

1 **Title:** Insights into mechanisms governing forest carbon response to nitrogen deposition: a
2 model-data comparison using observed responses to nitrogen addition

3

4 **Authors:** R. Q. Thomas^{1,2}, G. B. Bonan², and C. L. Goodale¹

5

6 ¹Department of Ecology and Evolutionary Biology, Cornell University, Ithaca, NY,

7 ²National Center for Atmospheric Research, Boulder, CO

8

9 **Running title:** Insights into mechanisms governing C and N interactions

10

11 **Corresponding Address:**

12 R. Quinn Thomas

13 NCAR/CGD/TSS

14 P.O. Box 3000

15 Boulder CO 80307-3000

16 USA

17

18

19

20

21

22

23

24 **Abstract**

25 In many forest ecosystems, nitrogen (N) deposition enhances plant uptake of carbon dioxide,
26 thus reducing climate warming from fossil fuel emissions. Therefore, accurately modeling how
27 forest carbon (C) sequestration responds to N deposition is critical for understanding how future
28 changes in N availability will influence climate. Here, we use observations of forest C response
29 to N inputs along N deposition gradients and at five temperate forest sites with fertilization
30 experiments to test and improve a global biogeochemical model (CLM-CN 4.0). We show that
31 the CLM-CN plant C growth response to N deposition was smaller than observed and the
32 modeled response to N fertilization was larger than observed. A set of modifications to the CLM-
33 CN improved the correspondence between model predictions and observational data (1) by
34 increasing the aboveground C storage in response to historical N deposition (1850–2004) from
35 14 to 34 kg C per additional kg N added through deposition and (2) by decreasing the
36 aboveground net primary productivity response to N fertilization experiments from 91 to 57 g C
37 $\text{m}^{-2} \text{yr}^{-1}$. Modeled growth response to N deposition was most sensitive to altering the processes
38 that control plant N uptake and the pathways of N loss. The response to N deposition also
39 increased with a more closed N cycle (reduced N fixation and N gas loss) and decreased when
40 prioritizing microbial over plant uptake of soil inorganic N. The net effect of all the
41 modifications to the CLM-CN resulted in greater retention of N deposition and a greater role of
42 synergy between N deposition and rising atmospheric CO_2 as a mechanism governing increases
43 in temperate forest primary production over the 20th century. Overall, testing models with both
44 the response to gradual increases in N inputs over decades (N deposition) and N pulse additions
45 of N over multiple years (N fertilization) allows for greater understanding of the mechanisms
46 governing C-N coupling.

47

48 **1. Introduction**

49
50 Reactive nitrogen (N) from fossil fuel combustion and agricultural activities influences
51 global climate by altering atmospheric chemistry, aerosols, and greenhouse gas concentrations
52 (Butterbach-Bahl et al., 2011; Pinder et al., 2012). However, the direction of the climate impact
53 of reactive N primarily depends on the balance of opposing processes: positive radiative forcing
54 from emissions of N₂O, a greenhouse gas, and negative radiative forcing from altered
55 atmospheric chemistry and carbon dioxide (CO₂) storage in N-fertilized forests (Arneth et al.,
56 2010; Pinder et al., 2012). Reactive N deposited on forest ecosystems can increase primary
57 production if the forest is N-limited (Nadelhoffer et al., 1999; Magnani et al., 2007; Thomas et
58 al., 2010), which results in less CO₂ in the atmosphere and consequently reduced climate
59 warming. Recent estimates show that this CO₂ uptake broadly offsets warming from N₂O
60 emissions, indicating that the N-induced forest sink of CO₂ has an important role in global
61 climate (Zaehle et al., 2011; Butterbach-Bahl et al., 2011; Pinder et al., 2012).

62 Accurately predicting how carbon (C) storage in forest ecosystems will respond to the
63 changing deposition of reactive N is critical for developing climate change targets for reducing
64 emissions and air pollution. Global biogeochemical models coupled to climate and atmospheric
65 chemistry models are powerful tools for exploring this carbon- nitrogen-climate interface
66 (Sokolov et al., 2008; Thornton et al., 2009; Yang et al., 2009; Zaehle and Friend, 2010), but it is
67 paramount to build confidence in predictions of how C uptake and storage respond to changing
68 N inputs.

69 Fortunately, a variety of observational and experimental data are available to test and
70 improve the sensitivity of global biogeochemical models to changes in N deposition and the
71 resulting C sequestration. Studies have generally shown that elevated N inputs often increase

72 plant growth and soil C sequestration (Magnani et al., 2007; Hyvonen et al., 2008; de Vries et al.,
73 2009; Janssens et al., 2010; Thomas et al., 2010), although some ecosystems can be harmed by
74 chronic elevated N inputs that lead to soil acidification and N saturation (Aber et al., 1998;
75 Hogberg et al., 2006; Wallace et al., 2007). The current range of estimates quantifying the
76 additional C sequestered per unit of N added (kg C per kg N; or dC/dN) is broad, in part due to
77 the myriad of approaches used to quantify dC/dN. These approaches include N fertilization
78 studies (Hyvonen et al., 2008; Liu and Greaver, 2009), where large inputs of N are added to
79 forests over short time scales, and N deposition gradient studies (Magnani et al., 2007; de Vries
80 et al., 2009; Thomas et al., 2010), where spatial variation in N deposition and forest growth are
81 used to estimate the impact of gradual increases N deposition on C storage over multiple
82 decades. Furthermore, there can be variation among studies in the C pools being measured, as
83 some studies calculate the dC/dN of aboveground stem C (de Vries et al., 2009; Thomas et al.,
84 2010), soil organic matter (Janssens et al., 2010), or net ecosystem production (NEP; Magnani et
85 al., 2007; Sutton et al., 2008). Finally, the observations span regions with very different historical
86 N deposition loads (i.e. the US compared to Western Europe). Successfully using the available
87 data to test and improve global biogeochemical models requires directly accounting for the
88 variation in magnitude and time-scale of N additions in the observational and experimental data.

89 Many different approaches have been used to model key processes influencing C and N
90 cycle interactions in terrestrial ecosystems (Zaehle and Dalmonech, 2011). For example, N
91 fixation has been modeled as a function of net primary production (NPP) (Thornton et al., 2007),
92 evapotranspiration (Felzer 2012; Tian et al. 2011; Yang et al., 2009; Zaehle and Friend, 2010) or
93 N demand (Gerber et al., 2010). Similarly, N uptake has been represented as a direct function of
94 photosynthesis and C : N stoichiometric constraints on building plant tissue (Thornton et al.,

95 2002, 2007) or based on allocation of C to plant roots (Gerber et al., 2010; Raich et al. 1991;
96 Zaehle and Friend, 2010). Soil and plant buffering of the C cycle to daily to annual changes in N
97 availability also differs among models (Gerber et al., 2010; Zaehle and Friend, 2010). Despite
98 these differences, global biogeochemical models predict reasonable levels of global NPP
99 (Thornton et al., 2007; Gerber et al., 2010; Zaehle et al., 2010a), suggesting that the
100 representation or parameterization of one C-N process may compensate for the representation or
101 parameterization of another. Understanding how the different model structures or
102 parameterizations influence the prediction of how ecosystems respond to N deposition requires
103 isolating key processes that govern C and N interactions. Unfortunately, inter-model
104 comparisons can be limited by broad differences in model structure that make it difficult to
105 isolate particular processes that differ among models. One approach to this problem is to
106 compare different representations of particular C and N cycle processes within the same general
107 model, thereby obtaining a better understanding of which processes influence predictions of how
108 terrestrial C storage and climate respond to changing N availability.

109 Here, we explored the influence of alternative approaches to modeling C and N
110 interactions on the sensitivity of C storage to N inputs in temperate forest ecosystems. To isolate
111 the alternative approaches, we implemented multiple alternative assumptions about C and N
112 cycling within a single global biogeochemical land surface model (CLM- CN 4.0). We focused
113 on five key assumptions about the N cycle in the CLM-CN 4.0: (1) the extent to which the N
114 cycle is open, based on N fixation inputs and N losses relative to internal N cycling, (2) the
115 buffering of the soil inorganic N pool and plant N pool, (3) the representation of plant N uptake,
116 (4) the pathways of N loss, and (5) the canopy scaling of photosynthesis. These alternative
117 assumptions are combined to create a modified version of the CLM-CN 4.0 that is compared to

118 observed ecosystem response to experimental N fertilization and to elevated N inputs across N
119 deposition gradients.

120

121 **2.0 Methods**

122

123 ***2.1 Baseline model description***

124 We used the CLM-CN 4.0 as the baseline model (Lawrence et al., 2011, 2012). The
125 CLM-CN 4.0 is the global land surface model in the Community Earth System Model (Gent et
126 al., 2011) and includes both terrestrial biogeophysical and biogeochemical processes. Our model
127 simulations include both the biogeophysical and biogeochemical components of the CLM-CN
128 but we focus our model evaluation and improvement on the biogeochemical component
129 (hereafter, referred to as the “clm4cn” model). A description of the key processes that relate to
130 new model modifications are described below, while a more thorough description of the
131 biogeochemical component can be found elsewhere (Thornton et al., 2002, 2007, 2009; Thornton
132 and Rosenbloom, 2005). In the clm4cn model, the C and N cycles are coupled through litter and
133 soil organic matter decomposition and through plant dynamics. The primary C and N coupling
134 occurs on the 30-min time scale, as plants compete for N with microbial immobilization into soil
135 organic matter, where N comes from a generic soil inorganic N pool (i.e. NH_4^+ and NO_3^- are
136 combined). Plant N demand is based on the N needed to match the demand set by non-N limited
137 photosynthesis and plant tissue C : N stoichiometric constraints. If the combined N demand
138 exceeds the available N in soil and retranslocated from sensed plant tissue, plant uptake and
139 microbial immobilization are reduced in proportion to the available N and their relative demands.
140 Sources of new N into the clm4cn model include N fixation and N deposition. N losses include

141 denitrification, leaching, fire, and harvest. N fixation is a saturating function of NPP derived
142 from Cleveland et al. (1999). Fixation and deposition are both directly added to the soil inorganic
143 N pool. The clm4cn model includes both denitrification and leaching processes; however, the
144 vast majority of N is lost as N gas in most ecosystems in the model (Table A2). Therefore, the
145 two loss pathways for N gases in the clm4cn model are very important: (1) a constant 1 % of net
146 mineralization is lost as N gas and (2) the soil inorganic N that exceeds plant uptake and
147 immobilization is denitrified at a rate of 50 % per day.

148

149 ***2.2. Modified model description***

150 The overall model modifications (referred to as “clm4mod”) build on recent
151 improvements to the calculations of canopy photosynthesis in the clm4cn (Bonan et al., 2011,
152 2012) by modifying the representations of plant N uptake, internal N cycling, N loss, and
153 biological N fixation in mature temperate and boreal forests. The modifications within the
154 clm4cn reflect differences between the clm4cn and other global biogeochemical models,
155 specially models that have alternative approaches to modeling N uptake (O- CN: Zaehle and
156 Friend, 2010; LM3V: Gerber et al., 2010), buffering of plant and soil N availability (O-CN:
157 Zaehle and Friend, 2010; LM3V: Gerber et al., 2010) and less N fixation in temperate and boreal
158 forests than the clm4cn (LM3V; Gerber et al., 2010). An overview of the modifications is found
159 below while a full description is found in the Appendix A.

160

161 ***2.2.1 Internal N cycling***

162 Plant N uptake in the clm4mod model is based on Michaelis-Menten kinetics, where

163 the rate of N uptake depends on a maximum uptake rate per gram of fine root C, as well as the
164 concentration of soil inorganic N in separate NH_4^+ and NO^{-3} pools (see Appendix A for detailed
165 information). Plant uptake increases with soil temperature and as the internal plant pool of N
166 decreases relative to a maximum internal pool. The formulation of N uptake is similar to that
167 used in other global biogeochemical models (Gerber et al., 2010; Zaehle and Friend, 2010) and
168 differs from the clm4cn by allowing the N uptake to be decoupled from photosynthesis at short
169 time scales (i.e. seconds to days); longer term N uptake (i.e. at days to years) remains ultimately
170 coupled to photosynthesis. The maximum internal plant N pool is equal to one year of live plant
171 tissue N turnover (Gerber et al., 2010). In the clm4mod model, the maximum uptake rate is
172 assumed to be equal for NH_4^+ and NO^{-3} , as implemented in other models(Gerber et al., 2010;
173 Zaehle and Friend, 2010). N uptake occurs any time during the growing season (i.e. when leaves
174 are present on the plant), rather than only during the day within the growing season, as
175 implemented in the clm4cn model. Plant uptake is assumed to be less competitive for N than soil
176 immobilization of N, in that plant uptake occurs after soil microbial immobilization demands are
177 met; in the clm4cn, neither plant uptake nor soil immobilization of N had first access to soil
178 inorganic N, rather they compete based on their demand for N. The clm4mod includes a plant
179 labile N (short/medium-term storage) pool that is used to buffer the demand for N from
180 photosynthesis from the uptake of N by roots. The buffering occurs by allowing only 2 % of the
181 plant labile N pool to be available for combining with new photosynthate to build plant tissue.
182 The 2 % buffering capacity leads to approximately a two-day turnover time of labile plant N.
183 The clm4cn does not include buffering of labile plant N.

