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## 1 INTRODUCTION

2

3 Nitrogen (N) is an essential nutrient, but reactive N has well-known deleterious effects in high  
4 concentrations. Agriculture and industry have strongly altered the N cycle in ways that impact the  
5 environment from local to global scales by contributing to increasing greenhouse gas emissions, acidic  
6 deposition, and impairing the functioning of ecosystems through the eutrophication of soils and waters.  
7 The N cycle is thus intrinsically coupled with various environmental processes and factors including the  
8 transformation of land-use, energy and food production and consumption, climate change, exploitation of  
9 natural resources, air, soil and water pollution, human health, ecosystem services, and other natural and  
10 anthropogenic drivers (Galloway et al. 2004). Future sustainable management and stewardship of both  
11 less disturbed and highly managed ecosystems require a more integrated approach to the assessment of  
12 linkages between these systems and their interaction with the human society (Collins et al. 2011).

13 Long-term monitoring of N biogeochemistry is a powerful research approach to understanding the  
14 dynamic features of ecosystem behavior influenced by natural and anthropogenic drivers, locally,  
15 regionally and globally. The Long-Term Ecological Research (LTER) program was first established in  
16 early 1980s in the USA. Since then, the LTER has been expanded to many other countries as an  
17 integrated ecological research network that enables long-term site-based research, field experiments, and  
18 database development. The US-LTER has produced important findings on the N dynamics in a broad  
19 geographical range of watersheds and landscapes, including the long-term impact of atmospheric N  
20 deposition on forest ecosystems, the impact of logging on stream N chemistry, the climate impacts on N  
21 cycles in ecosystems, effects on biodiversity, etc. (e.g., Likens et al. 1996; Clark and Tilman 2008;  
22 Fernandez et al. 2010; Groffman et al. 2012; Driscoll et al. 2012). Some European countries have also  
23 conducted long-term environmental monitoring, for example Sweden (e.g., Löfgren, et al. 2011), the UK  
24 (Curtis et al., 2014) and Finland (Rask et al. 2014). In addition to the LTER sites, long-term N

25 experiments have been also been conducted at other sites in the USA and Europe. Examples of European  
26 studies include the NITREX (Gundersen et al. 1998) and climate experiments linked with N dynamics  
27 (e.g., CLIMEX (Wright et al. 1998), CLIMOOR (Beier et al. 2004), and VULCAN (Peñuelas et al.  
28 2007)). Lake manipulation experiments have been undertaken in Canada, Norway, the USA and Finland  
29 (e.g., Carpenter et al 2001; Harris et al. 2014). There have also been a number of snow manipulation  
30 experiments in the USA, Norway and Germany (e.g., Kaste et al. 2008; Wipf and Rixen 2010). While  
31 contributing to our current understanding of N cycling in ecosystems, they also reveal significant gaps in  
32 knowledge which will require a continued commitment to long-term research and a broadening of  
33 international perspectives to address. The LTER program has expanded internationally since the early  
34 1990s and the International LTER (ILTER) was created in 1993. This currently comprises over 600 sites  
35 within 40 member networks, providing great potential for understanding altered N biogeochemistry and  
36 its impact in different environment and socio-ecological settings at an international scale. However,  
37 effective integration of this international effort has been impeded by the absence of a mechanism to bring  
38 the international research community together and the relative paucity of robust and directly comparable  
39 data that could be employed in meta-analyses at global and regional scales. Recent syntheses of nitrogen  
40 issues in the USA and Europe (e.g. Sutton et al. 2011; Suddick and Davidson 2012) bring to the fore the  
41 need to review the contributions that long term environmental research has made to the scientific  
42 understanding of the changing N cycle and consider how it might address the current major gaps in  
43 knowledge. Here we review current understanding of the impact of anthropogenic N on various  
44 ecosystems and environments to elucidate the consequences of globally increased N cycles for coupled  
45 social-ecological systems under a changing climate (Fig. 1). Particular attention is paid to the most recent  
46 trends in anthropogenic reactive N emissions, including: nitrous oxide (N<sub>2</sub>O); the complex interaction of  
47 N with carbon (C), phosphorus (P) and other elements; impacts of N on biodiversity; seasonal and  
48 long-term trends in N biogeochemistry associated with climate variability; the N cascade process from

49 terrestrial to aquatic ecosystem; and finally, societal challenges from ecosystem services to human health.

50 Emerging uncertainties and further research questions are also discussed.

51

## 52 **INCREASED ANTHROPOGENIC NITROGEN EMISSIONS**

53

54 Humans create more reactive N (Nr) than natural ecosystems do (Galloway et al. 2003), principally  
55 nitrogen oxides (NO<sub>x</sub>-N, i.e., sum of N<sub>2</sub>O, NO, and NO<sub>2</sub>) and ammonia (NH<sub>3</sub>), mostly through food and  
56 energy production and consumption and their various byproducts. Reactive N emissions into the  
57 atmosphere contribute to increasing greenhouse gases, acidic deposition, as well as excess inputs of N  
58 nutrients to receiving environments. One of the Nr forms, N<sub>2</sub>O, is an important greenhouse gas with an  
59 exceptionally long atmospheric half-life that is emitted through agricultural activities as well as natural  
60 processes such as denitrification within wetlands. Here we review the long-term trends of Nr and N<sub>2</sub>O  
61 emissions and their current knowledge gaps.

62

### 63 **Global long-term trends in anthropogenic emissions of reactive nitrogen**

64

65 Reactive N emissions associated with human-induced burning of biomass and animal husbandry  
66 have been entering the atmosphere for over 10,000 years. Emissions have increased sharply since the  
67 onset of the industrial revolution due to fossil fuel combustion, while the use of synthetic N-fertilizers  
68 became especially important in the 20<sup>th</sup> century. The global cumulative anthropogenic release of Nr to the  
69 atmosphere over the last 10,000 years has been estimated at ~17.4 Pg N, 28% of which was emitted  
70 during 1850–2000 and 42% during 1–1850 AD (Kopáček and Posch, 2011). Recent global emissions of  
71 NO<sub>x</sub> from anthropogenic and natural sources have been estimated to range from 44 to 50 Tg N yr<sup>-1</sup>, while  
72 the contribution from NH<sub>3</sub> has been estimated at 54 Tg N yr<sup>-1</sup> (Kopáček and Posch, 2011). About 70% of

73 global NH<sub>3</sub> emissions are closely related to food production and agricultural systems, predominantly  
74 livestock production and the use of synthetic N-fertilizers (Kopáček and Posch, 2011). Global Nr  
75 emissions have increased sharply since the 1950s (Fig. 2). Overall, Europe is the only continent where Nr  
76 emissions have begun to decrease in recent years (i.e. since the late 1980s) (Fig. 2). This decrease is  
77 attributed to NO<sub>x</sub> emission controls on energy production, lower NH<sub>3</sub> emissions due to reductions in  
78 cattle production, and reduced use of synthetic N-fertilizer (Kopáček and Posch, 2011).

79

## 80 **Greenhouse gas emissions**

81

82 Nitrous oxide is a potent greenhouse gas with a global warming potential that is ~300 times greater  
83 than CO<sub>2</sub> on a per molecule basis. The production of N<sub>2</sub>O occurs during both denitrification and  
84 nitrification. N<sub>2</sub>O in the atmosphere is estimated to have increased by 18% from its pre-industrial level  
85 (IPCC 2007). The rise is attributed primarily to human activities, particularly from agriculture and land  
86 use change.

87 Information on the processes influencing N<sub>2</sub>O emissions from soils is sparse, particularly that on the  
88 roles of temperature, moisture, redox potential, pH, and substrate availability (Wallenstein et al. 2006).  
89 While agricultural soils are considered a major source of N<sub>2</sub>O, the effect of N fertilizer on soil N<sub>2</sub>O  
90 emissions remains highly uncertain (Davidson 2009; Zaehle et al. 2011). Emission factors (N<sub>2</sub>O  
91 emissions per unit N addition) have been reported to vary between 0.1–7% of the N applied (Skiba and  
92 Smith 2000). Since multiple processes and drivers are involved, N<sub>2</sub>O emissions are highly variable and  
93 often associated with “hotspots” (high emissions from small areas) and “hot moments” (high emissions  
94 for brief periods), making measuring, modeling, and up-scaling challenging (Groffman et al. 2009; Reay  
95 et al. 2012).

96 High variability in the response of N<sub>2</sub>O to N inputs indicates nonlinearity of the response function  
97 (Hoben et al. 2011). However, there is also large global variation in levels of N-inputs to agricultural  
98 systems, ranging from 588 kg N ha<sup>-1</sup> yr<sup>-1</sup> in a wheat-maize double cropping system in North China to 7 kg  
99 N ha<sup>-1</sup> yr<sup>-1</sup> in maize systems in western Kenya, resulting in very large uncertainty over global N<sub>2</sub>O  
100 emissions (Vitousek et al. 2009). Assessing a decade of measurements from an ILTER site in Michigan,  
101 USA, Robertson et al. (2000) reported that N<sub>2</sub>O fluxes were similar among different cropping systems,  
102 suggesting that N<sub>2</sub>O fluxes were driven by soil N availability, rather than by additional N inputs. In  
103 contrast, Van Groenigen et al. (2010) found that N inputs stimulated a dramatic increase in N<sub>2</sub>O  
104 emissions when fertilizer rates reached 301 kg N ha<sup>-1</sup> yr<sup>-1</sup>, while N<sub>2</sub>O emissions were small when  
105 fertilizer rates were ~180–190 kg N ha<sup>-1</sup> yr<sup>-1</sup> or lower. Given the paucity of data for areas with low rates  
106 of fertilization such as Africa, there is currently insufficient information for establishing the response  
107 function of N<sub>2</sub>O fluxes following addition of N inputs in these systems (Van Groenigen et al. 2010).

108 Clearly, there is a need for considerable clarification of the factors determining N<sub>2</sub>O emissions from  
109 N inputs at representative sites around the globe. For example, assessments are urgently required to  
110 determine the global impact of the African Green Revolution, called for by the former United Nation  
111 secretary general Kofi Annan. Agricultural productivity across Sub-Saharan Africa is expected to increase  
112 substantially by major increases in fertilizer use (up to 100 kg ha<sup>-1</sup> yr<sup>-1</sup>, Sanchez et al. 2007). To assess the  
113 unintended N<sub>2</sub>O emissions and N leaching to the local environments, more research is urgently needed to  
114 understand the N fluxes in response to inputs.

115

## 116 **ALTERED NITROGEN BIOGEOCHEMISTRY IN ECOSYSTEMS**

117

118 Increasing anthropogenic N<sub>r</sub> emissions are a significant source of atmospheric N deposition to land and  
119 sea (Galloway et al. 2004) and also enhance global warming through N<sub>2</sub>O emissions (IPCC 2007),

120 disturbing N pools, cycling and transport in and among ecosystems. In this section, we review the current  
121 understanding of the impact of increased N deposition on N biogeochemistry over a period of changing  
122 climate in various ecosystems, with special attention to ILTER's findings.

