

1    **Title**

2    A soil matrix capacity index to predict mineral-associated but not particulate organic carbon across a range of  
3    climate and soil pH

4  
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25    **Keywords**

26    soil organic matter, carbon, size fractionation, physicochemical properties, particulate organic carbon, mineral-  
27    associated organic carbon

28    **Abstract**

29  
30        Understanding controls on soil organic carbon (SOC) will be crucial to managing soils for climate change  
31        mitigation and food security. Climate exerts an overarching influence on SOC, affecting both carbon (C) inputs to  
32        soil and soil physicochemical properties participating in C retention. To test our hypothesis that climate, C inputs,

33 and soil properties would differently affect particulate organic carbon (POC) and mineral-associated organic carbon  
34 (MAOC), we sampled 16 agricultural sites ( $n = 124$  plots) in the United States, ranging in climate (mean annual  
35 precipitation (MAP) - potential evapotranspiration (PET; MAP-PET)), soil pH (5.8 – 7.9), and soil texture (silt +  
36 clay = 13 – 96%). As MAP-PET increased, soils increased in oxalate-extractable iron ( $Fe_O$ ) and aluminum ( $Al_O$ ),  
37 decreased in exchangeable calcium ( $Ca_{ex}$ ) and magnesium ( $Mg_{ex}$ ), and received greater C inputs. Soil  
38 physicochemical properties did not strongly predict POC, confirming the relative independence of this SOC fraction  
39 from the soil matrix. In contrast, MAOC was well predicted by combining  $Al_O + [1/2]Fe_O$  with  $Ca_{ex} + Mg_{ex}$  in a  
40 ‘matrix capacity index’, which performed better than individual soil physicochemical properties across all pH levels  
41 ( $r > 0.79$ ). Structural equation modeling indicated a similar total effect of MAP-PET on MAOC and POC, which  
42 was mediated by total C inputs and the matrix capacity index for MAOC but not POC. Our results emphasize the  
43 need to separately conceptualize controls on MAOC and POC and justify the use of a unified soil matrix capacity  
44 index for predicting soil MAOC storage.

45

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58

#### 59 **Introduction**

60        Maintaining or increasing soil organic carbon (SOC) in agricultural soils will be crucial for mitigating  
61    climate change (Minasny et al. 2017; Lessmann et al. 2022) and for supporting soil functioning (King et al. 2020;  
62    Cotrufo and Lavallee 2022). To effectively manage agricultural SOC, we need to develop process-based models of  
63    SOC based on a sound understanding of how SOC responds to environmental controls. Although environmental  
64    controls on SOC storage have a rich history of theoretical and empirical work, encompassing SOC responses to  
65    climate (Jobbagy and Jackson 2000), soil texture (Hassink 1997) and other soil physicochemical properties  
66    (Rasmussen et al. 2018; Rowley et al. 2018; Heckman et al. 2020), and carbon (C) inputs (Six et al. 2002), on-going  
67    refinements are yet to be fully integrated. For instance, separating SOC into distinct physical fractions is  
68    increasingly leveraged to improve our understanding of environmental controls on SOC storage (Cotrufo et al. 2021;  
69    Yu et al. 2022). Nevertheless, to our knowledge no studies have synthesized climate, soil physicochemical, and C  
70    input controls on agricultural soil C fractions at a continental scale.

71        Conceptualizing SOC into contrasting fractions of mineral-associated organic carbon (MAOC) and  
72    particulate organic carbon (POC) has been proposed to aid in understanding controls on SOC storage (Lavallee et al.  
73    2020). The more stable MAOC pool forms primarily from microbial necromass and soluble, unprocessed plant  
74    compounds (Kallenbach et al. 2016; Liang et al. 2017) and is primarily stabilized through adsorption, wherein soil  
75    minerals protect adsorbed C from decomposition (Kleber et al. 2015). In contrast, POC is formed predominantly  
76    from structural plant inputs and has shorter residence times than MAOC (von Lützow et al. 2007), but may persist  
77    through a combination of physical and physiological constraints on decomposers (Cotrufo and Lavallee 2022).  
78        Given these contrasting pathways of formation and mechanisms of persistence for POC and MAOC (Lavallee et al.  
79    2020), these fractions may be regulated by different suites of controls from among those factors already widely  
80    recognized in controlling SOC.

81        Climate can be viewed as an overarching control on SOC pools, because it can affect factors that control  
82    both C inputs to soil and losses of C from soil (Cotrufo and Lavallee 2022). The control of climate on C inputs  
83    operates mainly via water limitations on net primary productivity – and consequently C inputs – at continental scales  
84    (Gentine et al. 2019). Water availability can be estimated via water balance as the difference between mean annual  
85    precipitation (MAP) and potential evapotranspiration (PET; MAP-PET). In turn, C inputs to soil often (Gulde et al.  
86    2008), but not always (Zhou et al. 2019), increase SOC. To date, it is unclear whether C inputs similarly affect POC  
87    and MAOC pools. As POC is minimally dependent on protection from the soil matrix, POC formation may be

88 expected to more directly reflect plant C inputs to soil than MAOC. The formation of MAOC is expected to depend  
89 on microbial transformations and soil matrix adsorption capacity (Cotrufo et al. 2013), and may therefore exhibit a  
90 moderated relationship to C inputs. Currently, many process-based models predict a saturating increase of SOC with  
91 increases in C inputs (Georgiou et al. 2021; Zhang et al. 2021), but these predictions may be refined by assessing the  
92 impact of C inputs on contrasting SOC fractions.

93 Climate also controls C losses from the soil, including via microbial activity and soil physicochemical  
94 properties. While microbial activity has received abundant attention (Zhang et al. 2008), soil physicochemical  
95 properties are increasingly acknowledged for their protective capacity over SOC (Rasmussen et al. 2018). Soil  
96 physicochemical properties are modified by MAP-PET: wetness decreases soil pH (Slessarev et al. 2016), increases  
97 oxalate-extractable iron and aluminum ( $Fe_O$  and  $Al_O$ ; Hall et al. 2020), and decreases exchangeable calcium ( $Ca_{ex}$ ;  
98 von Fromm et al. 2021). As  $Ca_{ex}$  and  $Al_O + Fe_O$  are stabilizing agents of SOC, they therefore introduce a climate-  
99 dependent role of soil physicochemical properties in C retention (Rasmussen et al. 2018; Rowley et al. 2018). The  
100 extent to which these soil properties influence retention of POC vs retention of MAOC has been rarely explored  
101 empirically, but it might be expected that soil physicochemical properties more closely control MAOC compared to  
102 POC given the dependence of MAOC on matrix protection (Kleber et al. 2015). Updating the soil physicochemical  
103 controls for different soil fractions is especially likely to improve soil C modeling, because currently soil C models  
104 rely on soil texture as the property that controls partitioning of new C inputs to soil (Georgiou et al. 2021; Zhang et  
105 al. 2021).

106 A tool that would aid in modeling soil physicochemical controls on MAOC (and potentially on POC)  
107 across climates would be a widely applicable, quantitative measure of the capacity of the soil matrix to stabilize C.  
108 Rasmussen et al. (2018) showed that soil texture was not a useful predictor of SOC in a global dataset and suggested  
109 that stabilization of SOC by soil physicochemical properties is pH- and climate-specific: exchangeable calcium  
110 ( $Ca_{ex}$ ) dominates soil C stabilization in high pH and arid environments, while  $Fe_O$  and  $Al_O$  dominate in low pH and  
111 humid environments. It remains unclear how to advance process-based SOC models with this division, i.e., whether  
112 is it necessary to introduce a pH cutoff at which some soil properties affect C stabilization but others do not, or if a  
113 synthetic index for the stabilization capacity of the soil matrix could serve universally to inform SOC dynamics  
114 across soil pH levels.

