UK Centre for Ecology & Hydrology

Cuilcagh ammonia monitoring and foliar ammonium in vegetation

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Title

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Contents

1 Introduction

Cuilcagh Mountain in County Fermanagh in Northern Ireland (NI) has been a Special Area of Conservation (SAC) since 2005 and is 2,751 ha in size. It is the second largest intact blanket bog in Northern Ireland. Cuilcagh Anierin Uplands in the Republic of Ireland (RoI) was designated a SAC in 1997 and is 9,736 ha. It contains one of the largest areas of intact mountain blanket bog in the RoI which is relatively undisturbed. Together the two neighbouring SACs form one of the largest areas of upland blanket bog in Ireland. They also form an important part of the wider Marble Arch Caves Global Geopark, which was the World's first UNESCO Global Geopark crossing an international border.

Cuilcagh Mountain SAC (NI) is largely privately owned with some areas of commonage and publicly owned land. Cuilcagh Anierin Uplands SAC is mostly commonage (over 70%) with the remainder being privately owned or owned by Coillte (semi state forestry body). Both sites are extensively grazed by sheep with a few small areas grazed by cattle. A large amount of the surrounding land is dominated by coniferous forestry (largely Sitka Spruce) with the remainder being mainly unimproved agricultural land.

The area is situated at a relatively high altitude (up to 665 m) in a high rainfall area (~1500 mm/year) and has a wide range of habitats which are scattered as a mosaic over the area and is home to rare wildlife. One of the integral species to blanket bog are Sphagnum mosses. Some of the Sphagnum species present are very sensitive to damage by atmospheric nitrogen (N) deposition. Research was required to determine the level of atmospheric nitrogen input to these systems, especially ammonia (NH_3) concentrations and nitrogen deposition across the area and its damaging effect on the vegetation.

Northern Ireland suffers from the highest levels of atmospheric nitrogen input in the UK and Ireland. This has been shown to have noticeable and significant negative impacts on a range of species and habitats but particularly those found on peatlands. While much monitoring and research has been carried out in a number of lowland settings in Northern Ireland, there has been little monitoring in upland habitats to date. Cuilcagh Mountain and Cuilcagh Anierin Uplands SACs were identified as ideal candidates for monitoring to provide an insight into levels of atmospheric ammonia in an Irish upland setting.

Passive samplers are the most efficient way of measuring NH_3 concentrations in the air, especially where there is no local power supply (electricity) available. UKCEH ALPHA® (Adapted Low-cost Passive High Absorption) samplers (Tang et al. 2001) were installed at five sites across the two SACs to capture typical concentrations.

The standard method to assess the effects of N deposition on vegetation is to measure the N-content (%N). Previous biomonitoring studies showed that differences in N content (%N) and foliar ammonium (foliar NH_4-N) in bryophytes (mosses) and lichens were closely related to atmospheric NH_3 concentrations, when there was a point NH_3 source (e.g. farm buildings) that emitted the gas (Leith et al 2005; Sutton et al 2011; Van Dijk et al 2009). Of the two indicators, foliar NH_4-N responds more strongly and probably also more quickly to NH_3 changes than %N. The report also showed that different plant species react differently to changes in NH_3 air concentration.

A comparison between different components of N deposition, i.e. dry NH_3, wet NO_3-N (nitrate) and NH_4-N (ammonium) inputs, at the long-term Whim Bog field manipulation site (Southern Scotland) http://www.whimbog.ceh.ac.uk/ shows that these different forms of N input do not all have the same impact on %N and foliar NH_4-N concentrations of mosses. For %N, the sensitivity appears to be highest for NH_3, intermediate for wet NH_4-N and lowest for NO_3-N. This differentiation is similar but even stronger for foliar NH_4-N in mosses, which were very sensitive to NH_3, but only responded to high levels of wet N deposition inputs (Leith et al 2005). The foliar NH_4-N method was chosen in this study, being the most sensitive approach, and also to remain within the agreed budget.

The Cuilcagh site is part of the Collaborative Action for Nature Network (CANN) project supported by the EU's INTERREG VA programme, which aims to identify and deliver conservation measures on a suit of SACs across Northern Ireland, the Republic of Ireland and Scotland to ensure their long-term sustainability.

A study into the NH_3 air concentrations and the effects of these on vegetation was carried out on Cuilcagh Mountain and Cuilcagh Anierin Uplands SAC's. The project started with the establishing of the ALPHA® monitoring sites and the collection of moss samples in February 2020.

2 Methods

2.1 Monitoring sites

The monitoring sites were chosen so that they were spread out over the whole site (both SACs), received 'incoming air' from as many areas as possible and were accessible to allow ALPHA® samplers to be changed on a monthly basis. The sites were jointly chosen by UKCEH staff (providing experimental needs and site requirements) and UW staff (providing site specific information and using local knowledge). The locations of the monitoring sites are shown in Figure 1 and the coordinates in Table 1.

There is no grazing during the winter months at the sites and only light grazing with sheep for the rest of the year. This made it necessary to fence off the sample posts so no sheep can reach the ALPHA® samplers. Two examples of the setup of the sites are shown in Figure 2.