123

#### 124 **Long-term effects of N deposition in watershed N cycles and leaching**

125

126 Excess atmospheric N deposition beyond the N requirement of the biota often causes N saturation,  
127 which has been observed in many forest ecosystems of Europe and the USA (Dise and Wright 1995; Aber  
128 et al. 1998). Elevated concentrations of  $\text{NO}_3^-$  in surface waters derived from non-point or point sources of  
129 N pollution usually indicate that there has been sufficient anthropogenic deposition of N for catchment  
130 soils to have reached a degree of N saturation (Stoddard 1994).

131 In recent years, attempts in the USA and Europe to reduce atmospheric emissions of acidic  
132 precursors and other pollutants have resulted in widespread reductions in sulfur (S) deposition, with  
133 corresponding substantial reductions in sulfate concentrations in run-off. However, in Western Europe,  
134 there have been less linear changes of atmospheric deposition with respect to N. While reductions in  
135 emissions of N have led to broadly comparable reductions in ammonium ( $\text{NH}_4^+$ ) deposition, reductions in  
136  $\text{NO}_3^-$  deposition have been much lower (Fowler et al. 2007). The combination of uncertainties associated  
137 with these non-linearities between reduction of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  and the various responses of N leaching to  
138 variation in winter climate make the future prediction of  $\text{NO}_3^-$  leaching to surface waters and the extent to  
139 recovery from acidification very difficult.

140 In contrast, further increases in N emissions in the East Asia region during the next few decades  
141 have been predicted as a consequence of rapid industrialization, urbanization and economic growth (e.g.  
142 Galloway et al. 2003, 2004; Fang et al. 2011). Fang et al. (2011) indicated that N deposition in China  
143 ranged 2.6 to 48  $\text{kg N ha}^{-1} \text{ yr}^{-1}$ , while the threshold of N deposition to N saturation in Chinese forest



144 differs from that in the USA and Europe (i.e., the relatively high N leaching in some Chinese forests  
145 receiving low N input). Niu et al. (2010) reported that an experimental addition of N deposition (100 kg N  
146 ha<sup>-1</sup> yr<sup>-1</sup>) for four years enhanced the ecosystem productivity by 27% in a temperate steppe ecosystem in  
147 China. Several comparative studies (Park et al. 2003; Fang et al. 2011; Mitchell 2011) suggest that  
148 regional climate, geology and hydrology result in different patterns and responses to elevated N  
149 deposition in forest ecosystems, when compared to previous findings of similar studies in the USA and  
150 Europe (Ohte et al. 2001), indicating that more comparative research is needed to generalize the impact of  
151 increased N deposition on ecosystems. Long-term studies of watershed N biogeochemistry are clearly  
152 limited outside the USA and Europe, especially in East Asia, South America and Africa, where  
153 anthropogenic N deposition will increase in future.

154

#### 155 **Complex interactions of N with other elements**

156

157 The N cycle is intimately coupled to the C cycle. Soils with large pools of organic C and high C:N  
158 ratios are generally associated with N accumulation and tend to export less NO<sub>3</sub><sup>-</sup> than soils with low C:N  
159 ratios (e.g., Aber et al. 1998; Gundersen et al. 1998). When Nr availability is elevated in an N-limited  
160 system (e.g. through atmospheric N deposition), soil inorganic N is readily utilized by plants, resulting in  
161 increased C uptake (Gruber and Galloway 2008) and reduced below-ground allocation of C (Deegan et al.  
162 2012). Elevated Nr in soil can also change the soil microbial community by, for example, a reduction of  
163 fungal:bacterial biomass ratios (Högberg et al. 2007; Boberg et al. 2010). These studies emphasize the  
164 importance of taking N-C interactions into account when considering the possible impact of climate  
165 change on ecosystems, carbon sequestration, and in the development of earth system models (Thornton et  
166 al. 2009). Various mechanisms have been proposed to explain the changes in N-C interactions following  
167 increased N availability: biomass increase with allocation changes in plants (i.e., reduction of

168 below-ground C allocation due to the N increase) (Högberg et al. 2010); enhanced soil respiration  
169 reflecting an increase in soil microbial activity with an increase in N availability (Gärdenäs et al. 2011);  
170 inhibition of litter decomposition through a change in litter quality with elevated N (Knorr et al. 2005;  
171 Pregitzer et al. 2008); a change in plant uptake of organic N as a nutrient source in N-limited  
172 environments (Gärdenäs et al. 2011); altered interaction with dissolved organic carbon (e.g., enhanced  
173 mineralization of DOC due to increased abundance of electron acceptors in the form of  $\text{NO}_3^-$  in anoxic  
174 soil micro-sites (Kopáček et al. 2013c)); and changes in abiotic N-C interactions in soil (e.g., abiotic  
175 reaction of nitrite with dissolved organic matter through nitration and nitrosation of aromatic ring  
176 structures) (Davidson et al. 2003).

177       Phosphorus (P) is also an essential nutrient for biota. N-C-P interactions in soil vary among biomes.  
178 Where P limits primary production, such as in some tropical ecosystems or acid alpine grasslands,  
179 increases in N deposition may have little impact on productivity (Matson et al. 1999), a finding that has  
180 recently been documented by field experiments at ILTER sites (Cusack et al. 2011; Bowman et al. 2008).  
181 In both N- and P- limited tundra ecosystems, C fluxes were found to respond positively to additions of  
182 both elements, although responses to P tended to be stronger than to N (Shaver et al. 1998). Bergström  
183 and Jansson (2006) have shown that increased N deposition may have changed lakes from N-limitation to  
184 P-limitation in remote and small lakes across the northern hemisphere, an observation supported by  
185 nutrient addition experiments in UK upland streams (Maberly et al., 2002). On the other hand, an  
186 assessment of long-term data from a Spanish ILTER lake site by Camarero and Catalan (2012) suggested  
187 that atmospheric P deposition may cause lakes to revert from P-limitation to N-limitation. There are clear  
188 needs for research into long-term C-N-P interactions for a much wider range of biomes.

189       Nitrogen deposition can serve as an acidifying as well as eutrophying agent (Oulehle et al. 2008).  
190 Bowman et al. (2008) reported that long-term acid deposition in the Western Tatra Mountains of Slovakia,  
191 central Europe has altered soil systems in alpine grasslands to an extreme level of acidification usually

192 associated with soils exposed to acid mine drainage. They showed that increases in N deposition had  
193 resulted in a depletion of base cations, increases in aluminium (Al) and extractable iron (Fe) in soil, and a  
194 reduction in the biomass of vascular plants associated with a decrease in shoot calcium and magnesium  
195 concentrations. They suggested that acidifying soils in central Europe have reached an unprecedented  
196 level of toxicity in which Al release into soil water has been superseded by Fe release (Bowman et al.  
197 2008).

198

### 199 **N leaching in dormant season**

200

201 Seasonal changes in nitrogen behavior of ecosystems are mostly driven by seasonal fluctuations of  
202 physical drivers (i.e. weather conditions) and biological factors (i.e., phenology in plant and microbial  
203 activity). The seasonality of plant growth in many biomes results in a seasonal N demand, while (with the  
204 exception of heavily N-saturated soils and catchments with little soil cover) most  $\text{NO}_3^-$  leached into  
205 surface and ground waters is increasingly being found to have undergone soil microbial processing  
206 (Stoddard 1994; Piatek et al. 2005; Curtis et al. 2012). Consequently, the dependence of biological  
207 systems on soil microclimate can lead to strong seasonal variation in N fluxes and concentrations in soils  
208 and drainage waters.

209 Time series analyses from boreal to temperate forested, moorland and alpine systems emphasize the  
210 importance of winter temperatures and snow cover in determining the export of  $\text{NO}_3^-$  in soil, ground and  
211 surface waters. Although winter has sometimes been considered to be the “dormant season,” due to cold  
212 temperatures, vegetation dormancy and a persistent snow cover, microbial processes can persist and exert  
213 a critical impact on N cycling (Campbell et al. 2005; Makoto et al. 2013). Snow also allows solutes to  
214 accumulate in the soil (Kurian et al. 2012) leading to pronounced fluxes when the snow melts.  
215 Watersheds throughout the Northeast USA export more than 85% of the annual  $\text{NO}_3^-$  loss during winter

216 (Mitchell et al. 1996), with most of this export occurring during spring snowmelt (Campbell et al. 2005),  
217 but mid-winter melt events and rain-on-snow events can also influence winter  $\text{NO}_3^-$  loads to streams  
218 (Casson et al. 2010). Individual rain-on-snow events can contribute as much as 40% of annual  $\text{NO}_3^-$   
219 export from forested watersheds in southeast Canada, and the contribution of rain-on-snow events to  
220 annual and winter  $\text{NO}_3^-$  loads has generally increased in recent decades (Eimers et al. 2007).

221 The insulating properties of snow can maintain soil temperatures sufficiently high to allow root  
222 growth, microbial respiration and other biotic activities to continue (Groffman et al. 2009). Soils devoid  
223 of a snowpack are more vulnerable to freezing and hence to physical and chemical changes, including the  
224 death of fine roots, cell lysis and the alteration of soil microbial processes (Tierney et al. 2001;  
225 Christopher et al. 2008; Shibata et al. 2013). Experimental snow removal in alpine Europe lowered soil  
226 temperatures and increased  $\text{NO}_3^-$  release (Freppaz et al. 2008). In mountainous and northern regions, soil  
227 temperatures and ecosystem respiration rates tend to be higher in winters with high amounts of snowfall  
228 than in winters with less or no snow (Monson et al. 2006). On the other hand, experimental snow  
229 manipulation at a mountain site in Norway indicated that no increase of inorganic N fluxes was associated  
230 with snow removal (Kaste et al. 2008), suggesting that the effects of decreased snow on the N cycle  
231 varies among locations. Coherent patterns of variation in  $\text{NO}_3^-$  leaching are sometimes evident over large  
232 spatial scales and across catchments covering wide altitudinal gradients and land-use classes (e.g. Evans  
233 et al. 2010; Rogora et al. 2008). In the UK, winters when  $\text{NO}_3^-$  leaching to remote surface waters have  
234 been strongly associated with negative excursions in the winter North Atlantic Oscillation (NAO) Index,  
235 most likely due to low winter temperatures, lower than average rainfall and larger contributions from  
236 more polluted air masses originating from the European continent (Monteith et al. 2000; George et al.  
237 2004a). However, as soil temperature is a dominant driver, opposing inter-annual patterns in  $\text{NO}_3^-$   
238 leaching may be observed in regions normally blanketed by snow in winter when they lack snow cover,  
239 since snow cover insulates the uppermost soil layer from the atmosphere (Groffman et al. 2009; Makoto

240 et al. 2013). Consequently, relationships between  $\text{NO}_3^-$  leaching and the NAO index in the UK and in  
241 northern Europe may vary regionally (George et al. 2004b; Blenckner et al. 2007; de Wit et al. 2008).

