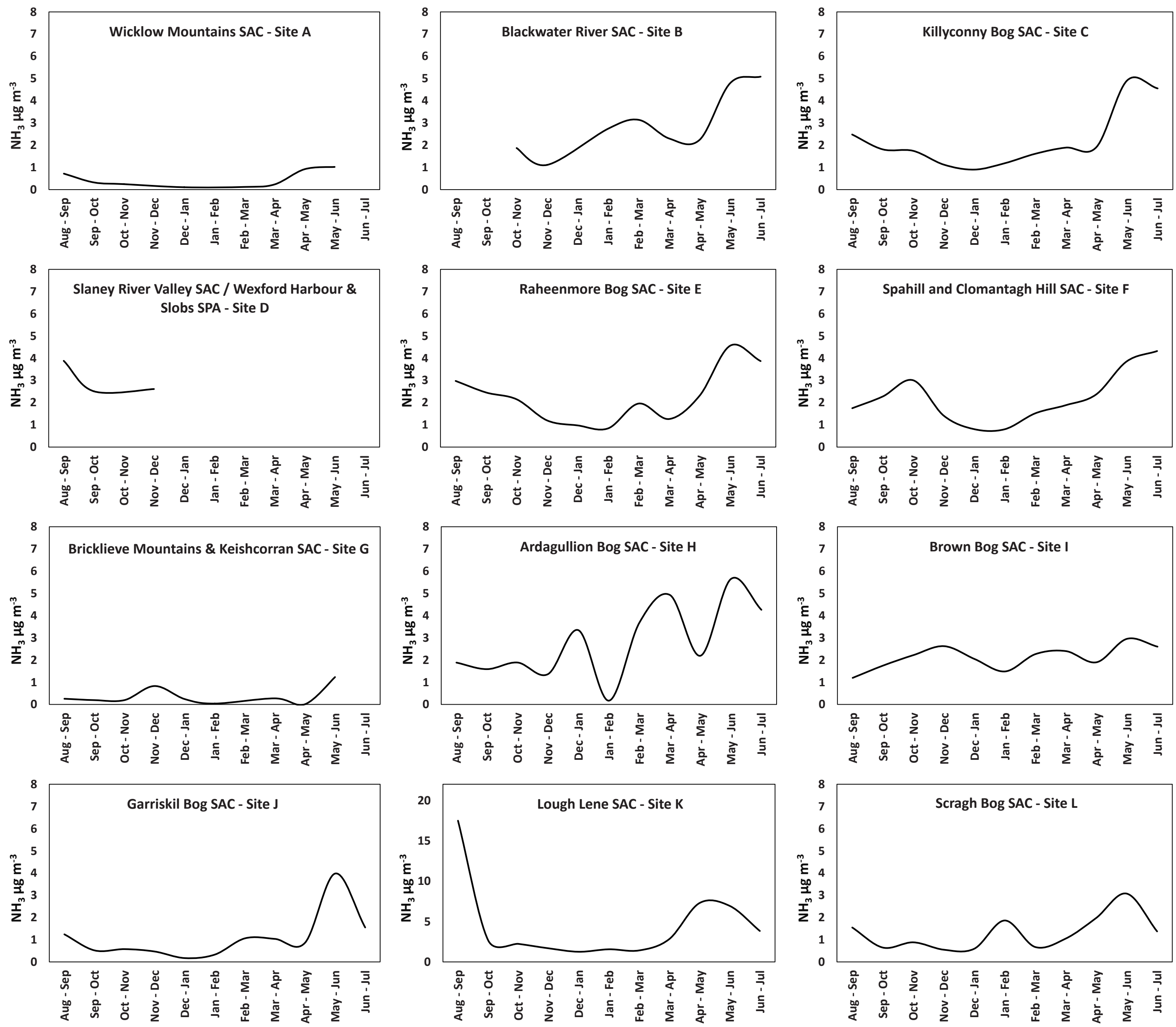

Fig. 2. Seasonal variation over 12-month period monitored across 12 Natura 2000 sites.

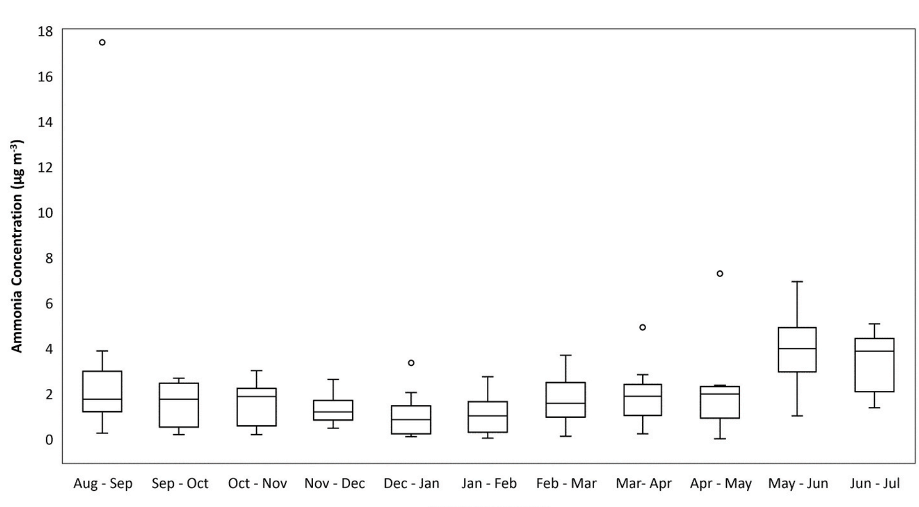

Fig. 3. Box and Whisker plot of NH_3 concentrations monitored within 11 monitoring periods covering 12 months on all sites.

