1	Updated framework and signal-to-noise analysis of soil mass balance
2	approaches for quantifying enhanced weathering on managed lands
3	
4	Tim Jesper Suhrhoff <sup>1,2*</sup> , Tom Reershemius <sup>3, 2</sup> , Jacob Jordan <sup>4</sup> , Shihan Li <sup>5</sup> , Shuang Zhang <sup>5</sup> , Ella
5	Milliken <sup>2</sup> , Boriana Kalderon-Asael <sup>2</sup> , Yael Ebert <sup>2</sup> , Rufaro Nyateka <sup>2</sup> , Christopher T. Reinhard <sup>6</sup> ,
6	Noah J. Planavsky <sup>2,1</sup>
7	
8	<sup>1</sup> Yale Center for Natural Carbon Capture, Yale University, New Haven, CT 06511, USA
9	<sup>2</sup> Department of Earth and Planetary Sciences, Yale University, New Haven, CT 06511, USA
10	<sup>3</sup> School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne,
11	England NE1 7RU, United Kingdom
12	<sup>4</sup> Mati Carbon, Houston, TX, USA
13	<sup>5</sup> Department of Oceanography, Texas A&M University, College Station, TX 77843, USA
14	<sup>6</sup> School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332,
15	USA
16	
17	* corresponding author: timjesper.suhrhoff@yale.edu
18	

# 19 Abstract

20

21 Enhanced weathering is a promising approach for removing carbon dioxide from the atmosphere 22 at scale while improving agricultural yields. However, accurately quantifying carbon dioxide 23 removal in the field is critical for this approach to scale, particularly given that nearly all of the 24 current deployment activity caters to the voluntary carbon market. Here, we present an updated 25 framework and a signal-to-noise analysis for using soil-based mass balance approaches to quantify 26 rock powder dissolution from field-scale data of soil composition. With additional assumptions, 27 the quantification of rock powder dissolution can be used to estimate carbon dioxide removal 28 potential of EW deployments. The framework we present explicitly accounts for the enrichment 29 of immobile elements in topsoil due to feedstock mass loss and demonstrates that omission of this 30 process systematically overestimates feedstock dissolution. We suggest that the framework should 31 only be used when average post-weathering sample compositions fall within the parameter space 32 representing physically meaningful results (i.e., set out by the mixing relationships between soil, 33 feedstock, and a hypothetical weathered feedstock residue endmember). Building from this, we 34 provide support for the idea that feedstock dissolution should be quantified using the sample 35 population mean rather than individual samples. Given the potential for signal-to-noise issues with

- 36 this framework, it is critical that it is utilized only when signals are statistically robust. To illustrate
- 37 this, we present a signal-to-noise analysis based on a new dataset of soil cation heterogeneity from
- high-density spatial sampling of 5 fields (0.6-19.2 samples  $ha^{-1}$ , 7.1-39.6 pooled cores  $ha^{-1}$ ). The
- analysis is based on simulated geolocated sample pairs and suggests that detecting rock powderdissolution via soil mass balance should be feasible when application rates, dissolution fractions,
- and sampling frequencies are above certain threshold values. When planning deployments, signal
- 41 and sampling frequencies are above certain threshold values. when planning deployments, signal 42 emergence can be optimized through careful selection of feedstock composition, strategic
- 43 feedstock application, and improved sampling protocols.
- 44

## 45 1 Introduction

46 Achieving the climate targets set out by the Paris agreement requires both deep and immediate 47 emissions cuts as well as the ability to remove emitted carbon from the atmosphere (IPCC, 2018; 48 Geden et al., 2024; UNEP, 2024). Removing up to 5-10 Gt CO<sub>2</sub> from the atmosphere annually will 49 ultimately require a portfolio of Carbon Dioxide Removal (CDR) approaches (Strefler et al., 2021). 50 Enhanced Weathering (EW) is one promising approach where CO<sub>2</sub> can be removed from the 51 atmosphere through the reaction with crushed rock feedstocks applied as soil amendments 52 (Seifritz, 1990; Schuiling & Krijgsman, 2006; Hartmann & Kempe, 2008; Köhler et al., 2010; ten 53 Berge et al., 2012; Hartmann et al., 2013; Beerling et al., 2018, 2020, 2024). In the ideal case, CO<sub>2</sub> 54 is transferred into bicarbonate and ultimately stored in the oceans for >10 kyrs (Renforth & 55 Henderson, 2017) or stored as carbonate in both soils and deep-sea sediments. This approach has 56 a unique set of advantages including that carbon is stored more durably compared to many 57 biomass-based approaches. Enhanced weathering can also boost crop yields and does not compete 58 for land resources (Haque et al., 2020; Kelland et al., 2020; Gunnarsen et al., 2023; Beerling et al., 59 2024), and the logistics and infrastructure to scale are readily available.

60

61 Currently, most CDR activity-including EW-is occurring on the voluntary carbon market 62 (Smith et al., 2023; Geden et al., 2024; CDR.fyi, 2025). This means that CDR credits are primarily 63 being used by companies with net-zero goals to balance ongoing emissions. There is a long 64 tradition of tracking soil carbon removal through biogeochemical modeling-foremost with soil 65 organic carbon (e.g., Parton et al., 1998)-and using models for emissions offsetting claims 66 (Oldfield et al., 2022; Potash et al., 2025). There are also geochemical models for enhanced weathering (Taylor et al., 2017; Kanzaki et al., 2022, 2024a; Bertagni et al., 2024). However, it 67 68 has been commonly argued that soil biogeochemical models have not progressed or been 69 sufficiently validated to make them fit for offsetting purposes at this stage (Kanzaki et al., 2024b; 70 Sutherland et al., 2024). Therefore, there is a need to develop a suite of tools to track weathering 71 rates and EW at the field scale, both for verification of ongoing compensatory offset claims and 72 for validation of predictive process-based models for quantifying soil carbon removal. 73

74 This is a challenge for EW because it is an open-system CDR pathway, and a large number of 75 approaches have been suggested to quantify CDR at the field scale (Almaraz et al., 2022; Clarkson 76 et al., 2024). Broadly speaking, Measurement, Reporting, and Verification (MRV) approaches for 77 EW rely on either solid soil, water, gas, or exchangeable phase measurements (Clarkson et al., 78 2024), and typically measurements of two phases are combined into reported CDR numbers 79 (Sutherland et al., 2024). Soil-based MRV approaches have a unique set of advantages, namely 80 that they yield a time-integrated signal (Reershemius et al., 2023; Clarkson et al., 2024), meaning 81 that in contrast to water and gas phase-based estimates, they resolve all rock feedstock weathering 82 that occurred between different sampling steps without need for high temporal sampling 83 frequencies. All field-based EW MRV approaches do not directly resolve downstream losses of 84 CO<sub>2</sub>, which according to current crediting frameworks must be accounted for based on empirically 85 informed but modeled based estimates (Campbell et al., 2023; Clarkson et al., 2024).

86

87 One promising variation of soil-based MRV approaches is the use of soil mass balance 88 (Reershemius et al., 2023; Clarkson et al., 2024; Suhrhoff et al., 2024). Soil mass balance 89 approaches rely on a sample-resample approach where the dissolution of rock powder feedstock 90 is tied to the loss of cations from mixed soil-feedstock samples. The loss of cations provides an 91 estimate of feedstock dissolution, and with additional assumptions can be translated into an 92 estimate of initial CDR. Here, we present an updated framework for this approach that explicitly 93 considers the impact of immobile element enrichment in soils due to feedstock mass loss from 94 topsoils. Furthermore, we demonstrate some of the intricacies of this approach with specific 95 examples, perform a signal-to-noise analysis, and share Python code and a spreadsheet-based 96 conceptual tool to help users explore and potentially constrain rock powder dissolution in their 97 own field deployments. The signal-to-noise analysis is grounded in a new dataset (5 fields, 998 98 total samples) where spatial heterogeneity in soil major and trace elemental concentration is 99 assessed at a high spatial sampling density.

## <sup>101</sup> 2 Soil mass balance framework

102 Soil mass balance approaches are based on the assumption that mobile base cations are lost from 103 the solid phase of the soil-feedstock mixture during feedstock dissolution, while immobile 104 elements are retained in the solid phase of the soil. Base cations mobilized during feedstock 105 dissolution can be temporarily retained on the soil exchange complex (Dietzen & Rosing, 2023; 106 Kanzaki et al., 2024b; te Pas et al., 2025), but these can also be readily quantified. Using these 107 assumptions, practitioners can calculate weathering rates of feedstock material based on the 108 mobility of base cations relative to immobile elements (Brimhall & Dietrich, 1987; Chadwick et 109 al., 1990, 1999; Brimhall et al., 1991; Kurtz et al., 2000; White et al., 2001; Anderson et al., 2002; 110 Riebe et al., 2003; Tabor et al., 2004; Sheldon & Tabor, 2009; Brantley & Lebedeva, 2011; Fisher 111 et al., 2017; Lipp et al., 2021). In the context of EW, this framework was first applied in 2023 112 (Kantola et al., 2023; Reershemius et al., 2023) and has since been built upon in several 113 publications (Reershemius & Suhrhoff, 2023; Beerling et al., 2024; Clarkson et al., 2024; Suhrhoff 114 et al., 2024; Derry et al., 2025) and preprints (Baum et al., 2024; Rogers & Maher, 2025).

115

116 For this approach to be effective, the rock feedstock added to fields must be enriched in base 117 cations, as compared with the background soil. If immobile element abundance is also being used 118 to evaluate the amount of feedstock in a given sample, at least one immobile element needs to be 119 enriched compared to the background soil. If these conditions are met, the enrichment of immobile 120 elements in topsoils can be used to constrain rock powder addition, and the loss of cations can be 121 used to estimate rock powder dissolution. If these conditions are not met, soil mass balance 122 approaches (SOMBA) are not suitable to detect CDR through EW (Reershemius et al., 2023; 123 Clarkson et al., 2024; Suhrhoff et al., 2024). This does not mean that for such feedstock-soil 124 combinations no CDR is occurring, only that quantification of CDR will need to rely on different 125 approaches (Suhrhoff et al., 2024). Using an immobile element to constrain rock powder addition 126 has the benefit that rock powder loss through, e.g., erosion, is not erroneously detected as 127 weathering, as may be the case if only changes in major cation concentration are considered. 128 Because first applications of this approach to EW have used the immobile element Ti as the proxy 129 for rock powder addition, this approach has also been called "TiCAT" (Reershemius et al., 2023),

but because other immobile elements may also be used (Suhrhoff et al., 2024), we now refer to

- 131 this approach more broadly as soil mass balance approaches (SOMBA).
- 132

133 The loss of cations from topsoils upon weathering can be used to constrain the fraction of rock 134 powder that has dissolved. This in turn can be a proxy for CDR, but translating rock powder 135 dissolution into CDR estimates requires additional assumptions as well as quantification of 136 downstream loss processes (Reershemius et al., 2023; Clarkson et al., 2024). For this reason, robust 137 quantification of CDR should rely on multiple methods based on two phase measurements (e.g., 138 solid and gas phases) (Sutherland et al., 2024). At scale, a multiple phase approach will be 139 impractical in every case at deployment scale, indicating the need to ultimately move away from 140 field level accounting, as for example also suggested for soil organic carbon management 141 (Bradford et al., 2023; Potash et al., 2025). Quantitative conversion of dissolution fraction into 142 CDR estimates as well as post-weathering CDR loss processes are discussed in detail elsewhere 143 (Campbell et al., 2023; Kanzaki et al., 2023; Clarkson et al., 2024; Zhang et al., 2024) and are 144 beyond the scope of this study. Our focus here is to present an updated framework for the 145 quantification of rock powder dissolution, as well as a signal-to-noise analysis of the utility of this 146 approach against background soil heterogeneity. We also share the accompanying code to provide 147 future ERW deployments with a solid foundation for the quantification of rock powder dissolution.

148

149

### 150 2.1 Calculation of feedstock dissolution fraction

151 After rock powder that has an elevated base cation content (/i), with the square brackets denoting 152 concentrations per mass of soil) and is enriched in at least one immobile element (i) is added to 153 fields, the composition of the initial soil-feedstock mixture falls onto a mixing line between the 154 soil and feedstock endmembers (Figure 1a). As the rock powder dissolves, mobile base cations are 155 leached from the mineral phase. This loss of cations is used to quantify the fraction of rock powder 156 that has weathered. This estimate of base cation loss reflects the dissolution of primary feedstock 157 when a chemical extraction of secondary phases or exchangeable cations is performed prior to 158 analysis. Alternatively, the estimate can reflect the proportion of the overall feedstock base cation 159 inventory that has been leached from topsoils entirely if bulk samples are used.

