Comments to Referees

Referee 1

The lack of data on moisture availability to key species is a major concern
to me. Judging from the vegetation it seems a rather dry example of bog vegetation.

Whim bog is not a pristine bog, but the present vegetation is commensurate with UK bog vegetation M19 NVC for UK, and is very similar to that highlighted in the majority of N manipulation studies on peatlands (Lund et al (Sweden) and the Mer Bleue site in Canada), so it is by no means atypical. Continuous water table measurements at the site since (2003) indicate means of (24, drought yr), 12, 12, 9, 5, 10, 6 cm below the soil surface, upto 2010, so relatively wet for most of the year. We agree that Whim does not exemplify bog vegetation where hummocks, e.g. with *S. capillifolium* and *Calluna,* are much less common, cf N Scandinavia. Significant areas of Whim do have the watertable at the surface and here *S. magellanicum, S. fallax,* and *S. cuspidatum* grow. We have amended the description of Whim vegetation to clarify that we are working on a bog /peatland dominated by hummocks with dwarf shrubs and hummock forming *Sphagnum*.

Conclusions based on bulk density data are questionable…

We realise that there are issues concerning BD in peats and our interpretation: we have re examined the literature on bulk density sampling and interpretation and the papers of Johnathon Price, but don't feel such papers have addressed situations such as the one we describe. We feel the major area of lack of clarity relates to what we call peat and thus what is included in the sample. We operated a strict sampling protocol whereby only the humified material was sampled on all plots thus we believe our samples are comparable and the differences real…that is as much as we can comment in reply. Thus we have left the data in but added a caveat in the discussion.

'When the peatland plant community remains intact and vital the additional N appears to remain in the peat and vegetation (Fig.7) with negligible leakage. In this study the accumulation of N in the peat partly reflects the increase in bulk density, a consequence of the loss of easily decomposed material at the surface leading to a compression of the peat (Johnson et al., 1990), increases in %N in the peat were quite variable across treatment plots. A much larger more extensive sampling of the plots, that takes account of the different proportions of plant functional groups would be required to detect significant changes in peat N'.

Thirdly, I was
wondering why nitrate and ammonium concentrations were substantially higher in the amm-treatment. The soil moisture N-concentration exceeded data from earlier studies applying similar N-loads. To what extend are loads comparable?

Differences in soil N availability when N was added as ammonia rather than in wet deposition as nitrate or ammonium have been addressed in response to referee 2 ('At Whim leakage of N as the greenhouse gas N_2O depended on the form of N. In response to high NH_3 concentrations / deposition the vegetation changed dramatically leading to a domino effect: *Calluna* was killed along with *S. capillifolium*, hypnaceous mosses and

Cladonia spp so that for a couple of years the peat was exposed before *E. vaginatum* expanded to dominate the area. This meant the floristic N sink was much smaller and as a result both KCl extractable NH_4^+ and concentrations of soil water NO_3^- rose significantly, the higher pH associated with NH_3 deposition probably accelerating nitrification rates').

We believe that the wet and dry N loads are comparable: having had a PhD student engaged looking at ammonia deposition to whim vegetation and based our calculations on the observations from this flux chamber work involving samples of whim vegetation undertaken as a PhD and then accepted as 5 peer reviewed papers, as explained in Sheppard et al 2011. We have not, as such, measured nitrification rates in the field to support our view that the increase in pH of approximately one pH unit to circa 4.8 to 5 with ammonia has enhanced nitrification.

The manuscript would benefit from a careful look through. The discussion is rather lengthy when touching the few N-emission data. Methods are not complete. Graphs are a bit rough.

We have tidied up the graphs and figure legends as requested and redrawn the figures as suggested and the manuscript generally and included more information in the methods section.

The discussion is rather lengthy when touching the few N-emission data….

While we appreciate there are not so many measurements of N_2O we feel the discussion does put those data in context and given that this paper addresses biogeochemical cycling rather than focussing just on species responses, which have been previously described we prefer to keep the balance as it is. Until all the data is available and peer reviewed we would prefer not to directly address the question are N deposition rates overrated. We feel we have provided valuable data but are also very aware that N deposition interacts very strongly with climate and feel we need to investigate this further first….see also later.

Minor remarks:
p.8144 L18 – sentence not clear, awkward question (manuscript is later on more concerned about N-forms at high deposition rates rather than a neat gradient)
Rewritten as …and reference to dose omitted. 'However, we do not know to what extent the form of N in deposition influences such processes'.

p.8148 L26 – Additional text has been added,
For how many days were syringes left in the field? One month as stated.
How was the oxidation of ammonium to nitrate in the syringe prevented when samples were left out for more than 2 days?
We cant exclude the possibility of N transformations in the syringes, but the small filter size and covering the syringes with a large clod of peat to exclude light and buffer temperature fluctuations, while they are left out helps restrict this possibility.

p.8149 L8 – Information on soil extractions are missing. Most KCl methods are inferior to methods using Strontium chloride or Barium chloride when estimating total cations attach to (peat) soils.
We did use KCl as our extractant for mineral N as it is a standard method (DL Rowell Soil Science Methods and Applications). We were not using this extract to measure cations. The full method has been added.

