Organic phosphorus cycling may control grassland responses to nitrogen deposition: a long-term field manipulation and modelling study

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Abstract

In many temperate ecosystems, nitrogen (N) limits productivity, meaning anthropogenic N deposition can stimulate plant growth and subsequently carbon (C) sequestration. Phosphorus (P) and N-P co-limited grasslands are widespread, yet there is limited understanding of their responses to N deposition. Here, we investigate the consequences of enhanced N addition on the C-N-P pools of two P-limited grasslands; one acidic and one limestone, occurring on contrasting soils and explore their responses to a long-term nutrient-manipulation experiment. We do this by combining data with an integrated C-N-P cycling model (N14CP). We explore the role of P-access mechanisms by allowing these to vary in the modelling framework, and comparing model plant-soil C-N-P outputs to empirical data. Combinations of organic P access and inorganic P availability most closely representing empirical data were used to simulate the grasslands and quantify their temporal response to nutrient manipulation. The model suggested that access to organic P is a key determinant of grassland nutrient limitation and responses to experimental N and P manipulation. A high rate of organic P access allowed the acidic grassland to overcome N-induced P limitation, increasing biomass C input to soil and promoting SOC sequestration in response to N addition. Conversely, poor accessibility of organic P for the limestone grassland meant N provision exacerbated P-limitation and reduced biomass input to the soil, reducing soil carbon storage. Plant acquisition of organic P may therefore play an important role in reducing P-limitation, and determining responses to anthropogenic changes in nutrient availability. We conclude that grasslands differing in their access to organic P may respond to N deposition in contrasting ways, and stress that should N deposition shift ecosystems toward stronger P-limitation, a globally important carbon sink risks degradation.

1. Introduction

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51   Grasslands represent up to a third of terrestrial net primary productivity (NPP) [Hoekstra *et al.*, 2005]

52   and potentially hold over 10% of the total organic carbon stored within the biosphere [Jones and

53   Donnelly, 2004]. The ecosystem services provided by grasslands, such as carbon storage, are highly

54   sensitive to perturbations in their nutrient cycling, including the perturbation of nitrogen (N) inputs

55   from atmospheric deposition [Phoenix *et al.*, 2012].

56   Since the onset of the industrial revolution, human activity has doubled the global cycling of N, with

57   anthropogenic sources contributing 210 Tg of fixed N per year to the global N cycle, surpassing

58   naturally fixed N by 7 Tg N yr^{-1} [Fowler *et al.*, 2013]. Much of this additional N is deposited on terrestrial

59   ecosystems from atmospheric sources. This magnitude of N deposition results in a range of negative

60   impacts on ecosystems (including grasslands) such as reductions in biodiversity [Bobbink *et al.*, 2010;

61   Southon *et al.*, 2013], acidification of soil, and the mobilisation of potentially toxic metals [Carroll *et*

62   *al.*, 2003; Horswill *et al.*, 2008; Phoenix *et al.*, 2012]

63   Despite large anthropogenic fluxes of N, most terrestrial ecosystems on temperate post-glacial soils

64   are thought to be N-limited (biomass production is most restricted by N availability) [Vitousek and

65   Howarth, 1991; Du *et al.*, 2020], as weatherable sources of phosphorus (P) remain sufficiently large to

66   meet plant P demand [Vitousek and Farrington, 1997; Menge *et al.*, 2012]. Both empirical and

67   modelling studies have shown that pollutant N, when deposited on N-limited ecosystems, can increase

68   productivity [Tipping *et al.*, 2019] and soil organic carbon (SOC) storage [Tipping *et al.*, 2017], largely

69   as a result of stimulated plant growth. This suggests that while there are negative consequences of N

70   deposition, there may also be benefits from enhanced plant productivity and increases in carbon

71   sequestration.

72   Whilst most research focuses on N-limited ecosystems [LeBauer and Treseder, 2008], a number of

73   studies have highlighted that P limitation and N-P co-limitation are just as prevalent, if not more

74   widespread, than N limitation [Fay *et al*., 2015; Du *et al*., 2020; Hou *et al*., 2020]. In a meta-analysis of

75   grassland nutrient addition experiments spanning five continents, Fay *et al*. [2015] found that

76   aboveground annual net primary productivity was limited by nutrients in 31 out of 42 sites, most

77   commonly through co-limitation of N and P [Fay *et al*., 2015]. Similarly, P additions in 652 field

78   experiments increased aboveground plant productivity by an average of 34.9% [Hou *et al*., 2020],

79   while it is estimated that P limitation, alone or through co-limitation with N, could constrain up to

80   82% of the natural terrestrial surface's productivity [Du *et al*., 2020].

81   Furthermore, P limitation may be exacerbated by N deposition [Johnson *et al*., 1999; Phoenix *et al*.,

82   2004], or become increasingly prevalent as previously N-limited ecosystems transition to N-sufficient

83   states [Goll *et al*., 2012]. For example, in parts of the Peak District National Park, UK, N deposition has

84   exceeded 3 g m^{-2} yr^{-1}, with further experimental additions of 3.5 g m^{-2} yr^{-1} leading to decreases rather

85   than increases in productivity of limestone grasslands [Carroll *et al*., 2003]. This makes P limitation

86   critical to understand in the context of global carbon and nutrient cycles. By definition, N deposition

87   should impact P-limited ecosystems differently to N-limited ones, yet there is little understanding of

88   how N deposition impacts these systems.

89   While N deposition may worsen P limitation in some instances, plant strategies for P acquisition may

90   require substantial investments of N, suggesting that increased N supply may facilitate enhanced P

91   uptake [Vance *et al.,* 2003; Long *et al*., 2016; Chen *et al*., 2020]. Indeed, previous work from long-term

92   experimental grasslands has shown strong effects of N deposition on plant enzyme production

93   [Johnson *et al.* 1999; Phoenix *et al.* 2004], whereby the production of additional extracellular

94   phosphatase enzymes was stimulated. While it is not clear if this response is driven by exacerbated P-

95   limitation resulting from N deposition or extra N availability making elevated enzyme production

96   possible, such changes in plant physiology may promote cleaving of P from organic soil pools. Over

97   time, the accumulation of plant-available P from organic sources may provide a mechanism by which

98   plants exposed to high levels of N deposition may overcome P limitation [Chen *et al.* 2020].

99   By using the integrated C-N-P cycle model N14CP, Janes-Bassett *et al.* [2020] suggest that the role of

100   organic P cycling in models may be poorly represented, as the model failed to simulate empirical yield

101   data in agricultural soils with low P fertiliser input. Organic P access is therefore likely an important

102   means of nutrient acquisition for plants in high N and low P soils [Chen *et al.* 2020], yet our

103   understanding of organic P cycling in semi-natural ecosystems is fairly limited [Janes-Bassett *et al.*

104   2020]. Such interdependencies of the C, N and P cycles make understanding an ecosystem's response

105   to perturbations in any one nutrient cycle challenging, particularly when ecosystems are not solely

106   limited in N. This highlights the need for integrated understanding of plant-soil nutrient cycling across

107   the C, N and P cycles, and in ecosystems that are not solely N-limited.

108   Process-based models have a role to play in addressing this, as they allow us to test our mechanistic

109   understanding and decouple the effects of multiple drivers. There has been increasing interest in

110   linking C with N and P cycles in terrestrial ecosystem models [Wang *et al*., 2010; Achat *et al*., 2016;

111   Jiang *et al*., 2019] as the magnitude of the effects that anthropogenic nutrient change can have on

112   biogeochemical cycling are realised [Yuan *et al*., 2018]. Yet, few modelling studies have explicitly

113   examined the effects of P limitation, or the role of organic P access in determining nutrient limitation,

114   likely mirroring the relatively fewer empirical studies of these systems.

115   By combining process-based models with empirical data from long-term nutrient-manipulation

116   experiments, we may simultaneously improve our understanding of empirical nutrient limitation, the

117   role(s) of organic P acquisition, and their interactions with anthropogenic nutrient pollution. In

118   particular, this approach offers a valuable opportunity for understanding ecosystem responses to

119   environmental changes that may only manifest after extended periods of time, such as with changes

120   in soil organic C, N and P pools, which typically occur on decadal timescales [Davies *et al*., 2016a, Janes-

121   Bassett *et al*., 2020]. Here, we combine new data from a long-term nutrient manipulation experiment

122   on two P-limited upland grasslands (acidic and limestone) occurring on contrasting soils, with the

123   mechanistic C-N-P plant-soil biogeochemical model; N14CP [Davies *et al*., 2016b].

124 We use these experimental data to explore the role of organic P access in determining ecosystem

125 nutrient limitation and grassland responses to long-term nutrient manipulations. Specifically, we aim

126 to explore how variation in P acquisition parameters, that control access to organic and inorganic

127 sources of P in the model, may help account for differing responses of empirical grassland C, N and P

128 pools to N and P additions. Second, we explore the effects of long-term anthropogenic N deposition

129 and experimental N and P additions on plant and soil variables of the simulated acidic and limestone

130 grasslands. This will help improve our understanding of organic P process attribution within the model

131 and may suggest how similarly nutrient limited grasslands could respond to similar conditions.

132 We hypothesise that 1) access to organic P will be an important determinant of ecosystem nutrient

133 limitation, 2) increased organic P availability may alleviate P limitation resulting from N deposition and

134 3) grasslands capable of accessing sufficient P from organic forms may overcome P limitation resulting

135 from N deposition and nutrient treatments, whereas grasslands lacking such accessibility will not.