161 Enrichment of immobile elements through rock powder dissolution occurs when they are retained 162 in topsoil while a soluble fraction of feedstock is lost from the system. Assuming that the topsoil 163 volume sampled does not change and that there is no change in porosity, lost feedstock in a sample 164 is replaced with soil that also contains immobile elements in addition to the retained immobile 165 elements added via the rock powder. Furthermore, if the density of feedstock is greater than that 166 of soil, as is true for most cases, this means that the mass being used to calculate the concentration 167 *[i]* is less than for the initial soil-feedstock mixture, such that  $[i]_{t=n} > [i]_{t=0}$  in all cases where feedstock is partially dissolved. As a result of cation loss and immobile element enrichment, the 168 169 soil-feedstock mixture composition is evolving from the pre-weathering composition on the 170 mixing line along a vector towards the bottom right in [j] vs. [i] space (Figure 1b).

171

172 One way to calculate the dissolution fraction (here denoted as the mass transfer coefficient  $\tau_j$ , used 173 synonymously to dissolution fraction in this manuscript) is from the loss of cations compared to 174 the pre-weathering soil-feedstock mix:

175

177 
$$[j]_{add} = [j]_0 - [j]_s$$
 2

178

179 where  $[j]_{add}$  is the increase in base cation concentrations due to the addition of rock powder,  $\Delta [j]$ 180 reflects the decrease of base cation concentrations due to feedstock dissolution, and the subscript 181 s corresponds to baseline soil. If the effect of immobile element enrichment is not taken into 182 account, and the fraction of feedstock in the pre-weathering soil-feedstock mix and associated 183 cation addition is calculated simply by vertically projecting the post-weathering composition onto 184 the mixing line (Figure 1c), the estimate of the cations lost from topsoils  $(\Delta [j]^*)$  is inflated, such that the erroneous estimate  $\tau_i^*$  would be larger than  $\tau_i$ . The impact of this enrichment process on 185 186 post-weathering soil concentrations as well as estimates of the fraction of feedstock that has 187 dissolved is demonstrated and discussed in section 3.1.

188

189 An alternative way to calculate the fraction of rock powder that has dissolved without exact 190 knowledge of the pre-weathering soil-feedstock mix composition is to describe the post-

191 weathering composition as a mix of three endmembers: pure soil, pure feedstock, as well as the 192 composition of a hypothetical weathered feedstock residue endmember (Figure 1d). The 193 composition of this hypothetical endmember is defined to be the composition that a layer of soil 194 would have after a layer of pure feedstock (corresponding to the soil sampling depth, d<sub>sample</sub>) has 195 dissolved. The overall dissolution fraction can then be calculated from the contributions to the 196 feedstock and weathered feedstock endmember to the mixed sample composition. Assuming mass 197 and volume conservation, this endmember mixing approach can be described by a system of 198 equations such that each endmember contributes a volume proportion (X) to the observed post-199 weathering composition, which together sum to unity:

200

$$201 X_s + X_f + X_{wf} = 1 3$$

202

Where subscripts *s*, *f*, and *wf* correspond to baseline soil, feedstock, and weathered feedstock. Because in practical field sampling based on constant soil sampling depths, a system of constant *volume* is sampled, these endmember contributions reflect *volume* contributions to the sampled soil volume defined by the sampling depth over a given area (all calculations and code shared here use 1 hectare (ha) by default). The endmember contributions reflect three unknowns. Hence, we set up two additional equations reflecting mass conservation of immobile elements as well as mobile base cations respectively.

210

211 
$$[j]_{s}X_{s}\rho_{s} + [j]_{f}X_{f}\rho_{f} + [j]_{wf}X_{wf}\rho_{wf} = [j]_{mix,t=n}(X_{s}\rho_{s} + X_{f}\rho_{f} + X_{wf}\rho_{wf})$$

$$4$$

212 
$$[i]_{s}X_{s}\rho_{s} + [i]_{f}X_{f}\rho_{f} + [i]_{wf}X_{wf}\rho_{wf} = [i]_{mix,t=n}(X_{s}\rho_{s} + X_{f}\rho_{f} + X_{wf}\rho_{wf})$$

213

Note that it is important to account for the impact of immobile element enrichment due to mass loss also for the composition of the hypothetical weathered feedstock endmember. These equations can be solved (see S1.1 for detailed derivation) to calculate the contribution of each endmember to the observed post-weathering composition.

5

218

This system of equations (3, 4, and 5) can be used to explicitly calculate the volume proportions of each of the three endmembers (for full derivation see supplement S1.1):

222 
$$X_f = \frac{\rho_s([j]_{mix,t=n}-[j]_s)}{\rho_s([j]_{mix,t=n}-[j]_s) - \rho_f([j]_{mix,t=n}-[j]_f)}$$
6

223 
$$X_{wf} = \frac{\rho_s([i]_{mix,t=n}-[i]_s)\rho_f([j]_{mix,t=n}-[j]_f)-\rho_s([j]_{mix,t=n}-[j]_s)\rho_f([i]_{mix,t=n}-[i]_f)}{\rho_f[i]_f(\rho_s([j]_{mix,t=n}-[j]_s)-\rho_f([j]_{mix,t=n}-[j]_f))}$$
7

224 
$$X_s = 1 - X_f - X_{wf}$$
 8

The fraction of feedstock that has dissolved is calculated from the proportion of the weathered feedstock residue endmember relative to the sum of feedstock and weathered feedstock residue endmembers:

229

231

232 Calculating  $\tau_i$  requires measuring the immobile element and base cation concentration of baseline 233 soils, feedstock, and post-weathering soil-feedstock mix samples, as well as soil and feedstock 234 density (i.e., the density of the ground rock powder, not the rock itself). Generally, EW 235 deployments should assess  $\tau_i$  values for all base cations to be used to estimate CDR. Because these will vary between base cations, setting the system of equations as an over-constrained system using 236 237 multiple equations for different base cations in combination with an inversion approach is not 238 recommended unless expanding the framework to explicitly consider different mineral phases and 239 loss processes. Some feedstocks may also contain mineral phases that are not expected to dissolve 240 on the timeline relevant for the EW deployment, which could be taken into account by modifying 241 the composition of the hypothetical weathered feedstock residue endmember accordingly (both in 242 terms of composition and density).

243

This endmember mixing approach is preferrable to quantifying feedstock dissolution exclusively from the loss of cations compared to the initial soil-feedstock mix composition (equations 1 and 2) because estimating this initial composition from post-weathering measurements without knowing the exact mixing proportions (which may vary throughout a field) is non-trivial given that the direction of the vector that the soil-feedstock mix composition will move along during weathering depends on the initial feedstock-soil mass mixing ratio ( $fM_{f, t=0}$ ) and the composition of each endmember. Instead, the endmember mixing approach quantifies the dissolution fraction while also explicitly accounting for the enrichment of immobile elements due to feedstock loss from the system. Alternatively, sampling after feedstock addition (and again after weathering has occurred) can be used resolve issues of mixing proportions. Mobile element loss should still be calculated relative to a detrital element, even when not using the detrital element to calculate feedstock addition rates (Brimhall & Dietrich, 1987; Chadwick et al., 1990; Brimhall et al., 1991; Anderson et al., 2002).

257

In addition to estimating feedstock dissolution, the framework presented here can also be used to estimate the amount of initial feedstock as well as the pre-weathering feedstock-soil mix composition from the post weathering composition as well as baseline soil and feedstock data (for detailed derivation see S.1.2):

262

$$263 \quad a = (X_f + X_{wf}) \, v_{sampled \, layer} \, \rho_f \tag{10}$$

264 
$$[j]_{mix, t=0} = \frac{\rho_s X_s [j]_s + \rho_f (X_f + X_{wf})[j]_f}{\rho_s X_s + \rho_f (X_f + X_{wf})}$$
11

265 
$$[i]_{mix,t=0} = \frac{\rho_s X_s [i]_s + \rho_f (X_f + X_{wf})[i]_f}{\rho_s X_s + \rho_f (X_f + X_{wf})}$$
12

266

267 Where  $v_{sample \ layer}$  is the volume of the sampled layer (per hectare if a is estimated per hectare). 268

269 Here, we supply Python code as well as an example use case. Generally, the relevant calculations 270 are defined as functions in the Python file SOMBA.py, where the calculation of  $\tau_i$  is defined in the 271 function SOMBA tau. The code also contains additional functions to estimate pre-weathering and 272 post-weathering mix composition from deployment data (functions SOMBA start and 273 SOMBA end; see supplement S1). In addition, SOMBA.py also contains the function 274 SOMBA tau meta, which in addition to  $\tau_i$  also returns the individual endmember contributions as 275 well as additional deployment parameters calculated from post-weathering samples as defined 276 below. We provide two Python scripts; one that loads input data and calculates the SOMBA 277 parameters, and a second one that demonstrates the internal consistency of the framework 278 presented here (see also supplement S1.5 and Figure S1). We furthermore provide an Excel 279 template that calculates the dissolution fraction based on eq. 6-9. This template may be used as a

tool to analyze initial results, but ultimately thorough statistical investigation should always bebased on advanced statistical modeling.

282

### 283 2.2 Signal-to-noise analysis

Soils are heterogeneous both on small and large spatial scales (Bahri et al., 1993; Jackson & Caldwell, 1993; Zhang et al., 1998; McGrath et al., 2004; Spijker et al., 2005; Ramsey et al., 2013; Smith et al., 2013; Webster & Lark, 2019), which may pose challenges for soil-based approaches to quantify rock powder dissolution in EW field trials (Suhrhoff et al., 2024; Derry et al., 2025; Rogers & Maher, 2025). To assess the efficacy of the soil-based mass balance approach to quantify rock powder dissolution outlined here against the backdrop of soil heterogeneity, we conduct a signal to noise analysis grounded in soil and basalt data for EW field trials in US agricultural lands.

291

292

### 293 2.2.1 Data constraints

294 To use a representative basalt composition, we calculate the mean composition (in terms of base 295 cations and Ti) of all basalts within the US that are contained in the GEOROC database (Lehnert 296 et al., 2000). Soil base cation and immobile element concentrations as well as representative soil 297 heterogeneity on these parameters are based on two separate datasets. We use an existing dataset 298 of US soils (Smith et al., 2013) to constrain the elemental composition of a large number of fields 299 (only data classified as "Row Crops" and "Small Grains" as LandCover2 variable considered, n =300 614). Here, each sample is considered to represent the "true" composition of a field. The analysis uses Ca+Mg as *i* (basalt  $[i]_f = 3.11 \text{ mol kg}^{-1}$ ), and Ti as *i* (basalt  $[i]_f = 0.206 \text{ mol kg}^{-1}$ ). Because the 301 302 soil mass balance framework requires a clear difference in [i] and [j] between soils and rock 303 powders (Suhrhoff et al., 2024), we only consider soil samples as suitable fields where both [i] and 304 [*j*] are at least 5 times lower than US basalt (n = 130 out of 614 Row Crop and Small Grain samples; 305 Figure 2). These data are used as "true" field compositions.

306

To constrain variance on field-level sample compositions resulting from spatial heterogeneity, we
utilize a new dataset based on high-density spatial sampling (Table 1; Figure S2). This dataset of

309 soil heterogeneity is based on new ICP-MS soil composition measurements (residual phase after

310 exchangeable cations were leached with 1M ammonium acetate) from 5 field sites in the US with 311 spatial sampling frequencies ranging from 0.6 - 19.8 samples ha<sup>-1</sup> (7.1 - 39.6 pooled sub samples 312 ha<sup>-1</sup>). For more information on sampling and analytical procedures, see supplement S2. We fit log-313 normal distributions to field data (using the Python scipy.stats module), and use fitted shape 314 parameters representing the standard deviations ( $\sigma$ ) of the underlying normal distribution to model 315 in-field variance. The shape parameters corresponding to field data are shown in Figure S3, and 316 uniform distributions between the range of observed shape parameters is used to generate synthetic 317  $\sigma$  values in Monte Carlo simulations.

318

#### 319 2.2.2 Statistical modeling

320

The signal-to-noise analysis developed here predicts the efficacy of detecting feedstock dissolution based on hypothetical application amounts and dissolution fractions ( $\tau_i$ ) and a paired sampling approach in a series of Monte Carlo simulations based on the following logic. For each modeled  $\tau_j$  value, application amount, and sampling frequency (1-20 samples ha<sup>-1</sup>), we:

Generate the number of samples to be simulated for each field from the product of sampling
 frequency and a simulated field size, ranging from 10-100 ha (uniform distribution). Within
 the US, most farms are smaller than 72 ha, but most farmland is in farms that are larger
 than 2000 ha (USDA, 2022, 2024), such that the values generated here represent a
 conservative choice.