184

185 ***2.2.2 N losses***

186 The clm4mod model introduces a nitrification algorithm, an alternative denitrification
187 algorithm, and a simple algorithm describing the production and hydrologic loss of dissolved
188 organic matter, including dissolved organic N (DON). Nitrification is a function of soil NH_4^+ ,
189 soil temperature, soil water, and net mineralization based on Parton et al. (2001) with 2 % of
190 nitrification lost as N_2O (Parton et al., 2001). Denitrification is an function of soil NO^{-3} , soil
191 water, and soil heterotrophic activity based on Bradbury et al. (Appendix A5; Bradbury et al.,
192 1993; Yang et al., 2009). To buffer the availability of soil inorganic N and approximate short-
193 term cation exchange processes, 10 % of total soil NH_4^+ is available for immobilization, plant
194 uptake, nitrification, and leaching (Gerber et al., 2010), and, since NO^{-3} is highly mobile in soils,
195 100 % of NO^{-3} is assumed to be available for soil, plant, and loss processes. Dissolved organic
196 matter is produced at a constant proportion (2 %) of the organic matter transfer between the slow
197 litter pool (lignin-based) and its receiving soil organic matter pool (based on Gerber et al., 2010).
198 Both dissolved organic C and N are lost in proportion to hydrologic export, similar to leaching
199 loss of soil inorganic N in the clm4cn model. The clm4cn does not include separate consideration
200 of NH_4^+ and NO^{-3} and cycling, nor does it include DOC and DON losses.

201

202 **2.2.3 N inputs**

203 In clm4mod N fixation is a function of actual evapotranspiration, based on the central
204 relationship in the Cleveland et al. (1999) review of N fixation measurements, rather than a
205 function of NPP, as implemented in clm4cn. In addition, symbiotic and non-symbiotic sources of
206 N fixation are separated. Symbiotic fixation is added to the labile N pool and non-symbiotic
207 fixation is added to the soil NH_4^+ pool. Symbiotic N fixation is assumed to be zero in mid- to
208 late-successional temperate and boreal forests (i.e. when leaf area index (LAI) > 1) and non-

209 symbiotic N fixation increases with actual evapotranspiration (Appendix A6). Both sources of
210 fixation are assumed to occur in grasslands and tropical forests. This N fixation routine reduces
211 the overall N inputs to mid- to late-successional extra-tropical forests (see Table A2 for the
212 magnitude of change in N fixation). A pathway for N fertilization was also added to facilitate the
213 simulation of N fertilization experiments.

214 N deposition in the clm4mod was equal to total N deposition in the clm4cn, except N
215 deposition in the clm4mod was divided into NH_4 and NO_3 based on the N deposition input
216 fields described in Lamarque et al. (2005).

217

218 ***2.2.4 Canopy photosynthesis***

219 Finally, the clm4mod model includes changes to the canopy scaling of photosynthesis,
220 maximum photosynthetic rates, radiative transfer, leaf photosynthesis, and stomatal conductance
221 as described in Bonan et al. (2011) and (2012). Bonan et al. (2012) introduced a multi-layer
222 canopy scaling approach that solved photosynthesis throughout the canopy rather than using a
223 whole canopy approximation. The model updates in Bonan et al. (2011, 2012) decreased GPP
224 and effectively reduced the photosynthetic potential of shaded leaves, but the impact of the
225 changes on C-N interactions has not been investigated. The clm4mod model also includes
226 specific values of maximum photosynthetic rate for each plant functional type from a synthesis
227 of a plant trait database (Kattge et al., 2009), although these values differed only slightly from
228 the values in the clm4cn model for the temperate broadleaf plant type used in this study (clm4cn,
229 52; clm4mod, 58; $\mu\text{mol m}^{-2} \text{s}^{-1}$).

230

231 ***2.3 Simulations***

232 The clm4cn and clm4mod models were used to simulate forest biogeochemistry at five
233 sites in North American broadleaf temperate deciduous forests. The five sites were chosen based
234 on the presence of long-term forest productivity measurements (10+ years), long-term N
235 fertilization experiments (10+ years), and are contained within the geographic boundaries of the
236 analysis of forest inventory data by Thomas et al. (2010), which estimated how forest C storage
237 has responded to N deposition across the northeastern US (see below). Basic descriptions of the
238 sites are included in Table 1. Four of the five sites were in Michigan, USA, with each site
239 receiving varying atmospheric deposition and a $3 \text{ g N m}^{-2} \text{ yr}^{-1}$ experimental addition of N over
240 ten years (Pregitzer et al., 2008; 1995–2005). The other site was at Harvard Forest in
241 Massachusetts, USA (Magill et al., 2004) and included two different 14-yr fertilization additions
242 (5 and $15 \text{ g N m}^{-2} \text{ yr}^{-1}$; 1988–2002). All data used in this study for the five sites and six N
243 fertilization experiments can be found in Magill et al. (2004) and Pregitzer et al. (2008). We
244 simulated ecosystem response to transient N deposition and N fertilization at each of the five
245 sites using the clm4cn and clm4mod models (Table 2). The simulations involved running each
246 model from 1850 to 2004 at each of the five sites with different combinations of forcing data
247 (Table 2). The baseline (control; Table 2 Sim. 1) simulation used transient N deposition (NH_x
248 and 15 NO_y ; Lamarque et al., 2005), atmospheric CO_2 , land use (by harvesting vegetation
249 biomass in the year that yields the reported stand age at the five sites), and climate. N deposition
250 and atmospheric CO_2 trends had reconstructions covering the entire simulation (1850–2004). A
251 57-yr meteorological dataset was available to force the model (1948–2004; Qian et al., 2006).
252 We created site-level meteorological data by using the corresponding grid cell in the global
253 gridded data (Qian et al., 2006). We used the data from 1948–1972 for the 1850–1972
254 simulation years, and the 1973–2004 meteorological dataset was used for the 1973–2004

255 simulation years (as in Randerson et al., 2009 and Bonan and Levis 2010). Each simulation
256 needed initial conditions that were attained by running the model to equilibrium using 1850
257 values for N deposition and atmospheric CO₂ and the 1948–1972 time-series for meteorological
258 data. All wildfire was excluded in the spin-up and other simulations due to uncertainties using
259 the statistical fire model at a single point location. Simulations used site-specific soil texture
260 (Magill et al., 2004; Pregitzer et al., 2008). We refer to the equilibrium state used as initial
261 conditions as the pre-industrial steady-state.

262 We isolated the influence of transient N deposition on C cycling at each site by repeating
263 the baseline simulation described above except for holding N deposition constant at 1850 values
264 (Table 2 Sim. 2). We also tested whether C cycle sensitivity was different for larger inputs of N
265 deposition than included in the baseline simulation (Table 2 Sim. 3). The higher N deposition
266 simulation used N deposition values found in Western Europe and allowed us to explore why N
267 deposition gradients in North America (Thomas et al. 2010) yielded steeper C responses than in
268 Western Europe (de Vries et al. 2009). The high N deposition simulation used a N deposition
269 trajectory from 1850 to 2004 with 1995–2004 mean deposition levels at the five sites of 2.2 g N
270 m⁻² yr⁻¹ (Table 1: EU deposition gradient) rather than the actual N deposition rates (1995- 2004)
271 at these sites that ranged from 0.68–1.18 g N m⁻² yr⁻¹ (Table 1: US deposition gradient).

272 Because the NPP response to rising atmospheric CO₂ is constrained by N availability, we
273 tested whether the sensitivity of NPP to rising atmospheric CO₂ changed as a result of the
274 modifications to clm4cn. To test this sensitivity we performed two additional simulations at the
275 five sites using the clm4cn and clm4mod: a simulation that held both N deposition and
276 atmospheric CO₂ constant at 1850 levels (Table 2 Sim. 4) and a simulation that held CO₂
277 constant at 1850 levels but included 1850–2004 N deposition levels (Table 2 Sim. 5)

278 Finally, we simulated the six N fertilization experiments (Table 1; four sites with one
279 experiment each and one site with two experiments) by adding N fertilization to the baseline
280 simulation to best approximate the field experiments by specifying the start year, duration,
281 magnitude and intra-annual distribution of N application (Table 2 Sim. 6). To test whether the N
282 fertilization treatments completely relieved N limitation, we simulated the six N fertilization
283 experiments again, this time adding a very large dose of enough additional N to the fertilized
284 treatment to meet any remaining N demand by plants and microbial immobilization ('Non-
285 nitrogen limited' treatment).

286

287

288 ***2.4 N fertilization and deposition analysis and observations***

289 The model comparison to observations focused on NPP, net ecosystem productivity
290 (NEP), and annual aboveground net C increment (ACI) in plants because these were the
291 variables measured in the N fertilization experiments and across the N deposition gradients. The
292 model response to N fertilization was assessed by comparing mean annual aboveground NPP
293 (ANPP) in the control and N-fertilized simulations to ANPP data from the corresponding control
294 and fertilized treatments in the field data. In both the models and observations, ANPP
295 corresponded to the sum of mean leaf and stem productivity over the course of the observational
296 data. We also report ACI for the fertilization experiments (the change of aboveground C stock
297 between years). ACI differs from NPP and ANPP in that ACI does not include the production
298 and turnover of wood or leaves within a year that are included in NPP measurements. However,
299 ACI includes the losses of C from mortality that are not included in NPP measurements. We
300 report the ACI response to fertilization by dividing by the N added ($dC_{ACI}/dN_{fertilization}$).

301 We compared the model response to N deposition to observations from the literature. We
302 calculated average ACI between 1994 and 2004 in the simulations with and without transient N
303 deposition (both including transient CO₂). The ACI response to N deposition was expressed as
304 the ACI difference divided by the difference in mean N deposition over the same time period
305 ($dC_{ACI}/dN_{deposition}$). We also report the difference in NEP divided by the difference in N
306 deposition ($dC_{NEP}/dN_{deposition}$). We compared the above metrics of N deposition response to the
307 corresponding metrics reported in analyses listed in Table 3.

308 We also assessed the contribution of N retention to the N deposition response in the
309 clm4cn and clm4mod model. The total N deposition retained between 1970 and 2004 and
310 between 2000 and 2004 was calculated to determine the long- and short-term retention of N
311 deposition, respectively. Over each time period, we calculated total deposition retained in the
312 ecosystem and the fate of N deposition into soil organic matter (including litter and coarse
313 woody debris) and vegetation.

314 In addition, we assessed the relative contribution of CO₂ fertilization to how NPP
315 responds to N deposition for each site using the method developed by Churkina et al. (2009) and
316 Zaehle et al. (2010b). That is, we isolated the pure N deposition (i.e. N deposition enhancement
317 without an interaction with CO₂ fertilization), the pure CO₂ fertilization, and the synergistic
318 effect of CO₂ fertilization and N deposition on NPP by calculating the mean NPP (1994–2004) in
319 the simulations with (1) N deposition and atmospheric CO₂ at pre-industrial levels (Table 2 Sim.
320 4), (2) only transient N deposition (CO₂ at pre-industrial levels; Table 2 Sim. 5), (3) only
321 transient CO₂ (N deposition at pre-industrial levels; Table 2 Sim. 2), and (4) both transient N
322 deposition and CO₂ (i.e. control simulation described above; Table 2 Sim 1). The pure N
323 deposition response was the difference in NPP between (1) and (2), while the pure CO₂

324 fertilization response was the difference between (1) and (3). The additional NPP needed to
325 reach the difference between (1) and (4) was the synergy between N deposition and CO₂
326 fertilization.

