

1 **Reviewer 1 comments and response**

2 The manuscript by Walker et al. presents results from a study investigating atmospheric
3 deposition of reactive nitrogen to a deciduous forest at the USDA Forest Service Coweeta
4 Hydrologic Laboratory in the southern Appalachian Mountains. The authors use several well-
5 established measurement methods to differentiate between oxidized and reduced as well as
6 organic and inorganic compounds found in wet and dry deposition. Finally, they apply a bi-
7 directional resistance-based model driven with the observed measurements of Nr air
8 concentrations, micrometeorology, canopy structure, and biogeochemical parameters to present
9 the full reactive nitrogen budget for the site.

10 While the character of the paper is a report-style compilation of results from a multitude of
11 methods rather than following a clear scientific question, the authors do a great job in thoroughly
12 describing the complexity of reactive nitrogen field investigations and long-term observation.
13 Though continuous eddy-covariance observations are not included, the study represents the state-
14 of-the-art in Nr monitoring and data interpretation. I particularly appreciate the inclusion of field
15 investigations of the ammonia emission potential of green and senescent leaves as well as from
16 litter, which is crucial for model parameterization and rarely conducted. The results are put into a
17 broader context and discussed with regard to air quality regulations in the past, e.g. reduction in
18 oxidized N is now clearly visible. Method uncertainties are sufficiently considered and
19 presented.

20 The text is very well written and easy to follow. Figures are clear and easy to grasp. The
21 supplemental material is useful and the selection of graphs and tables that were put into this
22 section is good. This is the most comprehensive single-site study I am aware of and definitely
23 deserves publication.

24 I only have a few, rather minor, points that should be considered before final presentation in the
25 BG journal:

26 **Response:** We sincerely thank the reviewer for their comments and questions. We have
27 addressed each in detail below.

28 **Comment:** With regard to Section 2.2.7, how exactly were the NH₃ data from hourly
29 measurements used to impose diurnal variability on the biweekly data to be used as hourly input
30 for the model? It is stated in line 393 that continuous NH₃ concentrations were only measured
31 during the last two intensives (in spring and summer, I guess?). The diurnal variability is known
32 to be driven by temperature, humidity, light availability, phenology, etc., how was the amplitude
33 of the variability from these two campaigns transferred to the other – probably much cooler –
34 seasons?

35 **Response:** The reviewer is correct that continuous hourly measurements were only conducted
36 during the last two intensives. To account for diurnal variability in the NH₃ air concentration,
37 the diel concentration pattern determined during the spring and summer intensives
38 (Supplemental Figure S7) was imposed on the bi-weekly AMoN NH₃ concentration. First, the
39 hourly profile of NH₃ concentrations was normalized by the corresponding overall mean

40 concentration to produce a normalized mean diel concentration profile. This profile was then
41 applied to each biweekly AMoN air concentration, temporally scaling the NH₃ concentration by
42 time of day while maintaining the measured biweekly AMoN concentration. In this way, the
43 hourly time series derived for the entire year from AMoN measurements displays the diel
44 variability observed during the spring and summer.

45 The reviewer is correct, the amplitude of the diel concentration profile would be expected to
46 change throughout the year in response to a number of factors, e.g., temperature, local NH₃
47 emissions, boundary layer dynamics, biogeochemistry. Our approach does not incorporate the
48 seasonality that may be observed in the diel profile for winter and fall. However, while the
49 amplitude of the diel cycle may differ from our observations during these seasons, the
50 seasonality of the air concentration on a longer averaging period (i.e., two weeks) is reflected in
51 the AMoN concentrations. An alternative approach that could be employed in the future would
52 be to derive diel profiles from a chemical transport model at shorter than seasonal time scales,
53 perhaps monthly, to scale the AMoN measurement to the hourly time scale for flux modeling.

54 **Comment:** The method section is very informative, but quite long. I'm wondering whether it
55 would make sense to put all detailed descriptions from 2.2.1 up to 2.2.5 into the supplement, just
56 adding a few sentences to 2.2 what has been done and referring to the respective part in the
57 Supplemental Material. It's not a must, but would significantly reduce length and better highlight
58 the findings given the potential readership of people who work in conservation and are likely
59 more interested in the results and their interpretation than in every technical detail of the
60 methodology.

61 **Response:** We appreciate the reviewer's comment and admittedly it was difficult to decide how
62 much detail on methods to include in the primary text as opposed to supplemental. Ultimately,
63 we felt that the methods themselves, and particularly the combination thereof to assess the
64 deposition budget, were worth describing in the main text along with the results.

