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Atmospheric ammonia, acid gas and aerosol monitoring network in Northern Ireland: 2023

Report for 2023 calendar year

31/03/2026

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1. Summary

A Northern Ireland-wide ammonia monitoring network was established in March 2019 across the country with 25 ammonia (NH_3) monthly monitoring sites, implementing the UKCEH ALPHA® method (Adapted Low-cost Passive High Absorption sampler®) and 4 reactive gas and aerosol monitoring sites implementing the UKCEH DELTA® method (DEnuder for Long Term Atmospheric sampling® system). From March 2022, all ALPHA® sites were added into the UK National Ammonia Monitoring Network (NAMN), while only one DELTA® site from the original NI network was retained to join the UK Acid Gases and Aerosol Network (AGANet). This resulted in a total number of 26 sites for the Northern Ireland network from March 2022 onwards, with only the Hillsborough AFBI25-A continuing monitoring outside of the UKEAP until July 2023.

The aim of these measurements is to provide sufficient data to (i) explore spatial and temporal patterns in NH_3 concentrations in Northern Ireland, (ii) compare results with atmospheric transport model output, and (iii) to enable longer-term trend analysis and potential for quantifying change over time due to changes in activities and/or the implementation of policy measures, and (iv) monitor and assess the relationship between NH_3 and interacting acid gases (nitric acid: HNO_3, sulphur dioxide: SO_2) and inorganic particulate phase composition (ammonium: NH_4^+, nitrate: NO_3^-, sulphate: SO_4^{2-}, chloride: Cl^-, sodium: Na^+, calcium: Ca^{2+}, magnesium: Mg^{2+}).

Monthly measurements from March 2019 to December 2023 are presented in this report. Annual mean concentrations for calendar years are reported as time-weighted means to ensure that individual sampling periods contribute proportionally to the calculated annual mean, accounting for slightly longer or shorter monitoring periods.

Spatial patterns and seasonal variability (January to December 2023)

- Annual mean NH_3 concentrations in NI in 2023 show high spatial variability, in line with data across the 26 sites, albeit with a general decrease of concentrations for most sites compared to 2022. The lowest NH_3 annual mean concentrations continued to be observed at rural background sites (e.g., 0.56 µg NH_3 m^{-3} for 2022 at Beaghs Burn (UKA00383), while the highest annual mean concentrations occurred in an area dominated by emissions from dairy farming (6.28 µg NH_3 m^{-3} at Drumclamph 2 (AFBI29-A).
- In 2023 only one site surpassed a monthly concentration ≥ 20 µg m^{-3} (Inch Abbey; UKA00948), in contrast with 2022 when 6 monitoring sites surpassed that threshold.
- All sites showed seasonal variability in NH_3 concentrations, with key drivers relating to agricultural activities and meteorological conditions. The highest monthly concentrations are typically observed in spring and autumn when manure applications take place. In 2023, the spring peak occurred early, influenced by very dry conditions in February followed by intense precipitation in March with associated lower land spreading activity. It is important to note that a spring concentration peak

was also observed at background sites (across all years), suggesting a wider regional influence of agricultural emissions at these more remote locations.

- Warmer and drier conditions in the summer months are likely to have contributed to elevated monthly concentrations, coupled to seasonal grazing of animals and the displacement of the NH_3 /NH_4^+ equilibrium towards the gas phase. Lower concentrations during the winter months across the network reflected a reduction in emissions in cold, wet conditions with little agricultural activity as well as an enhancement of the partitioning of NH_3 (g) into ammonium (NH_4^+) (p) aerosols.
- Data coverage for annual representativity (>274 days) was not achieved for the DELTA samplers at Ballynahone Bog and Lough Navar due to sampling and technical issues.
- Ammonia continues to be the largest component in the gas and aerosol measurements for the inorganic N species reported in the DELTA® network. This means that NH_3 was the dominant contributor to atmospheric nitrogen input to sensitive receptors over many parts of Northern Ireland.
- Aerosol phase continued to be dominated by secondary inorganic aerosols (SIA) NH_4NO_3 and $(NH_4)_2SO_4$, and Na & Cl, related to sea salt sources.

Comparison with model estimates

- Annual average measured NH_3 concentrations were compared with outputs from the UK European Monitoring and Evaluation Programme model (EMEP4UK, e.g. Vieno et al., 2016), a 3-D Eulerian chemical transport model widely utilized in scientific research and policy support at both global and regional scales. The annual average NH_3 concentrations across the network agree with modelled predictions (R^2 = 0.62, FAC2 = 78%) in 2023.

2. NI ALPHA® and DELTA® network

A network of 25 ammonia (NH_3) monitoring sites was established in early March 2019 across Northern Ireland by UKCEH and AFBI, implementing the same methodology as in the UK's National Ammonia Monitoring Network (NAMN[1]) using UKCEH ALPHA® samplers (Adapted Low-cost Passive High Absorption sampler®; Tang et al., 2001). In addition, 4 sites were established to monitor reactive gases and inorganic aerosols, implementing the UKCEH DELTA® method (DEnuder for Long Term Atmospheric sampling® system; Sutton et al., 2001) as used in the UKs Acid Gases and Aerosols Network (AGANet[2]) and NAMN.

In March 2022, 24 ALPHA sites and 1 DELTA site were transferred from the old NI NH_3 network under the UK Eutrophying and Acidifying Pollutants (UKEAP[3]) contract.

The 24 ALPHA sites (without Hillsborough, AFBI25-A) joined the NAMN ALPHA site Coleraine, while the DELTA site of Ballynahone Bog (AFBI26-D) was added to the UK's National Ammonia Monitoring Network (NAMN) and Acid Gases and Aerosol Network (AGANet) DELTA sites alongside Hillsborough and Lough Navar (Figure 1).

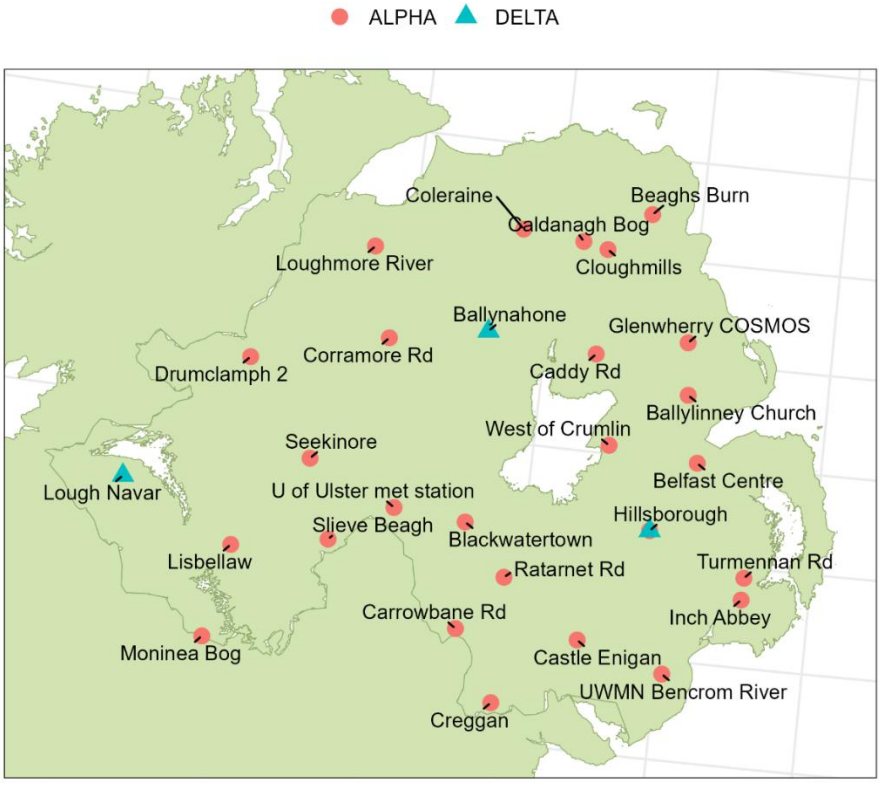


Figure 1. Map of Northern Ireland ALPHA® and DELTA® network (total = 29 sites) for 2023, established across Northern Ireland in March 2019.

[1] https://uk-air.defra.gov.uk/networks/network-info?view=nh3
[2] https://uk-air.defra.gov.uk/networks/network-info?view=aganet
[3] https://uk-air.defra.gov.uk/networks/network-info?view=ukeap

Table 1 shows the equivalent UKAIR codes for each of the NI network sites that were incorporated into the UKEAP network. The pre-UKEAP site codes are shown here for ease of comparison with previous reports in this series, however from 2023 onwards the UKAIR codes will be used to identify each site. Additionally, AFBI25-A is present in this report for data completion purposes, as the monitoring continued there until July 2023.

Table 1. Equivalence between the pre-UKEAP site codes and their correspondent UKAIR code from March 2022 onwards.

Site name	Code pre-UKEAP	UKAIR code
U of Ulster met station	AFBI01-A	UKA00938
Castle Enigan	AFBI02-A	UKA00939
Beaghs Burn	AFBI03-A	UKA00383
Slieve Beagh	AFBI04-A	UKA00940
Moninea Bog	AFBI05-A	UKA00941
Seekinore	AFBI07-A	UKA00942
Lisbellaw	AFBI08-A	UKA00943
Glenwherry COSMOS	AFBI09-A	UKA00944
UWMN Bencrom River	AFBI10-A	UKA00945
Blackwatertown	AFBI11-A	UKA00946
Ratarnet Rd	AFBI12-A	UKA00947
Inch Abbey	AFBI13-A	UKA00948
Belfast Centre	AFBI14-A	UKA00212
Ballylinney Church	AFBI15-A	UKA00949
West of Crumlin	AFBI16-A	UKA00950
Loughmore River	AFBI17-A	UKA00951
Caldanagh Bog	AFBI18-A	UKA00952
Cloughmills	AFBI19-A	UKA00953
Caddy Rd	AFBI20-A	UKA00954
Turmennan Rd	AFBI21-A	UKA00955
Carrowbane Rd	AFBI22-A	UKA00956
Creggan	AFBI23-A	UKA00957
Corramore Rd	AFBI24-A	UKA00958
Ballynahone Bog	AFBI26-D	UKA00959
Drumclamph 2	AFBI29-A	UKA00960
Lough Navar	S45-D	UKA00166
Hillsborough	S44-D	UKA00293
Coleraine	S79-A	UKA00401

The ALPHA® sites had been selected to provide representative coverage at the time of network design (2018) of (i) the range of modelled concentrations from the FRAME chemical transport and deposition model (replaced with EMEP4UK for model/measurement intercomparisons since the Year 2022 report in this series), (ii) each of seven major dominant emission source classifications: cattle (beef and dairy), pigs & poultry, sheep, mixed agriculture, non-agricultural, fertiliser and background (very low emission density, < 1 kg N ha^{-1} yr^{-1}), and (iii) spatial coverage across Northern Ireland.

The DELTA® sites provide monthly measurements of NH_3 as well as concurrent measurement of acid gases (nitric acid: HNO_3, sulphur dioxide: SO_2) and inorganic aerosols (ammonium: NH_4^+, nitrate: NO_3^-, sulphate: SO_4^{2-}, chloride: Cl^-, sodium: Na^+, Ca^{2+}, magnesium: Mg^{2+}). This evidence is useful for evaluating atmospheric transport models and for estimating a budget of reduced nitrogen (NH_3 and NH_4^+) vs. oxidised nitrogen (sum of HNO_3 and NO_3^-), as well as sulphur.

2.1. Historic changes in the NI NH_3 Network

Table 2 shows the current number of sites with ALPHA® and DELTA® samplers in NI that are part of the UKEAP network. Some changes were made since the establishment of the network (in 2019) to keep it as representative as possible:

- AFBI06 (Drumclamph: cattle dairy) was discontinued in August 2019 due to a large local source and was relocated to AFBI29 Drumclamph 2 in September 2019.
- AFBI25 (Hillsborough: mixed cattle) is not representative for the surrounding area as it was deliberately set up close to a large emission source. This site had installed an ALPHA® sampler (AFBI25-A), a DELTA® sampler (AFBI25-D) and a Picarro Cavity Ring-Down Spectroscopy (CRDS) NH_3 gas analyser (Picarro model Q2103; https://www.picarro.com) with high time-resolution, continuous measurement of NH_3. An Automatic Weather Station (Campbell Scientific; www.campbellsci.eu) was also installed at the same time and these instruments were operated alongside the existing long-term UKEAP network measurements at Hillsborough, for local scale assessment rather than representativity within the NI NH_3 network.
- AFBI25-D (Hillsborough DELTA; mixed cattle), AFBI27-D (U of U Coleraine Met Station; mixed cattle) and AFBI28-D (Sandholes; Mixed cattle) were discontinued after March 2022.

Table 2: Operational NH_3 monitoring sites in Northern Ireland during 2023 calendar year.

Site Type	Air pollutants measured	# Sites
ALPHA®	Gas: NH_3	26
DELTA®	Gases: NH_3, HNO_3, SO_2 Aerosols: NH_4^+, NO_3^-, SO_4^2, Cl^-, Na^+, Ca^{2+}, Mg^{2+})	3
Total number of sites		**29**

2.2. Data Quality Management

The ALPHA® and DELTA® samplers are prepared and analysed at the UKAS-accredited UKCEH Lancaster laboratory, following standard protocols developed by UKCEH (Tang et al., 2001) and implemented in the UK NAMN (Tang et al., 2018a) and UK Acid Gas and Aerosol Monitoring Network (Tang et al., 2018b). Detailed descriptions of the ALPHA® and DELTA® methods were provided in the Year 1 report (Tang et al., 2021). Starting from March 2022, the NI NH_3 network follows the UKEAP data ratification process explained in Twigg et al. (2024). This process includes:

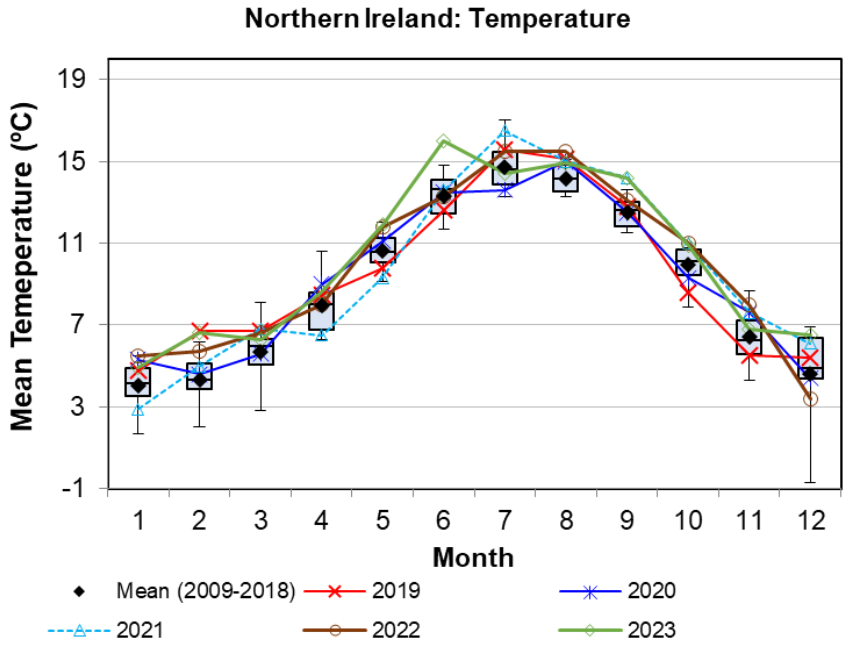
1. Review and flagging of data based on field and laboratory comments.
2. Automated processes and flagging based on metadata and quality controls.
3. Expert scientist review including site specific reviews.

All data presented in this report have undergone QA/QC and are fully ratified.
The minimum number of valid monthly measurement data needed to calculate an annual mean (based on calendar years) is 9 (75 % data capture); in the case of time weighted averages, the number of valid days needs to be ≥273.75 days. This is to avoid bias in the estimated annual mean, particularly since NH_3 is known to exhibit large seasonal variability.

3. Results and Discussions

3.1. Meteorological conditions

The monthly averaged temperature and precipitation data for Northern Ireland from March 2019 to December 2023 are shown in Figure 2, alongside the longer-term average for the 2009-2018 period.



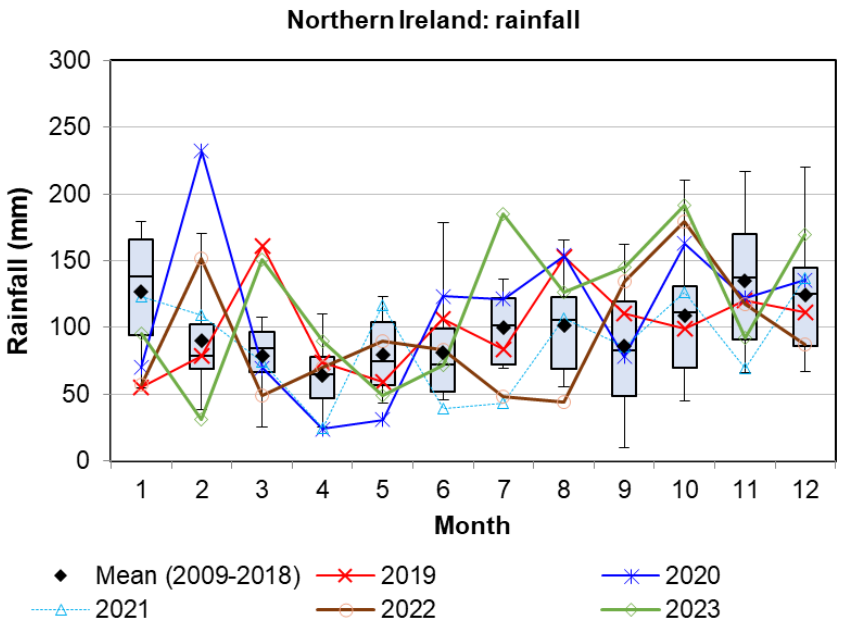


Figure 2: Comparison of 2019 to 2023 mean monthly temperature (top) and rainfall (bottom) data against the 10-year averaged monthly data (2009 to 2018) in NI. The diamonds in the boxplots show the mean, with the grey boxes indicating the median and interquartile range, and the error bars showing the minimum and maximum. Source: https://www.metoffice.gov.uk/pub/data/weather/uk/climate/datasets/, accessed 24/01/2025).