327

328 ***2.5 Sensitivity Analysis to model structure***

329 We explored the sensitivity of the N deposition response ($dC_{ACI}/dN_{deposition}$) to the
330 mechanisms and processes that differ between the clm4cn and clm4mod models. We created
331 intermediate models that sequentially step through the 15 model modifications that were
332 included in the shift from the clm4cn to the clm4mod (Table 4; Fig. 1). The sensitivity analysis
333 was sequential in that each intermediate model in Table 4 includes all the modifications in the
334 intermediate models listed above it. To quantify the influence of each process on the N
335 deposition response, we ran simulations with and without transient N deposition using each of
336 the intermediate models at a single site (Harvard Forest). The change in $dC_{ACI}/dN_{deposition}$
337 associated with each modification was used to quantify the sensitivity of N deposition response
338 to assumptions about the structure of the C and N cycles.

339 In most of the modifications, we were interested in the influence of the model structure
340 on the N deposition response in the absence of altered baseline productivity (the pre-industrial
341 steady-state; see Sect. 2.3). We manually adjusted the denitrification parameter to maintain the
342 same baseline production so that Model 4 had the same baseline production (NPP and total C
343 stocks) as Model 3 and Models 5–14 had the same baseline production as Model 15. To maintain
344 the same baseline production, we altered the proportion excess soil inorganic N (Models 4–10;
345 Table 4) or NO₃⁻ (Models 11–15; Table 4) that is denitrified. A detailed description of the
346 intermediate models can be found in Appendix B.

347

348 **3.0 Results**

349

350 ***3.1 Model response to N fertilization experiments***

351 The clm4mod model better predicted mean ANPP measured at the control plots at
352 the five field sites (i.e. no N additional fertilization added) than the clm4cn model. The mean
353 observed ANPP across the five sites was $464 \pm 36 \text{ g C m}^{-2} \text{ yr}^{-1}$ (1 S.E. across sites), while the
354 mean in the clm4mod and clm4cn model was 411 ± 28 and $352 \pm 50 \text{ g C m}^{-2} \text{ yr}^{-1}$ (1S.E.),
355 respectively (Table 5). Both models predicted lower ANPP than observed in the most productive
356 sites (MI-B, MI-C and MI-D; Fig. 2). Neither model was consistently higher or lower than
357 observed ANPP in the two least productive sites (HF and MI-A; Fig. 2a).

358 The clm4mod also better predicted both the mean ANPP in the N fertilized simulations
359 and the increase in ANPP over the control simulation than the clm4cn. The fertilized ANPP in
360 the clm4mod model ($474 \pm 8 \text{ g C m}^{-2} \text{ yr}^{-1}$) compared better to the observed fertilized ANPP in the
361 six experiments at the five sites ($504 \pm 40 \text{ g C m}^{-2} \text{ yr}^{-1}$) than the clm4cn model ($420 \pm 41 \text{ g C m}^{-2}$
362 yr^{-1} ; Table 5). The mean increase in ANPP in the fertilization experiments was similar between
363 the observations ($55 \pm 8 \text{ g C m}^{-2} \text{ yr}^{-1}$) and the clm4mod ($57 \pm 18 \text{ g C m}^{-2} \text{ yr}^{-1}$) with the clm4cn
364 fertilization response 65% higher ($91 \pm 19 \text{ g C m}^{-2} \text{ yr}^{-1}$) than the observed response. At individual
365 sites, the clm4mod corresponded substantially better to observations from the two N fertilization
366 experiments at Harvard Forest than the clm4cn (Fig. 2c). At the MI-A site, the clm4cn performed
367 better compared to the observations than the clm4mod (Fig. 2c). Both the fertilization responses
368 in the clm4cn and clm4mod models were within the bounds of uncertainty in the observations at
369 MI-B, MI-C, and MI-D (Fig. 2c).

370 Despite differences in ANPP response to N fertilization, both the clm4cn and 20
371 clm4mod models predicted similar aboveground C increments per unit N fertilizer added
372 ($dC_{ACI}/dN_{fertilizer}$; clm4cn: $10.7 \pm 1.3 \text{ kgC}(\text{kgN})^{-1}$; clm4mod: $10.6 \pm 4.5 \text{ kgC}(\text{kgN})^{-1}$), that was on
373 average 1.5 times larger than the observed $dC_{ACI}/dN_{fertilizer}$ ($4.0 \pm 2.7 \text{ kgC}(\text{kgN})^{-1}$; Table 3).
374 However, the site-to-site variability in the clm4mod $dC_{ACI}/dN_{fertilizer}$ was larger than the
375 variability in clm4cn, leading to overlapping uncertainty with the observations. The mean annual
376 net ecosystem production response to N fertilization ($dC_{NEP}/dN_{fertilizer}$) across all five sites was
377 27.9 ± 2.8 and $23.2 \pm 9.4 \text{ kgC}(\text{kgN})^{-1}$ for the clm4cn and clm4mod models, respectively (Table
378 3). The clm4cn compared better to the observed $dC_{NEP}/dN_{fertilizer}$ at the six fertilization
379 experiments ($31 \pm 10 \text{ kgC}(\text{kgN})^{-1}$; Table 3), although both models were contained in the
380 observational uncertainty. Additionally, both net ecosystem production responses were within
381 the uncertainty ($24 \pm 8.7 \text{ kgC}(\text{kgN})^{-1}$) reported by Lui and Greaver (2009) in a meta-analysis of
382 forest NEP response to N fertilization.

383

384 ***3.2 Model response to historical N deposition***

385 The clm4mod model had a 144 % larger response of aboveground C increment to N
386 deposition ($dC_{ACI}/dN_{deposition}$) than the clm4cn model (Table 3). The $dC_{ACI}/dN_{deposition}$
387 was 14.0 and $34.2 \text{ kgC}(\text{kgN})^{-1}$ in the clm4cn and clm4mod models, respectively (Table 3). Both
388 models predicted lower responses than reported for aboveground C increment across the
389 Northeastern US ($50 \text{ kgC}(\text{kgN})^{-1}$; adjusted from Thomas et al., 2010 for higher rates of N
390 deposition); however, the bias was substantially reduced in the clm4mod model (Table 3).

391 In the simulations with higher rates of N deposition (1995–2004 mean= 15.2 g N m^{-2}
392 yr^{-1}), the aboveground C increment response to N deposition ($dC_{ACI}/dN_{deposition}$) decreased in

393 both models (Table 3). The simulations with a large increase in N deposition were designed to
394 test model sensitivity to N deposition levels larger than typically found in the US but similar to
395 levels found in parts of Western Europe. Comparing the model results to observations from
396 Western Europe, the mean $dC_{ACI}/dN_{deposition}$ across all sites in the clm4mod model (26.2
397 $kgC(kgN)^{-1}$) was contained within the range reported from inventory measurements of European
398 forests across a N deposition gradient (Table 2; 15–40 $kgC(kgN)^{-1}$; DeVries et al., 2009), while
399 the mean clm4cn model result was lower than the reported range (11.8 $kgC(kgN)^{-1}$).

400 For the NEP response to N, adding the belowground vegetation and soil response
401 increased average $dC_{NEP}/dN_{deposition}$ across the five sites to 30.0 and 74.1 $kg C (kgN)^{-1}$ in the
402 clm4cn and clm4mod models, respectively (Table 3). The $dC_{NEP}/dN_{deposition}$ using the EU N
403 deposition values for the clm4mod model (49.5 $kgC(kgN)^{-1}$) was within the range of values
404 recalculated for European forest by Sutton et al. (2008; 50–75 $kgC(kgN)^{-1}$) using eddy flux
405 observations reported by Magnani et al. (2007). The mean $dC_{NEP}/dN_{deposition}$ using the EU N
406 deposition from the clm4cn model (24.5 $kgC(kgN)^{-1}$) was 50% less than the lower bound
407 reported in Sutton et al. (2008).

408

409 ***3.3 Mechanisms explaining the increased responsiveness of the modified model to N***

410 ***deposition and fertilization***

411 The mean retention of N deposition within ecosystem was larger in clm4mod than
412 clm4cn, mirroring the $dC_{ACI}/dN_{deposition}$ response. Across all five sites, the mean retention of N
413 deposition was higher in the clm4mod model than the clm4cn model (Fig. 3). In both the clm4cn
414 and clm4mod, ecosystem N retention (Fig. 3; sum of N recovery in vegetation and soil) was
415 lower when integrated over a 34-yr period (1970–2004: clm4cn = 51 %; clm4mod = 81 %) than

416 a 4-yr period (2000–2004: clm4cn = 55 %, clm4mod = 94 %). The fate of N retained in the
417 ecosystem was predominately in soil organic matter in both models and at both time scales (Fig.
418 3). However, the proportion of N deposition retained in both vegetation and soil was higher in
419 the clm4mod than the clm4cn model (Fig. 3) with particularly large increases in N retained in
420 soil. The response to N deposition ($dC_{ACI}/dN_{deposition}$) was most sensitive to the use of a
421 Michaelis-Menten approach to plant N uptake in the clm4mod that describes N up- take as a
422 function of soil inorganic N and fine root C, rather than the approach in clm4cn that represents N
423 uptake as a function of photosynthesis and the N required by stoichiometric constraints (Model
424 6; Table 3; Fig. 4). Implementing the Michaelis-Menten approach increased the $dC_{ACI}/dN_{deposition}$
425 by $27 \text{ kgC}(\text{kgN})^{-1}$. The next largest sensitivity was associated with the pathway of N loss (Model
426 10; Table 4; Fig. 4); the removal of the N gas loss process simulated in clm4cn as 1 % of net N
427 mineralization decreased the $dC_{ACI}/dN_{deposition}$ by $15 \text{ kgC}(\text{kgN})^{-1}$ (Fig. 4). Because we increased
428 the proportion of excess N that was denitrified to maintain the same total N loss at pre-industrial
429 steady-state, the change in $dC_{ACI}/dN_{deposition}$ was associated with modifying the particular
430 pathways of N loss, rather than being associated with a modification to the total pre-industrial N
431 export.

432 The implementation of a less open N cycle with lower N input and outputs increased
433 $dC_{ACI}/dN_{deposition}$ by $6 \text{ kgC}(\text{kgN})^{-1}$ (Model 4; Table 4; Fig. 4). $dC_{ACI}/dN_{deposition}$ increased by 8
434 $\text{kgC}(\text{kgN})^{-1}$ in the simulation that isolated the influence of reduced denitrification on the
435 response to N deposition (Model 5; Table 4; Fig. 4). This simulation had the same pre-industrial
436 primary productivity as the simulation with Michaelis- Menten plant N uptake (Model 6) but
437 without the Michelis-Menten uptake mechanism (same model structure as Model 4 but with a
438 lower denitrification parameter). In contrast, allowing microbial immobilization to have first

439 access to soil inorganic N (Model 8; Fig. 1; Fig. 4) and implementing a representation of
440 nitrification with separated NH_4^+ and NO_3^- pools (Model 11; Table 4; Fig. 4) decreased
441 $dC_{\text{ACI}}/dN_{\text{deposition}}$ by 7 and 5 $\text{kgC}(\text{kgN})^{-1}$, respectively. All other processes described in Table 4
442 had little impact on $dC_{\text{ACI}}/dN_{\text{deposition}}$ ($< 3 \text{ kgC}(\text{kgN})^{-1}$).

443

444 **3.4. Synergy between N deposition and atmospheric CO_2**

445 Averaged across all five sites, the clm4mod and clm4cn models predicted similar
446 increases in NPP over pre-industrial NPP, attributed to the increase in both N deposition and
447 atmospheric CO_2 over the period from 1850 to 2004 (clm4cn = $84.1 \text{ gCm}^{-2} \text{ yr}^{-1}$; clm4mod =
448 $87.2 \text{ gCm}^{-2} \text{ yr}^{-1}$; 1994–2004; Fig. 5a). However, the relative contribution of N deposition and
449 CO_2 fertilization differed strongly between the two models (Fig. 5b). The increase in NPP
450 predicted by the clm4cn model was comprised of a pure N deposition response (46 %) and a pure
451 CO_2 fertilization response (57 %) that were largely independent of each other, as the synergy
452 only explained 7% of the NPP change (Fig. 5b). In contrast, the pure CO_2 fertilization response
453 in the clm4mod model was small (12%) while the majority of the NPP increase was explained by
454 a pure N deposition response (58 %) and a synergy between N deposition and rising CO_2 (30 %;
455 Fig. 5b).