115 To investigate a suite of interacting environmental controls on SOC, POC, and MAOC in agricultural soils,  
116 we studied topsoils (0–20 cm) from 16 long-term agricultural research sites and 124 plots across the United States.  
117 We selected sites to include soils of the broadest pH range feasible under agriculture – expected to result in a range  
118 of soil polyvalent exchangeable cations ( $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$ ) and  $\text{Al}_\text{O} + \text{Fe}_\text{O}$ . We asked: how does climate influence C  
119 inputs, soil physicochemical properties, and SOC, POC, and MAOC? As soil physicochemical properties and C  
120 inputs are potential drivers of SOC, POC, and MAOC, we aimed to investigate relationships between them  
121 independently and to evaluate whether synthesizing soil physicochemical properties could be used to calculate a  
122 widely applicable soil matrix capacity index. Finally, we aimed to assess the extent to which effects of MAP-PET on  
123 POC and MAOC storage were mediated by C inputs and soil physicochemical properties. We hypothesized,  
124 broadly, that POC and MAOC would exhibit distinct responses to environmental controls. Specifically, we  
125 hypothesized that C inputs would be a stronger control on POC than on MAOC due to the independence of POC  
126 from matrix protection, and that MAOC would be better explained by soil physicochemical properties than POC due  
127 to the dependence of MAOC on matrix protection.

128

129

## 130 **Methods**

### 131 *Site selection and soil sampling*

132 Soils were sampled from 0–20 cm in the fall of 2020 from 16 agricultural sites (SI Table 1). From each site,  
133 6–10 plots were sampled, which represented two replicated treatments of contrasting management practices. As our  
134 aim was to assess continental-scale relationships, we did not assess soil response to management histories, but used  
135 the contrasting management to achieve differences in C inputs within the same climate and soil type. All plots  
136 received agronomically realistic rates of synthetic N fertilizer, most were under no-till, and no plots received  
137 exogenous organic amendments or irrigation. For complete information on sites, soil sampling, and sample  
138 processing, see supplementary information text and SI Tables 1–3.

139

### 140 *Soil physicochemical properties*

141 We assessed a suite of soil physicochemical properties on each plot-level soil sample. Soil pH was  
142 measured in a slurry of 1:1 soil:water by mass after 10 minutes of rest. Soil texture was assessed using the

143 hydrometer method to determine clay content and mass recovery of sand particles ( $> 53 \mu\text{m}$ ) was used to determine  
144 sand content. Soil exchangeable cations were extracted in ammonium acetate following Thomas (1982). Briefly,  
145  $\sim 2.5\text{-g}$  of 2-mm sieved, air-dry soil was shaken for 30 minutes with 25-mL 1N ammonium acetate at pH 7, then  
146 filtered through a Whatman #1 filter paper (nominal pore size =  $11 \mu\text{m}$ ) and analyzed via inductively coupled  
147 plasma optical emission spectrometer (ICP-OES, Optima 7300 DV, PerkinElmer, Waltham, MA, USA) for  $\text{Ca}^{2+}$  and  
148  $\text{Mg}^{2+}$ , reported by total positive charge ( $\text{cmol kg soil}^{-1}$ ). These polyvalent cations provide mechanism of C retention  
149 via their role in cation bridging (Wiesmeier et al. 2019). Soil Fe and Al were extracted via the acid ammonium  
150 oxalate method following Loeppert and Inskeep (1996). This method estimates Fe and Al in amorphous phases  
151 (referred to as  $\text{Fe}_0$  and  $\text{Al}_0$ ). For the acid ammonium oxalate extraction,  $\sim 0.5\text{-g}$  ground, air-dry soil was mixed with  
152 30-mL 0.175 mol/L ammonium oxalate at pH 3 and shaken for 2 hours in the dark, then filtered through a Whatman  
153 #1 filter paper. Calcareous soils were identified by reaction with HCl, as described below, and their carbonates  
154 removed before the acid ammonium oxalate extraction by reacting the sample with 30-mL 1 mol/L ammonium  
155 acetate at pH 5.5. Ammonium oxalate extracts were also run on the ICP-OES, and summation of  $\text{Al}_0$  and  $\text{Fe}_0$  was  
156 corrected to larger atomic mass of Fe by dividing Fe by half ( $[1/2]\text{Fe}_0$ , Wagai et al. 2020). All analyses performed  
157 were air-dry soils and are reported in oven-dry equivalents.

158

#### 159 *Soil size fractionation into POC and MAOC*

160 Soils were separated by size into sand + POC ( $> 53 \mu\text{m}$ ) and silt + clay + MAOC ( $< 53 \mu\text{m}$ ) following  
161 Cambardella and Elliott, (1992). These fractions are hereafter referred to as ‘POC’ and ‘MAOC’, respectively.  
162 Briefly, 5.75–6.25-g of 2-mm sieved bulk soil dried at  $60^\circ \text{C}$  was shaken for 18 hours with 12 glass beads in 30-mL  
163 0.5% sodium hexametaphosphate to disrupt all aggregates. The resulting soil slurry was rinsed with DI water over a  
164 53  $\mu\text{m}$  sieve to isolate POC and remove glass beads. Soil solution passing through the sieve was deemed MAOC.  
165 Both the POC and MAOC fractions were dried at  $60^\circ \text{C}$  until reaching constant mass. Recoveries of the initial soil  
166 masses in the summed fractions were between 95 and 103% for all samples, with a mean recovery of 100.5%. Soils  
167 and fractions containing carbonates (identified by effervescence after addition of 5% HCl, 18 samples) were treated  
168 to remove inorganic carbon via HCl fumigation (Harris et al. 2001). SOC, MAOC, and POC were ground using a  
169 mortar and pestle before running on a Costech elemental analyzer (Costech ECS4010, Analytical Technologies, Inc.,  
170 Milano, Italy). The average recovery of SOC in POC and MAOC fractions was 92% (standard error = 0.9%).

171

172 *Crop C inputs to soil and climate data*

173 The best available crop yield data from across the history of each site were used to estimate C inputs from  
174 crops to soil (SI Table 4). Allometric equations (Bolinder et al. 2007) were used to estimate shoot and root + exudate  
175 inputs for each crop; belowground inputs were truncated to the 20-cm soil depth sampled using crop-specific root  
176 distributions (Fan et al. 2016). For perennial crops grown over multiple years, annual root inputs were estimated as  
177 62% of root inputs from the initial year, following an assumption of partial root turnover (King and Blesh 2018).  
178 Shoot inputs were reduced by the proportions of shoots that were removed for stover production, if any, and  
179 rotation-average crop inputs were calculated ( $\text{Mg C ha}^{-1} \text{ yr}^{-1}$ ). As yield information was not consistently available  
180 for all harvests across site history, we did not investigate interannual variability in C inputs. For each site, mean  
181 annual precipitation (MAP) and mean annual air temperature (MAT) were extracted from WorldClim at 30 s  
182 resolution (Fick and Hijmans 2017, 1970–2000). Potential evapotranspiration (PET), calculated using a Penman-  
183 Montieth equation, was extracted from the Global Aridity Index Database v2 (Trabucco and Zomer 2018, 1970–  
184 2000), and was used to estimate ecosystem water balance (MAP-PET; Slessarev et al. 2016).