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 2. Methods

140 **2.1. Field experiment description**

141 The empirical data is from Wardlow Hay Cop (henceforth referred to as Wardlow), a long-term

142 experimental grassland site in the Peak District National Park (UK) [Morecroft *et al.*, 1994]. There are

143 two distinct grassland communities occurring in close proximity; acidic (National vegetation

144 classification U4e) and limestone (NVC CG2d) semi-natural grasslands (Table S2). Both grasslands

145 share a carboniferous limestone hill but the limestone grassland sits atop a thin humic ranker

146 [Horswill *et al.*, 2008] and occurs predominantly on the hill brow. In contrast, the acidic grassland

147 occurs in the trough of the hill, allowing the accumulation of wind-blown loess and the formation of

148 a deeper soil profile of a palaeo-argillic brown earth [Horswill *et al.*, 2008].

149 Despite contrasting soil types, both the acidic and limestone grasslands are largely P-limited

150 [Morecroft *et al.* 1994; Carroll *et al.* 2003], though occasional N and P co-limitation can occur

151 [Phoenix *et al.* 2003] and more recently, positive growth responses in solely N-treated plots have

152 been observed, in line with the latest understanding that long-term N loading may increase P supply

153 by increasing phosphatase enzyme activity [Johnson et al. 1999; Phoenix et al.2004; Chen et al.

154 2020].

155 Nutrients (N and P) have been experimentally added to investigate the effects of elevated N

156 deposition and the influence of P limitation [Morecroft *et al.*, 1994]. Nitrogen treatments simulate

157 additional N deposition to the background level and the P treatment acts to alleviate P limitation.

158 Nutrients are added as solutions of distilled water and applied as fine spray by backpack sprayer, and

159 have been applied monthly since 1995, and since 2017 bi-monthly. Nutrient additions are in the

160 form of NH_4NO_3 for nitrogen and $NaH_2PO_4.H_2O$ for phosphorus. Nitrogen is applied at rates of 0

161 (distilled water control – 0N), 3.5 (low nitrogen – LN) and 14 g N m^{-2} yr^{-1} (high nitrogen – HN). The P

162 treatment is applied at a rate of 3.5 g P m^{-2} yr^{-1} (phosphorus – P).

163   Data collected from the Wardlow grasslands for the purpose of this work are; aboveground biomass

164   C, SOC, and total N, which is assumed to be equivalent to modelled SON. This new data is combined

165   with total P data that was collected by Horswill *et al.* at the site [Horswill *et al.*, 2008]. Summaries of

166   these data are available within the supplementary material (Table S4) and details of their collection

167   and conversion to model-compatible units in supplementary section S1.

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169   **2.2. Summary of model processes**

170   2.2.1. N14CP model summary

171   The N14CP ecosystem model is an integrated C-N-P biogeochemical cycle model that simulates net

172   primary productivity (NPP), C, N and P flows and stocks between and within plant biomass and soils,

173   and their associated fluxes to the atmosphere and leachates [Davies *et al.*, 2016b]. N14CP was

174   originally developed and tested on 88 northern Europe plot-scale studies, including grasslands,

175   where C, N and P data were available. All but one of the tested ecosystems exhibited N limitation

176   [Davies *et al.*, 2016b]. It has also been extensively and successfully blind-tested against SOC [Tipping

177   *et al.*, 2017] and NPP data from unimproved grassland sites across the UK [Tipping *et al.*, 2019].

178   However, N14CP has not been extensively tested against sites known to exhibit P limitation,

179   especially where these are explicitly manipulated by long term experimental treatments. While the

180   importance of modelled weatherable P (P_{Weath0}) and historic N deposition on N-limited C, N and P

181   have been investigated [Davies *et al.* 2016b], the potential influence of organic P on ecosystem

182   nutrient limitation and responses to nutrient perturbations have yet to be explored.

183   Here, we modify N14CP to add experimental N and P additions to simulate a long-term nutrient

184   manipulation experiment similar to that at the limestone and acidic grasslands at Wardlow, and we

185   use empirical data from Wardlow to explore the role of organic P cleaving in determining ecosystem

186   state. A full model description can be found in Davies *et al.*, [2016b], however, a summary of the

187   most relevant features is given here for convenience.

188   2.2.2. Net primary productivity and nutrient limitations

189   Plant biomass is simulated in the model as two sets of pools of coarse and fine tissues representing

190   both above and belowground plant C, N and P, with belowground biomass for each plant functional

191   type (PFT) represented by a root fraction. NPP adds to these on a quarterly basis with growth

192   occurring in quarters 2 and 3 (spring and summer). In N14CP, NPP depends on a single limiting

193   factor, in accordance with Liebig's law of the minimum. The factors that can limit growth in the

194   model include available N and P, temperature or precipitation, the latter two being provided as

195   input driver data (see section 2.3.2).

196   First, the potential maximum NPP limited by climate is calculated using regression techniques, as in

197   Tipping *et al.* [2014]. The corresponding plant demand for N and P to achieve this potential NPP is

198   then calculated [Davies *et al*., 2016b; Tipping *et al*., 2017]. This demand is defined by PFT

199   stoichiometry, which changes through time in accordance with ecosystem succession (see section

200   2.3.2). Stoichiometry of coarse tissue is constant but each PFT's fine tissue has two stoichiometric

201   end members, allowing the model to represent transitions from N-poor to N-rich species or an

202   enrichment of the fine tissues within a single species (or a combination of both) [Davies *et al*.,

203   2016b], dependent on available N. This allows a degree of flexibility in plant C:N ratios in response to

204   environmental changes such as N deposition. If the available nutrients cannot meet the calculated

205   plant nutrient demand, the minimum calculated NPP based on either N or P availability is used,

206   giving an estimation of the most limiting nutrient to plant growth.

207   Nutrient co-limiting behaviour can occur in the model through increased access to organic P sources

208   in the presence of sufficient N (see 2.2.3), and by having the rate of N fixation dependent on plant

209   and microbial available P [Davies *et al*., 2016b]. The initial rate of N fixation is based on literature

210   values for a given PFT but is downregulated by anthropogenic N deposition and related to P

211   availability. The degree to which P availabilty limits this maximum rate of fixation is determined by a

212   constant; K_{Nfix} [Davies *et al.* 2016b]. This means that while modelled NPP is limited by availability of a

213   single nutrient, co-limitation may occur through P limitation of N fixation [Danger *et al.* 2008].

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215   2.2.3. Plant and soil N and P cycling

216   A simplified summary of key pools and processes regarding plant-soil nutrient cycling are detailed in

217   Figure 1. Details such as initial base cation pools, their effects on soil pH, and most parameter names

218   have been omitted for clarity but are available from the original model development study [Davies *et*

219   *al.* 2016b]. Key changes for the purpose of this work are highlighted in red.

220   Plant available N is derived from biological fixation, the decomposition of coarse litter and SOM,

221   atmospheric deposition and direct N application. Plant available P also comes from SOM and coarse

222   litter decomposition, direct treatment, desorption of inorganic P from soil surfaces, and sometimes

223   cleaving of organic P [Davies *et al.*, 2016b]. The sorbed inorganic P pool builds over time with inputs

224   of weathered P and sorption of any excess plant available inorganic P, and desorption occurs as a

225   first order process.

226   Phosphorus enters the plant-soil system by weathering of parent material, the initial value of which

227   (P_{Weath0} within the model) can be set to a default value, or made site-specific by calibrating this initial

228   condition to soil observational data (as in methods section 2.3.3). From this initial pool, annual

229   releases of weathered P are determined by first-order rate constants that are temperature

230   dependent, with the assumption that no weathering occurs below 0 degrees Celsius. This weathered

231   P can then contribute toward plant-available P in soil water or be sorbed to soil surfaces. In principle,

232   P can be added in small quantities by atmospheric deposition [Ridame and Guieu, 2002] or by local

233   redistribution [Tipping *et al.*, 2014]. For the purpose of this study, P deposition is set to zero as its

234   net contribution to the total P pool in comparison to weathering is assumed to be minimal.

235   The size of the available P pool is determined by summing: P retained within plant biomass prior to

236   litterfall, inorganic P from decomposition, dissolved organic P and P cleaved from SOP by plants.

237   Accessibility of each P form is determined by a hierarchal relationship in the order mentioned above,

238   whereby plants and microbes access the most readily available P sources first and only move onto

239   the next once it has been exhausted.

240   When N is in sufficient supply and more bioavailable P forms have been exhausted from the total

241   available pool, simulated plants can access P from SOM via an implicit representation of extracellular

242   P-cleaving enzymes with a parameter termed P_{Cleave}. While empirical data quantifying this parameter

243   is scarce, N14CP constrains P_{Cleave} by utilising a maximum SOM C:P ratio; $[C:P]_{fixlim}$, that ensures SOM

244   stoichiometry is not unrealistically disrupted by excessive removal of organic P (Equation 1).

245

$$P_{Cleave} = SOP - \frac{SOC}{[C:P]_{fixlim}}$$

246   Equation 1

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248   The functioning of the P_{Cleave} parameter, including its stoichiometric constraint, remains the same in

249   this work but we have introduced a modifier to adjust the rate at which plants can access this P

250   source. This parameter; $P_{CleaveMax}$, represents the maximum amount (g m^{-2} season^{-1}) of cleaved P that

251   plants can acquire from the available P pool to satiate P demand.