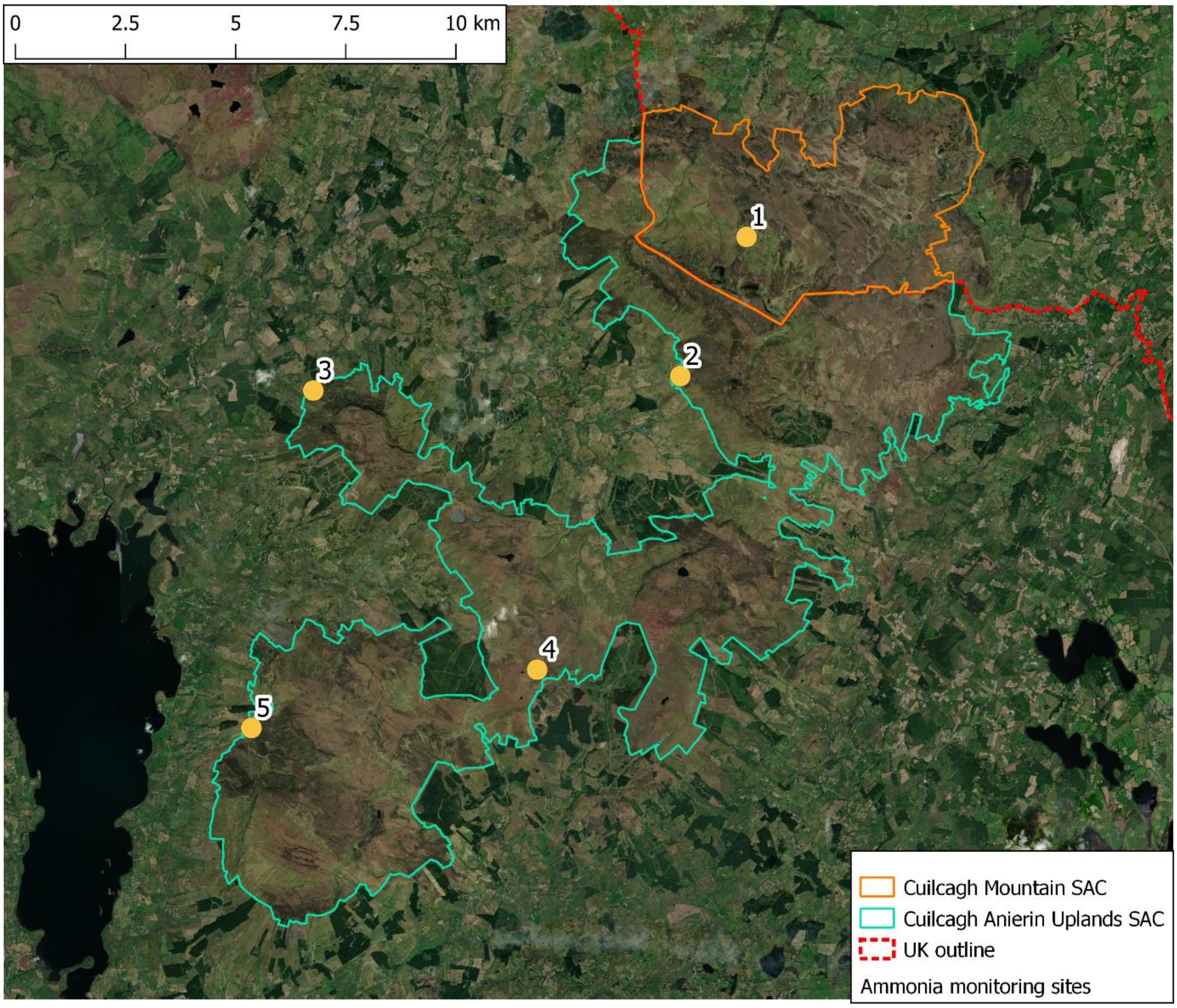

Figure 1: Location of the 5 Cuilcagh NH_3 monitoring sites. With Site 1: Boardwalk (NI); Site 2: Eshvagh (ROI), Site 3: Corcashel (ROI), Site 4: Grouse Project (ROI) and Site 5: Shridrinagh (ROI)

Table 1: Location of the 5 monitoring sites with their names, coordinates and date the site was set up.

Cuilcagh NH_3 monitoring sites				
		Coordinates		
site number	**name**	**Latitude**	**Longitude**	**set up date**
Northern Ireland				
1	Boardwalk	54.218694	-7.823424	19/02/2020
Republic of Ireland				
2	Eshvagh	54.190490	-7.846421	19/02/2020
3	Corcashel	54.187614	-7.973803	20/02/2020
4	Grouse Project	54.130905	-7.896038	20/02/2020
5	Shridrinagh	54.119063	-7.995085	20/02/2020

Figure 2: Two of the NH_3 monitoring sites. Left: Site 3 Corcashell looking to the west. Right: Site 5 Shridrinagh looking to the south.

2.1.1 Additional Site Information

These notes were mainly recorded at time of site set up.
Site 2: Eshvagh is near farm buildings (just south, about a mile away). It is not clear if there is any livestock kept in the buildings, but if so only in low numbers.

Site 4: Grouse Project. This site was to be expected to have the lowest NH_3 concentrations due to its re mote location, distance from any kind of improved agriculture and significant levels of forest nearby. A lot of *Cladonia portentosa* was found here. This lichen is very sensitive for NH_3 damage. To see so much of it here is a sign that the NH_3 concentrations in the air are quite low.

Site 5: Shridrinagh seems to have supplementary feeding and is close to the entrance gate. It was expected to have higher stock concentrated in that area compared to other sites and therefore higher NH_3 concentrations are expected. The vegetation at this site looked quite damaged, probably due to overgrazing in the past.

NH_3 levels at the other 3 locations were expected to be fairly similar due to their similar settings.

For comparison of the foliar (NH_4-N) content of the moss samples it is important to collect the same moss species at all 5 sites. *Sphagnum fallax* and *Pleurozium schreberi* were the only species that were growing at all 5 sites. These two species are not the most NH_3 sensitive but slightly more N tolerant. The more sensitive species are not found at all 5 sites and this is an indication that there is some N damage to the vegetation.

2.2 Ammonia measurements

UKCEH ALPHA® Samplers

Atmospheric NH_3 concentrations were monitored using the UKCEH ALPHA® (Adapted Low-cost Passive High Absorption) samplers, shown in Figure 3 (Tang et al., 2001).

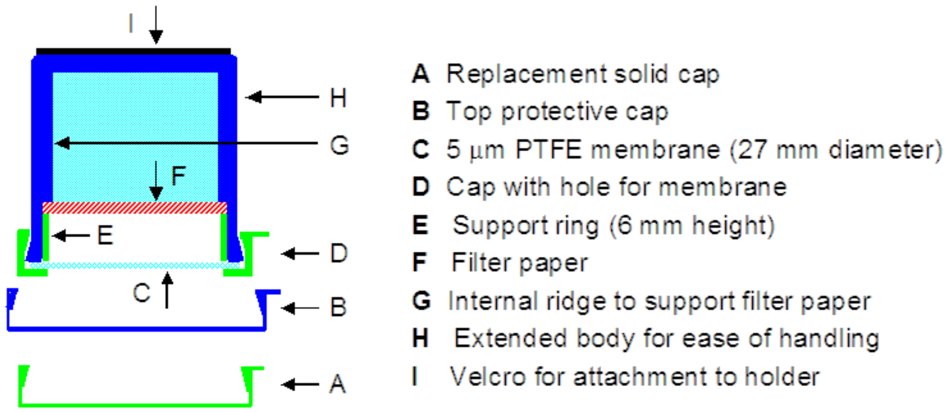

Figure 3: Outline diagram of a sing UKCEH ALPHA® sampler.

Preparation of Samples

ALPHA® samplers were prepared in accordance with standard UKCEH protocols (Tang et al., 2021), using filter circles impregnated with citric acid. Triplicate samplers were prepared for each monitoring site and were placed in a sealed container together with spare caps, which were used to replace the membrane caps at the end of sampling.

Exposure of Samples

ALPHA® samplers are attached by the use of Velcro to shelter on a post at about 1.5 m height above ground or vegetation. The sampling height of 1.5 m above ground is standard, which provides a representative NH_3 concentration in the atmosphere and is in line with heights featured in modelling outputs. Plastic bird spikes deter birds from perching. Triplicate samples are used at each site in order to give a more reliable estimation of the air concentration of NH_3.