The 2023 annual average temperature ± standard deviation of 10.2 ± 4 °C constitutes a historical maximum in Northern Ireland since records began back in 1910, and the first time the annual mean surpassed 10 °C.

Monthly mean temperatures in 2023 in some months were higher than the 10-year average (2009-2018). June was notably warm, with mean T = 16 °C, and ranked as one of the sunniest Junes recorded since 1957 as well as the hottest June since 1887 (Met Office, 2023a & 2023b). The precipitation measurements show February (31.3 mm) was an unusually dry month, below the 10-year average minimum value (38 mm). In contrast to this dry period, March and July were exceptionally wet (151.2 and 185.4 mm rain, respectively) compared to the 10-year average maximum for each month (107.3 and 136.3 mm) (Met Office, 2023c).

3.2. Annual mean NH_3 concentrations

3.2.1. Annual Mean Calculation Approach comparison

In more recent reporting years, annual mean concentrations were calculated by assuming that each individual measurement represented an equal one-month period. Under this approach, all monthly sample values were treated as 1/12 of a 12-month year, regardless of the actual exposure duration, i.e., the number of days represented by each monthly sample.

From 2023 onwards, a time-weighted (TW) annual mean method has been adopted. This approach accounts for differences in exposure durations and varying lengths of

calendar month, assigning each monthly measurement a weight proportional to the number of days it represents. This ensures that longer exposure periods contribute proportionally more to the calculated annual mean than shorter periods. The method is consistent with the UKEAP procedure, bringing the dataset into closer alignment with national reporting standards and best practice.

To assess the impact of adopting the revised method, the previous "equal-month" calculation was compared with TW approach, using four years of historical data as shown in **Error! Reference source not found.**. Further information on the regression parameters can be found in the Appendix.

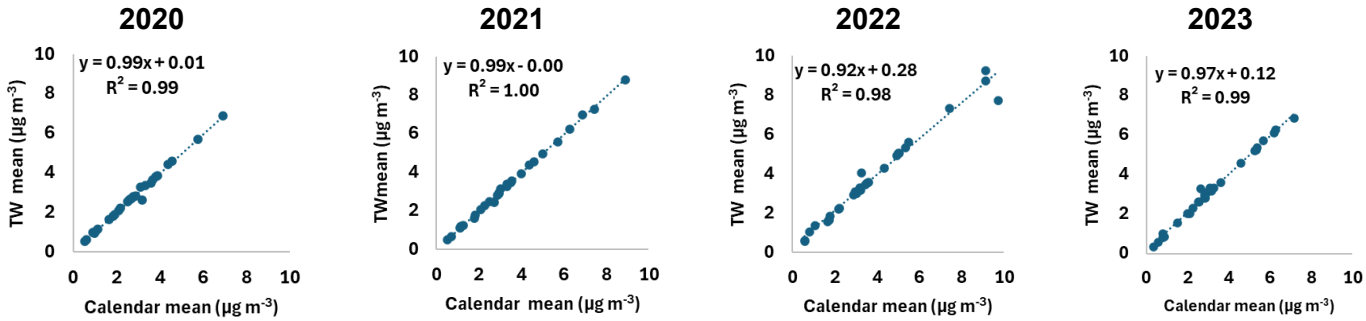


Figure 3: Comparison of annual mean concentrations calculated using the previous "equal-month" averaging method and the new time-weighted approach accounting for actual exposure periods.

The comparison between the two methods shows that they agree closely, with very few minor numerical differences at sites where exposure periods varied substantially from calendar months (i.e. Hillsborough AFBI 25 in 2022 or Drumclamph 2 in 2023). This evidence the high compliance of the local site operators with the sampler exchange protocols and provides confidence that historic trends remain unaffected. However, the TW method offers a more accurate representation of annual average concentrations without altering overall interpretation.

This report presents both the calendar and TW averages for continuity purposes and comparability with previous reports; however, from the 2024 report onwards annual mean values will only use the TW calculation.

3.2.2. NH_3 annual average concentrations

Annual mean concentrations were derived using the TW approach (Table 3). For comparison purposes, the calendar annual averages are shown in Appendix 1 (Table S1).

Figure 4 shows the TW annual NH_3 concentrations for all sites in the NI NAMN network from 2020 until 2023. In 2023 only 5 sites show increased annual concentrations, albeit this increase is relatively low, ≤0.5 µg NH_3 m^{-3}: Moninea Bog (UKA0094) Lisbellaw

(UKA00943), Blackwater Town (UKA00946), Belfast Centre (UKA00212), and Ballylinney Church (UKA00949).

The remaining sites show a decrease in annual averages from 2022, especially at Ratarnet Rd (UKA00947), Caddy Rd (UKA00954) and Drumclamph 2 (UKA00960), where annual average concentrations decreased by ≥ 2 µg NH_3 m^{-3}. These sites displayed historical maximum concentrations in 2022, as a consequence of meteorology favourable for high emission rates (i.e., warm and dry weather) and enhanced local activity during spreading periods (Espina Martin et al. 2026); in 2023 the meteorological conditions were less favourable during the March and April months, with increased precipitation compared to 2022, likely influencing the concentration decrease observed at several sites (see Section 3.4 for further details).

As a consequence of the decrease in concentrations, several sites did not exceed the annual average critical level for lichens and bryophytes (1 µg NH_3 m^{-3}): Beaghs Burn (UKA00383, background, 0.56 µg NH_3 m^{-3}), Bencrom River (UKA00945, background, 0.82 µg NH_3 m^{-3}), Loughmore River (UKA00951, mixed cattle, 0.8 µg NH_3 m^{-3}), Corramore Rd (UKA00958, mixed agriculture, 0.86 µg NH_3 m^{-3}); other sites such as Lough Navar retained the low concentration levels from previous years. It is however noted that in 2023 Lough Navar data capture (DC) was not sufficient to be representative for an annual mean. All DELTA sites were below the required DC, due to several issues, such as increased water ingress, damage during shipping and restricted site access for some sites (Twigg et al., 2024).

Table 3: Time-weighted annual concentrations for each site. In the Type column, A represents ALPHA® sites and D DELTA® sites. Concentrations are expressed in µg NH_3 m^{-3}, and "N" corresponds to the number of valid sampling days per site used for calculating annual mean. *N days < 274 equates to <75% data capture - coloured in red; mean concentrations at these sites are expected to be less representative of the average yearly concentrations and are coloured in light grey to indicate the increased uncertainty.

			2020		2021		2022		2023	
ID	Type	Name	mean	N	mean	N	mean	N	mean	N
UKA00938	A	U of Ulster met station	2.67	216*	3.29	365	5.04	335	2.85	273*
UKA00939	A	Castle Enigan	3.49	366	3.15	365	3.28	365	2.94	339
UKA00383	A	Beaghs Burn	0.53	366	0.67	331	0.6	365	0.56	312
UKA00940	A	Slieve Beagh	1.15	334	1.12	360	1.56	365	0.84	337
UKA00941	A	Moninea Bog	2.1	366	2.27	365	2.19	365	2.27	365
UKA00942	A	Seekinore	2.79	366	3.96	365	3.52	336	2.81	338
UKA00943	A	Lisbellaw	3.88	366	4.39	365	5.03	365	5.35	365
UKA00944	A	Glenwherry COSMOS	1.66	366	2.08	365	2.24	360	2	338
UKA00945	A	UWMN Bencrom River	0.98	366	1.2	178*	1.36	279	0.82	364
UKA00946	A	Blackwatertown	3.82	161*	5.61	365	5.31	337	5.38	364
UKA00947	A	Ratarnet Rd	2.73	155*	8.83	309	7.34	365	5.25	365
UKA00948	A	Inch Abbey	1.83	366	1.65	365	4.3	365	2.63	365
UKA00212	A	Belfast centre	2.54	366	2.81	365	2.99	270*	3.15	365
UKA00949	A	Ballylinney Church	4.43	334	4.98	365	5.6	365	5.68	365
UKA00950	A	West of Crumlin	2.58	366	2.91	365	3.58	365	2.55	334
UKA00951	A	Loughmore River	1.02	366	1.13	300	1.04	229*	0.8	300
UKA00952	A	Caldanagh Bog	2.64	335	2.97	365	3.01	365	2.84	365
UKA00953	A	Cloughmills	3.64	366	3.57	365	3.44	365	3.26	365
UKA00954	A	Caddy Rd	4.6	366	7.3	304	8.75	336	6.19	337
UKA00955	A	Turmennan Rd	1.91	366	1.79	291	1.83	360	1.53	365
UKA00956	A	Carrowbane Rd	3.39	216*	4.56	338	4.91	330	4.59	365
UKA00957	A	Creggan	2.79	360	3.39	365	3.07	365	2.54	310
UKA00958	A	Corramore Rd	0.97	366	1.27	365	1.65	365	0.86	329
AFBI25-A	A	Hillsborough	6.89	366	6.24	365	7.74	319	7.17	174*
UKA00401	A	Coleraine	2.21	183*	3.48	365	4.04	365	3.61	365
UKA00960	A	Drumclamph 2	5.71	366	7.01	365	9.25	365	6.28	365
UKA00293	D	Hillsborough	3.31	277	2.48	276	2.92	271*	2.11	267*
UKA00959	D	Ballynahone	2.84	329	2.46	170*	3.18	197*	3.09	234*
UKA00166	D	Lough Navar	0.61	275	0.53	242*	0.57	213*	0.35	270*

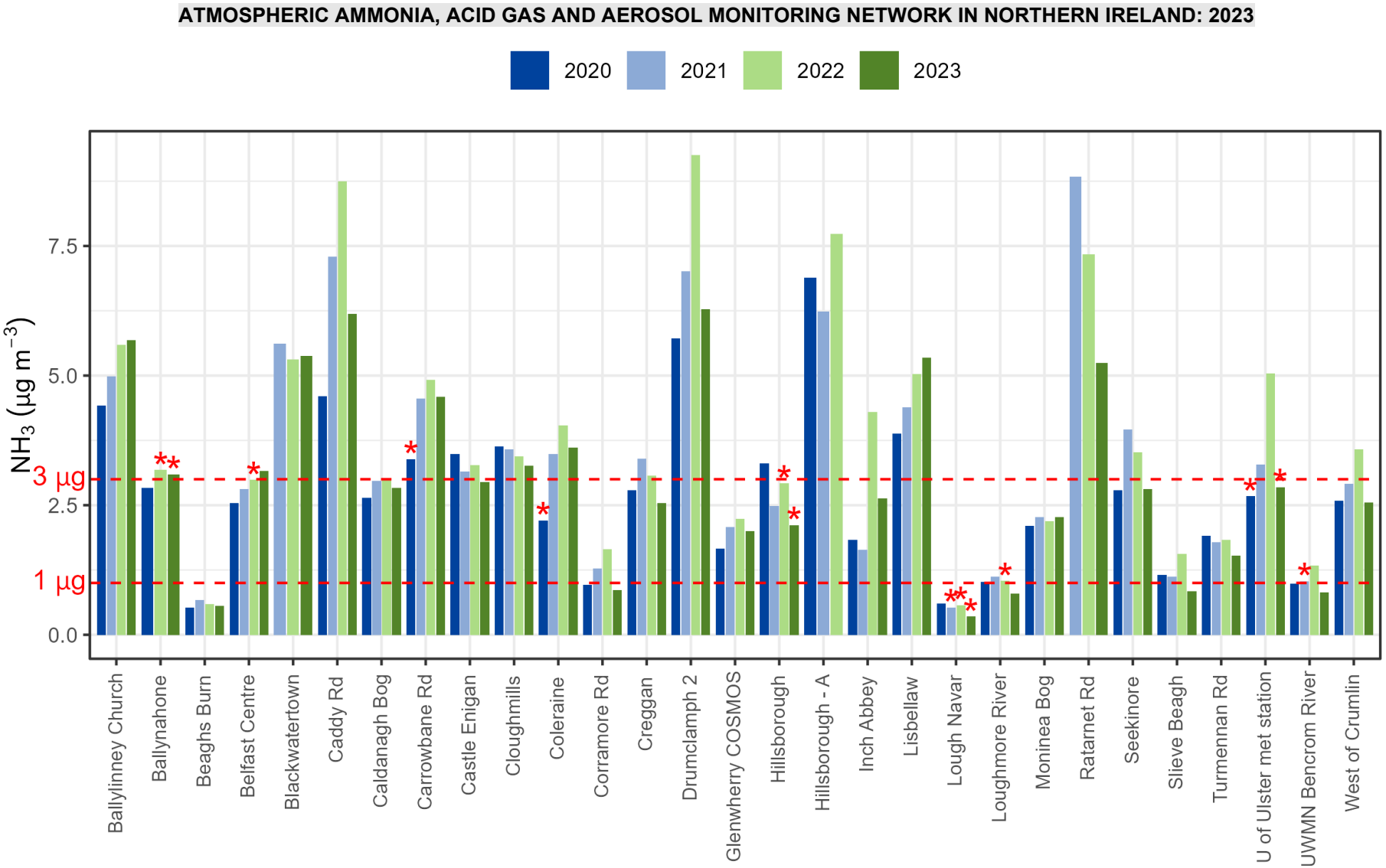


Figure 4. Annual time-weighted NH_3 concentrations for 2020-2023 years at the NI NH_3 network. Bars with red asterisks have monitoring data for less than 75% of the year and are not representative of their respective annual concentrations. The red dashed lines represent the annual critical levels of 1 and 3 µg NH_3 m^{-3}. Hillsborough – A is the ALPHA® sampler, whereas Hillsborough is the DELTA®. Where data capture is less than 50% (< 183 days) annual averages are not presented.

3.3. Spatial patterns

Figure 5 shows the spatial distribution of mean annual concentrations across NI NH_3 network, both for 2023 and for the 3-year period 2020-2023 for comparison purposes. As in previous years, the map shows no clear geographical trend in 2023 as NH_3 concentrations were highly variable over the country due to the presence of many agricultural emission sources near the monitoring sites rather than specific geographical reasons.

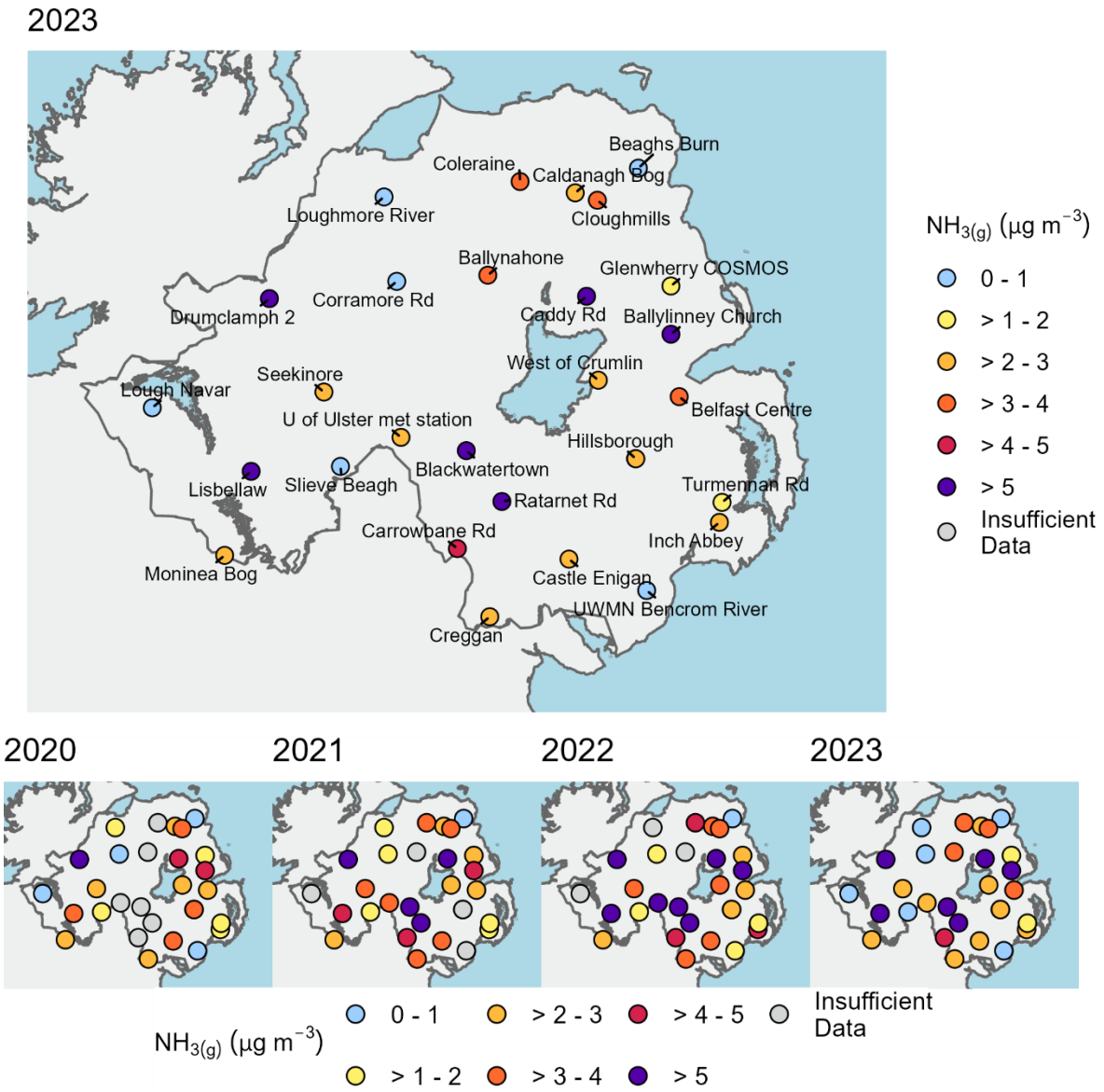


Figure 5: Annual 2023 time-weighted mean NH_3 concentrations (top); Annual time-weighted mean concentrations from 2020 to 2023 (bottom). Grey dots represent sites with insufficent data to be annually representative (DC< 75%). In 2023, AFBI25A site is located 1 km away to the Hillsborough NAMN site and its marker is hidden by Hillsborough NAMN; AFBI25A has a DC≤75% and thus represented by a grey dot.