(Site K) August–September, where a concentration of 17.5 μg m^{-3} was observed. The NPWS volunteer noted that this high concentration was likely due to slurry spreading occurring within neighbouring fields. Slurry spreading was also observed in April–May, when a concentration of 7.3 μg m^{-3} was recorded. The lowest concentrations observed across all sites typically occurred in December–January, with Ardagullion Bog SAC (Site H) being an exception seeing a peak (3.4 μg m^{-3}) in December–January, followed by a dip in January–February. Slight increases were observed on Brown Bog SAC (Site I) and Bricklieve Mountains & Keishcorran SAC (Site G) in November–December. .

The Box and Whisker plot presented in Fig. 3 summarises the monitoring conducted across 12 Natura 2000 sites. A distinct seasonal pattern is observed, where concentrations typically decrease from August–September through to December–January, followed by increases through to summer peaks in May–July. May–Jun exhibits the greatest range, followed by Feb–Mar and Aug–Sep.

ANOVA single factor analysis indicates there is a statistically significant difference between monitoring periods across all 12 sites. Where $P < 0.005$ and F (2.85)is higher than F critical value (1.92).

3.3. Spatial variation

Annual average concentrations from this monitoring programme (Kelleghan et al., 2020), are presented in Table 2. NH_3 concentrations across sites varied substantially from 0.47 μg m^{-3} in the Bricklieve Mountains and Keishcorran SAC (Site G) to 4.59 μg m^{-3} in Lough Lene SAC (Site K). Of the Natura 2000 sites designated for bog related qualifying features, annual average concentrations of 0.57, 2.3, 2.34, 2.92, 2.24, 1.18, and 1.4 μg m^{-3} were observed on Wicklow Mountains SAC (Site A), Killyconny Bog (Cloghbally) SAC (Site C), Raheenmore Bog SAC (Site E), Ardagullion Bog SAC (Site H), Brown Bog SAC (Site I), Garriskil Bog SAC (Site J), Scragh Bog SAC (Site L) respectively. Averaging monitored values for Blackwater River (Cork/Waterford) SAC and Slaney River Valley SAC/Wexford Harbour and Slobs SPA resulted in concentrations of 2.7 and 3.11 μg m^{-3}. The annual average concentration monitored on Spahill and Clomantagh Hill SAC (Site F) was 2.29 μg m^{-3}.

Uncertainty was applied to data collected by ALPHA samplers using uncertainty (11.4–11.5%) previously identified for ALPHA samplers (Martin et al., 2019). This resulted in an uncertainty ranging from ±0.05–0.52 μg m^{-3} across monitored sites (Fig. 4).

The estimated dry deposition of NH_3 based on the concentration and habitat type is also presented in Table 2, alongside EMEP modelled wet reduced and oxidised nitrogen deposition, in addition to dry oxidised nitrogen deposition. The estimated dry deposition of nitrogen from the monitored NH_3 ranges from 1.22 kg N ha^{-1} yr^{-1} to 11.92 kg N ha^{-1} yr^{-1} for the same sites. The lowest level of wet NH_4 deposition was observed on Bricklieve Mountains and Keishcorran SAC (Site G) at 2.98 kg N ha^{-1} yr^{-1}, where the highest was in Killyconny Bog (Cloghbally) SAC (Site C) with 5.31 kg N ha^{-1} yr^{-1}. Oxidised N in the form of wet and dry deposited NOx is deposited across sites at a lower range compared to reduced N, where dry deposition of NOx varies from 0.67 to 2.14 kg N ha^{-1} yr^{-1}, and wet NOx on a range of 0.99–2.03 kg N ha^{-1} yr^{-1}. The highest total nitrogen deposition is expected to occur on Lough Lene (Site K) with 17.78 kg N ha^{-1} yr^{-1}, though Ardagullion Bog SAC (Site H) is a close second with 17.32 kg N ha^{-1} yr^{-1}. The lowest total N deposition occurs in the Bricklieve Mountains and Keishcorran SAC (Site G) with 5.93 kg N ha^{-1} yr^{-1} deposited, followed by Wicklow Mountains SAC (Site A) with 9.52 kg N ha^{-1} yr^{-1} and the Garriskil Bog SAC (Site J) with 10.01 kg N ha^{-1} yr^{-1}. All other Natura 2000s site receive a total N deposition greater than 11 kg N ha^{-1} yr^{-1}.

Monitored concentration and estimated deposition data from Table 2 is presented in Fig. 5, which shows the concentration of NH_3 monitored on each Natura 2000 site (Fig. 5, Left) and the total nitrogen deposition with relative contributions from wet and dry oxidised and reduced nitrogen deposition (Fig. 5, Right).

Dry deposition of NH_3 typically comprised the greatest contribution

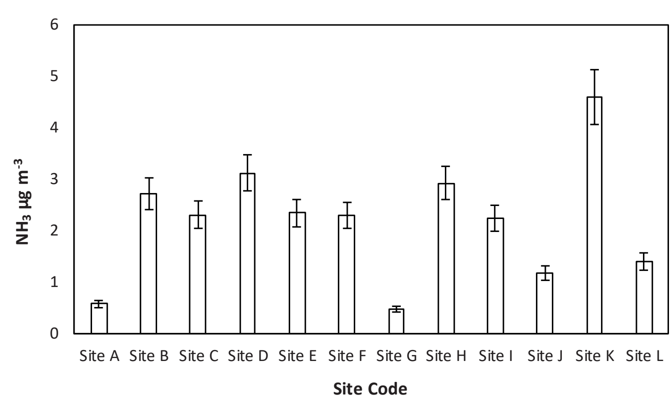

Fig. 4. Mean monitored concentrations per site, where error bars represent uncertainty as defined by Martin et al. (2019).

Table 2
NH_3 concentration and nitrogen (N) deposition rates on monitored sites.