Monitoring was carried out on a monthly frequency from February 2020 until April 2021, using continuous time-integrated sampling over each period. Due to COVID-19 restrictions it was not possible to change the samples after the initial set up in February 2020 until June 2020, therefore resulting in longer-term average concentrations for this period**.**

Site Set Up and Site Operator Duties

The initial establishment of the sampling sites was carried out by Roisin Grimes, Simon Gray and Ronald Surgenor from Ulster Wildlife and guided by Netty van Dijk from UKCEH. After the initial set up, sites were visited on a monthly basis by an Ulster Wildlife member of staff trained to carry out the required monthly changeover of samples. A recording card was used by the site operator to record dates and times of the sample changes at each site, together with relevant local information (e.g. agricultural activities taking place in the vicinity, such as manure spreading, during the month or at the time of visit).

Chemical Analysis

Exposed samples were stored in a cold room at 4°C until analysis. Impregnated filter circles from the exposed ALPHA® samplers were extracted into deionised water and analysed for ammonium on the SEAL AA3 system at UKCEH. This analysis system is based on detection of a colour change response which is selective for ammonium. The method is an adapted (by UKCEH) standard instrument method to account for the pH of the citric acid in samples.

Calculation of Air Ammonia Concentrations

Processing of raw data was performed in accordance with UKCEH standard protocols. From 2019 this involved the use of the AAGA (ammonia, acid gases and aerosol) data processing tool. Details of the calculations are included below for reference (Tang et al., 2021)

The amount of ammonia collected (Q) on an ALPHA sampler due to air sampling is given by:

$$Q = (ce-cb)*v \qquad (1)$$

Where ce is the liquid concentration of san exposed sampler, cb is the liquid concentration of a blank sampler and v is the liquid volume of the extraction solution.

The air concentrations (Xa) of ammonia is then determined as:

$$Xa = Q/V \qquad (2)$$

Where V is the effective volume of air sampled (V, m^3), which is be found by:

$$V = DAt/L \qquad (3)$$

Where D is the diffusion coefficient of NH_3 in air, A is the cross sectional area, t is sampling duration and L is the diffusion path length. (Tang et al. 2001) An uptake rate of 0.003241315 was used (Edinburgh laboratory calibrated uptake rate for 2020/2021).

Quality Assurance and Calibration

The accuracy of the SEAL AA3 system for analysis of ammonium in aqueous solution is assured by participation in international laboratory proficiency schemes (GAW). Replicate ALPHA® samplers were also used for each measurement (triplicate samplers in this study) and should, when performing well, agree to within 15 % (CV). Large discrepancies are most likely due to contamination of samples, or other factors that affect the performance of the samplers.

Results have been quality assured and flagged appropriately according to EMEP protocols (https://projects.nilu.no//ccc/flags/index.html). All field blanks demonstrated contamination levels within the acceptable range. The dataset is considered to be of high quality.

2.3 Vegetation sampling

Sample collection and preparation

Samples of *Sphagnum fallax* and *Pleurozium schreberi* were collected at the same time as the ammonia monitoring sites were set up (19 and 20 February 2020) at each monitoring site by Netty van Dijk (UKCEH). Back in the lab they were sorted and cleaned. Only the top 1 to 1.5 cm of the *P. schreberi* shoots and the capitula of *S. fallax* were used. After a quick rinse with de-ionised water they were blot-dried and stored in the freezer at -20°C until they were extracted.

2g fresh weight (FW) of each frozen sample was weighed out (in duplicate were possible) and 20 ml de-ionised water was added. After an extraction time of 4 hours the solution was filtered through 0.45 µm pore syringe filter and stored in the freezer at -20°C until analysis (Leith et al 2005; Van Dijk et al 2009)

Sample analysis

The samples were analysed following the standard protocol (same as for ALPHA® samples) on the SEAL AA3 analyser. The SEAL AA3 is an instrument utilising a colorimetric reaction to detect the concentration of ammonium in water (modified Berthelot). It is important to note the reaction chemistry is specifically corrected for the impact of the low pH of the sample.

Calculating the NH_4-N concentration in the vegetation samples FW (fresh weight)

NH_4-N (µg g^{-1}) FW

The foliar NH4-N concentrations are calculated following the method below (Leith et al 2005; Van Dijk et al 2009)

$$N_{f,NH4\text{-}N} = [N_{NH4\text{-}N}\text{-}N_{blank}] *(M_{extractant} + M_{f,sample})/ M_{f,sample} \quad (1)$$

Where:

$N_{f,NH4\text{-}N}$ is the foliar NH_4-N concentration (µg g^{-1} fresh weight (FW)) in the vegetation sample

$N_{NH4\text{-}N}$ is the NH_4-N concentration in the extraction solution (µg g^{-1})

N_{blank} is the NH_4-N concentration in the blanks (µg g^{-1})

$M_{extractant}$ is the mass of extractant (de-ionised water) used (20 g as standard)

$M_{f,sample}$ is the fresh mass (FM) of the vegetation sample (g)

3 Results

3.1 Ammonia concentrations

The average concentrations for the study period for the 5 sites are quite low and vary from 0.53 at the Grouse Project to 0.64 µg NH_3 m^{-3} at the Boardwalk and Eshvagh. (Table 2 and Figure 4). See for full details Appendix I (Data Report) and Appendix II: Cuilcagh NH_3 concentrations per site.

Table 2: Monthly NH3 concentrations (µg m-3) from February 2020 until April 2021. The concentrations are the average of triplicate sampling. * Due to COVID restrictions access to the sites was not possible and the samples stayed on for this extended time ** Samples not returned

2020	Boardwalk NH$_3$ (µg m^{-3})	Eshvagh NH$_3$ (µg m^{-3})	Corcashel NH$_3$ (µg m^{-3})	Grouse Project NH$_3$ (µg m^{-3})	Shridrinagh NH$_3$ (µg m^{-3})
February*	1.248	1.271	1.193	1.100	1.301
March*	1.248	1.271	1.193	1.100	1.301
April*	1.248	1.271	1.193	1.100	1.301
May*	1.248	1.271	1.193	1.100	1.301
June	0.473	0.484	0.433	0.327	0.489
July	0.222	0.222	0.169	0.166	0.194
August	0.611	0.640	0.577	0.556	0.497
September	0.488	0.509	0.419	0.414	0.449
October	0.382	0.356	0.324	0.311	0.319
November	0.200	0.265	0.264	0.158	0.198
December	0.112	0.141	0.108	0.101	0.129
2021					
January	0.257	0.214	0.186	0.153	0.225
February	0.415	0.413	0.362	0.380	0.280
March	0.744	0.627	0.588	0.523	0.665
April**					
Average	**0.64**	**0.64**	**0.59**	**0.53**	**0.62**