Figure 6 shows the mean annual NH_3 concentrations for 2023 grouped by their dominant NH_3 emission source classifications, based on emission modelling output. Figure 7 shows the historical graphs for the years 2020 – 2022. This metric was

assigned according to the dominant modelled NH_3 source for each 5 km grid cell, to aid interpretation of seasonal patterns in NH_3 concentrations. Since there are no 5 km grid squares in NI with emissions dominated by either sheep or the application of mineral fertilizers, these two categories have no representation. Sources are calculated as dominant NH_3 emissions sources if they are the largest source and contribute > 45% of the total NH_3 emissions.

The five dominant emission source sectors covered by the NI network sites are:

- Cattle (beef, dairy, mixed)
- Pigs & Poultry (combined for data disclosure reasons)
- Non-agricultural sources
- Mixed agriculture (where no single source sector dominates, i.e. represents at least 45% of the total emissions)
- Background (very low NH_3 emissions of <1 kg N ha^{-1} y^{-1}).

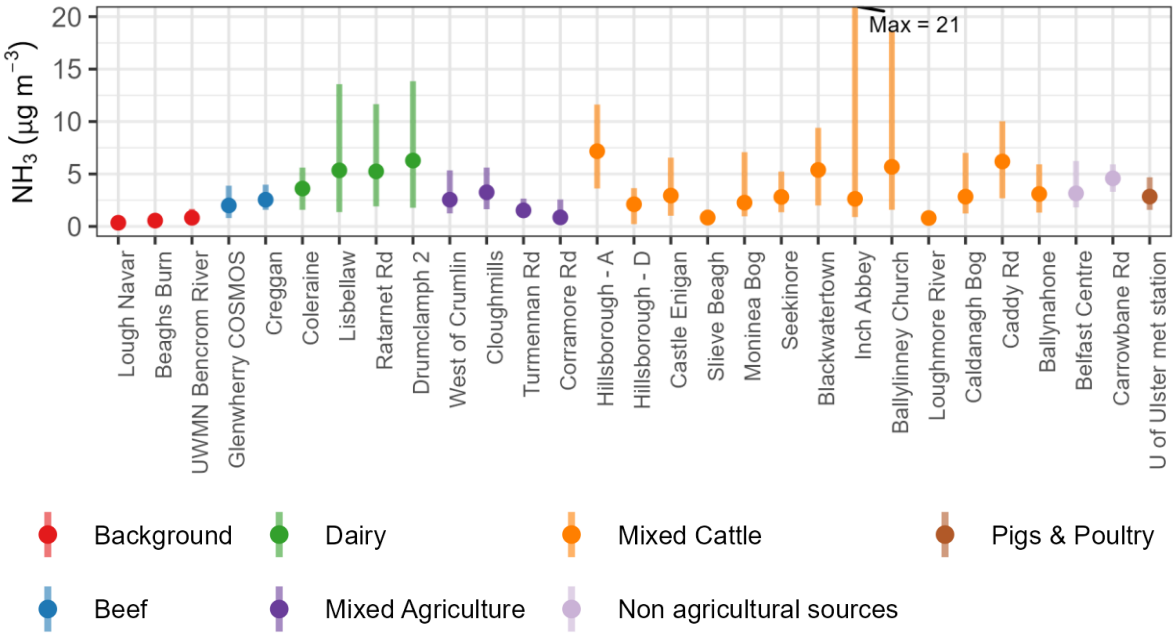


Figure 6. Annual mean time-weighted NH_3 concentrations in 2023. The graph also displays the minimum and maximum monthly values for each site in the NI ALPHA® and DELTA® network. The sites are grouped according to their dominant NH_3 emission source classifications, where dominant are those sources which contribute > 45% of the total NH_3 emissions.

In 2023, the maximum concentrations were lower than those observed during 2022 and instead were more comparable with the values previously observed during 2020 and 2021 (Figure 7). In 2023, ten sites exceeded 3 µg NH_3 m^{-3}, five fewer than 2022, reflecting the overall observed concentration decrease.

The higher values occurred in areas dominated by dairy emissions (4 sites: Lisbellaw, UKA00943; Ratarnet Rd, UKA00947; Drumclamph 2, UKA00960; Coleraine, UKA00401), mixed cattle (3 sites: Blackwater Town, UKA00946; Ballylinney Church, UKA00949; Caddy Rd, UKA00954), and sites dominated by non-agricultural sources and mixed agricultural sources (3 sites: Belfast Centre, UKA00212; Carrowbane Rd., UKA00956; Cloughmills, UKA00953).

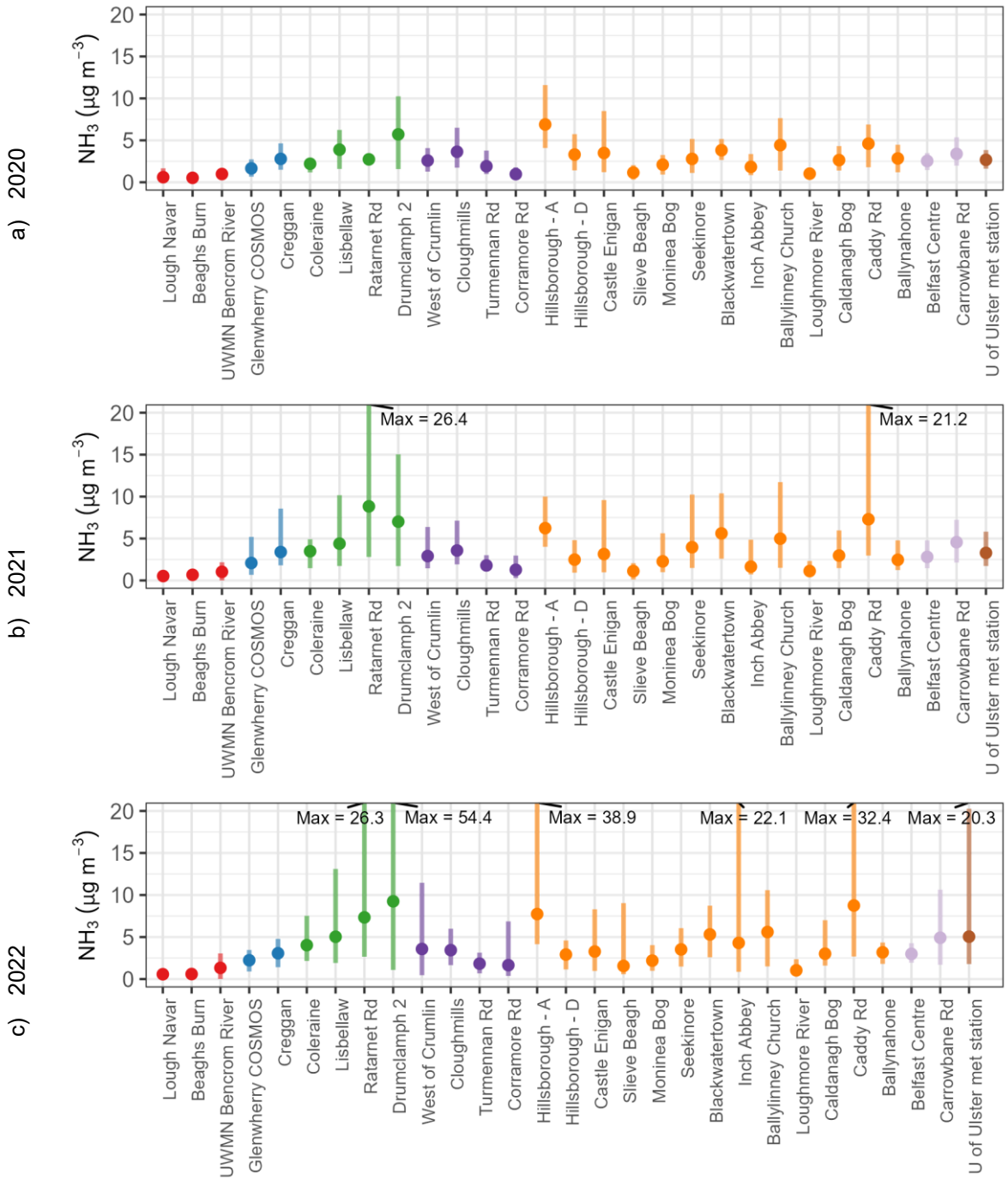


Figure 7. Comparison of annual mean time-weighted NH_3 concentrations in 2020 (a), 2021 (b) and 2023 (c). The graphs also display the minimum and maximum monthly values for each site in the NI ALPHA® and DELTA® network. The sites are grouped according to their dominant NH_3 emission source classifications, where dominant are those sources which contribute > 45% of the total NH_3 emissions

3.4. Seasonal variability

The full time series of monthly NH_3 concentrations from March measured for the 26 sites in the NI ALPHA network during 2023 is shown in Figure 8. Sites are grouped according to their dominant emission source categories in each of the graphs. The sites are grouped according to their dominant NH_3 emission source classifications, where dominant are those sources which contribute > 45% of the total NH_3 emissions.

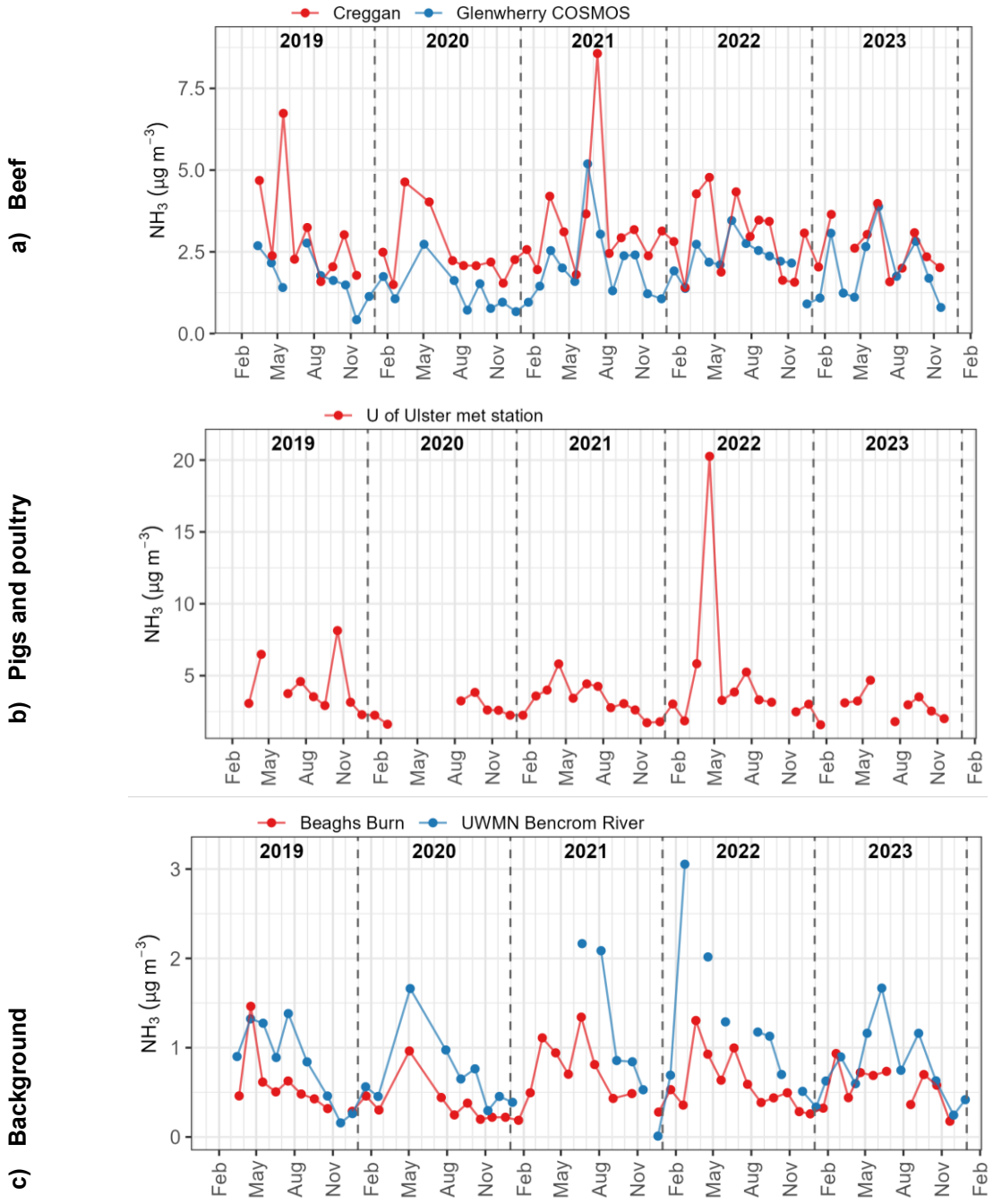


Figure 8. Time series of monthly time-weighted NH_3 concentrations measured at sites in the NAMN ALPHA ® network across Northern Ireland between March 2019 - December 2023, grouped according to dominant emission source sectors. Monthly concentrations are displayed for the middle date of each exposure period. NOTE: The y-axis is different on each panel.

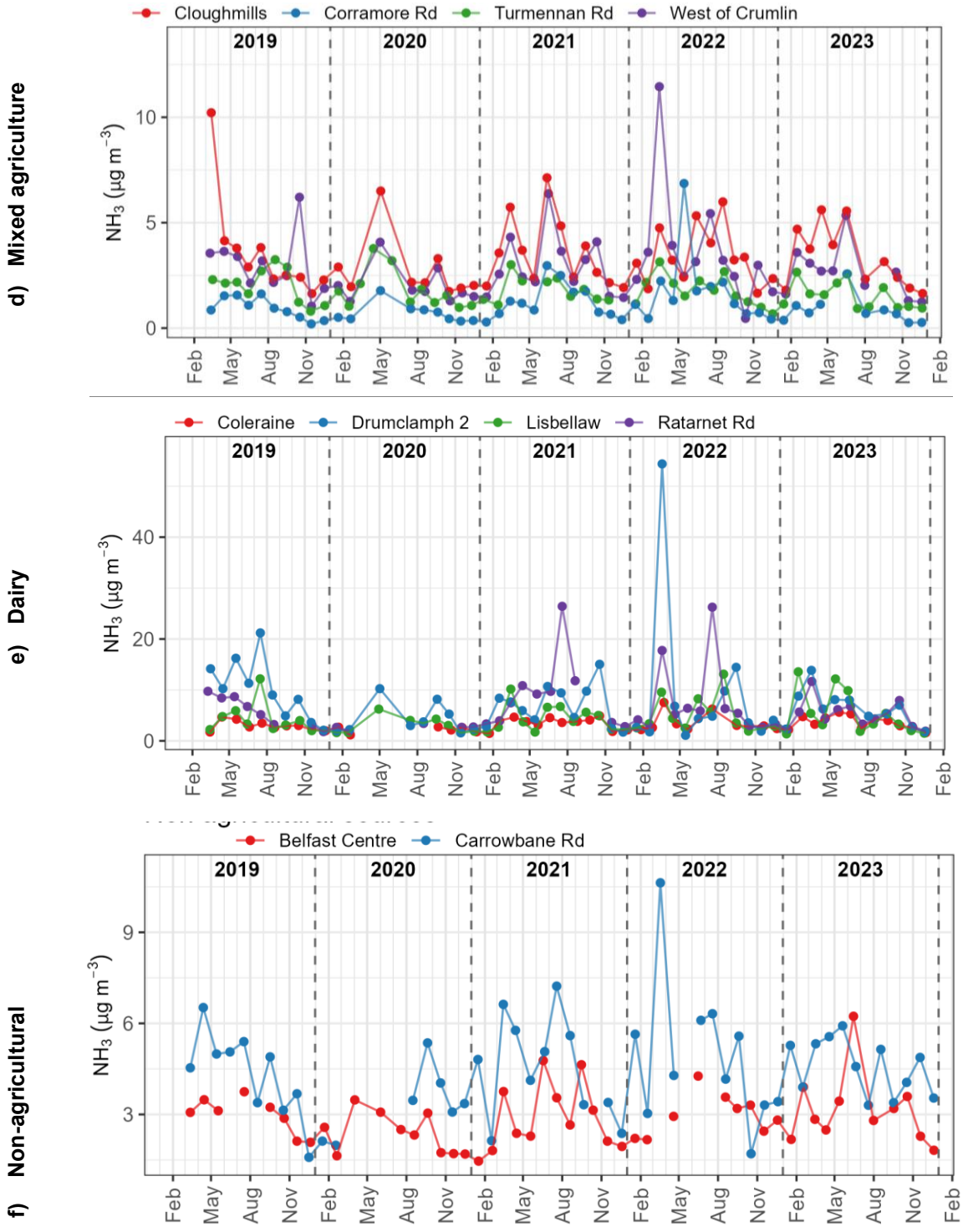


Figure 8 (cont.). Time series of monthly time-weighted NH_3 concentrations measured at sites in the NAMN ALPHA ® network across Northern Ireland between March 2019 - December 2023, grouped according to dominant emission source sectors. Monthly concentrations are displayed for the middle date of each exposure period. NOTE: The y-axis is different on each panel.