65 Other:

66 **Comment:** Introduction: I suggest adding information on measurement period, length, etc.

67 **Response:** This information will be added.

68 **Comment:** Line 41-42: "many areas" and "some regions", please specify where, e.g. near
69 hotspots of animal husbandry, chemical industry, etc.

70 **Response:** Additional detail will be added.

71 **Comment:** Line 153: Is 8 m the correct height? What was the reason for this height?

72 **Response:** Yes, 8 m is correct. This was the height of a permanent tower immediately adjacent
73 to the shelter housing the TD-PC-CL instrument. The tower was used opportunistically and 8 m
74 happened to be the maximum height. Reviewer 2 also asked about the choice of measurement
75 heights and corresponding treatment of measurements at different heights for flux modeling. As

76 discussed in the response to reviewer 2, we made no correction for differing measurement
77 heights and will clarify that point and limitation in the revised text.

78 **Comment:** Line 170: What was the selection criteria for the two respective heights?

79 **Response:** In this case, the heights were chosen to maximize the separation between sampling
80 boxes to maximize the concentration gradient. 34 m is just above the top of the canopy and 37.5
81 m and 43.5 m were the total height of the tower in 2015 and 2016, respectively. Ultimately, the
82 MARGA data were not used for gradient flux calculations because colocation experiments to
83 remove systematic bias between the sample boxes were not successful. As described in the
84 primary text, gradient fluxes were instead calculating using measurements from the time-
85 integrated denuder measurements.

86 **Comment:** Line 178: “to the analytical box for analysis Ion Chromatography (IC)”, is there a
87 word missing?

88 **Response:** Yes, this will be corrected.

89 **Comment:** Line 270: Check for consistency in unit notation: “g⁻¹ tissue” vs. “kg tissue⁻¹”

90 **Response:** Thank you for pointing out this inconsistency. We will make the correction here and
91 check throughout.

92 **Comment:** Line 312: Delete “is R_a” after “z₀”

93 **Response:** OK

94 **Comment:** Line 449: Is RH defined before?

95 **Response:** RH will be defined at line 236 in the revised text.

96 **Comment:** Line 505-506: Do two decimal places reflect the measurement accuracy?

97 **Response:** Two decimal places are appropriate for the corresponding detection limits (0.018 –
98 0.038 ppb).

99 **Comment:** Line 605-606: 61.4% wet plus 38.7% dry deposition equals 100.1%, check rounding.

100 **Response:** Thank you for point this out. Rounding will be checked here and throughout.

101 **Comment:** Line 617: Can a bit more explanation given why stomatal fluxes are so low
102 compared to cuticular fluxes?

103 **Response:** We will add more detail to the explanation of the low stomatal fluxes compared to
104 the cuticular flux. First, the stomatal resistance is generally larger than the cuticular resistance
105 even during the summer when the stomatal resistance reaches a minimum. Second, the gradients

106 that drive the leaf-level stomatal (F_s) and cuticular (F_{cut}) fluxes can be defined as $X_s - X_l$ and $X_{cut} -$
107 X_l , respectively. X_s and X_{cut} are the stomatal and cuticular compensation points, respectively,
108 and X_l is the concentration of NH_3 above the leaf. In the current model formulation X_{cut} is zero
109 and X_s is non-zero and a function of the stomatal emission potential and temperature. Thus, the
110 concentration gradient is always larger for the cuticular versus the stomatal pathway. Together
111 the larger stomatal resistance and smaller concentration gradient ($X_s - X_l$) result in $F_s < F_{cut}$.

112 **Comment:** Line 708: Why would the aerodynamic resistance become zero at steep forested
113 slopes? R_a is turbulence and wind speed driven, so why would it approach zero?

114 **Response:** Over flat homogeneous terrain, vertical exchange between the atmosphere and
115 vegetation is driven by vertical turbulent diffusion. In the traditional resistance analogy, the
116 resistance to turbulent transfer is referred to as the aerodynamic resistance (R_a). Hicks (2008)
117 describes an extreme example in which horizontal flow approaching a steep slope penetrates the
118 canopy. In this example, the transfer of material (deposition) to the canopy elements becomes
119 dominated by horizontal advection and filtration rather than vertical diffusion. Thus, this
120 situation can be described as analogous to R_a tending to zero, i.e., no aerodynamic resistance to
121 transfer.

122 **References**

123 Hicks, B.B., 2008. On estimating dry deposition rates in complex terrain. *Journal of Applied*
124 *Meteorology and Climatology*, 47, 1651 – 1658.

