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

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Abstract

Phosphorus (P) limited ecosystems are widespread, yet there is limited understanding of how these ecosystems may respond to anthropogenic deposition of nitrogen (N), and the interconnected effects on the biogeochemical cycling of carbon (C), N and P. 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 where access is limited, soil organic carbon stocks could decline.

1. Introduction

Grasslands represent up to a third of terrestrial net primary productivity (NPP) [Hoekstra *et al.* 2005] and potentially hold over 10% of the total organic carbon stored within the biosphere [Jones and Donnelly, 2004]. The ecosystem services provided by grasslands, such as carbon storage, are highly sensitive to perturbations in their nutrient cycling, including the perturbation of nitrogen (N) inputs from atmospheric deposition [Phoenix *et al.* 2012].

Since the onset of the industrial revolution, human activity has doubled the global cycling of N, with anthropogenic sources contributing 210 Tg of fixed N per year to the global N cycle, surpassing naturally fixed N by 7 Tg N yr^{-1} [Fowler *et al.* 2013]. Much of this additional N is deposited on terrestrial ecosystems from atmospheric sources. This magnitude of N deposition results in a range of negative impacts on ecosystems (including grasslands) such as reductions in biodiversity [Bobbink *et al.* 2010; Southon *et al.* 2013], acidification of soil, and the mobilisation of potentially toxic metals [Carroll *et al.* 2003; Horswill *et al.* 2008; Phoenix *et al.* 2012]

Despite large anthropogenic fluxes of N, most terrestrial ecosystems on temperate post-glacial soils are thought to be N-limited (biomass production is most restricted by N availability) [Vitousek and Howarth, 1991; Du *et al.* 2020], as weatherable sources of phosphorus (P) remain sufficiently large to meet plant P demand [Vitousek and Farrington, 1997; Menge *et al.* 2012]. Both empirical and modelling studies have shown that pollutant N, when deposited on N-limited ecosystems, can increase productivity [Tipping *et al.* 2019] and soil organic carbon (SOC) storage [Tipping *et al.* 2017], largely as a result of stimulated plant growth. This suggests that while there are negative consequences of N deposition, there may also be benefits from enhanced plant productivity and increases in carbon sequestration.

Whilst most research focuses on N-limited ecosystems [LeBauer and Treseder, 2008], a number of studies have highlighted that P limitation and N-P co-limitation are just as prevalent, if not more

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

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

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

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

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

78   it is estimated that P limitation, alone or through co-limitation with N, could constrain up to 82% of

79   the natural terrestrial surface's productivity [Du *et al.* 2020].

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

81   2004], or become increasingly prevalent as previously N-limited ecosystems transition to N-sufficient

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

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

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

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

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

87   how N deposition impacts these systems.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

103 2020]. Such interdependencies of the C, N and P cycles make understanding an ecosystem's response

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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2. Methods

2.1. Field experiment description

The empirical data is from Wardlow Hay Cop (henceforth referred to as Wardlow), a long-term experimental grassland site in the Peak District National Park (UK) [Morecroft *et al.* 1994]. Details of empirical data collection are available in supplementary section 1. There are two distinct grassland communities occurring in close proximity; acidic (National vegetation classification U4e) and limestone (NVC CG2d) semi-natural grasslands (Table S2). Both grasslands share a carboniferous limestone hill but the limestone grassland sits atop a thin humic ranker [Horswill *et al.* 2008] and occurs predominantly on the hill brow. In contrast, the acidic grassland occurs in the trough of the hill, allowing the accumulation of wind-blown loess and the formation of a deeper soil profile of a palaeo-argillic brown earth [Horswill *et al.* 2008].

Despite contrasting soil types, both the acidic and limestone grasslands are largely P-limited [Morecroft *et al.* 1994; Carroll *et al.* 2003], though occasional N and P co-limitation can occur [Phoenix *et al.* 2003] and more recently, positive growth responses in solely N-treated plots have been observed, in line with the latest understanding that long-term N loading may increase P supply by increasing phosphatase enzyme activity [Johnson et al. 1999; Phoenix et al.2004; Chen et al. 2020].