456

457 **4.0 Discussion**

458 Overall, our modifications to the CLM-CN 4.0 substantially improved predictions of C
459 storage in response to historical N deposition. The modifications in the clm4mod model
460 increased the aboveground C increment response to historical N deposition by 144 % compared
461 to the clm4cn model and compared more closely with observations across N deposition gradients

462 in the Northeastern US and Western Europe. Modifications to the representation of plant N
463 uptake and pathways of N losses were the most important mechanisms that were responsible for
464 the increased aboveground C increment response to N deposition in the clm4mod model. The net
465 effect of the modifications increased ecosystem retention of N deposition and increased synergy
466 between N deposition and fertilization from elevated atmospheric CO₂.

467

468 ***4.1 Response to historical N deposition***

469 The response to N deposition was most sensitive to the implementation of a Michaelis-
470 Menten approach to plant N uptake (Model 6; Fig. 4). By adding the Michaelis-Menten uptake,
471 plant N uptake depended on the fine root C stock, the soil inorganic N concentration,
472 temperature, and N status of the plant rather than the N demand set by photosynthesis, allocation,
473 and C : N ratios of the allocated tissues. The Michaelis-Menten uptake increased the N
474 deposition response by increasing N retention (2000–2004) by 9%, likely due to greater ability of
475 plants to compete against N loss processes. The increased N retention was also associated with a
476 lower parameter value for the proportion of excess N lost as N gas in the model with Michaelis-
477 Menten uptake (Model 6; Fig. 4). The lower parameter was necessary to yield the same steady-
478 state N gas loss at pre-industrial conditions in the Michaelis-Menten uptake simulation because
479 this approach to N uptake requires larger stocks of soil inorganic N to retain the same N uptake
480 rate as a model without Michaelis-Menten uptake. The lower N gas loss parameter likely
481 allowed more N deposition to be retained in the ecosystem in the transient simulations.
482 Michaelis-Menten uptake also increased soil inorganic N stocks necessary to yield the same N
483 uptake as the clm4cn model. This reduced the competition between plants and immobilization,
484 thus increasing the total assimilation into N soil organic matter. A range of N uptake approaches

485 are used in ecosystem and global biogeochemical models suggesting the choice of how N uptake
486 is represented can strongly influence the sensitivity to N deposition in the model.

487 The N deposition response was also sensitive to the pathway of N loss (Model 10; Fig. 4).
488 Broadly there are two pathways of gas and leaching N loss used in ecosystem and global
489 biogeochemical models: turnover-dependent and concentration-dependent pathways (Menge,
490 2011). Turnover dependent pathways refer to N losses that are proportional to the turnover of an
491 internal nitrogen pool (i.e. litter N, soil organic N, or vegetation N). Concentration-dependent
492 pathways refer to N losses that are proportional to the concentration of soil inorganic N and
493 typically only occur under periods of N saturation. As an example of a turnover-dependent
494 pathway, the clm4cn has a pathway of N gas loss that is proportional to the net N mineralization
495 associated with soil organic matter turnover (1 % of net N mineralization). The sensitivity
496 analysis found that substituting concentration- dependent for a turnover-dependent gas loss
497 pathway decreased the plant C response to N deposition; the substitution occurred through
498 removing the N gas loss associated with net mineralization and compensating the reduced N loss
499 by increasing denitrification of excess soil inorganic N, a concentration-dependent pathway
500 (Model 10; Fig. 4). Similarly, DON leaching in the clm4mod is another example of a turnover-
501 dependent loss pathway (Menge, 2011) because it is proportional to the decomposition of litter.
502 We found that by including DON leaching and reducing the denitrification of NO_3^- (Model 14;
503 Fig. 4), the plant C response to N deposition response increased. Overall it is clear that models
504 with a greater role of turnover-dependent N losses had a greater plant C response to N deposition
505 than models with N loss dominated concentration- dependent pathways; We hypothesize that
506 concentration-dependent pathways are able to more quickly lose N deposition when N

507 availability is elevated, while turnover-dependent pathways increase N retention by requiring N
508 deposition to cycle through the plants and soil before being lost.

509 Another important change to the CLM-CN that was responsible for increasing the
510 $dC_{ACI}/dN_{deposition}$ response in the clm4mod model was the implementation of a less open N cycle
511 (Model 4; Fig. 4). N cycles range from being open to closed depending on the importance of the
512 inputs and outputs of N relative to the internal N cycling fluxes. For example, at steady state in
513 global biogeochemical models, all N fixation inputs are balanced by N losses from the
514 ecosystem. As such, assuming equal stocks of N, models with larger N inputs will have larger
515 outputs at steady state, resulting in faster and a more open N cycle. The degree of openness of
516 the N cycle in an ecosystem is not explicitly specified in ecosystem models; rather, it is
517 controlled by the balance of N inputs to outputs. The magnitude and mechanisms governing N
518 fixation and N losses vary widely among global biogeochemical models, likely indicating that
519 the degree of openness of the N cycle also varies among models. Indeed, in comparison to
520 another global biogeochemical model, in the extra-tropics the clm4cn model reports both a
521 greater role of N availability in the C cycle and greater N fixation (Thornton et al., 2007) than the
522 LM3V model (Gerber et al., 2010). The LM3V model uses a demand- driven approach to N
523 fixation that recognizes that N fixation is limited in closed-canopy temperate and boreal forests
524 (Crews, 1999) rather than the relationship between NPP and N fixation, derived from Cleveland
525 et al. (1999), used in the clm4cn.

526 The net effect of all the modifications (Models 2–15) was to increase the $dC_{ACI}/dN_{deposition}$
527 response to N deposition by increasing the retention of N deposition within the ecosystem, as
528 greater long-term N retention increased the availability of N to plants and allowed them to
529 respond to rising atmospheric CO₂. Retention of N deposition within the five simulated forests at

530 the 4 to 30 yr time horizon in the clm4mod model was between 81 and 95 %, and only 51 to 55
531 % in the clm4cn model. The higher N retention rate in the clm4mod model than the clm4cn
532 model better matches observations from field tracer experiments in which isotopically labeled N
533 (¹⁵N) was added to forests and total isotope recovery was used to measure N retention
534 (Nadelhoffer et al., 1999, 2004; Templer et al., 2012). At the Harvard Forest site, retention of
535 added ¹⁵N in two experiments after 7 yr ranged from 88 to 100%, which compares well to
536 clm4mod (Nadelhoffer et al., 2004; treatments with no additional N fertilization added). In
537 contrast, a ¹⁵N tracer experiment at one of the Michigan sites (MI-B) only recovered 17.5% of
538 added ¹⁵N, which is substantially lower than both the clm4cn and clm4mod models (Zak et al.,
539 2004). This tracer study differed markedly from most others. That is, a meta-analysis of ¹⁵N
540 experiments found that approximately 78 % of added N was recovered in 11 temperate
541 deciduous broadleaf forest ecosystems, and 75 % was recovered across all forests (Templer et
542 al., 2012). A similar analysis on nine sites, many of which were included in the meta-analysis
543 conducted by Templer et al. (2012), found 90 % recovery of ¹⁵N after 1–3 yr of addition
544 (Nadelhoffer et al., 1999). Overall, on the balance of evidence, the increased N retention in the
545 clm4mod better reflects the ¹⁵N retention observed in most temperate forest tracer studies.

546 The net effect of all the modifications also increased synergy between N deposition and
547 atmospheric CO₂ in the clm4mod. Surprisingly, when averaged across all five sites, the increase
548 in NPP resulting from N deposition was similar between the two models in the simulations when
549 rising atmospheric CO₂ was not included (Fig. 5b). However, when rising atmospheric CO₂ was
550 included, the synergy between N deposition and CO₂ led to a larger total response to N
551 deposition in the clm4mod model than clm4cn model. This increase in synergy was due to the
552 greater retention of N deposition in the clm4mod than the clm4cn model. The reduction of N

553 limitation resulting from the additional ecosystem N allowed an enhancement of photosynthesis
554 by the next most limiting resource in the model, CO₂, whereas the clm4cn model remained N
555 limited. Consequently, the clm4mod model exhibited CO₂ fertilization in the simulation with
556 both rising CO₂ and N deposition, enabled in part by rising N deposition. Overall, the increased
557 enhancement of NPP due to synergy between N deposition and CO₂ from 7 % in clm4cn to 30 %
558 in clm4mod led to better correspondence with other studies: a 25 % synergistic effect measured
559 in field-based CO₂ fertilization experiment of needle leaf pine forest (Oren et al., 2001) and a 28
560 % synergistic effect reported by a global modeling analysis using BIOME-BGC model
561 (Churkina et al., 2009). It is important to note that the sites used in the analysis were not in arid
562 environments where soil moisture can regulate N limitation and CO₂ fertilization (Felzer et. al
563 2011). Future studies can expand the analysis beyond temperate deciduous forests and explore
564 how the set of model modifications influences C-N interactions in a range of ecosystem types.

565

566 ***4.2 Response to N fertilization***

567 Overall, the clm4mod either improved or had no impact on the comparison to
568 observations from N fertilization experiments, depending on the metric used in the model
569 evaluation. In this study, we used three metrics to compare model predictions from clm4cn and
570 clm4mod to N fertilization experiments, with each metric testing different aspects of model
571 representation of N limitation. The first metric, the increase of ANPP in response to N
572 fertilization, tested the productivity response, particularly wood and leaf production, to N
573 fertilization. The ANPP response metric showed that, on average, the clm4mod corresponded
574 better to observations than the clm4cn, with particular improvements at the Harvard Forest site.
575 The improved correspondence at the Harvard Forest site was attributable to both a decrease in

576 potential ANPP when N was not limiting (see discussion below) and an increase in the ANPP of
577 the control treatment.

578 However, the ANPP increase metric did not include changes in mortality that were
579 included in the second metric, $dC_{ACI}/dN_{fertilization}$ (i.e. the change in standing stock of
580 aboveground C between years). The model modifications did not have an impact on the mean
581 $dC_{ACI}/dN_{fertilization}$ response to N fertilization and both the clm4mod and clm4cn predicted larger
582 $dC_{ACI}/dN_{fertilization}$ than observed. The two key differences between the ANPP responses and
583 $dC_{ACI}/dN_{fertilization}$ to fertilization were: one, increased mortality from N fertilization in the field
584 studies may not decrease ANPP but will decrease dC/dN , and two, increased foliar production in
585 the models increases ANPP without directly increasing dC/dN . Neither model included
586 mechanisms through which elevated N inputs could increase tree mortality and tissue turnover,
587 and both models predicted an increase in foliar productivity not found in the fertilization
588 experiments (Magill et al.,2004; Pregitzer et al., 2008).

589 The productivity of the N fertilized treatment alone is the third metric describing how
590 productivity responded to N fertilization. The ANPP in the field fertilized plots can be viewed
591 as an approximation of the N unlimited productivity, assuming the fertilization level was high
592 enough to meet plant demand and low enough to prevent negative effects of soil acidification. If
593 so, the measure of N unlimited productivity is a metric that does not test the model response to N
594 per se; rather, it tests the representation of the next most limiting resource in the models.

595 Averaged across all six fertilization experiments, the clm4mod model did improve predictions of
596 ANPP in the fertilized treatment. Higher ANPP in the fertilization treatments in the clm4mod
597 model than the clm4cn model was surprising because the clm4mod model included changes to
598 the CLM-CN 4.0, described in Bonan et al. (2012), that decreased canopy level photosynthesis.

599 Therefore, including the modifications that lowered photosynthesis should have decreased the
600 simulated productivity when N limitation was relieved. However, a key difference between the
601 clm4cn and clm4mod models was that the simulated N fertilization experiments relieved N
602 limitation in the clm4mod simulations while it did not in the clm4cn simulations, potentially due
603 to the high ecosystem retention of N in the clm4mod. Table 4 shows that the N unlimited ANPP
604 in the clm4mod did not differ from the ANPP in the fertilization simulations, while the N
605 unlimited ANPP in the clm4cn was 77 % greater than the ANPP in the fertilization simulations.
606 The low ecosystem retention of N in the clm4cn maintained N limitation even at fertilization
607 levels over double net N mineralization rates.