Site Code	Site name	NH_3 concentration (μg NH_3 m^{-3})	Dry NH_y Deposition (kg N ha^{-1} yr^{-1})	Wet NH_y Deposition (kg N ha^{-1} yr^{-1})	Dry NOx Deposition (kg N ha^{-1} yr^{-1})	Wet NOx Deposition (kg N ha^{-1} yr^{-1})	Total Reduced N Deposition (kg N ha^{-1} yr^{1})
	Source	Monitored	Calculated	EMEP 2017	EMEP 2017	EMEP 2017	Calculated
Site A	Wicklow Mountains SAC	0.57	2.22	3.16	2.14	2.01	9.52
Site B	Blackwater River (Cork/ Waterford) SAC	2.7	7.01	4.54	0.77	1.32	13.64
Site C	Killyconny Bog (Cloghbally) SAC	2.3	8.96	5.31	0.73	1.26	16.26
Site D	Slaney River Valley SAC/ Wexford Harbour and Slobs SPA	3.11	8.08	4.04	1.12	2.03	15.27
Site E	Raheenmore Bog SAC	2.34	9.12	3.85	0.8	1.04	14.81
Site F	Spahill and Clomantagh Hill SAC	2.29	5.95	4.19	0.87	0.99	12
Site G	Bricklieve Mountains and Keishcorran SAC	0.47	1.22	2.98	0.67	1.06	5.93
Site H	Ardagullion Bog SAC	2.92	11.37	4.24	0.68	1.04	17.32
Site I	Brown Bog SAC	2.24	8.73	3.3	0.75	0.99	13.78
Site J	Garriskil Bog SAC	1.18	4.6	3.81	0.67	1.01	10.1
Site K	Lough Lene SAC	4.59	11.92	4.03	0.74	1.1	17.78
Site L	Scragh Bog SAC	1.4	5.45	3.88	0.72	1.01	11.07

to total nitrogen deposition, ranging from 23.3% to 67% with an average of 50.4% across all sites. Wet deposition of NH_4 was the second greatest contributor to total nitrogen deposition, with an average of 31.7% across all sites and a range of 22.7–50.3%. Both dry and wet deposited NOx contributed the least to total nitrogen deposition with averages of 7.5 and 10.3% respectively across all sites. This varied across sites with ranges of 3.9%–22.5% for dry deposited and 6–21.1% for wet deposited NOx (Table 3).

The Box and Whisker plot presented in Fig. 6 displays the variation of concentrations recorded at each different site monitored. Sites with high and low whiskers such as Blackwater River (Cork/Waterford) SAC (Site B), Raheenmore Bog SAC (Site E), Spahill and Clomantagh Hill SAC (Site F) and Ardagullion Bog SAC (Site H) are sites which displayed a greater seasonal variation concentration recorded. Lough Lene (Site K) has the highest third quartile, though its median is similar to a number of other sites.

3.4. Trend analysis

Analysis of land use influence on NH_3 concentration used CORINE Landcover data to infer agricultural activity proximal to each monitoring site. The percentage of each habitat type within 2 km from the monitoring site was calculated, from which the percentage cover of both “Pasture” and “Non-irrigated arable land” were summed to represent land within 2 km dedicated to agriculture. Annual average ambient concentrations exhibited a Pearson correlation coefficient of 0.8 with landuse in Fig. 7. Similarly, the relationship with average monthly temperature is shown in Fig. 7, as a proxy for influence of time of year and the direct influence of temperature. This relationship exhibits a Pearson correlation coefficient of 0.9, highlighting season and temperature also have an influence on concentrations alongside land use.

4. Discussion

4.1. Source of nitrogen

The strong correlation of proximal agricultural land and monitored NH_3 concentration supports agriculture as its dominant source on monitored Natura 2000 sites (Kelleghan et al., 2019; Sutton et al., 2001; Tang et al., 2018). While seasonal variation observed supports the link to both temperature and seasonally variable agricultural activity (e.g.

Table 3
Proportion of dry and wet deposited reduced and oxidised nitrogen to monitored sites.

Site Code	Site name	Dry NH_3 Deposition % of Total N	Wet NH_4 Deposition % of Total N	Dry NOx Deposition % of Total N	Wet NOx Deposition % of Total N
Site A	Wicklow Mountains SAC	23.3	33.2	22.5	21.1
Site B	Blackwater River (Cork/ Waterford) SAC	51.4	33.3	5.6	9.7
Site C	Killyconny Bog (Cloghbally) SAC	55.1	32.7	4.5	7.7
Site D	Slaney River Valley SAC/ Wexford Harbour and Slobs SPA	52.9	26.5	7.3	13.3
Site E	Raheenmore Bog SAC	61.6	26	5.4	7
Site F	Spahill and Clomantagh Hill SAC	49.6	34.9	7.3	8.3
Site G	Bricklieve Mountains and Keishcorran SAC	20.6	50.3	11.3	17.9
Site H	Ardagullion Bog SAC	65.6	24.5	3.9	6
Site I	Brown Bog SAC	63.4	23.9	5.4	7.2
Site J	Garriskil Bog SAC	45.5	37.7	6.6	10
Site K	Lough Lene SAC	67	22.7	4.2	6.2
Site L	Scragh Bog SAC	49.2	35	6.5	9.1
Average		50.4	31.7	7.5	10.3