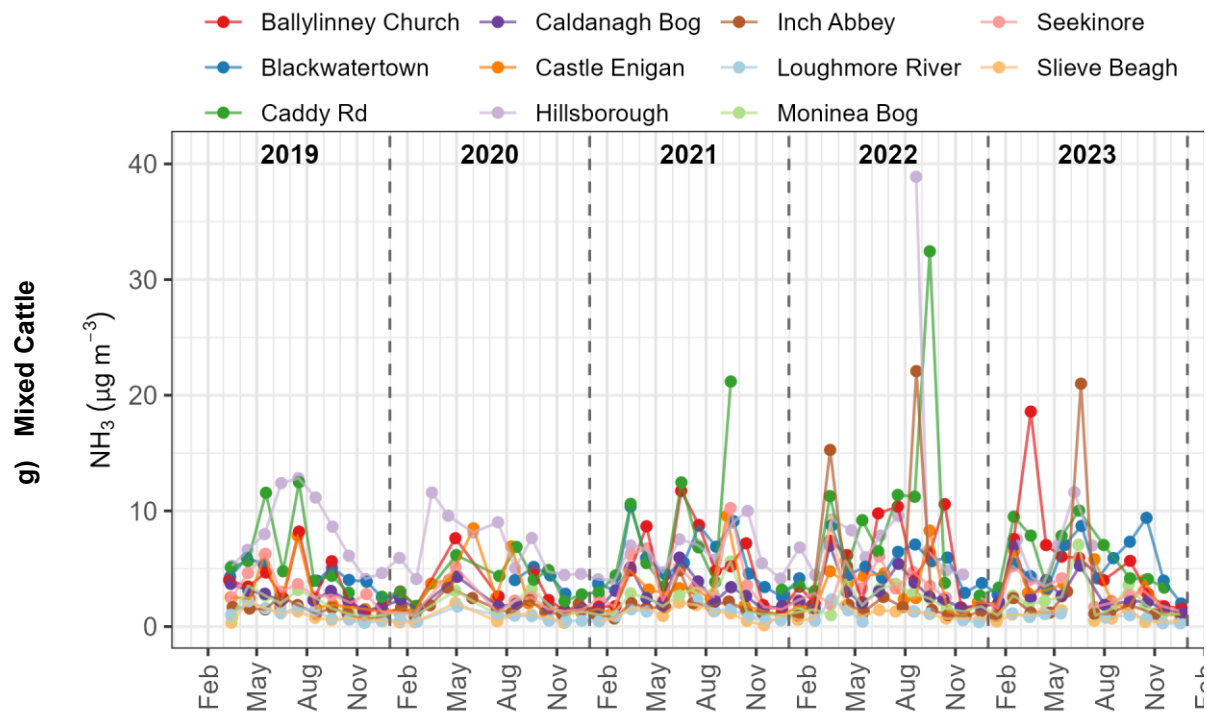


Figure 8 (cont.). Time series of monthly time-weighted NH3 concentrations measured at sites in the NAMN ALPHA ® network across Northern Ireland between March 2019 - December 2023, grouped according to dominant emission source sectors. Monthly concentrations are displayed for the middle date of each exposure period. NOTE: The y-axis is different on each panel.

Ammonia concentrations in 2023 showed typical high concentration periods during spring and autumn months, as expected with seasonal agricultural activities, coinciding with land spreading of manures and slurries during this period. However, the highest concentrations in 2023 occurred during June, and to a lesser degree in February and April. June 2023 had a historic record of sunlight hours since 1957 and was characterized by high pressure systems across the UK (Met Office, 2023b); these conditions, combined with the relatively low amount of precipitation (Figure 2), would explain the high concentrations due to the increased emissions from sources, enhanced partitioning of semi-volatile SIA's back into the gas phase, and the accumulation of NH_3 in the atmosphere due lack of dispersion from the drop in wind speed (Met Office, 2023d). Additionally, there is anecdotal evidence that the proportion of dairy cows being housed year-round rather than grazing during the summer months has increased. The consequence is that there are related changes in farming practice with higher levels of silage production and additional slurry spread events throughout the summer.

Background (low concentration) sites

- The background concentration sites are mainly influenced by meteorology, including by the gas-aerosol partitioning in the atmosphere. In summer, increased NH_3 emissions with an increase in temperature favour secondary NH_4^+ aerosol to remain in the gas phase as NH_3, while during the winter months lower concentrations were observed, most likely as a consequence of NH_3 partitioning into NH_4^+ aerosol (Tang et al., 2018).
- Bi-directional exchange of ammonia with vegetation will also influence the reported NH_3 concentrations at background sites, where warm, dry conditions in the summer months may promote NH_3 emission from vegetation (Sutton et al., 1995; Sutton et al., 2020).

Sites in emission source areas

- Higher levels of precipitation tends to decrease NH_3 emissions because rain events dilute the available NH_3 pool and increase the potential to wash urea and N species in solution from the surface through run-off and/or leaching. As NH_3 is soluble and is washed out of the atmosphere by precipitation, this is also likely to contribute to lower atmospheric NH_3 concentrations during wet periods.

- February 2023 was exceptionally dry compared to the 10-year average of 2009-2018, which likely advanced the start of slurry and manure spreading in February; in March very high precipitation likely temporarily delayed further land spreading until April. After July precipitation was high until November, compared to the 10-year average.

- Livestock manure (mostly slurry-based systems in Northern Ireland, except for poultry and sheep farming) is typically spread during the spring and autumn months and this can be related to the observed peaks in monthly NH_3 concentrations. During February and April 2023, several peaks are clearly visible in the temporal profiles for all main source sectors, while in March 2023 the abundant precipitation limited spreading activities and accumulation processes of NH_3, resulting in lower atmospheric concentrations. Ballylinney Church (UKA00949, 18.6 µg NH_3 m^{-3}) and Drumclamph 2 (UKA00960, 13.9 µg NH_3 m^{-3}) showed the maximum concentrations during the spring months' fertilisation events. The autumn concentrations were slightly lower compared to 2022, especially near sites dominated by mixed cattle farming where the peak intensities were not as strong as in previous years.

- Most sites showed increased concentrations during June 2023 most likely due to the record temperatures registered for the month, resulting in increased NH_3 emissions. The warm temperatures drove volatilization of NH_3 (e.g., high-density grazing livestock, any mineral/organic fertiliser application following silage cuts). It is however noted that none of the peak concentrations observed

in 2023 were as high as those in 2022, with only Inch Abbey (UKA00948) recording a peak of 21 µg NH_3 m^{-3} average over 23 days (8-30 June 2023), which is comparable to 2022 peak months.

The general patterns described above are also observed in the mean seasonal profiles for the years 2020-23 for the different NH_3 emission source categories (Figure 9). N.B. Sites AFBI25 (Hillsborough: and UKA00960 (Drumclamph 2: dairy cattle) were not included in this analysis as they were not considered representative for the wider surrounding area due to their close proximity to specific sources.

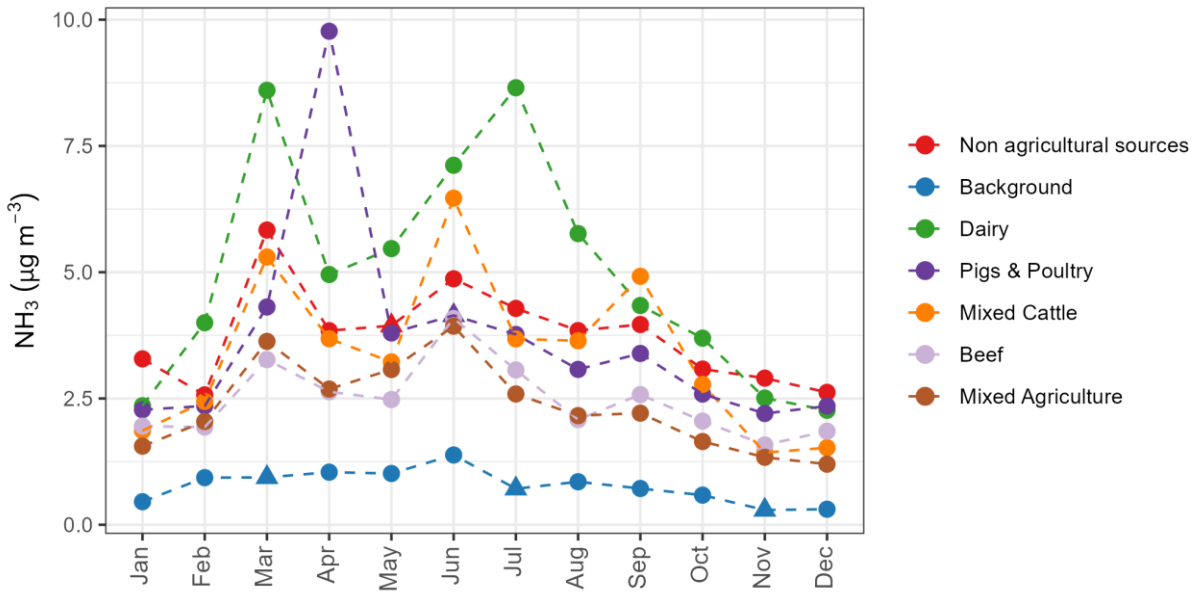


Figure 9. Seasonal cycles of NH_3 concentrations from January 2020 to December 2023 for all sites in the NI ALPHA® network (except AFBI25-A and UKA00960), grouped according to dominant emission source sectors, where dominant are those sources which contribute > 45% of the total NH_3 emissions. The shape of points depict data capture, where data capture of 75% of over shown as a circle and under 75% a triangle.

Most source categories typically record maximum concentrations during March and/or April, when agricultural activity such as slurry spreading is at its peak. Dairy and mixed cattle sites have additional peaks occurring in July and June, respectively (perhaps linked to post-silage cut land spreading under warmer temperatures). The June 2023 peak seems to have been occurring especially around mixed cattle sites, as the monthly profile showed values that were ≈1 µg NH_3 m^{-3} higher compared with other years. However, this peak is also seen across sites associated with other dominant source types and its strength may have been related to June being exceptionally warm (Figure 3).

3.5. Monitored vs modelled NH_3

Annual average NH_3 concentration data from the calendar year 2023 (January to December 2023) from the ALPHA® and DELTA® networks were compared with modelled annual mean NH_3 concentrations. Modelled NH_3 concentrations for each site's location in the ALPHA® and DELTA® network were provided by the UK European Monitoring and Evaluation Programme (EMEP4UK) model version rv5.0, an offline atmospheric chemistry transport model based on the EMEP MSC-W model with an output resolution of ~3km x ~3km (http://www.emep4uk.ceh.ac.uk/) (e.g. Vieno et al., 2016; Ge et al., 2021) for the year 2023 (using 2023 emissions data published by the National Atmopsheric Emissions Inventory in 2025). Modelled NH_3 concentrations are direct model outputs and have not been calibrated.

Any sites with less than 75% of the year with observations (273.75 days of the year) were excluded due to insufficient temporal coverage (see Table 3 and Table S1). The following sites were not used (i.e. only representative data according to the criteria were included in the comparison):

- Ballynahone Bog (Delta sampler, UKA00959) – 64% coverage.
- Hillsborough (Alpha sampler, AFBI25) – 48% coverage.
- Hillsborough (Delta sampler, UKA00293) – 73% coverage.
- Lough Navar (Delta sampler, UKA00166) – 74% coverage.
- University of Ulster (Alpha sampler, UKA00938) – 75% coverage (74.5%)

The sites removed from the comparison concur with those noted in Table 3, but it is recognised that three of the excluded sites are very close to the requirement threshold. Any monthly mean concentrations exceeding 3 standard deviations from the annual mean of 2023 measurements for a given site (i.e. z-score > 3) were also excluded from annual mean derivation as numerical outliers.

As part of the outlier exclusion, the following data were removed from this analysis:

- Inch Abbey (Alpha sampler, UKA00948) – June 2023. This reduced the annual mean concentration from 2.63 (see Table 3) to 1.45 μg m^{-3} $year^{-1}$, and the annual coverage from 100% to 94%.

Figure 10 shows the gridded annual concentrations of NH_3 in Northern Ireland as predicted by the EMEP4UK model for 2023 (with no calibration), with an overlay of the site locations used in the model comparison. Concentrations of NH_3 from both data sources are plotted with a common colour scale.

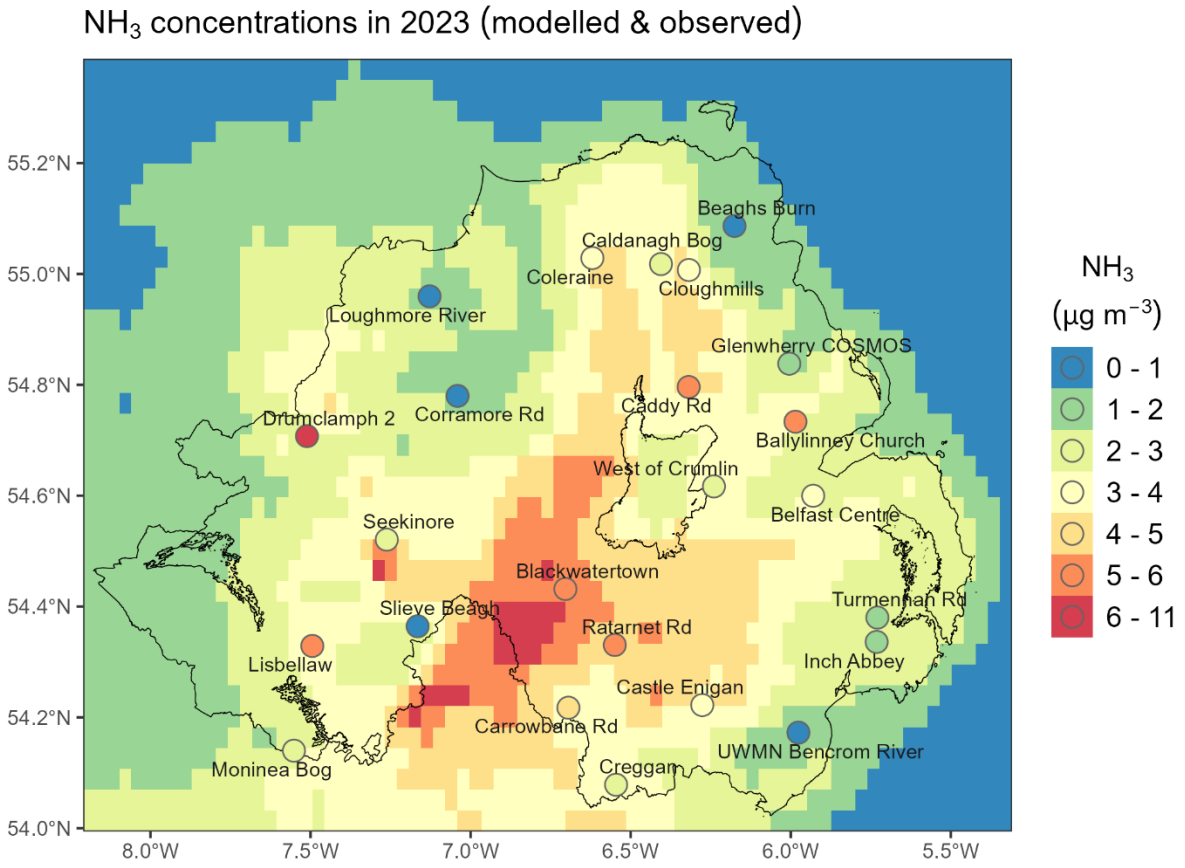


Figure 10. Comparison between annual mean modelled (shaded cells) and observed (coloured dots) NH_3 concentrations in 2023 for the NI NH_3 network.

Figure 11 shows a scatterplot comparing modelled and observed annual mean concentrations of NH_3 at the 24 locations, classified by the NH_3 dominant source emissions. Modelled values represent the corresponding ~3 km x ~3 km EMEP4UK grid cell in which the monitoring sites are located. 19 of the 24 sites (79%) have modelled concentrations within a factor of 2 (FAC2), or between double or half of the observed annual average NH_3 concentration. This is a key metric of atmospheric model performance and should be 50% as a minimum (Hanna and Chang, 2012).