Generate a set of baseline soil samples for each field based on log-normal distributions
where the variance is constrained from fits to empirical data (Figure S2, Figure S3), and
the generated log-normal sample distributions scaled to ensure the expected population
mean is the same as the "true" field mean. How the log-normal fits to soil data are used to
generate synthetic in-field heterogeneity is explained in more detail in supplement S2.3.

335 3. Calculate the "true" post-weathering composition for each baseline sample, based on
336 deployment parameters (based on functions SOMBA\_start and SOMBA\_end)—reflecting
337 a paired sampling approach.

Generate variance around "true" post-weathering compositions as in 1 assuming the same
 variance as for baseline samples, as well as reduced variance reflecting the expected
 improvement due to a paired sampling approach, implemented by reducing shape

- parameters by 50%—while this is somewhat arbitrary, the efficacy of a paired sampling
  approach to reduce sampling variance can be tested for any real deployment such that these
  conditions can be verified at a field level.
- 5. Randomly generate uncertainty on feedstock composition from 5–10% (uniform distribution; i.e.  $\sigma$  values of 0.05 to 0.1 for generated log normal distirbutions). To reflect increasing thoroughness of the sampling approach, as soil sampling frequency increases from 1 to 20 samples ha<sup>-1</sup> we also increase the number of total samples that the composition of the feedstock endmember is calculated from (from 1 to 20 samples).
- 349
  6. Calculate the average baseline, post-weathering soil-feedstock mix, and feedstock
  350 composition based on the generated samples, each called one "realization".
- 351 7. For each realization we calculate the dissolution fraction (based on SOMBA\_tau) and
  352 calculate the absolute difference compared to the true dissolution fraction (which is
  353 assumed *a priori*).
- 8. We repeat this procedure one hundred times (100 realizations) and calculate the average error on  $\tau_j$  over all fields and realizations. This average error represents the expected error on  $\tau_j$  if applying this framework based on data-constrained soil heterogeneity and representative US soil composition.

### 358 3 Results and discussion

359

### 360 3.1 Impact of immobile element enrichment on calculated dissolution

- 361 fractions
- 362

363 Accurately accounting for immobile element enrichment in soils due to feedstock loss from the 364 topsoil system is essential to quantifying feedstock dissolution. Here, we demonstrate the impact 365 of this process (see 2.1) by simulating the increase in immobile element concentrations in post-366 weathering soil-feedstock mixtures for three different feedstock application amounts, the whole 367 range of dissolution fractions, as well as soils with a Ti content that is 2-10 times depleted 368 compared to US-average basalt. As expected from mass balance considerations, the enrichment of 369 immobile elements is highest at high dissolution fractions,  $\tau_i$ , as well as at low feedstock-to-soil immobile element ratios  $(r_i)$ , as shown in Figure 3a where the impact is visualized by showing the 370 371 difference in post-weathering to pre-weathering soil-feedstock mix composition ( $\Delta i$ ). At constant 372  $r_i$ , this effect is linear with increasing  $\tau_i$ , demonstrating that it scales with the amount of feedstock 373 volume that has been lost from the system and is replaced with soil when considering constant 374 sampled topsoil volumes. There are also instances where this process will have a negligible (>5%)375 effect.

376

The effect also increases with increasing application amounts, because at the same dissolution fraction the volume of feedstock that is lost from topsoils increases. When  $r_i$  is defined via depletion relative to a fixed feedstock composition,  $\Delta i$  increases with decreasing  $r_i$ , reflecting the fact that when sampling constant soil volumes, soil that replaces lost feedstock has a higher immobile element concentration. Because  $r_i$  is defined as the ratio of feedstock to soil immobile element concentrations, lower  $r_i$  reflects higher soil concentrations of i:

383

$$384 \quad [i]_s = \frac{[i]_f}{r_i}$$

386 Note that there is also an impact of feedstock dissolution on soil base cation concentrations beyond387 the pure loss of feedstock (Figure S4).

388

389 When this enrichment is not accounted for, the resulting dissolution fractions are overestimated. 390 Here we demonstrate this effect by comparing the erroneously high  $\tau_i^*$  as calculated from equation 391 1 based on pre-weathering base cation concentrations estimated by vertically projecting post-392 weathering [i] concentrations onto the mixing line between soil and feedstock endmembers 393 without accounting for enrichment of *i* (i.e., the horizontal component of the vector in Figure 1b). 394 The difference between the erroneous  $\tau_i^*$  and  $\tau_i$  as calculated from the endmember approach is 395 largest at intermediate  $\tau_i$  and low  $r_i$ , where it goes up to a  $\Delta$  value of 0.12 (Figure 3b). The relative 396 effect is the highest at low  $\tau_i$  and approaches 100% at low dissolution fractions and differences 397 between soil and feedstock immobile element concentrations.

398

399 In theory, one could use an immobile element that is strongly depleted in feedstock relative to soil 400 to calculate feedstock addition from the depletion of *i* in the mixed sample. However, in addition 401 to being undesirable from a signal-to-noise perspective, the utility of this approach is limited as 402 the vector caused by the enrichment of immobile elements through feedstock mass loss will align 403 with the mixing line, making it difficult to discern significant trends (Figure S5). Hence, the 404 framework discussed here in which addition of feedstock is quantified from changes in soil 405 immobile element content should only be applied when immobile concentrations in feedstock are 406 greater than those present in background soil.

407

408 In contrast to immobile element enrichment due to feedstock mass loss, calculated  $\tau_i$  may be 409 erroneously small because immobile elements used as a proxy for feedstock addition may not 410 always be truly immobile. While detrital trace element concentrations in rivers are significantly 411 depleted relative to their abundance in catchment lithologies (Gaillardet et al., 2014), mobilization 412 of "immobile" elements such as Ti and Zr has been observed in some extremely weathered and 413 cation depleted soils (e.g., Melfi et al., 1996; Cornu et al., 1999; Hodson, 2002). This phenomenon 414 would cause underestimation of the amount of initially added feedstock when immobile elements 415 are used as a proxy for feedstock addition, resulting in estimates of base cation loss and dissolution 416 fractions that would be biased low. While this is of less concern than potentially overestimating 417 weathering for the purpose of verifying CDR credits, it is in the interest of practitioners to test the 418 immobility of chosen proxy elements and potentially account for immobile element loss from 419 topsoils provided this can be achieved at adequate signal-to-noise levels.

- 420
- 421

## 422 3.2 Calculated dissolution fractions outside of the mixing triangle

423

424 The framework introduced here should only be applied when the post-weathering composition of 425 the feedstock-soil mixture falls within mass balance constraints-the mixing triangle defined by 426 the soil, feedstock, and hypothetical weathered feedstock residue endmembers (Figure 1d). For 427 this to be the case, the application amount and dissolution fraction need to be large enough and the 428 difference in soil and feedstock immobile element as well as base cation content needs to be 429 sufficiently large (Suhrhoff et al., 2024; Rogers & Maher, 2025) such that weathering of rock 430 powder results in a statistically significant signal within the endmember framework. If a significant 431 portion of the samples in the sample-resampling approach fall outside of the mass balance 432 constraints, it is most likely a sign that the sampling strategy was not optimized for capturing the 433 underlying spatial variation in soil chemistry and/or that soil and feedstock compositions were too 434 similar to one another (Suhrhoff et al., 2024). Given that soil sampling methods have been 435 discussed in detail in numerous places (Campbell et al., 2023; Sutherland et al., 2024; Rogers & 436 Maher, 2025), we will not belabor this point.

437

438 For the framework developed here to explain compositions outside of the endmember mixing 439 triangle, at least one of the endmember contributions to the post-weathering sample would need to 440 be negative. Because  $\tau_i$  is computed as the contribution of the weathered feedstock residue 441 endmember relative to the sum of the same endmember and the residual feedstock endmember 442 contributions (equation 9), if either of these contributions is negative the denominator of this 443 fraction can approach 0, which causes instability outside of the mixing triangle. This is 444 demonstrated in Figure 4, where  $\tau_i$  is shown as a function of [i] and [j] for two hypothetical soil 445 and feedstock compositions. As evident from Figure 4, outside of the mixing triangle  $\tau_i$  tends to 446 increase to unrealistically large absolute values. To the left of the soil endmember (indicating a 447 hypothetical negative amount of feedstock), reasonable but unphysical  $\tau_i$  can be achieved as a 448 result of noise. These observations suggest: (1) when applied to field settings, this framework 449 requires thorough statistical investigation to ensure that the post-weathering composition is 450 significantly different to pure soil and pre-weathering soil-feedstock mixtures. This requires, for 451 example, Monte Carlo-type statistical approaches in which the uncertainty introduced by all 452 parameters (including potential corrections for control site trends to baseline data) is fully 453 propagated into final estimates (see also Derry et al., 2025); (2) although individual samples may 454 fall outside of the mixing triangle as a result of soil heterogeneity even if there is a robust signal 455 overall, because mixing compositions outside the mixing plane are unstable,  $\tau_i$  should always be 456 computed based on sample population averages rather than from the average of  $\tau_i$  calculated for 457 individual samples.

- 458
- 459

### 460 3.3 Non-self averaging behavior

461 The framework presented here is non-self-averaging. This means that calculating  $\tau_j$  for each 462 individual sample and then taking the average does not give the same result as calculating  $\tau_j$  based 463 on the sample population average *i* and *j* concentrations. This phenomenon is particularly acute 464 when some samples fall outside of the mixing triangle.

465

466 We demonstrate this behavior with a simple simulation (Figure 5 & Table 2). We calculate the true 467 pre- and post-weathering soil-feedstock mixture compositions for two hypothetical deployments 468 (250 t ha<sup>-1</sup>,  $\tau_i$  of 0.5 and 50 t ha<sup>-1</sup>,  $\tau_i$  of 0.25) and endmember compositions (using the Python 469 functions SOMBA start and SOMBA end). For the calculated post-weathering composition, we 470 simulate a set of samples based on assumed soil heterogeneities (here implemented as normal 471 distributions with relative standard deviations of 25% and 10%, respectively) such that these two 472 sets correspond to exemplary low- and high-resolvability deployments. As demonstrated in Figure 473 5c, for the first deployment many samples fall outside of the mixing triangle. For both populations, 474  $\tau_i$  as calculated from the average of each individual sample  $\tau_i$  is not the same  $\tau_i$  calculated from the 475 population mean *i* and *j* concentrations (Table 2), with an extreme difference for the first low-476 resolvability scenario. This is important to consider in statistical modelling of post-deployment 477 data, where Monte Carlo approaches (incl. bootstrapping) should always first calculate population

478 means based on sample chemical compositions before calculating  $\tau_j$  for a specific average model

479 composition, rather than statistically resampling from distributions of sample  $\tau_j$ .

480

### 481 3.4 Signal-to-noise analysis

The framework presented here can only yield accurate estimates of rock powder dissolution in soils when weathering signals can be picked out against background soil heterogeneity (Reershemius & Suhrhoff, 2023; Suhrhoff et al., 2024; Derry et al., 2025; Rogers & Maher, 2025). Here, we assess signal-to-noise in the updated framework by estimating the average error on detected dissolution fractions practitioners would observe based on specific deployment choices and spatial sampling frequencies. This analysis is based on a novel in-field dataset of high spatial density (0.6 – 19.2 ha<sup>-1</sup>; Table 1), which are used to simulate in-field heterogeneity.

489

490 The average error on detected dissolution fractions decreases with increasing sampling frequency, 491 application amounts, and dissolution fractions (Figure 6), which is consistent with previous 492 investigations (Suhrhoff et al., 2024; Rogers & Maher, 2025). As a function of spatial sampling 493 density, average errors on detected dissolution fractions have similar shapes to exponential decay 494 curves where marginal gains in detection accuracy decrease as sampling frequency increases. 495 Based on conservative estimates of spatial heterogeneity (Figure 6a&b); the signal-to-noise 496 analysis suggests that when cumulative application amounts exceed 100 t ha<sup>-1</sup>, expected errors are 497 on average <15% when sampling frequencies exceed 10 samples ha<sup>-1</sup>. At higher dissolution 498 fractions ( $\tau_i = 0.5$ ), average errors below 10% are possible with high sample density. If paired-499 sampling is implemented effectively the average error decreases significantly (Figure 6c&d). 500 While the way that the reduction in variance is implemented here is somewhat arbitrary ( $\sigma/2$ ), we 501 would like to stress that both variance of baseline sampling as well as of reduction of variance due 502 to paired sampling can be constrained at a field level based on deployment data. Monte Carlo 503 simulations should then be tailored to specific field conditions to gauge the uncertainty of detected 504 values and applicability of soil mass balance approaches.