608 One important caveat when using N fertilization studies to evaluate C-N interactions in
609 models is accounting for potential harmful affects of fertilization-induced inorganic N leaching
610 on base cation exchange and forest health (i.e., Hogberg et al. 2007; Wallace et al. 2007). The
611 clm4mod simulates greater inorganic N leaching than the clm4cn (Table A2). This increased N
612 leached would likely lead to greater cation depletion and acidification. However, neither clm4cn
613 nor clm4mod simulates other element cycles, such as calcium and aluminum, nor links between
614 soil solution chemistry and growth or mortality needed to mechanistically represent the negative
615 impacts of N leaching on forest productivity and tree survival. While some N fertilization
616 studies across the Northeast US have reported harmful impacts of N fertilization (e.g. Wallace et
617 al. 2007; Magill et al. 2004 – Pine site; McNulty et al. 2005), all of the studies used in this
618 analysis yielded neutral or positive effects of fertilization on ANPP and C accumulation (Magill
619 et al. 2004; Pregitzer et al. 2008).

620

621 ***4.3 Implications***

622 The set of model simulations presented in this study also provide insight into the
623 observational data. The reported dC/dN was lower for the fertilization experiments than for the
624 dC/dN from N deposition gradients (Table 3). Furthermore, there was a lower reported dC/dN in
625 gradient studies in Europe than in the US (Table 3). Despite these disparities, we show that the
626 reported dC/dN data are reconcilable if the differences in the magnitude and time-scale of N
627 additions are considered. The clm4mod model simulations overlapped or were near the
628 uncertainty bounds in the observations across the different times scales and magnitudes of N
629 additions. The N deposition gradient studies measured the response to lower N inputs over a
630 longer period of time (decades to a century), while the N fertilization experiments measured the
631 response to higher inputs over a shorter time scale (years to decades). This indicates that the
632 differences in ecosystem N use efficiencies reported for different fertilization studies and N
633 deposition gradients may be explained by differences in the magnitude and time scale of N
634 addition.

635 Overall, the substantial increase in C storage response to N deposition that occurred as a
636 result of modifications to the CLM-CN 4.0 model resulted in a better comparison to observations
637 of temperate broadleaf forest growth across N deposition gradients and to N fertilization
638 experiments. The improved sensitivity to N inputs was driven primary by altering the
639 mechanisms governing plant N uptake and the pathways of N loss. At the global scale, the
640 modifications to CLM-CN presented are likely to improve the model correspondence to the
641 globally distributed set of N fertilization experiments, ^{15}N tracer studies, and small catchment N
642 budgets that have been previously used to benchmark global biogeochemical models (Thomas,
643 2013). Furthermore, we show that due to non-linearity in ecosystem response to N addition,
644 testing models with both the response to gradual increases in N inputs over decades (N

645 deposition) and N pulse additions of N over multiple years (N fertilization) allows for greater
646 understanding of the mechanisms governing C-N coupling.

647

648 *Acknowledgements*

649 We would like to thank Cayelan Carey, Timothy Fahey, and Natalie Mahowald for helpful
650 comments on the manuscript. Eric Kluzek, Dan Ricutto, and Peter Thornton provided assistance
651 with the CLM-CN simulations. National Science Foundation (NSF) awards to Peter Hess et al.
652 (NSF-ETBC award #1021613), the NSF IGERT in Cross-Scale Biogeochemistry and Climate,
653 and the Cornell Biogeochemistry and Environmental Biocomplexity Small Grant Program
654 financially supported the project. NCAR is sponsored by the National Science Foundation. We
655 thank the researchers at the Harvard Forest Chronic Nitrogen Amendment Study and the
656 Michigan Nitrogen Deposition Gradient Study for their hard work producing the N fertilization
657 data cited in this study.

658 **Appendix A**

659 *clm4mod model description*

660 The clm4mod model includes changes to the canopy scaling of photosynthesis, maximum
661 photosynthetic rates, radiative transfer, leaf photosynthesis, and stomatal conductance described
662 in Bonan et al. (2012) and (2011). Additional modifications are described below.

663

664 *AI Nitrogen uptake by plants*

665 Plant uptake of inorganic nitrogen (N) in CLM-CN 4.0 (“clm4cn”) is based on the N required to
666 match the demand set by N unlimited photosynthesis (i.e. potential gross primary productivity)
667 and plant tissue C:N stoichiometric constraints. In the clm4cn model, N uptake is independent of
668 allocation to fine root mass. The clm4mod model represents N uptake as a function of fine root
669 carbon (C) mass (C_{root}), soil inorganic N availability ($\text{NH}_{4,\text{av}} + \text{NO}_{3,\text{av}}$), soil temperature ($f(T)$),
670 and plant demand for N ($f(N_{\text{labile}})$).

671

$$U_{N,\text{plant}} = V_{n,\text{max}} \frac{\text{NH}_{4,\text{av}} + \text{NO}_{3,\text{av}}}{(\text{NH}_{4,\text{av}} + \text{NO}_{3,\text{av}}) + K_{\text{min}}} C_{\text{root}} f(N_{\text{labile}}) f(T)$$

672

673 where $f(N_{\text{labile}})$ down regulates the uptake capacity based on the stock of labile N in the plant. As
674 N_{labile} approaches one year’s worth of N turnover of live tissue (x ; leaves, fine roots, and live
675 wood), the maximum uptake capacity decreases. The down regulation function is based on Aber
676 et al. (1997).

677

$$f(N_{\text{labile}}) = \sqrt{1 - \frac{N_{\text{labile}}}{x}}$$

678

679 The temperature function $f(T)$, is the same function governing soil decomposition, nitrification
680 (see below), and denitrification (see below). $\text{NH}_{4,\text{av}}^+$ $\text{NO}_{3,\text{av}}$ are the concentrations of ammonium
681 and nitrate that are available for plant uptake (see below). V_{nmax} is the maximum uptake capacity
682 at 25 °C when N demand was large (i.e. $f(\text{N}_{\text{labile}})=1$). K_{min} is the half saturation constant for plant
683 uptake.

684 The availability of N within the plant for growth is buffered so that a proportion (2 %) of
685 the labile N pool is available to build plant tissue.

686

687 ***A2 Fine root turnover***

688 In the clm4cn model, the turnover of fine root C is linked to the turnover of leaf C. In the
689 clm4mod version, the root turnover is an explicit parameter and is decoupled from leaf turnover.
690 Root turnover occurs throughout the year, rather than only when leaves senesce. Root turnover is
691 maintained at the same rate as the clm4cn model for all species (1.0yr^{-1}), except boreal and
692 temperate needleleaf species, which has a turnover of 0.3 yr^{-1} based on White et al. (2000).
693 Decoupling fine root turnover from leaf turnover allows fine roots to be present throughout the
694 year and permits a fast response of plant N uptake in the spring.

695

696 ***A3 Soil N dynamics***

697 The clm4mod version of the model includes soil inorganic pools of NH_4^+ and NO_3^- , rather than
698 a single inorganic N pool, as implemented in the clm4cn model. The NH_4^+ pool is buffered to
699 represent an exchangeable pool and a pool in solution that is available for plants, immobilization,
700 nitrification, and leaching.

$$NH_{4,av} = b_{NH_4}NH_4$$

701
 702 where b_{NH_4} is assumed to be 10 % of total soil NH_4^+ (Gerber et al., 2010). Constant buffering
 703 capacity is a first approximation for a more complex process of resorption/desorption. Future
 704 model development could parameterize non-linearity into the buffering capacity that is a function
 705 of the total soil organic matter and the bulk density of the soil. NO_3^- is assumed to have no
 706 buffering capacity in the soil therefore
 707 $NO_{3,av}=NO_3^-$.

708
 709 ***A4 Internal N cycling***

710 The clm4mod model assumes that microbes have priority for soil inorganic N to meet the
 711 immobilization demand. Plant uptake and immobilization of N is divided between NH_4^+ and
 712 NO_3^- in proportion to the availability of each N species ($NH_{4,av}$; $NO_{3,av}$). The conversion of NH_4^+
 713 to NO_3^- (nitrification) is represented as function of net N mineralization, NH_4^+ availability,
 714 temperature, and water availability based on Parton et al. (2001). Nitrifiers are assumed to be less
 715 competitive for NH_4^+ than plants and immobilization into soil organic matter

$$N_{nitr} = K_{nitr1}N_{mineralization} + K_{nitr2}NH_{av,nitr}f(T)f(W)$$

717
 718 where the $NH_{4,av,nitr}$ is the NH_4^+ available for nitrification

$$NH_{4,av,nitr} = NH_{4,av} - U_{NH_4,plant} - U_{NH_4,soil}$$

720

721 K_{nitr1} , K_{nitr2} , $f(T)$, and $f(W)$ are the proportion of net mineralization that is nitrified, maximum
 722 nitrification rate (s^{-1}) based on available $NH_{4,av,nitr}$, temperature modifier, and water availability
 723 modifier, respectively. $f(T)$ and $f(W)$ are the same temperature and water functions that
 724 modified decomposition and plant N uptake (Thornton et al., 2007, 2009). The clm4mod model
 725 ignores the effect of pH on nitrification (Parton et al., 1996). A proportion (0.02) of the
 726 nitrification is lost to N_2O and not converted to NO_3^- (Parton et al., 2001).

727 ***A5 Inorganic N loss***

728 In the clm4mod model, the leaching of NH_4^+ is a function of the soil water drainage and
 729 $NH_{4,av}$, minus the NH_4^+ uptake by plants, immobilization, and nitrifiers during the model time
 730 step. Likewise, the leaching of NO_3^- is a function of the soil water drainage and NO_3^- , minus the
 731 NO_3^- taken up by plants and immobilization during the model timestep.

732 The loss of NO_3^- through denitrification is modeled as a function of the available nitrate
 733 $NO_{3,av}$ (minus nitrate uptake by plants, immobilization, and leaching), the ratio of soil water to
 734 saturated soil water, and total respiration from soil organic matter decomposition (a proxy for
 735 microbial activity and oxygen composition; $CO_{2,soil}$). The representation is described in
 736 Bradbury et al. (1993) and Yang et al. (2010).

737

$$N_{denit} = DCO_{2,soil}NO_{3,av}\frac{W}{W_s}$$

738

739 where D is the denitrification rate per g of CO_2 respiration of soil organic matter, the W is soil
 740 water in the top five soil layers and W_s is water holding capacity at saturation.

741

742 ***A6 Biological N fixation***

743 The biological N fixation in temperate and boreal forests is modified to better represent
 744 observations that N fixing tree species are largely absent from mid- to late- successional forests,
 745 but can be present in earlier successional forests (Crews, 1999). Based on biome specific data on
 746 N fixation and evapotranspiration in Cleveland et al. (1999), annual non-symbiotic fixation is a
 747 function of annual evapotranspiration and occurs in all ecosystems:

$$N_{fix,nonsym} = 0.0006AAET + 0.0117$$

748
 749 where AAET is annual evapotranspiration of the previous year. Non-symbiotic N fixation
 750 is added to the soil NH_4^+ pool.

751 Symbiotic N fixation is function of the plant functional type, proportion of grid cell
 752 occupied by the plant function type, leaf area index, and annual evapotranspiration. Symbolic N
 753 fixed is determined by subtracting the non-symbiotic relationship described above from the
 754 relationship between total N fixation and evapotranspiration in Cleveland et al. (1999: central
 755 relationship; Figure A1). In grasslands and tropical ecosystems, symbiotic N fixation is added to
 756 the plant labile N pool. In temperate and boreal forests with leaf area index < 1 , symbiotic N
 757 fixation is also added to the plant labile N pool, as they are assumed to be early successional and
 758 contain some N fixing plants. No symbiotic N fixation is added to the plant labile N pool in
 759 temperate and boreal forest with leaf area index ≥ 1 . The overall relationship describing
 760 symbiotic N fixation is

$$N_{fix,sym} = \begin{cases} w_{pft}(0.0018AAET - 0.0289) & \text{temperate or boreal trees and LAI} < 1 \\ 0 & \text{temperate or boreal trees and LAI} \geq 1 \\ w_{pft}(0.0018AAET - 0.0289) & \text{all other pfts} \end{cases}$$

762

763 where w_{pft} is the proportion of the grid cell occupied by the plant functional type. N fixation is
764 constrained to be $\geq 0 \text{ g N m}^{-2} \text{ yr}^{-1}$

765

766 ***A7 Dissolved organic matter dynamics***

767 Dissolved organic N losses can be important for maintaining N limitation (Menge, 2011),
768 especially in ecosystems with low anthropogenic N inputs (Hedin et al., 1995). A simple
769 representation of the production and leaching of dissolved organic matter is added to the CLM-
770 CN. As presented in Gerber et al. (2010), DOM production is assumed to be a fraction of the
771 turnover of the structural litter pool. In the clm4mod model, DOM production is parameterized to
772 be 1.5% (p_{dom}) of the transfer from the lignin-based litter pool (Litter 3) to its receiving soil
773 organic matter pool (SOM 3). So that DOM production does not alter the decomposition rate of
774 the litter pool, the C : N ratio of DOM must equal that of receiving SOM pool. Therefore, the C :
775 N of DOM is set to be 10 : 1 (CN_{DOM}). Future research should focus on improving the
776 representation of DOM production so that the C : N better match observations (i.e. more C
777 produced for the same N production). However, increasing the C : N ratio of the DOM while
778 maintaining the same production of DON will likely have little effect on N cycle. All DOM
779 produced is assumed to be unavailable for plant uptake and immobilization. The leaching of
780 DOM is based on the water drainage and the total soil water.