185

186 *Calculation of soil matrix capacity index*

187 To investigate the capacity for combined values of  $\text{Al}_0 + [1/2]\text{Fe}_0$  and  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$  to stabilize SOC, we  
188 calculated a matrix capacity index (MCI) for all 124 plots across the 16 sites. First, to overcome different reporting  
189 units for  $\text{Al}_0 + [1/2]\text{Fe}_0$  and  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$  (Rasmussen et al. 2018), we calculated their standardized values for each  
190 observation in the sample ( $n=124$ ) using the z-score approach:

$$191 \quad Z = \frac{x - u}{\sigma} \quad [1]$$

192 where  $Z$  is the standardized value,  $x$  is the observed value,  $u$  is the mean of the sample and  $\sigma$  is the  
193 standard deviation of the sample. The Z-score standardization results in a vector with the same relative distances  
194 between all points as the original vector but with a mean of zero and a standard deviation of 1. In our data, means of  
195 samples were  $2.22 \text{ g kg soil}^{-1}$  for  $\text{Al}_0 + [1/2]\text{Fe}_0$  and  $18.02 \text{ cmol kg soil}^{-1}$  for  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$ , and standard deviations  
196 were  $0.75 \text{ g kg soil}^{-1}$  for  $\text{Al}_0 + [1/2]\text{Fe}_0$  and  $8.70 \text{ cmol kg soil}^{-1}$  for  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$ . To calculate the reported MCI, we  
197 summed standardized values for each observation:

198

$$MCI = Z_{Ca_{ex}+Mg_{ex}} + Z_{Al_0+[1/2]Fe_0} \quad [2]$$

199 where  $Z_{Ca_{ex}+Mg_{ex}}$  is the standardized value of  $Ca_{ex} + Mg_{ex}$  and  $Z_{Al_0+[1/2]Fe_0}$  is the standardized value of  $Al_0 + [1/2]Fe_0$ . Plot-level MCI values were averaged within each site for subsequent analyses, to align with data  
 200 treatment for all other soil physicochemical properties. Multiple regression using all possible model subsets of  $Al_0$ ,  
 201  $Fe_0$ ,  $Ca_{ex}$ ,  $Mg_{ex}$  and silt + clay identified  $Al_0$ ,  $Fe_0$ , and  $Ca_{ex}$  as the best predictors of MAOC based on adjusted  $R^2$   
 202 values (SI Table 5), whereas the same model selection with summed soil physicochemical properties identified  $Al_0$   
 203 + [1/2] $Fe_0$  and  $Ca_{ex} + Mg_{ex}$  as the best predictors (SI Table 6). Thus, model selection did not include Mg in the best  
 204 model initiated with individual soil properties across these sites. In light of acknowledged soil chemical controls on  
 205 SOC (Wiesmeier et al. 2019), and considering previous efforts to synthesize soil matrix controls on SOC (Possinger  
 206 et al. 2021), we retained  $Mg_{ex}$  in the proposed MCI in all main figures but also include tests with the MCI as  
 207 calculated with  $Al_0 + [1/2]Fe_0$  and  $Ca_{ex}$  in SI Tables 8-10.

209

#### 210 *Statistical methods*

211 We used simple linear regression to test for relationships between soil physicochemical and climatic factors  
 212 and their relationships with SOC, POC, and MAOC across the entire dataset. We did not use mixed models with a  
 213 random effect for site, which would have estimated common slopes aggregated from within-site relationships,  
 214 because the focus of this study was on between-site relationships. In some cases, relationships between predictor and  
 215 response variables exhibited heteroskedasticity of variance (Bruesch-Pagan test p-value < 0.05). In these cases, we  
 216 attempted to remove heteroskedasticity by log or square root transforming either predictor or response. Where a data  
 217 transformation was successful, we applied it to the reported regression coefficients and indicate in every instance  
 218 where a transformation was used. Where these data transformations did not improve variance distributions, we used  
 219 raw data in regressions. We used z-score standardized parameters only for the MCI data; no other data were z-score  
 220 standardized. Low and high soil pH groups were delineated based on the median of the sample (pH = 6.5), with n =  
 221 8 for the low pH group and n = 8 for the high pH group.

222 We used structural equation modeling using the R package ‘*lavaan*’, to investigate the direct and indirect  
 223 effects of MAP-PET, C inputs, and soil physicochemical properties on POC and MAOC. To construct the structural  
 224 equation models (SEM), we chose the C input and the soil physicochemical parameters that were most closely  
 225 related to MAOC or POC based on our linear regressions ( $Al_0 + Fe_0$  only for POC, as no C input variables were

226 significant; total C and the MCI for MAOC). Each model allowed for a direct effect of MAP-PET on the SOC  
227 fraction as well as indirect pathways for an effect of MAP-PET on SOC via C inputs (MAOC only) and the other via  
228 a soil physicochemical property. Despite the relatively low number of observations in our SEMs, the model fit  
229 criteria were met: both models had a comparative fit index (CFI) of  $> 0.9$ , root mean square error of approximation  
230 (RMSEA) of  $< 0.08$ , and standardized root mean square residual (SRMR) of  $< 0.08$ ; (Hooper et al. 2008). We  
231 assessed direct and indirect effects of MAP-PET on POC and MAOC by extracting coefficients from individual  
232 pathways, then multiplying these coefficients to calculate indirect pathways (e.g., effect of MAP-PET on total C  
233 inputs and effect of total C inputs on MAOC); we summed indirect coefficients for both indirect pathways to  
234 estimate total indirect effects (SI Tables 12–13). All analyses were carried out in R version 4.1.2.

235

## 236 **Results and Discussion**

237

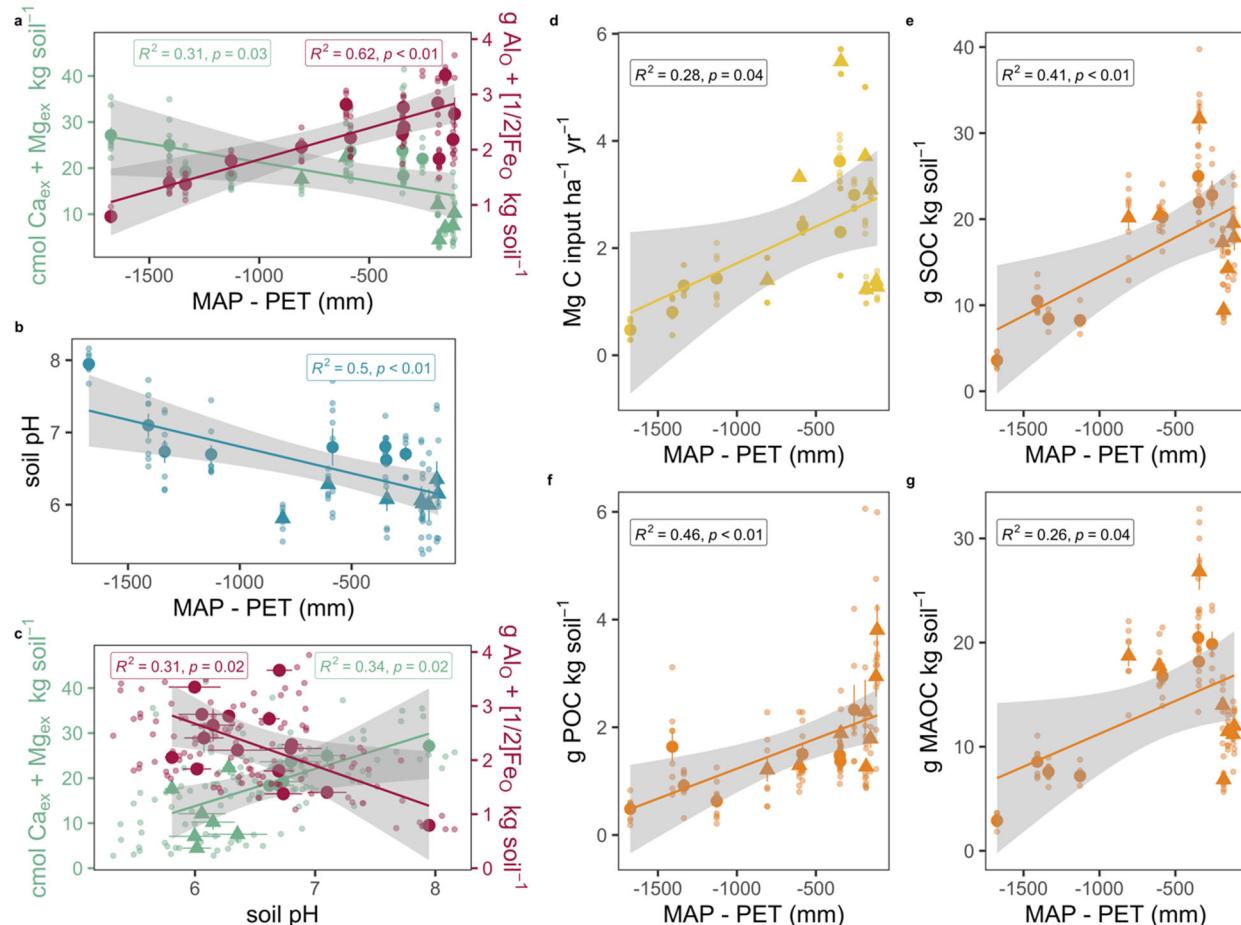
### 238 *Climate influence on soil physicochemical properties and C inputs, SOC, POC, and MAOC*