Nutrients (N and P) have been experimentally added to investigate the effects of elevated N deposition and the influence of P limitation [Morecroft *et al.* 1994]. Nitrogen treatments simulate additional N deposition to the background level and the P treatment acts to alleviate P limitation. Nutrients are added as solutions of distilled water and applied as fine spray by backpack sprayer, and have been applied monthly since 1995, and since 2017 bi-monthly. Nutrient additions are in the form of NH_4NO_3 for nitrogen and $NaH_2PO_4.H_2O$ for phosphorus. Nitrogen is applied at rates of 0 (distilled water control – 0N), 3.5 (low nitrogen – LN) and 14 g N m^{-2} yr^{-1} (high nitrogen – HN). The P 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 S1) and details of their collection

167   and conversion to model-compatible units in supplementary section 1.

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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 represented by a root fraction. NPP adds to these on a quarterly basis with growth occurring in

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

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

194   available N and P, temperature or precipitation, the latter two being provided as input driver data

195   (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 plant functional

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

200   section 2.3.2). Stoichiometry of coarse tissue is constant but the fine tissue of each plant functional

201   type has two stoichiometric end members. This allows the model to represent transitions from N-

202   poor to N-rich plant communities or an enrichment of the fine tissues within plants (or a

203   combination of both) [Davies *et al.* 2016b], dependent on available N. This allows a degree of

204   flexibility in plant C:N ratios in response to environmental changes such as N deposition. If the

205   available nutrients cannot meet the calculated plant nutrient demand, the minimum calculated NPP

206   based on either N or P availability is used, giving an estimation of the most limiting nutrient to plant

207   growth.

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

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

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

211   values for a given plant functional type and is downregulated by anthropogenic N deposition, but

212   not soil N content more generally, as it is assumed that atmospherically deposited N is readily

213   available to N-fixers. Nitrogen fixation in the model is also related to P availability. The degree to

214   which P availabilty limits this maximum rate of fixation is determined by a constant; K_{Nfix} [Davies et

215   al. 2016b]. This means that while modelled NPP is limited by availability of a single nutrient, co-

216   limitation may occur through P limitation of N fixation [Danger *et al.* 2008].

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218   2.2.3. Plant and soil N and P cycling

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

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

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

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

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

224   atmospheric deposition and direct N application. Fine plant litter enters the SOM pool directly due

225   to its rapid rate of turnover whereas coarse litter contributes N and P through decomposition and

226   does not join the SOM pool. Plant available P also comes from SOM and coarse litter decomposition,

227   direct treatment, desorption of inorganic P from soil surfaces, and sometimes cleaving of organic P

228   [Davies *et al.* 2016b]. The sorbed inorganic P pool builds over time with inputs of weathered P and

229   sorption of any excess plant available inorganic P, and desorption occurs as a first order process.

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

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

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

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

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

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

236   P can be added in small quantities by atmospheric deposition [Ridame and Guieu, 2002] but for the

237   purpose of this work, P deposition is set to zero in the model. While the contribution of P through

238   atmospheric deposition is increasingly realised [Aciego et al. 2017], we cannot account for the losses

239   of P that may also occur through landscape redistribution [Tipping et al. 2014].

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

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

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

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

244   the next once it has been exhausted.

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

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

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

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

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

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$$P_{Cleave} = SOP - \frac{SOC}{[C:P]_{fixlim}}$$
Equation 1

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

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

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

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

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

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

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

260   SOC and SON using C:N:P stoichiometries of coarse and fine plant biomass. Decomposition of SOP,

261   and its contribution to the available P pool, is subject to the same turnover rate constants as for SOC

262   and SON.

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

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

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

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

267   plant demand.