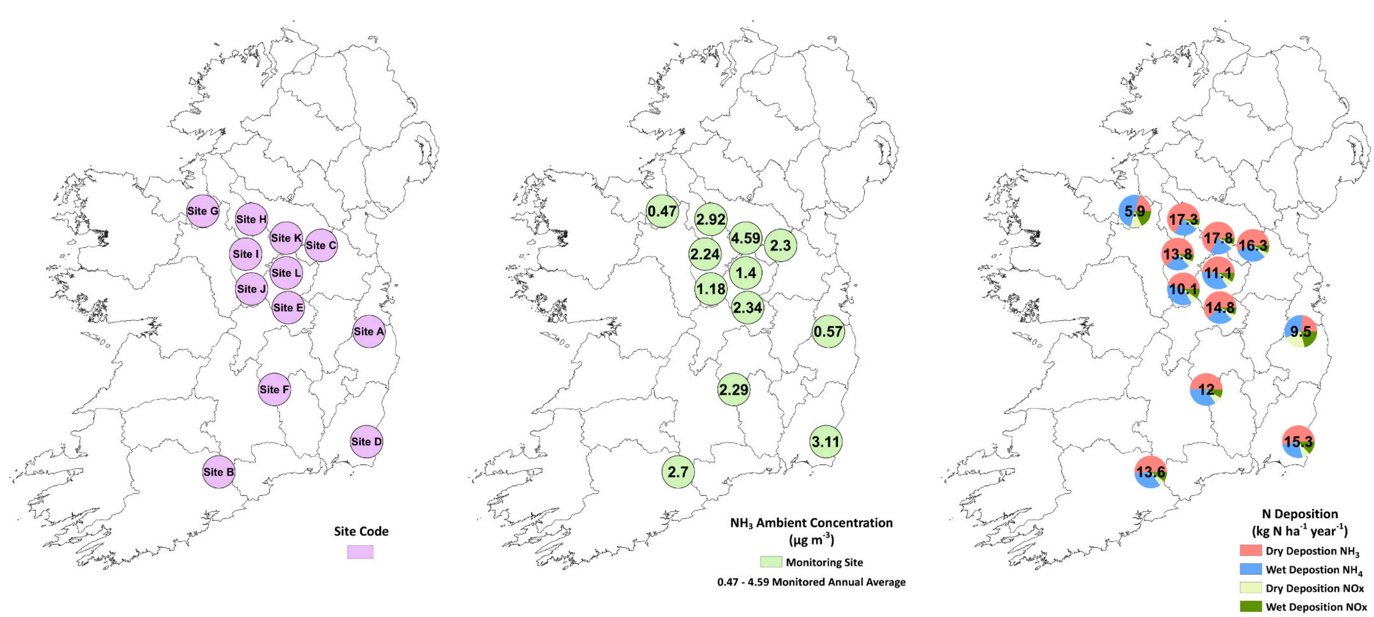

Fig. 5. Left – Site Codes. Middle - Monitored concentrations on Natura 2000 sites. Right – Total nitrogen (N) deposition at monitored locations.

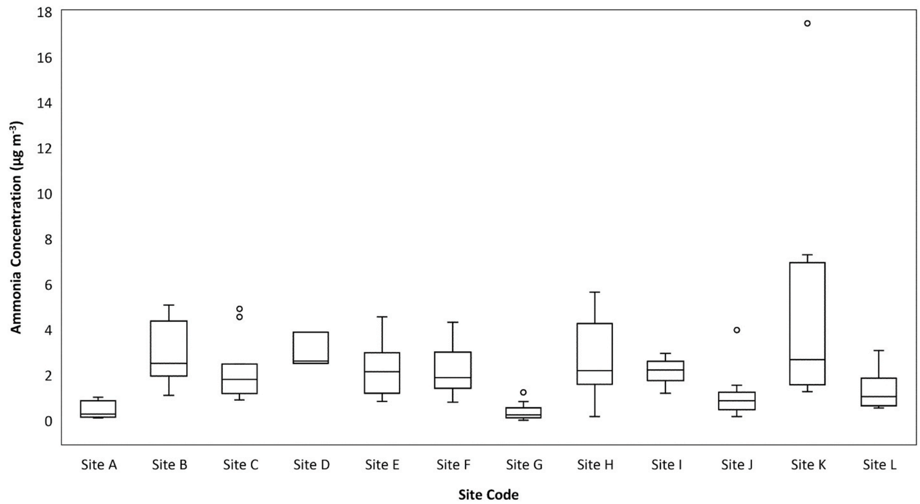

Fig. 6. Box and Whisker plot of NH_3 concentrations monitored on different sites over 12-month period. ANOVA single factor analysis indicates there is a statistically significant difference between concentrations on different sites. Where $P < 0.005$ and F (3.97) is higher than F critical (1.88).

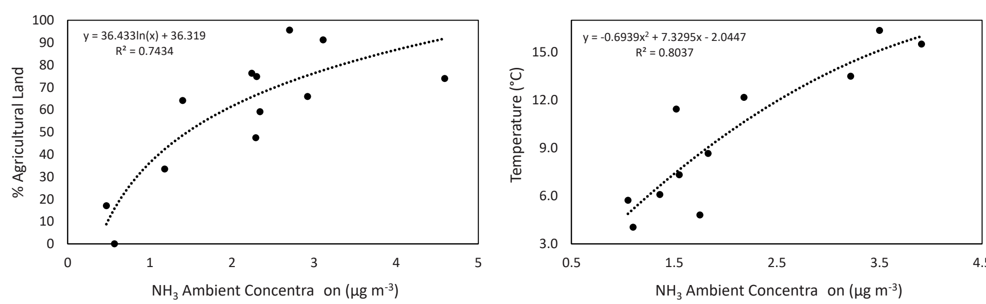

Fig. 7. Left: Scatterplot of annual average ambient NH_3 concentrations against percentage agricultural land within 2 km of the monitoring site. Right: Scatterplot of monthly average ambient NH_3 concentrations against average monthly temperature.

Doyle et al., 2017; Lalor and Schulte, 2008). The proportion of CORINE habitats "Pasture" and "Non-irrigated arable land" within 2 km acts as a proxy for agricultural intensity near monitoring locations. It is accepted that agriculture contributes to 99% of Irish NH_3 emissions (Environmental Protection Agency, 2020), thereby contributing to the majority of NH_4 production (Asman et al., 1998; Gong et al., 2013). NH_3 and NH_4 combined, forming total reduced nitrogen deposition contribute an average of 82.1% to total nitrogen deposition. While oxidised nitrogen accounts for the remaining 17.9%, agriculture is responsible for 32.4% of these emissions (Environmental Protection Agency, 2020). However, as reduced nitrogen has been shown to illicit greater biodiversity impacts than oxidised nitrogen (Haddad et al., 2000; Paulissen et al., 2004; Pitcairn et al., 2003), agriculture's contribution to NH_3 production is more important than its contributions to NOx emissions.