239 The sampling sites spanned a climatic gradient in MAP-PET (-1675 to -112 mm, Fig. 1, SI Table 1). Although  
240 the study area also encompassed a range of MAT (5.7–12.4 °C) and MAP (357–1066 mm), MAP-PET emerged as a  
241 more consistent driver of soil physicochemical properties and C inputs than either MAP or MAT. Compared to  
242 MAP-PET, MAP exhibited similar but less defined relationships to soil physicochemical properties and C inputs,  
243 while MAT was minimally related to both (SI Table 7). As expected following previous work (Slessarev et al. 2016;  
244 von Fromm et al. 2021), MAP-PET was associated with decreasing soil pH and  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$  and increasing  $\text{Al}_{\text{o}} +$   
245  $[1/2]\text{Fe}_{\text{o}}$  (Fig 1a-b). In our dataset, a particularly high pH site (pH = 7.9) contributed to producing these previously  
246 established relationships between soil pH,  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$  and  $\text{Al}_{\text{o}} + [1/2]\text{Fe}_{\text{o}}$ . The observed variability in some  
247 relationships, for instance between MAP-PET and  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$  ( $R^2 = 0.23$ ), likely emerges from soil factors not  
248 assessed, such as soil age, which interacts with climate and parent material in creating soil weathering status.

249 Greater MAP-PET was also associated with increased total C inputs (Fig 1d), which aligns with reduced  
250 moisture constraints on plant productivity (Gentine et al. 2019). Variability in total C inputs around the upper range  
251 of MAP-PET (Fig 1d) may also reflect a loosening of moisture constraints on plant productivity and introduction of  
252 soil or agricultural management influences. In a similar vein, shoot C inputs were less sensitive to MAP-PET than  
253 root C inputs (SI Table 7,  $R^2 = 0.05$  vs.  $R^2 = 0.50$ ), which was likely due to variable harvesting of aboveground

254 biomass across these sites. For instance, at some sites, crop aboveground biomass was fully removed (e.g., for hay  
 255 or biofuel), whereas at other sites all the stem and leaf biomass were returned after grain harvest. Given the  
 256 relatively consistent return of root inputs to soil, root inputs more closely reflect a moisture constraint on overall  
 257 crop productivity for agricultural systems. Soil C pools also exhibited positive relationships to MAP-PET (Fig 1e-g);  
 258 we used SEMs to explore the direct vs. indirect effects of MAP-PET on these soil C pools.

259



260

261 **Fig. 1** Relationships between mean annual precipitation minus potential evapotranspiration (MAP-PET), soil pH,  
 262 and soil physicochemical properties (left panels), and relationships between MAP-PET, carbon (C) inputs, and soil  
 263 C (right panels). Soils measured 0–20 cm depth across 16 agricultural sites in the United States. Large points  
 264 represent site-level averages and small points represent plots within sites (n = 124). Large point circles = soil pH >  
 265 6.5 large points triangles = soil pH < 6.5. Error bars represent standard errors; standard errors not available for C  
 266 inputs. Gray bars represent 95% confidence intervals. Axis text colors for panels (a) and (c) correspond to color of

267 points and regression lines. In panels (d-g), orange points correspond to soil C observations while yellow points  
268 correspond to C input observations. Regression coefficients for data shown, with related tests, are reported in SI  
269 Table 7.

270

271

272 *Effect of soil physicochemical properties and C inputs on SOC, POC, and MAOC*

273 We show that SOC response to soil physicochemical factors is a composite of the responses of various controls  
274 that operate distinctly on POC vs MAOC pools (Fig 2). Consistent with our hypothesis, soil physicochemical factors  
275 were stronger controls on MAOC than POC. Our finding that MAOC depends on stabilization by reactive surfaces  
276 of the soil matrix is supported by previous work (Kleber et al. 2015). We find that  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$  and  $\text{Al}_0 + [1/2]\text{Fe}_0$   
277 better represent these effects on MAOC stabilization than silt + clay. Predictors of total SOC were more similar to  
278 those of MAOC than of POC, which was expected as MAOC made up the bulk of SOC (average = 81%), as is  
279 common in agricultural soils (Lugato et al. 2021). While there was evidence of a positive association between  $\text{Al}_0 +$   
280  $[1/2]\text{Fe}_0$  and increased POC (Fig 2), our finding that POC overall was not as well predicted by soil physicochemical  
281 properties as MAOC is mirrored in findings from previous work (Hassink 1997; Six et al. 2002).