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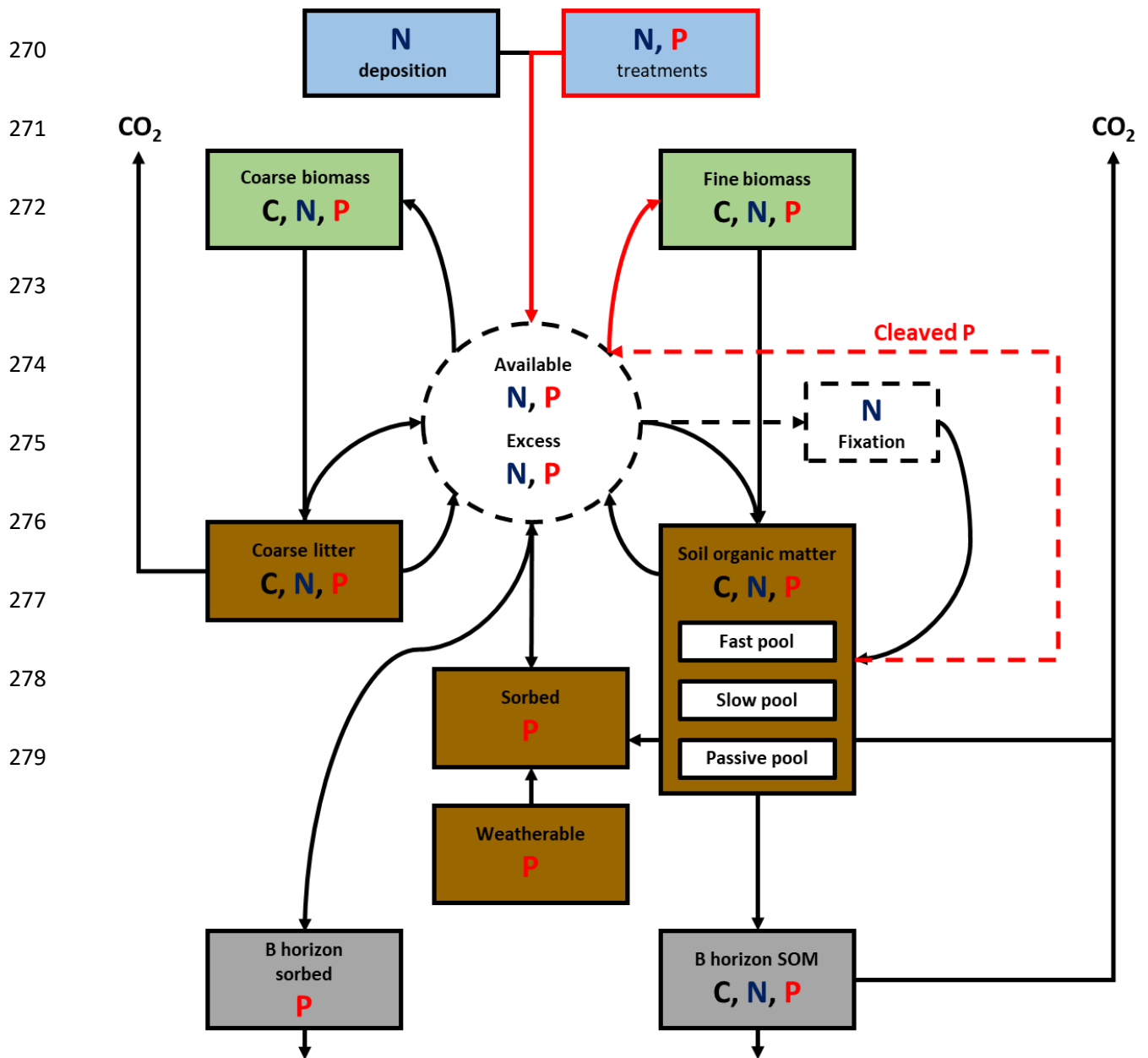
Figure 1: A simplified schematic of the key flows and pools of C, N and P within N14CP, adapted from the full schematic available in Davies *et al.* (2016b). Red lines highlight modifications to N14CP for the purpose of this work, including adding experimental nutrients and allowing uptake of cleaved 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.

2.3. Simulating the field manipulation experiment with the model

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

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

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

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

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

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

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

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

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

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

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

different P forms.

2.3.1. Nutrient applications

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

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

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

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

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

during all quarters.

302   2.3.2. Input drivers

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

304   (10,000 BP in the model). This is to capture the length of time required for soil formation following

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

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

307   know about the site's history and forcings.

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

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

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

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

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

313   availability. Input driver data include plant functional type history, climatic data and N deposition

314   data. A summary of the data used for model input is provided in supplementary Table S3. To

315   simulate the sites' plant functional type history, we used data on Holocene pollen stratigraphy of the

316   White Peak region of Derbyshire [Taylor *et al.* 1994], which captures important information

317   regarding Wardlow's land-use history for the entire duration of the model spin up phase.

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

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

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

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

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

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

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

325   N deposition of the site.

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

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

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

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

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

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

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

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334 2.3.3. Model parameters for the acidic and limestone grasslands

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

354   to observations. We simulated the two grasslands and their treatment blocks with a set of 200

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

356   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

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

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

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

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

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

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

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

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

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

366   measure of error across multiple observation variables.

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

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

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

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

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

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

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

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

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

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

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

382 accurately simulate grassland responses to long-term nutrient manipulation. The pattern of

383 grassland response, i.e. how a variable responds to nutrient treatment, is an important

384 consideration and is determined in the model by the most limiting nutrient. Consequently, the

385 parameter combination with the lowest F value, that still maintained a grassland's empirical

386 response to nutrient additions, was used within the analysis.