4.2. Seasonal variation

A significant correlation (Pearson's correlation co-efficient of 0.9) between monitored concentrations with monthly average temperature indicates a clear effect of temperature. This influence is likely due to a combination of seasonally variable agricultural activity and the temperature itself. Both monitoring (Bourdin et al., 2014) and modelling (Lalor and Lanigan, 2010) in Ireland have in the past highlighted the influence of seasonally variable temperatures on NH_3 emission rates, with peak rates typically in the hottest summer months (i.e. June–August). Both temperatures and windspeeds affect the emission rate and dispersion potential of NH_3 (Misselbrook et al., 2005; Sommer et al., 1991).

Most sites monitored had their highest monthly average concentrations recorded in May–June, corresponding with peak silage harvesting and nutrient application. Across Ireland, an estimated 62% of total annual slurry application occurs from April to June (Lalor and Schulte, 2008), with most sites showing a slight decrease in NH_3 before the May to June peak. Though seasonal patterns of NH_3 concentration varied across sites, the trend observed (Fig. 3) is broadly representative of the nutrient application period, where the spreading season opens January 13th – February 1st through to September 14th – October 31st, depending on location and material. The slight increase towards the end of the year seen on a number of sites could be attributed to farmers emptying slurry tanks before or after the closed period. Across most sites, this increase is minimal, though concentrations observed on Spahill and Clomantagh Hill SAC (Site F) and Brown Bog SAC (Site I) both exceed 2 μg m^{-3} for October–November indicating potential spreading immediately prior to the closed period. While a peak above 3 μg m^{-3} in December–January on Ardagullion Bog SAC (Site H) may be a clearer indicator of potential out of season spreading, it could also be from spreading after January 12th – 15th or be attributed to other agricultural sources (Department of Agriculture and Food, 2008). The highest concentration observed of 17.5 μg m^{-3} occurred in August–September on Lough Lene SAC (Site K), where the source was recorded by the site operator as being from slurry spreading. This site saw the highest annual average concentration, primarily as a result of the peaks in April–June, and August–September, where slurry spreading was recorded by the site operator for both peaks. It should be noted that observations could only be made when samples were being changed and may not be representative of conditions throughout the 30-day monitoring period. Measured concentrations across many sites were lowest during the closed period between December and January. The concentration on the Bricklieve

Mountains and Keishcorran SAC (Site G) however increased slightly in December but was still comparable to concentrations on all other sites at the same time. The typical grass-growing season in Ireland begins in March slowing down in August before growth ceases from October to March as a result of lower soil temperatures (Hennessy and Roosen, 2003). The patterns observed roughly correspond with the grazing period, though this varies from farm to farm it is typically from March to November (Läpple et al., 2012).

Both of the previous NH_3 monitoring studies in Ireland also exhibited similar seasonal patterns, with the 2013–14 survey showing on average lows from December–February, July, and October (Doyle et al., 2017). Doyle et al. (2017) showed a more pronounced peak in November concentrations compared to this study, but echoed peaks observed from March–April, and June. In contrast to this study, Doyle et al. (2017) exhibited an increase in concentrations from August–October. The 1999–2000 survey (de Kluizenaar and Farrell, 2000) reported high concentrations in March and June, again echoing the influence of agricultural practices on NH_3 emission and concentration. However, the 1999–2000 survey (de Kluizenaar and Farrell, 2000) highlights peak concentrations also observed in January which are not supported by either the 2013–2014 survey or this study. In both previous projects, monitoring sites were located >2 km from intensive sources such as pig or poultry farms, as the networks were focused on monitoring ambient conditions. As indicated in both previous studies, a continuous national NH_3 network is required to establish long-term trends to adequately identify seasonal variation. All analysis conducted on seasonal variation of NH_3 concentrations attribute varying concentration to a combination of agricultural practices (primarily slurry spreading) and meteorological conditions (e.g. Anderson et al., 2003; Hellsten et al., 2007). The strong seasonal variation observed supports past work carried out in Ireland which highlighted that emissions from slurry spreading are higher with higher temperatures, and can be reduced by spreading when temperatures are lower (Bourdin et al., 2014). Bourdin et al.'s (2014) work however also highlights that though NH_3 emissions from spreading in Spring with lower temperatures reduce NH_3 emissions, they typically increase N_2O emissions. Hence Spring applications may be more important where nitrogen deposition to biodiversity is a concern, whereas areas not proximal to protected biodiversity could focus on reducing N_2O reductions.

4.3. Critical threshold exceedance

The spatial variation of concentrations between sites monitored echoes previous calls for detailed national modelling to account for the spatial diversity of emissions, concentration and deposition (Doyle et al., 2017; Kelleghan et al., 2019; Singles et al., 1998). Table 4 details critical levels, critical loads (Bobbink and Hettelingh, 2011) and vegetation community change points previously identified from Irish research (Wilkins et al., 2016).

Of the sites monitored, only two fell below the critical level for lichens and mosses of 1 μg m^{-3}. These were both upland sites in areas with relatively low levels of agriculture. The Bricklieve Mountains and Keishcorran SAC (Site G) had an annual average NH_3 concentration of 0.47 μg m^{-3} with an estimated total nitrogen deposition 5.93 kg N ha^{-1} yr^{-1}, well below the empirical critical load of 15–25 kg N ha^{-1} yr^{-1} for semi-natural dry grasslands and scrubland facies on calcareous substrates (*Festuco-Brometalia*) (*important orchid sites) [Annex I Habitat Code 6210]. Similarly, concentrations recorded at the Wicklow Mountains SAC (Site A) site were below the lower critical level at 1 μg m^{-3}, though the south east of Ireland is exposed to higher levels of wet deposition with an estimated total nitrogen deposition of 9.52 kg N ha^{-1} yr^{-1}, higher than the lower end of the empirical critical loads for Blanket Bogs (Active)* [Annex I Habitat Code 7130]. In Ireland, due to pressures from other sources, it is recommended that the lower CL (5 kg N ha^{-1} yr^{-1}) be applied to bogs (Air Pollution Information System, 2016). This is a good example of a site where the CLE is not exceeded but the CL is, highlighting the importance of assessing exceedance of both thresholds in practice.