252   A fraction of plant biomass is converted to litter in each quarterly time step and contributes a

253   proportion of its C, N and P content to SOM, which is sectioned intro three pools (fast, slow and

254   passive) depending on turnover rate [Davies *et al.*, 2016b]. Soil organic P (SOP) is simulated

255   alongside SOC and SON using C:N:P stoichiometries of coarse and fine plant biomass. Decomposition

256   of SOP, and its contribution to the available P pool, is subject to the same turnover rate constants as

257   for SOC and SON.

258   Carbon is lost as CO_2 following temperature-dependent decomposition and as dissolved organic

259   carbon. Likewise, N and P are lost via dissolved organic N and P in a proportion consistent with the

260   stoichiometry of each SOM pool. Inorganic N is lost via denitrification and inorganic P can be sorbed

261   by soil surfaces. Both inorganic N and P can be leached in dissolved forms if they are in excess of

262   plant demand.

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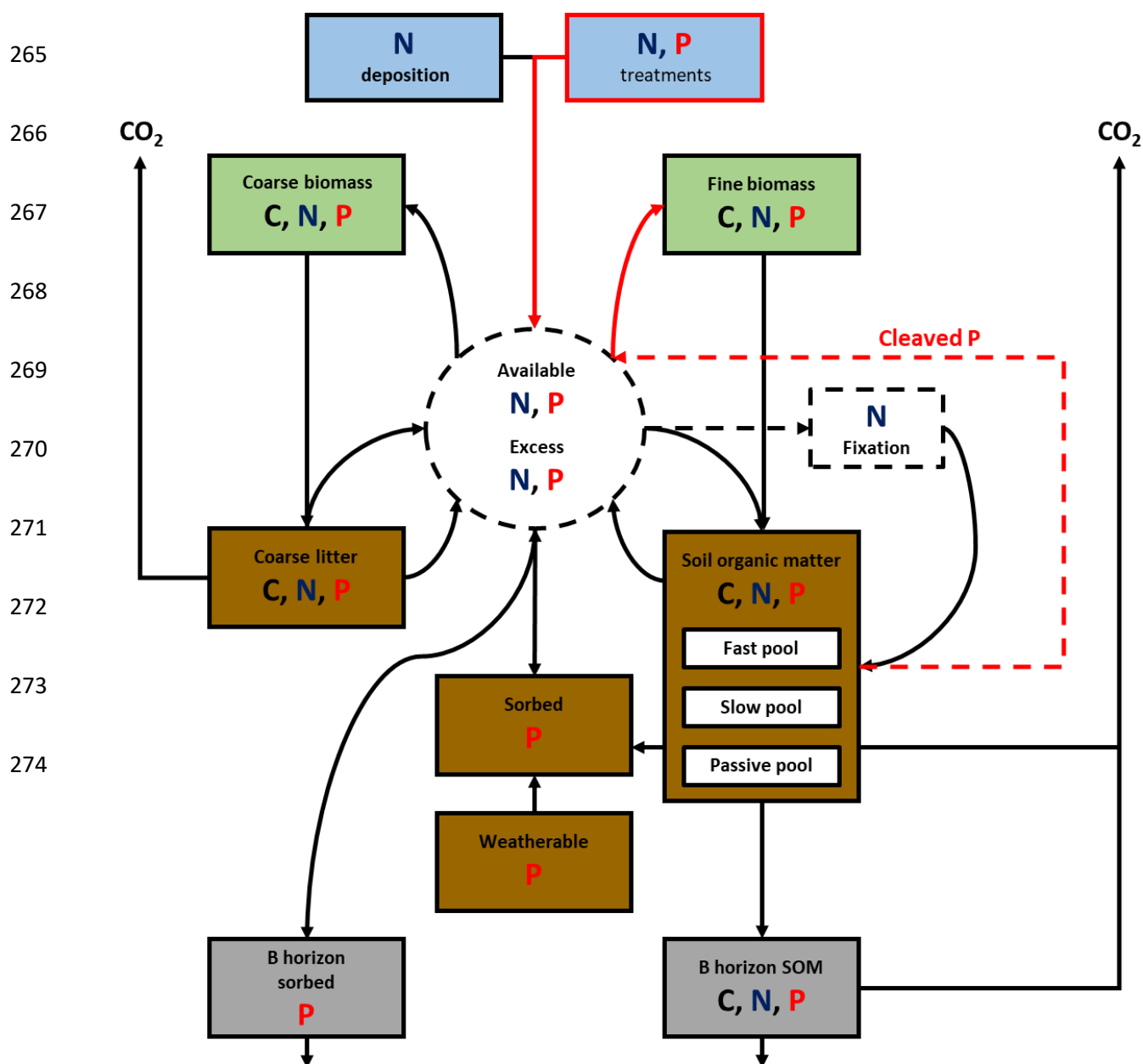
Figure 1: A simplified schematic of the key flows and pools of C, N and P within N14CP, adapted from the full schematic available in Davies *et al.* (2016a). Red lines highlight modifications to N14CP for the purpose of this work, including adding experimental nutrients and allowing uptake of cleaved P to be more flexible. Solid lines indicate input to another pool and a dashed line indicates either a feedback or interaction with another pool. In the model, N can enter the available pool via atmospheric deposition, nutrient treatments, biological fixation, and decomposition of coarse litter and SOM. For P, the two main sources are the inorganic sorbed pool and from the turnover of SOM. The former is derived initially from the weatherable supply of P, defined by its initial condition (P_{Weath0}). P can also be added to this pool experimentally as with N. The dashed line going from available N and P to N fixation represents the downregulation of N fixation by N deposition and the dependency of N fixation on P availability. The cleaving of organic P from SOM and its incorporation into the plant-available nutrient pool, is represented by the dashed red line and its uptake by plants, determined by $P_{CleaveMax,}$ shown with a solid red line.

275   **2.3. Simulating the field manipulation experiment with the model**

276   We use data from the Wardlow limestone and acidic grasslands to explore the potential role organic

277   P access may have in determining grassland nutrient limitation when exposed to long-term N

278   deposition and more recently, experimental nutrient manipulation. We use environmental input

279   data collated from Wardlow to drive model processes. Empirical data regarding contemporary soil C,

280   N and P for the contrasting grasslands is used to calibrate the initial size of the weatherable P pool

281   within the model, and to allow access to organic cleaved P to vary to account for patterns in the

282   data. We do not aim to perfectly replicate the Wardlow grasslands but rather use the unique

283   opportunity that Wardlow provides to test our understanding of such P-limited ecosystems and how

284   our conceptualisation of P access mechanisms within the model may affect them. In addition, we

285   can use the model-simulated grasslands to investigate the potential effects of long-term N

286   deposition and nutrient manipulation on ecosystems which may differ in their relative availability of

287   different P forms.

288

289   2.3.1. Nutrient applications

290   Nutrient treatments are treated in N14CP as individual plots in the simulations with differing

291   amounts of inorganic N and P applied in line with the field experimental treatments (section 2.1).

292   The N and P treatments are added to the bioavailable N and P pools of the model on a quarterly

293   basis in line with the model's time-step. While Wardlow nutrient treatments are applied monthly

294   and N14CP quarterly, the annual sum of applied N or P is equivalent, and nutrients are applied

295   during all quarters.

296

297   2.3.2. Input drivers

298   N14CP simulations run on a quarterly time step and are spun up from the onset of the Holocene

299   (10,000 BP in the model). This is to capture the length of time required for soil formation following

300   deglaciation in north west Europe and is not an attempt to truly model this long term period.

301   Instead, it allows us to form initial conditions for modern day simulations that takes in what we

302   know about the site's history and forcings.

303   To use this spin up phase and simulate contemporary soil C, N and P stocks, we use a variety of input

304   driver data. Inputs nearer the present are more accurately defined based on site-scale

305   measurements and assumptions are made regarding past conditions. This approach of spinning up

306   to present-day observations avoids the assumption that ecosystems are in a state of equilibrium,

307   which is likely inaccurate for ecosystems exposed to long-term anthropogenic changes in C, N and P

308   availability. Input driver data include PFT history, climatic data and N deposition data. A summary of

309   the data used for model input is provided in supplementary Table S3. To simulate the sites' PFT

310   history, we used data on Holocene pollen stratigraphy of the White Peak region of Derbyshire

311   [Taylor *et al*. 1994], which captures important information regarding Wardlow's land-use history for

312   the entire duration of the model spin up phase.

313   Input drivers are provided as annual time series to drive the model and as the acidic and limestone

314   sites are co-located, these input timeseries are shared for both grasslands. It is assumed in the

315   model that anthropogenic N deposition was negligible prior to 1800 and the onset of the industrial

316   revolution. After 1800, N deposition is assumed to have increased similarly across Europe [Schopp *et*

317   *al*., 2003]. In N14CP, this trend is linearly extrapolated from the first year of data (1880) back to 1800

318   [Tipping *et al*., 2012]. Data regarding N deposition that is specific to Wardlow was incorporated

319   between the years 2004 and 2014 and the Schöpp *et al*. [2003] anomaly scaled to represent the high

320   N deposition of the site.

321 To provide climate forcing data, daily minimum, mean and maximum temperature and mean

322 precipitation records beginning in 1960 were extracted from the UKPC09 Met office CEDA database

323 (Table S3). The data nearest to Wardlow was calculated by triangulating latitude and longitude data

324 and using Pythagoras' theorem to determine the shortest distance. These data were converted into

325 mean quarterly temperature and precipitation. Prior to this, temperature was assumed to follow

326 trends described in Davies *et al*. [2016b] and mean quarterly precipitation was derived from Met

327 Office rainfall data between 1960 to 2016 and held constant.

328

329 2.3.3. Model parameters for the acidic and limestone grasslands

330 The N14CP model has been previously calibrated and tested against a wide range of site data to

331 provide a general parameter set that is applicable to temperate semi-natural ecosystems, without

332 extensive site-specific calibration [Davies *et al*., 2016b]. The majority of those parameters are used

333 here for both grasslands. However, two parameters relating to P sources and processes were

334 allowed to vary between the sites: the initial condition for the weatherable P pool, P_{Weath0}; and the

335 rate of plant access to organic P sources, $P_{CleaveMax}$ (Figure 1). We allowed P_{Weath0} to vary for each

336 grassland as variation in a number of factors including lithology and topography mean that we

337 should expect the flux of weathered P entering the plant-soil system to vary on a site-by-site basis

338 [Davies *et al*. 2016b]. Indeed, we should expect that P_{Weath0} differs between the acid and limestone

339 grasslands, as despite their proximity, they have differing lithology. Davies *et al*. [2016b], show that

340 variation in this initial condition considerably helps explain variance in contemporary SOC, SON and

341 SOP stocks between sites. However, it is difficult to set this parameter directly using empirical data,

342 as information on lithology and P release is limited at the site scale.