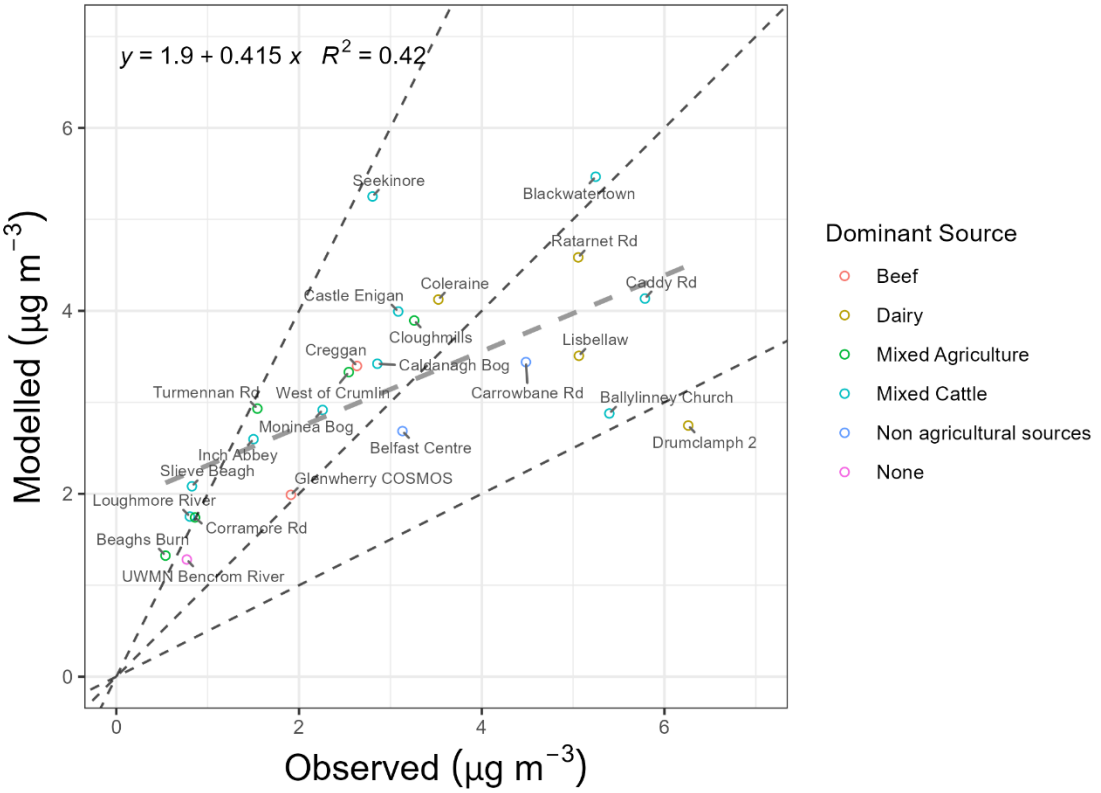


Figure 11: Observed annual average NH_3 concentrations (time-weighted) at the ALPHA® and DELTA® sites in Northern Ireland (x-axis), with annual average modelled NH3 concentrations from the EMEP4UK model (y-axis) for 2023. The 3 diagonal dashed lines represent 1:1 (middle), 2:1 (upper) and 0.5:1 (lower) ratios, from the perspective of the modelled data. The colour of each plotted site represents the dominant source of NH_3 in the site's vicinity. A further grey dashed line with longer dashes is the coefficient of determination (R^2 = 0.42, equation in figure)

Other metrics of model performance are shown in Table 4, illustrating that the EMEP4UK model performed reasonably well for the 2023 calendar year, compared to observations in the network. The R = 0.65 (R^2 = 0.42, y = 1.9 + 0.415x) indicates a correlation between modelled and observed values but suggests the model tends to over-estimate the lower observations and does not represent the largest peaks as well – the skew of the R^2 slope in Figure 11 reflects this. In conjunction with this, there is a low overall mean bias (MB) of 0.14 (units = ug m^{-3}) (~5% of the mean). While this value of MB does not, in itself, indicate good or bad model performance (due to some cancelling of error that can be seen in Figure 11), it does indicate the model has slight systematic bias to 'over-model' measurements in 2023 in general, compared to 2022, influenced by four sites with low annual mean measurements. The normalised mean gross error (NMGE; the mean absolute error divided by the mean of the observations) of 36% indicates errors are moderate relative to the observed mean of 3.0 ug m^{-3} and the nRMSE (RMSE / mean observed value) is ~44%, higher than in 2022, reflecting the larger spread of values. Similarly, the RMSE of 1.33 is lower than the observed standard deviation of 1.77 ug m^{-3}, indicating that the model error was somewhat smaller than the large variability in the measurement data.

Table 4. Model performance metrics for EMEP4UK against annual observations of NH3 in 2022 and 2023. FAC2 = fraction of sites modelled within a factor of 2 of measurements (min = 50%); r = the (Pearson) correlation coefficient; MB = mean bias (same units as data); normalised mean gross error; RMSE = root mean square error.

Year	n. sites	FAC2	r	MB	NMGE	RMSE
2022	24	92%	0.64	-0.11	0.29	1.25
2023	24	79%	0.65	0.14	0.36	1.33

In this context it is important to consider the uncertainties in both components of the model/monitoring comparison. The following paragraphs have been retained from the previous version of this report, for the year 2023.

The monitoring sites were set up to be as representative as possible across Northern Ireland, from several perspectives: geographical coverage, concentration gradient (low/medium/high) and different emission source sectors ("dominant sources"). However, the exact spatial location of each sampler influences which sources are captured over the monthly exposure period. This varies with local activities and weather conditions, both inter- and intra-annually, with closer sources being "seen" by the sampler more strongly that those further afield which are more likely to have been dispersed and diluted before the air parcels reach the sampler.

This is why representative samplers require careful site selection to avoid undue influences of individual local sources on the data. However, in areas with high levels of emitting activities, such as the Northern Irish countryside, this can be difficult due to the density of emission sources and practicalities such as landowner permissions for establishing a monitoring site etc. In addition, there are also uncertainties inherent in any monitoring technique (Martin et al., 2019; Twigg et al., 2022).

The modelled concentrations are heavily influenced by the preceding emission modelling carried out under the UK's National Atmospheric Emission Inventory projects. The emission data are necessarily derived from available national and regional activity statistics (such as livestock number and crop area data, agricultural practice information, land use data for agricultural emissions; road traffic and vehicle fleet statistics, etc), and relevant "emission factors" to represent emission source strength. This means that, on average, emissions are well represented across the country, but emissions from each individual source, such as a dairy cow, or a slurry tank, will, in reality, vary considerably, depending on the individual characteristics of the source, weather conditions, local farm management etc. The agricultural emission modelling also requires aggregation of individual sources to avoid breach of data agreements of the underlying agricultural statistics (where emissions from at least 5 farms need to be aggregated to preserve confidentiality), by using statistical modelling techniques.
In other words, uncertainties are inherent in both monitored and modelled atmospheric ammonia concentrations, and the analysis carried out here provides evidence that the two methods agree well overall.

3.6. DELTA measurements

Data from the NI DELTA sites (Ballynahone Bog (UKA00959), Hillsborough (UKA00293) and Lough Navar (UKA00166)) are interpreted in this section. Table 5 shows the mean TW concentrations alongside other statistics for the three sites. In Table S2 are the mean NI DELTA concentrations using the calendar-based system for comparison with previous reports.

Table 5. Summary statistics for 2023 for reactive gas and aerosol measurement data from the three DELTA® sites in Northern Ireland. Mean annual averages have been calculated as TW averages. All concentrations are expressed in µg m^{-3}. Cells in red correspond to sites whose annual statistics have been calculated with n ≤ 274, the average is coloured in grey as they are considered not representative for 2023.

Species	Statistic	Ballynahone Bog (UKA00959)	Hillsborough (UKA00293)	Lough Navar (UKA00166)
HNO_3	**Min**	-0.04	-0.03	-0.03
	Max	1.28	0.13	0.15
	TW mean	0.2	0.05	0.04
	DC (days)	**266**	**267**	**244**
SO_2	**Min**	0.24	0.04	0.01
	Max	0.71	0.54	0.29
	TW mean	0.29	0.19	0.11
	DC (days)	280	294	**271**
NH_3	**Min**	1.32	0.22	0.03
	Max	5.92	3.65	0.79
	TW mean	3.10	2.11	0.35
	DC (days)	**234**	**267**	**271**
NO_3^-	**Min**	0.36	0.31	0.19
	Max	2.02	1.8	0.91
	TW mean	0.82	1	0.56
	DC (days)	**202**	296	**271**
SO_4^{2-}	**Min**	0.47	0.09	0.24
	Max	1.02	1.08	0.89
	TW mean	0.66	0.61	0.52
	DC (days)	**202**	329	**271**
NH_4^+	**Min**	0.12	0.17	0.10
	Max	0.99	0.77	0.43
	TW mean	0.44	0.47	0.27
	DC (days)	**180**	299	**238**
Na^+	**Min**	0.39	0.22	0.3
	Max	2.82	1.28	1.17
	TW mean	1.09	0.68	0.68
	DC (days)	**240**	329	**238**
Cl^-	**Min**	1.08	0.39	0.77
	Max	1.95	2.26	1.84
	TW mean	1.37	1.32	1.26
	DC (days)	**202**	299	**271**
Ca^{2+}	**Min**	-0.01	0	-0.03
	Max	0.25	0.25	0.19
	TW mean	0.13	0.11	0.14
	DC (days)	**240**	329	**271**
Mg^{2+}	**Min**	-0.01	0.02	0.05
	Max	0.14	0.15	0.14
	TW mean	0.09	0.09	0.1
	DC (days)	**240**	329	**271**

The number of days with valid monitoring data at Ballynahone Bog and Lough Navar were below the minimum number for representativity (n ≥ 274) due to several issues decreasing total data coverage (Twigg et al., 2024), however several species at Ballynahone Bog (HNO_3), Hillsborough (HNO_3 and NH_3) and Lough Navar (HNO_3, NH_3, NO_3, SO_4^{2-}·Cl-, Ca^{2+}, Mg^{2+} have data coverage close to n ≥ 274, hence their interpretation must be handled with caution.

Annual concentrations for the inorganic precursor gases, secondary inorganic aerosols (SIA), main sea salt and minor alkaline aerosol species are presented in Figure 12 and Figure 13. The lowest concentrations for most species were found at Lough Navar (S45), a remote site in the west of Northern Ireland away from local emission sources, and where the influence of continental Europe in terms of long-range transboundary transport of pollutants is also smallest, based on modelling (see source attribution data https://www.apis.ac.uk/).

The precursor gases SO_2 and HNO_3 were present at low concentrations, however HNO_3 at Ballynahone Bog shows double concentrations compared to the other two sites (see Section 3.6.2 for further discussion). SO_2 remains at the levels observed in 2022 and within the limit of detection (LOD) of the DELTA® method. Ammonium aerosols (NH_4NO_3, $(NH_4)_2SO_4$) are secondary inorganic aerosols that are formed from reactions between precursor gases (NH_3, HNO_3 and SO_2). They have longer atmospheric lifetimes and tend to vary on a regional scale rather than a local scale. SIA concentrations are similar across all three sites with ranges between 0.4 - 2 µg m^{-3}, however Lough Navar shows the lowest concentrations for SIA, again representing the background nature of this site.

Figure 13 shows that the minor alkaline cations (Mg^{2+} and Ca^{2+}) and sea salt components (Na^+ and Cl^-) are relatively consistent across sites. However, only the Hillsborough site has sufficient data capture to be considered representative for the calendar year 2023. The minor alkaline components remained within the LOD of the DELTA® method.

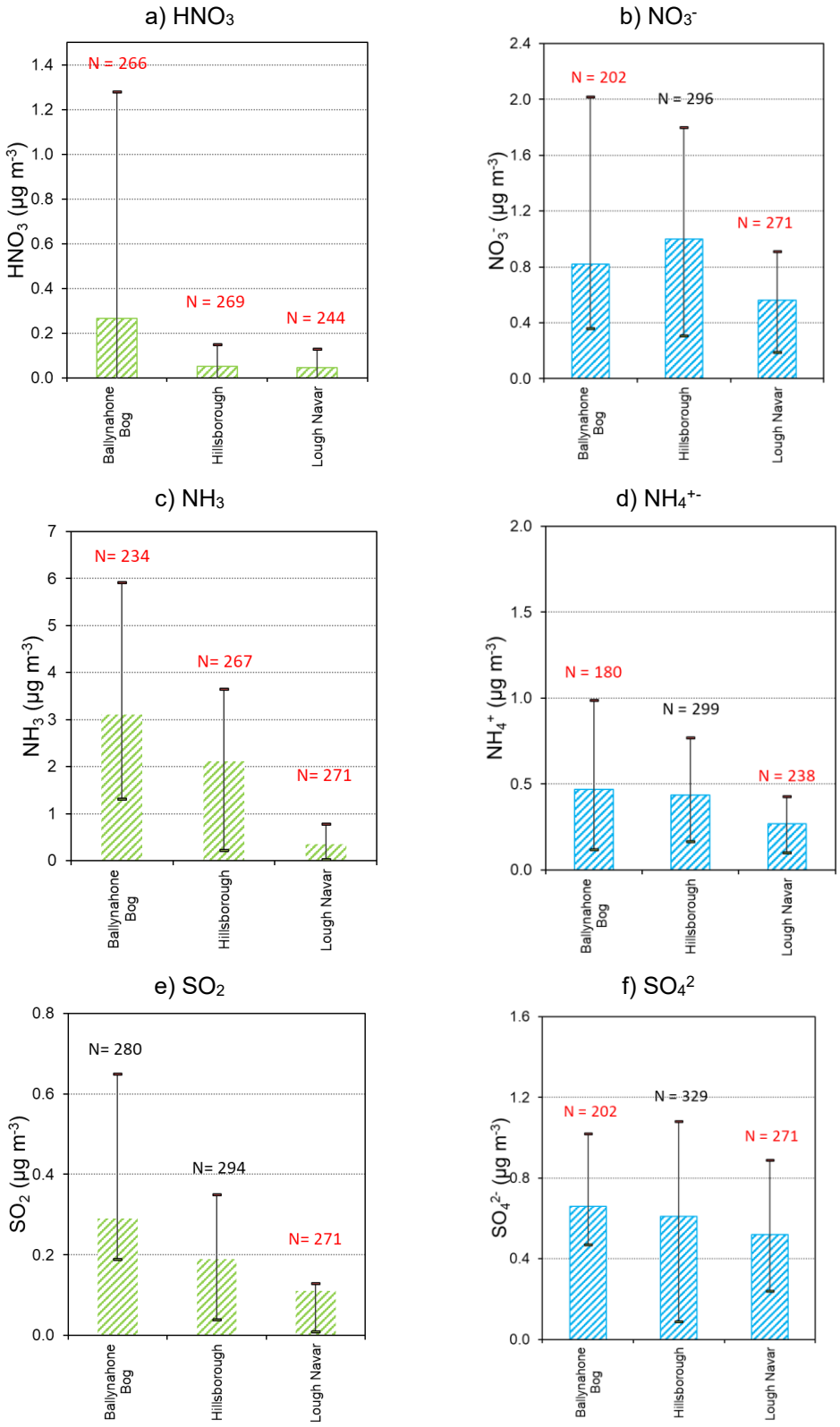


Figure 12. 2023 calendar year average concentrations of reactive gases (NH_3, HNO_3 and SO_2) and counterpart aerosols (NH_4^+, NO_3^- and SO_4^{2-}) at Ballynahone Bog (UKA00959), Hillsborough (UKA00166) and Lough Navar (UKA00293). The bars represent the annual TW average concentration and the whiskers the minimum and maximum monthly concentrations. The numbers next to the bars correspond to the number of valid monthly data used in the analysis, if DC ≤ 274 days, the number is highlighted in red.

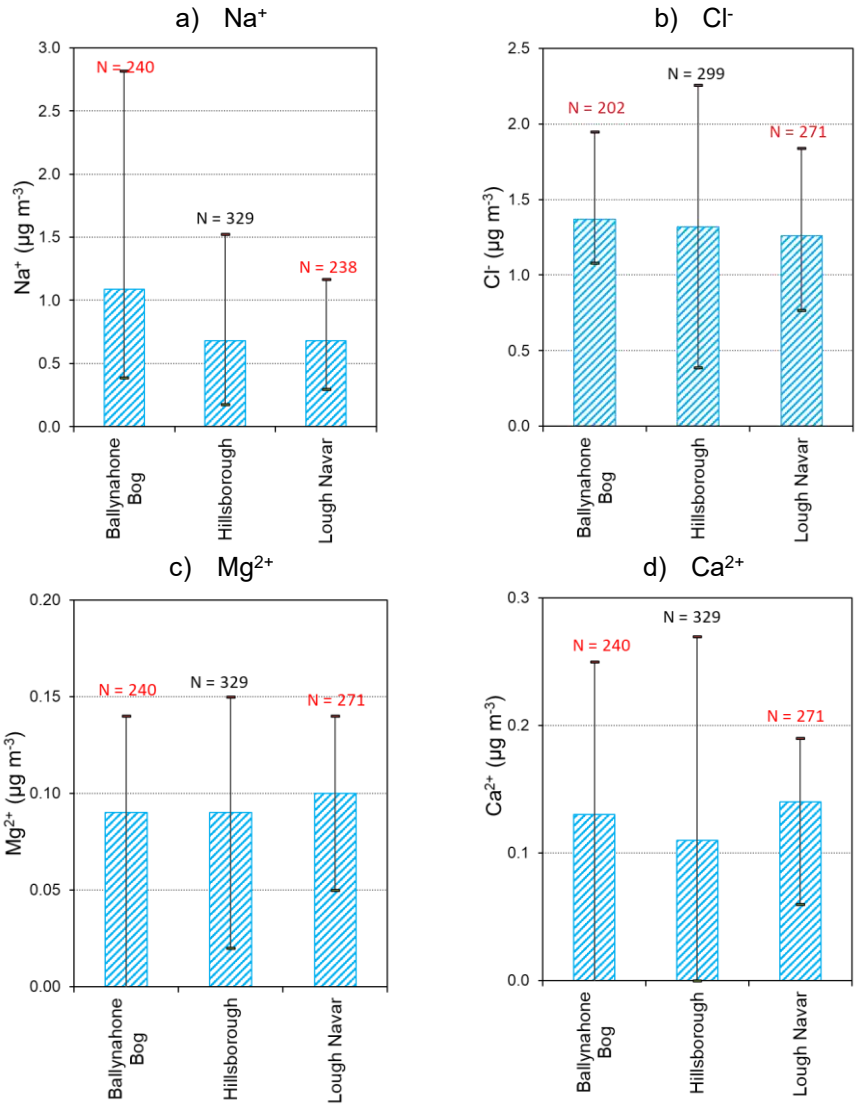


Figure 13. 2023 annual TW average concentrations of Na^+, Cl^-, Mg^{2+} and Ca^{2+} at Ballynahone Bog (UKA00959), Hillsborough (UKA00166) and Lough Navar (UKA00293). The bars represent the annual TW average concentration and the whiskers the minimum and maximum monthly concentrations. The numbers next to the bars correspond to the number of valid monthly data used in the analysis. If DC ≤ 274 days, the number is highlighted in red.