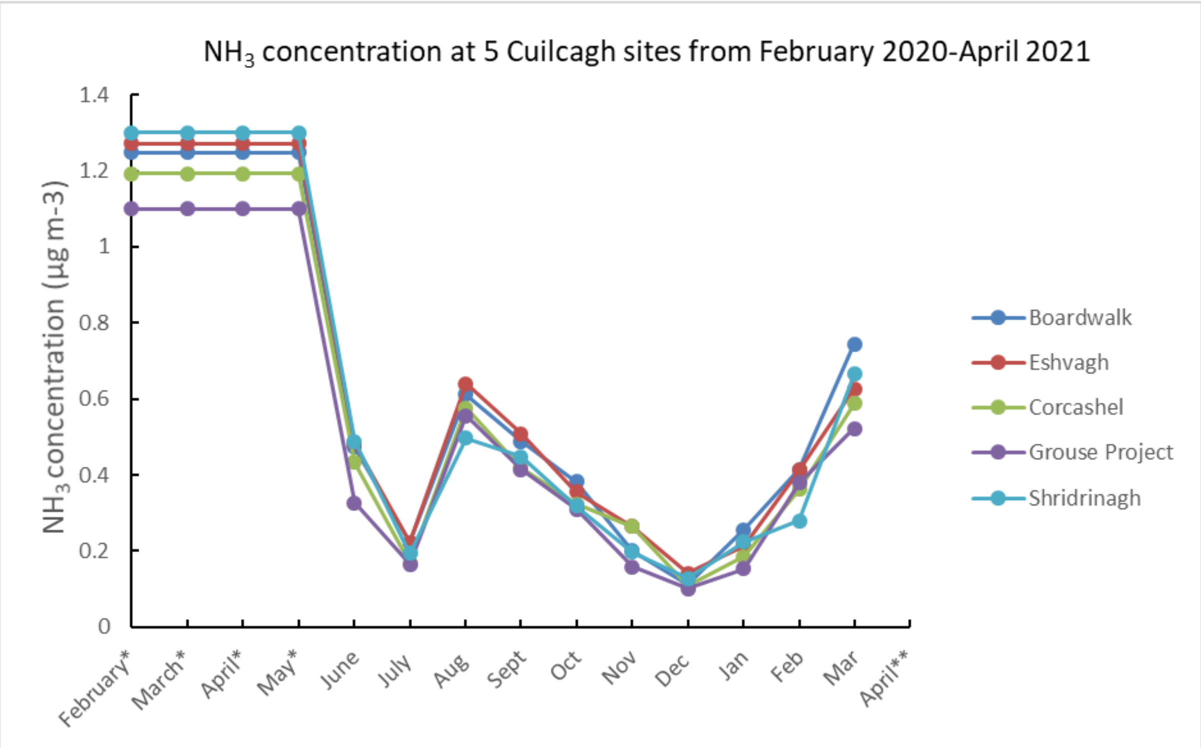

Figure 4: Monthly NH$_3$ concentrations (µg m^{-3}) from February 2020 until April 2021. The concentrations are the average of tri-plicate sampling.
* Due to COVID restrictions it was not possible to change the samples for the first 4 months. ** Samples not returned

After setting up the sites the monitoring sites were not accessible for 4 months due to COVID-19 restrictions and therefore it was not possible to change the samples until June 2021. So samples stayed on for much longer than the usual exposure time of 1 month. For this reason we extended the monitoring period at the end of the project duration by 2 months.

As expected, the NH_3 concentration was the lowest at the Grouse Project (Site 4) with an average concentration of 0.53 $\mu g\ m^{-3}$. Contrary to expectations, the concentrations at Shridrinagh (Site 5) were in the middle, with an average of 0.62 $\mu g\ m^{-3}$. But the concentrations at all 5 sites were more similar than expected. Not only the average concentration over the project-period but also the monthly concentrations were very similar across the 5 monitoring sites.
The annual cycle of ammonia concentrations at each of the sites is as expected for a rural background site, with peaks in spring and autumn, though the COVID pandemic impacts on the monitoring makes this difficult to observe clearly.
However as the monitoring at the Boardwalk site will continue in a follow-up project, this annual cycle will become clearer.

The average NH_3 concentrations for the Cuilcagh sites were between 0.53 and 0.64 NH_3 ($\mu g\ m^{-3}$) and are below the annual, long-term, critical level of to 1 $\mu g\ NH_3\ m^{-3}$ for lichens and bryophytes (apis website) and 3 $\mu g\ NH_3\ m^{-3}$ for higher plants. Based on the condition of the vegetation, especially at Shridinagh (Site 5) much higher NH_3 concentrations had been expected.

3.2 Foliar NH_4-N concentration in vegetation

The foliar NH_4-N (FW) concentrations in *Pleurozium schreberi* were higher than in *Sphagnum fallax* (Table 3 and Figure 5), as expected. The foliar NH_4-N (FW) concentrations in both moss species were higher than expected, given the low atmospheric NH_3 concentrations. For comparison, NH_4-N (FW) concentrations < 1 (μg g-1) FW have been found at sites with NH_3 air concentrations even up to 2 $\mu g\ NH_3\ m^{-3}$. Concentrations of a similar level as found in the Cuilcagh vegetation samples have been found at sites with far higher NH_3 air concentrations of 3-7 $\mu g\ NH_3\ m^{-3}$ (Figure 6, Van Dijk et al 2021). For full details Appendix III: Tables with the calculations of foliar NH_4-N in the vegetation samples from Cuilcagh. As there was already visible damage to the vegetation and the most sensitive species were missing, the relatively high foliar NH_4-N (FW) concentrations were not surprising.

Table 3: NH_4-N (µg g^{-1}) FW concentrations in *Sphagnum fallax* and *Pleurozium schreberi* at the 5 Cuilcagh sites vs. atmospheric NH_3 concentrations.

	NH_3 (µg m^{-3})	**foliage NH_4-N** NH_4-N (µg g^{-1}) FW	
SITENAME		*S. fallax*	*P. schreberi*
Boardwalk	0.64	18.77	22.16
Eshvagh	0.64	11.62	14.16
Corcashel	0.59	10.81	34.47
Grouse Project	0.53	10.34	25.25
Shridrinagh	0.62	8.01	24.55