506 In the context of sampling densities, it should be noted that as long as the spatial distance between 507 sub-sample cores used to pool samples is larger than the spatial wavelength of soil heterogeneity, 508 these required high sample rates can also partially be achieved by pooling samples, as is commonly 509 practiced in most agronomic soil sampling protocols (Sawyer et al., 2016). Additionally, there are 510 well established methods for characterizing contaminants in soils and other particulate media 511 (Hewitt et al., 2007; Hadley et al., 2011; Clausen et al., 2013a, 2013b, 2013c; ITRC, 2020). A key 512 aspect of these methodologies, such as Incremental Sampling Methods (ISMs), is that they 513 acknowledge a-priori that contaminants, or in this case, crop amendments are distributed unevenly 514 at the scales of interest relevant to signal detection. When implemented properly, incremental 515 sample pooling and averaging strategies result in highly representative soil data at the field scale 516 (Hewitt et al., 2007; Hadley et al., 2011; Clausen et al., 2013a, 2013b, 2013c; ITRC, 2020), with 517 high numbers of pooled sub-samples of sufficient individual mass having a higher utility compared 518 to more measured samples reflecting less pooled cores, not least because the former tend to be 519 normally distributed due to the central limit theorem. We assert that if the mean and variance of a 520 field or fields can be well established, averaged mixing models such as SOMBA can be utilized 521 with confidence commensurate to the established population statistics.

522

523 This analysis is based on a subset of samples for which soil mass balance approaches are suitable 524 for MRV, here operationally defined as soil [i] and [j] being at least 5 times below US-average 525 basalt composition (Lehnert et al., 2000). Approximately ~22% of all agricultural soils contained 526 in the used geochemical soil database (Smith et al., 2013) fulfill this condition. This fraction 527 strongly increases when all soils with concentrations at least 2 times lower are considered (n = 594528 out of 614 samples; ~95%), primarily due to more samples fulfilling the Ti cutoff (Figure S6). 529 When the same signal-to-noise analysis is applied to this larger set of fields the average error on 530 detected mass transfer coefficients is larger (Figure S7). This is expected based on lower soilfeedstock compositional differences (Suhrhoff et al., 2024). Note also that the modeled 531 532 deployment size (10-100 ha) has a direct impact on the signal-to-noise analysis as the number of 533 generated samples is the product between field/deployment size and sampling frequency.

534

In addition to increasing application amounts and optimizing deployment parameters e.g., through
the choice of an above-average Ti containing basalt (Suhrhoff et al., 2024), improving sampling

protocols (Rogers & Maher, 2025) can all help to improve the robustness of soil mass balance approaches. An alternative way to increase both accuracy and precision could be to quantify dissolution fractions at the aggregate level over multiple deployments rather than for individual field sites, as has for example been demonstrated for the quantification of changes in soil organic carbon stocks (Bradford et al., 2023; Potash et al., 2025). Furthermore, the modelled average USbasalt composition may also not be optimal in terms of soil-feedstock differences.

543

544 Our signal-to-noise analysis also demonstrates that soil mass balance approaches can produce 545 robust estimates of rock powder dissolution fractions when sampling frequencies, application 546 amounts, dissolution fractions, and soil-feedstock compositional differences are sufficiently high. 547 Nevertheless, resolvability also depends on the practice decisions with respect to acceptable 548 uncertainty. While achieving an error of less than, e.g., 10% for 90% of the realizations (Rogers 549 & Maher, 2025) is challenging in most settings unless application rates are high, larger 550 uncertainties can still be acceptable in the context of crediting CDR if crediting is done at lower 551 bounds of uncertainty (Sutherland et al., 2024). In addition, it is important to keep in mind that this 552 approach requires an adequate difference in soil and feedstock composition; for a given feedstock 553 and immobile element some soils will be extremely unlikely to yield a significant signal. A signal-554 to-noise analysis for a given feedstock should hence only be based on the subset of soils that are 555 potential targets for robust signals for this MRV approach, rather than through approaches that 556 group all signals together regardless of soil fitness. Furthermore, it is important to note that what 557 is relevant for this framework is the total application *amount*, not the annual *rate*. Hence, settings 558 for which feedstock dissolution may not be resolvable initially can become resolvable over time 559 through the gradual increase of cumulative application amounts as well as increases in the 560 dissolution fraction over time.

561

### 562 3.5 Additional Assumptions and Limitations

563 One key assumption that is made in the signal-to-noise analysis is that baseline soil [i] and [j] does 564 not change with time, and that therefore as long as sampling and spatial heterogeneity is correctly 565 accounted for, a change in [i] and [j] can be solely attributed to feedstock addition and dissolution. 566 This assumption may not always hold in cases where weathering of a labile constituent of the soil, aeolian deposition, or other process might unexpectedly result in loss or gain of elements in the soil. Changes through time in soil [i] and [j] in controls that cannot be explained by sampling practice and spatial heterogeneity should be factored into estimates for feedstock weathering generated using SOMBAs; and results treated with caution where a mechanistic understanding of the elemental concentration change of the system cannot be found.

572

573 We have not included baseline trend corrections in the signal-to-noise analysis presented here due 574 to a lack of data on covariance for temporal trends in adjacent fields. Any simulation would hence 575 depend more on our assumptions than realistic processes. As has been demonstrated, e.g., for soil 576 organic carbon monitoring (Bradford et al., 2023), including such a correction would increase 577 average detection errors but not systematically change trends relating to different application 578 amounts and sampling protocols. Importantly, we suggest that for the purpose of crediting, cation 579 losses from control sites should be deducted from treatment site EW signals, but that control site 580 gains in base cations must not be used to increase weathering signals from treatment sites unless 581 the cation gain in control site composition can be explained by known manipulations that has also 582 occurred on treatment sites (e.g., fertilizer input etc.).

### 583 4 Conclusion

584 We have presented an updated framework for using soil mass balance approaches (SOMBA) to 585 quantify rock powder dissolution in EW field settings and provide a Python code base for 586 implementing this framework. The updated framework explicitly accounts for the enrichment of 587 immobile elements in topsoils due to feedstock mass loss (Brimhall & Dietrich, 1987; Anderson 588 et al., 2002). Failing to account for these processes can cause detected dissolution fractions to be 589 up to  $\sim 0.12$  too high. Depending on deployment parameters, this may be an error of up to 100% 590 for low dissolution fractions and relatively small compositional differences between feedstock and 591 soil.

592

593 We strongly suggest that the framework presented here should only be used when post-weathering 594 sample compositions fall robustly within the mass balance constraints defined by the baseline soil, 595 pure feedstock, as well as the composition the topsoil would have after a layer of pure feedstock 596 had dissolved. Solutions are unstable outside of this parameter space, which may yield dissolution 597 fractions that are unphysically high or low and should not be used to estimate CDR. When this 598 occurs albeit reasonable application amounts (Suhrhoff et al., 2024), it is most likely a sign that 599 sampling was not designed or optimized to capture the underlying spatial variability in soil 600 chemistry and/or that soil-feedstock compositional differences are too small. The code presented 601 here generates sensible dissolution fractions when the post-weathering composition falls within 602 the mass balance dictated mixing triangle. However, this does not necessarily mean that this signal 603 can be resolved statistically, particularly at low feedstock application amounts. It is the 604 responsibility of practitioners to thoroughly investigate the statistical significance of changes in 605 soil compositions and deduced rock dissolution parameters, for example through stochastic 606 simulations that propagate uncertainties pertaining to all relevant parameters (Derry et al., 2025), 607 including resulting from trends in control sites and through downsampling statistical tests. 608 Sampling protocols should generally be defined *a priori* informed by desired sampling power 609 (Chow et al., 2008). Lastly, we suggest that the framework should always be applied to calculate 610 dissolution fractions based on the sample population mean, rather than for each individual sample 611 because of the non-self-averaging character of this framework as well as instability outside of the 612 endmember mixing triangle, where individual samples may fall due to soil heterogeneity even if there is a clear signal for the overall distribution. This consideration will change the statistical modelling of weathering dynamics, e.g. via Monte Carlo simulations. Future studies should include incremental sampling strategies at predefined field and sub-field scales. In effect, averaging strategies should be fit-for-purpose and built in concert with the soil sampling procedures that researchers or EW suppliers design. We would also like to stress that alternative parametrizations of SOMBA are feasible and may be advantageous for certain settings such that the framework presented here should not be viewed as un-amendable.

620

621 Our signal-to-noise analysis suggests that field-level quantification of rock powder dissolution 622 based on soil mass balance is possible when application amounts, dissolution fractions, soil-623 feedstock compositional differences, and sampling frequencies are sufficient. This may for 624 example imply that signal emergence will only become resolvable after multiple years of repeated 625 deployments and after substantial feedstock weathering. Our analysis suggests that soil mass balance approaches can be a useful tool in tracking weathering rates, but it must be acknowledged 626 627 that this approach will not work in all settings and will typically require higher sampling densities 628 than those currently being implemented in commercial deployments. Signal emergence can 629 furthermore be optimized using tailored sampling strategies (Rogers & Maher, 2025) as well as 630 feedstock-soil-matching (Suhrhoff et al., 2024).

# 631 5 Acknowledgements

- TJS acknowledges funding by the Swiss National Science Foundation (Grant P500PN\_210790).
- 633 NP and CR acknowledge funding from the United States Department of Agriculture (USDA) and
- 634 the Grantham Foundation for the Environment. TS and NP acknowledge support from the Yale
- 635 Center for Natural Carbon Capture. SL and SZ acknowledge support from College of Arts &
- 636 Sciences Environment and Sustainability Initiative (ESI) at Texas A&M University.

# 638 6 Conflict of interest

- 639 JJ is funded through the public benefit corporation, Mati Carbon, a subsidiary of the not-for profit-
- 640 Swaniti Initiative.
- 641 The remaining authors declare that the research was conducted in the absence of any commercial
- 642 or financial relationships that could be construed as a potential conflict of interest.

#### 7 Bibliography 644

- 645 Almaraz, M., Bingham, N. L., Holzer, I. O., Geoghegan, E. K., Goertzen, H., Sohng, J., & 646 Houlton, B. Z. (2022). Methods for determining the CO2 removal capacity of enhanced 647 weathering in agronomic settings. Frontiers in Climate, 4.
- 648 https://doi.org/10.3389/fclim.2022.970429
- 649 Anderson, S. P., Dietrich, W. E., & Brimhall, G. H. (2002). Weathering profiles, mass-balance 650 analysis, and rates of solute loss: Linkages between weathering and erosion in a small, steep 651 catchment. Bulletin of the Geological Society of America, 114(9), 1143–1158. 652 https://doi.org/10.1130/0016-7606(2002)114<1143:WPMBAA>2.0.CO
- 653 Bahri, A., Berndtsson, R., & Jinno, K. (1993). Spatial Dependence of Geochemical Elements in a 654 Semiarid Agricultural Field: I. Scale Properties. Soil Science Society of America Journal,
- 655 57(5), 1316–1322. https://doi.org/10.2136/sssaj1993.03615995005700050026x 656 Baum, M., Liu, H., Schacht, L., Schneider, J., & Yap, M. (2024). Mass-Balance MRV for
- 657 Carbon Dioxide Removal by Enhanced Rock Weathering: Methods, Simulation, and 658 Inference. https://doi.org/10.48550/arXiv.2407.01949
- 659 Beerling, D. J., Epihov, D. Z., Kantola, I. B., Masters, M. D., Reershemius, T., Planavsky, N. J.,
- 660 Reinhard, C. T., Jordan, J. S., Thorne, S. J., Weber, J., Martin, M. V., Freckleton, R. P., 661 Hartley, S. E., James, R. H., Pearce, C. R., DeLucia, E. H., & Banwart, S. A. (2024). 662 Enhanced weathering in the US Corn Belt delivers carbon removal with agronomic benefits. 663 Proceedings of the National Academy of Sciences, 120, 2017.
- 664 https://doi.org/10.1073/pnas.2319436121
- 665 Beerling, D. J., Kantzas, E. P., Lomas, M. R., Wade, P., Eufrasio, R. M., Renforth, P., Sarkar, B., 666 Andrews, M. G., James, R. H., Pearce, C. R., Mercure, J., Pollitt, H., Holden, P. B., & 667 Edwards, N. R. (2020). Potential for large-scale CO2 removal via enhanced rock weathering 668 with croplands. Nature, 583(May 2018), 242-248. https://doi.org/10.1038/s41586-020-669 2448-9
- 670 Beerling, D. J., Leake, J. R., Long, S. P., Scholes, J. D., Ton, J., Nelson, P. N., Bird, M., Kantzas, 671 E., Taylor, L. L., Sarkar, B., Kelland, M., Delucia, E., Kantola, I., Müller, C., Rau, G. H., & 672 Hansen, J. (2018). Farming with crops and rocks to address global climate, food and soil 673 security. Nature Plants, 4(March). https://doi.org/10.1038/s41477-018-0108-y
- 674 Bertagni, M. B., Calabrese, S., Cipolla, G., Valerio Noto, L., & Porporato, A. M. (2024). 675 Advancing Enhanced Weathering Modeling in Soils: Systematic Comparison and 676 Validation with Experimental Data. Journal of Advances in Modeling Earth Systems, 1–25.
- 677 https://doi.org/10.1029/2024MS004224
- 678 Bradford, M. A., Eash, L., Polussa, A., Jevon, F. V., Kuebbing, S. E., Hammac, W. A., 679 Rosenzweig, S., & Oldfield, E. E. (2023). Testing the feasibility of quantifying change in
- 680 agricultural soil carbon stocks through empirical sampling. Geoderma, 440(July), 116719. 681 https://doi.org/10.1016/j.geoderma.2023.116719
- 682 Brantley, S. L., & Lebedeva, M. (2011). Learning to read the chemistry of regolith to understand 683 the critical zone. Annual Review of Earth and Planetary Sciences, 39, 387–416. 684 https://doi.org/10.1146/annurev-earth-040809-152321
- 685 Brimhall, G. H., Christopher J., L., Ford, C., Bratt, J., Taylor, G., & Warin, O. (1991).
- 686 Quantitative geochemical approach to pedogenesis: importance of parent material reduction, 687 volumetric expansion, and eolian influx in lateritization. Geoderma, 51(1-4), 51-91.
- 688 https://doi.org/10.1016/0016-7061(91)90066-3