242 Over the last decade, trends in  $\text{NO}_3^-$  concentrations in waters across the UK Upland Waters  
243 Monitoring Network have lost coherence and begun to diverge (Monteith et al., 2014). Inter-annual  
244 variation in  $\text{NO}_3^-$  concentrations in some northern sites remains tightly linked to the winter NAO Index,  
245 and shows a long term (>20 years) increase consistent with the long term decline in the NAO over the  
246 same period (Fig. 3). At other sites further south, however,  $\text{NO}_3^-$  concentrations, while still showing  
247 evidence of influence of the NAO on short term variability, are trending downwards (Fig. 3), possibly in  
248 response to more marked reductions in N deposition in this region. The divergence provides evidence for  
249 regional differences in the relative importance of N deposition and climate variability on  $\text{NO}_3^-$  leaching to  
250 surface waters, with the latter exerting greater influence in areas where N deposition has been more  
251 stable.

252

### 253 **Cascading influences from terrestrial watersheds to estuaries**

254

255 Nitrogen losses from agricultural land are often several times higher than those from natural  
256 systems. In typical agrarian systems, exported N represents 10–40% (~25% on average) of net  
257 anthropogenic nitrogen inputs (Howarth et al. 2011), depending on the amounts of leachable  $\text{NO}_3^-$  in the  
258 soil and surplus water to transport the solutes out of the watershed. Kopáček et al. (2013a, b) indicated  
259 that, in Slapy Reservoir, an ILTER site in central Europe, the reservoir of leachable  $\text{NO}_3^-$  in agricultural  
260 and forested watersheds originates from both external (fertilization and atmospheric deposition) and  
261 internal (mineralization of soil organic N) sources, with relative contributions dependent on topography  
262 and land use practices such as drainage and tillage. Fluctuations in the export of N from Slapy Reservoir  
263 (Vltava river) from 1920–2010 were strongly related to the change in the mineralization of soil organic N

264 enhanced by more drainage of farmlands (up to 43%) rather than to the external N sources (Kopáček et al.  
265 (2013a, b). Boyer and Howarth (2002) evaluated the anthropogenic N source in large watersheds based on  
266 intensive monitoring of N cycles, indicating that fertilizer N inputs, N fixation in crop land and animal  
267 feed N imports were the dominant sources of Nr from agricultural land to the riverine N exports in sixteen  
268 large catchments of northeastern USA.

269 At watershed, landscape and regional scales, cascades and interactions are key to understanding N  
270 dynamics. Riparian zones function as the interface (“buffer zone”) between terrestrial and aquatic  
271 ecosystems, and may act as either net sources or sinks of N depending on timescales, hydrological  
272 conditions and the history of N inputs. Anaerobic conditions in shallow groundwater in the riparian zone  
273 stimulate denitrification (microbial transformation of  $\text{NO}_3^-$  to reduced gaseous forms such as  $\text{N}_2\text{O}$  and  $\text{N}_2$ ),  
274 thus reducing the potential flux of  $\text{NO}_3^-$  leaching to stream water (Chestnut and McDowell 2000).  
275 Hyporheic exchange, mixing saturated ground water (relatively anaerobic) with stream water (mostly  
276 aerobic), may provide “hot spots” for dynamic microbial N transformation near riparian boundaries and at  
277 the surfaces of channel beds (Shibata et al. 2004).

278 A substantial proportion of Nr can be buried in accumulating sediments of lakes and swamps (Noe  
279 and Hupp 2005). However, sediment anoxia may lead to the reduction of  $\text{NO}_3^-$  and nitrite ( $\text{NO}_2^-$ ) to  $\text{N}_2$  (or  
280  $\text{N}_2\text{O}$ ) by denitrification (Rissanen et al. 2011). Recently, “anaerobic ammonium oxidation” (*anammox*)  
281 has been identified as another process of  $\text{N}_2$  release under anoxic conditions (Jetten et al. 2005).

282 In contrast to many freshwater systems, coastal systems may be N-limited as a consequence of  
283 eutrophication associated with high P inputs (Howarth and Marino 2006). Substantial denitrification rates  
284 have even been found in N-rich downstream riverine systems, whereas no comparable P-removal process  
285 occurs (Vermaat et al. 2012; Billen et al. 2009). Consequently, this may lead to N-limitation that  
286 enhances the dominance of diazotrophic cyanobacteria in periods when the high energy demand for  
287 N-fixation can be satisfied (Stal and Zehr 2008). This can even lead to temporal N limitation (Schubert et

288 al. 2010), whereby P-concentration increases during summer in response to the constant supply of P by  
289 runoff and release from the sediment (Figure 4; Schubert and Wasmund 2005). Further investigations of  
290 denitrification rates and their driving factors including regional comparisons of diverse riverine systems  
291 and their connections to marine systems would reduce the uncertainty of N budgets of coastal systems fed  
292 by terrestrial N inputs.

293

## 294 **IMPACT ON BIODIVERSITY AND HUMAN SOCIETY**

295

296 As described above, increases of anthropogenic Nr emission and deposition substantially alter N  
297 pools, cycles and transport among ecosystems. The altered N behavior also influences structures and  
298 characteristics of organisms in natural ecosystems and anthropogenically dominated systems. Here we  
299 review how increased Nr affects (i) biological structures in the context of biodiversity and also (ii) human  
300 society in the context of human health and ecosystem services.

301

### 302 **Terrestrial biodiversity impacts**

303

304 Numerous studies have reported a decline in species diversity (vascular plants, lichens, mosses,  
305 phytoplankton microbes, etc.) associated with both N fertilization and N gradients across a range of  
306 different ecosystem types in forest and semi-natural areas (Clark and Tilman 2008; Bobbink et al. 2010).  
307 Clark and Tilman (2008) demonstrated that chronic low-level nitrogen addition ( $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  above  
308 ambient atmospheric N deposition) reduced plant species numbers by 17% relative to controls receiving  
309 ambient N deposition based on the multi-decadal experiment of N fertilization in the grassland ecosystem  
310 of Cedar Creek LTER. Recent studies suggested that even low-level N deposition could influence the  
311 changes in ground vegetation (Johansson et al. 2012; Hedwall et al. 2013). Nitrogen pollution stimulates

312 competitive interactions that lead to compositional change, making conditions unfavorable for some  
313 species (Bobbink et al. 2010; Bobbink and Hettelingh, 2011). Deprivation of light and nutrients resulting  
314 from the increased cover of aggressive dominant species can outweigh the potential benefits of N  
315 fertilization for subordinate species. These changes in biodiversity can have cascading impacts on  
316 primary production, soil C storage, microbial activity, rates of decomposition, N mineralization and  
317 immobilization, tissue chemistry, trophic interactions (herbivory), and can ultimately disrupt ecosystem  
318 functions and services (Ochoa-Hueso et al. 2011; Dias et al. 2011).

319 The sensitivity of terrestrial biodiversity to the deposition of oxidized and reduced N provides the  
320 basis for setting critical loads for N deposition both in Europe and North America (Cape et al. 2009;  
321 Pinho et al. 2011, 2012; Bobbink and Hettelingh, 2011). Independently-derived critical levels for lichens  
322 and moss diversity have been found to be similar for northern and southern Europe, thus emphasizing the  
323 universal applicability of these plant groups as ecological indicators of N deposition. Pardo et al. (2011)  
324 showed that, in the USA, empirical critical loads for N tend to increase according to the following  
325 sequence: lichens and bryophytes, mycorrhizal fungi, herbaceous plants and shrubs, and trees. In several  
326 studies in the USA, lichens invariably showed the lowest  $\text{NH}_3$  critical levels ( $1 \mu\text{g m}^{-3}$ ) and N critical  
327 loads ( $1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ ) of all biological indicators (Jovan et al. 2012).

328 Currently, there is no coordinated global observation system capable of providing real-time tracking  
329 of biodiversity change around the globe (Pereira et al. 2013). The scientific understanding of how  
330 biodiversity is reacting to increasing N inputs, and how this is affecting ecosystem resilience and  
331 ecosystem services remains limited. However, biodiversity seems to be a relatively sensitive metric for  
332 measuring the effects of N at the ecosystem level, i.e., loss of particular species from an ecosystem (Cape  
333 et al. 2009). Changes in biodiversity can also be used to help identify those species most sensitive to  
334 increased N. We expect that various assessments of biodiversity will exhibit differences in scalability,  
335 temporal sensitivity, feasibility, and relevance.



336

337 **Human health**

338

339 Human-induced changes in response to changes in the N cycle also have both negative and positive  
340 implications for human health. The most obvious health benefit of increased use of Nr is decreased  
341 hunger and malnutrition through the use of fertilizers, while N-related air pollutants are hazardous for  
342 humans. Atmospheric N pollution can affect human health by increasing respiratory problems especially  
343 those caused by smaller particulate matter (PM<sub>2.5</sub>), since they have the ability to penetrate deeper into the  
344 respiratory tract. Approximately 40% of PMs are NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>. High levels of atmospheric NO<sub>x</sub> lead to  
345 increases in tropospheric O<sub>3</sub> that strongly affect human respiratory function (von Mutius 2000). In  
346 addition, high concentrations of NO<sub>2</sub> in urban air can lengthen and worsen common viral infections such  
347 as human rhinovirus, significantly elevating the risks to asthmatics and individuals with compromised  
348 immune systems (Spannhake et al. 2002).

349 Nitrogen also affects human health via water pollution. Concentrations of NO<sub>3</sub><sup>-</sup> in drinking water  
350 exceeding 10 mg L<sup>-1</sup> put children at risk of methemoglobinemia (“blue-baby” syndrome; Gupta et al.  
351 2000). Even nitrate levels below the WHO standard may stimulate the endogenous formation of  
352 N-nitrosamines (van Mannen et al. 1996), compounds strongly implicated in cancer risks. Long-term  
353 consumption of water with NO<sub>3</sub><sup>-</sup> concentrations of 6.3 mg L<sup>-1</sup> and above has been linked to a higher risk  
354 for Non-Hodgkin’s lymphoma (Ward et al. 1996). In Iowa, rising NO<sub>3</sub><sup>-</sup> levels well below the 10 mg L<sup>-1</sup>  
355 standard were associated with an increased risk of bladder and ovarian cancers (Weyer et al. 2001).

356 One way to maintain good nourishment of the human population while decreasing fertilizer  
357 consumption would be to reduce meat consumption and increase consumption of a diversity of vegetables.  
358 Typically most NO<sub>3</sub><sup>-</sup> exposure (86%) to humans comes from vegetables, whereas the primary contributors  
359 to nitrite (NO<sub>2</sub><sup>-</sup>) intake are cured meats (39%), baked goods and cereals (34%), and vegetables (16%). It is

360 possible that a diet based on a diversity of vegetables provides man with adequate levels of  $\text{NO}_2^-$  which  
361 contributes to the whole-body NO production and homeostasis (Landberg et al. 2011).