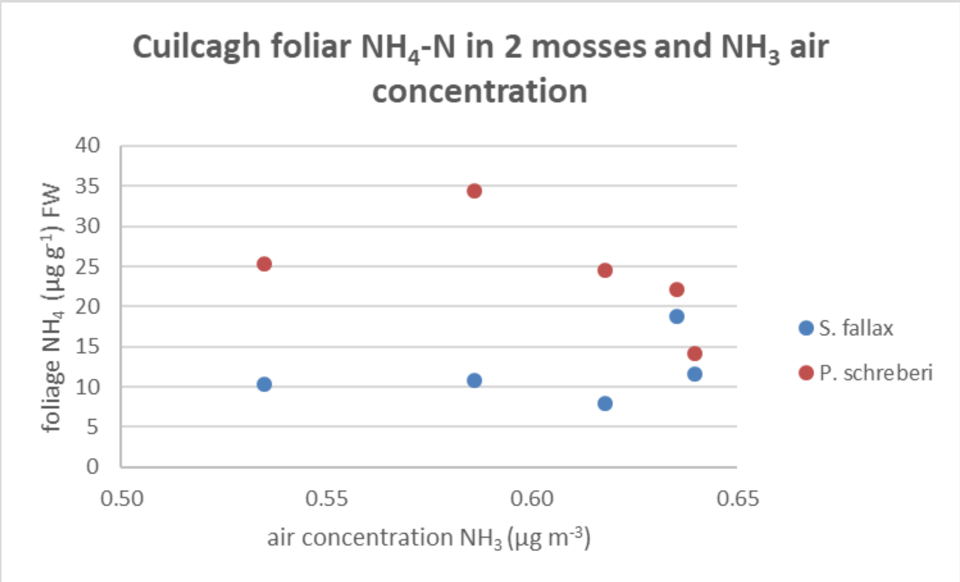

Figure 5: NH_4-N (µg g^{-1}) FW in *Sphagnum fallax* and *Pleurozium schreberi* at the 5 Cuilcagh sites against the average NH_3 concentration.

Ideally a year of NH_3 air concentrations would be collected before taking vegetation samples so that NH_4-N concentrations in the vegetation can be directly associated as an effect of the NH_3 concentrations measured. Unfortunately that was not possible in this short project and the NH_4-N concentrations are related to the measured concentrations (for the project time) assuming the air concentrations are not so different from the year before the samples were taken. Agricultural activities are the main source for the ammonia concentrations and these were, despite the pandemic, pretty much as normal and we had not expected the pandemic to have caused big differences in the measurements.

3.3 Comparison with other sites

Although the foliar ammonium in bryophytes are species/site specific it is still useful to compare the results with results from other sites (Figure 6).

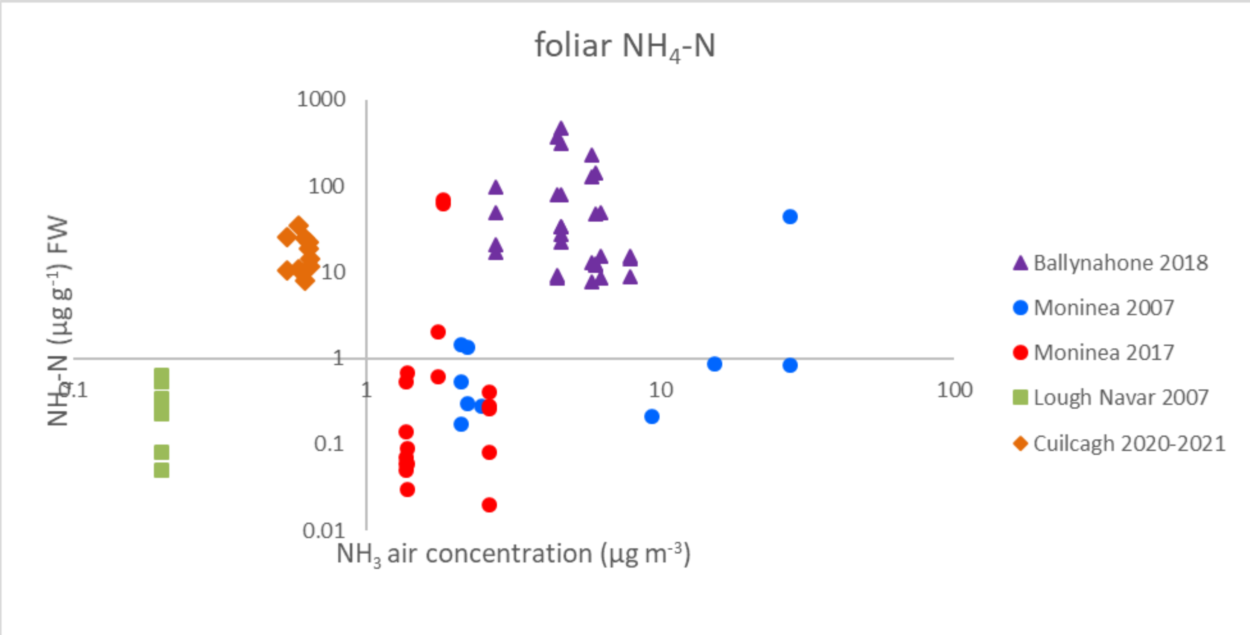

Figure 6: Foliar NH_4-N (µg g^{-1}) FW concentrations in vegetation at Cuilcagh in comparison with other sites. Lough Navar is a clean background site; Ballynahone Bog is a site where the vegetation is in a poor condition due to high NH_3 concentrations and Moninea shows the results before (2007) and after (2017) the closing of a poultry farm.

Figure 6 shows clearly that the foliar content (NH_4-N) at Cuilcagh is relatively high in relation to the NH_3 air concentration and in comparison with other sites. The results from Lough Navar (forested upland area in west Fermanagh), a clean background site are much lower than from the other sites. The foliar content (NH_4-N) of the vegetation samples from Cuilcagh are comparable with the levels found at Ballynahone Bog, which has much higher NH_3 air concentrations (Van Dijk et al 2021; Sutton et al 2011).

In summary, the vegetation was found to be more damaged by atmospheric N input (as shown by the high foliar N concentrations than could be expected based on the relatively low NH_3 concentrations. This is an indication that there are other sources of atmospheric N input at the site. High grazing numbers result in a higher NH_3 air concentration, but grazing densities are low across the Cuilcagh sites. Only at Site 3 Shridrinagh are the grazing numbers slightly higher. This indicates that there is an important other N source. As all these sites are high precipitation sites, it is most likely that this is the N depositing in rain (wet deposition). To test this hypothesis, a wet deposition collector has been placed close to the ALPHA® monitoring site1: Boardwalk in a follow up project. Rain samples are being collected approx. twice per month, with initial results expected in 2022.

4. Conclusions

The average annual concentrations for the study period at the 5 sites are relatively low and vary from 0.53 at the Grouse Project to 0.64 NH_3 (µg m^{-3}) at the Boardwalk and Eshvagh. All sites are below the annual, long-term, critical level of to 1 µg NH_3 m^{-3} for lichens and bryophytes.

The higher than expected foliar NH_4-N (FW) concentrations in *S. fallax* and *P. schreberi* at these low NH_3 concentrations and the absence of very sensitive moss species at most of the monitoring sites, indicate that there is damage from atmospheric N input to the vegetation from a source other than local ammonia emissions. It is most likely that this is nitrogen from further afield depositing in rain (wet deposition), arriving at the site through medium/long-range transport. To study this, a wet deposition collector has been placed close to the ALPHA® monitoring Site1: Boardwalk in a follow-up project and data collection is being continued by Ulster Wildlife.