343 As this is the first time that N14CP has been knowingly applied to ecosystems of a largely P-limited

344 nature, we also allowed the maximum rate at which plants could access cleaved P ($P_{CleaveMax}$) to vary,

345 to investigate how plant P acquisition might change when more readily accessible P forms become

346   scarcer. Empirical quantification of organic P access is poor [Janes-Bassett *et al.* 2020], hence we use

347   a similar data-driven calibration for $P_{CleaveMax}$ as we do for P_{Weath0}.

348   We ran a series of simulations systematically varying P_{Weath0} and $P_{CleaveMax}$ and comparing the results

349   to observations, we simulated the two grasslands and their treatment blocks with a set of 200

350   parameter combinations. This captured all combinations of 20 values of P_{Weath0} between 50 and 1000

351   g m^{-2} and 10 values of $P_{CleaveMax}$ between 0 to 1 g m^{-2} per growing season using a $\log_{10}$ spacing to focus

352   on the lower range of $P_{CleaveMax}$ values. The P_{Weath0} range was set to capture the lower end of P_{Weath0}

353   estimates described in Davies *et al.* [2016b], which were more likely to be appropriate for these P-

354   poor sites. We explored a range of values for $P_{CleaveMax}$, from zero where no access to organic sources

355   is allowed, to 1 g m^{-2} per growing season – a rate in the order of magnitude of a fertilizer application.

356   The model outputs were compared to measured, SOC, SON and total P (Table S4) for each grassland.

357   We tested how these parameter sets performed by calculating the error between the observations

358   and model outputs of the same variables for each combination of $P_{CleaveMax}$ and P_{Weath0}. The sum of

359   the absolute errors between modelled and observed soil C, N and P data were scaled (to account for

360   differing numbers of observations) and summed to provide an F value (Equation 2) as an overall

361   measure of error across multiple observation variables. The parameter combination with the lowest

362   F value that still maintained the grassland's empirical response to nutrient additions for both the

363   acidic and limestone grasslands (Supplementary section S1.1.), was used within the analysis.

364

$$F = (\frac{SAE[C_{SOM}]}{\bar{C}_{SOM,Obs}})/C_n + (\frac{SAE[N_{SOM}]}{\bar{N}_{SOM,Obs}})/N_n + (\frac{SAE[P_{Total}]}{\bar{P}_{Total,Obs}})/P_n \qquad \text{(Equation 2)}$$

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368   Plant biomass C data were excluded from the cost function to allow for blind testing of the model's

369   performance against empirical observations. As the variable most responsive to nutrient additions,

370   both in terms of rapidity and magnitude of the response, we deemed these the most rigorous data

371   to use for separate testing. We included soil C, N and P data from all nutrient treatments rather than

372   just the control to ensure that the selected parameter combination could better account for

373   patterns in empirical data. For instance, we know that empirical N treatments can increase plant and

374   soil enzyme activity in both Wardlow grasslands, [Johnson *et al.* 1999; Phoenix *et al.* 2004; Keane *et*

375   *al.* 2020] which a calibration to control-only data may not have captured.

376   While the cost function is a useful tool in allowing the model to simulate the magnitude of

377   contemporary C, N and P pools, it does not allow us to capture all necessary information to

378   accurately simulate grasslands of contrasting nutrient limitation. The pattern of grassland response,

379   i.e. how a variable responds to nutrient treatment, is an important consideration and is determined

380   in the model by the most limiting nutrient. Consequently, the parameter combination with the

381   lowest F value, that still maintained a grassland's empirical response to nutrient additions

382   (Supplementary section S1.1.), was used within the analysis.

383

384

3. Results

Below, we first present data regarding the results of the calibration of P_{Weath0} and $P_{CleaveMax}$ for each grassland, and how simulated grassland C, N and P using these parameter combinations compares to the empirical data (section 3.1, Figure 2). Second, we explore how the limiting nutrient of the modelled grasslands has changed through time in response to N deposition and experimental treatment (section 3.2, Figure 3). Third, we explore how C, N and P pools in the simulated grasslands have responded to N deposition and nutrient treatment within the model, and include empirical data to contextualise changes (section 3.3, Figure 4). Finally, we present the C, N and P budgets for both modelled grasslands to examine changes in C, N and P pools more closely, in order to better our mechanistic understanding of changes in nutrient flows within the model (section 3.3, Figure 5).

3.1. Varying phosphorus source parameters

The model calibration selected parameter values for P_{Weath0} and $P_{CleaveMax}$ that indicate contrasting use of P sources by the two simulated grasslands, with the acidic grassland capable of acquiring more P from organic sources, having a $P_{CleaveMax}$ value of 0.3162 g m^{-2} season^{-1} compared to the limestone, with a value 10 times smaller at 0.0316 g m^{-2} season^{-1}. Conversely, inorganic P availability was greater in the limestone grassland due to the larger weatherable pool of P, P_{Weath0}, at 300 g m^{-2} compared to 150 g m^{-2} in the acidic.

The selected parameter combinations resulted in the model simulating the acidic grassland as N-limited and the limestone as P-limited, with reasonable congruence between observed and modelled data. The outputs for the calibrated model are shown in Figure 2 against the observations for above-ground biomass C, soil organic C, and N for both the acidic and limestone grasslands (Fig 2). Raw data used for Figure 2 are provided in supplementary tables S5 and S6.

410   Overall, N14CP more accurately simulated the magnitude of limestone grassland C, N and P pools

411   than the acidic, and it generally captured the pattern of responses to nutrient treatment, albeit this

412   is not always supported by high r^2 values. The model estimates of above ground biomass C are

413   broadly aligned with the observations: capturing variation between the grasslands and treatments

414   (r^2 = 0.58), and on average overestimating the magnitude by 12.9% (SE ± 11.9) and 12.1% (SE ± 9.4)

415   for the acidic and limestone grasslands respectively (Fig 2a).

416   Soil organic C on average was slightly overestimated (7.1% with SE ± 3.3) for the limestone grassland

417   (Fig 2b), with a larger average overestimate for the acidic grassland (39.9% with SE ± 6.8). However,

418   in this latter case the variation between treatments was better captured. Despite a low r^2 value for

419   SOC (0.01), the model broadly captured the patterns we observe in the empirical data, with N

420   addition increasing SOC in the acidic and P addition increasing SOC in the limestone. However, the

421   intermediate increase in SOC with P in the acidic grassland is not captured by the model, nor is the

422   magnitude of the negative effect of LN treatment on limestone SOC.

423   Simulated magnitudes of SON are well-aligned with observations for the acidic grassland, with an

424   average error of 2.3% (SE ± 3.2), whilst SON for the limestone grassland was on average

425   underestimated by 17.8% (SE ± 3.6) (Fig 2c). The variation between treatments was better captured

426   for acidic than limestone SON but was overall reasonable (r^2 = 0.39).

427   Finally, the model overestimated total soil P (defined in the model as organic P plus sorbed P) by an

428   average of 6.0% (SE ± 4.3) for the limestone but underestimated by 54.7% (SE ± 8.0) in the acidic

429   grassland, which was the least accurately predicted variable out of those investigated (Fig 2d). With

430   only two empirical data points for TP across only two nutrient treatments, it is difficult to discern the

431   relationship between treatments and TP so an r^2 value is of little relevance here.