362 Global food and feed trades are one of the important drivers of global, regional and local N  
363 circulation (Galloway et al. 2008). International trade in N has increased eightfold (from 3 to 24 Tg N)  
364 during 1961–2010 and a small number of countries (e.g., USA, Argentina and Brazil) currently feed much  
365 of the rest of the world in terms of proteins and N (Lassaletta et al. 2014). The spatial imbalance of  
366 production and consumption of feed and food contributes to the spatial imbalance of risk for human  
367 health and environment quality (e.g., animal feed imports from Africa, where the export of N contributed  
368 to N limitation of human food production with negative consequences for human health locally). Also, the  
369 influence of the global trade in N is more complex than merely the N flows associated with import or  
370 export of food and feed because part of the reactive N added by fertilizers and feed during the production  
371 of crop and animal products is lost to the environment, becoming a source of water and air pollution  
372 (Leach et al. 2012).

373

#### 374 **Impact on societal and economic value**

375

376 The concept of ecosystem services (Millennium Ecosystem Assessment Board 2005) recognizes the  
377 vital importance of the natural environment and the biodiversity it supports in underpinning human  
378 wellbeing. The nitrogen cycle is central to several key ecosystem processes including: water quality  
379 regulation (regulating services); ecosystem productivity that is often limited by N (provision of services  
380 via food, timber, and fiber); C sequestration and control of  $\text{N}_2\text{O}$  emissions (via climate regulation  
381 services). Nitrogen also indirectly impacts all ecosystem services through its influence on biodiversity  
382 (e.g. Suddick and Davidson 2012). Clearly, a range of N-related ecosystem services may be threatened by  
383 anthropogenic disturbances of biogeochemical cycles.

384 To date, economic valuation of N-related ecosystem services and human health has been conducted  
385 mainly in Europe and the USA (Compton et al. 2011; Sutton et al. 2011), while assessment in other  
386 region such as Asia-Pacific, Africa and South America is still limited and entails great uncertainty. The  
387 European Nitrogen Assessment (ENA) estimated that the highest social costs of N are associated with air  
388 pollution effects of NO<sub>x</sub> on human health (10 to 30€ per kg of N). A similar value (\$28 per kg NO<sub>x</sub>-N)  
389 relating to the USA was obtained by Compton et al. (2011). The effects of N loss to water on aquatic  
390 ecosystems were evaluated by the ENA as: 5 to 20€ per kg of N. The ENA also estimated N-related  
391 environmental damage from agriculture in the EU to be 20 to 150 billion € year<sup>-1</sup>, which is comparable  
392 with a benefit of N-fertilizer for farmers of 10 to 100 billion € per year<sup>-1</sup> (Sutton et al. 2011).

393

## 394 **THE NEED FOR INTERNATIONAL INTEGRATION OF LONG-TERM ECOSYSTEM** 395 **RESEARCH**

396

397 Based on the above literature review, we propose that several areas require more attention to  
398 develop a better understanding and reduce uncertainties with respect to the environmental effects of N.

399 The long-term monitoring and analysis of N deposition, N cycles in various ecosystems,  
400 biodiversity, and N export to water are needed to provide the fundamental information necessary to  
401 address a spectrum of research questions concerning N dynamics in coupled human and ecological  
402 systems (Robertson et al. 2012; Driscoll et al. 2012). Modeling and analysis coupled with long-term  
403 monitoring and field experiments provide powerful research tools to help understand the dynamic features  
404 of the N cycle driven by multiple environmental factors, and to address new parameters to be monitored  
405 or examined (e.g., Aber et al. 2002; Driscoll et al. 2003). There are clearly regional research gaps in the  
406 context of long-term site-based research on N biogeochemistry: East Asia, South America and Africa (e.g.  
407 Anderson et al. 2012; Urakawa et al. 2012) where increased N<sub>r</sub> pollution has been predicted for the

408 coming decades (Galloway et al. 2004). Also, long-term research sites in agricultural and urban  
409 ecosystems are currently limited despite their large importance in global N cycles. Increased international  
410 collaboration and integration offers the potential for further significant scientific advances, particularly  
411 with respect to the elucidation of: (i) responses of N<sub>2</sub>O emission to elevated Nr inputs; (ii) biodiversity  
412 changes associated with changes in N deposition; (iii) spatial heterogeneity of temporal trends among  
413 different deposited N species; (iv) spatial patterns in N leaching from a wide spectrum of catchments  
414 including a range of altitudinal and latitudinal gradients and different land-use types; (v) long-term trends  
415 in N concentrations in surface waters and potential linkages with inter-annual climate change.

416         Second, studying N dynamics at the ecosystem level should be coupled with socio-economic issues.  
417 Reactive nitrogen in the environment presents society with a global problem that must be addressed at a  
418 global scale over the long-term by uniting the analyses of natural and human systems. Continued  
419 maintenance of our best long-term environmental observation systems and the development of new  
420 long-term experiments will be necessary to clarify these complex interactions and their long- and  
421 short-term impacts.

422         At the international scale, our environmental observation capacity remains extremely limited. Based  
423 on the analysis in this review, some research questions have emerged:

- 424 - To what extent do ecosystems exhibit common or unique responses to elevated Nr across different  
425 environmental and social landscapes?
- 426 - What features of socio-ecological N interactions are likely to be most sensitive to global changes in  
427 human population and climate?
- 428 - What are the political and management options to mitigate or adapt the N-related social issues (e.g.  
429 diet, human health and ecosystem services)?
- 430 - Will future climate change have major impacts on N biogeochemistry, and what feedbacks from N  
431 cycling will be most important in influencing the climate?

432 Even though the answers to these questions remain unclear, some strategies need to be developed.  
433 For example, some previous studies have suggested that very sensitive organisms, such as lichens and  
434 mosses could be effective early warning indicators of atmospheric Nr pollution in the early stages of  
435 anthropogenic disturbance of N cycles in an ecosystem (Pinho et al. 2011). The functional diversity of  
436 lichens and/or mosses coupled with measures of their nitrogen content and isotopic composition have the  
437 potential to be explicit spatial indicators of the early effects of Nr pollution., It would therefore be  
438 possible to use lichens and mosses in the long-term ecological site to develop an early-warning biological  
439 monitoring system of atmospheric N pollution in regional and global scales. Other responses of  
440 ecosystem structure and functioning to altered N cycle often vary among sites, influenced not only by  
441 current driving factors but also by long-term socio-ecological legacies (Aber et al. 1998). Therefore,  
442 investigations need to include international comparisons of the impact of socio-ecological legacies on  
443 current N cycling processes by analyzing the relationship between current monitoring data and previous  
444 land history and other parameters. The historical records of site-management, land-use, natural  
445 disturbances, climate, atmospheric deposition, etc. should be used to help to understand how historical  
446 factors are affecting current N cycles. Such analyses should be facilitated by using the results from  
447 long-term ecological sites such as the ILTER worldwide network. Meta-analysis of comprehensive and  
448 integrated N databases and the organization of workshops on focused topics using international  
449 researchers networks (e.g. ILTER) should be encouraged. The outcomes of collaborative international  
450 research should also include analyses of the complete spectrum of socio-ecological factors related to N.  
451 This information must to be provided to both the scientific community as well as other stakeholders,  
452 including policy makers.

453

454 **References**

455

456 Aber, J., W. McDowell, K. Nadelhoffer, A. Magill, G. Berntson, M. Kamakea, S. McNulty, W. Currie, et  
457 al. 1998. Nitrogen saturation in temperate forest ecosystems: hypotheses revisited. *Bioscience* 48:  
458 921–34.

459 Aber, J.D., S.V. Ollinger, C.T. Driscoll, G.E. Likens, R.T. Holmes, R.J. Freuder, and C.L. Goodale, 2002.  
460 Inorganic nitrogen losses from a forested ecosystem in response to physical, chemical, biotic, and  
461 climatic perturbations. *Ecosystems* 5: 648–658.

462 Anderson, C.B., J.L. Celis-Diez, B.J. Bond, G.M. Pastur, C. Little, J.J. Armesto, C. Ghersa, A. Austin, et  
463 al. 2012. Progress in creating a joint research agenda that allows networked long-term  
464 socio-ecological research in southern South America: Addressing crucial technological and human  
465 capacity gaps limiting its application in Chile and Argentina. *Austral Ecology* 37: 529–536.

466 Beier, C., B. Emmett, P. Gundersen, A. Tietema, J. Peñuelas, M. Estiarte, C. Gordon, A. Gorissen, et al.  
467 2004. Novel approaches to study climate change effects on terrestrial ecosystems in the field:  
468 drought and passive nighttime warming. *Ecosystems* 7: 583–597.

469 Bergström, A., and M. Jansson. 2006. Atmospheric nitrogen deposition has caused nitrogen enrichment  
470 and eutrophication of lakes in the northern hemisphere. *Global Change Biology* 12:635–643.

471 Billen, G., V. Thieu, J. Garnier, and M. Silvestre, 2009. Modelling the N cascade in regional watersheds:  
472 The case study of the Seine, Somme and Scheldt rivers. *Agriculture, Ecosystems and Environments*  
473 133: 234–246.

474 Blenckner, T., R. Adrian, D.M. Livingstone, E. Jennings, G.A. Weyhenmeyer, D.G. George, T.  
475 Jankowski, M. Järvinen. et al. 2007. Large-scale climatic signatures in lakes across Europe: a  
476 meta-analysis. *Global Change Biology* 13: 1314–1326.

477 Bobbink, R., K. Hicks, J. Galloway, T. Spranger, R. Alkemade, M. Ashmore, M. Bustamante, S.  
478 Cinderby. et al. 2010. Global assessment of nitrogen deposition effects on terrestrial plant diversity:  
479 a synthesis. *Ecological Applications* 20: 30–59.

480 Bobbink, R., and J.P. Hettelingh, 2011. Review and revision of empirical critical loads and dose-response  
481 relationships, Coordination Centre for Effects, National Institute for Public Health and the  
482 Environment (RIVM)

483 Boberg, J.B., R.D. Finlay, J. Stenlid, and B.D. Lindahl. 2010. Fungal C translocation restricts  
484 N-mineralization in heterogeneous environments. *Functional Ecology* 24: 454–459.

485 Bowman, W.D., C.C. Cleveland, L. Halada, L. J. Hresko, and J.S. Baron. 2008. Negative impact of  
486 nitrogen deposition on soil buffering capacity. *Nature Geoscience* 1: 767–770.

487 Boyer, E.W., and R.W. Howarth, 2002. *The nitrogen cycle at regional to global scales*, Kluwer Academic  
488 Publishers.

489 Camarero, L., and J. Catalan. 2012. Atmospheric phosphorus deposition may cause lakes to revert from  
490 phosphorus limitation back to nitrogen limitation. *Nature Communications* 3: 1118.

491 Campbell, J.L., M.J. Mitchell, P.M. Groffman, and L.M. Christenson. 2005. Winter in northeastern North  
492 America: An often overlooked but critical period for ecological processes. *Frontiers in Ecology and*  
493 *the Environment* 3: 314–322.