5. References

http://www.apis.ac.uk/critical-loads-and-critical-levels-guide-data-provided-apis

Leith I.D., van Dijk N., Pitcairn C.E.R., Wolseley P.A., Whitfield C.P., and Sutton M.A. 2005. Biomonitoring methods for assessing the impacts of nitrogen pollution: refinement and testing. JNCC Report 386

M. A. Sutton, I. D. Leith, W. J. Bealey, N. van Dijk and Y. S. Tang. 2011. Moninea Bog - Case study of atmospheric ammonia impacts on a Special Area of Conservation, chapter in Nitrogen Deposition and Natura 2000, Science and practice in Determining Environmental Impacts. 59-71

Tang, Y., Cape, J. and Sutton, M. 2001. Development and types of passive samplers for monitoring atmospheric NO2 and NH3 concentrations', *The Scientific World Journal,* 1, pp. 513-529.

Tang Y.S., Stephens A. and Poskitt J. 2021. UKCEH ALPHA Sampler, User instructions, Issue Number 1.5, UKCEH Protocol

Van Dijk N., Leith I.D., Pitcairn C.E.R. and Sutton M.A. 2009. Soluble ammonium in plants as a bioindicator for atmospheric nitrogen deposition: refinement and testing of a practical method**.** In: Sutton M.A., Baker S.M.H., Reis S.: Atmospheric Ammonia - Detecting emission changes and environmental impacts. Springer Publishers, 281-289

Van Dijk N., Thomas I. N., Iwanicka A. K., Harvey D., Stephens A., Tang Y. S., Sutton M., Dragosits U. 2021. Ballynahone Bog ammonia project, vegetation analysis/bioindicator checks, report to NIEA/DAERA

Appendix I: Data Report

UK Centre for Ecology & Hydrology

Cuilcagh – Data Report
Results
The dataset is provided in a separate CSV file. Measurements represent the average air concentration of NH_3 for the exposure period in µg m^{-3}. The calibrated uptake rate used is provided at the top of the file, and is representative for the Edinburgh Laboratory during 2020/2021.

2020 data have been published on the EIDC, the remaining data will be published in April 2022. The published dataset and supporting documentation can be found here: https://catalogue.ceh.ac.uk/documents/21562c80-96dc-4642-bfcf-285846000ceb

Data Quality
All data have been blank corrected and quality checked. All values measured at a value above the detection limit and within calibration limits. The dataset provided has been flagged in accordance with EMEP flagging (https://projects.nilu.no//ccc/flags/index.html)

The majority of sites had replicates which gave a coefficient of variation of less than 10% when outliers with known issues were removed. This indicates good data quality. Transport blanks measured within acceptable range, demonstrating no/low levels of contamination on transport/storage.

Appendix II: Cuilcagh NH_3 concentrations per site

Site 1: Boardwalk

Month	Date out	Date in	Sampled time (hrs)	Sampled volume (m^3)	measured concentration in extraction solution: sample 1 NH_4 (mg L^{-1})	sample 2 NH_4 (mg L^{-1})	sample 3 NH_4 (mg L^{-1})	mean NH_4 (mg L^{-1})	% CV	lab blank NH_4 (mg L^{-1})	NH_3 estimated (µg m^{-3})	**NH_3 calibrated* (µg m^{-3})**
2020												
February	2020/02/19 12:15:00	2020/06/17 14:24:00	2857.2	12.4	4.545	3.927	3.982	4.151	8.2	0.073	0.931	**1.248**
March												
April												
May												
June	2020/06/17 14:24:00	2020/07/02 13:05:00	358.7	1.6	0.366	0.221	0.199	0.262	34.6	0.068	0.353	**0.473**
July	2020/07/02 13:05:00	2020/08/03 16:45:00	771.7	3.4	0.251	-	0.264	0.257	3.5	0.061	0.166	**0.222**
August	2020/08/03 16:45:00	2020/09/04 13:30:00	764.8	3.3	0.648	0.647	0.599	0.631	4.4	0.097	0.456	**0.611**
September	2020/09/04 13:30:00	2020/10/06 18:30:00	773.0	3.4	0.553	0.509	0.507	0.523	5.0	0.091	0.364	**0.488**
October	2020/10/06 18:30:00	2020/11/03 16:20:00	670.8	2.9	-	0.346	0.337	0.341	1.9	0.048	0.285	**0.382**
November	2020/11/03 16:20:00	2020/12/03 16:40:00	720.3	3.1	0.234	0.215	0.269	0.239	11.4	0.075	0.149	**0.200**
December	2020/12/03 16:40:00	2021/01/13 13:40:00	981.0	4.3	0.207	0.201	0.234	0.214	8.3	0.089	0.083	**0.112**
2021												
January	2021/01/13 13:40:00	2021/02/01 14:24:00	456.7	2.0	0.195	0.253	0.216	0.222	13.2	0.087	0.192	**0.257**
February	2021/02/01 14:24:00	2021/03/01 14:08:00	671.7	2.9	-	0.397	0.393	0.395	0.7	0.076	0.31	**0.415**
March	2021/03/01 14:08:00	2021/04/01 15:38:00	744.5	3.2	0.643	0.734	0.707	0.695	6.8	0.061	0.555	**0.744**
April												**-**

* uptake rate: 0.003241315

Due to covid-19 first batch of samples have been out from February -June 2020

April 2021 samples not returned

- sample missing

Site 2: Eshvagh

Month	Date out	Date in	Sampled time (hrs)	Sampled volume (m^3)	measured concentration in extraction solution: sample 1 NH_4 (mg L^{-1})	sample 2 NH_4 (mg L^{-1})	sample 3 NH_4 (mg L^{-1})	mean NH_4 (mg L^{-1})	% CV	lab blank NH_4 (mg/L^{-1})	NH_3 estimated (µg m^{-3})	**NH_3 calibrated* (µg m^{-3})**
2020												
February	2020/02/19 15:10:00	2020/06/17 11:08:00	2851.0	12.4	4.377	4.173	4.107	4.219	3.3	0.073	0.949	**1.271**
March												
April												
May												
June	2020/06/17 11:08:00	2020/07/01 10:20:00	335.2	1.5	0.312	0.231	0.217	0.254	20.2	0.068	0.361	**0.484**
July	2020/07/01 10:20:00	2020/08/03 11:15:00	792.9	3.4	0.221	0.220	0.347	0.263	27.8	0.061	0.166	**0.222**
August	2020/08/03 11:15:00	2020/09/02 12:07:00	720.9	3.1	0.665	0.608	0.600	0.624	5.6	0.097	0.477	**0.640**
September	2020/09/02 12:07:00	2020/10/06 11:55:00	815.8	3.5	0.631	0.530	0.537	0.566	10.0	0.091	0.380	**0.509**
October	2020/10/06 11:55:00	2020/11/03 12:20:00	673.4	2.9	0.315	0.312	0.339	0.322	4.6	0.048	0.265	**0.356**
November	2020/11/03 12:20:00	2020/12/04 09:20:00	741.0	3.2	0.284	0.275	0.339	0.300	11.6	0.075	0.198	**0.265**
December	2020/12/04 09:20:00	2021/01/13 09:00:00	959.7	4.2	0.28	0.210	0.242	0.244	14.5	0.089	0.106	**0.141**
2021												
January	2021/01/13 09:00:00	2021/02/01 09:56:00	456.9	2.0	0.211	0.192	0.194	0.199	5.3	0.087	0.159	**0.214**
February	2021/02/01 09:56:00	2021/03/01 09:06:00	671.2	2.9	0.399	0.369	0.414	0.394	5.8	0.076	0.309	**0.413**
March	2021/03/01 09:06:00	2021/04/01 12:40:00	746.6	3.2	0.580	0.649	0.559	0.596	7.9	0.061	0.468	**0.627**
April												**-**