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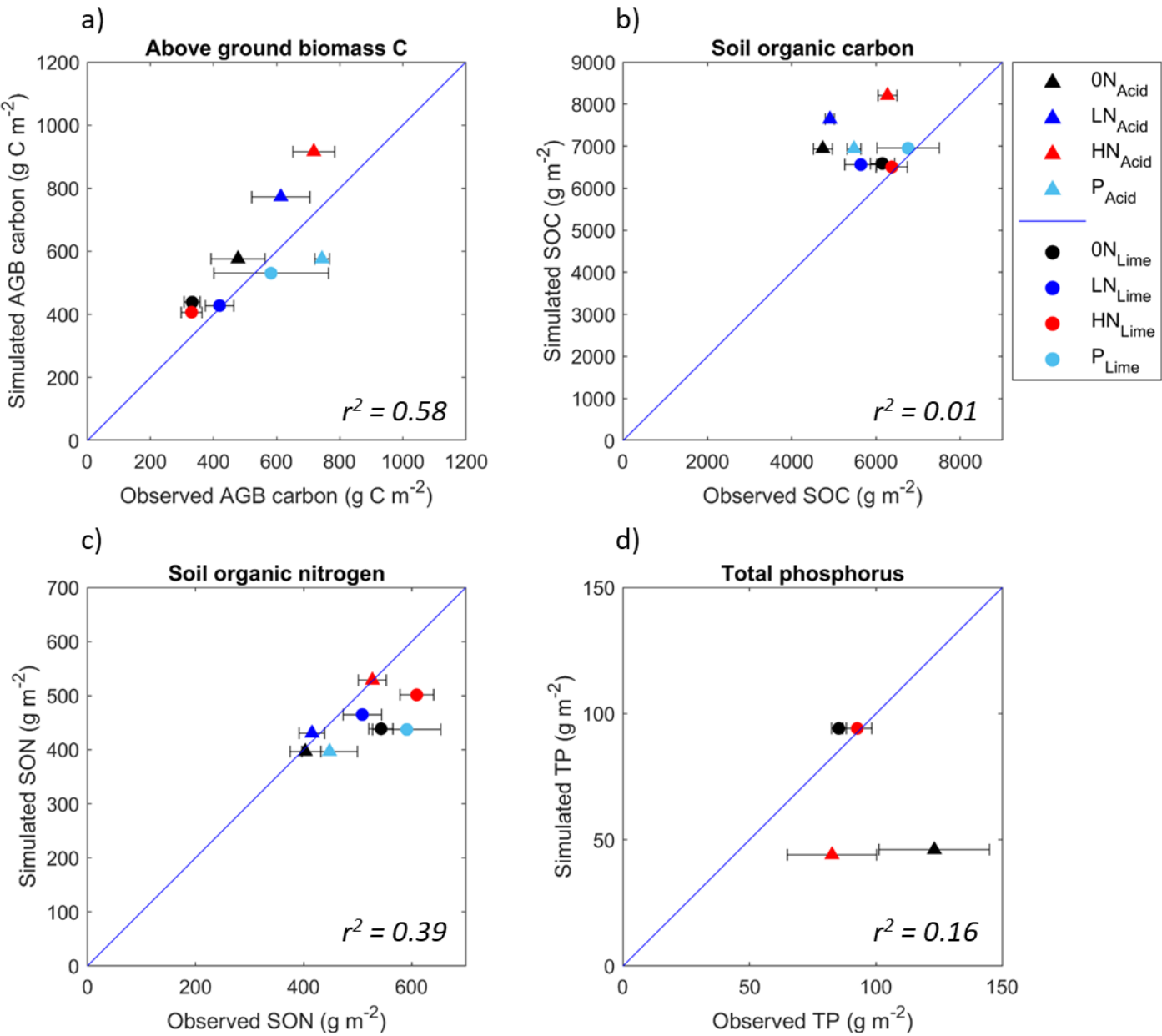
Figure 2: A comparison of the observed values of a) aboveground biomass carbon, b) soil organic carbon, c) soil organic nitrogen and d) total soil phosphorus from both grasslands, with simulated values from the model. The blue line represents a 1 to 1 relationship and the closer the data points are to the line, the smaller the discrepancy between observed and modelled data. All data are in grams per metre squared and all treatments for which data were collected are presented. The horizontal error bars represent the standard error of the empirical data means. The r^2 value of regression models fitted to the data give an overall indication of the direction of response of each variable to nutrient addition, hence a low value is not necessarily indicative of poor model fit

3.2. The limiting nutrient through time

Modelled acid grassland NPP remained N-limited from 1800 through to 2020 under most nutrient treatments (Fig 3). Nitrogen deposition increased the potential NPP through time and the grassland moved toward co-limitation in the LN treatment (i.e. the N and P lines were closer) but remained N-limited (Fig 3b). In the HN treatment, the acidic grassland shifted to P limitation as N-limited NPP surpasses P-limited NPP (Fig 3c).

The simulated limestone grassland was also initially N-limited, but was driven through a prolonged (c. 100 year) state of apparent co-limitation until clearly reaching P-limitation in 1950, solely as a result of N deposition (Fig 3). In the 0N treatment, the grassland remained P-limited but the potential NPP values for N and P are similar, suggesting the grassland is close to co-limitation (Fig 3e). The LN and HN treatment amplified pre-existing P-limitation, lowering the potential NPP of the grasslands (Fig 3f, g). With the addition of P in 1995, P limitation is alleviated, and the ecosystem transitions to a more productive N-limited grassland (Figure 3h).

Another way to interpret the extent of nutrient limitation within N14CP with specific reference to P-demand, is to assess the rate of P cleaving through time. These data corroborate the N and P-limited NPP data, showing that in the limestone grassland, the maximum amount of cleavable P is accessed by plants in the 0N, LN and HN treatments from approximately 1900 through to the end of the experimental period in 2020 (Fig S1, Table S14), highlighting its consistent state of P limitation.

Conversely, while cleaved P is used in the 0N treatment in the acidic grassland, it occurs at approximately one third of the total rate, hence the grassland is not entirely P-limited (Fig S1, Table S10). The LN treatment increases the rate of access to cleaved P and HN causes it to reach its maximum value, confirming the shift to P limitation suggested by the NPP data (Fig S1, Table S10). Soil organic P cleaving does not occur in the P-treated plots of either grassland.
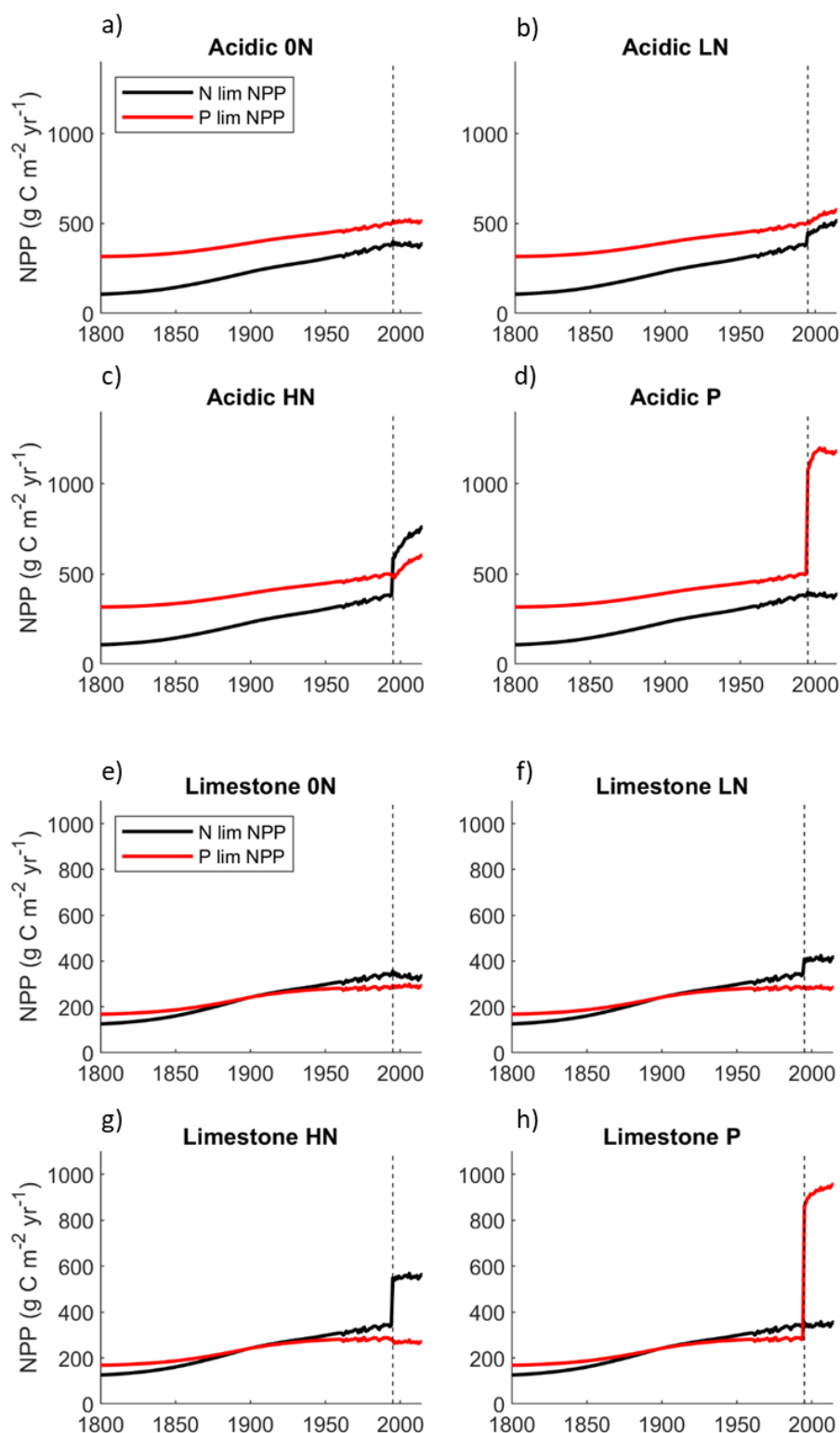
Figure 3: Plots showing the nutrient most limiting productivity for all nutrient treatments in both simulated grasslands. The vertical dashed line is the year of first nutrient addition within the model (1995). The value of the lines represents the maximum amount of productivity attainable given the availability of N and P separately. Due to a Liebig's law of the minimum approach to plant growth, it is the lowest of the two lines that dictates the limiting nutrient of the grassland and represents actual modelled productivity. Where lines share a value, it can be considered in a state of N-P co-limitation.