Figure 14 shows the mean absolute and relative composition of inorganic species measured in the DELTA network for 2023. As in previous years, NH_3 continues to dominate the inorganic gases reported (Mean DELTA NI NH_3 = 1.9 ± 1.5 µg NH_3 m^{-3}), compared to low concentrations of SO_2 (Mean DELTA NI SO_2 = 0.2 ± 0.11 µg SO_2 m^{-3}) and HNO_3 (Mean DELTA NI HNO_3 = 0.12 ± 0.13 µg HNO_3 m^{-3}). This is also reflected in the percentage composition of total mass of gas and aerosol components measured. NH_3 (expressed as nitrogen, NH_3-N), on average accounts for 30.7 % (range = 5.2 - 42 %) of the total speciation measured, highlighting the dominance of atmospheric NH_3 in NI compared to SO_2 and HNO_3 (2.5 % and 0.5 %, respectively). SIA species contributed 19.4 % of the monitored components. Interestingly the proportion of NO_3^- and SO_4^{2-} at Lough Navar was notably higher compared to the other two sites, even though it is a background site - this may imply enrichment through long range transport processes.

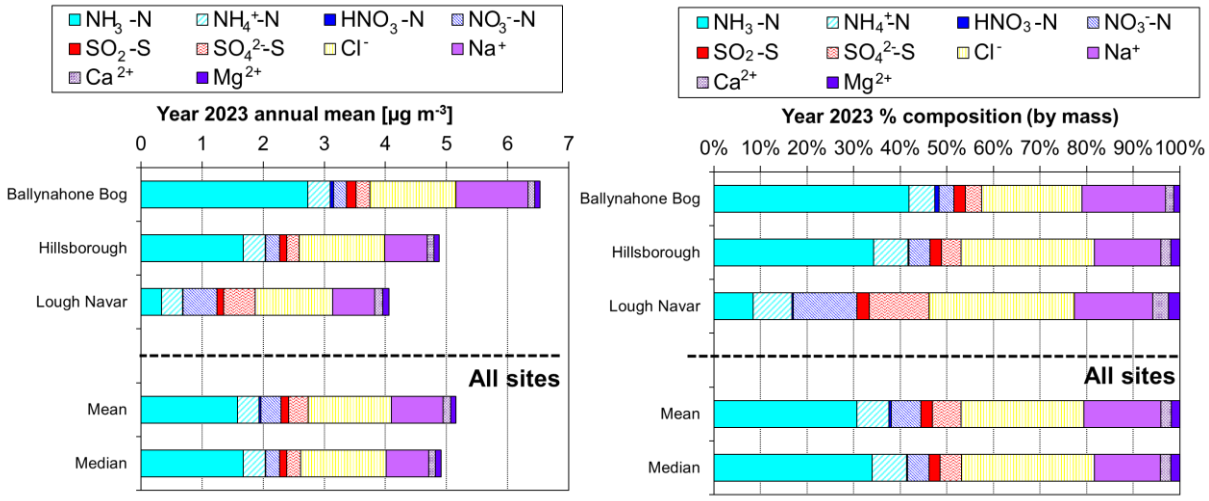


Figure 14. Atmospheric inorganic composition data for 2022 (Left) Mean gas and aerosol concentrations at DELTA® sites in Northern Ireland. (Right) the same data expressed as annual average composition by total mass of both the gas and aerosol components measured.

Concentrations of NaCl accounted for 43 % of the total mass measured across sites as marine sources are located ≤100 km from the monitoring sites, while Mg^{2+} and Ca^{2+} levels were on average near LOD levels and contributed less than 5% to the overall measured species pool.

3.6.1. Ion balance and relationships between species measured by the DELTA samplers

The validity of the DELTA® measurements was assessed by checking the ion balance (IB) neutrality between the cation (Na^+, NH_4^+, Mg^{2+} and Ca^{2+}) and anion (Cl^-, NO_{3-} and SO_4^{2-}) species in nanoequivalents (neq) of charge (Twigg et al., 2015).

The IB is calculated as follows:

$$Anions = \left(\frac{[NO_3^-]}{62} + \frac{2[SO_4^{2-}]}{96} + \frac{[Cl^-]}{35.5}\right) \quad \textbf{Equation 1}$$

$$Cations = \left(\frac{[NH_4^+]}{18} + \frac{[Na^+]}{23} + \frac{2[Ca^{2+}]}{40} + \frac{2[Mg^{2+}]}{24.3}\right) \quad \textbf{Equation 2}$$

Where all species concentrations are expressed as µg m^{-3} *10^3, and the numbers represent the molar mass in g mol^{-1}. Figure 15 shows the total sum of cations against the total sum of anions for the entire monitoring period (March 2019 – Dec 2023).

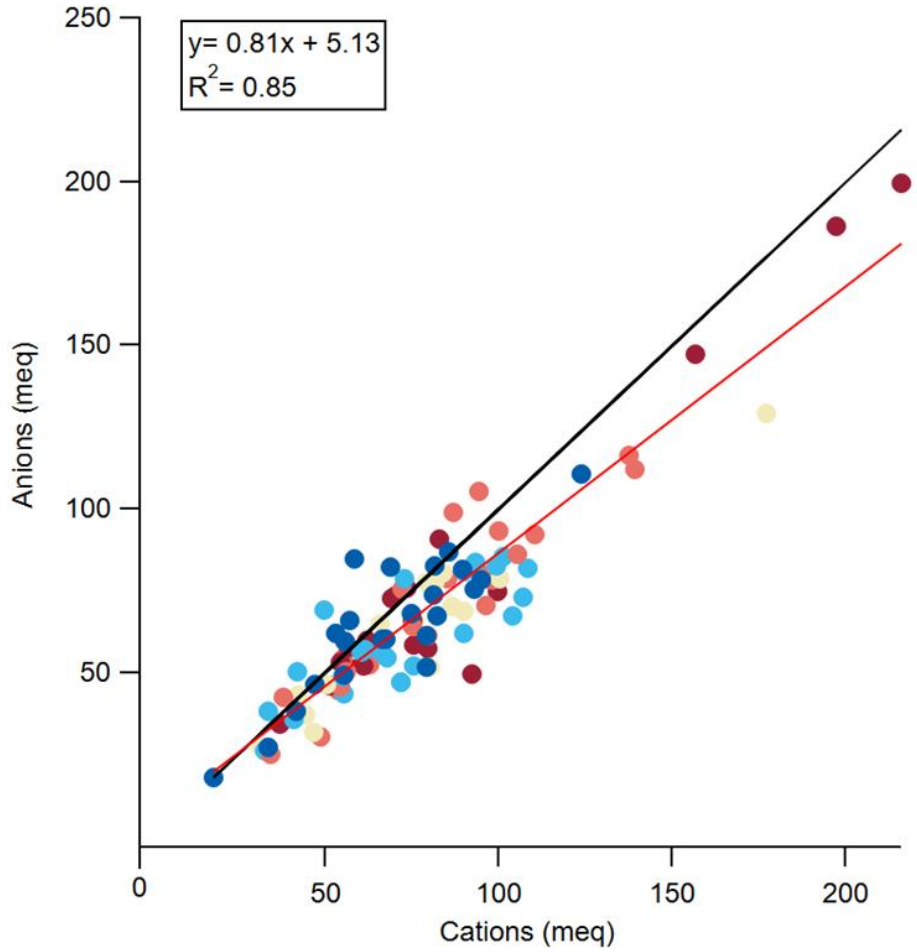


Figure 15. Ion balance for the NI DELTA network (Ballynahone Bog, Hillsborough and Lough Navar) from 2019 until 2023. Each year of sampling is shown with a different colour. The black line represents the 1:1 line, representing aerosol full neutrality, while the red line represents the Ion Balance linear regression.

The NI DELTA ion balance shows a good linearity coefficient (slope = 0.81) and high correlation between the cation and anion species (R^2= 0.85). This implies that particulate matter is mostly neutralized but there is a lack of acidic species (19%) to fully neutralize the alkaline aerosols. This shows a slight increase towards alkaline species (+2%) compared to 2022 (Figure S1); this may be related to the lower data capture from the DELTA samplers in 2023, but most likely it may be caused by the lower concentrations of organic acidic species in the atmosphere not reported by the DELTA®. The high correlation between the aerosol species also provides confidence in the quality of the measurements, since any uncertainty in the measurements would propagate through to scatter in the ion balance plots. For the base cations Ca^{2+} and Mg^{2+}, there is high uncertainty in the measurements as the concentrations are mainly at or below the limit of detection of the analytical method, therefore these data must be treated with caution.

A high correlation is expected between NH_4^+ and the sum of NO_3^- and SO_4^{2-} (slope = 0.88, R^2 = 0.86; Figure 16.), as these components are mostly present in the particulate phase as NH_4NO_3 and $(NH_4)_2SO_4$, coming from the neutralisation reaction between NH_3, HNO_3 and SO_2 oxidation products (Seinfeld and Pandis, 2016).

When comparing NH_4^+ with NO_3^- (Figure 16.b) and SO_4^{2-} (Figure 16.c), NH_4^+ shows larger molar concentrations associated to NO_3^- than SO_4^{2-}. This continues the trend observed for previous years reports (Tang et al. 2022, Espina-Martin et al., 2026) where SIA species in Northern Ireland are more nitrate-rich than sulphate rich, similar to those observed in the wider UK (Tang et al. 2018b; Twigg et al., 2025), as a consequence of the major reductions in SO_2 emissions since the 1980s following effective national and international policy implementation.

Cl^- & Na^+ have an almost 1:1 relationship with high correlation (slope = 0.99, R^2 = 0.83). They are marine sources and data sit within the sea salt (ss) ratio for Na:Cl (0.85, Seinfeld & Pandis 2016; Twigg et al., 2015). In Figure 16d it can be seen that some data points are outside the marine ss ratio; this may be linked to depletion of Cl due to long range transport processes and subsequent acid displacement by HNO_3 to form $NaNO_3$ (Dasgupta et al., 2007; Spindler et al., 2012).

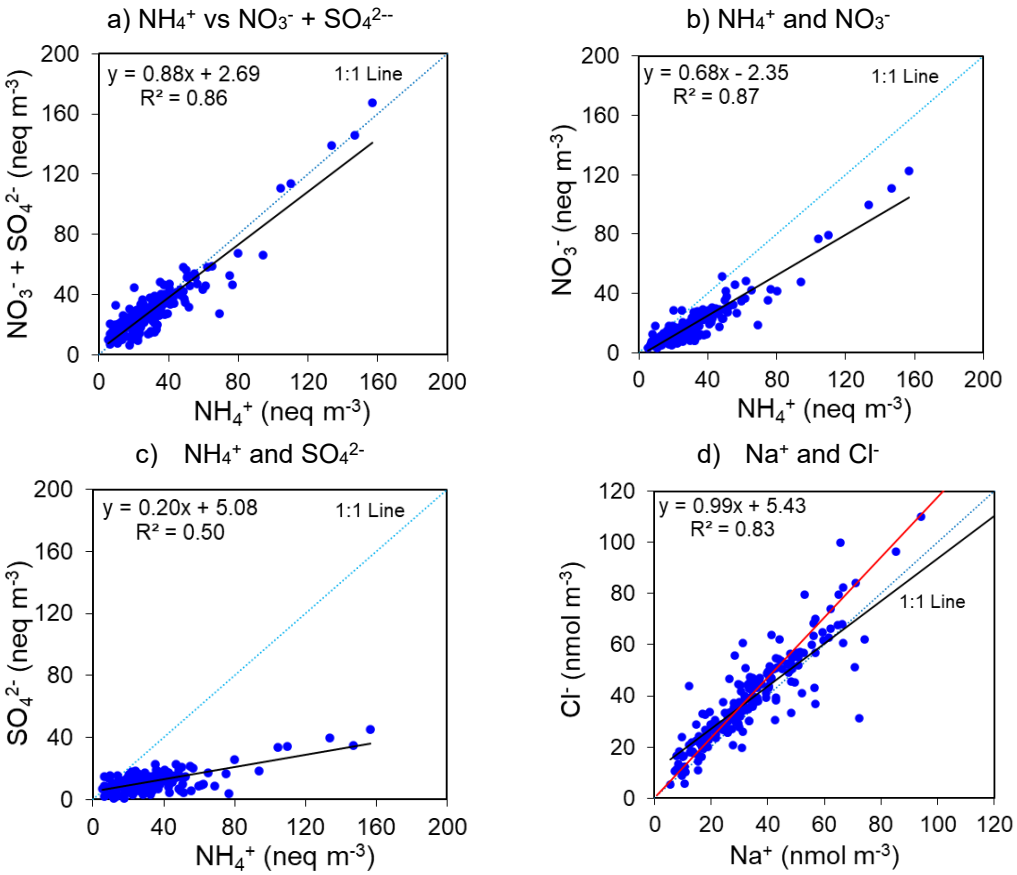


Figure 16. Scatter plots of concentrations between (a) NH_4^+ and NO_3^- + SO_4^{2-}, (b) NH_4^+ and NO_3^-, (c) NH_4^+ and SO_4^{2-}, and (d) Na^+ and Cl^- between 2019 - 2023 in the NI DELTA network. The red line in (d) corresponds to the known ratio of Cl^- to Na^+ in seawater (Seinfeld and Pandis, 2016).

3.6.2. Seasonal trends of DELTA components

Seasonal profiles were derived from the three continuous DELTA samplers in the network after the revision and incorporation into the UKEAP network in 2022: (Ballynahone Bog (UKA00959), Hillsborough (UKA00293) and Lough Navar (UKA00166).

Ammonia shows consistent peak concentrations during the spring and autumn, likely related to the agricultural activities already discussed in Section 3.4. Figure 17 shows that DELTA® NH_3 concentrations in 2023 were comparable to previous years, ranging from 0.3 to 6 µg NH_3 m^{-3}. As with the ALPHA® samplers, the 2023 spring peak was recorded in February followed by a sharp decrease in March due to the rainy conditions washing out the atmosphere; the June peak was also recorded by the Ballynahone Bog DELTA® sampler and on a lesser scale, also at Lough Navar. Higher concentrations were recorded at Hillsborough during the summer and autumn months, likely coming from increased local emissions at the large nearby farm (Figure 2).

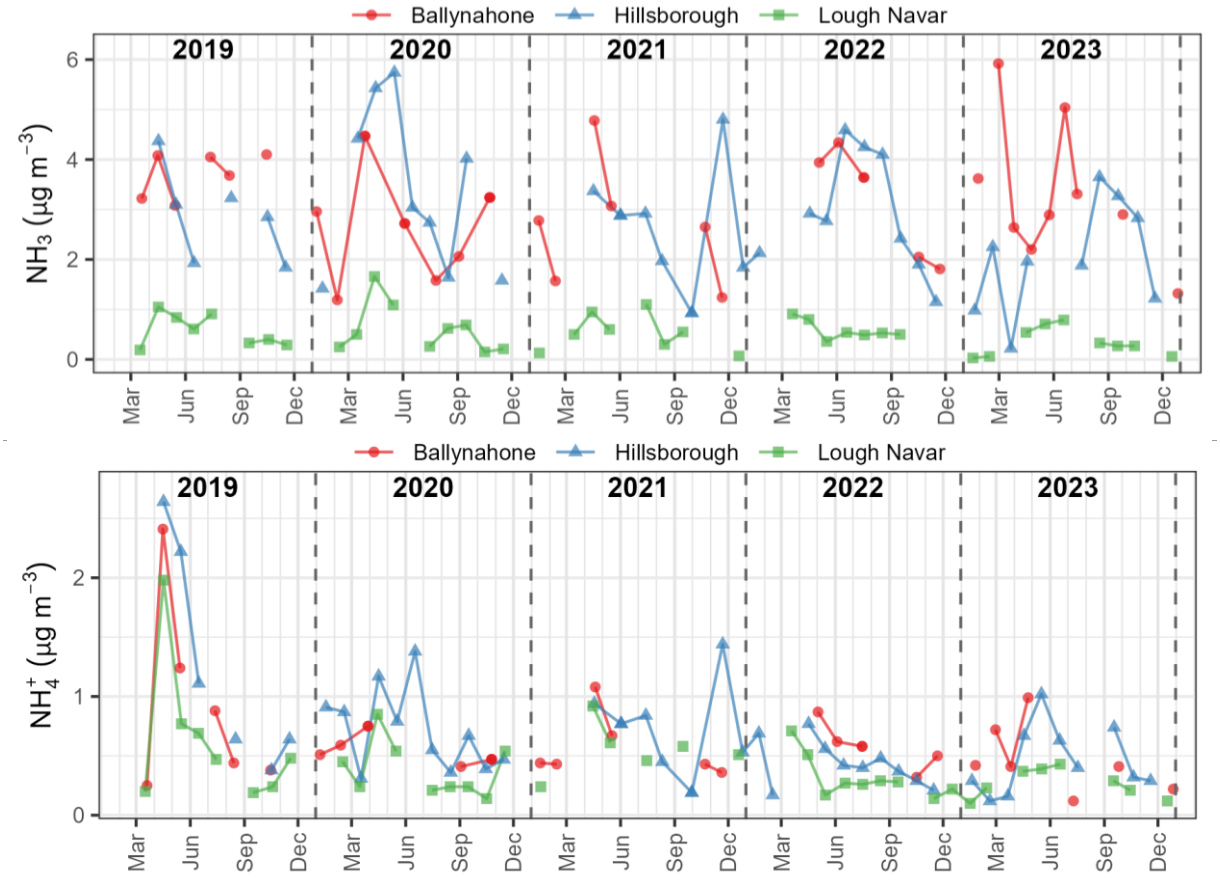


Figure 17. Time series of monthly NH_3 and associated NH_4^+ concentrations reported by the DELTA® systems in Northern Ireland. The data points in the graph are aligned with the assigned exposure months for each DELTA sampler.

In 2023, NH_4^+ concentrations were comparable with previous years and show an indicative decrease over time, similar to SO_4^{2-} (Figure 18) and to a lesser degree, to NO_3^- (Figure 19). Additional years of data will provide further insight whether this is interannual variability, an effect of the NI Network downsize back in March 2022 from 5 to 3 DELTA locations, or it is related to changes in the atmospheric composition.