494 Cape, J.N., L.J.V.D. Eerden, L.J. Sheppard, I.D. Leith, and M.A. Sutton. 2009. Evidence for changing the  
495 critical level for ammonia. *Environmental Pollution* 157: 1033–1037.

496 Carpenter, S.R., J.J. Cole, J.R. Hodgson, J.F. Kitchell, M. L. Pace, D. Bade, K.L. Cottingham, T.E.  
497 Essington, J.N. Houder. et al. 2001. Trophic cascades, nutrients, and lake productivity: whole-lake  
498 experiments. *Ecol Monogr* 71: 163–186.

499 Casson, N.J., M.C. Eimers, and J.M. Buttle. 2010. The Contribution of Rain-On-Snow Events to Nitrate  
500 Export in the Forested Landscape of South-Central Ontario, Canada. *Hydrological Process* 24:  
501 1985–1993.

502 Chestnut, T.J., and W.H. McDowell 2000. C and N dynamics in the riparian and hyporheic zones of a  
503 tropical stream, Luquillo mountains, Puerto Rico. *Journal of the North American Benthological*  
504 *Society* 19: 199–214.

505 Christopher, S.F., H. Shibata, M. Ozawa, Y. Nakagawa, and M.J. Mitchell. 2008. The effect of soil  
506 freezing on N cycling: Comparison of two headwater subcatchments with different vegetation and  
507 snowpack conditions in the northern Hokkaido Island of Japan. *Biogeochemistry* 88: 15–30.

508 Clark, C.M., and D. Tilman. 2008. Loss of plant species after chronic low-level nitrogen deposition to  
509 prairie grasslands. *Nature* 451: 712–715.

510 Collins, S.L., S.R. Carpenter, S.M. Swinton, D.E. Orenstein, D.L. Childers, T.L. Gragson, N.B. Grimm,  
511 J.M. Grove et al. 2011. An integrated conceptual framework for long-term social–ecological  
512 research. *Frontiers in Ecology and the Environment* 9: 351–357.

513 Compton, J.E., J.A. Harrison, R.L. Dennis, T.L. Greaver, B.H. Hill, S.J. Jordan, H. Walker, H.V.  
514 Campbell. 2011. Ecosystem services altered by human changes in the nitrogen cycle: a new  
515 perspective for US decision making. *Ecological Letters* 14: 804–815.

516 Curtis, C.J., T.E.H. Heaton, G.L. Simpson, C.D. Evans, J. Shilland, and S. Turner. 2012. Dominance of  
517 biologically produced nitrate in upland waters of Great Britain indicated by stable isotopes.  
518 *Biogeochemistry* 111: 535–554.

519 Curtis, C.J., R.W. Battarbee, D.T. Monteith, E.M. Shilland. 2014 The future of upland water ecosystems  
520 of the UK in the 21st century: A synthesis. *Ecol Indic* 37 Part B: 412–430.

521 Cusack, D.F., W.L. Silver, M.S. Torn, and W.H. McDowell. 2011. Effects of nitrogen additions on  
522 above- and belowground carbon dynamics in two tropical forests. *Biogeochemistry* 104: 203–225.

523 Davidson, E.A., J. Chorover, and D.B. Dail. 2003. A mechanism of abiotic immobilization of nitrate in  
524 forest ecosystems: the ferrous wheel hypothesis. *Global Change Biology* 9: 228–236.



- 525 Davidson, E.A. 2009 The contribution of manure and fertilizer nitrogen to atmospheric nitrous oxide  
526 since 1860. *Nature Geoscience* 2: 659–662.
- 527 De Wit, H.A., A. Hindar, and L. Hole. 2008. Winter climate affects long-term trends in stream water  
528 nitrate in acid-sensitive catchments in southern Norway. *Hydrology and Earth System Sciences* 12:  
529 393–403.
- 530 Deegan, L.A., D.S. Johnson, R.S. Warren, B.J. Peterson, J.W. Fleeger, S. Fagherazzi, and W.M.  
531 Wollheim. 2012. Coastal eutrophication as a driver of salt marsh loss. *Nature* 490: 388–392.
- 532 Dias. T., S. Malveiro, M.A. Martins-Loução, L.J. Sheppard, and C. Cruz. 2011. Linking increased  
533 N-driven biodiversity changes with soil N availability in a Mediterranean-Type Ecosystem. *Plant  
534 and Soil* 341: 125–136.
- 535 Dise, N., and R. Wright 1995. Nitrogen leaching from European forests in relation to nitrogen deposition.  
536 *Forest Ecology and Management* 71: 153–161.
- 537 Driscoll C.T., D. Whitall, J. Aber, E. Boyer, M. Castro, C. Cronan, C.L. Goodale, P. Groffman et al. 2003.  
538 Nitrogen Pollution in the Northeastern United States: Sources, Effects, and Management Options.  
539 *BioScience* 53: 357–374.
- 540 Driscoll, C.T., K.F. Lambert, F.S. Chapin III, D.J. Nowak, T.A. Spies, F.J. Swanson, D.B. Kittredge,  
541 and C.M. Hart. 2012. Science and society: The role of long-term studies in environmental  
542 stewardship. *BioScience* 62: 354–366.
- 543 Eimers, M.C., J.M. Buttle, and S.A. Watmough. 2007. The contribution of rain-on-snow events to annual  
544 no<sub>3</sub>-n export from a forested catchment in south-central Ontario, Canada. *Applied Geochemistry* 22:  
545 1105–1110.
- 546 Evans, C.D., D.M. Cooper, D.T. Monteith, R.C. Helliwell, F. Moldan, J. Hall, E.C. Rowe, and B.J. Cosby.  
547 2010. Linking monitoring and modelling: can long-term datasets be used more effectively as a basis  
548 for large-scale prediction? *Biogeochemistry* 101: 211–227.

549 Fang, Y., P. Gundersen, R.D. Vogt, K. Koba, F. Chen, X.Y. Chen, and M. Yoh. 2011. Atmospheric  
550 deposition and leaching of nitrogen in Chinese forest ecosystems. *Journal of Forest Research* 16:  
551 341–350.

552 Fernandez, I.J., M.B. Adams, M.D. SanClements, and S.A. Norton. 2010. Comparing decadal responses  
553 of whole-watershed manipulations at the Bear Brook and Fernow experiments. *Environmental*  
554 *Monitoring and Assessment* 171: 149–161.

555 Fowler, D., R. Smith, J. Muller, J.N. Cape, M. Sutton, J.W. Erisman, and H. Fagerli. 2007. Long term  
556 trends in sulphur and nitrogen deposition in Europe and the cause of non-linearities. *Water, Air, &*  
557 *Soil Pollution: Focus* 7: 41–47.

558 Freppaz, M., L. Ceili, M. Marcheilli, and E. Zanini. 2008. Snow removal and its influence on temperature  
559 and N dynamics in alpine soils (Vallée d'Aoste, northwest Italy). *Journal of Plant Nutrition and Soil*  
560 *Science* 171: 672–680.

561 Galloway, J.N., F.J. Dentener, D.G. Capone, E.W. Boyer, R.W. Howarth, S.P. Seitzinger, G.P. Asner, C.C.  
562 Cleveland, et al. 2004. Nitrogen Cycles: Past, Present and Future. *Biogeochemistry* 70: 153–226.

563 Galloway, J.N., J.D. Aber, J.W. Erisman, S.P. Seitzinger, R.W. Howarth, E.B. Cowling, and B.J. Cosby.  
564 2003. The nitrogen cascade. *Bioscience* 53: 341–356.

565 Galloway, J.N., A.R. Townsend, J. W. Erisman, M. Bekunda, Z. Cai, J.R. Freney, L.A. Martinelli, S.P.  
566 Seitzinger, et al. 2008. Transformation of the Nitrogen Cycle: Recent Trends, Questions, and  
567 Potential Solutions. *Science* 320: 889–892.

568 Gårdenäs, AI, G.I. Ågren, J.A. Bird, M. Clarholm, S. Hallin, P. Ineson, T. Kätterer, H. Knicker, S.I.  
569 Nilsson, et al. 2011. Knowledge gaps in soil carbon and nitrogen interactions – From molecular to  
570 global scale. *Soil Biology and Biochemistry* 43: 702–717.

571 George, D.G., S.C. Maberly, and D.P. Hewitt. 2004b. The influence of the North Atlantic Oscillation on  
572 the physical, chemical and biological characteristics of four lakes in the English Lake District.  
573 *Freshwater biology* 49: 760–774.

574 Groffman, P., K. Butterbach-Bahl, R.W. Fulweiler, A.J. Gold, J.L. Morse, E.K. Stander, C. Tague, C.  
575 Tonitto, et al. 2009. Challenges to incorporating spatially and temporally explicit phenomena  
576 (hotspots and hot moments) in denitrification models. *Biogeochemistry* 92: 49–77.

577 Groffman, P.M., L.E. Rustad, P.H. Templer, J.L. Campbell, L.M. Christenson, N.K. Lany, A.M. Socci,  
578 M.A. Vadeboncoeur, et al. 2012. Long-term integrated studies show complex and surprising effects  
579 of climate change in the northern hardwood forest. *BioScience* 62: 1056–1066.

580 Gruber, N., and J.N. Galloway. 2008. An Earth-system perspective of the global nitrogen cycle. *Nature*  
581 451: 293–296.

582 Gundersen, P., B.A. Emmett, O.J. Kjønaas, C.J. Koopmans, A. Tietemad, 1998. Impact of nitrogen  
583 deposition on nitrogen cycling in forests: a synthesis of NITREX data, *For Ecol Manage* 101: 37–  
584 55.

585 Gupta, S.K., R.C. Gupta, and A.K. Seth. 2000. Methaemoglobinaemia in areas with high nitrate  
586 concentration in drinking water. *National Medical Journal of India* 13: 58–61.

587 Harris, T.D., F.M Wilhelm, J.L. Graham, K.A. Loftin, 2014. Experimental manipulation of TN:TP ratios  
588 suppress cyanobacterial biovolume and microcystin concentration in large-scale in situ microcosms  
589 -. *Lake Reserv Manag* 30: 72–83.

590 Hedwall, P.O, A. Nordin, J. Strengbom, J. Brunet, B. Olsson. 2013. Does background nitrogen deposition  
591 affect the response of boreal vegetation to fertilization? *Oecologia* 173: 615–624.

592 Högberg M.N., M.J.I. Briones, S.G. Keel, D.B. Metcalfe, C. Campbell, A.J. Midwood, B. Thornton, V.  
593 Hurry, et al. 2010. Quantification of effects of season and nitrogen supply on tree below-ground

594 carbon transfer to ectomycorrhizal fungi and other soil organisms in a boreal pine forest. *New*  
595 *Phytologist* 187: 485–493.

596 Högberg, M.N., Y. Chen, and P. Högberg. 2007. Gross nitrogen mineralisation and fungi-to-bacteria  
597 ratios are negatively correlated in boreal forests. *Biology and Fertility of Soils* 44: 363–366.