125

126 **Reviewer 2 comments and response**

127 Reviewer's comments on Biogeosciences manuscript "Atmospheric Deposition of Reactive
128 Nitrogen to a Deciduous Forest in the Southern Appalachian Mountains" by J.T. Walker

129 General Comments

130 This manuscript describes the atmospheric reactive nitrogen (Nr) deposition budget over a
131 deciduous forest in the Southern Appalachian Mountains. Extensive measurements of the wet
132 and dry deposition components of total deposition of inorganic and organic, reduced and
133 oxidized, gas- and aerosol-phase Nr, are reported for the years 2015-2016, when intensive
134 measurement campaigns were conducted at a forest site in Coweeta Basin as part of the SANDS
135 programme.

136 Wet deposition was measured in straightforward manner by precipitation collectors, while dry
137 deposition was mostly modelled from measured air concentrations and surface-atmosphere
138 exchange (inferential) modelling. Some aerodynamic gradient-flux measurements were made for
139 gases and aerosols over a limited period of time, providing measured reference points to assess
140 the performance of the surface-atmosphere exchange model.

141 The detailed, speciated, multi-season, multi-site measurements of most of the dominant and also
142 less documented (e.g. organic) forms of Nr concentrations in air and water offer a rare,
143 measurement-based glimpse into the diversity of all Nr forms contributing to total Nr deposition
144 over a US forest, and into the technical challenges and solutions implemented to close the
145 deposition budget.

146 The data from the 2015-2016 SANDS intensive campaigns are examined in the light of multi-
147 year or multi-decadal observation datasets from CASTNET, AMoN, NADP and EPA
148 measurement networks, showing the decreases observed in total Nr deposition to the site over the
149 last 3-4 decades (mostly from a long-term reduction in NO_x emissions), but highlighting the
150 increasing importance of reduced nitrogen in total deposition and the continued exceedance of
151 critical loads for this ecosystem. The paper is therefore very well suited for the readership and
152 scope of Biogeosciences.

153 The manuscript presents a very detailed and clear description of the measurement methods used
154 in the extensive data collection, and assimilation by inferential modelling, which I find very
155 useful for this type of paper, where the objective and scope include a thorough methodological
156 component to document the manifold aspects required to compute a comprehensive Nr
157 deposition budget. Such methodological aspects deserve not to be trivialized and glossed over,
158 and will be useful to other researchers in this field, confronted by the complexities of total Nr
159 deposition budgeting.

160 The paper is very well written, and I have only very few and minor comments before
161 recommending eventual publication in Biogeosciences.

162 **Response:** We sincerely thank the reviewer for their comments and questions. We have
163 addressed each in detail below.

164 Specific Comments

165 **Comment:** line 153: some gas and aerosol components of total Nr were measured at 1-10m
166 above ground, while the canopy height is 30m. I presume this means the samplers were located
167 in a clearing of the forest. How was this accounted for in inferential modelling of dry deposition,
168 knowing that the model supposes that concentrations are measured above the canopy, and that
169 concentrations measured in a (small) clearing are likely to represent sub-canopy levels rather
170 than above-canopy concentrations? Was there a correction scheme to account for this effect?

171 **Response:** This is a good point. As the reviewer points out, some measurements were taken
172 above the canopy on the eddy flux tower while another set of measurements was collected in an
173 open area nearby the tower. We did not make any attempt to correct for potential differences in
174 concentration due to measurement height but will clarify this point in the text.

175 **Comment:** line 265 and lines 564-569: the Gamma_s parameter in the bi-directional NH₃
176 exchange model should represent the emission potential (NH₄⁺/H⁺) of the apoplast, i.e. the
177 inter-cellular fluid that is exposed to the air within sub-stomatal cavities. Here the assumption is
178 made (implicitly) that the NH₄⁺/H⁺ ratio of bulk tissue extracts (whole leaf, i.e. whole cells inc.
179 vacuole, symplast and apoplast all mixed) is equal to the apoplastic emission potential. Many
180 publications have previously reported vastly different NH₄⁺/H⁺ ratios for bulk tissue and
181 apoplast (e.g. Sutton et al, Biogeosciences, 6, 2907–2934, 2009, fig.7 over grassland, 1-2 orders
182 of magnitude difference; Wang et al., Plant Soil (2011) 343:51–66, conclude p64: "...bulk leaf
183 tissue Γ_s can not be used as a tool to predict the potential NH₃ exchange of beech leaves").
184 Some publications do assert that there is a positive relationship between bulk and apoplastic
185 Gamma ratios, and bulk ratios are of course much more easily measured than apoplastic
186 extraction methods, so it is tempting to use the bulk tissue ratio as a proxy, for simplicity. Do the
187 authors have evidence that it is justified in the case of this particular forest ecosystem? They do
188 present a sensitivity analysis later on, using upper and lower percentiles, but I didn't see any
189 explicit discussion of why or how the bulk tissue ratio could be used as a proxy for the apoplastic
190 ratio. Please comment.