- Brimhall, G. H., & Dietrich, W. E. (1987). Constitutive mass balance relations between chemical composition, volume, density, porosity, and strain in metasomatic hydrochemical systems:
  Results on weathering and pedogenesis. *Geochemica et Cosmochemica Acta*, 51(4).
  https://doi.org/10.1016/0016-7037(87)90070-6
- 693 Campbell, J., Bastianini, L., Buckman, J., Bullock, L., Foteinis, S., Furey, V., Hamilton, J.,
- Harrington, K., Hawrot, O., Holdship, P., Knapp, W., Maesano, C., Mayes, W., Pogge von
- 695 Strandmann, P., Reershemius, T., Rosair, G., Sturgeon, F., Turvey, C., Wilson, S., &
- 696 Renforth, P. (2023). *Measurements in Geochemical Carbon Dioxide Removal* (1st ed.).
- 697 Heriot-Watt University. https://doi.org/10.17861/2GE7-RE08
- 698 CDR.fyi. (2025). Keep Calm and Remove On The CDR fyi 2024 Year in Review.
- Chadwick, O. A., Brimhall, G. H., & Hendricks, D. M. (1990). From a black to a gray box a
  mass balance interpretation of pedogenesis. *Geomorphology*, 3(3–4), 369–390.
  https://doi.org/10.1016/0169-555X(90)90012-F
- Chadwick, O. A., Derry, L. A., Vitousek, P. M., Huebert, B. J., & Hedin, L. O. (1999). Changing
  sources of nutrients during four million years of ecosystem development. *Nature*,
  397(6719), 491–497. https://doi.org/10.1038/17276
- Chow, S. C., Cheng, B., & Cosmatos, D. (2008). On power and sample size calculation for QT
  studies with recording replicates at given time point. *Journal of Biopharmaceutical Statistics*, *18*(3), 483–493. https://doi.org/10.1080/10543400801995452
- Clarkson, M. O., Larkin, C. S., Swoboda, P., Reershemius, T., Suhrhoff, T. J., Maesano, C. N., &
  Campbell, J. S. (2024). A Review of Measurement for Quantification of Carbon Dioxide
  Removal by Enhanced Weathering in Soil. *Frontiers in Climate*, 6(June), 1–20.
  https://doi.org/10.3389/fclim.2024.1345224
- Clausen, J., Gerogian, T., & Bednar, A. (2013a). *Incremental Sampling Methodology (ISM) for Metallic Residues* (Issue August 2013).
- Clausen, J. L., Georgian, T., & Bednar, A. (2013b). Cost and Performance Report of Incremental
   Sampling Methodology for Soil Containing Metallic Residues Engineer Research and
   Development Center (Issue September).
- Clausen, J. L., Georgnian, T., Bednar, A., Perron, N., Bray, A., Tuminello, P., Gooch, G.,
  Mulherin, N., Gelvin, A., Beede, M., Saari, S., Jones, W., & Tazik, S. (2013c).
  Demonstration of Incremental Sampling Methodology for Soil Containing Metallic
  Residues. In *Microchemical Journal* (Issue September).
- Cornu, S., Lucas, Y., Lebon, E., Ambrosi, J. P., Luizão, F., Rouiller, J., Bonnay, M., & Neal, C.
  (1999). Evidence of titanium mobility in soil profiles, Manaus, central Amazonia.
- 723 *Geoderma*, 91(3–4), 281–295. https://doi.org/10.1016/S0016-7061(99)00007-5
- Derry, L. A., Chadwick, O. A., & Porder, S. (2025). Estimation of Carbon Dioxide Removal via
   Enhanced Weathering. *Global Change Biology*, *31*, 1–3. https://doi.org/10.1111/gcb.70067
- Dietzen, C., & Rosing, M. T. (2023). Quantification of CO2 uptake by enhanced weathering of
   silicate minerals applied to acidic soils. *International Journal of Greenhouse Gas Control*,
   *125*(March), 103872. https://doi.org/10.1016/j.ijggc.2023.103872
- Fisher, B. A., Rendahl, A. K., Aufdenkampe, A. K., & Yoo, K. (2017). Quantifying weathering
  on variable rocks, an extension of geochemical mass balance: Critical zone and landscape
- evolution. *Earth Surface Processes and Landforms*, 42(14), 2457–2468.
- 732 https://doi.org/10.1002/esp.4212

Gaillardet, J., Viers, J., & Dupré, B. (2014). Trace Elements in River Waters. In H. D. Holland &
K. K. Turekian (Eds.), *Treatise on Geochemistry: Second Edition* (Vol. 7, pp. 195–235).
https://doi.org/10.1016/B978-0-08-095975-7.00507-6
Geden O. Gidden M. I. Lamb W. F. Miny, J. C. Nemet G. F. & Smith S. M. (2024). *The*

Geden, O., Gidden, M. J., Lamb, W. F., Minx, J. C., Nemet, G. F., & Smith, S. M. (2024). *The State of Carbon Dioxide Removal.*

- Gunnarsen, K. C., Jensen, L. S., Rosing, M. T., & Dietzen, C. (2023). Greenlandic glacial rock
   flour improves crop yield in organic agricultural production. *Nutrient Cycling in Agroecosystems*, *126*(1), 51–66. https://doi.org/10.1007/s10705-023-10274-0
- Hadley, P. W., Crapps, E., & Hewitt, A. D. (2011). Time for a Change of Scene. *Environmental Forensics*, 12(4), 312–318. https://doi.org/10.1080/15275922.2011.622344
- Haque, F., Santos, R. M., & Chiang, Y. W. (2020). Optimizing Inorganic Carbon Sequestration
  and Crop Yield With Wollastonite Soil Amendment in a Microplot Study. *Frontiers in Plant Science*, 11(July), 1–12. https://doi.org/10.3389/fpls.2020.01012
- Hartmann, J., & Kempe, S. (2008). What is the maximum potential for CO2 sequestration by
  "stimulated" weathering on the global scale? *Naturwissenschaften*, 95(12), 1159–1164.
  https://doi.org/10.1007/s00114-008-0434-4
- Hartmann, J., West, A. J., Renforth, P., Köhler, P., De La Rocha, C. L., Wolf-Gladrow, D. A.,
  Dürr, H. H., & Scheffran, J. (2013). Enhanced chemical weathering as a geoengineering
  strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean
  acidification. *Reviews of Geophysics*, *51*(2), 113–149. https://doi.org/10.1002/rog.20004
- Hewitt, A. D., Jenkins, T. F., Walsh, M. E., Walsh, M. R., Bigl, S. R., & Ramsey, C. A. (2007).
   *Protocols for Collection of Surface Soil Samples at Military Training and Testing Ranges for the Characterization of Energetic Munitions Constituents* (Issue July).
- Hodson, M. E. (2002). Experimental evidence for mobility of Zr and other trace elements in
  soils. *Geochimica et Cosmochimica Acta*, 66(5), 819–828. https://doi.org/10.1016/S00167037(01)00803-1
- 759 IPCC. (2018). Global warming of 1.5°C. An IPCC Special Report on the impacts of global
  760 warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission
  761 pathways, in the context of strengthening the global response to the threat of climate
  762 change, *Ipcc Sr15*, 2(October), 17–20. https://www.ipcc.ch/sr15/
- 763 ITRC. (2020). Incremental Sampling Methodology (ISM) Update The Interstate Technology &
   764 Regulatory Council (ITRC) (Issue October).
- Jackson, R. B., & Caldwell, M. M. (1993). Geostatistical Patterns of Soil Heterogeneity Around
   Individual Perennial Plants. *The Journal of Ecology*, *81*(4), 683.
   https://doi.org/10.2307/2261666
- Kantola, I. B., Blanc-Betes, E., Master, M. D., Chang, E., Marklein, A., Moore, C. E., von
  Haden, A., Bernacchi, C. J., Wolf, A., Epihov, D. Z., Beerling, D. J., & Delucia, E. H.
  (2023). Improved net carbon budgets in the US Midwest through direct measured impacts
  of enhanced weathering. *Global Change Biology*, *May*, 1–17.
- 772 https://doi.org/10.1111/gcb.16903
- Kanzaki, Y., Chiaravalloti, I., Zhang, S., Planavsky, N. J., & Reinhard, C. T. (2024a). In silico
  calculation of soil pH by SCEPTER v1.0. *Geoscientific Model Development*, 17(10), 4515–
  4532. https://doi.org/10.5194/gmd-17-4515-2024
- Kanzaki, Y., Planavsky, N. J., & Reinhard, C. T. (2023). New estimates of the storage
  permanence and ocean co-benefits of enhanced rock weathering. *PNAS Nexus*, 2(4), 1–9.
  https://doi.org/10.1093/pnasnexus/pgad059

- Kanzaki, Y., Planavsky, N., Zhang, S., Jordan, J., & Christopher, T. (2024b). Soil cation storage
   as a key control on the timescales of carbon dioxide removal through enhanced weathering.
   *ESS Open Archive*. https://doi.org/10.22541/essoar.170960101.14306457/v1
- Kanzaki, Y., Zhang, S., Planavsky, N. J., & Reinhard, C. T. (2022). Soil Cycles of Elements
  simulator for Predicting TERrestrial regulation of greenhouse gases: SCEPTER v0.9. *Geoscientific Model Development*, 15(12), 4959–4990. https://doi.org/10.5194/gmd-154959-2022
- Kelland, M. E., Wade, P. W., Lewis, A. L., Taylor, L. L., Sarkar, B., Andrews, M. G., Lomas,
  M. R., Cotton, T. E. A., Kemp, S. J., James, R. H., Pearce, C. R., Hartley, S. E., Hodson, M.
  E., Leake, J. R., Banwart, S. A., & Beerling, D. J. (2020). Increased yield and CO2
  sequestration potential with the C4 cereal Sorghum bicolor cultivated in basaltic rock dustamended agricultural soil. *Global Change Biology*, *26*(6), 3658–3676.
- 791 https://doi.org/10.1111/gcb.15089
- Köhler, P., Hartmann, J., & Wolf-Gladrow, D. A. (2010). Geoengineering potential of artificially
  enhanced silicate weathering of olivine. *Proceedings of the National Academy of Sciences*of the United States of America, 107(47), 20228–20233.
- 795 https://doi.org/10.1073/pnas.1000545107
- Kurtz, A. C., Derry, L. A., Chadwick, O. A., & Alfano, M. J. (2000). Refractory element
   mobility in volcanic soils. *Geology*, 28(8), 683–686. https://doi.org/10.1130/0091 7613(2000)028<0683:REMIVS>2.3.CO;2
- Lehnert, K., Su, Y., Langmuir, C. H., Sarbas, B., & Nohl, U. (2000). A global geochemical
  database structure for rocks. *Geochemistry, Geophysics, Geosystems*, 1(5).
  https://doi.org/10.1029/1999gc000026
- Lipp, A. G., Shorttle, O., Sperling, E. A., Brocks, J. J., Cole, D. B., Crockford, P. W., Del
  Mouro, L., Dewing, K., Dornbos, S. Q., Emmings, J. F., Farrell, U. C., Jarrett, A., Johnson,
  B. W., Kabanov, P., Keller, C. B., Kunzmann, M., Miller, A. J., Mills, N. T., O'Connell, B.,
  ... Yang, J. (2021). The composition and weathering of the continents over geologic time.
- *Geochemical Perspectives Letters*, *17*, 21–26. https://doi.org/10.7185/geochemlet.2109
- McGrath, D., Zhang, C., & Carton, O. T. (2004). Geostatistical analyses and hazard assessment
  on soil lead in Silvermines area, Ireland. *Environmental Pollution*, 127(2), 239–248.
  https://doi.org/10.1016/j.envpol.2003.07.002
- Melfi, A. J., Subies, F., Nahon, D., & Formoso, M. L. L. (1996). Zirconium mobility in bauxites
  of southern Brazil. *Journal of South American Earth Sciences*, 9(3–4), 161–170.
  https://doi.org/10.1016/0895-9811(96)00003-x
- Oldfield, B. E. E., Eagle, A. J., Rubin, R. L., Rudek, J., & Gordon, D. R. (2022). Crediting
  agricultural soil carbon sequestration; Regional consistency is necessary for carbon credit
  integrity. *Science*, 375(6586), 1222–1225.
- Parton, W. J., Hartman, M., Ojima, D., & Schimel, D. (1998). *Daycent description and testing*.
  35–48.
- Potapov, P., Turubanova, S., Hansen, M. C., Tyukavina, A., Zalles, V., Khan, A., Song, X. P.,
  Pickens, A., Shen, Q., & Cortez, J. (2022). Global maps of cropland extent and change
  show accelerated cropland expansion in the twenty-first century. *Nature Food*, 3(1), 19–28.
  https://doi.org/10.1038/s43016-021-00429-z
- Potash, E., Bradford, M. A., Oldfield, E. E., & Guan, K. (2025). Measure-and-remeasure as an
- 823 economically feasible approach to crediting soil organic carbon at scale. *Environmental* 824 *Research Letters*, 20(2). https://doi.org/10.1088/1748-9326/ada16c