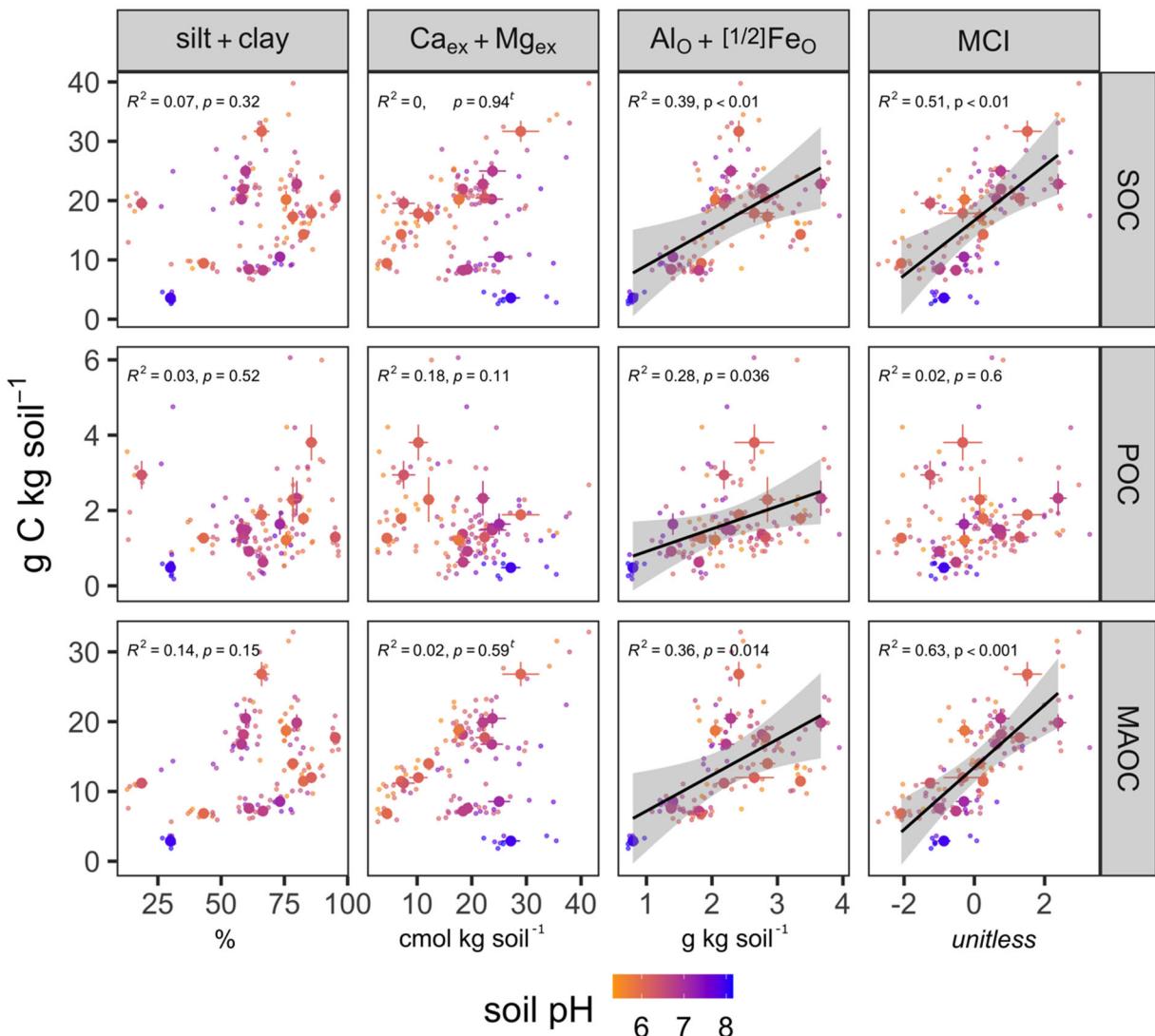
282 When soils were divided into low and high pH groups, soil  $\text{Ca}_{\text{ex}}$ ,  $\text{Mg}_{\text{ex}}$ ,  $\text{Al}_0$ , and  $\text{Fe}_0$  emerged as having stronger  
283 association with MAOC in the pH group in which they were less abundant (Fig 3). We observed that  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$   
284 exhibited much weaker association with MAOC in high pH soils compared to low pH soils, while  $\text{Al}_0 + [1/2]\text{Fe}_0$   
285 exhibited weaker associations with MAOC in the low pH soils (Fig 3, SI Table 7). To some extent, this observation  
286 may be explained by soil interactions with climate. For instance, some high pH, arid soils containing  $\text{CaCO}_3$  (which  
287 enters into  $\text{Ca}_{\text{ex}}$  during extraction) also supported low C inputs, likely due to a moisture constraint on crop  
288 productivity. While we removed inorganic C from these soils prior to analysis, the effect of low C inputs *in situ* may  
289 have outweighed any effect of  $\text{CaCO}_3$  in contributing to aggregate- or mineral-associated C stabilization (Rowley et  
290 al. 2021). The lower  $R^2$  of the relationship between  $\text{Al}_0 + [1/2]\text{Fe}_0$  and MAOC in the low pH soils in which these  
291 compounds are more abundant may be explained by an excess of  $\text{Al}_0 + [1/2]\text{Fe}_0$  relative to MAOC, although  
292 confirmation of this concept requires further investigation.

293 Contrary to our hypothesis, C inputs were a better predictor of MAOC than POC, which held when analyzed  
294 across shoot, root, and total C inputs (Fig 4). This finding overturned our expectation of matrix-mediated soil C

295 stabilization contrasting with C input-dependent POC pools. We now propose that C inputs are a poor predictor of  
296 POC in agricultural soils because POC pools are more controlled by loss pathways, being less protected (supported  
297 by more rapid turnover times, Poeplau et al. 2018) and more vulnerable to the micro-climate effects of  
298 decomposition than MAOC. Differences in C input chemistry between sites due to the range of crop species planted,  
299 from leguminous annual cover crops to perennial grasses, likely also contributed to differential rates of retention of  
300 C inputs (Johnson et al. 2007). While it is surprising that root inputs in particular were poorly associated with an  
301 overall increase in POC given their preferential retention in soil (Austin et al. 2017), an increase in minimum values  
302 of POC with root inputs does support the current understanding of the role of root inputs for SOC. Total C and shoot  
303 C inputs best predicted MAOC levels, and we explore interrelationships between C inputs and MAOC through the  
304 use of SEM below.

305

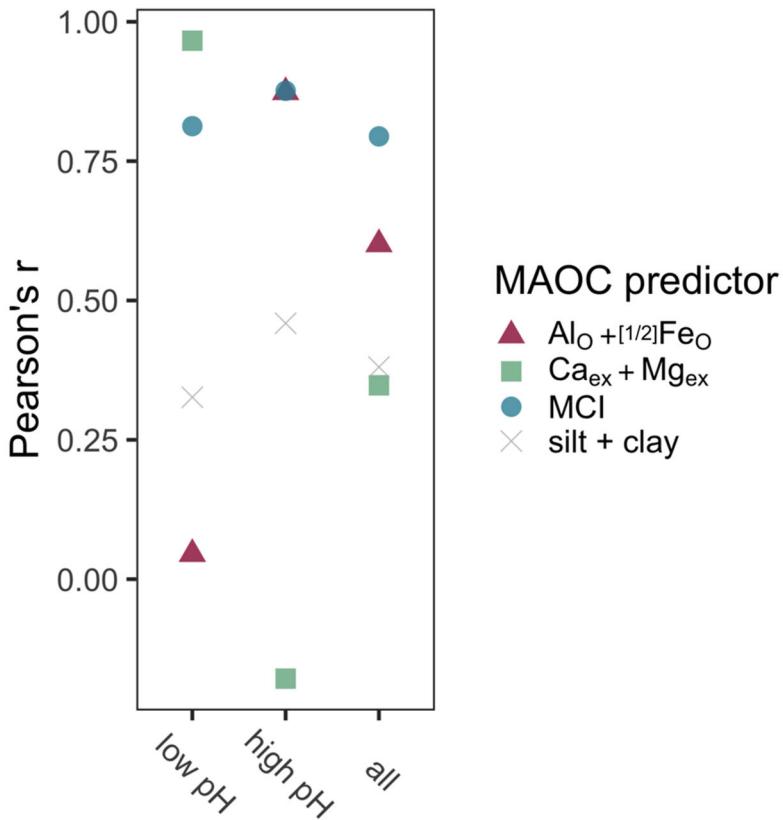
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307

308 **Fig. 2** Effect of soil physicochemical properties on soil organic carbon (SOC), particulate organic carbon (POC),  
 309 and mineral-associated organic carbon (MAOC), 0–20 cm depth, across 16 agricultural sites (n = 124 plots) in the  
 310 United States. Large points represent site-level averages and small points represent plots within sites (n = 124).  
 311 Error bars represent standard errors. Regression lines plotted when p < 0.05. A 't' indicates the p-value and R<sup>2</sup>  
 312 reflect response variables that were log-transformed to reduce heteroskedasticity. Ca<sub>ex</sub> + Mg<sub>ex</sub> = sum of  
 313 exchangeable Ca and Mg. Al<sub>O</sub> + [1/2]Fe<sub>O</sub> = sum of oxalate-extractable Al and oxalate-extractable Fe. MCI = matrix  
 314 capacity index, defined in Methods. Complete regression coefficients for all observations and separate pH groups,  
 315 and with Ca<sub>ex</sub>, Mg<sub>ex</sub>, Fe<sub>O</sub>, and Al<sub>O</sub> separated, are reported in SI Tables 8–10.