781 **Appendix B. Model descriptions for intermediary models used in sensitivity analysis**

782 The series of intermediary models using to the sensitivity analysis are described below:

783

784 **Model 1 (*clm4cn*):** Model 1 is the same as the *clm4cn* model described in the main text.

785

786 **Model 2 (*Model 1 + Multi-layer canopy*):** Model 2 adds modifications to the canopy
787 scaling of photosynthesis using a multi-layer approach with updated maximum photosynthetic
788 rates, radiative transfer, leaf photosynthesis, stomatal conductance described in Bonan et al.
789 (2012) and (2011). Model 2 uses Kattge et al. (2009) values for V_{cmax} (see main text).

790

791 **Model 3 (*Model 2 + soil buffering*):** Model 3 adds a soil buffering parameter to Model
792 2. The soil buffering assumes that 19 % of the generic soil inorganic N pool is available for plant
793 uptake, immobilization into soil organic matter, leaching, and denitrification. The parameter (19
794 %) was chosen to represent a distribution of the generic soil inorganic N pool into 90% NH_4^+ and
795 10% NO_3^- with the same buffering parameters used in the *clm4mod* model. By assuming 10 %
796 of N is NO_3^- , the model is consistent with the preexisting parameterization of N available for
797 leaching losses in Models 1 and 2.

798

799 **Model 4 (*Model 3 + less open N cycle*):** Model 4 creates a less open N cycle by reducing N
800 fixation (see Appendix A6). To isolate the impact of a less open N cycle rather from the
801 sensitivity to N reduced N inputs, we decreased the proportion of excess soil inorganic N that
802 was loss as denitrification (from 0.50 day^{-1} to 0.0475 day^{-1}) to maintain the same pre-industrial
803 productivity as Model 3.

804

805 **Model 5 (Model 4 + reduced denitrification):** Model 5 reduces the proportion of excess N that is
806 lost through denitrification (0.013 day^{-1}), setting the pre-industrial steady state equal to
807 clm4mod.

808

809 **Model 6 (Model 5 + Michaelis-Menten approach to plant N uptake):** Model 5 adds the
810 Michaelis-Menten approach (described in Appendix A1) for simulating plant N uptake. The
811 parameters used are listed in Table A1. N uptake is only allowed to occur when vegetation is
812 photosynthesizing, thus matching the diurnal cycle of N uptake found in Models 1–5. To
813 maintain the same pre-industrial steady state as model clm4mod, the proportion of excess N that
814 is denitrified was set to 0.0011 day^{-1} .

815

816

817 **Model 7 (Model 6 + N uptake throughout day):** Model 7 is equivalent to Model 6 except that N
818 uptake is allowed to occur throughout the day when leaves are present. To maintain the same
819 pre-industrial steady state as clm4mod, the proportion of excess N that is denitrified was set to
820 0.00165 day^{-1} .

821

822 **Model 8 (Model 7 + priority to microbial immobilization):** In Models 1–7 competition between
823 plant N uptake and microbial N uptake was based on the relative N demand by the two
824 processes. Soil inorganic N is distributed based on the relative demand. In the Model 8,
825 microbial immobilization is given first priority to the soil inorganic N required meet its demand

826 for N. To maintain the same pre-industrial steady state as clm4mod, the proportion of excess N
827 that is denitrified was set to 0.0022 day^{-1} .

828
829 **Model 9 (Model 8 + temperate and soil water limitation of denitrification):** In Models 1–8, the
830 proportion of excess N that is denitrified depended only available N. Model 9 limits
831 denitrification based on soil water and soil temperature (see Appendix A5). To maintain the
832 same pre-industrial steady state as clm4mod, the proportion of excess N that is denitrified was
833 set to 0.0011 day^{-1} .

834
835
836 **Model 10 (Model 9 + removed N gas loss that is proportion to net N mineralization):** Model
837 10 removes the turnover-dependent pathway of N loss by setting the proportion of net N
838 mineralization lost as N gas to zero. To maintain the same pre-industrial steady state as
839 clm4mod, the proportion of excess N that is denitrified, a concentration-dependent N loss
840 pathway, was set to 0.029 day^{-1} .

841
842 **Model 11 (Model 10 + NH_4^+ pool, NO_3^- pool, and nitrification):** Model 11 separates
843 the generic soil inorganic N pool in Models 1–10 into NH_4^+ and NO_3^- pools. Model 11 also adds
844 the nitrification process described in Appendix A4. To maintain the same pre-industrial steady
845 state as clm4mod, the proportion of NO_3^- that is denitrified was set to 0.17 day^{-1} .

846
847 **Model 12 (Model 11 + Denitrification a function of heterotrophic respiration):** Model replaces
848 the temperature limitation of denitrification with a parameter that sets denitrification as a

849 proportion of heterotrophic respiration (see Appendix A5). The proportion is set to 0.097 (g C)^{-1}
850 to maintain the same pre-industrial steady state as clm4mod.

851
852 **Model 13 (Model 12 + N_2O loss that is proportion to nitrification):** Model 13 adds a N_2O loss
853 process where N_2O production is a proportion (0.2) of nitrification (see Appendix A4). To
854 maintain the same pre-industrial steady state as clm4mod, the parameter describing the
855 denitrification rate per g of soil respiration $0.077(\text{gC})^{-1}$.

856
857 **Model 14 (Model 13 + DON leaching):** Model 14 adds the production and leaching of dissolved
858 organic C and N (see Appendix A6). To maintain the same pre-industrial steady state as
859 clm4mod, the parameter describing the denitrification rate per g of soil
860 respiration was set to $0.05(\text{gC})^{-1}$.

861
862 **Model 15 (Model 14 + plant N buffering, clm4mod):** Model 15 includes all the
863 changes described for the clm4mod model (main text and Appendix A). It adds to Model 14 a
864 plant labile N pool that buffers the availability of N to meet the N demand set by the
865 photosynthetic rate, tissue allocation, and tissue C : N ratios (see Appendix A1).

866

867

868

869

870 **References**

- 871 Aber, J. D., Ollinger, S. V., and Driscoll, C.: Modeling nitrogen saturation in forest ecosystems
872 in response to land use and atmospheric deposition, *Ecol. Model.*, 101, 61–78, 1997.
- 873 Aber, J. D., McDowell, W. H., Nadelhoffer, K. J., Magill, A. H., Berntson, G., Kamakea, M.,
874 McNulty, S. G., Currie, W., Rustad, L., and Fernandez, I. J.: Nitrogen saturation in
875 temperate forest ecosystems – hypotheses revisited, *Bioscience*, 48, 921–934, 1998.
- 876 Arneeth, A., Harrison, S. P., Zaehle, S., Tsigaridis, K., Menon, S., Bartlein, P. J., Feichter, J.,
877 Korhola, A., Kulmala, M., O’Donnell, D., Schurgers, G., Sorvari, S., and Vesala, T.:
878 Terrestrial biogeochemical feedbacks in the climate system, *Nat. Geosci.*, 3, 525–532, 2010.
- 879 Bonan, G. B. and Levis, S.: Quantifying carbon-nitrogen feedbacks in the Community Land
880 Model (CLM4), *Geophys. Res. Lett.*, 37, L07401, doi:10.1029/2010GL042430, 2010.
- 881 Bonan, G. B., Lawrence, P. J., Oleson, K., Levis, S., Jung, M., Reichstein, M., Lawrence, D. M.,
882 and Swenson, S. C.: Improving canopy processes in the Community Land Model version 4
883 (CLM4) using global flux fields empirically inferred from FLUXNET data, *J. Geophys.*
884 *Res.*, 116, G02014, doi:10.1029/2010JG001593, 2011.
- 885 Bonan, G. B., Oleson, K. W., Fisher, R. A., Lasslop, G., and Reichstein, M.: Reconciling leaf
886 physiological traits and canopy flux data: Use of the TRY and FLUXNET databases in the
887 Community Land Model version 4 (CLM4), *Biogeosciences*, 117, G02026,
888 doi:10.1029/2011JG001913, 2012.
- 889 Bradbury, N., Whitmore, A., Hart, P., and Jenkinson, D.: Modeling the fate of nitrogen in crop
890 and soil in the years following application of ¹⁵N-labeled fertilizer to winter-wheat, *J. Agr.*
891 *Sci.*, 121, 363–379, 1993.
- 892 Butterbach-Bahl, K., Nemitz, E., and Zaehle, S.: Nitrogen as a threat to the European

893 greenhouse balance, in: The European Nitrogen Assessment, edited by: Sutton, M. A., Howard,
894 C. M., Erisman, J. W., Billen, G., Bleeker, A., Grennfelt, P., van Grinsven, H., and Grizzetti,
895 B., Cambridge University Press, Cambridge, 434–462, 2011.

896 Churkina, G., Caldeira, T. R., von Bloh, W., Trusilova, K., Jung, M., and Dentener, F.: Synergy
897 of rising nitrogen depositions and atmospheric CO₂ on land carbon uptake moderately offsets
898 global warming, *Global Biogeochem. Cy.*, 23, GB4027, doi:10.1029/2008GB003291, 2009.

899 Cleveland, C., Townsend, A., Schimel, D. S., Fisher, H., Howarth, R., Hedin, L. O., Perakis, S.,
900 Latty, E., von Fischer, J. C., Elseroad, A., and Wasson, M.: Global patterns of terrestrial
901 biological nitrogen (N₂) fixation in natural ecosystems, *Global Biogeochem. Cy.*, 13, 623–
902 645, 1999.

903 Crews, T. E: The presence of nitrogen fixing legumes in terrestrial communities: evolutionary vs.
904 ecological considerations, *Biogeochemistry*, 46, 233–246, 1999.

905 de Vries, W., Solberg, S., Dobbertin, M., Sterba, H., Laubhahn, D., van Oijen, M., Evans, C. D.,
906 Gundersen, P., Kros, J., Wamelink, G. W. W., Reinds, G. J., and Sutton, M. A.: The impact
907 of nitrogen deposition on carbon sequestration by European forests and heathlands, *Forest
908 Ecol. Manag.*, 258, 1814–1823, 2009.

909 Felzer, B.: Carbon, nitrogen, and water response to climate and land-use changes in
910 Pennsylvania during the 20th and 21st centuries. *Ecological Modelling*, 240, 49-63, 2012

911 Felzer, B. S., Cronin, T. W., Melillo, J. M., Kicklighter, D. W., Schlosser, C. A., and Dangal, S.
912 R. S.: Nitrogen effect on carbon-water coupling in forests, grasslands, and shrublands in the
913 arid western United States. *Journal of Geophysical Research- Biogeosciences* 116, G03023,
914 doi: 10.1029/2010JG001621, 2011

915 Gent, P. R., Danabasoglu, G., Donner, L. J., Holland, M. M., Hunke, E. C., Jayne, S. R.,

916 Lawrence, D. M., Neale, R. B., Rasch, P. J., Vertenstein, M., Worley, P. H., Yang, Z.-L., and
917 Zhang, M.: The Community Climate System Model Version 4, *J. Climate*, 24, 4973–4991,
918 2011.

919 Gerber, S., Hedin, L. O., Oppenheimer, M., Pacala, S. W., and Shevliakova, E.: Nitrogen cycling
920 and feedbacks in a global dynamic land model, *Global Biogeochem. Cy.*, 24, GB1001,
921 doi:10.1029/2008GB003336, 2010.