* uptake rate: 0.003241315
Due to covid-19 first batch of samples have been out from February -June 2020
April 2021 samples not returned
- sample missing

Site 3: Corcashel

Month	Date out	Date in	Sampled time (hrs)	Sampled volume (m^3)	measured concentration in extraction solution: sample 1 NH_4 (mg L^{-1})	sample 2 NH_4 (mg L^{-1})	sample 3 NH_4 (mg L^{-1})	mean NH_4 (mg L^{-1})	% CV	lab blank NH_4 (mg L^{-1})	NH_3 estimated (µg m^{-3})	**NH_3 calibrated* (µg m^{-3})**
2020												
February	2020/02/20 12:50:00	2020/06/17 10:06:00	2828.3	12.3	3.587	3.883	4.329	3.933	9.5	0.073	0.89	**1.193**
March												
April												
May												
June	2020/06/17 10:06:00	2020/07/01 11:55:00	337.8	1.5	0.247	0.206	0.255	0.236	11.1	0.068	0.323	**0.433**
July	2020/07/01 11:55:00	2020/08/03 12:18:00	792.4	3.4	0.213	0.210	0.221	0.215	2.7	0.061	0.126	**0.169**
August	2020/08/03 12:18:00	2020/09/02 13:05:00	720.8	3.1	0.613	0.563	0.541	0.573	6.4	0.097	0.431	**0.577**
September	2020/09/02 13:05:00	2020/10/06 13:10:00	816.1	3.5	0.508	0.468	0.469	0.482	4.7	0.091	0.312	**0.419**
October	2020/10/06 13:10:00	2020/11/02 16:10:00	652.0	2.8	0.269	0.253	0.347	0.29	17.4	0.048	0.242	**0.324**
November	2020/11/02 16:10:00	2020/12/04 10:03:00	761.9	3.3	0.225	0.300	0.391	0.305	27.2	0.075	0.197	**0.264**
December	2020/12/04 10:03:00	2021/01/13 10:33:00	960.5	4.2	0.226	0.190	0.206	0.207	8.7	0.089	0.081	**0.108**
2021												
January	2021/01/13 10:33:00	2021/02/01 11:12:00	456.7	2.0	0.190	0.156	0.207	0.184	14.2	0.087	0.139	**0.186**
February	2021/02/01 11:12:00	2021/03/01 09:47:00	670.6	2.9	0.360	0.346	0.356	0.354	2.1	0.076	0.270	**0.362**
March	2021/03/01 09:47:00	2021/04/01 13:34:00	746.8	3.2	0.564	0.557	0.57	0.564	1.1	0.061	0.439	**0.588**
April												**-**

* uptake rate: 0.003241315

Due to covid-19 first batch of samples have been out from February -June 2020

April 2021 samples not returned

- sample missing

Site 4: Grouse project

Month	Date out	Date in	Sampled time (hrs)	Sampled volume (m^3)	measured concentration in extraction solution: sample 1 NH_4 (mg L^{-1})	sample 2 NH_4 (mg L^{-1})	sample 3 NH_4 (mg L^{-1})	mean NH_4 (mg L^{-1})	% CV	lab blank NH_4 (mg L^{-1})	NH_3 estimated (µg m^{-3})	**NH_3 calibrated* (µg m^{-3})**
2020												
February	2020/02/20 10:50:00	2020/06/17 16:45:00	2836.9	12.3	3.531	3.709	3.69	3.643	2.7	0.073	0.821	**1.100**
March												
April												
May												
June	2020/06/17 16:45:00	2020/07/01 14:25:00	333.7	1.4	0.197	0.185	0.198	0.193	3.7	0.068	0.244	**0.327**
July	2020/07/01 14:25:00	2020/08/03 14:50:00	792.4	3.4	0.233	0.195	0.207	0.212	9.0	0.061	0.124	**0.166**
August	2020/08/03 14:50:00	2020/09/02 15:45:00	720.9	3.1	-	0.602	0.509	0.555	11.8	0.097	0.415	**0.556**
October	2020/10/06 16:40:00	2020/11/02 13:55:00	646.3	2.8	0.291	0.260	0.284	0.278	5.9	0.048	0.232	**0.311**
September	2020/09/02 15:45:00	2020/10/06 16:40:00	816.9	3.5	0.537	0.465	0.432	0.478	11.3	0.091	0.309	**0.414**
November	2020/11/02 13:55:00	2020/12/04 12:30:00	766.6	3.3	0.221	0.217	0.202	0.213	4.8	0.075	0.118	**0.158**
December	2020/12/04 12:30:00	2021/01/13 11:56:00	959.4	4.2	0.204	0.184	0.211	0.200	7.1	0.089	0.076	**0.101**
2021												
January	2021/01/13 11:56:00	2021/02/01 12:55:00	457.0	2.0	0.150	0.186	0.165	0.167	10.9	0.087	0.114	**0.153**
February	2021/02/01 12:55:00	2021/03/01 11:45:00	670.8	2.9	0.440	0.357	0.306	0.368	18.3	0.076	0.283	**0.380**
March	2021/03/01 11:45:00	2021/04/01 15:45:00	747.0	3.2	0.492	0.519	0.512	0.508	2.7	0.061	0.390	**0.523**
April												-