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389   **3. Results**

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391   Below, we first present data regarding the results of the calibration of P_{Weath0} and $P_{CleaveMax}$ for each

392   grassland, and how simulated grassland C, N and P using these parameter combinations compares to

393   the empirical data (section 3.1, Figure 2). Raw empirical data is available in table S1 in section 2 of

394   the supplementary material. Second, we explore how the limiting nutrient of the modelled

395   grasslands has changed through time in response to N deposition and experimental treatment

396   (section 3.2, Figure 3). Third, we explore how C, N and P pools in the simulated grasslands have

397   responded to N deposition and nutrient treatment within the model, and include empirical data to

398   contextualise changes (section 3.3, Figure 4). Finally, we present the C, N and P budgets for both

399   modelled grasslands to examine changes in C, N and P pools more closely, in order to better our

400   mechanistic understanding of changes in nutrient flows within the model (section 3.3, Figure 5).

401

402   **3.1. Varying phosphorus source parameters**

403

404   The model calibration selected parameter values for P_{Weath0} and $P_{CleaveMax}$ that indicate contrasting

405   use of P sources by the two simulated grasslands, with the acidic grassland capable of acquiring

406   more P from organic sources, having a $P_{CleaveMax}$ value of 0.32 g m^{-2} season^{-1} compared to the

407   limestone, with a value 10 times smaller at 0.03 g m^{-2} season^{-1}. Conversely, inorganic P availability

408   was greater in the limestone grassland due to the larger weatherable pool of P, P_{Weath0}, at 300 g m^{-2}

409   compared to 150 g m^{-2} in the acidic.

410   The selected parameter combinations resulted in the model simulating the acidic grassland as N-

411   limited and the limestone as P-limited, with reasonable congruence between observed and

412   modelled data. The outputs for the calibrated model are shown in Figure 2 against the observations

413   for above-ground biomass C, soil organic C, and N for both the acidic and limestone grasslands (Fig

414   2). Raw data used for Figure 2 are provided in supplementary tables S4 and S5.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

437

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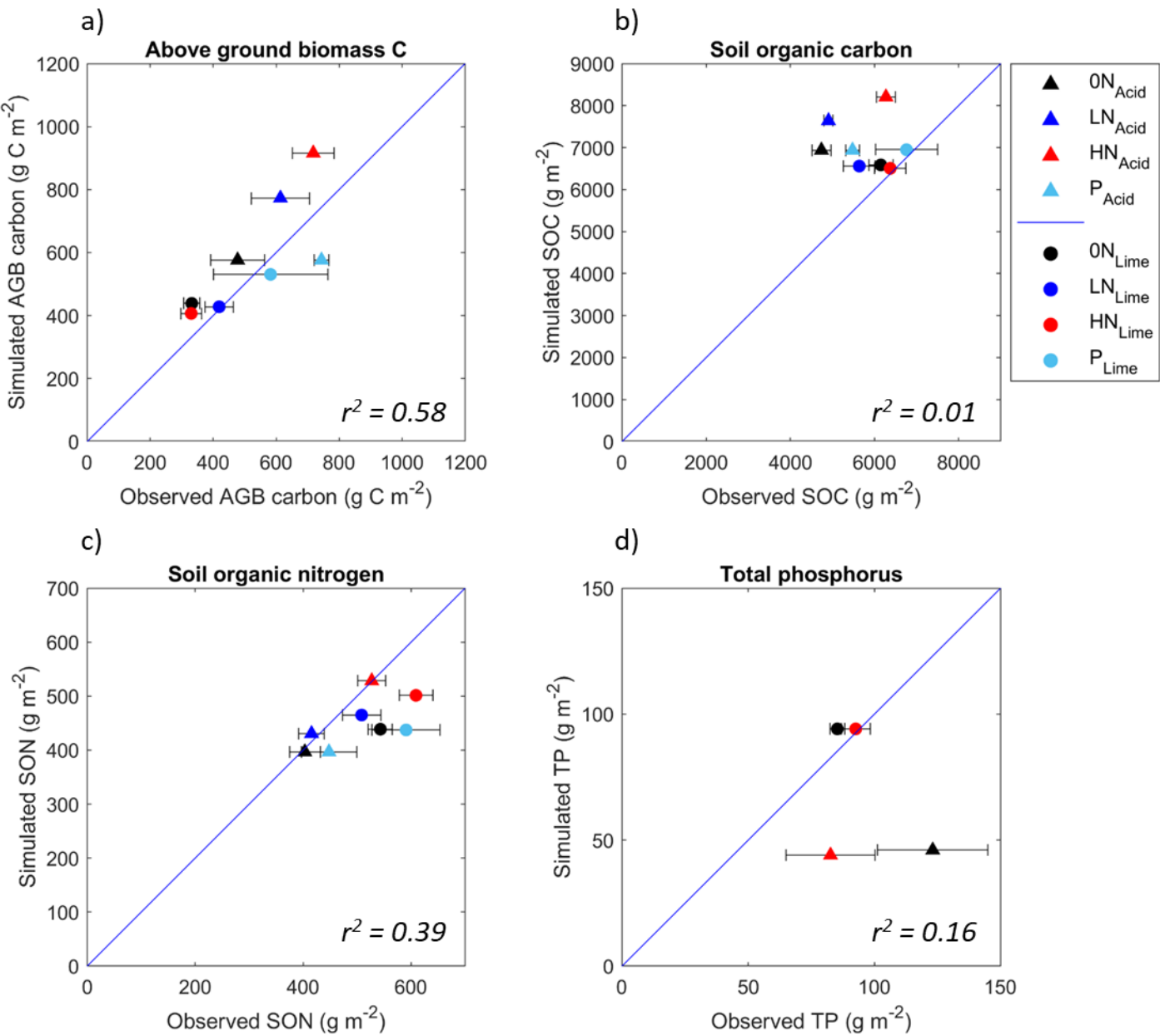
Figure 2: A comparison of the observed values of a) aboveground biomass carbon, b) soil organic carbon, c) soil organic nitrogen and d) total soil phosphorus from both grasslands, with simulated values from the model. The blue line represents a 1 to 1 relationship and the closer the data points are to 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 S13), 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 S9). 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 S9). 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.