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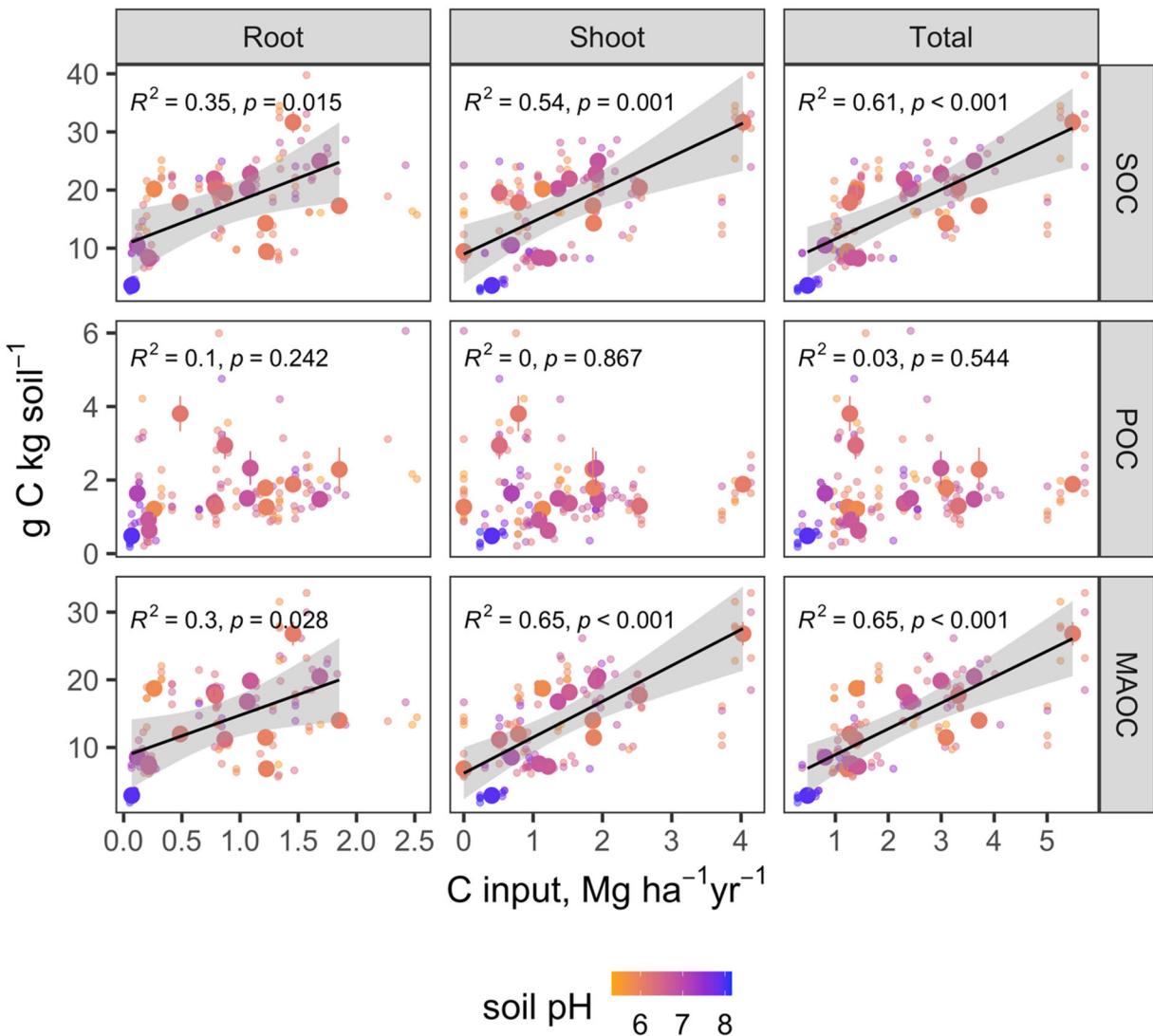


317

318 **Fig. 3** Pearson correlation coefficients between soil physicochemical properties and soil mineral-associated organic  
 319 carbon (MAOC), 0–20 cm depth, across 16 agricultural sites (averaged from 124 plots) in the United States. Site-  
 320 level average soil pH ranged from 5.8–6.4 in the low pH group and 6.6–7.9 in the high pH group. MCI = matrix  
 321 capacity index, the sum of z-score standardized values of Ca<sub>ex</sub> + Mg<sub>ex</sub> and Al<sub>O</sub> + [1/2]Fe<sub>O</sub>, defined in Methods.

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325

326 **Fig. 4** Relationships between root, shoot, and total average C inputs and soil organic carbon (SOC), particulate  
 327 organic carbon (POC), and mineral-associated organic carbon (MAOC), 0–20 cm depth, across 16 agricultural sites  
 328 (n = 124 plots) in the United States. Large points represent site-level averages and small points represent plots  
 329 within sites (n = 124). Regression lines plotted when p < 0.05. Error bars represent standard errors; standard errors  
 330 not available for C inputs. Complete regression coefficients for all observations are reported in SI Table 11.

331

332

333 *A unified index for soil matrix capacity to stabilize MAOC*

334 Our approach of creating an MCI to predict MAOC, based on the unified stabilization capacity of  $\text{Ca}_{\text{ex}} +$   
335  $\text{Mg}_{\text{ex}}$  with  $\text{Fe}_0$  and  $\text{Al}_0$ , appears justified, as the MCI had more predictive power over MAOC than other  
336 physicochemical properties (Fig 2, Fig 3; SI Tables 5–6). The MCI also predicted MAOC when calculated with only  
337  $\text{Ca}_{\text{ex}}$  as the exchangeable cation (SI Table 10), likely due to greater abundance of  $\text{Ca}_{\text{ex}}$  compared to  $\text{Mg}_{\text{ex}}$  in our soils.  
338 Further investigation is needed to determine if  $\text{Mg}_{\text{ex}}$  is required in an MCI than spans a broader range of climate and  
339 vegetation covers. Mechanisms of  $\text{Ca}_{\text{ex}}$ ,  $\text{Mg}_{\text{ex}}$ ,  $\text{Fe}_0$  and  $\text{Al}_0$  in stabilizing soil C, which have been proposed and  
340 examined elsewhere, include cation bridging and ligand exchange with organic complexes, as well as aggregate  
341 formation (Rowley et al. 2018; Wagai et al. 2020).

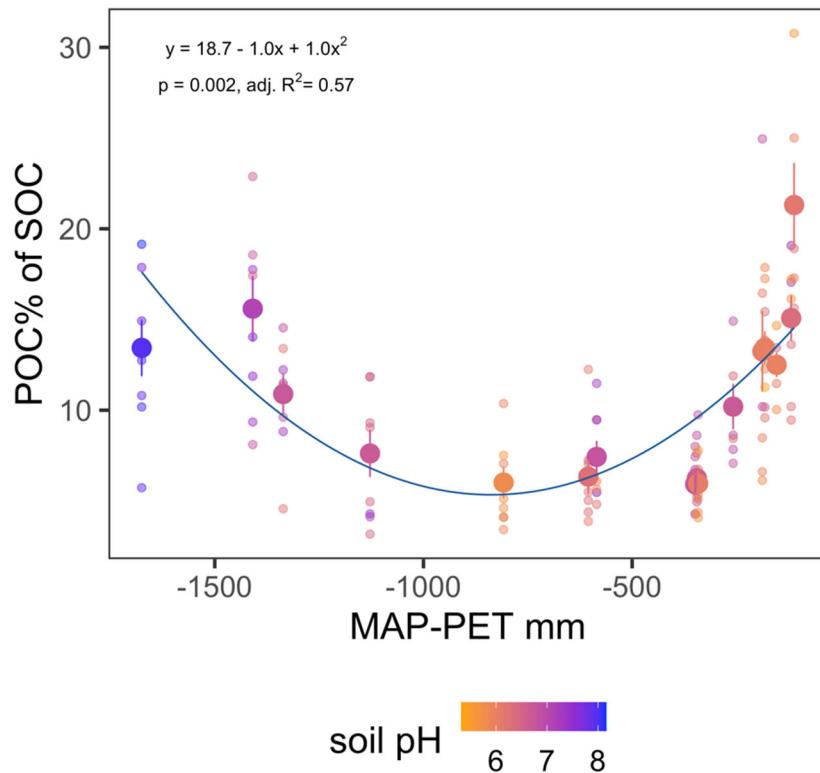
342 The pH-independent MCI proposed here (Fig 2, Fig 3) appears at first to contrast findings of Rasmussen et  
343 al. (2018). Rasmussen et al. (2018) showed that soil physicochemical properties associated with SOC differ in arid  
344 vs. humid climates, i.e.,  $\text{Fe}_0$  and  $\text{Al}_0$  were positively related to SOC in humid climates and  $\text{Ca}_{\text{ex}}$  was positively  
345 related to SOC in arid climates, with only a moderate degree of overlap. Rasmussen et al. (2018) attributed these  
346 patterns to a differential abundance of  $\text{Fe}_0$ ,  $\text{Al}_0$ , and  $\text{Ca}_{\text{ex}}$  with changes in water balance and soil pH. The same  
347 patterns of differential abundance of these compounds across soil pH are evident in this study (Fig 1 a–c). By  
348 dividing SOC into POC and MAOC, however, we observed that  $\text{Al}_0 + [1/2]\text{Fe}_0$  are associated with increasing levels  
349 of MAOC in both low pH and high pH soils, and that  $\text{Ca}_{\text{ex}} + \text{Mg}_{\text{ex}}$  are associated with increasing MAOC even in low  
350 pH soils (Fig 3, SI Table 10).