3.3. Modelled trends and responses to nutrient additions

The model allows the temporal trends and responses to nutrient additions to be further explored. Figure 4 provides the temporal responses for the treatments, and Figure 5 a full nutrient budget for the year 2020. Full data for changes in soil C, N and P and plant biomass C pools since the onset of large-scale N deposition (1800 within the model) for both grasslands are included in supplementary Table S15. All data used for determining responses of biomass C and soil organic C, N and P pools to experimental nutrient additions are in supplementary Tables S16 (acidic) and S17 (limestone).

3.3.1. Acidic grassland

The modelled time series suggest that in the 0N (control) treatment for the acidic grassland, background levels of atmospheric N deposition between the period 1800-2020 resulted in an almost four-fold increase in biomass C, a near-twofold increase in SOC and SON and increased the size of the SOP pool by almost a fifth (Fig 4).

Since initiated in 1995, all C and N pools responded positively to N but not P treatments (Fig 5a, c, Tables S7, S8). The LN and HN treatments further increased aboveground biomass C by 36.2% and 61.7% (Fig 4a) and increased the size of the total SOC pool by 11.5% and 20.6% respectively (Fig 4c). Similarly, the total SON pool in the acidic grassland increased by 9.7% in the LN treatment and 36.6% in the HN (Fig 4e).

Responses of the SOP pool are in contrast to those of the SOC and SON pools, with LN and HN decreasing SOP by 4.4% and 9.1% respectively, while P addition substantially increased the size of the SOP pool by 76.7% (Fig 4g). Nitrogen treatments facilitated access to SOP from both subsoil and topsoil, increasing plant available P and facilitating its uptake into biomass material (Fig 5e, Table S9).

486   3.3.2. Limestone grassland

487   Model simulations for the limestone grassland also suggest N deposition between 1800 and 2020

488   considerably increased aboveground biomass C, SOC and SON pools (Fig. 4), but to a lesser extent

489   than in the acidic grassland. Soil organic C and SON increased by almost half and biomass C more

490   than doubled. Soil organic P accumulated at a faster rate than in the acidic grassland, increasing by

491   about a third (Fig 4, Table S15).

492   Responses of the aboveground biomass C and SOC pools in the limestone grassland differ greatly to

493   those of the acidic, declining with N addition and increasing with P addition (Fig 4). This response

494   was ubiquitous to all C pools, with declines in subsoil, topsoil and biomass C (Fig 5b, Table S11).

495   Biomass C declined by 2.4% and 7.3% with LN and HN addition (Fig 4b) and SOC declined by 0.5%

496   and 1.4% with the same treatments (Fig 4d). Phosphorus addition increased biomass C and SOC by

497   22.0% and 6.1% respectively (Fig 4b, d).

498   Nitrogen treatments increased the size of subsoil, topsoil and available N pools, but led to small

499   declines in biomass N (Fig 5d, Table S12). The P treatment slightly reduced subsoil and topsoil SON

500   compared to the control yet increased available N and biomass N, to the extent where biomass N is

501   greater in the P than HN treatment (Fig 5d, Table S12). Total SON increased by 6.4% and 15.0% with

502   LN and HN respectively and declined by 0.2% with P treatment (Fig 4f).

503   The response of the limestone P pools mirrors that of carbon, with declines in subsoil SOP, topsoil

504   SOP, available P and biomass P with LN and HN addition (Fig 5f, Table S13). The limestone grassland

505   SOP pool declined by 0.2% with LN and 0.5% with HN addition, with an increase of 20.0% upon

506   addition of P (Fig 4h). The P treatment substantially increased total ecosystem P in the limestone

507   grassland, particularly in the topsoil sorbed pool (Fig 5f, Table S13).

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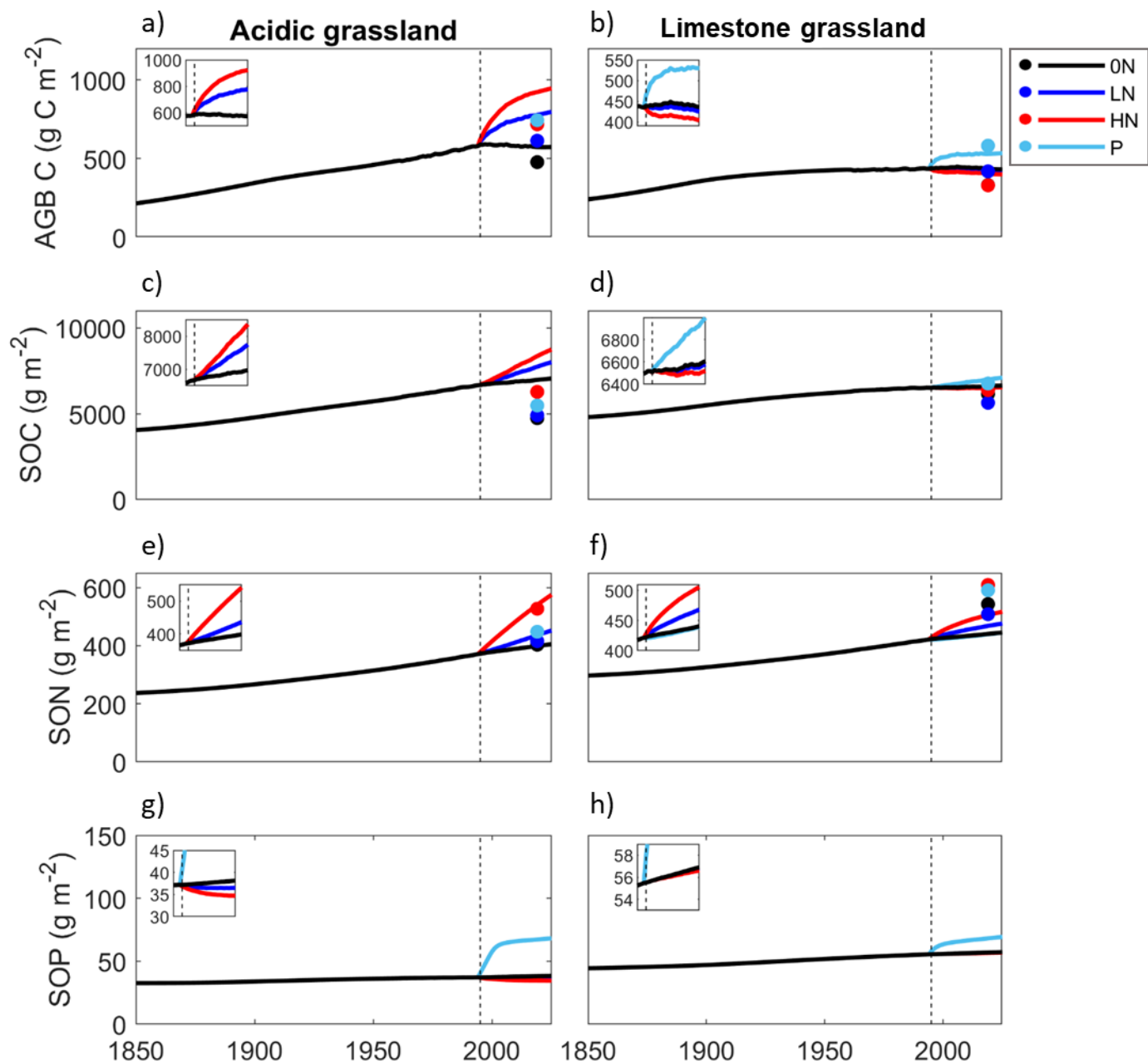
Figure 4: Time series plots of aboveground biomass C, soil organic C, N and P for the acidic (panels a, c, e and g respectively) and limestone modelled grasslands (panels b, d, f and h respectively). The vertical dashed line represents the first year of nutrient addition (1995) and marks the beginning of the experimental period. The inset subplots focus on this experimental period (1995-2020) and highlight changes occurring as a result of nutrient additions rather than background N deposition. All nutrient treatments at Wardlow are represented in all panels though not all lines are visible if they do not differ from 0N. Both grassland share a y axis. Empirical data from figure 2 are plotted on the respective panels, with the exception of panels g and h, where empirical data is incompatible with modelled data (total P versus organic P).
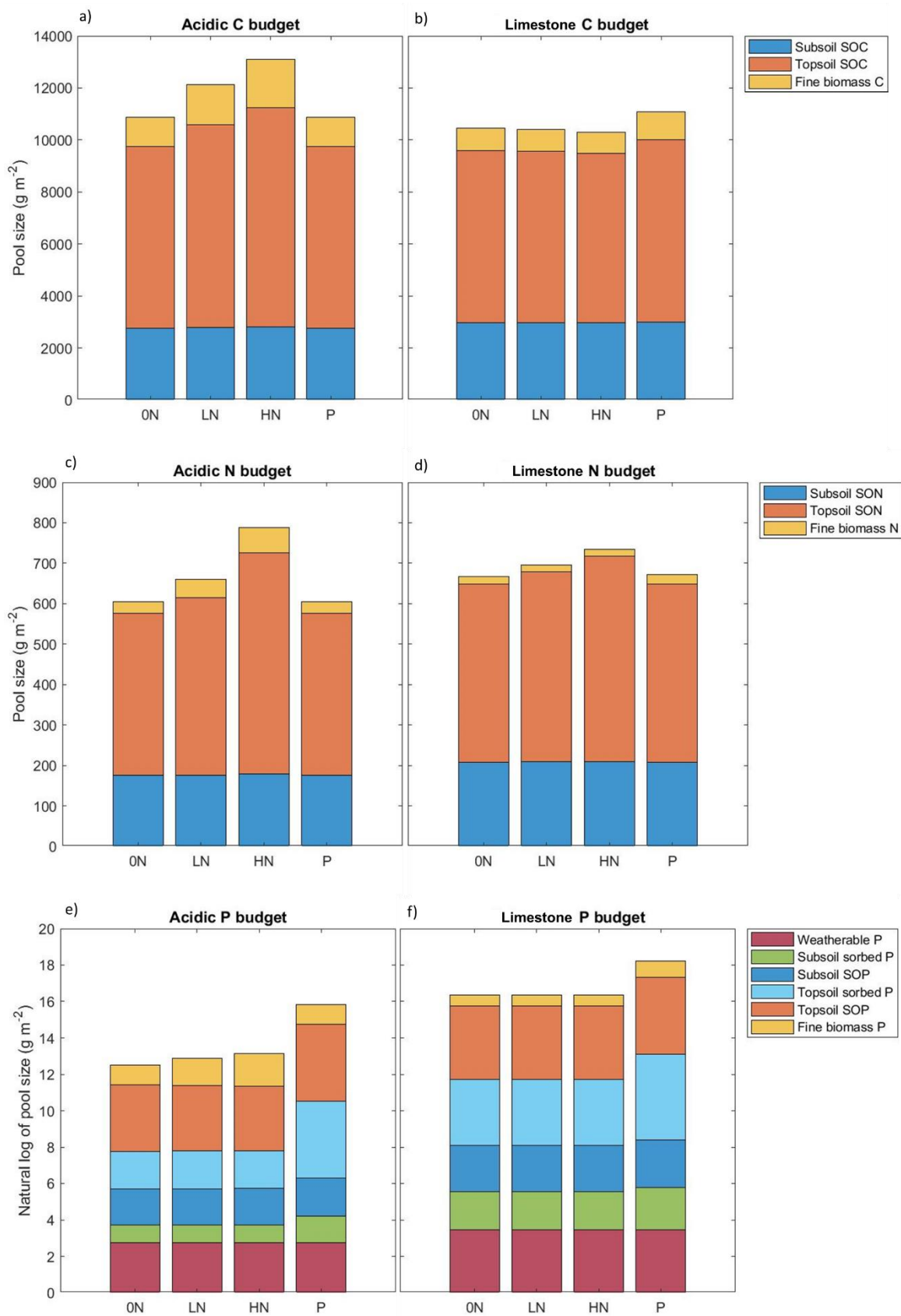
Figure 5: Modelled C, N and P budgets for the acidic (panels a, c and e) and limestone (panels b, d, f) grasslands for the year 2020. Modelled sizes of C and N pools are in grams per metre squared, and P pools are presented as $\log_n$ grams per metre squared. Temporary pools such as available N and P and fixed N are not presented here to avoid 'double counting' in other pools and wood litter C, N and P are not presented due to their negligible sizes.