598 Howarth, R.W., and R. Marino. 2006. Nitrogen as the limiting nutrient for eutrophication in coastal  
599 marine ecosystems: Evolving views over three decades. *Limnology and Oceanography* 51: 364–376.

600 Howarth, R., D. Swaney, G. Billen, J. Garnier, B. Hong, C. Humborg, P. Johnes, C-M. Mörth, et al. 2011.  
601 Nitrogen fluxes from the landscape are controlled by net anthropogenic nitrogen inputs and by  
602 climate. *Frontiers in Ecology and the Environment* 10: 37–43.

603 IPCC. 2007. Climate change 2007: The Physical Science Basis. Contribution of Working Group I to the  
604 Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge  
605 University Press, Cambridge, United Kingdom and New York, NY, USA.

606 Jetten, M.S., I. Cirpus, B. Kartal, L. van Niftrik, K.T. van de Pas-Schoonen, O. Sliemers, S. Haaijer, W.  
607 van der Star, M. Schmid, et al. 2005. 1994–2004: 10 years of research on the anaerobic oxidation of  
608 ammonium. *Biochemical Society Transactions* 33: 119–123.

609 Johansson, O., K. Palmqvist, J. Olofsson, 2012 Nitrogen deposition drives lichen community changes  
610 through differential species responses. *Glob Chang Biol* 18: 2626–2635.

611 Jovan, S., J. Riddell, P.E. Padgett, and T.H. Nash III. 2012. Eutrophic lichens respond to multiple forms  
612 of N: implications for critical levels and critical loads research. *Ecological Applications* 22: 1910–  
613 1922.

614 Kaste, Ø., K. Austnes, L.S. Vestgarden, R.F. Wright, 2008. Manipulation of snow in small headwater  
615 catchments at Storgama, Norway: Effects on leaching of inorganic nitrogen. *AMBIO* 37: 29–37.

616 Knorr, M., S.D. Frey, and P.S. Curtis. 2005. Nitrogen additions and litter decomposition: A meta-analysis.  
617 *Ecology* 86: 3252–3257.

618 Kopáček, J., and M. Posch. 2011. Anthropogenic nitrogen emissions during the Holocene and their  
619 possible effects on remote ecosystems. *Global Biogeochemical Cycles* 25: GB2017.  
620 doi:10.1029/2010GB003779.

621 Kopáček, J., J. Hejzlar, and M. Posch. 2013a. Factors controlling the export of nitrogen from agricultural  
622 land in a large central European catchment during 1900–2010. *Environmental Science &*  
623 *Technology* 47: 6400–6407.

624 Kopáček, J., J. Hejzlar, and M. Posch. 2013b. Quantifying nitrogen leaching from diffuse agricultural and  
625 forest sources in a large heterogeneous catchment. *Biogeochemistry* 115: 149–165.

626 Kopáček, J., B.J. Cosby, C.D. Evans, J. Hruška, F. Moldan, F. Oulehle, H. Šantrůčková, K. Tahovská, et  
627 al. 2013c. Nitrogen, organic carbon and sulphur cycling in terrestrial ecosystems: linking nitrogen  
628 saturation to carbon limitation of soil microbial processes. *Biogeochemistry* 115: 33–51.

629 Kurian, L.M., L.K. Lutz, M.J. Mitchell. 2012. Winter hydrology and NO<sub>3</sub><sup>-</sup> concentrations in a forested  
630 watershed: a detailed field study in the Adirondack Mountains of New York. *Journal of the*  
631 *American Water Resources Association* 49: 264–283.

632 Landberg, J.O., M. Carlstrom, F.J. Larsen, and E. Weitzberg. 2011. Roles of dietary inorganic nitrate in  
633 cardiovascular health and disease. *Cardiovascular Research* 89: 525–532.

634 Lassaletta, L., G. Billen, B. Grizzetti, J. Garnier, A.M. Leach, and J.N. Galloway, 2014. Food and feed  
635 trade as a driver in the global nitrogen cycle: 50-year trends. *Biogeochemistry* 118: 225–241.

636 Leach, A.M., J.N. Galloway, A. Bleeker, J.W. Erisman, R. Kohn, J. Kitzes, 2012. A nitrogen footprint  
637 model to help consumers understand their role in nitrogen losses to the environment. *Environmental*  
638 *Development* 1:40–66.

639 Likens, G.E., C.T. Driscoll, and D.C. Buso. 1996. Long-term effects of acid rain: response and recovery  
640 of a forest ecosystem. *Science* 272: 244–246.

641 Löfgren, S., M. Aastrup, L. Bringmark, H. Hultberg, L. Lewin-Pihlblad, L. Lundin, G.P. Karlsson, and B  
642 Thunholm, 2011. Recovery of Soil Water, Groundwater, and Streamwater from Acidification at the  
643 Swedish Integrated Monitoring Catchments. *AMBIO* 40: 836–856.

644 Maberly, S.C., L. King, M.M. Dent, R.I. Jones, C.E. Gibson, 2002. Nutrient limitation of phytoplankton  
645 and periphyton growth in upland lakes. *Freshw Biol* 47: 2136–2152.

646 Makoto, K., T. Kajimoto, L. Koyama, G. Kudo, H. Shibata, Y. Yanai, and J.H.C. Cornelissen. 2013  
647 Winter climate change in plant–soil systems: summary of recent findings and future perspectives.  
648 *Ecological Research* (In press).

649 Matson, P.A., W.H. McDowell, A.R. Townsend, and P. M. Vitousek. 1999. The globalization of N  
650 deposition: ecosystem consequences in tropical environments. *Biogeochemistry* 46: 67–83.

651 Millennium Ecosystem Assessment Board. 2005. *Ecosystems and Human Well-Being: Current State and*  
652 *Trends*, Volume 1. Washington D.C., USA: Island Press.

653 Mitchell MJ, C.T. Driscoll, J.S. Kahl, G.E. Likens, P.S. Murdoch, and L.H. Pardo. 1996. Climatic control  
654 of nitrate loss from forested watersheds in the northeast United States. *Environmental Science &*  
655 *Technology* 30: 2609–2612.

656 Mitchell, M.J. 2011. Nitrate dynamics of forested watersheds: spatial and temporal patterns in North  
657 America, Europe and Japan. *Journal of Forest Research* 16: 333–340.

658 Monson, R.K., D.L. Lipson, S.P. Burns, A.A. Turnipseed, A.C. Delany, M.W. Williams, and S.K.  
659 Schmidt. 2006. Winter forest soil respiration controlled by climate and microbial community  
660 composition. *Nature* 439: 711–714.

661 Monteith, D.T., C.D. Evans, P.A. Henrys, G.L. Simpson, and I.A. Malcolm. 2014. Trends in the  
662 hydrochemistry of acid-sensitive surface waters in the UK 1988–2008. *Ecological Indicators* 37:  
663 287–303.

664 Monteith, D.T., C.D. Evans, and B. Reynolds. 2000. Are temporal variations in the nitrate content of UK  
665 upland freshwaters linked to the North Atlantic Oscillation? *Hydrological Processes* 14: 1745–1749.

666 Niu, S., M. Wu, Y. Han, J. Xia, Z. Zhang, H. Yang, and S. Wan. 2010. Nitrogen effects on net ecosystem  
667 carbon exchange in a temperate steppe. *Global Chang Biol* 16: 144–155.

668 Noe, G.B., and C.R. Hupp. 2005. Carbon, nitrogen, and phosphorus accumulation in floodplains of  
669 Atlantic coastal plain rivers, USA. *Ecological Applications* 15: 1178–1190.

670 Ochoa-Hueso, R., E.B. Allen, C. Branquinho, C. Cruz, T. Dias, M.E. Fenn, E. Manrique, M.E.  
671 Pérez-Corona, et al. 2011. Nitrogen deposition effects on Mediterranean-type ecosystems: an  
672 ecological assessment. Review. *Environmental Pollution* 159: 2265–2279.

673 Ohte, N., M.J. Mitchell, H. Shibata, N. Tokuchi, H. Toda, and G. Iwatsubo, 2001. Comparative  
674 evaluation on nitrogen saturation of forest catchments in Japan and northeastern United States.  
675 *Water Air Soil Pollut* 131: 649–654.

676 Oulehle F, W.H. McDowell, J.A. Aitkenhead-Peterson, P. Krám, J. Hruška, T. Navrátil, F. Buzek, and D.  
677 Fottová, 2008. Long-Term Trends in Stream Nitrate Concentrations and Losses Across Watersheds  
678 Undergoing Recovery from Acidification in the Czech Republic. *Ecosystems* 11: 410–425.

679 Pardo, L.H., M.E. Fenn, C.L. Goodale, L.H. Geiser, C.T. Driscoll, E.B. Allen, J.S. Baron, R. Bobbink, et  
680 al. 2011. Effects of nitrogen deposition and empirical nitrogen critical loads for ecoregions of the  
681 United States. *Ecological Applications* 21: 3049–3082.

682 Park, J., M.J. Mitchell, P.J. McHale, S.F. Christopher, and T.P. Myers. 2003. Interactive effects of  
683 changing climate and atmospheric deposition on N and S biogeochemistry in a forested watershed of  
684 the Adirondack Mountains, New York State. *Global Change Biology* 9: 1602–1619.

685 Peñuelas, J., P. Prieto, C. Beier, C. Cesaraccio, P. De Angelis, G. De Dato, B.A. Emmett, M. Estiarte, et  
686 al. 2007. Response of plant species richness and primary productivity in shrublands along a north–

687 south gradient in Europe to seven years of experimental warming and drought: reductions in primary  
688 productivity in the heat and drought year of 2003. *Glob Chang Biol* 13: 2563–2581.

689 Pereira, H.M., S. Ferrier, M. Walters, G.N. Geller, R.H.G. Jongman, R.J. Scholes, M.W. Bruford,  
690 N.Brummitt, et al. 2013. Essential Biodiversity Variables. *Science* 339: 277–278.

691 Piatek, K.B., M.J. Mitchell, S.R. Silva, and C. Kendall. 2005. Sources of nitrate in snowmelt discharge:  
692 Evidence from water chemistry and stable isotopes of nitrate. *Water, Air, & Soil Pollution* 165: 13–  
693 35.

694 Pinho, P., T. Dias, C. Cruz, Y.S. Tang, M.A. Sutton, M-A. Martins-Loução, C. Máguas, and C.  
695 Branquinho. 2011. Using lichen functional-diversity to assess the effects of atmospheric ammonia in  
696 Mediterranean woodlands. *Journal of Applied Ecology* 48: 1107–1116.

697 Pinho, P., M.R. Theobald, T. Dias, Y.S. Tang, C. Cruz, M.A. Martins-Loucao, C. Maguas, M. Sutton, et  
698 al. 2012. Critical loads of nitrogen deposition and critical levels of atmospheric ammonia for  
699 semi-natural Mediterranean evergreen woodlands. *Biogeosciences* 9: 1205–1215.