351 Although this study is limited to agricultural soils, we speculate that if the MCI proposed here were  
352 investigated in a global dataset in which SOC were fractionated into POC and MAOC, the MCI may similarly  
353 predict MAOC storage, and we present this hypothesis as an important topic of future work. Fractionating SOC  
354 gains importance in non-agricultural soils because non-agricultural soils store a greater proportion of SOC as POC  
355 (Lugato et al. 2021), and the effect of soil physicochemical controls on MAOC may be obscured by this abundance  
356 of POC. ). In the global dataset of Rasmussen et al. (2018), which contained grassland and forest soils, POC may  
357 have comprised a greater proportion of SOC in extremes of water balance (Fig 5), where microbial decomposition  
358 may be limited (Cotrufo et al. 2021). In arid environments,  $\text{Fe}_0$  and  $\text{Al}_0$  may poorly correlate to SOC (Rasmussen et  
359 al., 2018) due to the prevalence of  $\text{Ca}_{\text{ex}}$  and the presence of POC, which was not related to  $\text{Ca}_{\text{ex}}$  in this study (SI  
360 Table 9). In contrast, in humid environments,  $\text{Fe}_0$  and  $\text{Al}_0$  may be related to total SOC (Rasmussen et al., 2018) due  
361 to both their prevalence and to their moderate contribution to POC stabilization (Fig 2). While the soils in this study

362 are a continental rather than global dataset, by fractionating SOC and studying a range of soil pH and  
363 physicochemical properties we identify the efficacy of an MCI across agricultural soils. Our data do not support the  
364 concept of a pH threshold in which a single feature of the soil matrix begins to stabilize SOC, and instead suggest  
365 that a milieu of soil compounds, differing in abundance, can operate concurrently to stabilize MAOC and that  
366 considering their unified stabilization potential offers a comprehensive view of SOC dynamics.

367 The utility of this MCI will vary with research aims, its generalizability across non-agricultural systems,  
368 and community reporting practices. This MCI may prove a valuable tool for parsimonious, process-based SOC  
369 modeling in that it may quantify matrix stabilization capacity beyond that of clay while avoiding the complication of  
370 representing multiple soil physicochemical properties separately. While soil pH may appear a reasonable substitute  
371 for soil texture given *pH-dependent* MAOC stabilization mechanisms, soil pH was a poor predictor of MAOC  
372 compared to the MCI (SI Table 10), likely because total matrix stabilizing agents are independent of soil pH.  
373 However, if the research aim is to understand the relative importance of soil physicochemical properties for MAOC  
374 in specific contexts, then keeping soil properties separate will enable more granular investigation than combining  
375 them in an MCI. The extent to which a similar relationship of the MCI with MAOC holds across non-agricultural  
376 ecosystems requires investigation, as do interactions of matrix stabilization with climate (Possinger et al. 2021) and  
377 stocks vs. persistence of MAOC (*sensu* Heckman et al. 2020). Finally, as the MCI of a given soil will change  
378 depending on the mean and standard deviation used to calculate z-scores, we emphasize the need for consistent  
379 reporting of means and standard deviations if MCI values are to be comparable across studies.

380  
381



382 **Fig. 5** Quadratic relationship between MAP-PET and particulate organic carbon (POC) as a percentage of soil  
383 organic carbon (SOC), where raw C data are in g C kg soil<sup>-1</sup>. Quadratic regression was performed log transformed  
384 response; coefficients are back-transformed for presentation. Large points represent site-level averages and small  
385 points represent plots within sites (n = 124).

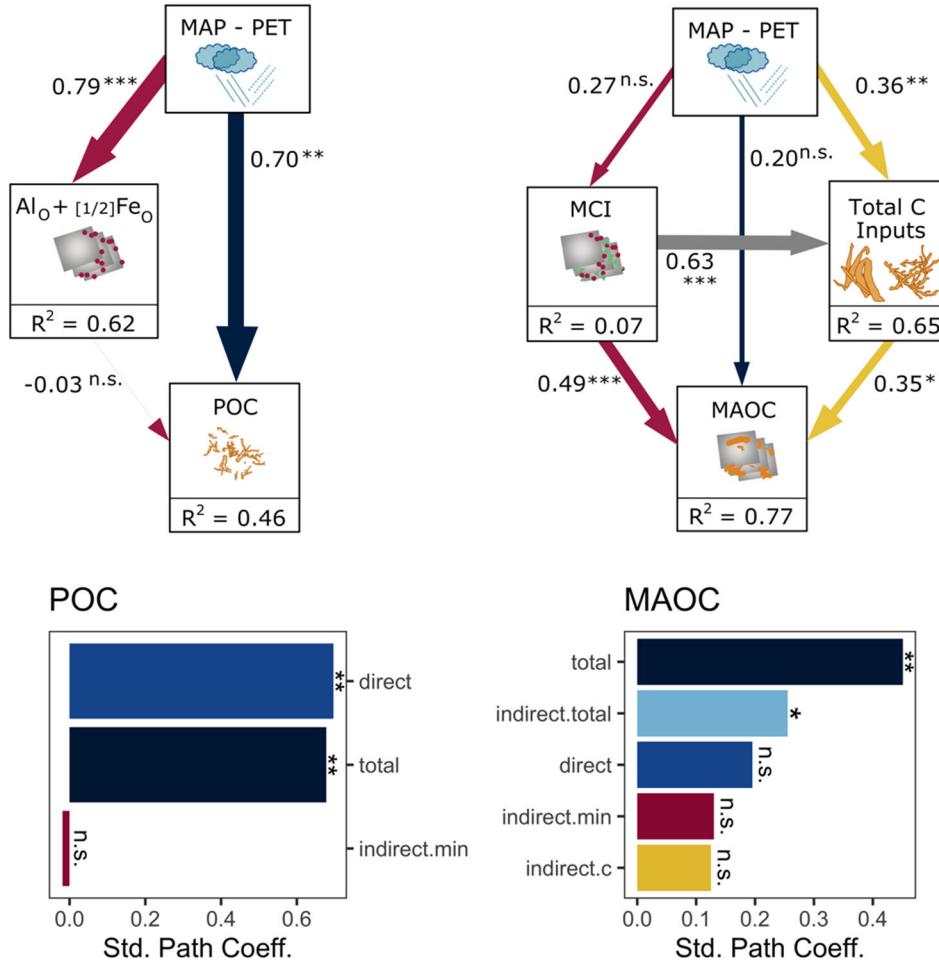
387

388 *Direct and indirect effects of MAP-PET on POC and MAOC*

389 To assess the direct and indirect effects of MAP-PET on soil C, we constructed two SEMs, one each for  
390 POC and MAOC (Fig 6). As potential mediators of an indirect effect of MAP-PET on POC, we used Al<sub>0</sub> + [1/2]Fe<sub>0</sub>  
391 because it was the only factor related to POC in simple linear regression (Fig 2). Since there were many  
392 environmental properties correlated with MAOC, we used the MCI and total C inputs in the SEM, as they were the  
393 factors exhibiting the strongest relationship to MAOC in simple linear regressions (Fig 2, Fig 3). Here, we use  
394 'direct' and 'indirect' to describe pathways elaborated in the structural equation model, acknowledging that  
395 pathways established as 'direct' in the model may nevertheless be mediated by properties not measured in this study.  
396 Structural equation modeling revealed that MAP-PET exerted only a direct effect on POC and a combination of  
397 direct and indirect effects of MAOC (Fig 6).