191 **Response:** The reviewer raises an important point here. We are indeed using the NH₄⁺/H⁺ ratio
192 (stomatal emission potential, Γ_s) from measurements on leaf bulk tissue as a proxy for that of the
193 apoplast. As rightly pointed out by the reviewer, while a number of studies have shown positive
194 correlations between bulk tissue chemistry, apoplastic chemistry, and independently quantified
195 compensation points (David et al., 2009; Hill et al. 2002; Massad et al. 2010; Mattsson and
196 Schjoerring 2002; Mattsson et al. 2009), absolute differences between ratios derived from bulk
197 tissue versus apoplast measurements can be large. For example, Sutton et al. (2009) and
198 Personne et al. (2015) both show that ratios derived from bulk tissue chemistry exceed those
199 derived from apoplast chemistry. As will be clarified in the text, we did not perform experiments
200 to validate the use of bulk tissue as a proxy for apoplast chemistry.

201 To put our bulk tissue derived Γ_s into broader context, our results fall within the range, but on the
202 lower end, of Γ_s reported for forests in the meta-analysis of Massad et al., 2010. Using data from
203 studies in which Γ_s was reported along with the concentration of NH₄⁺ in bulk tissue, Massad et
204 al. (2010) derived a general relationship:

205 $\Gamma_s = 19.3 \times \exp(0.0506 \times [NH_4^+]_{bulk})$ (1)

206 where $[NH_4^+]_{bulk}$ is the concentration of NH_4^+ in leaf tissue ($\mu g\ g^{-1}$ tissue). Using our measured
207 median value of $[NH_4^+]_{bulk}$ in equation (1) gives $\Gamma_s = 210$, which is larger than our tissue derived
208 median value of $\Gamma_s = 36$ but on the same order as the 75th percentile ($\Gamma_s = 171$) used as the upper
209 value in our model sensitivity analysis. In general, our estimates of Γ_s are reasonable in the
210 context of existing observations and the general relationship between $[NH_4^+]_{bulk}$ and Γ_s put forth
211 by Massad et al. (2010). That being said, we certainly acknowledge the reviewer's point
212 regarding uncertainty in the validity of our use of bulk tissue chemistry as a proxy for apoplastic
213 chemistry and will expand on this point in the text. As the reviewer points out, measurements on
214 bulk tissue are easier and therefore more tempting to use compared to apoplastic extractions.
215 More studies comparing apoplast and bulk tissue derived Γ_s are needed to extend the meta-
216 analysis of Massad et al. (2010) to a wider range of natural ecosystems, particularly deciduous
217 forests. This point will also be emphasized in the revised text.

218 **Comment:** line 647: "This pattern largely reflects the seasonal cycle in leaf area index". Could
219 seasonal patterns in wind speed, turbulence, surface wetness (rainfall), also contribute to
220 seasonal V_d patterns, aside from LAI?

221 **Response:** Yes, we agree that seasonal patterns in other drivers could also contribute to
222 seasonality in V_d and will clarify this point in the text.

223 line 758-9: "more temporally extensive measurements of the litter NH_3 emission potential are
224 also needed". I would add that a better understanding (and modelling) of the leaf litter decay
225 dynamics, constrained by weather (temperature, moisture) are needed if one aims to reproduce
226 litter N emissions in surface exchange models.

227 **Response:** Thank you for the comment. We agree and will add this point to the text.

228 Technical corrections

229 **Comment:** line 290: add "by eddy covariance" after "heat flux measured..."

230 **Response:** OK

231 **Comment:** lines 427-428: the sentence " To estimate the concentration of NO_2 from the
232 measured "other" NO_y , we examined the ratio of NO_2 to the quantity $NO_y - HNO_3 - PANS -$
233 NTR (e.g., "other" NO_y) simulated by CMAQ (V5.2.1) for the Coweeta site over the year
234 2015418-419..." feels a little like a repeat of lines 418-419

235 **Response:** Thank you for point this out. We will shorten the sentence at line 418 to eliminate
236 redundancy.