700 Pritzger, K.S., A.J.  
701 Burton, D.R. Zak, and A.F. Talhelm. 2008. Simulated chronic nitrogen deposition increases carbon  
702 storage in Northern Temperate forests. *Global Change Biology* 14: 142–153.

703 Rask, M., L. Arvola, M. Forsius and J. Vuorenmaa. 2014. Preface to the special issue “Integrated  
704 monitoring in the Valkea-Kotinen catchment during 1990–2009: Abiotic and biotic responses to  
705 changes in air pollution and climate. *Boreal Environ Res* 19:1–3.

706 Reay, D.S., E. A. Davidson, K. A. Smith, P. Smith, J.M. Melillo, F. Dentener, and P.J. Crutzen. 2012.  
707 Global agriculture and nitrous oxide emissions. *Nature Climate Change* 2: 410–416.

708 Rissanen, A., M. Tirola, and A. Ojala. 2011. Spatial and temporal variation in denitrification and in the  
denitrifier community in a boreal lake. *Aquatic Microbial Ecology* 64: 27–40.



709 Robertson, G.P., E.A. Paul, and R.R. Harwood. 2000. Greenhouse Gases in Intensive Agriculture:  
710 Contributions of Individual Gases to the Radiative Forcing of the Atmosphere. *Science* 289: 1922–  
711 1925.

712 Robertson, G.P., S.L. Collins, D.R. Foster, N. Brokaw, H.W. Ducklow, T.L. Gragson, C. Gries, S.K.  
713 Hamilton, et al. 2012. Long-Term Ecological Research in a Human-Dominated World. *BioScience*  
714 62: 342–353.

715 Rogora, M., C. Arese, R. Balestrini, and A. Marchetto. 2008. Climate control on sulphate and nitrate  
716 concentrations in alpine streams of Northern Italy along a nitrogen saturation gradient. *Hydrology*  
717 *and Earth System Sciences* 12: 371–381.

718 Sanchez, P., C. Palm, J. Sachs, G. Denning, R. Flor, R. Harawa, B. Jama, T. Kiflemariam, et al. 2007.  
719 The African millennium villages. *Proceedings of the National Academy of Sciences of the United*  
720 *States of America* 104: 16775–16780.

721 Schubert, H., and N. Wasmund. 2005. Das Phytoplankton des Strelasundes und des Kubitzer Boddens.  
722 *Meer Museum* 18: 83–92. (in Germany)

723 Schubert, H., N. Wasmund, and K. Sellner. 2010. Long-term investigations in brackish ecosystems. In  
724 *Long-term Ecological research*, ed. F. Müller, C. Baessler, H. Schubert, S. Klotz, 163–178:  
725 Springer-Verlag. (in Germany)

726 Shaver, G.R., L.C. Johnson, D.H. Cades, G. Murray, J.A. Laundre, E.B. Rastetter, K.J. Nadelhoffer, and  
727 A.E. Giblin. 1998. Biomass and CO<sub>2</sub> flux in wet sedge tundras: Responses to nutrients, temperature,  
728 and light. *Ecological Monographs* 68: 75–97.

729 Shibata, H., O. Sugawara, H. Toyoshima, S. M. Wondzell, F. Nakamura, T. Kasahara, F. J. Swanson, and  
730 K. Sasa. 2004. Nitrogen dynamics in the hyporheic zone of a forested stream during a small storm,  
731 Hokkaido, Japan. *Biogeochemistry* 69: 83–104.

732 Shibata, H., Y. Hasegawa, T. Watanabe, and K. Fukuzawa (2013) Impact of snowpack decrease on net  
733 nitrogen mineralization and nitrification in forest soil of northern Japan. *Biogeochemistry* 116: 69–  
734 82.

735 Skiba, A., and K.A. Smith. 2000. The control of nitrous oxide emissions from agricultural and natural  
736 soils. *Chemosphere - Global Change Science* 2: 379–386.

737 Spannhake, E.W., S.P.M. Reddy, D.B. Jacoby, X.Y. Yu, B. Saatian, and J. Tian. 2002. Synergism  
738 between rhinovirus infection and oxidant pollutant exposure enhances airway epithelial cell cytokine  
739 production. *Environmental Health Perspectives* 110: 665–670.

740 Stal, L.J., and J.P. Zehr. 2008. Cyanobacterial nitrogen fixation in the ocean: Diversity, regulation and  
741 ecology. In *The Cyanobacteria: Molecular Biology, Genomics and Evolution*, ed. A. Herrero, E.  
742 Flores, 423–446, Caister: Academic Press.

743 Stoddard, J.L. 1994. Long-term changes in watershed retention of nitrogen: Its causes and aquatic  
744 consequences. In *Environmental chemistry of lakes and reservoirs*. ed. L.A. Baker, 223–284.  
745 Washington, DC: American Chemical Society

746 Suddick, E.C., and E.A. Davidson. 2012. The Role of Nitrogen in Climate Change and the Impacts of  
747 Nitrogen-Climate Interactions on Terrestrial and Aquatic Ecosystems, Agriculture, and Human  
748 Health in the United States: A Technical Report Submitted to the US National Climate Assessment.  
749 North American Nitrogen Center of the International Nitrogen Initiative (NANC-INI), Woods Hole  
750 Research Center, 149 Woods Hole Road, Falmouth, MA.

751 Sutton, M.A., C.M. Howard, J.W. Erisman, G. Billen, A. Bleeker, P. Grennfelt, H. van Grinsven, and B.  
752 Grizzetti, 2011. The European Nitrogen Assessment. Cambridge: Cambridge University Press,

753 Thornton, P.E., S.C. Doney, K. Lindsay, J.K. Moore, N. Mahowald, J.T. Randerson, I. Fung, J.-F.  
754 Lamarque, et al. 2009. Carbon-nitrogen interactions regulate climate-carbon cycle feedbacks: results  
755 from an atmosphere-ocean general circulation model. *Biogeosciences* 6: 2099–2120.

756 Tierney, G.T., T.J. Fahey, P.M. Groffman, J.P. Hardy, R.D. Fitzhugh, and C.T. Driscoll. 2001. Soil  
757 freezing alters fine root dynamics in a northern hardwood forest. *Biogeochemistry* 56: 175–190.

758 Townsend, A.R., B.H. Braswell, E.A. Holland, and J.E. Penner. 1996. Spatial and temporal patterns in  
759 terrestrial carbon storage due to deposition of fossil fuel nitrogen. *Ecological Applications* 6: 806–  
760 814.

761 Urakawa, R., H. Toda, K. Haibara, and Y. Aiba, 2012. Long-term hydrochemical monitoring in an  
762 Oyasan Experimental Forest Watershed comprised of two small forested watersheds of Japanese  
763 cedar and Japanese cypress. *Ecol Res (Data paper)* 27: 245.

764 Van Groenigen, J.W., G.L. Velthof, O. Oenema, K.J. Van Groenigen, and C. Van Kessel. 2010. Towards  
765 an agronomic assessment of N<sub>2</sub>O emissions: a case study for arable crops. *European Journal of Soil  
766 Science* 61 :903–913.

767 Van Maanen, J.M.S, I.J. Welle, G. Hageman, J.W. Dallinga, P.L. Mertens, and J.C. Kleinjans. 1996.  
768 Nitrate contamination of drinking water: relationship with HPRT variant frequency in lymphocyte  
769 DNA and urinary excretion of N- nitrosamines. *Environmental Health Perspectives* 104: 522–528.

770 Vermaat, J.E., S. Broekx, B. Van Eck, G. Engelen, F. Hellmann, J.L. De Kok, H. Van der Kwast, J. Maes,  
771 W. Salomons, et al. 2012. Nitrogen source apportionment for the catchment, estuary, and adjacent  
772 coastal waters of the river Scheldt. *Ecology and Society* 17: 30.  
773 <http://dx.doi.org/10.5751/ES-04889-170230>

774 Vitousek, P.M., R. Naylor, T. Crews, M.B. David, L.E. Drinkwater, E. Holland, P.J. Johnes, and J.  
775 Katzenberger. 2009. Nutrient Imbalances in Agricultural Development. *Science* 324: 1519–1520/.

776 Von Mutius, E. 2000. Current review of allergy and immunology. *Journal of Allergy and Clinical  
777 Immunology* 105: 9–19.

778 Wallenstein, M.D., D.D. Myrold, M. Firestone, and M. Voytek. 2006. Environmental controls on  
779 denitrifying communities and denitrification rates: Insights from molecular methods. *Ecological*  
780 *Applications* 16: 2143–2152.

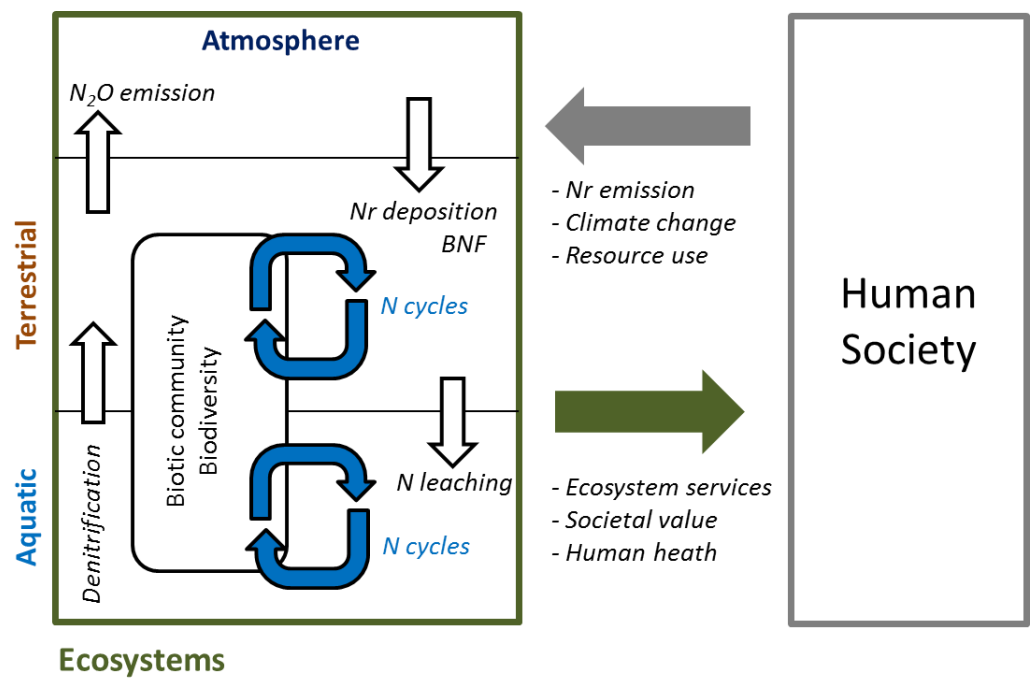
781 Ward, M.H., S.D. Mark, K.P. Cantor, D.D. Weisenburger, A. Correa-Villaseñor, and S.H. Zahm. 1996.  
782 Drinking water nitrate and the risk of non-Hodgkin’s lymphoma. *Epidemiology* 7: 465–471.