Table 4
Critical thresholds for most sensitive qualifying feature for each Natura 2000 site monitored.

Site Code	Site name	Most Sensitive Feature	Critical Level (μg NH_3 m^{-3})	Critical Load (kg N ha^{-1} $year^{-1}$)	Vegetation Change Point (kg N ha^{-1} $year^{-1}$)
Site A	Wicklow Mountains SAC	Blanket bogs (active)[a] [7130]	1	5–10	4.9
Site B	Blackwater River (Cork/ Waterford) SAC	Old sessile oak woods with *Ilex* and *Blechnum* in the British Isles [91A0]	1	10–15	8.8
Site C	Killyconny Bog (Cloghbally) SAC	Active raised bogs[a] [7110]	1	5–10	4.9[b]
Site D	Slaney River Valley SAC/ Wexford Harbour and Slobs SPA	Old sessile oak woods with *Ilex* and *Blechnum* in the British Isles [91A0]	1	10–15	8.8
Site E	Raheenmore Bog SAC	Active raised bogs[a] [7110]	1	5–10	4.9[b]
Site F	Spahill and Clomantagh Hill SAC	Semi-natural dry grasslands and scrubland facies on calcareous substrates (*Festuco-Brometalia*) ([a] important orchid sites) [6210]	1	15–25	8.3
Site G	Bricklieve Mountains and Keishcorran SAC	Semi-natural dry grasslands and scrubland facies on calcareous substrates (*Festuco-Brometalia*) ([a] important orchid sites) [6210]	1	15–25	8.3
Site H	Ardagullion Bog SAC	Active raised bogs[a] [7110]	1	5–10	4.9[b]
Site I	Brown Bog SAC	Active raised bogs[a] [7110]	1	5–10	4.9[b]
Site J	Garriskil Bog SAC	Active raised bogs[a] [7110]	1	5–10	4.9[b]
Site K	Lough Lene SAC	Hard oligo-mesotrophic waters with benthic vegetation of *Chara* spp. [3140]	3	3–10	–
Site L	Scragh Bog SAC	Transition mires and quaking bogs [7140]	1	5–10	4.9[b]

[a] Annex I priority habitat.
[b] Based on vegetation community change point for active blanket bogs.

Bogs are particularly sensitive to impacts from atmospheric nitrogen pollution (e.g. Gunnarsson and Rydin, 2000; Sheppard et al., 2009) as they are ombrotrophic systems, adapted to a low-nutrient environment.

As such, 7 of the 12 Natura 2000 sites monitored were previously designated for containing peatland specific conservation features. The Wicklow Mountains SAC (Site A) site was Blanket Bogs (Active)* [Annex I Habitat Code 7130], Scragh Bog SAC (Site L) for its Transition mires and quaking bogs [Annex I Habitat Code 7140], while the remaining sites were all Active raised bogs* [Annex I Habitat Code 7110]. All active raised bog sites exceeded the CLE for lichens and moss species of 1 μg m^{-3}, with a range of 1.18–2.92 μg m^{-3}. The total nitrogen deposition across all active raised bog sites exceed the higher band of the CL range (10 kg N ha^{-1} yr^{-1}) with rates of 10.1–17.32 kg N ha^{-1} yr^{-1}.

Only two sites monitored exceeded the CLE for higher plants at 3 μg m^{-3}: Slaney River Valley SAC/Wexford Harbour & Slobs SPA (Site D) and Lough Lene SAC (Site K). Slaney River Valley SAC/Wexford Harbour & Slobs SPA (Site D) constitutes two overlapping Natura 2000 sites encompassing Wexford Harbour within which monitoring was conducted. Slaney River Valley (Site D) is designated for old sessile oak woods with *Ilex* and *Blechnum* in the British Isles [91A0], amongst other potentially sensitive conservation features. It is not recommended to apply the annual average concentration from this monitoring period as it is derived from only three samples. However, previous monitoring was conducted on the same site in the 1999–2000 study indicating an annual average concentration of 3.12 μg m^{-3} (de Kluizenaar and Farrell, 2000), which indicates the monitored 3.11 μg m^{-3} may be representative; though, it is also possible that this similarity is coincidence and conditions could have changed on site. Applying the monitored concentration estimates total nitrogen deposition as 13.3 kg N ha^{-1} yr^{-1} exceeding the lower CL for old sessile oak woods with *Ilex* and *Blechnum* in the British Isles [91A0] of 10–15 kg kg N ha^{-1} yr^{-1} (Bobbink and Hettelingh, 2011).

Lough Lene SAC (Site K) while qualifying features are not directly associated with impacts from NH_3, hard oligo-mesotrophic waters with benthic vegetation of *Chara* spp [3140] can be linked with the empirical critical load for "permanent oligotrophic lakes, ponds and pools" with an empirical critical load of 3–10 kg N ha^{-1} yr^{-1}. An annual average of 4.59 μg m^{-3} exceeding the CLE for higher plants is supported by total nitrogen deposition of 17.78 kg N ha^{-1} yr^{-1} a rate higher than both the upper and lower range for the relevant empirical critical load.