466 **3.3. Modelled trends and responses to nutrient additions**

467

468 The model allows the temporal trends and responses to nutrient additions to be further explored.

469 Figure 4 provides the temporal responses for the treatments, and Figure 5 a full nutrient budget for

470 the year 2020. Full data for changes in soil C, N and P and plant biomass C pools since the onset of

471 large-scale N deposition (1800 within the model) for both grasslands are included in supplementary

472 Table S14. All data used for determining responses of biomass C and soil organic C, N and P pools to

473 experimental nutrient additions are in supplementary Tables S15 (acidic) and S16 (limestone).

474

475 3.3.1. Acidic grassland

476 The modelled time series suggest that in the 0N (control) treatment for the acidic grassland,

477 background levels of atmospheric N deposition between the period 1800-2020 resulted in an almost

478 four-fold increase in biomass C, a near-twofold increase in SOC and SON and increased the size of

479 the SOP pool by almost a fifth (Fig 4).

480 Since initiated in 1995, all C and N pools responded positively to N but not P treatments (Fig 5a, c,

481 Tables S7, S8). The LN and HN treatments further increased aboveground biomass C by 36.2% and

482 61.7% (Fig 4a) and increased the size of the total SOC pool by 11.5% and 20.6% respectively (Fig 4c).

483 Similarly, the total SON pool in the acidic grassland increased by 9.7% in the LN treatment and 36.6%

484 in the HN (Fig 4e).

485 Responses of the SOP pool are in contrast to those of the SOC and SON pools, with LN and HN

486 decreasing SOP by 4.4% and 9.1% respectively, while P addition substantially increased the size of

487 the SOP pool by 76.7% (Fig 4g). Nitrogen treatments facilitated access to SOP from both subsoil and

488 topsoil, increasing plant available P and facilitating its uptake into biomass material (Fig 5e, Table

489 S8).

490

491   3.3.2. Limestone grassland

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

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

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

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

496   about a third (Fig 4, Table S14).

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

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

499   was ubiquitous to all C pools, with declines in subsoil, topsoil and biomass C (Fig 5b, Table S10).

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

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

502   22.0% and 6.1% respectively (Fig 4b, d).

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

504   declines in biomass N (Fig 5d, Table S11) The P treatment slightly reduced subsoil and topsoil SON

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

506   greater in the P than HN treatment (Fig 5d, Table S11) Total SON increased by 6.4% and 15.0% with

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

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

509   SOP, available P and biomass P with LN and HN addition (Fig 5f, Table S12). The limestone grassland

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

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

512   grassland, particularly in the topsoil sorbed pool (Fig 5f, Table S12).