922 Hedin, L. O., Armesto, J., and Johnson, A.: Patterns of nutrient loss from unpolluted, old-growth
923 temperate forests – evaluation of biogeochemical theory, *Ecology*, 76, 493–509, 1995.

924 Hogberg, P., H. Fan, M. Quist, D. Binkley, and C. Tamm: Tree growth and soil acidification in
925 response to 30 years of experimental nitrogen loading on boreal forest, *Global Change*
926 *Biology*, 12, 489–499, 2006.

927 Hyvonen, R., Persson, T., Andersson, S., Olsson, B., Agren, G. I., and Linder, S.: Impact of
928 long-term nitrogen addition on carbon stocks in trees and soils in northern Europe,
929 *Biogeochemistry*, 89, 121–137, 2008.

930 Janssens, I. A., Dieleman, W., Luyssaert, S., Subke, J.-A., Reichstein, M., Ceulemans, R., Ciais,
931 P., Dolman, A. J., Grace, J., Matteucci, G., Papale, D., Piao, S. L., Schulze, E. D., Tang, J.,
932 and Law, B. E.: Reduction of forest soil respiration in response to nitrogen deposition, *Nat.*
933 *Geosci.*, 3, 315–322, 2010.

934 Kattge, J., Knorr, W., Raddatz, T., and Wirth, C.: Quantifying photosynthetic capacity and its
935 relationship to leaf nitrogen content for global-scale terrestrial biosphere models, *Glob.*
936 *Change Biol.*, 15, 976–991, 2009.

937 Lamarque, J.-F., Kiehl, J., Brasseur, G., Butler, T., Cameron-Smith, P., Collins, W., Collins, W.
938 J., Granier, C., Hauglustaine, D., Hess, P. G., Holland, E. A., Horowitz, L. W., Lawrence,

939 M., McKenna, D., Merilees, P., Prather, M., Rasch, P., Rotman, D., Shindell, D. T., and
940 Thornton, P. E.: Assessing future nitrogen deposition and carbon cycle feedback using a
941 multi- model approach: analysis of nitrogen deposition, *J. Geophys. Res.-Atmos.*, 110,
942 D19303, doi:10.1029/2005JD005825, 2005.

943 Lawrence, D. M., Oleson, K., Flanner, M. G., Thornton, P. E., Swenson, S. C., Lawrence, P. J.,
944 Zeng, X., Yang, Z.-L., Levis, S., Sakaguchi, K., Bonan, G. B., and Slater, A. G.:
945 Parameterization improvements and functional and structural advances in Version 4 of the
946 Community Land Model, *J. Adv. Mod. Earth Sys.*, 3, M03001, doi:10.1029/2005JD005825,
947 2011.

948 Lawrence, P. J., Feddema, J. J., Bonan, G. B., Meehl, G. A., O'Neill, B. C., Oleson, K., Levis,
949 S., Lawrence, D. M., Kluzek, E., Lindsay, K., and Thornton, P. E.: Simulating the
950 biogeochemical and biogeophysical impacts of transient land cover change and wood harvest
951 in the Community Climate System Model (CCSM4) from 1850 to 2100, *J. Climate*, 25,
952 3071–3095, 2012.

953 Liu, L. and Greaver, T. L.: A review of nitrogen enrichment effects on three biogenic GHGs: the
954 CO₂ sink may be largely offset by stimulated N₂O and CH₄ emission, *Ecol. Lett.*, 12, 1103–
955 1117, 2009.

956 Magill, A. H., Aber, J. D., Currie, W., Nadelhoffer, K. J., Martin, M. E., McDowell, W. H.,
957 Melillo, J. M., and Steudler, P.: Ecosystem response to 15 years of chronic nitrogen
958 additions at the Harvard Forest LTER, Massachusetts, USA, *Forest Ecol. Manag.*, 196, 7–28,
959 2004.

960 Magnani, F., Mencuccini, M., Borghetti, M., Berbigier, P., Berninger, F., Delzon, S., Grelle, A.,
961 Hari, P., Jarvis, P. G., Kolari, P., Kowalski, A. S., Lankreijer, H., Law, B. E., Lindroth, A.,

962 Loustau, D., Manca, G., Moncrieff, J. B., Rayment, M., Tedeschi, V., Valentini, R., and
963 Grace, J.: The human footprint in the carbon cycle of temperate and boreal forests, *Nature*,
964 447, 848–850, 2007

965 McNulty, S. G., Boggs J., Aber, J. D., Rustad L., and Magill, A. H: Red spruce ecosystem level
966 changes following 14 years of chronic N fertilization. *Forest Ecology and Management*, 219,
967 279–291, 2005.

968 Menge, D. N. L.: Conditions under which nitrogen can limit steady-state net primary production
969 in a general class of ecosystem models, *Ecosystems*, 14, 519–532, 2011.

970 Nadelhoffer, K. J., Emmett, B. A., Gundersen, P., Kjonaas, O. J., Koopmans, C., Schleppi, P.,
971 Tietema, A., and Wright, R. F.: Nitrogen deposition makes a minor contribution to carbon
972 sequestration in temperate forests, *Nature*, 398, 145–148, 1999.

973 Nadelhoffer, K. J., Colman, B., Currie, W., Magill, A. H., and Aber, J. D.: Decadal-scale fates of
974 ¹⁵N tracers added to oak and pine stands under ambient and elevated N inputs at the Harvard
975 Forest (USA), *Forest Ecol. Manag.*, 196, 89–107, 2004.

976 Oren, R., Ellsworth, D., Johnsen, K., Phillips, N., Ewers, B., Maier, C., Schafer, K., McCarthy,
977 H., Hendrey, G., McNulty, S. G., and Katul, G.: Soil fertility limits carbon sequestration by
978 forest ecosystems in a CO₂-enriched atmosphere, *Nature*, 411, 469–472, 2001.

979 Parton, W., Holland, E., Del Grosso, S., Hartman, M., Martin, R., Mosier, A., Ojima, D., and
980 Schimel, D. S.: Generalized model for NO_x and N₂O emissions from soils, *J. Geophys. Res.-*
981 *Atmos.*, 106, 17403–17419, 2001.

982 Pinder, R. W., Davidson, E. A., Goodale, C. L., Greaver, T. L., Herrick, J. D., and Liu, L.:
983 Climate change impacts of US reactive nitrogen, *P. Natl. Acad. Sci. USA*, 15, 7671–7675,
984 2012.

985 Pregitzer, K. S., Burton, A. J., Zak, D. R., and Talhelm, A. F.: Simulated chronic nitrogen
 986 deposition increases carbon storage in Northern Temperate forests, *Glob. Change Biol.*, 14,
 987 142–153, 2008.

988 Qian, T., Dai, A., Trenberth, K. E., and Oleson, K. W.: Simulation of global land surface
 989 conditions from 1948 to 2004, Part I: forcing data and evaluations, *J. Hydrometeorol.*, 7,
 990 953–975, 2006.

991 Raich, J. W., Rastetter, E. B., Melillo, J. M., Kicklighter, D. W., Steudler, P. A., Peterson B. J.,
 992 Grace, A. L., Moore III, B., and Vorosmarty, C. J.: Potential Net Primary Productivity in
 993 South America: Application of a Global Model. *Ecological Applications* 1:399–429, 1991.

994 Sokolov, A. P., Kicklighter, D. W., Melillo, J. M., Felzer, B. S., Schlosser, C. A., and Cronin, T.
 995 W.: Consequences of considering carbon nitrogen interactions on the feedbacks between
 996 climate and the terrestrial carbon cycle, *J. Climate*, 21, 3776–3796, 2008.

997 Sutton, M. A., Simpson, D., Levy, P. E., Smith, R. I., Reis, S., van Oijen, M., and de Vries, W.:
 998 Uncertainties in the relationship between atmospheric nitrogen deposition and forest carbon
 999 sequestration, *Glob. Change Biol.*, 14, 2057–2063, 2008.

1000 Templer, P. H., Mack, M. C., Chapin III, F. S., Christenson, L. M., Compton, J. E., Crook, H. D.,
 1001 Currie, W. S., Curtis, C. J., Dail, D. B., D’Antonio, C. M., Emmett, B. A., Epstein, H.,
 1002 Goodale, C. L., Gundersen, P., Hobbie, S. E., Holland, K., Hooper, D. U., Hungate, B. A.,
 1003 Lamontagne, S., Nadelhoffer, K. J., Osenberg, C., Perakis, S., Schleppei, P., Schimel, J.,
 1004 Schmidt, I. K., Sommerkorn, M., Spoelstra, J., Tietema, A., Wessel, W., and Zak, D. R.:
 1005 Sinks for nitrogen inputs in terrestrial ecosystems: a meta-analysis of ¹⁵N tracer field studies,
 1006 *Ecology*, 93, 1816–1829, 2012.

1007 Thomas, R. Q.: Nitrogen Constraints on Terrestrial Carbon Sequestration, From Trees to the

1008 Globe, Ph. D. dissertation, Department of Ecology and Evolutionary Biology, Cornell
1009 University, Ithaca, NY, USA, 162 pp., 2013.

1010 Thomas, R. Q., Canham, C. D., Weathers, K. C., and Goodale, C. L.: Increased tree carbon
1011 storage in response to nitrogen deposition in the US, *Nat. Geosci.*, 3, 13–17, 2010.

1012 Thornton, P. E. and Rosenbloom, N. A.: Ecosystem model spin-up: Estimating steady state
1013 conditions in a coupled terrestrial carbon and nitrogen cycle model, *Ecol. Model.*, 189, 25–
1014 48, 2005.

1015 Thornton, P. E., Law, B. E., Gholz, H., Condit, M. T., Falge, E., Ellsworth, D., Golstein, A.,
1016 Monson, R. K., Hollinger, D. Y., Falk, M., Chen, J., and Sparks, J. P.: Modeling and
1017 measuring the effects of disturbance history and climate on carbon and water budgets in
1018 evergreen needleleaf forests, *Agr. Forest Meteorol.*, 113, 185–222, 2002.

1019 Thornton, P. E., Lamarque, J.-F., Rosenbloom, N. A., and Mahowald, N. M.: Influence of
1020 carbon- nitrogen cycle coupling on land model response to CO₂ fertilization and climate
1021 variability, *Global Biogeochem. Cy.*, 21, GB4018, doi:10.1029/2006GB002868, 2007.

1022 Thornton, P. E., Doney, S. C., Lindsay, K., Moore, J. K., Mahowald, N., Randerson, J. T., Fung,
1023 I., Lamarque, J.-F., Feddema, J. J., and Lee, Y.-H.: Carbon-nitrogen interactions regulate
1024 climate-carbon cycle feedbacks: results from an atmosphere-ocean general circulation
1025 model, *Biogeosciences*, 6, 2099–2120, doi:10.5194/bg-6-2099-2009, 2009.

1026 Tian, H., Melillo J., Lu, C., Kicklighter D., Liu, M., Ren, W., Xu, X., Chen, G., Zhang, C., Pan,
1027 S., Liu, J., and Running, S.: China’s terrestrial carbon balance: contributions from multiple
1028 global change factors. *Global Biogeochemical Cycles* 25, GB1007, doi:
1029 10.1029/2010GB003838, 2011.

1030 Wallace, Z. P., Lovett, G. M., Hart, J. E., and Machona, B.: Effects of nitrogen saturation on tree

1031 growth and death in a mixed-oak forest, *Forest Ecol. Manag.*, 243, 210–218, 2007.

1032 Yang, X., Wittig, V., Jain, A. K., and Post, W. M.: Integration of nitrogen cycle dynamics into
1033 the Integrated Science Assessment Model for the study of terrestrial ecosystem responses to
1034 global change, *Global Biogeochem. Cy.*, 23, GB4029, doi:10.1029/2009GB003474, 2009.

1035 Zaehle, S. and Dalmonech, D.: Carbon–nitrogen interactions on land at global scales: current
1036 understanding in modelling climate biosphere feedbacks, *Curr. Opin. Environ. Sust.*, 3, 311–
1037 320, 2011.

1038 Zaehle, S. and Friend, A. D.: Carbon and nitrogen cycle dynamics in the O-CN land surface
1039 model: 1. Model description, site-scale evaluation, and sensitivity to parameter estimates,
1040 *Global Biogeochem. Cy.*, 24, GB1005, doi:10.1029/2009GB003521, 2010.