Habitat-specific CLs have been highlighted as being an "inefficient approach to managing nitrogen deposition" to protect biodiversity as species community changes occur at rates lower than empirical critical loads (Payne et al., 2017). In Ireland, detailed analysis of species community changes along a gradient of nitrogen deposition identified vegetation community change points at rates typically lower than empirical CLs (Wilkins et al., 2016). Where the empirical CL for Semi-natural dry grasslands and scrubland facies on calcareous substrates (*Festuco-Brometalia*) (*important orchid sites) [Annex I Habitat Code 6210] is 15–25 kg N ha^{-1} yr^{-1}, work by Wilkins et al. (2016) showed that species changes occur at 8.3 kg N ha^{-1} yr^{-1}. This distinction is vitally important for Spahill and Clomantagh Hill SAC (Site F), where the CLE is exceeded at 2.29 μg m^{-3}, but total reduced nitrogen deposition only reaches 12 kg N ha^{-1} yr^{-1}. This rate is below the empirical CL but above the vegetation community change point. Empirical CLs are intended to be iterative, so there is potential this rate could be lowered upon the next review (De Vries et al., 2007).

The Blackwater River (Cork/Waterford) SAC (Site B) monitoring site is the only location that was within 15 m of a roadway, which could have contributed to its measurements. Every other site was of significant distance from roadsides and thereby contributions from traffic are not expected to be significant. The CLE for this site was exceeded and was quite close to exceeding the CLE for higher plants at 2.7 μg m^{-3}. The Blackwater River (Cork/Waterford) SAC (Site B) comprises several distinct habitat sub-units, a number of which are potentially sensitive to NH_3 or nitrogen pollution; particularly old sessile oak woods with *Ilex* and *Blechnum* in the British Isles [Annex I Habitat Code 91A0] with a CL of 10–15 kg N ha^{-1} yr^{-1}. The lower end of this CL range was exceeded with a rate of 13.64 kg N ha^{-1} yr^{-1}, in addition to the vegetation change point of 8.8 kg N ha^{-1} yr^{-1} (Wilkins et al., 2016). While it is possible Blackwater River (Cork/Waterford) SAC (Site B) is receiving some NH_3 from vehicular traffic, it appears to follow the same seasonal trend as other sites. This could indicate traffic may not be an issue for this isolated case, but that is not clear from the data available.

4.4. Implications for Irish agriculture

Typically, areas with more intensive agriculture have higher NH_3 concentrations, such as in the east and south of the Netherlands (Lolkema et al., 2015) and as recorded in areas with higher numbers of intensive sources (Tang et al., 2018). Doyle et al. (2017) showed a strong correlation between livestock numbers and the ambient monitoring network in the 2013–2014 Irish survey. All monitored exceedances from the current study are likely a result from agricultural pollution with the exception of the Blackwater Valley SAC (Site B), which may also be in receipt of emissions from traffic. Contribution of NOx to sites was relatively minimal, accounting for 17.8% of total nitrogen deposition. As 99% of Irish NH_3 emissions are from agriculture (Environmental Protection Agency, 2020), and NH_4 is formed from NH_3 pollution (Gong et al., 2013; Russell et al., 1983), assessing exceedance of CLs based on these two elements alone would focus the assessment on contributions from agriculture. As it is also possible for these sites to be receiving contributions from agricultural NOx from fertilizers and urine and dung from grazing animals, the contribution of oxidised nitrogen was included (Environmental Protection Agency, 2020). An important distinction between this study and the two previous Irish studies is that the current study focused on monitoring concentrations on Natura 2000 sites whereas the previous two were carried out as national ambient networks. Considering the strict protection required for Natura 2000 sites and the apparent failure of maintaining concentration and deposition below CLEs and CLs, current practices need to be questioned.

The Dutch Nitrogen Case (C 293/17 & C 294/17)(CJEU, 2019) has clarified that any source of NH_3 should be assessed in AA of Natura (2000) sites, specifically grazing cattle and land spreading. This logic is extended to other agricultural activities such as cattle housing (including farms receiving derogation under Nitrates Directive (91/676/EEC) (European Comission, 1991), and pig and poultry farms below Industrial Emissions Directive (2010/75/EU)(European Union, 2010) thresholds. A current failing of the Irish assessment process is consideration of cumulative impacts from multiple sources. If included in assessments, background concentrations are derived from kriged estimations of concentration from 25 to 40 sites more than 2 km away from intensive sources are typically used as a baseline across all Natura 2000 sites. As this monitoring specifically excluded intensive sources of pig and poultry farms assessments, using this baseline alone cannot be representative of local concentration and deposition rates. Shropshire Council has recognised this as an issue in the UK, requiring new agricultural developments to include a review of all potential contributing intensive sources into their assessment (Shropshire Council, 2018). When carrying out AA of a new agricultural facility or practice, cognisance needs to be given to the baseline concentration and deposition on neighbouring Natura 2000 sites. As the Dutch Nitrogen Case (C 293/17 & C 294/17)(CJEU, 2019) points out, if a site already exceeds its CLEs or CLs, any additional contribution could be considered as causing a significant negative effect to the site's integrity (Anker et al., 2019).

Further discussion and research are required concerning whether a significant negative effect on a Natura 2000 site's integrity is achieved when either a CL or a vegetation change point is exceeded. Vegetation change points identified by Wilkins et al. (2016) are typically lower than CLs and would therefore be more difficult to enforce. However, international research supports the use of vegetation change points to conserve biodiversity rather than empirical CLs, as CLs have been described as an inefficient approach to managing such pollution (Payne et al., 2017).