237 **Comment:** line 442, figure 2 and figure S9: the decrease of SO_x emissions and concentrations
238 over 30 years had a large impact on NH_x chemistry, and is useful to explain the NH_x trends. It

239 would be good to show the SO₂/SO₄= data of Fig S9 in Fig.2 of the main text, alongside long-
240 term trends of Nr?

241 **Response:** Good suggestion. We will add the sulfur time series to Figure 2 of the main text.

242 **Comment:** line 505, fig. 5: NO_y concentrations are expressed in ppb, it might be good to
243 harmonize with the rest of the figures as μg m⁻³ (easier to compare NO_y with TNO₃- and NH_x
244 of figs 6-7, for example) ?

245 **Response:** Agreed. Concentrations will be harmonized to μg N m⁻³ in the revised text.

246 **Comment:** line 517: suggest change "the same proportions of the NO_y budget..." to "the same
247 proportions of the atmospheric NO_y load ..." ? The word budget may suggest deposition ?

248 **Response:** Agreed. Wording will be changed to "atmospheric NO_y load"

249 **Comment:** line 631, similar to above, suggest change to "NH₄⁺ contributed more to the
250 atmospheric NH_x load than NH₃..."

251 **Response:** Agreed. Wording will be changed to "atmospheric NH_x load"

252 **Comment:** line 556: "The contributions of NO₃⁻ and NO₂⁻ were negligible." This refers to Fig.
253 8, but in the top part (a) of Fig. 8, I don't see that NO₃⁻ was negligible (here, WSON is
254 negligible, as is NO₂⁻). And subsequently, "Organic compounds (WSON) contributed 11.6% of
255 WSTN...", again that is not what the top figure shows, but it is what the lower part (b) of Fig. 8
256 apparently shows. There is a contradiction between the two parts (a) and (b): which is WSON,
257 and which is NO₃⁻ ? Amend text if necessary.

258 **Response:** This was a mistake in the color coding of the top chart and will be corrected.

259 **Comment:** Fig. 8 caption: suggest change to "Contributions of N aerosol species to WSTN..."
260

261 **Response:** Thank you. Wording will be changed as suggested.
262

263 References

264
265 David M, Loubet B, Cellier P, Mattsson M, Schjoerring JK, Nemitz E, Roche R, Riedo M,
266 Sutton MA (2009) Ammonia sources and sinks in an intensively managed grassland canopy.
267 *Biogeosciences* 6: 1903–1915. doi:10.5194/bg-6-1903-2009

268 Hill PW, Raven JA, Sutton MA (2002) Leaf age-related differences in apoplastic NH₄⁺
269 concentration, pH and the NH₃ compensation point for a wild perennial. *J Exp Bot* 53: 277–286.
270 doi:10.1093/jexbot/53.367.277

271 Massad RS, Nemitz E, Sutton MA (2010) Review and parameterization of bi-directional
272 ammonia exchange between vegetation and the atmosphere. *Atmos Chem Phys* 10:10359–
273 10386. doi:10.5194/acp-10-10359-2010

- 274 Mattsson M, Schjoerring JK (2002) Dynamic and steady-state responses of inorganic nitrogen
275 pools and NH₃ exchange in leaves of *Lolium perenne* and *Bromus erectus* to changes in root
276 nitrogen supply. *Plant Physiol* 128:742–750. doi:10.1104/pp.010602
- 277 Mattsson M, Herrmann B, Jones S, Neftel A, Sutton MA, Schjoerring JK (2009) Contribution of
278 different grass species to plant-atmosphere ammonia exchange in intensively managed grassland.
279 *Biogeosciences* 6:59–66. doi:10.5194/bg-6-59-2009
- 280 Personne, E., Tardy, F., Genermont, S., et al. (2015) Investigating sources and sinks for ammonia
281 exchanges between the atmosphere and a wheat canopy following slurry application with trailing
282 hose. *Agricultural and Forest Meteorology* 207:11-23.
- 283 Sutton, M. A., Nemitz, E., Milford, C., Campbell, C., Erisman, J. W., Hensen, A., Cellier, P.,
284 David, M., Loubet, B., Personne, E., Schjoerring, J. K., Mattsson, M., Dorsey, J. R., Gallagher,
285 M. W., Horvath, L., Weidinger, T., Meszaros, R., Dämmgen, U., Neftel, A., Herrmann, B.,
286 Lehman, B. E., Flechard, C., and Burkhardt, J. (2009) Dynamics of ammonia exchange with cut
287 grassland: synthesis of results and conclusions of the GRAMINAE Integrated Experiment,
288 *Biogeosciences* 6: 2907–2934. <https://doi.org/10.5194/bg-6-2907-2009>