L17 – 8 times per year or in two years'time?

Inserted ‘both’ before the years

p.8151 L1 - interesting finding that Sphagnum capillifolium capitula contained > 2% N in the Nitrate treatment while showing rather small differences in cover compared to the control. This finding is in contrast to many N-addition experiments in European bogs.

The 2% N was found in the ammonium not the nitrate treatment…there was no *Sphagnum* in the ammonia treatment therefore there is no %N reported for this treatment. We have regularly measured higher %N in *S. capillifolium* than previously reported so we will mention this in the discussion.
Probably give it more attention as older experiments mostly used ammonium and nitrate combined (even in combination with sulphur)

We are now aware of up to 30% differences in %N depending on which pigmented form of S. capillifolium is sampled, so would prefer not to develop a discussion on %N in Sphagnum in this paper.

p.8151 L15 - bulk density of surface peats is an important variable for N-storage but difficult to draw conclusions from as it ingrates time-dependent processes. Bulk density is driven by litter burial and compaction following changes in hydraulic pressure and peat decomposition (see literature of Jonathan Price and others)….see earlier reply.

p.8153 L4 – Why would the authors expect an increase in vegetation cover at Whim bog with increasing N deposition: even in the controls N-availability is supposed to be rather higher due to desiccation of the surface peat (drainage) and N-deposition rates of some 10 kg N/ha/yr.
We have no data or evidence to support the view that the surface peat is oxidising, the site was drained over 100 years ago but not since except in the adjacent area over 200 m from the site.
p.8154 L5-18 – The assumption that bog vegetation is a priori N-limited seems old-fashioned to me. There’s growing evidence in the global literature that P-limitation is common not only at increased N-deposition rates > 10 kg N/ha/yr but also at rates as low as 2 kg N/ha/yr. I would strongly recommend to include this aspect in the discussion/introduction.

We concur with the comment about P limitation and are currently developing this in another paper, but it is now addressed in the discussion.
‘One reason why N retention has not been effective at Whim bog could be linked to P availability. The availability of N is not the only nutrient that can affect growth in semi-natural systems and at Whim phosphorus (P) availability and possibly potassium (K) influenced the N response, at least in the early years (Carfrae et al., 2007). When PK was added in a 1:14 ratio of N:P there was indirect evidence of an improvement in *Sphagnum* growth and a reduction in %N. Measurement of shoot elongation and %N in 2008 (Kivimaki, 2012) indicated the PK effects on *S. capillifolium* were sustained and there was no interaction with N form. As found in previous studies co-limitation by P / K will reduce the effectiveness of *Sphagnum* and most likely other species present e.g. *Calluna* to retain N (Pilkington et al., 2007)’.

There was some increase in growth / cover, particularly evident from the increase in litter cover in permanent quadrats over the years in the Nred plots, (Sheppard et al., 2011), but it only reached significance once. Co-limitation by P availability may also be contributing to *Calluna*s’ muted N response, in the presence of PK shoot extension was significantly albeit only by 7 % increased, although not in every year. Although, Rowe et al., (2008) showed that N deposition led to higher phosphatase activity and thus could improve the P supply and acquisition.

p.8159 L9 – also toxic to other bryophytes that …….. NH_3 is toxic to this keystone moss and other hypnaceous mosses which contribute to N immobilisation
L13 –spelling should read bypasses ….corrected thankyou
L18 – I can only partly agree with this conclusion. The
data presented here showed a surprisingly low decrease in the cover of Sphagnum mosses – something like 30% to 20% of total cover. If 30% per cent is supposed to be 'healthy, vital : : :' why should 20% already be the dusk of carbon sequestration through Sphagnum mosses? Dry spells will probably impose an evenly high or higher stress on the mosses compared N-deposition. I'd like to see more thoughts in the paper questioning whether N-deposition rates are 'overrated' or likely to be overruled by N-form.

We agree with this comment and have changed the wording accordingly, so the statement is more appropriate for the data presented, the general trend is down and we feel that all the signs are for detrimental effects all be they will be slow to occur, but agree that at the present time the data indicate a downward trend, rather than eradication.
The focus of this paper was the coupling between vegetation and biogeochemical cycling…..we would prefer to address the issue of whether N deposition is overrated and make comparisons with the wider literature covering surveys separately, once we have published more of this large dataset and make those topics the focus a paper.

Comment [MSOffice1]: Remember form to address

Figures: Fig. 1 – no error bars? These have been added as also an explanation of the sampling along the ammonia transect ….Cover and sampling along the NH_3 transect was measured in two 2 m by 1 m quadrats positioned parallel to the release pipes, one on either side of the central board walk that splits the transect. Sample values represent the mean of these two sampling points where at 4 subsamples were bulked to provide the sample for analysis.

Fig. 2 – tissue samples of Calluna before it disappeared from the amm-treatment?
We have amended the figure caption to remove confusion but we have not presented values if the vegetation type was not present ie had no cover value in Fig 1.