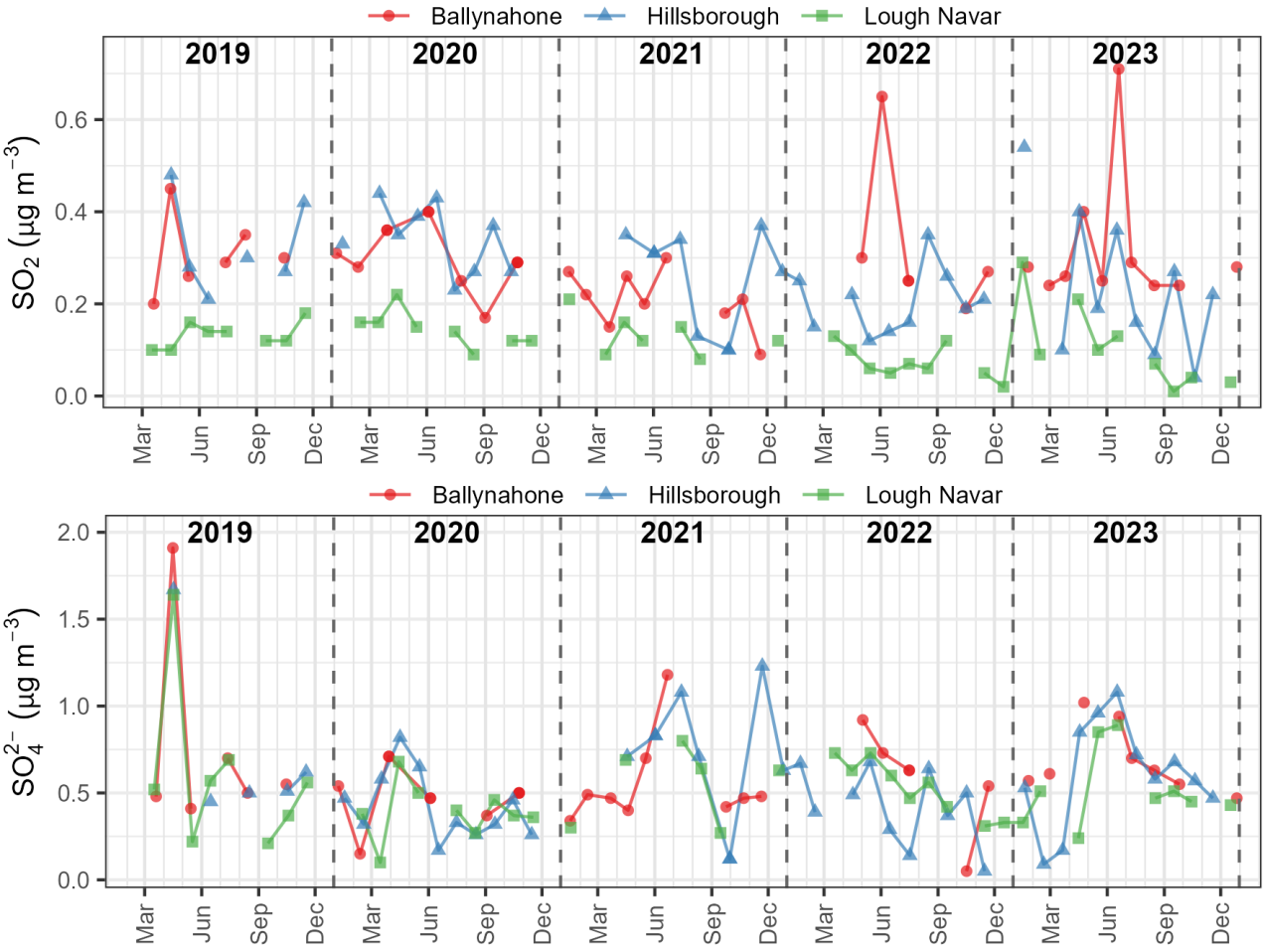


Figure 18. Time series for SO_2 and SO_4^{2-} reported by the DELTA® systems at the Northern Ireland network monitoring sites. The data points in the graph are aligned with the assigned exposure months for each DELTA sampler.

In 2023, the highest SO_2 concentration were reported in June (Figure 18) for the second consecutive year at Ballynahone Bog, suggesting a specific local event or events rather than a network generalized increase; this increase in concentrations were not observed across the wider AGAnet; SO_2 concentrations tend to be highest in the colder months due to seasonal combustion processes (heating), with coal burning still a considerable source of heating in Northern Ireland. The concentrations increase during periods with stable atmospheric conditions that allow the build-up of concentrations at ground level. SO_4^{2-} shows an increase during late spring and early summer months, as SO_2 oxidation towards SO_4^{2-} is enhanced during warm and dry periods (Twigg et al., 2015; Figure 21).

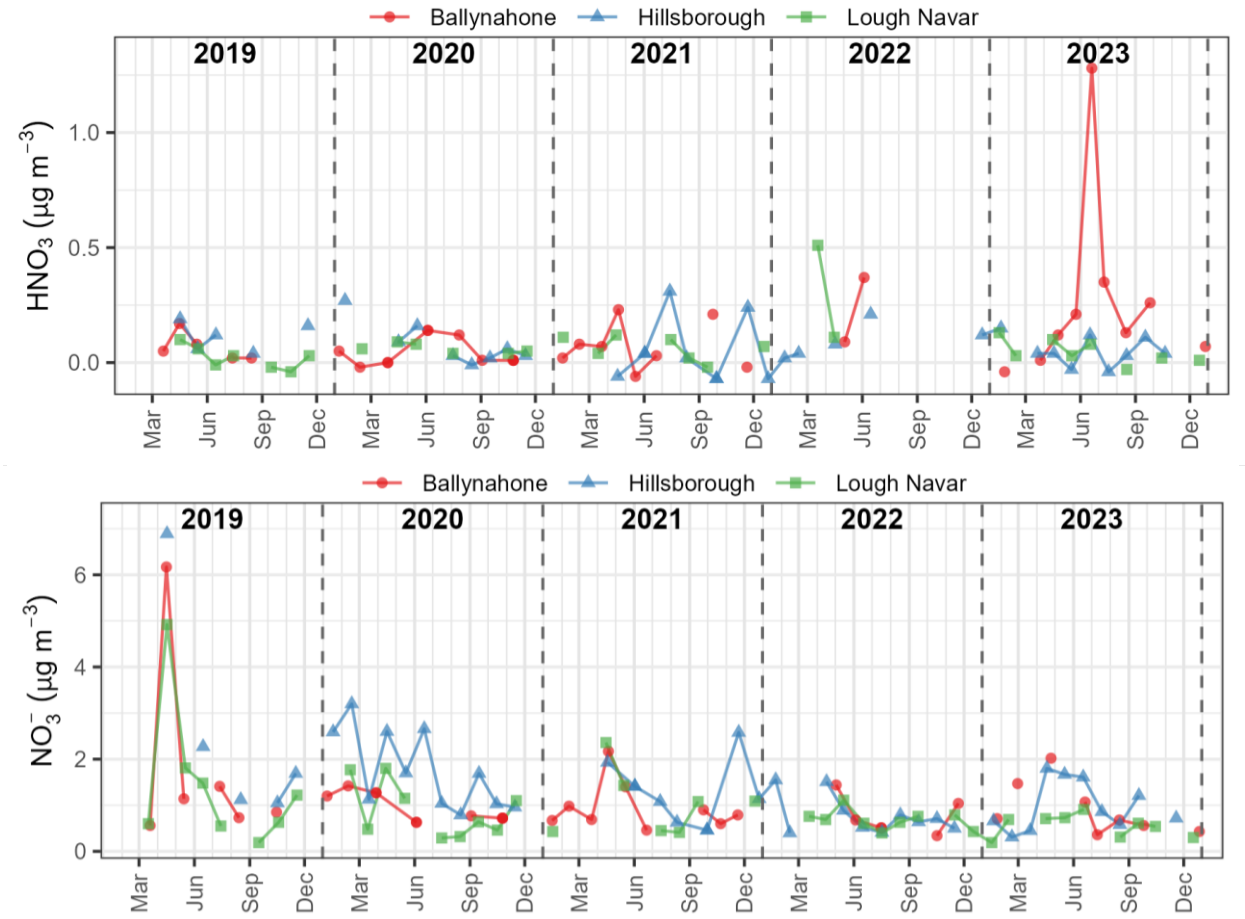


Figure 19. Time series of monthly HNO_3 and NO_3^- concentrations reported by the DELTA® systems in the Northern Ireland network. The data points in the graph are aligned with the assigned exposure months for each DELTA sampler.

For HNO_3, the following processes influence its seasonal distribution:

i) Formation of HNO_3 from NO_x through photochemical processes (Pope et al., 2016).

ii) Removal of HNO_3 by reaction with NH_3 to form NH_4NO_3 - smaller concentrations of HNO_3 in spring and autumn due to high seasonal concentrations of NH_3 to promote aerosol formation.

iii) Temperature and humidity effects on the equilibrium between the gas phase HNO_3 (and NH_3) and aerosol phase NH_4NO_3. Cooler, more humid conditions favour the aerosol formation, whereas warmer, drier conditions will see partitioning back to the gas phase as NH_3 and HNO_3.

iv) Long-range transboundary transport of NH_4NO_3 to the sites (Vieno et al., 2014). Typically, this is observed across the UK in spring when high pressure systems result in the import of particulate matter from Europe.

In 2023, a very high HNO_3 peak was observed in June at Ballynahone Bog; this could be partially explained by the high temperatures (Figure 2) and the fact that 2023 was the eighth sunniest year on record for Northern Ireland (Met Office, 2022b), leading to increased photochemical production as a secondary pollutant. This was also reflected in the rest of the AGAnet data, where HNO_3 concentrations increased in June and September; summer conditions allowed enhanced HNO_3 formation due to higher atmospheric oxidative capacity and less partitioning towards NH_4NO_3 (Twigg et al., 2024). The May and June peaks may be attributed to a combination of the processes i) and iii) mentioned above. NO_3^- peaks were observed between April to June, when processes ii, iii) and iv) above were likely taking place.

Usually, the largest concentrations of Na^+ and Cl^- tend to occur during winter, likely due to the increased wind speeds from storms generating more sea spray, highlighting the importance of marine sources in winter (Twigg et al. 2015; Figure 21g). Figure 20 shows sporadic events during winter, spring and summer months, outside of the typical storm season (Met Office, 2023e).

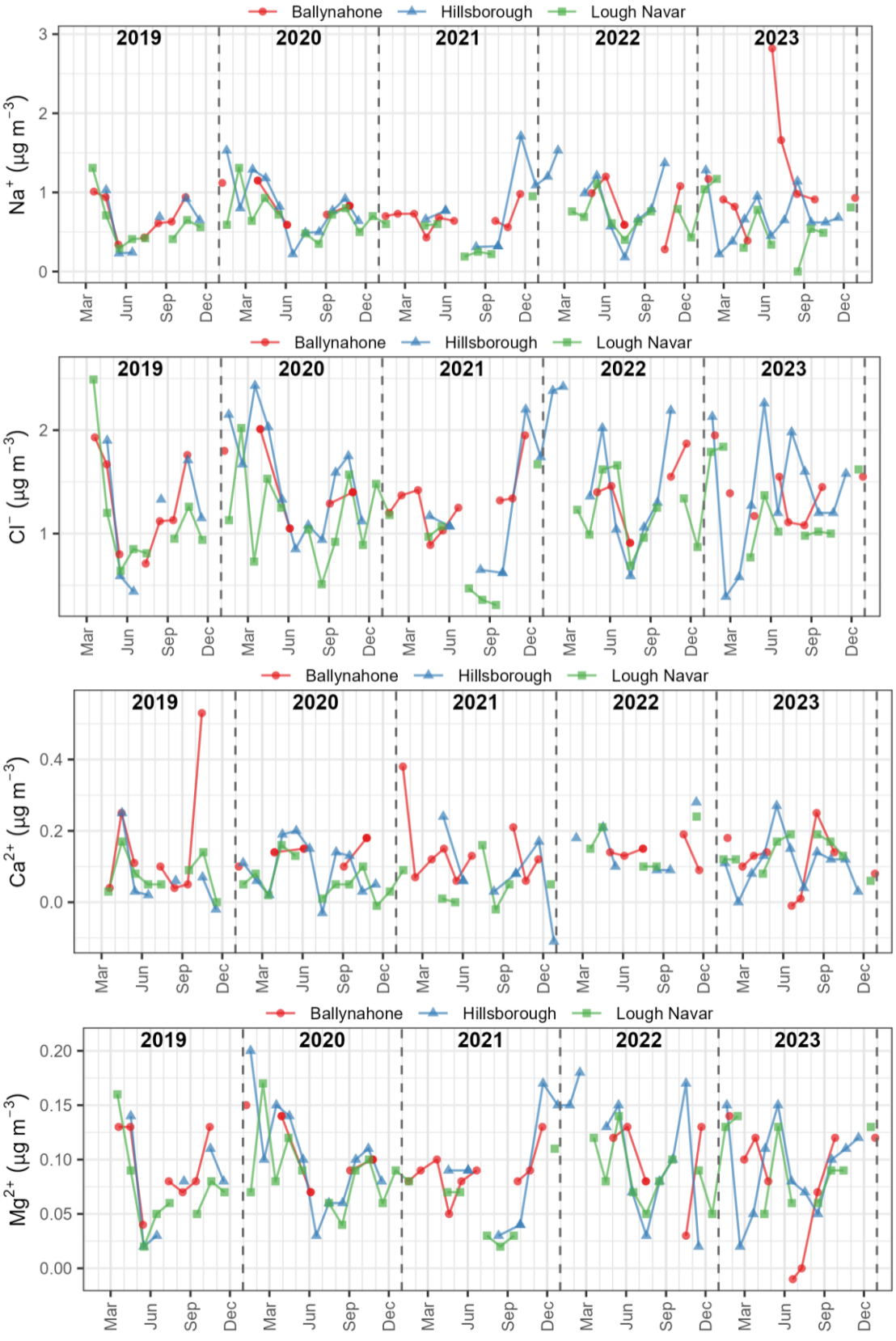


Figure 20. Time series for Na^+, Cl^-, Ca^{2+} and Mg^{2+} measured by the DELTA® sampler. The data is nested within the assigned exposure months for each DELTA sampler. The data points in the graph are aligned with the assigned exposure months for each DELTA sampler.

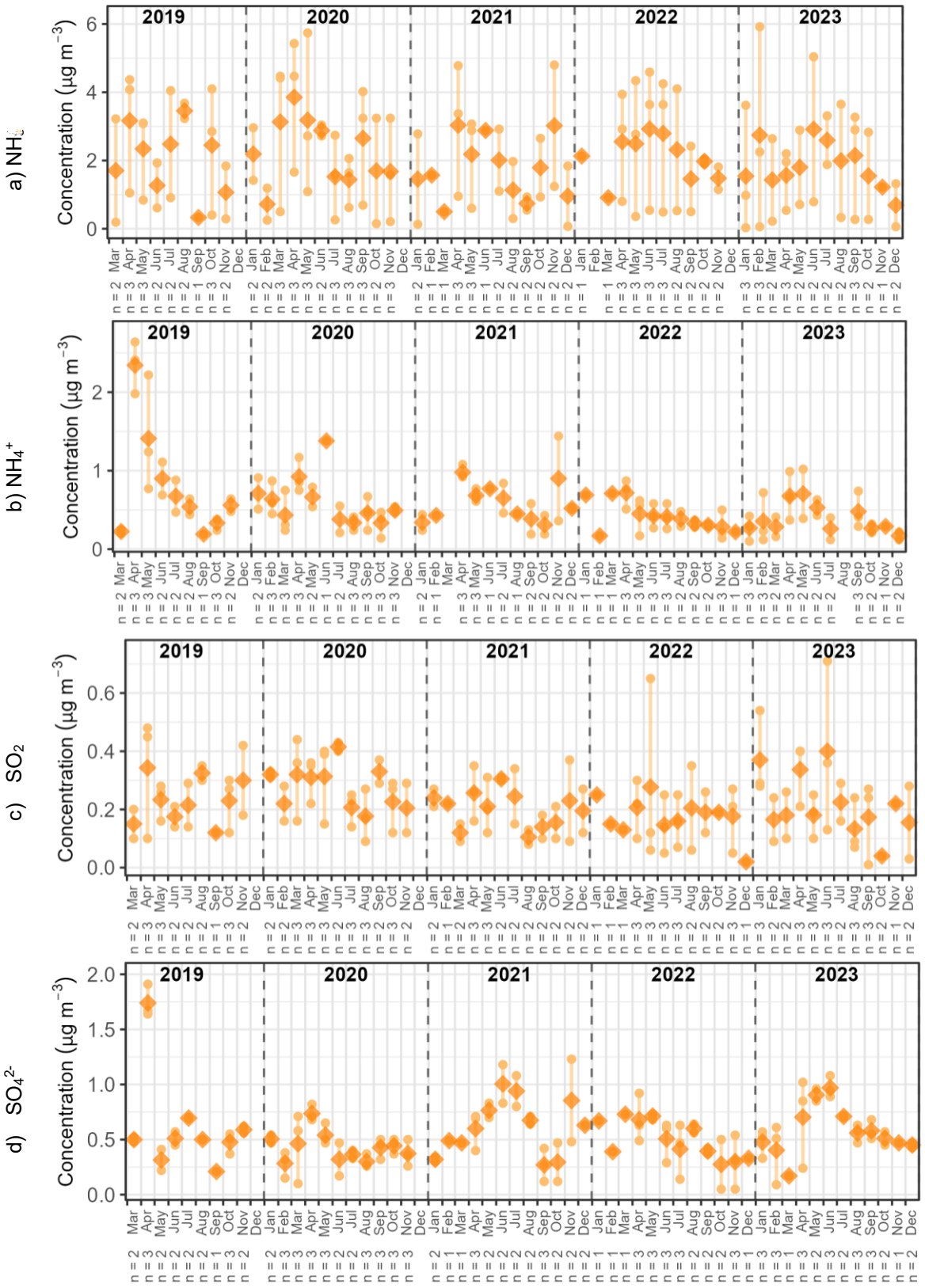


Figure 21. Mean concentrations for all DELTA samplers in the NI network. The time series represent the mean concentration, and the whiskers represent the minimum and maximum concentrations recorded during the exposure month.