783 Weyer, P.J., J. Cerhan, B.C. Kross, G.R. Hallberg, J. Kantamneni, G. Breuer, M.P. Jones, W. Zheng, et al.  
784 2001. Municipal drinking water nitrate level and cancer risk in older women: the Iowa Women’s  
785 Health Study. *Epidemiology* 12:327–338

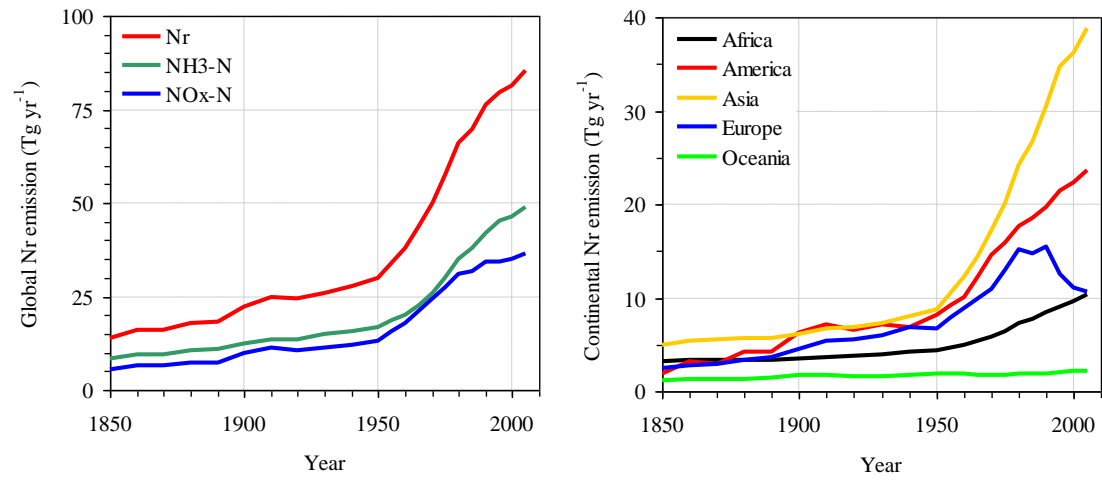
786 Wipf, S. and C. Rixen 2010. A review of snow manipulation experiments in Arctic and alpine tundra  
787 ecosystems. *Polar Research* 29: 95–109.

788 Wrigit, R.F., 1998. Effect of increased carbon dioxide and temperature on runoff chemistry at a forested  
789 catchment in southern Norway (CLIMEX Project). *Ecosystems* 1: 216–225.

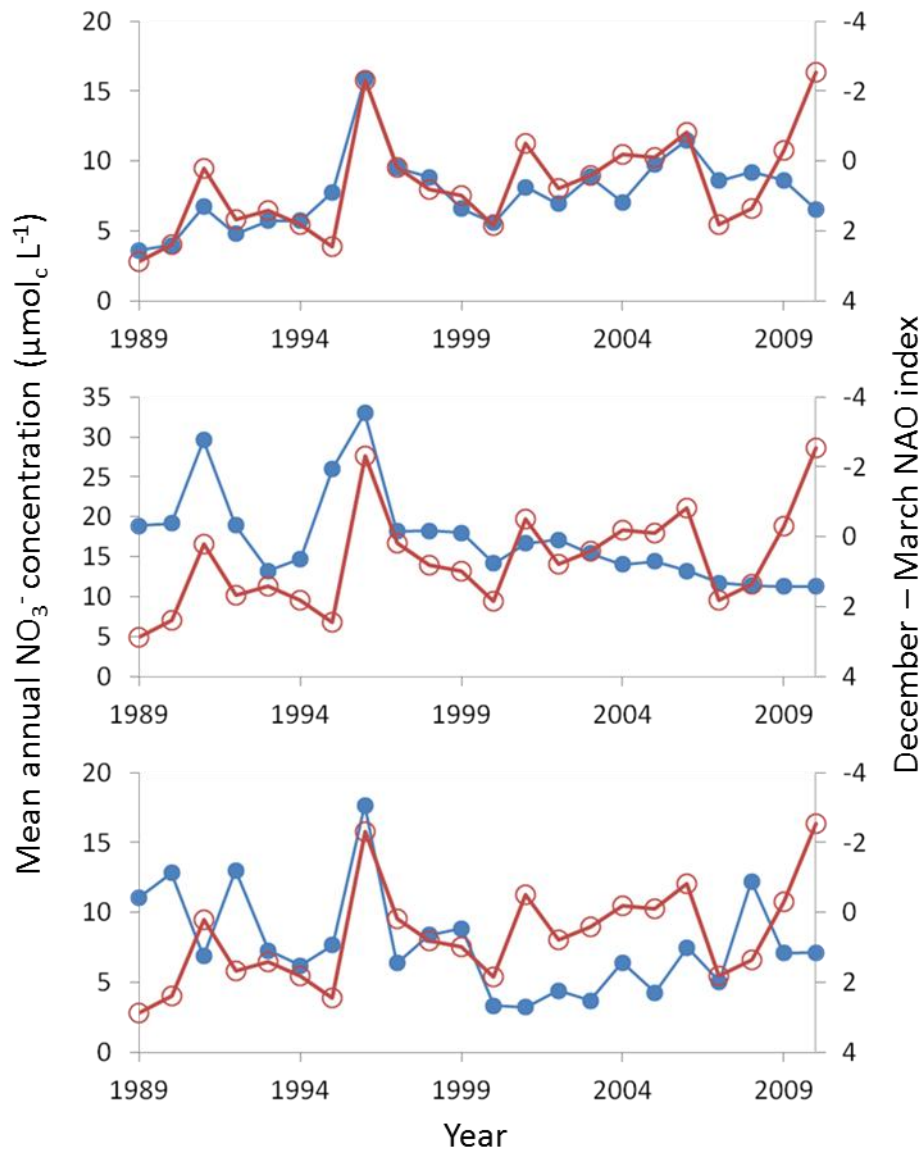
790 Zaehle, S., P. Ciais, A.D. Friend, and V. Priour. 2011. Carbon benefits of anthropogenic reactive nitrogen  
791 offset by nitrous oxide emissions. *Nature Geoscience* 4: 601–605.



**Fig.1** Conceptual framework of Nitrogen (N) biogeochemistry in coupled human and ecological systems in this review. Black arrows indicate anthropogenic disturbance and ecosystem feedbacks among both systems. White arrows represent dominant reactive nitrogen (Nr) flow; Nr deposition, Biological N fixation (BNF), N leaching and emission of nitrous oxide ( $N_2O$ ). Blue arrow shows N cycles among plant-soil-microbe systems.

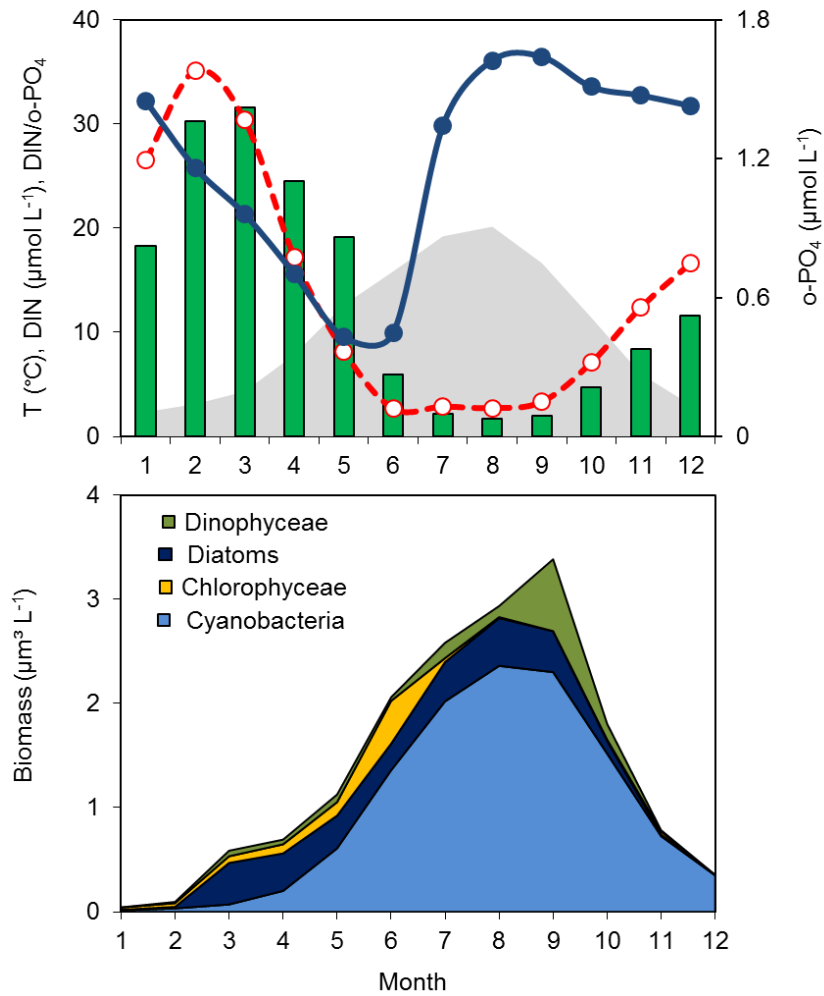


**Fig.2** Global (left panel) and continental (right panel) annual rates of Nr ( $\text{NO}_x\text{-N} + \text{NH}_3\text{-N}$ ) emissions (derived from Kopáček and Posch, 2011).



**Fig. 3** Long-term observation of nitrate concentrations in 3 small upland UK lakes (The UK Upland Waters Monitoring Network).

From the top, the sites are Round Loch of Glenhead (southwest Scotland), Scoat Tarn (English Lake District), and Llyn Llagi (North Wales - Snowdonia). The blue circles represent the annual means of seasonal (4 samples per year) nitrate concentrations. The open red circles represent the December to March North Atlantic Oscillation Index. The NAO scale is reversed so the most negative values are uppermost.



**Fig. 4** Seasonality of dissolved nutrient concentration, temperature and phytoplankton biomass in a coastal water body. Shown are seasonal changes in dissolved inorganic nitrogen (DIN in  $\mu\text{mol L}^{-1}$ ; open circles), ortho-phosphate ( $\text{o-PO}_4$  in  $\mu\text{mol L}^{-1}$ ; closed circles), temperature (T in  $^{\circ}\text{C}$ ; grey background area), DIN/o- $\text{PO}_4$  ratio (bars; upper panel) and phytoplankton biomass ( $\mu\text{m}^3 \text{L}^{-1}$ , lower panel, resolved for main taxonomic groups) of a coastal inlet (Kubitzer Bodden and Strelasund, Southern Baltic Sea coast, Germany). All values are averages over a 10-year period (1988-1999). For further details see Schubert and Wasmund (2005).