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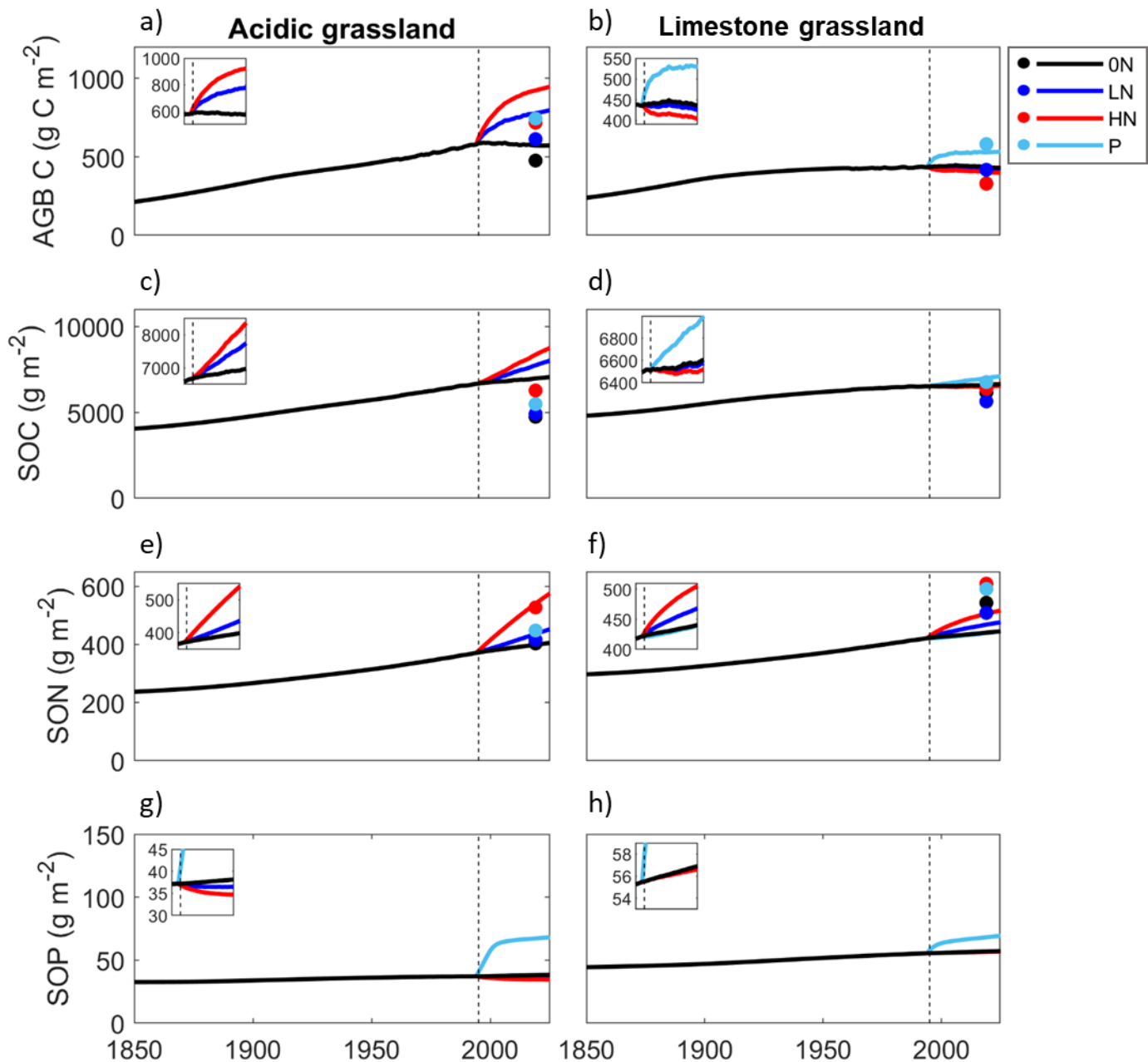
Figure 4: Time series plots of aboveground biomass C, soil organic C, N and P for the acidic (panels a, c, e and g respectively) and limestone modelled grasslands (panels b, d, f and h respectively). The vertical dashed line represents the first year of nutrient addition (1995) and marks the beginning 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 grasslands 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).