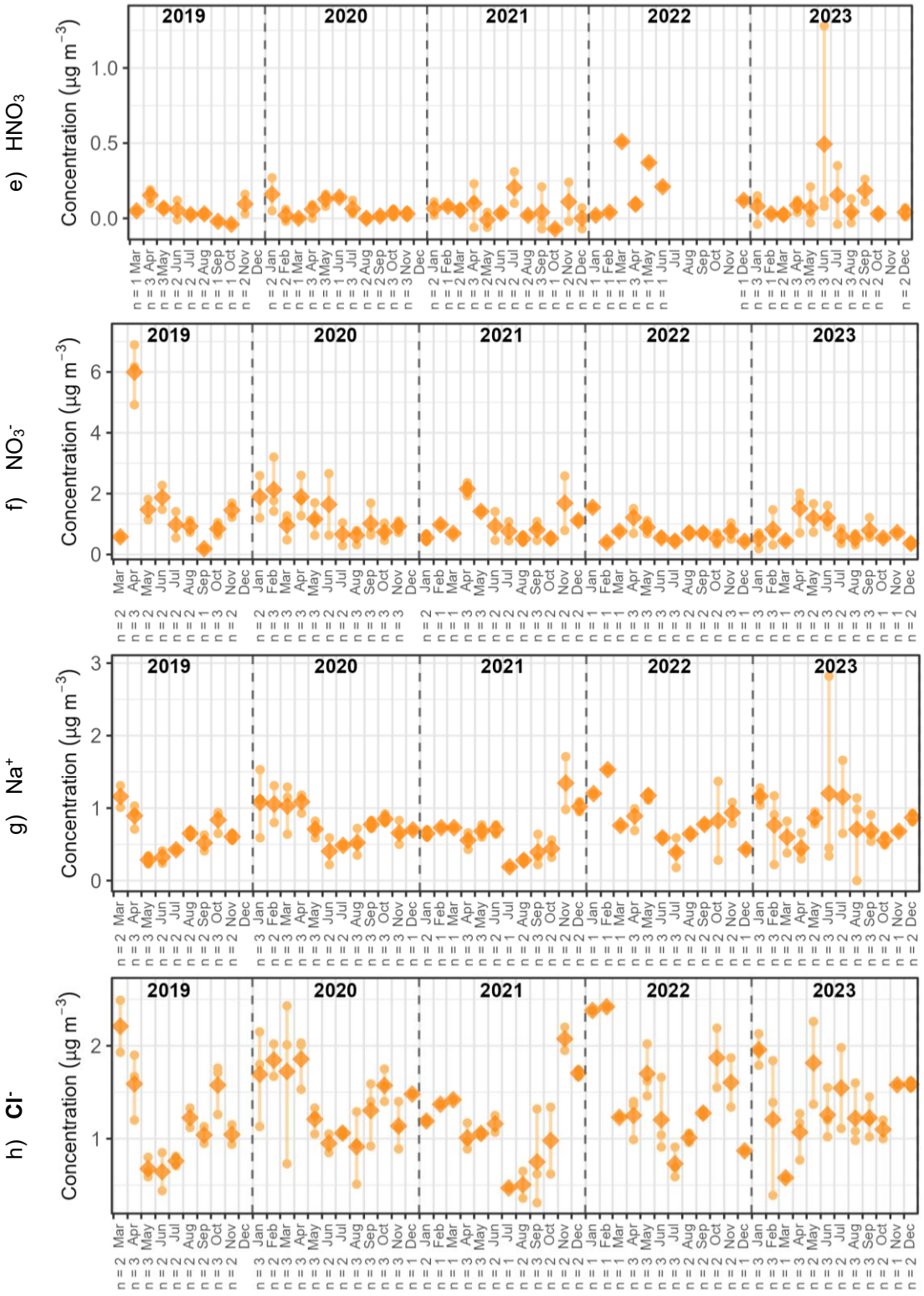


Figure 21. (cont). Mean concentrations for all DELTA® samplers in the NI network. For each monitoring period, the light orange circles represent all DELTA® data points, the darker orange diamonds represent the mean ammonia concentration, and the whiskers represent the range (minimum and maximum) of concentrations recorded during the exposure period.

4. Conclusions and next steps

2023 was the first full year where all sites in the NI ALPHA NH_3 and DELTA network were included in the NAMN/AGAnet (with the exception of AFBI25A which was set up to measure local concentrations for different purpose and was discontinued in August 2023). All data from ALPHA and DELTA sites are available via the Defra UK-AIR website (https://uk-air.defra.gov.uk/data/data_selector) as part of the UKEAP outputs (excluding AFBI25).

This report showed a comparison between calendar-year averages (based on calendar-month averages) vs time weighted averages, with the latter considered to be more accurate and representative of the sampling periods. The comparison between the two methods provides a transition from calendar months to time weighting of individual sampling periods allows for a comparison between this report and previous iterations.

Annual mean NH_3 concentrations in NI in 2023 showed high spatial variability across the 26 sites, similar to previous years. Measured annual average concentrations saw a general decrease for most sites compared to 2022. The NI NH_3 network displayed typical seasonal NH_3 patterns with key drivers related to agricultural activities, meteorological conditions and the thermodynamic partitioning of partitioning of NH_3 (g) into ammonium (NH_4^+) (p) aerosols.

The lowest NH_3 concentrations continued to occur at rural background sites while the highest concentrations occurred in areas dominated by mixed cattle and dairy sources. The maximum monthly concentration spike was recorded at Inch Abbey in June (21 µg NH_3 m^{-3}), most likely triggered by a combination of enhanced emissions, favourable meteorology and local events. Other notable spring peaks were observed in March-April at Ballylinney Church (UKA00949, 18.6 µg NH_3 m^{-3}) and Drumclamph 2 (UKA00960, 13.9 µg NH_3 m^{-3}), likely triggered by local events, making these sites less representative of the wider surrounding area. Annual average measured NH_3 concentrations agree well with modelled predictions from the EMEP4UK CTM (R^2 = 0.62, FAC2 = 78%) for 2023.

Ballynahone Bog and Lough Navar DELTA sites had several components were below the minimum DC to be considered representative (n ≥ 274), although Lough Navar was close to that value for most of the measured species; caution is required to not over-interpretate their results. Ammonia continues to be the largest component in the gas and aerosol measurements for the inorganic N species reported in the DELTA® network in Northern Ireland. Inorganic water-soluble aerosol phase concentrations reported continue to be dominated by secondary inorganic aerosols (SIA) NH_4NO_3 and $(NH_4)_2SO_4$, as well as from Na and Cl from marine sea salt sources.

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Published datasets

EIDC-Monthly atmospheric ammonia, acid gas, inorganic aerosols, and base cation concentrations from Northern Ireland ALPHA® Ammonia Monitoring Network 2019-2020 and DELTA gas and aerosol monitoring network, 2019 – 2020

UKAIR – Annual ALPHA and DELTA sampler datasets for the 2022 and 2024 year period available in the data selector: https://uk-air.defra.gov.uk/data/data_selector_service?show=non-auto&submit=Reset&f_limit_was=1

Appendices

Mean annual concentrations of NH_3 for NI ALPHA sites using the calendar-based method.

Table *S1*. Annual mean NH_3 concentrations measured at 29 sites in the AFBI ALPHA® and DELTA® networks for the calendar years 2020, 2021 and 2022. A for ALPHA® sites and D for DELTA® sites. Concentrations are expressed in µg NH_3 m^{-3}.

			2020		2021		2022		2023	
ID	Type	Name	Mean	n	Mean	n	Mean	n	Mean	n
UKA00938	A	U of Ulster met station	**2.63**	*7	**3.31**	12	**5.03**	11	2.83	9
UKA00939	A	Castle Enigan	**3.60**	12	**3.03**	12	**3.18**	12	3.09	11
UKA00383	A	Beaghs Burn	**0.53**	12	**0.68**	10	**0.60**	12	0.57	10
UKA00940	A	Slieve Beagh	**1.15**	11	**1.11**	12	**1.68**	12	0.84	11
UKA00941	A	Moninea Bog	**2.10**	12	**2.27**	12	**2.20**	12	2.30	12
UKA00942	A	Seekinore	**2.77**	12	**3.98**	12	**3.51**	11	2.83	11
UKA00943	A	Lisbellaw	**3.88**	12	**4.37**	12	**5.02**	12	5.24	12
UKA00944	A	Glenwherry COSMOS	**1.67**	12	**2.10**	12	**2.23**	12	2.01	10
UKA00945	A	UWMN Bencrom River	**0.92**	12	**1.14**	*6	**1.09**	10	0.82	10
UKA00946	A	Blackwater town	**3.82**	*5	**5.71**	12	**5.33**	11	5.37	12
UKA00947	A	Ratarnet Rd	**2.69**	*5	**8.91**	10	**7.41**	12	5.20	12
UKA00948	A	Inch Abbey	**1.83**	12	**1.80**	12	**4.35**	12	3.27	11
UKA00212	A	AURN Belfast centre	**2.53**	12	**2.88**	12	**3.01**	*8	3.16	11
UKA00949	A	Ballylinney Church	**4.36**	11	**5.02**	12	**5.49**	12	5.72	11
UKA00950	A	West of Crumlin	**2.54**	12	**2.96**	12	**3.60**	12	2.63	11
UKA00951	A	Loughmore River	**1.03**	12	**1.12**	10	**0.82**	*8	1.00	11
UKA00952	A	Caldanagh Bog	**3.18**	12	**2.95**	12	**3.04**	12	2.96	11
UKA00953	A	Cloughmills	**3.68**	12	**3.53**	12	**3.44**	12	3.34	11
UKA00954	A	Caddy Rd	**4.55**	12	**7.45**	10	**9.12**	11	6.10	10
UKA00955	A	Turmennan Rd	**1.91**	12	**1.83**	10	**1.77**	12	1.54	12
UKA00956	A	Carrowbane Rd	**3.34**	*7	**4.59**	11	**4.93**	11	4.57	12
UKA00957	A	Creggan	**2.76**	12	**3.33**	12	**2.97**	12	2.63	10
UKA00958	A	Corramore Rd	**0.98**	12	**1.25**	12	**1.74**	12	0.86	10
UKA00960	A	Drumclamph 2	**5.77**	12	**6.88**	12	**9.14**	12	6.26	11
AFBI25-A	A	Hillsborough	**6.92**	12	**6.3**	12	**9.71**	11	6.85	*6
UKA00959	D	Ballynahone Bog	**2.90**	11	**2.74**	*7	**3.24**	*6	3.32	9
UKA00293	D	Hillsborough	**3.12**	9	**2.50**	9	**2.91**	9	2.03	9
UKA00166	D	Lough Navar	**0.60**	9	**0.53**	*8	**0.59**	*7	0.34	9
UKA00401	A	Coleraine	**2.18**	*6	**3.50**	12	**3.28**	12	3.62	12

*n = no. of valid monthly measurement periods used in calculating annual mean. *Sites with n < 9 months of data are expected to be less representative of the average yearly concentrations and are highlighted in red.*

Mean annual concentrations of acid gases and aerosols for NI DELTA sites using the calendar-based method.

Table S2. Summary statistics for 2023 for reactive gas and aerosol measurement data from the three DELTA® sites in Northern Ireland. Mean annual averages have been calculated as calendar averages. All concentrations are expressed in µg m-3. Cells in red correspond to sites whose annual statistics have been calculated with n ≤ 9, therefore the mean average is coloured in grey as they are considered not representative for 2023.

Species	Statistic	Ballynahone Bog (UKA00959)	Hillsborough (UKA00293)	Lough Navar (UKA00166)
HNO_3	**Mean**	0.27	0.05	0.05
	Min	-0.04	-0.03	-0.03
	Max	1.28	0.13	0.15
	SD	0.40	0.06	0.05
	N	9	9	8
SO_2	**Mean**	0.32	0.24	0.11
	Min	0.24	0.04	0.01
	Max	0.71	0.54	0.29
	SD	0.15	0.16	0.09
	N	10	10	9
NH_3	**Mean**	3.32	2.03	0.34
	Min	1.32	0.22	0.03
	Max	5.92	3.65	0.79
	SD	1.41	1.11	0.28
	N	9	9	9
NO_3^-	**Mean**	0.91	0.99	0.55
	Min	0.36	0.31	0.19
	Max	2.02	1.8	0.91
	SD	0.58	0.54	0.24
	N	8	10	9
SO_4^{2-}	**Mean**	0.69	0.61	0.52
	Min	0.47	0.09	0.24
	Max	1.02	1.08	0.89
	SD	0.19	0.30	0.22
	N	8	11	9
NH_4^+	**Mean**	0.47	0.44	0.27
	Min	0.12	0.17	0.10
	Max	0.99	0.77	0.43
	SD	0.30	0.20	0.12
	N	7	10	8
Na^+	**Mean**	1.18	0.94	0.61
	Min	0.39	0.22	0.3
	Max	2.82	1.28	1.17
	SD	0.70	0.43	0.38
	N	9	9	9
Cl^-	**Mean**	1.41	1.40	1.27
	Min	1.08	0.39	0.77
	Max	1.95	2.26	1.84
	SD	0.29	0.59	0.40
	N	8	11	9
Ca^{2+}	**Mean**	0.11	0.11	0.14
	Min	-0.01	0	-0.03
	Max	0.25	0.25	0.19
	SD	0.08	0.07	0.05
	N	9	11	9
Mg^{2+}	**Mean**	0.07	0.09	0.10
	Min	-0.01	0.02	0.05
	Max	0.14	0.15	0.14
	SD	0.06	0.04	0.04
	N	10	11	9

Ion Balance for Ballynahone Bog, Hillsborough and Lough Navar DELTA samplers for years 2019-2022

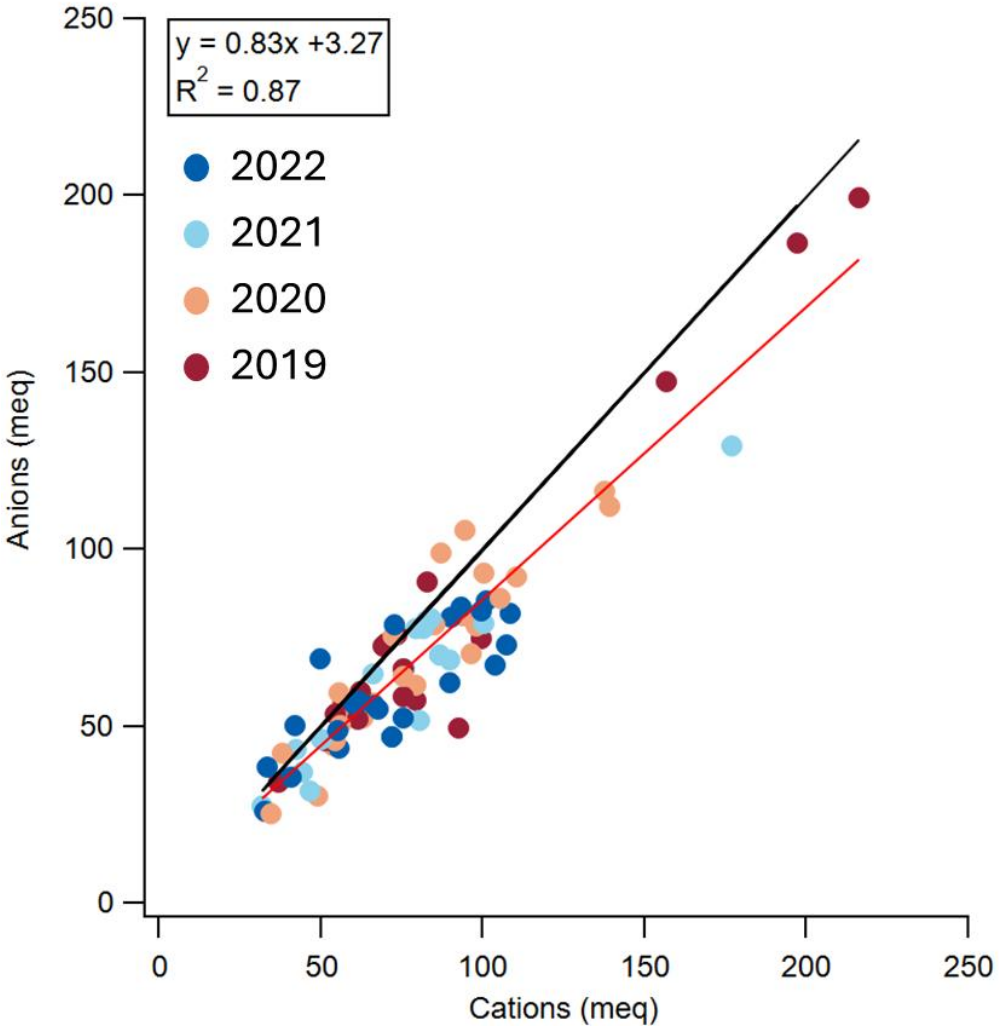


Figure S1. Ion balance for the NI DELTA network (Ballynahone Bog, Hillsborough and Lough Navar for years 2019 to 2022. Each year of sampling is shown with a different colour. The black line represents the 1:1 line, representing aerosol full neutrality, while the red line represents the Ion Balance linear regression.

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