* uptake rate: 0.003241315

Due to covid-19 first batch of samples have been out from February -June 2020

April 2021 samples not returned

- sample missing

Site 5: Shridrinagh

Month	Date out	Date in	Sampled time (hrs)	Sampled volume (m^3)	measured concentration in extraction solution: sample 1 NH_4 (mg L^{-1})	sample 2 NH_4 (mg L^{-1})	sample 3 NH_4 (mg L^{-1})	mean NH_4 (mg L^{-1})	% CV	lab blank NH_4 (mg L^{-1})	NH_3 estimated (µg m^{-3})	**NH_3 calibrated* (µg m^{-3})**
2020												
February	2020/02/20 10:50:00	2020/06/17 12:09:00	2832.3	12.3	4.119	4.105	4.639	4.288	7.1	0.073	0.971	**1.301**
March												
April												
May												
June	2020/06/17 12:09:00	2020/07/01 13:25:00	337.3	1.5	0.235	0.292	0.244	0.257	11.8	0.068	0.365	**0.489**
July	2020/07/01 13:25:00	2020/08/03 13:35:00	792.2	3.4	0.255	0.216	0.242	0.237	8.3	0.061	0.145	**0.194**
August	2020/08/03 13:35:00	2020/09/02 14:40:00	721.1	3.1	0.518	0.471	0.531	0.507	6.3	0.097	0.371	**0.497**
September	2020/09/02 14:40:00	2020/10/06 15:05:00	816.4	3.5	0.535	0.503	0.492	0.510	4.3	0.091	0.335	**0.449**
October	2020/10/06 15:05:00	2020/11/02 15:00:00	648.9	2.8	0.284	0.291	0.28	0.285	1.8	0.048	0.238	**0.319**
November	2020/11/02 15:00:00	2020/12/04 11:17:00	764.3	3.3	0.228	0.269	0.247	0.248	8.3	0.075	0.148	**0.198**
December	2020/12/04 11:17:00	2021/01/13 09:56:00	958.7	4.2	0.243	0.252	0.197	0.231	12.9	0.089	0.097	**0.129**
2021												
January	2021/01/13 09:56:00	2021/02/01 11:59:00	458.1	2.0	0.221	0.172	0.222	0.205	13.9	0.087	0.168	**0.225**
February	2021/02/01 11:59:00	2021/03/01 11:02:00	671.1	2.9	0.293	0.297	0.284	0.291	2.3	0.076	0.209	**0.280**
March	2021/03/01 11:02:00	2021/04/01 14:39:00	746.6	3.2	0.636	0.564	0.687	0.629	9.8	0.061	0.496	**0.665**
April												-

* uptake rate: 0.003241315
Due to covid-19 first batch of samples have been out from February -June 2020
April 2021 samples not returned
- sample missing

Appendix III: Tables with the calculations of foliar NH_4-N in the vegetation samples from Cuilcagh

								based on **fresh** weight	based on **dry** weight
site name	species	replicate	frozen weight (g)	dry weight (g)	extraction volume (ml)	**N** (mg L^{-1})	**blanks** (mg L^{-1})	**NH_4-N foliage** **NH_4-N(μg g^{-1})**	**NH_4-N foliage** **NH_4-N(μg g^{-1})**
Boardwalk	*Sphagnum fallax*	A	2.0332	0.3057	20	1.775	0.010	19.127	117.238
Boardwalk	*Sphagnum fallax*	B	2.1771	0.3100	20	1.817	0.010	18.407	118.388
Eshvagh	*Sphagnum fallax*	A	2.0606	0.2629	20	1.158	0.010	12.290	88.482
Eshvagh	*Sphagnum fallax*	B	2.3114	0.2880	20	1.145	0.010	10.956	79.954
Corcashel	*Sphagnum fallax*	A	2.1694	0.2807	20	1.146	0.010	11.609	82.077
Corcashel	*Sphagnum fallax*	B	2.0499	0.2507	20	0.941	0.010	10.014	75.203
Grouse Project	*Sphagnum fallax*	A	1.9913	0.2780	20	1.009	0.010	11.033	72.870
Grouse Project	*Sphagnum fallax*	B	2.0554	0.2881	20	0.909	0.010	9.647	63.308
Shridrinagh	*Sphagnum fallax*	A	2.0986	0.2878	20	0.732	0.010	7.603	50.896
Shridrinagh	*Sphagnum fallax*	B	2.0038	0.2575	20	0.777	0.010	8.422	60.340
Boardwalk	*Pleurozium schreberi*	A	1.9810	0.4184	20	2.007	0.010	22.159	97.456
Boardwalk	*Pleurozium schreberi*	B	NA	NA					
Eshvagh	*Pleurozium schreberi*	A	1.9829	0.4436	20	1.405	0.010	15.465	64.289
Eshvagh	*Pleurozium schreberi*	B	2.0040	0.4507	20	1.181	0.010	12.858	53.135
Corcashel	*Pleurozium schreberi*	A	2.0410	0.4680	20	3.666	0.010	39.482	159.895
Corcashel	*Pleurozium schreberi*	B	1.9820	0.4304	20	2.666	0.010	29.457	126.076
Grouse Project	*Pleurozium schreberi*	A	2.0516	0.4657	20	1.838	0.010	19.648	80.333
Grouse Project	*Pleurozium schreberi*	B	2.0389	0.5212	20	2.864	0.010	30.849	112.371
Shridrinagh	*Pleurozium schreberi*	A	2.0653	0.4455	20	2.444	0.010	26.004	111.704
Shridrinagh	*Pleurozium schreberi*	B	2.0207	0.4304	20	2.129	0.010	23.092	100.586

based on **fresh** weight		NH$_4$-N foliage NH$_4$-N(μg g^{-1})				
site number	Site name	species	replicate A	B	average	STDEV
1	Boardwalk	*Sphagnum fallax*	19.127	18.407	**18.767**	0.5
2	Eshvagh	*Sphagnum fallax*	12.290	10.956	**11.623**	0.9
3	Corcashel	*Sphagnum fallax*	11.609	10.014	**10.812**	1.1
4	Grouse Project	*Sphagnum fallax*	11.033	9.647	**10.340**	1.0
5	Shridrinagh	*Sphagnum fallax*	7.603	8.422	**8.013**	0.6
1	Boardwalk	*Pleurozium schreberi*	22.159	*	**22.159**	
2	Eshvagh	*Pleurozium schreberi*	15.465	12.858	**14.161**	1.8
3	Corcashel	*Pleurozium schreberi*	39.482	29.457	**34.469**	7.1
4	Grouse Project	*Pleurozium schreberi*	19.648	30.849	**25.249**	7.9
5	Shridrinagh	*Pleurozium schreberi*	26.004	23.092	**24.548**	2.1

based on **dry** weight		NH$_4$-N foliage NH$_4$-N(μg g^{-1})				
site number	Site name	species	replicate A	B	average	STDEV
1	Boardwalk	*Sphagnum fallax*	117.238	118.388	**117.813**	0.8
2	Eshvagh	*Sphagnum fallax*	88.482	79.954	**84.218**	6.0
3	Corcashel	*Sphagnum fallax*	82.077	75.203	**78.640**	4.9
4	Grouse Project	*Sphagnum fallax*	72.870	63.308	**68.089**	6.8
5	Shridrinagh	*Sphagnum fallax*	50.896	60.340	**55.618**	6.7
1	Boardwalk	*Pleurozium schreberi*	97.456	*	**97.456**	
2	Eshvagh	*Pleurozium schreberi*	64.289	53.135	**58.712**	7.9
3	Corcashel	*Pleurozium schreberi*	159.895	126.076	**142.986**	23.9
4	Grouse Project	*Pleurozium schreberi*	80.333	112.371	**96.352**	22.7
5	Shridrinagh	*Pleurozium schreberi*	111.704	100.586	**106.145**	7.9

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