398 A direct, positive association of MAP-PET with POC was not anticipated in this study but suggests that  
399 POC pools are more sensitive to decomposition than C input rates. We predicted that higher MAP-PET would  
400 correlate with greater C inputs or greater matrix protective capacity created by  $Al_o + [1/2]Fe_o$ , potentially resulting  
401 in higher POC through aggregation (Wagai et al. 2020). These hypotheses were not supported by the results of the  
402 simple linear regression, which showed no relationship between C inputs and POC (Figure 4), or the results of the  
403 SEM, which showed that despite increases with MAP-PET,  $Al_o + [1/2]Fe_o$  had a relatively little subsequent  
404 relationship to POC (Figure 6). Although MAP-PET likely mediates soil moisture and thereby controls rates of  
405 microbial decomposition, the extent to which increasing soil moisture in these agricultural soils could reduce  
406 microbial decomposition – and, therefore, the retention of C inputs in POC – remains an open question (Keiluweit et  
407 al. 2017). Another pathway through which MAP-PET could influence POC is that of root tissue chemistry. There is  
408 suggestive evidence that roots decrease nitrogen (N) content with increasing precipitation (Ordóñez et al. 2020),  
409 which could delay decomposition, however, this putative mechanism requires further investigation to verify.

410 Increasing MAP-PET had a total, positive association with MAOC, comprised primarily of indirect effects  
411 that were mediated by both increasing MCI and increasing total C inputs (Fig 5). The association of MAP-PET with  
412 the MCI was weaker than with  $Al_o + [1/2]Fe_o$  but still significant, likely due to contrasting effects of MAP-PET on  
413  $Al_o + [1/2]Fe_o$  and on  $Ca_{ex} + Mg_{ex}$  (Fig 1). The SEM also showed a series of positive interactions between the MCI,  
414 total C inputs, and MAOC (Fig 6). The clearest interpretation of these interactions is that both the MCI (Kleber et al.  
415 2015; Rowley et al. 2021) and C inputs (Gulde et al. 2008) lead to higher MAOC. However, iterations of the model  
416 without an MCI – C input relationship specified were returned as poorly fit ( $CFI < 0.90$ , Hooper et al. 2008),  
417 suggesting that higher MCI also promoted crop productivity. We speculate that components of the MCI may have  
418 contributed to crop nutrient requirements: while Al is not an essential plant nutrient, Fe and Ca are, and oxalate-  
419 extractable Fe in soil can correspond to crop Fe uptake (Morris et al. 1990). As a major component of SOC, MAOC  
420 may have also positively affected crop productivity (Oldfield et al. 2018) and therefore C inputs through its benefits  
421 for soil available water holding capacity, N mineralization, and soil structure (King et al. 2020).



422

423 **Fig. 6** Structural equation model (SEM) showing direct and indirect effects of mean annual precipitation – potential  
424 evapotranspiration (MAP-PET, mm) on particulate (POC, left) and mineral-associated (MAOC, right) organic  
425 carbon. Soils measured 0–20 cm depth across 16 agricultural sites (n = 124 plots) in the United States; site-level  
426 averages used in SEM. The SEM for POC includes  $Al_0 + [1/2]Fe_0$  ( $g kg soil^{-1}$ ), while the SEM for MAOC includes  
427 a matrix capacity index (MCI, unitless) and total C inputs ( $Mg C ha^{-1} yr^{-1}$ ). The widths of the arrows correspond to  
428 the standardized path coefficients, which are also shown in numbers next to each arrow.  $R^2$  values represent total  
429 proportion of variability explained by all paths. Yellow arrows and bars represent pathway from MAP-PET to C  
430 fraction as mediated by C inputs. Red arrows and bars represent pathway from MAP-PET to C fraction as mediated  
431 by soil physicochemical property. Navy arrow represents direct effect of MAP-PET on C fraction. Effects of  
432 complete paths are shown in the barplot, where ‘indirect.min’ = effect of MAP-PET on soil C via  $Al_0 + Fe_0$  or the  
433 MCI, and ‘indirect.c’ = effect of MAP-PET on MAOC via total C inputs. In all cases, n.s. = ‘not significant’; \* p <  
434 0.01; \*\* p < 0.05, and \*\*\*p < 0.01. The SEM fit the data well, as indicated by comparative fit index (CFI > 0.9) and

435 root mean square error of approximation (RMSEA < 0.08) and standardized root mean square residual (SRMR <  
436 0.08; Hooper et al. 2008). Full model output provided in SI Table 10 and SI Table 11.

437

438 *Implications*

439 Here, we show that fractionating cropland SOC into POC and MAOC allows for improved resolution of  
440 their environmental controls at the continental scale, aligning with findings from forests and grasslands. Given the  
441 strong relationship of the proposed MCI to MAOC, updating process-based soil C models to incorporate an MCI  
442 may offer a promising path for their improvement. However, the data necessary to support this effort, including  
443 MAOC, Fe<sub>o</sub>, Alo, Ca<sub>ex</sub> and Mg<sub>ex</sub> are not currently a consistent part of large-scale data products (Poggio et al. 2021).  
444 Future research will need to investigate the MCI demonstrated here for croplands across other ecosystems to  
445 understand its generalizability, as the MCI may show different relationships to MAOC in other ecosystems. Larger  
446 datasets could also allow more exhaustive weighing of different approaches for summing values of soil Fe<sub>o</sub>, Alo,  
447 Ca<sub>ex</sub>, Mg<sub>ex</sub>, as well as the interacting roles of soil age, parent material, and climate in driving an MCI. Coupling  
448 investigations of an MCI with processes of C transformation, C turnover, and determinants of maximum MAOC  
449 storage, including in subsoils, will also be valuable for advancing soil C modeling. Our work shows that  
450 understanding POC dynamics requires information beyond C input quantity and soil physicochemical properties to  
451 adequately describe its variation at continental scales. Soil temperature and moisture sensors, information on C input  
452 chemistry, and/or alternative fractionation of the POC pool (i.e., by density) could allow for improved resolution of  
453 POC dynamics.

454 Finally, we observed a series of positive associations between crop C inputs, MAOC, and the MCI. These  
455 relationships indicate the possibility of reinforcing feedbacks between crop productivity, soil MAOC accumulation,  
456 and soil fertility, where soil fertility is measured by Ca<sub>ex</sub> and Fe<sub>o</sub> but is also associated with N supply to crops from  
457 soil organic matter. While these pathways are individually acknowledged, considering and quantifying feedbacks  
458 between these pathways over broad spatial scales and beyond croplands may allow for improved understanding of  
459 future interacting between of soils, plant growth, and climate.

460

461 **Conflict of interest**

462 Co-author M. Francesca Cotrufo is co-founder of Cquester Analytics, which offers soil fractionation for service. The  
463 other authors have no competing interests to declare that are relevant to the content of this article.

464

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