Fig. 3 – Graphs are difficult to read – make additional
Y-axis for the amm treatment. Or switch to log-scale. It should read amm rather than NH3 in the legend. Last sentence is a bit misleading sounds like 56 plots in the amm treatment
Graphs redrawn on log scale, figure caption amended as recommended by omitting 56.
Fig. 4 – lower panel: Large error bars in water extractions raises concerns.
What was the background NO3-concentration of the water used for extractions?
Deionised water was used but we have omitted the data and redrawn the graph

Fig. 5 – How many samples taken to estimate bulk density of the amm-treatment? The graph doesn't show an error bar. As mentioned earlier, it's not that straightforward to draw conclusions from the upper 10 cm of peat as the base of these samples can vary greatly in age. Plots with reasonably high peat formation rates will reveal much younger compared to plots where vegetation forms peat at low rates.
Two soil samples were taken from the NH_3 transect, one on each side. All samples for bulk density were taken from underneath a thin layer of hypnaceous moss, and the surface ie 0 cm was taken at the point where the peat soil started. We accept that the methodology is open to comment but all plots were treated in the same way so we would expect differences to be treatment related

Referee 2

We thank the referee for identifying and acknowledging the strengths of this paper.

1. As requested we have included a summary of previously published results and how they differ from this paper.

The vegetation responses in permanent quadrats to different loads of reduced N as NH_3 or NH_4^+ were reported in detail for the sampling period 2002-2009 (Sheppard et al., 2011). This paper demonstrated conclusively that NH_3 reduces the cover of sensitive species at much lower N doses than NH_4^+ and that the threshold concentration for detrimental effects decreases with the length of exposure. Photographs of the visible damage associated with the reductions in cover, and the interactions with biotic and abiotic stress are described there and in Sheppard et al. (2008). In this paper we examine links between species change and biogeochemical cycling based on the whole plot vegetation cover after 7 years of N inputs.

2. Text rewritten to improve clarity re replicate number

Inserted (ie. 4 replicate plots per treatment)

3. Inserted how the Ev was measured

the area of the Eriophorum clump was measured by placing a wire grid over the top

4. 2.3. p 8148, lines 17-18. What does “proportioned depending on the depth of the hummock” mean. Not quite clear.

Clarified by rewriting:The N concentration was measured in both the capitula and the ‘brown’ stems. The relative weights of capitulum and stem were estimated from 10 destructive harvests off plot for a range of hummock depths and this was used together with the respective %N to estimate the g N m^2.

5. 2.3. p 8149, lines 8-9. Were the static chambers inserted beforehand and the system allowed to stabilize before the sampling?

The static chambers were inserted in 2006, several years before measurements started… adjusted text to read, In 2006, chambers

6. 3.1. The cover of several species declined. Did you make observations on the visible injuries preceding the death of the plants?

Comprehensive and photographic descriptions of visible damage were given in Sheppard et al 2011 where they formed a pertinent part of the results, so we made the decision to leave them out of this paper where the focus is on the biogeochemical cycling.

7. 4.2. p 8154, line 16. “accumulation of potentially toxic NH4+ ions”. It would be nice to know something about the mechanisms behind the toxicity. A short addition of this, if possible.

These are described in Krupa et al 2003 and this reference and the following text have been inserted Krupa SV (2003). Effects of atmospheric ammonia (NH3) on terrestrial vegetation: a review. Environmental Pollution, 12, 179–221.

Mechanisms behind NH_4^+ toxicity are described in detail by Solga (2003) and at the cellular level revolve around cell membranes. Ammonium ions function as an electron acceptor, enabling them to uncouple electron transport along membranes and also attack membrane lipids, disabling their functionality.

8. 4.3. p8156, lines 3-5. The first sentence of the paragraph is somewhat confusing. I do not quite get the message , and suggest rephrasing this.
we agree and this has been rephrased

At Whim leakage of N as the greenhouse gas N_2O depended on the form of N. In response to high NH_3 concentrations / deposition the vegetation changed dramatically leading to a domino effect: *Calluna* was killed along with *S. capillifolium*, hypnaceous mosses and *Cladonia* spp so that for a couple of years the peat was exposed before *E. vaginatum* expanded to dominate the area. This meant the floristic N sink was much smaller and as a result both KCl extractable NH_4^+ and concentrations of soil water NO_3^- rose significantly, the higher pH associated with NH_3 deposition probably accelerating nitrification rates.

8. 4.3. p 8157, line 1. I suggest term "calculations" is missing after emissions.
Replaced with …….Values for N_2O emissions from Whim bog

9. Fig. 2. "slime" is mentioned in the fig and the caption. What does it mean?
Defined in figure caption as (senescing lower plant biomass).

10. Fig. 5.
In the figure caption add the explanation of bars (%N?) and small squares (BD?
Done **Fig. 5.** Percentage of N (dry wt), the bars, (+/- st err) in the 0-10 cm peat from the control (no added N) and N treated (oxidised (Nox), reduced (Nred) and ammonia (amm)) plots (~56 kg N $ha^{-1}y^{-1}$) at Whim bog in 2009 (November) and on the right hand axis, the bulk density (BD), indicated by small squares within the bars.