- 825 Ramsey, M. H., Solomon-Wisdom, G., & Argyraki, A. (2013). Evaluation of in situ
- heterogeneity of elements in solids: Implications for analytical geochemistry. *Geostandards and Geoanalytical Research*, 37(4), 379–391. https://doi.org/10.1111/j.1751908X.2013.00236.x
- Reershemius, T., Kelland, M. E., Davis, I. R., D'Ascanio, R., Kalderon-Asael, B., Asael, D.,
- 830 Suhrhoff, T. J., Epihov, D. E., Beerling, D. J., Reinhard, C. T., & Planavsky, N. J. (2023).
- Initial Validation of a Soil-Based Mass-Balance Approach for Empirical Monitoring of
   Enhanced Rock Weathering Rates. *Environmental Science & Technology*, 57(48), 19497–
- Enhanced Rock Weathering Rates. *Environmental Science & Technology*, 57(48), 19497–
  19507. https://doi.org/10.1021/acs.est.3c03609
- Reershemius, T., & Suhrhoff, T. J. (2023). On error, uncertainty, and assumptions in calculating
   carbon dioxide removal rates by enhanced rock weathering in Kantola et al., 2023. *Global Change Biology, October*, 1–3. https://doi.org/10.1111/gcb.17025
- Renforth, P., & Henderson, G. (2017). Assessing ocean alkalinity for carbon sequestration.
   *Reviews of Geophysics*, 55(3), 636–674. https://doi.org/10.1002/2016RG000533
- Riebe, C. S., Kirchner, J. W., & Finkel, R. C. (2003). Long-term rates of chemical weathering
  and physical erosion from cosmogenic nuclides and geochemical mass balance. *Geochimica et Cosmochimica Acta*, 67(22), 4411–4427. https://doi.org/10.1016/S0016-7037(03)00382X
- Rogers, B., & Maher, K. (2025). A Framework for Integrating Spatial Uncertainty into Critical
  Zone Models : Application to Enhanced Weathering. *CDRXIV*.
  https://doi.org/10.70212/cdrxiv.2025334.v1
- Sawyer, J., Mallarino, A., & Killorn, R. (2016). *Take a Good Soil Sample to Help Make Good Fertilization Decisions* (Issue December).
- Schuiling, R. D., & Krijgsman, P. (2006). Enhanced Weathering: An Effective and Cheap Tool
  to Sequester CO2. *Climatic Change*, 74(1–3), 349–354. https://doi.org/10.1007/s10584005-3485-y
- 851 Seifritz, W. (1990). CO2 disposal by means of silicates. *Nature*, *345*(June), 486.
- Sheldon, N. D., & Tabor, N. J. (2009). Quantitative paleoenvironmental and paleoclimatic
  reconstruction using paleosols. *Earth-Science Reviews*, 95(1–2), 1–52.
  https://doi.org/10.1016/j.earscirev.2009.03.004
- Smith, D. B., Cannon, W. F., Woodruff, L. G., Solano, F., Kilburn, J. E., & Fey, D. L. (2013).
  Geochemical and mineralogical data for soils of the conterminous United States. U.S.
- 857 Geological Survey Data Series, 801(April), 1–26. https://doi.org/10.3133/ds801
- Smith, S. M., Geden, O., Affairs, S., Minx, J. C., & Change, C. (2023). *The State of Carbon Dioxide Removal.*
- Spijker, J., Vriend, S. P., & Van Gaans, P. F. M. (2005). Natural and anthropogenic patterns of
  covariance and spatial variability of minor and trace elements in agricultural topsoil. *Geoderma*, 127(1–2), 24–35. https://doi.org/10.1016/j.geoderma.2004.11.002
- Strefler, J., Bauer, N., Humpenöder, F., Klein, D., Popp, A., & Kriegler, E. (2021). Carbon
  dioxide removal technologies are not born equal. *Environmental Research Letters*, 16(7).
  https://doi.org/10.1088/1748-9326/ac0a11
- Suhrhoff, T. J., Reershemius, T., Wang, J., Jordan, J. S., Reinhard, C. T., & Planavsky, N. J.
- 867 (2024). A tool for assessing the sensitivity of soil-based approaches for quantifying
- 868 enhanced weathering: a US case study. *Frontiers in Climate*, 6(1346117), 1–17.
   869 https://doi.org/10.3389/fclim.2024.1346117

870	Sutherland, K., Holme, E., Savage, R., Gill, S., Matlin-Wainer, M., He, J., Marsland, E., & Patel,
871	C. (2024). Isometric Enhanced Weathering in Agriculture v1.0. Isometric.
872	https://registry.isometric.com/protocol/enhanced-weathering-agriculture
873	Tabor, N. J., Montanez, I. P., Zierenberg, R., & Currie, B. S. (2004). Mineralogical and
874	geochemical evolution of a basalt-hosted fossil soil (Late Triassic, Ischigualasto Formation,
875	northwest Argentina): Potential for paleoenvironmental reconstruction. Bulletin of the
876	Geological Society of America, 116(9–10), 1280–1293. https://doi.org/10.1130/B25222.1
877	Taylor, L. L., Beerling, D. J., Quegan, S., & Banwart, S. A. (2017). Simulating carbon capture
878	by enhanced weathering with croplands: An overview of key processes highlighting areas of
879	future model development. Biology Letters, 13(4). https://doi.org/10.1098/rsbl.2016.0868
880	te Pas, E. E. E. M., Chang, E., Marklein, A. R., Comans, R. N. J., & Hagens, M. (2025).
881	Accounting for retarded weathering products in comparing methods for quantifying carbon
882	dioxide removal in a short-term enhanced weathering study. Frontiers in Climate,
883	1524998(February), 1-10. https://doi.org/10.3389/fclim.2024.1524998
884	ten Berge, H. F. M., van der Meer, H. G., Steenhuizen, J. W., Goedhart, P. W., Knops, P., &
885	Verhagen, J. (2012). Olivine weathering in soil, and its effects on growth and nutrient
886	uptake in ryegrass (Lolium perenne L.): A pot experiment. PLOS ONE, 7(8), 1-8.
887	https://doi.org/10.1371/journal.pone.0042098
888	UNEP. (2024). Emissions Gap Report 2024: No more hot air please! With a massive gap
889	between rhetoric and reality, countries draft new climate commitments. United Nations
890	Environment Program, Nairobi, Kenya. https://doi.org/10.59117/20.500.11822/46404 This
891	USDA. (2022). Farms and Land in Farms 2021 Summary. United States Department of
892	Agriculture: National Agricultural Statistics Service, February, 1995–2004.
893	https://www.nass.usda.gov/Publications/Todays_Reports/reports/fnlo0222.pdf
894	USDA. (2024). Farms and Farmland. In 2022 Census of Agriculture Highlights (Issue March).
895	U.S. Department of Agriculture, National Agricultural Statistics Service.
896	Webster, R., & Lark, R. M. (2019). Analysis of variance in soil research: Examining the
897	assumptions. <i>European Journal of Soil Science</i> , 70(5), 990–1000.
898	https://doi.org/10.1111/ejss.12804
899	White, A. F., Bullen, T. D., Schulz, M. S., Blum, A. E., Huntington, T. G., & Peters, N. E.
900	(2001). Differential rates of feldspar weathering in granitic regoliths. Geochimica et
901	Cosmochimica Acta, 65(6), 847-869. https://doi.org/10.1016/S0016-7037(00)00577-9
902	Zhang, C., Selinus, O., & Schedin, J. (1998). Statistical analyses for heavy metal contents in till
903	and root samples in an area of southeastern Sweden. Science of the Total Environment,
904	212(2-3), 217-232. https://doi.org/10.1016/S0048-9697(97)00341-0
905	Zhang, S., Reinhard, C. T., Liu, S., Kanzaki, Y., & Noah, J. (2024). Constraining carbon loss
906	from rivers following terrestrial enhanced rock weathering. ESS Open Archive.
907	https://doi.org/10.22541/essoar.171052489.97497425/v1
908	

910 8 Figures



911

912 913 914 915 916 917 Figure 1: Sketch of the soil-based mass balance framework to quantify rock powder dissolution in soils. After rock powder of an elevated base cation and immobile element concentration compared to baseline soils is added to a field, the composition of the initial soil-feedstock mix falls on the mixing line between both endmembers (a). As feedstock dissolves base cations are released and either stored on the soil exchange complex or flushed out of topsoils. At the same time immobile element concentrations increase as a result of feedstock mass and volume loss, resulting in a vector starting at the pre-weathering soil-feedstock mix composition towards the bottom right (b). This is important to take into account, because simply projecting the post-weathering 918 919 soil-feedstock mix composition from its immobile element concentration up to the mixing line between soil and feedstock endmembers will cause inflated estimates of cation mass loss and deduced dissolution fractions (c). One way to estimate the 920 dissolution fraction while taking into account the impact of feedstock mass loss is to use a three endmember mixing model where 921 the post-weathering composition is described as a mix of the baseline soil, pure feedstock, and a hypothetical weathered feedstock <u>9</u>22 residue endmember (d). Note that the offset in immobile element concentrations (i.e., enrichment of immobile element 923 concentrations due to mass loss) for the post-weathering soil-feedstock mix sample is exaggerated in panels b-d for the purpose of 924 visualization. In a realistic system the horizontal component of this vector would be smaller compared to the vector between basalt 925 as well as soil + weathered basalt residue (proportionally to the position of the pre-weathering soil-feedstock mix composition on 926 the missing line).



Figure 2: Sites of the data utilized to constrain soil composition as well as in-field spatial heterogeneity (Table 1).

9**3**0 <sup>*a*</sup> Novel soil heterogeneity dataset reported here. <sup>*b*</sup> (Smith et al., 2013)

931 932 <sup>c</sup> (Potapov et al., 2022)

#### a) Immobile element enrichment due to feedstock mass loss





b)  $\Delta \tau_i$  (absolute) as a result of immobile element enrichment

c)  $\Delta \tau_i$  (relative) as a result of immobile element enrichment





Figure 3: The dissolution of added rock powder increases the immobile element concentration of topsoils of constant volume as the lost rock powder is replaced by soil from the bottom of the soil column (a). The difference between erroneously high  $\tau_j^*$  when not taking this process into account and the actual  $\tau_j$  is shown in b for absolute values  $(\tau_j^* - \tau_j)$  and in c relative to the respective  $\tau_j$ .  $((\tau_j^* - \tau_j) / \tau_j)$ .



941 Figure 4: Quantified feedstock dissolution fractions  $(\tau_j)$  for a hypothetical soil and rock powder for a range of immobile element 942 (i) and base cation (j) concentrations. The framework developed here should only be applied within the mixing triangle set out by 943 baseline soil, rock powder, and the hypothetical weathered feedstock residue endmember. Outside of this domain, the results of the

framework are unstable, and absolute values can approach infinity because negative contributions of endmembers can cause the

945 dominator of equation 9 to approach 0. Generally, the framework developed here should only be applied when post-weathering

946 soil-feedstock mix composition robustly falls within the mixing triangle.