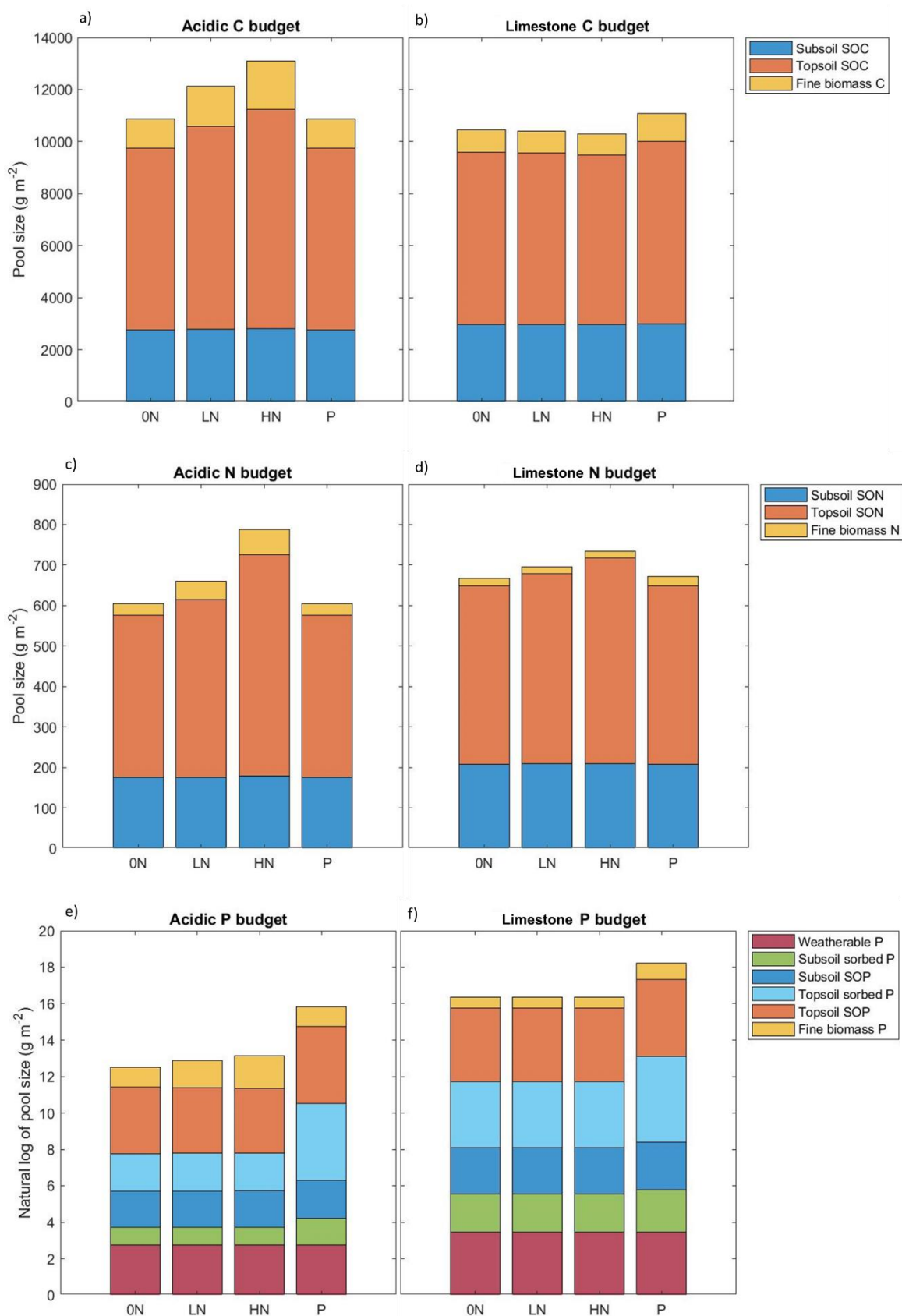
Figure 5: Modelled C, N and P budgets for the acidic (panels a, c and e) and limestone (panels b, d, f) grasslands for the year 2020. Modelled sizes of C and N pools are in grams per metre squared, and P pools are presented as $\log_n$ grams per metre squared. Temporary pools such as available N and 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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