1041 Zaehle, S., Friend, A. D., Friedlingstein, P., Dentener, F., Peylin, P., and Schulz, M.: Carbon and
1042 nitrogen cycle dynamics in the O-CN land surface model: 2. Role of the nitrogen cycle in the
1043 historical terrestrial carbon balance, *Global Biogeochem. Cy.*, 24, GB1006,
1044 doi:10.1029/2009GB003522, 2010a.

1045 Zaehle, S., Friedlingstein, P., and Friend, A. D.: Terrestrial nitrogen feedbacks may accelerate
1046 future climate change, *Geophys. Res. Lett.*, 37, L01401, doi:10.1029/2009GL041345,
1047 2010b.

1048 Zaehle, S., Ciais, P., Friend, A. D., and Prieur, V.: Carbon benefits of anthropogenic reactive
1049 nitrogen offset by nitrous oxide emissions, *Nat. Geosci.*, 4, 601–605, 2011.

1050 Zak, D. R., Pregitzer, K. S., Holmes, W. E., Burton, A. J., and Zogg, G. P.: Anthropogenic N
1051 deposition and the fate of $^{15}\text{NO}_3^-$ in a northern hardwood ecosystem, *Biogeochemistry*, 69,
1052 143–157, 2004.

1053

Tables

Table 1: Descriptions of sites used in model simulations.

Site	Harvard Forest	Michigan gradient A	Michigan gradient B	Michigan gradient C	Michigan gradient D
Code	HF	MI-A	MI-B	MI-C	MI-D
Latitude (N)	42° 30' N	46° 52'	45° 33'	44° 23'	43° 40'
Longitude (W)	72° 10' W	88° 53'	84° 51'	85° 50'	86° 09'
Stand Age (years) [^]	52	97	91	92	96
MAT* (°C)	7.1	4.7	6.0	6.9	7.6
MAP [#] (mm)	1120	873	871	888	812
Aboveground carbon (g C m ⁻²) [^]	6597	14,700	14,150	15,800	14,450
Vegetation type	temperate deciduous broadleaf				
Years of experiment	1988-2002	1995-2004	1995-2004	1995-2004	1995-2004
Nitrogen fertilization rate (g N m ⁻² yr ⁻¹)	5 & 15	3	3	3	3
Nitrogen deposition (g N m ⁻² yr ⁻¹)	0.8	0.68	0.91	1.17	1.18
Citation	Magill et al. 2004	Pregitzer et al. 2008			

* Mean annual temperature

Mean annual precipitation

[^] Age and carbon stocks in the year 1994

Table 2. Description of simulations and years of driver data used in each simulation

Simulation ¹	N deposition	N fertilization	CO ₂ concentration
(1) Control (baseline)	1850-2004	None	1850-2004
(2) Hold N deposition	1850	None	1850-2004
(3) Elevated N deposition; EU N deposition gradient	1850-2004; values more similar to EU deposition levels	None	1850-2004
(4) Hold N deposition and CO ₂	1850	None	1850
(5) Hold CO ₂	1850-2004	None	1850
(6) N fertilization	1850-2004	Yrs. of field study, rate of study (see Table 1)	1850-2004
(7) Non-N limited	1850-2004	Yrs. of field study, rate necessary to match N demand	1850-2004

¹ All simulations included transient land-use with a harvest at the year that yields the observed stand age in 1994 (see Table 1)

Table 3. Model simulations and observations of the vegetation and ecosystem carbon increment response to nitrogen deposition and fertilization. Model uncertainty estimates correspond to variation among sites (1 S.E.).

Response metric	Carbon measurement	Nitrogen input	clm4cn model	clm4mod model	Observations	Citation
$dC_{ACI}/dN_{deposition}$	Aboveground carbon increment	U.S. deposition gradient	14.0±1.1	34.2±3.0	50 (41-66)	Thomas et al. 2010*
$dC_{ACI}/dN_{deposition}$	Aboveground carbon increment	E.U. deposition gradient	11.8±0.8 [#]	26.2±2.6 [#]	15-40	DeVries et al. 2009
$dC_{ACI}/dN_{fertilization}$	Aboveground carbon increment	Fertilization experiments	10.7±1.3	10.6±4.5	4±2.7	Magill et al. 2004, Pregitzer et al. 2008
$dC_{NEP}/dN_{deposition}$	Net ecosystem production	U.S. deposition gradient	30.0±1.8	74.1±8.17	no data	
$dC_{NEP}/dN_{deposition}$	Net ecosystem production	E.U. deposition gradient	24.5±1.5 [#]	49.5±4.4 [#]	50-75	Sutton et al. 2008
$dC_{NEP}/dN_{fertilization}$	Net ecosystem production	Fertilization experiments	27.9±2.8	23.2±9.4	31 ± 10	Magill et al. 2004, Pregitzer et al. 2008

* The reported 61 dC/dN was divided by a factor of 1.23 to account for unmeasured nitrogen deposition. See Pinder et al. (2012) for more information.

These model simulations used higher N deposition (1994-2004 mean = 2.2 g N m⁻² yr⁻¹) to approximate nitrogen deposition in regions that have experience higher historical N deposition loads.

Table 4. Description of model modifications. Letters (a–l) refer to the processes shown in Fig. 1.

Model	Model modifications
Model 1	Same as clm4cn
Model 2	Decreased plant N uptake (d) by reducing the canopy photosynthesis (Bonan et al., 2011, 2012)
Model 3	Buffered the soil inorganic N available for immobilization (c) and plant N uptake (d).
*Model 4	Introduced a less open N cycle by decreasing denitrification (f) and N fixation (h). Maintains same pre-industrial steady-state as model 3.
*Model 5	Decreased denitrification (f) to increase productivity to match pre-industrial steady state of the models 5–15. Isolates the influence of higher baseline (pre-industrial steady-state) primary productivity on the N deposition response.
*Model 6	Replaced (d) with a Michaelis-Menten approach to modeling plant N uptake. N uptake only occurs when the plants are photosynthesizing. Adjusted (f) to maintain same pre-industrial steady-state as models 5–15.
Model 7	Same as model 6 except plant N uptake also occurs at night when plants are not photosynthesizing. Adjusted (f) to maintain same pre-industrial steady-state as models 5–15.
*Model 8	Altered immobilization (c) and plant N uptake (d) by allowing immobilization to have first access to soil inorganic N. Adjusted (f) to maintain same pre-industrial steady-state as models 5–15.
Model 9	Added temperature and soil water limitations to denitrification (f). Adjusted (f) to maintain same pre-industrial steady-state as models 5–15.
*Model 10	Removed the N gas loss (g) that was proportional to net N mineralization (b–c). Adjusted (f) to maintain same pre-industrial steady-state as models 5–15.
*Model 11	Added NH_4^+ and NO_3^- pools; added nitrification (j). Adjusted (f) to maintain same pre-industrial steady-state as models 5–14.
Model 12	Replaced temperature limitation of denitrification (f). Now proportional to SON & litter N respiration. Adjusted (f) to maintain same pre-industrial steady-state as models 5–15.
Model 13	Added N_2O loss (k) that is proportional to nitrification (i). Adjusted (f) to maintain same pre-industrial steady-state as models 5–15.
Model 14	Added dissolved organic N leaching (l). Proportional to the turnover of lignin litter pool. Adjusted (f) to maintain same pre-industrial steady-state as models 5–15.
Model 15 (clm4mod)	Added internal plant N pool to buffer plant N demand. Pre-industrial steady-state for the models 5–14 are calibrated to match model 15. Model 15 is equivalent to clm4mod.

* Denotes the model modifications that had the largest impact on the N deposition response ($> 3 \text{ dC}_{\text{ACI}}/\text{dN}_{\text{deposition}}$). See Fig. 4.

Table 5. Mean annual net primary productivity ($\text{g C m}^{-2} \text{ yr}^{-1}$) in the six nitrogen fertilization experiments at five temperate broadleaf deciduous forests. The field observations are compared to simulations from the clm4cn model, and clm4mod model. Error estimates correspond to variation among sites (1 S.E.).

	Observations	clm4cn	clm4mod
Control ANPP (n = 5)	464 ± 36	352 ± 50	411 ± 28
Fertilized ANPP (n = 6)	504 ± 40	420 ± 41	474 ± 8
Δ ANPP (n = 6) *	55 ± 8	91 ± 19	57 ± 18
Non-nitrogen limited ANPP (n = 6)	Not measured	742 ± 10	474 ± 8

*The mean fertilization responses for the observations and model simulations were different than the difference between the mean control and mean fertilization ANPP because two experiments at Harvard Forest shared the same control treatment

Table A1. New parameters introduced to the CLM-CN 4.0.

Parameter	Value	Units	Description	Reference
V_{nmax}	$2.7 \cdot 10^{-8}$	$g\ N\ g\ C^{-1}\ sec^{-1}$	Maximum N uptake per unit fine root C at 25C	none
K_{min}	1	$gN\ m^{-2}$	Half saturation constant for plant nitrogen uptake	Yang et al. 2010
x	1	proportion	Proportion of 1 years worth of live tissue nitrogen turnover	Gerber et al. 2010
b_{NH4}	0.10	proportion	Proportion of soil NH_4^+ available for plant uptake, immobilization and loss processed	Gerber et al. 2010
b_{NO3}	1	proportion	Proportion of soil NO_3^- available for plant uptake, immobilization and loss processed	Gerber et al. 2010
$b_{nlabile}$	0.02	proportion	Proportion of plant labile nitrogen available to build tissue per 30 minute time step	none
K_{nitr1}	0.2	proportion	Proportion of net mineralization that is nitrified	Parton et al. 2000
K_{nitr2}	0.1	day^{-1}	Maximum proportion of available NH_4^+ nitrified	Parton et al. 2000
K_{n2o}	0.02	proportion	Proportion of nitrification lost as N_2O	Parton et al. 2000
D	0.05	$g\ C^{-1}$	Maximum denitrification rate per g of soil respiration	Bradberry et al. 1993
p_{DOM}	0.015	proportion	Proportion of litter mass transferred from litter 3 pool to soil 3 pool that produces dissolved organic carbon and nitrogen	Gerber et al. 2010

Table A2. Mean simulated pre-industrial nitrogen fluxes ($\text{g N m}^{-2} \text{ yr}^{-1}$) average across all five sites in Table 1 (± 1 S. E.).

Flux	clm4cn	clm4mod
Nitrogen fixation	1.3 ± 0.1	0.26 ± 0.01
Nitrogen deposition	0.15 ± 0.01	0.15 ± 0.01
Nitrogen gas loss	1.4 ± 0.1	0.26 ± 0.01
Mineral nitrogen leaching	0 ± 0	0.07 ± 0.01
DON leaching	NA	0.1 ± 0.004
Plant nitrogen uptake	6.2 ± 0.67	6.9 ± 0.29
Net nitrogen mineralization	6.1 ± 0.66	6.5 ± 0.25
Nitrification	NA	3.6 ± 0.06

Figure captions.

Figure 1. Overview of the clm4cn and clm4mod model structure.

Figure 2. Mean annual aboveground net primary production (ANPP) for the five temperate deciduous forests in Table 1. The measured values, clm4cn model predictions, and clm4mod model predictions are shown for (a) the control (non-fertilized) plots and (b) the nitrogen fertilized plots, along with (c) the differences between the control and fertilized treatments. The model simulations include transient nitrogen deposition, atmospheric CO₂, and land-use. Error bars represent the S. E. reported in Pregitzer et al. (2008).

Figure 3. Model predictions of ecosystem retention of nitrogen deposition, partitioned among soil organic matter and vegetation averaged across all five sites for two time periods: 1970–2004 and 2000–2004. Error bars represent variation among sites (1 S.E.).

Figure 4. The sensitivity of the nitrogen deposition response to key changes in model structure for a single site (Harvard Forest). The figure shows the nitrogen deposition response, expressed as an annual aboveground carbon increment ($dC_{ACI}/dN_{deposition}$) for the clm4cn model (Model 1), clm4mod (Model 15), and intermediary models (Model 2–14). Each model builds on the modifications in the previous models and the difference in $dC_{ACI}/dN_{deposition}$ between a model and the previous model is shown in black. See Table 3 for a description of the mechanisms isolated in each model.

Figure 5. Model predictions of net primary production (NPP) response to rising nitrogen