947



948

Figure 5: Two exemplary EW deployments of 50 t ha<sup>-1</sup>,  $\tau_j$  of 0.25 and relative ISD on sampled soil compositions of 25% (a and c) and 250 t ha<sup>-1</sup>,  $\tau_j$  of 0.5 and ISD on soil samples of 10% (b and d), representative for a low- and high- resolvability scenarios. Panels c and d show the compositions of 10 random samples generated for the post-weathering soil-feedstock mixture (exact composition and associated sample  $\tau_j$  values listed in Table 2).



954 955 956 957 Figure 6: Average errors on detected dissolution fractions for two simulated mass transfer coefficients ( $\tau_i = 0.25$  in a and c,  $\tau_i = 0.25$ ) 0.5 in b and d). The top row shows simulations where the variance imposed onto paired samples is equivalent to the variance of initial baseline samples. Because is likely an overestimate for accurate sample and resample strategies, the lower row shows the 958 959 same simulations based on reduced variance for resampled sample composition ( $\sigma/2$ ). The simulations are based on compositions of US soil (Smith et al., 2013) and basalt (Lehnert et al., 2000) considering soils with base cation and Ti concentrations at least 5 960 times lower than basalt. The simulated in-field soil heterogeneity is based on the novel field trial dataset presented in Table 1.

# 962 9 Tables

								soil hetero	geneity (o	<del>,</del> ; log-no	rmal)
Site name	Lat	Lon	size	# samples	# pooled cores	sample density	core density	Ca	Mg	Na	Ti
_	[°]	[°]	[ha]			[ha <sup>-1</sup> ]	[ha <sup>-1</sup> ]	[]	[]	[]	[]
Elmbrook	45.25194	-87.59694	6.42	40	2	6.23	12.46	0.493	0.278	0.072	0.120
Hawthorne	42.26161	-73.60088	5.08	41	2	8.07	16.14	0.395	0.309	0.250	0.288
Longleaf Ridge	31.26212	-84.37106	2.02	40	2	19.80	39.60	0.582	0.218	0.630	0.264
Bisette - Tower	35.75976	-78.16533	42.44	25	12	0.59	7.07	0.519	0.523	0.510	0.154
Bisette - Ike Lewis	35.75701	-78.18675	26.85	38	12	1.42	16.98	0.355	0.687	0.391	0.177

Table 2: Realized sample compositions and their calculated $\tau_j$ as well as population average sample composition and its $\tau_j$ for two hypothetical EW deployments (50 t ha <sup>-1</sup> , $\tau_j = 0.25$ , SD of randomly generated soil compositions = 25% as well as 250 t ha <sup>-1</sup> , $\tau_j = 0.5$ , ISD = 10%).

exam 50 t ha <sup>-1</sup>	ple deployment 1 , $\tau_j = 0.25$ , SD = 0.25	5	exam 250 t ha	ple deployment 2 $\tau^{-1}, \tau_{j} = 0.5, SD = 0.1$	
i [mol kg <sup>-1</sup> ]	j [mol kg <sup>-1</sup> ]	τ <sub>j</sub> []	i [mol kg <sup>-1</sup> ]	j [mol kg <sup>-1</sup> ]	τ <sub>j</sub> []
I. random samples (post-	deployment composi	tion)			
0.033	0.569	1.300	0.089	0.707	0.652
0.054	0.777	-1.525	0.082	0.808	0.400
0.053	0.389	8.379	0.093	0.698	0.694
0.076	0.522	0.940	0.085	0.764	0.515
0.078	0.365	1.374	0.096	0.924	0.413
0.035	0.723	2.392	0.096	0.893	0.452
0.061	0.564	0.631	0.072	0.846	0.078
0.051	0.455	6.083	0.079	0.880	0.217
0.063	0.641	0.313	0.096	0.751	0.635
0.066	0.623	0.506	0.093	0.817	0.519
random sample average	$ au_j$	2.039			0.457
II. sample average [i], [j], and related $\tau_j$					
0.057	0.563	0.433	0.088	0.809	0.481
III. calculated true comp	osition				
0.057	0.591	0.25	0.089	0.802	0.5

972	Supplementary information to
973	
974	Updated framework and signal-to-noise analysis of soil mass balance
975	approaches for quantifying enhanced weathering on managed lands
976	
977	Tim Jesper Suhrhoff <sup>1,2</sup> *, Tom Reershemius <sup>3, 2</sup> , Jacob Jordan <sup>4</sup> , Shihan Li <sup>5</sup> , Shuang Zhang <sup>5</sup> , Ella
978	Milliken <sup>2</sup> , Boriana Kalderon-Asael <sup>2</sup> , Christopher T. Reinhard <sup>6</sup> , Noah J. Planavsky <sup>2,1</sup>
979	
980	<sup>1</sup> Yale Center for Natural Carbon Capture, Yale University, New Haven, CT 06511, USA
981	<sup>2</sup> Department of Earth and Planetary Sciences, Yale University, New Haven, CT 06511, USA
982	<sup>3</sup> School of Natural and Environmental Sciences, Newcastle University, Newcastle upon Tyne,
983	England NE1 7RU, United Kingdom
984	<sup>4</sup> Mati Carbon, Houston, TX, USA
985	<sup>5</sup> Department of Oceanography, Texas A&M University, College Station, TX 77843, USA
986	<sup>6</sup> School of Earth & Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA 30332,
987	USA
988	
989	* corresponding author: timjesper.suhrhoff@yale.edu
990	
991	Python code and Excel templates for the soil mass balance framework can be found here:
992	
993	
994	Content of this file:
995	S1: Additional derivations of the soil mass balance framework (incl. Figure S1)
996	S2: Soil data (incl. Figure S2 & Figure S3)
997	S3: Impact of feedstock mass loss on base cation and immobile element concentrations (incl.
998	Figure S4 & Figure S5)
999	S4: Impact of soil composition on signal-to-noise analysis (incl. Figure S6 & Figure S7)

1000	S1 Additional derivations of the soil mass balance framework
1001	
1002	This supplement contains all derivations relating to section 2.1 of the manuscript. In addition to
1003	quantifying rock powder dissolution and deployment parameters based on post-weathering soil
1004	sample composition (see section 2.1 of the main text), we also present a framework to calculate
1005	expected pre- and post-weathering compositions for soil-feedstock mixtures. The associated
1006	Python functions are included in the Python file SOMBA.py and were used in the analyses
1007	presented here. The code can be assessed here:
1008	https://doi.org/10.5281/zenodo.15696933
1009	
1010	S1.1 Derivation of soil mass balance framework
1011	
1012	We continue from section 2.1 after the introduction of the hypothetical weathered feedstock
1013	endmember. The composition of this hypothetical endmember is defined to be the composition
1014	that a layer of soil would have after a layer of pure feedstock (corresponding to the soil sampling
1015	depth, d <sub>sample</sub> ) has dissolved.
1016	
1017	Since cations are assumed to be lost from the system, it has the same cation content as an equivalent
1018	layer of pure soil, i.e.:
1019	
1020	$[j]_{wf} = [j]_s $
1021	
1022	where the subscripts $wf$ and $s$ correspond to weathered feedstock residue and baseline soil (and $f$
1023	denotes pure feedstock in the following equations). The immobile element concentration of this
1024	endmember is given by summing the amount of immobile elements in the fully weathered
1025	feedstock as well as the soil that has replaced the feedstock in the reference volume, and dividing
1026	by the system mass after weathering (assumed to be the same as background soil mass/density for
1027	the equivalent soil volume):
1028	
1029	$[i]_{wf} = \frac{\rho_s v_{sampled  layer}  [i]_s + \rho_f v_{sampled  layer} [i]_f}{\rho_s v_{sampled  layer}} = \frac{\rho_s [i]_s + \rho_f [i]_f}{\rho_s} = [i]_s + \frac{\rho_f}{\rho_s} [i]_f \qquad S2$

1031 where  $v_{sampled \ layer}$  corresponds to the sampled soil volume and  $\rho$  to the density of feedstock and 1032 soil. We make the assumption that post-weathering density is equivalent to background soil density 1033 (see also eq. S6b) within the frame of reference assuming no change in porosity, though we note 1034 that this ignores weathering congruency and compositional difference between the soil parent 1035 material and the rock feedstock applied.

1036

1037 Assuming mass and volume conservation, this endmember mixing approach can be described by 1038 a system of equations such that each endmember contributes a volume proportion (X) to the 1039 observed post-weathering composition, which together sum to unity:

1040

1041 
$$X_s + X_f + X_{wf} = 1$$
 S3

1042

Because in practical field sampling based on constant soil sampling depths, a system of constant *volume* is sampled, these endmember contributions reflect *volume* contributions to the sampled soil volume defined by the sampling depth over a given area (all calculations and code shared here use 1 hectare (ha) by default). The endmember contributions reflect three unknowns. Hence, we set up two additional equations reflecting mass conservation of immobile elements as well as mobile base cations respectively.

1049

1050 
$$[j]_{s}X_{s}\rho_{s} + [j]_{f}X_{f}\rho_{f} + [j]_{wf}X_{wf}\rho_{wf} = [j]_{mix,t=n}(X_{s}\rho_{s} + X_{f}\rho_{f} + X_{wf}\rho_{wf})$$
S4

1051 
$$[i]_{s}X_{s}\rho_{s} + [i]_{f}X_{f}\rho_{f} + [i]_{wf}X_{wf}\rho_{wf} = [i]_{mix,t=n}(X_{s}\rho_{s} + X_{f}\rho_{f} + X_{wf}\rho_{wf})$$
S5

- 1052
- 1053 Assuming that:
- 1054

1055 
$$[j]_{wf} = [j]_s$$
, and S6a

- 1056  $\rho_{wf} = \rho_s$
- 1057
- 1058 gives:
- 1059

1060 
$$[j]_{s}X_{s}\rho_{s} + [j]_{f}X_{f}\rho_{f} + [j]_{s}X_{wf}\rho_{s} = [j]_{mix,t=n}(X_{s}\rho_{s} + X_{f}\rho_{f} + X_{wf}\rho_{s})$$
S7

S6b

1061 
$$[i]_{s}X_{s}\rho_{s} + [i]_{f}X_{f}\rho_{f} + [i]_{wf}X_{wf}\rho_{s} = [i]_{mix,t=n}(X_{s}\rho_{s} + X_{f}\rho_{f} + X_{wf}\rho_{s})$$
S8

1063 Now, rearranging eq. S7 and S8 to isolate the endmember contributions on one side of theequation:

1065

1066 
$$X_{s}\rho_{s}([j]_{mix,t=n} - [j]_{s}) + X_{f}\rho_{f}([j]_{mix,t=n} - [j]_{f}) + X_{wf}\rho_{s}([j]_{mix,t=n} - [j]_{s}) = 0$$
 S9

1067 
$$X_{s}\rho_{s}([i]_{mix,t=n} - [i]_{s}) + X_{f}\rho_{f}([i]_{mix,t=n} - [i]_{f}) + X_{wf}\rho_{s}([i]_{mix,t=n} - [i]_{wf}) = 0$$
 S10  
1068

1069 Next, we substitute  $[i]_{wf}$  from eq. S2 into S10:

1071 
$$X_{s}\rho_{s}([i]_{mix,t=n} - [i]_{s}) + X_{f}\rho_{f}([i]_{mix,t=n} - [i]_{f}) + X_{wf}\rho_{s}([i]_{mix,t=n} - [i]_{s} + \frac{\rho_{f}}{\rho_{s}}[i]_{f}) = 0 \quad S11$$

- 1072
- 1073 For clarity, we rewrite the system of equations (S3, S7, S8) in matrix form:

1075 
$$\begin{pmatrix} \rho_s([j]_{mix,t=n} - [j]_s) & \rho_f([j]_{mix,t=n} - [j]_f) & \rho_s([j]_{mix,t=n} - [j]_s) \\ \rho_s([i]_{mix,t=n} - [i]_s) & \rho_f([i]_{mix,t=n} - [i]_f) & \rho_s([i]_{mix,t=n} - [i]_s + {\rho_f}/{\rho_s}[i]_f) \end{pmatrix} * \begin{pmatrix} X_s \\ X_f \\ X_{wf} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} S12$$

1076

### 1077 For clarity, defining the following shorthand notions:

1079 
$$a = \rho_s([j]_{mix,t=n} - [j]_s)$$
 S13a

1080 
$$b = \rho_f([j]_{mix,t=n} - [j]_f)$$
 S13b

1081 
$$c = \rho_s([i]_{mix,t=n} - [i]_s)$$
 S13c

1082 
$$d = \rho_f([i]_{mix,t=n} - [i]_f)$$
 S13d

- 1084
- 1085 With these shorthand notations, equation S12 becomes:
- 1086

1087 
$$\begin{pmatrix} a & b & a \\ c & d & c+e \\ 1 & 1 & 1 \end{pmatrix} * \begin{pmatrix} X_s \\ X_f \\ X_{wf} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$
S14