567   formation of iron and aluminium complexes and immobilising P [Kooijman *et al.* 1998].

568   In addition to physico-chemical processes reducing P availability, in P-limited grassland soils,

569   microbial processes may be dominant drivers of ecosystem P fluxes [Bünemann et al. 2012]. For

570   instance, while mineralisation of organic P may increase inorganic P in solution [Schneider *et al.*

571   2017], this can be rapidly and almost completely immobilised by microbes, particularly when soil P

572   availability is low [Bünemann et al. 2012]. As the model lacks a mechanism for increasing access to

573   secondary mineral P forms comparable to organic P-cleaving, and microbial P immobilisation is

574   incompletely represented for P-limited conditions, it is possible that the uptake of organic P by the

575   acidic grassland in the model is exaggerated.

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

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

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

579   when N deposition exceeds fixation (as at Wardlow), fixation is essentially nullified (as in Tables S7,

580   S11), meaning deposition becomes the sole source of N to the grassland. This in effect, removes the

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

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

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

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

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

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

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

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

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

590   *al.* 2018].

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

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

593 reasonable accuracy, albeit with the previously mentioned caveats.

594

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

596 While the model's estimation of $P_{CleaveMax}$ for the acidic grassland is likely overestimated, the model

597 experiment has highlighted that differences in organic versus inorganic P availability are a key

598 determinant of an ecosystem's nutrient limitation, and consequently, how they respond to changes

599 in anthropogenic N and P availability. For instance, while being exposed to the same background

600 level of N deposition and the same magnitude of experimental treatment, the modelled acidic

601 grassland was able to stimulate growth in response to LN and HN treatment whereas the modelled

602 limestone grassland was negatively affected by it.

603 Nitrogen addition increases plant demand for P and can shift ecosystems toward a state of P

604 limitation or increase the severity of limitation where it already exists [Menge and Field, 2007; An *et*

605 *al.* 2011; Goll *et al.* 2012]. Consistent with this, both simulated grasslands saw SOP decline with LN

606 and HN treatment, worsening P limitation in the limestone grassland, and depleting the SOP pool in

607 the acidic. As P cleaved from organic pools is the least bioavailable within the model hierarchy

608 (methods 2.2.3), this is indicative of increasing P stress in both grasslands. While SOP declined in

609 both grasslands, the responses of available and biomass P to nutrient treatments differed markedly

610 between the grasslands. Due to the higher rate of $P_{CleaveMax}$ in the acidic grassland, more P was in

611 plant-available forms and hence P does not become the limiting factor under N treatments (Table

612 S8). Conversely, available and biomass P decline under LN and HN addition in the limestone

613 grassland (Table S12), highlighting how the grassland's $P_{CleaveMax}$ capability is insufficient to meet

614 increased P demand.

615   Such high access to organic P sources in the modelled acidic grassland likely led it to respond to

616   nutrient enrichment in an N-limited manner, increasing productivity in response to N deposition and

617   LN and HN treatments as the model's limiting nutrient stimulated plant growth. Detrital C inputs

618   from plant biomass are the primary source of SOC accumulation within N14CP [Davies *et al.* 2016b]

619   and as such, changes in SOC integrate long term trends in net primary productivity in systems where

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

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

622   SOC (Fig 4c).

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

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

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

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

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

628   2017].

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

630   accumulate biomass with N addition as the grassland's greater access to topsoil SOP (Table S8)

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

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

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

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

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

636   2020]. Organic P release from SOM and its potential immobilisation, is poorly represented in models

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

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

639   experimental LN and HN treatments, and in reality, such rapid degradation of SOP may eventually

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

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

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

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

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

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

646   reductions in bioavailable P (Table S12), occurring via N-driven increases in stoichiometric P demand,

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

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

649   decreasing net biomass C input to the SOC pool. This suggests that in P-limited limestone grasslands

650   such as at Wardlow, where access to organic P forms may be comparatively limited, N deposition

651   may worsen pre-existing P limitation and reduce ecosystem C stocks [Goll *et al.* 2012, Li *et al.* 2018].

652

653   **4.3. Model limitations**

654
655   While N14CP is a fairly simple ecosystem model by design, it is one of few models to integrate the C,

656   N and P cycles for semi-natural ecosystems and has been extensively tested against empirical NPP

657   and soil C, N and P data [Davies *et al.* 2016a; Davies *et al.* 2016b; Tipping *et al.* 2017; Tipping *et al.*

658   2019; Janes-Bassett *et al.* 2020]. Previous work with N14CP has identified the need to enhance its

659   ability to simulate organic P cycling [Janes-Bassett *et al.* 2020], which we aimed to do in this study by

660   using long-term experimental data from contrasting P-limited grasslands.

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

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

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

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

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

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

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

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

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

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

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

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

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

674   2016; Phoenix *et al.* 2020], which likely contributes toward the poor representation of the acidic

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

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

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

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

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

680   2016b].

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

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

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

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

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

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

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

688

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 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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