It is vital that, when compliance is being sought with the NEC limit, a focus on compliance with the Habitats Directive (92/43/EEC) is not lost. Considering that a substantial proportion of the Irish Natura 2000 network is at risk to exceed site specific CLEs (Kelleghan et al., 2019), action is required not just to adequately assess new agricultural plans and projects but to assess existing practices. Reducing impacts is a more challenging task than merely reducing emissions, where Dutch measures to restore habitats from nitrogen impacts are underway (Schoukens, 2017). It is estimated that emission reduction targets in the UK will lead to only "modest increases in species richness" (Payne et al., 2017). There are several approaches to reduce emissions, and thereby negative effects on Natura 2000 sites. Air scrubbers are required on farm buildings proximal to Natura 2000 sites in Denmark, and are typical across the Netherlands (Jacobsen et al., 2019). Air scrubbers have been shown to be an effective measure to reduce ammonia emissions from housing (Melse and Ogink, 2005; Ogink and Bosma, 2007; Zhao et al., 2011), often with co-benefits of reducing odour and particulate matter emissions. Scrubbers are one of the most expensive forms of mitigation, where cheaper approaches such as reducing nitrogen content in feed or substituting urea with ammonium nitrate or protected urea are preferred due to low cost (Guthrie et al., 2018). Acidification of slurry is another viable option, though this practice is also expensive on a per animal basis, it is competitive when assessed in terms of national emission reductions. Denmark, for example, acidifies 20% of slurry produced, resulting in 60–70% reduction in NH_3 emissions from livestock buildings, and 50% during field applications (Jacobsen, 2017). Alternative techniques for applying fertiliser/slurry to fields, can also reduce emissions (Dowling et al., 2008; Misselbrook et al., 2002; Smith et al., 2000), though it remains to be seen if these or any combination of approaches above could reduce impacts observed on monitored Natura 2000 sites. Jacobsen et al. (2019) reported it to be very difficult to reduce emissions within 400 m of Natura (2000) site in order to meet allowable contributions to concentration and deposition, with estimated costs of up to €30,000 per year in addition to legally required emission reduction approaches e.g. reductions achieved from implementing BAT (Best Available Techniques) under the Industrial Emissions Directive (2010/75/EU). In the Netherlands, the cost of reducing emissions beyond BAT requirements decreases to €20,000 within 2000 m. Jacobsen et al. (2019) also clarified that, where critical loads were already exceeded as with many of the sites monitored by this project, it was not possible to reduce emissions to a permissible quantity.

5. Conclusions & recommendations

The monitoring in this study confirms for the first time CLE and CL exceedances of Irish Natura (2000) sites as a direct result of agricultural NH_3 pollution. With continued agricultural expansion expected under Food Wise 2025 (Department of Agriculture Food and the Marine, 2015) and predicted increases in national emissions (Donnellan et al., 2018), cognisance needs to be given to sites which are already impacted and those which will become impacted through an increase in emissions. For nitrogen-sensitive habitats such as bogs, heathland or many semi-natural grasslands, this is extremely problematic, as these exceedances are in direct conflict with conservation objectives of Natura (2000) sites. A strategy needs to be put in place to assess and manage current exceedances not just to ensure compliance with the Habitats Directive (92/43/EEC) but to guarantee these habitats are protected for future generations. Site-specific "Nitrogen Action Plans" to manage emissions near and impacts on Natura 2000 sites have been recommended (Whitfield and McIntosh, 2014). These would require collaboration between the competent authority for protecting Natura 2000 sites (National Parks and Wildlife Service) and the Department of Agriculture, Food and Marine.

A Pearson correlation co-efficient of 0.8 indicates a clear relationship between the amount of nearby agricultural land and the atmospheric concentration of NH_3. While temperature has an even stronger statistical correlation with a Pearson correlation co-efficient of 0.9, this relationship is both a direct result of temperature and seasonally variable agricultural practices.

All midlands raised bogs monitored exceeded both their CLEs and CLs, as a priority Annex I habitat under the Habitats Directive (92/43/EEC), this is cause for concern. Due to their sensitivity, priority designation, prevalence of other pressures and exhibited levels of deposition on these sites, action is recommended immediately to develop plans to monitor and restore these sites in light of atmospheric pollution. Both the Wicklow Mountains SAC (Site A) and Bricklieve Mountains and Keishcorran SAC (Site G) fell below the CLE for NH_3 were the two upland sites, where the contribution from other forms of nitrogen resulted in the Wicklow Mountains SAC (Site A) exceeding its empirical critical load. Hence, of the twelve Natura 2000 sites monitored, only the Bricklieve Mountains and Keishcorran SAC (Site G) was likely to not be impacted by nitrogen deposition. Likely due to the combination of few proximal sources and upland nature.

It is unclear if emission reduction approaches to land spreading of slurry/fertiliser would be sufficient to reduce concentrations on these sites. It is likely that additional management practices are required to reduce emissions, concentrations and deposition of harmful nitrogenous compounds. However, based on this monitoring, international approaches, and the findings of the Dutch Nitrogen Case (C 293/17 & C 294/17) the authors wish to highlight six points intended to improve compliance with the Habitats Directive (92/43/EEC), which apply not only to Ireland but every European Member State:

1. Appropriate Assessment should be carried out for all sources of NH_3, including slurry spreading, fertiliser application, cattle grazing, livestock housing, etc.
2. Semi-continuous national ambient modelling is required, supported by an extensive continuous monitoring network. An approach similar to the UK, Denmark or the Netherlands is recommended, where an extensive passive sampler network is supported by intensive monitoring on selected sites. This would generate more detailed maps not just for ammonia, but also other forms of nitrogen deposition improving on the resolution of European models (i.e. EMEP).
3. Detailed source apportioned concentration and deposition models are required for at-risk Natura 2000 sites, including all local hotspot sources in modelling to best represent cumulative contributions to the Natura 2000 site.
4. Site specific nitrogen management plans, inclusive of detailed concentration monitoring are recommended for potentially at-risk Natura 2000 sites.
5. Interpreting the monitoring results as being reflective of conditions across the whole site is problematic as, in reality, concentration and deposition tends to be heterogeneous within any one site (Vogt et al., 2013). A more spatially detailed study monitoring this variability across a number of affected sites is recommended in order to identify appropriate management to reduce local emissions and subsequent impacts.
6. Due to differing monitoring periods, exposure lengths, and missing samples, a monthly adjustment could not be calculated by this study and the same adjustment was applied equally to all periods. In future, this could be accounted for by conducting monitoring for the same time periods as the DELTA sampler. Additionally, this adjustment bias would benefit from co-location beside a DELTA sampler exposed to higher concentrations in order to provide a range.

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.

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