4. Discussion

4.1. Simulating contrasting grasslands by varying plant access to P sources

This is the first instance in which N14CP, and to the best of our knowledge, any other integrated C-N-P cycle model, has explicitly modelled P-limited ecosystems and investigated their responses to N deposition and additional nutrient treatments. By using empirical data from long-term experimental grasslands to drive and calibrate N14CP, we could test the model's ability to simulate two contrasting P-limited grasslands, and how organic P access may affect this ability. While the purpose of this work was not to explicitly reproduce the Wardlow grasslands within N14CP, by comparing data from Wardlow to the simulated grasslands, we can simultaneously develop our understanding of the model's representation of under-studied P cycling processes and contextualise what this may mean for empirical systems such as Wardlow.

The model suggests that the acidic grassland was characterised by high access to organic P, with comparatively low inorganic P availability, whereas the limestone grassland was the opposite, with low organic and high inorganic P availability. These simulated differences could reflect the relative availability of different P sources at Wardlow. As the acidic grassland formed in a hillside depression, loess has accumulated, thickening the soil profile and distancing the plant community from the limestone bedrock. The plant rooting zone of the acidic grassland is therefore not in contact with the bedrock, and roots almost exclusively occur in the presence of organic P sources which can be cleaved and utilised by plants [Caldwell, 2005; Margalef *et al*., 2017]. Conversely, the limestone grassland soil rarely exceeds 10 cm depth, and the rooting zone extends to the limestone beneath, providing plants with greater access to weatherable calcium phosphate [Smits *et al*., 2012].

Such parameter combinations allowed for reasonable congruence between empirical and simulated data, with an average discrepancy of only 6.6% (SE ± 9.1) and 1.2% (SE ± 4.4) for the acidic and limestone grasslands respectively across all variables (Table S5). However, model performance differed greatly between the two grasslands. For instance, the model accurately captured the

538   magnitude of limestone C, N and P data and their expected P-limited responses to nutrient

539   treatment, but was less effective at simulating the acidic grassland. N14CP did not simulate an

540   increase in biomass C or SOC with P addition in the acidic grassland, instead simulating a solely N-

541   limited grassland. While this may be expected of a model that employs a law-of-the-minimum

542   approach, N14CP has a number of mechanisms to account for N and P interdependence, meaning

543   that in principle, it is capable of simulating positive responses to LN, HN and P treatment, as

544   observed in the empirical data from 2017 (section 2.2.2).

545   The overestimation of acidic C pools and underestimation of total P suggests that the model is

546   simulating that too much organic P is being accessed by plants in response to N addition and

547   transferred into plant biomass pools (Fig 2d). Few parameter sets where simultaneously able to

548   simulate the magnitude of the empirical TP pool and the positive response of biomass to N addition

549   in the acidic grassland. This may also be due to limitations in the empirical P data, as P data used for

550   calibrating P cycling were available for only two nutrient treatments and represented total soil P, not

551   organic P. While we acknowledge the technical and theoretical issues associated with distinguishing

552   between organic and inorganic P pools [Lajtha *et al.* 1999; Barrow *et al.* 2020], such distinctions

553   would help in understanding this discrepancy and likely improve the model's ability to simulate P-

554   limited systems, particularly when organic P availability may be important.

555   Additionally, N14CP's representation of organic P cleaving likely underestimates the ability of soil to

556   rapidly occlude and protect organic P that enters solution. For example, inositol phosphate, a major

557   constituent of organic P, has been found to be used extensively by plants grown in sand but is hardly

558   accessed by plants grown in soil [Adams and Pate 1992]. Such organic phosphates become strongly

559   bound to oxides in the soil, protecting them from attack by phosphatase enzymes [Barrow 2020].

560   This may be particularly prevalent in the acidic grassland at Wardlow where N deposition has

561   resulted in acidification and base cation depletion [Horswill *et al.* 2008], potentially enhancing the

562   formation of iron and aluminium complexes and immobilising P [Kooijman *et al.*, 1998]. As the

563   model lacks a mechanism for increasing access to secondary mineral P forms comparable to organic

564   P-cleaving, the uptake of organic P by the acidic grassland is very likely exaggerated.

565   The model's inability to simulate a positive response to both N and P addition in the acidic grassland

566   may be an unintended consequence of the downregulation of N fixation by N deposition included

567   within N14CP [Davies *et al.* 2016b]. While this representation is appropriate [Gundale *et al.* 2013],

568   when N deposition exceeds fixation (as at Wardlow), fixation is essentially nullified (as in Tables S8,

569   S12), meaning deposition becomes the sole source of N to the grassland. This in effect, removes the

570   dependence of N acquisition on P availability, and could make modelling behaviour akin to N-P co-

571   limitation [Harpole *et al*., 2011] under high levels of N deposition challenging. This suggests that

572   current C-N-P cycle models that employ a Liebig's law of the minimum can provide a broad

573   representation of multiple variables by calibrating access to both organic and inorganic P sources

574   [Davies *et al.* 2016b], provided the ecosystem in question's limiting nutrient leans towards N or P

575   limitation. Furthermore, where access to organic P forms is likely to be lower, as in the limestone

576   grassland, model performance may improve. This could be further explored by allowing N fixation

577   limits in the model to adapt to P nutrient conditions or by attenuating the suppression of N

578   deposition on N fixation, to represent acclimatisation of N-fixers to greater N availability [Zheng *et*

579   *al.* 2018].

580   Ultimately, differences in modelled accessibility to organic forms of P enabled N14CP to distinguish

581   between the two empirical grasslands, and simulate the magnitude and pattern of data with

582   reasonable accuracy, albeit with the previously mentioned caveats.

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4.2. Consequences of differential P access on ecosystem C, N and P

While the model's estimation of $P_{CleaveMax}$ for the acidic grassland is likely overestimated, the model experiment has highlighted that differences in organic versus inorganic P availability are a key determinant of an ecosystem's nutrient limitation, and consequently, how they respond to changes in anthropogenic N and P availability. For instance, while being exposed to the same background level of N deposition and the same magnitude of experimental treatment, the modelled acidic grassland was able to stimulate growth in response to LN and HN treatment whereas the modelled limestone grassland was negatively affected by it.

Nitrogen addition increases plant demand for P and can shift ecosystems toward a state of P limitation or increase the severity of limitation where it already exists [Menge and Field, 2007; An *et al*., 2011; Goll *et al*., 2012]. Consistent with this, both simulated grasslands saw SOP decline with LN and HN treatment, worsening P limitation in the limestone grassland, and depleting the SOP pool in the acidic. As P cleaved from organic pools is the least bioavailable within the model hierarchy (methods 2.2.3), this is indicative of increasing P stress in both grasslands. While SOP declined in both grasslands, the responses of available and biomass P to nutrient treatments differed markedly between the grasslands. Due to the higher rate of $P_{CleaveMax}$ in the acidic grassland, more P accumulated in the plant-available pool and hence P does not become the limiting factor under N treatments (Table S9). Conversely, available and biomass P decline under LN and HN addition in the limestone grassland (Table S13), highlighting how the grassland's $P_{CleaveMax}$ capability is insufficient to meet increased P demand.

Such high access to organic P sources in the modelled acidic grassland likely led it to respond to nutrient enrichment in an N-limited manner, increasing productivity in response to N deposition and LN and HN treatments as the model's limiting nutrient stimulated plant growth. Detrital C inputs from plant biomass are the primary source of SOC accumulation within N14CP [Davies *et al*., 2016b] and as such, changes in SOC integrate long term trends in net primary productivity in systems where

612   external nutrients are supplied. The provision of additional N in the modelled LN and HN treatments

613   therefore led to large increases in biomass accumulation and consequently, almost linearly increased

614   SOC (Fig 4c).

615   Similar increases in N-limited grassland SOC under N addition have been shown, resulting from

616   significant increases in below-ground carbon input from litter, roots [He *et al*., 2013] and detrital

617   inputs [Fornara *et al*., 2013], mechanisms similar to those reported by the model. Similarly, Tipping

618   *et al*. [2017] used N14CP to show that N deposition onto N-limited UK ecosystems ubiquitously

619   increased SOC storage by an average of 1.2 kgCm^{-2} (c. 10%) between 1750 and 2010 [Tipping *et al*.,

620   2017].

621   Despite its P-limited condition under the HN treatment (Fig 3c), the acidic grassland continued to

622   accumulate biomass with N addition as the grassland's greater access to topsoil SOP (Table S9)

623   allowed it to acquire sufficient P to stimulate additional growth but not necessarily to alleviate P

624   limitation. This is consistent with the acidic grassland at Wardlow, where N treatment stimulated

625   root surface phosphatases, likely supplying more SOP to plants [Johnson *et al*., 1999]. Our simulated

626   acidic grassland therefore supports the hypothesis that prolonged N deposition may increase SOP

627   access to such an extent that P limitation is alleviated and growth can be stimulated [Chen *et al.*

628   2020]. Organic P release from SOM and its potential immobilisation, is poorly represented in models

629   and we encourage further study aimed at quantifying these processes [Chen *et al.* 2020; Janes-

630   Bassett *et al*., 2020; Phoenix *et al*., 2020]. However, such high rates of SOP access only occurred

631   under experimental LN and HN treatments, and in reality, such rapid degradation of SOP may

632   eventually degrade the pool to such an extent that P limitation soon returns.

633   Conversely, biomass C and SOC in the modelled limestone grassland responded positively to P

634   addition, via similar mechanisms to the N-response in the modelled acidic grassland. However, in

635   contrast to the acidic grassland, N addition caused declines in limestone biomass and SOC, the

636   former of which has been observed at the limestone grassland at Wardlow [Carroll *et al*., 2003].

637   Reductions in limestone biomass C (and consequently SOC) in the model are a combined result of

638   reductions in bioavailable P (Table S13), occurring via N-driven increases in stoichiometric P demand,

639   in addition to an inability to access sufficient P from the SOP pool (Table S14). Plants therefore

640   cannot meet P demand and new biomass is insufficient to replace senesced plant material,

641   decreasing net biomass C input to the SOC pool. This implies that in ecosystems where plants are not

642   well-adapted to acquiring organic forms of P [Phoenix *et al.* 2020], or where organic P is scarce, N

643   deposition may worsen pre-existing P limitation and reduce ecosystem C stocks [Goll *et al.* 2012; Li

644   *et al.* 2018].

645

646   **4.3. Model limitations**

647
648   While N14CP is a fairly simple ecosystem model by design, it is one of the first process-based

649   biogeochemical models to explicitly incorporate P with the C and N cycles for semi-natural

650   ecosystems, and to simulate NPP and soil C, N and P dynamics, for which it has been extensively

651   tested [Davies *et al.* 2016a; Davies *et al.* 2016b; Tipping *et al.* 2017; Tipping *et al.* 2019; Janes-Bassett

652   *et al.* 2020]. Previous work with N14CP has identified the need to enhance its ability to simulate

653   organic P cycling [Janes-Bassett *et al.* 2020], which we aimed to do in this study using long-term

654   experimental data from contrasting P-limited grasslands.

655   N14CP's simplified representation of plant nutrient pools and plant control over nutrient uptake, is

656   largely controlled by stoichiometric demand [Davies *et al.* 2016a], and does not incorporate many

657   plant strategies for P acquisition [Vance *et al.* 2003]. Indeed, by allowing $P_{CleaveMax}$ to vary to account

658   for empirical data, we attempt to somewhat increase plant control over organic P uptake. We

659   acknowledge earlier that such an approach likely underestimates the ability of soil surfaces and

660   microbes to protect newly-cleaved P from plant uptake. As such, where we may expect access to

661   organic P to be high, such as the acidic grassland at Wardlow, such modelled representation of

662   plant-mediated P access may lead to unrealistic depletions in soil P and increases in biomass and soil

663   C, and we would encourage further work aimed at improving model-representation of plant controls

664   on organic P cycling [Fleischer *et al.* 2019].

665   While we feel incorporating a suite of plant strategies for acquiring P would represent over-

666   parameterisation, we acknowledge that a modelled equivalent to $P_{CleaveMax}$ for accessing inorganic P

667   forms is lacking, such as carbon-based acid exudation to increase mineral P weathering [Achat *et al.*

668   2016; Phoenix *et al.* 2020], which likely contributes toward the poor representation of the acidic

669   total P pool. Biota-enhanced P weathering and nutrient redistribution by mycorrhizal hyphae are

670   important for nutrient cycling [Quirk *et al.* 2012], and fungal community structure and function is

671   strongly influenced by perturbations in the C and N cycles [Moore *et al.* 2020]. Such processes are

672   not included within N14CP as the extent to which weathering can be controlled by such mechanisms

673   and the manner in which these can be represented in C-N-P cycle models is debated [Davies *et al.*

674   2016b].

675   Currently, N14CP assumes C to be in unlimited supply, with its uptake by plants and consequent

676   input into soil pools controlled by C:N:P stoichiometry, hence C availability has little effect on N and

677   P dynamics within the model. Increasing atmospheric CO_2 may increase nutrient availability, as

678   plants may reallocate additional carbon resources toward nutrient acquisition [Keane *et al.* 2020] or

679   elevated CO_2 (eCO_2) may increase limitation of other nutrients such as N [Luo *et al.* 2004]. The

680   inclusion of eCO_2 into N14CP poses a particularly enticing research opportunity, and we aim to use

681   this study as a foundation for future work to include this process.

682

5. Conclusions

We have shown that by varying two P-acquisition parameters within N14CP, we can account for contrasting responses of two P-limited grasslands of differing soil P chemistry, and with reasonable accuracy. However, such coarse representation of organic P cycling in the model likely overestimates the ability of plants to use newly-cleaved P and limits our ability to simulate grasslands where N and P interact to control plant productivity, including the potential for N inputs to alleviate P limitation.

Differences in organic P access was a key factor distinguishing the contrasting responses of the modelled grasslands to nutrient manipulation, with high plant access allowing the acidic grassland to acquire sufficient P to match available N from chronic deposition and prevent 'anthropogenic P limitation'. In the acidic grassland, N treatment stimulated plant access of organic P, promoting growth and C sequestration. However, the model suggests that this is an unsustainable strategy, as the SOP pool rapidly degrades, and if N additions are sustained, P limitation may return. Conversely in the limestone grassland, which was less able to access organic P, additional N provision exacerbated pre-existing P limitation by simultaneously increasing plant P demand and reducing P bioavailability. This reduced productivity and consequently C input to soil pools declined, resulting in SOC degradation exceeding its replacement.

We further show that anthropogenic N deposition since the onset of the industrial revolution has had a substantial impact on the C, N and P pools of both the modelled acidic and limestone grasslands, to the extent where almost half of contemporary soil C and N in the model could be from, or caused by, N deposition.

Our work therefore suggests that with sufficient access to organic P, long-term N addition may alleviate P limitation. Where organic P access is limited, N deposition could shift more ecosystems toward a state of P limitation or strengthen it where it already occurs [Goll *et al.*, 2012], reducing productivity to the point where declines in grassland SOC stocks - one of our largest and most labile carbon pools – may occur.

Data availability: Data archiving is underway with the NERC's Environmental Information Data Centre (EIDC) and a DOI will be available once this process is complete. All data to be archived is present in the supplementary information for review purposes.

Author contributions:

CRT: Conceptualistion, data curation, formal analysis, investigation, methodology, project administration, software, validation, visualisation, writing – original draft preparation, writing – review and editing

VJB: Conceptualisation, formal analysis, investigation, methodology, supervision, software, writing – review and editing

GKP: Conceptualisation, methodology, funding acquisition, project administration, resources, supervision, writing – review and editing

BK: Investigation, methodology, supervision, writing – review and editing

IPH: Funding acquisition, methodology, resources, supervision, writing – review and editing

JD: Conceptualisation, formal analysis, investigation, resources, methodology, supervision, project administration, software, writing – review and editing

Competing interests: The authors declare that they have no competing interests.

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6. References

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