1088		
1089	Now defining a new variable reflecting the sum of the soil and weathered feedstock resid	due
1090	endmembers:	
1091		
1092	$X'_s = X_s + X_{wf}$	S15
1093		
1094	Inserting S15 into S14, the system of equations reduces to:	
1095		
1096	$aX'_s + bX_f = 0$	S16
1097	$cX'_s + dX_f + eX_{wf} = 0$	S17
1098	$X'_s + X_f = 1$	S18
1099		
1100	Now we solve for $X'_s$ by substituting $X_f = 1 - X'_s$ from equation S18 into S16:	
1101		
1102	$aX_s' + b(1 - X_s') = 0$	S19a
1103	$aX'_s + b - bX'_s = 0$	S19b
1104	$(a-b)X'_s+b=0$	S19c
1105	$X'_{s} = \frac{-b}{a-b}$	S19d
1106		
1107	Now, substituting, S19d into $X_f = 1 - X'_s$ from equation S18:	
1108		
1109	$X_f = 1 - \frac{-b}{a-b} = \frac{a-b}{a-b} - \frac{-b}{a-b} = \frac{a-b+b}{a-b} = \frac{a}{a-b}$	S20
1110		
1111	Substituting S13a and S13b into S20:	
1112		
1113	$X_f = \frac{\rho_s([j]_{mix,t=n} - [j]_s)}{\left(\rho_s([j]_{mix,t=n} - [j]_s) - \rho_f([j]_{mix,t=n} - [j]_f)\right)}$	S21
1114		
1115	Now we substitute S20 and S19d into S17 to solve for $X_{wf}$ :	
1116		

1117 
$$c \frac{-b}{a-b} + d \frac{a}{a-b} + e X_{wf} = 0$$
 S22

1118 
$$\frac{-bc+ad}{a-b} + eX_{wf} = 0$$
 S23

1119 
$$X_{wf} = \frac{bc-ad}{e(a-b)}$$
 S24

#### 1121 Finally, substituting S13a-S13e into S24:

1122

1123 
$$X_{wf} = \frac{\rho_f([j]_{mix,t=n}-[j]_f)\rho_s([i]_{mix,t=n}-[i]_s)-\rho_s([j]_{mix,t=n}-[j]_s)\rho_f([i]_{mix,t=n}-[i]_f)}{\rho_f[i]_f(\rho_s([j]_{mix,t=n}-[j]_s)-\rho_f([j]_{mix,t=n}-[j]_f))}$$
S25

- 1124
- 1125

### 1126 S1.2 Calculation of deployment parameters from post-weathering samples

1127

From the estimates of endmember contributions to the post-weathering soil-feedstock mix sample as well as the rock powder dissolution calculated using the approach outlined above, additional deployment parameters can be calculated that may be valuable for the purposes of MRV. First, we can calculate the mass of rock powder initially added to the sampled soil volume (a, t ha<sup>-1</sup>):

1132

1133 
$$a = f V_{f,t=0} v_{sampled \, layer} \rho_f$$
 S26

1134

1135 where  $fV_{f,t=0}$  is the pre-weathering feedstock volume fraction, defined as the sum of the volume 1136 fraction comprising residual feedstock as well as the initial feedstock present that has since 1137 weathered:

1138

1139 
$$fV_{f,t=0} = X_f + X_{wf}$$
 S27

1140

1141 and the sampled layer volume per hectare is calculated from the sampling depth ( $d_{sampling}$ ):

1143 
$$v_{sampled \ layer}[m^3 \ ha^{-1}] = 10000 \ m^2 ha^{-1} * d_{sampling}[m]$$
 S28  
1144

1145 Note that in cases where the sampling depth is not the same as the soil mixing depth, it is important 1146 to use the depth of soil sampling. If the two depths are not the same, using calculated parameters 1147 that are based only on the sampled layer for the entire mixed layer assumes that the sampled layer composition is representative of the entire mixed layer. This is not necessarily the case, particularly 1148 1149 when feedstock distribution is not uniform with depth. In cases where the mixing depth is larger 1150 than the sampling depth, one could assume that the calculated dissolution fraction ( $\tau_i$ ) applies to 1151 the known application amount, but this would trade off against the benefit that feedstock addition 1152 can be calculated from the enrichment of immobile elements. To make sure that the calculation of 1153 initial CDR from a combination of  $\tau_i$  with the applied feedstock mass is entirely constrained in 1154 empirical measurements the choice of sampling depth should ideally be equal to the mixing depth. 1155

In addition, we can calculate the initial soil-feedstock mix composition from the post-weathering composition and mixing model outputs. Initial concentrations can be calculated by combining the amounts of base cations as well as immobile elements contributed to the initial mix from both soil and feedstock divided by the mass of the system:

1160

1161 
$$[j]_{mix, t=0} = \frac{\rho_s v_{s,t=0} [j]_s + \rho_f v_{f,t=0} [j]_f}{\rho_s v_{s,t=0} + \rho_f v_{f,t=0}}$$
 S30

1162 
$$[i]_{mix, t=0} = \frac{\rho_s v_{s,t=0}[i]_s + \rho_f v_{f,t=0}[i]_f}{\rho_s v_{s,t=0} + \rho_f v_{f,t=0}}$$
 S31

1163

1164 where  $v_{s,t=0}$  and  $v_{f,t=0}$  are the area normalized volumes (m<sup>3</sup> ha<sup>-1</sup>) of soil and feedstock within the 1165 sampled topsoil volume:

1167 
$$v_{s,t=0} = v_{sampled \ layer} X_s$$
 S32

1168 
$$v_{f,t=0} = v_{sampled \ layer} fV_{f,t=0} = v_{sampled \ layer}(X_f + X_{wf})$$
 S33

- 1169
- 1170 Substituting 20 and 21 in 18 and 19:
- 1171

1172 
$$[j]_{mix, t=0} = \frac{\rho_s v_{sampled \, layer} X_s[j]_s + \rho_f v_{sampled \, layer}(X_f + X_{wf})[j]_f}{\rho_s v_{sampled \, layer} X_s + \rho_f v_{sampled \, layer}(X_f + X_{wf})} = \frac{\rho_s X_s[j]_s + \rho_f(X_f + X_{wf})[j]_f}{\rho_s X_s + \rho_f(X_f + X_{wf})}$$
S34

1173 
$$[i]_{mix,t=0} = \frac{\rho_s v_{sampled \ layer} X_s [i]_s + \rho_f v_{sampled \ layer} (X_f + X_{wf})[i]_f}{\rho_s v_{sampled \ layer} X_s + \rho_f v_{sampled \ layer} (X_f + X_{wf})} = \frac{\rho_s X_s [i]_s + \rho_f (X_f + X_{wf})[i]_f}{\rho_s X_s + \rho_f (X_f + X_{wf})}$$
S35

1175 The calculation of feedstock application mass as well as pre-weathering composition from post-1176 weathering composition and deployment data is included in the SOMBA\_TAU\_meta function 1177 defined in the SOMBA.py file in the supplement.

- 1178
- 1179

### 1180 S1.3 Pre-weathering mix composition

1181

After addition of rock powder to soils, the composition of the soil-rock-powder mix falls on a mixing line between both endmembers (Figure 1a). Provided the rock powder is enriched in both base cations as well as at least one immobile element compared to the baseline soil, the addition of rock powder causes an increase of both base cation and immobile element concentrations. The pre-weathering mix concentrations of both major cations (j) and an immobile element (i; both in mol/kg) can be calculated from the mix of both endmembers:

1188

1189 
$$j_{mix,t=0} = j_f r_{m,t=0} + j_s (1 - f M_{f,t=0})$$
 S36

1190 
$$i_{mix,t=0} = i_f r_{m,t=0} + i_s (1 - f M_{f,t=0})$$
 S37

1191

1192 Where the subscripts f and s denote feedstock and soil respectively, and  $fM_f$  refers to the mass 1193 mixing ratio of feedstock in the soil-feedstock mix, which can be calculated as:

1194

1195 
$$fM_{f,t=0} = \frac{a}{(a+m_{soil,t=0})}$$
 S38

1196

1197 where *a* is the application amount of rock powder (in t ha<sup>-1</sup>), and  $m_{topsoil,t=0}$  is the mass of soil in 1198 the mixed soil rock powder topsoil layer right after deployment (in t ha<sup>-1</sup>). The application amount 1199 *a* is in this case given from deployment data, while the mass of topsoil can be calculated from the 1200 topsoil volume that is not rock powder (units in square brackets):

1202 
$$m_{soil,t=0} [t ha^{-1}] = v_{soil,t=0} [m^3 ha^{-1}] \rho_{soil} [t m^{-3}]$$
 S39

1203 
$$v_{soil,t=0}[m^3ha^{-1}] = v_{mixed\ layer}[m^3ha^{-1}] - v_f[m^3ha^{-1}]$$
 S40

1204 
$$v_{f,t=0}[m^3ha^{-1}] = \frac{a[t ha^{-1}]}{\rho_f[t m^3]}$$
 S41

1205 
$$v_{mixed \ layer}[m^3ha^{-1}] = 10000 \ [m^2ha^{-1}] \ d_{mix} \ [m]$$
 S42

1207 where *m* refers to mass, *v* to volume, and  $\rho$  to density of the soil within the mixed layer (subscript 1208 topsoil), the total mixed layer (mixed layer) as defined by the mixing depth ( $d_{mix}$ ), as well as the 1209 feedstock (f). Substituting S39-42 into S38:

1210

1211 
$$fM_{f,t=0} = \frac{a}{(a+(10000 \, d_{mix} - a/\rho_f) \, \rho_{soil})}$$
 S43

1212

1213

### 1214 S1.4 Post-weathering composition

1215

1216 As feedstock dissolves, both base cation as well as immobile element concentrations change. 1217 While base cation concentrations decrease as these mobile elements are leached from topsoils, immobile element concentrations increase due to the loss of feedstock mass (and volume) from 1218 1219 topsoils, resulting in a vector originating at the pre-weathering composition towards the bottom 1220 right in *j* vs. *i* space (Figure 1a). The post-weathering soil-rock powder mix composition can be 1221 calculated as a function of feedstock dissolution (mass transfer coefficient  $\tau_i$ ) fraction through 1222 system mass conservation where the denominate describes the mass of the post-weathering mix 1223 and the numerator its amount base cations or immobile elements:

1224

1225 
$$j_{mix,t=n} = \frac{\rho_s v_{s,t=n}[j]_s + \rho_f v_{f,t=n}[j]_f}{\rho_s v_{s,t=n} + \rho_f v_{f,t=n}}$$
 S44

1226 
$$i_{mix,t=n} = \frac{\rho_s v_{s,t=n}[i]_s + \rho_f v_{f,t=0}[i]_f}{\rho_s v_{s,t=n} + \rho_f v_{f,t=n}}$$
 S45

1227

where the t = 0 in the numerator of eq. S45 reflects the fact that immobile elements added through feedstock are retained within topsoils upon weathering. Post-weathering soil and feedstock volumes can be calculated as:

1232 
$$v_{f,t=n} = v_{f,t=0} (1 - \tau_j)$$
 S46

1233 
$$v_{s,t=n} = v_{f,t=0} + v_{f,t=0} - v_{f,t=n} = v_{s,t=0} + v_{f,t=0} \tau_i$$
 S47

- 1234
- 1235

#### 1236 S1.5 Internal consistency of the SOMBA framework

1237

1238 One of the script contained in the code supplement (SOMBA verification.py) demonstrates the 1239 internal consistency of the SOMBA framework. In the first part of the script, an example dataset 1240 is generated based on assumed deployment parameters. Some of these parameters—such as the 1241 amount of feedstock applied, the dissolution fraction, and others—are specifically required for the 1242 SOMBA start and SOMBA end functions. These functions estimate the composition of the soilfeedstock mix before and after weathering, respectively, using deployment-specific inputs. 1243 1244 However, when using the soil mass balance framework to estimate rock powder dissolution fractions from post-weathering samples, these parameters may not be necessary. 1245

1246

1247 In the second part of the script, the generated dataset is used to sequentially call a series of soil 1248 mass balance functions defined in the SOMBA.py file, which are derived here. The functions 1249 called include: (1) SOMBA start, which calculates the pre-weathering soil-feedstock mix 1250 composition from deployment parameters; (2) SOMBA end, which estimates the post-weathering 1251 composition based on the output from SOMBA start and an assumed rock powder dissolution 1252 fraction; (3) SOMBA tau, which calculates the rock powder dissolution fraction from deployment 1253 data, including baseline soil, feedstock, and post-weathering compositions; and (4) 1254 SOMBA tau meta, which performs the same calculation as SOMBA tau but also provides 1255 metadata such as endmember contributions and detected feedstock amounts.

1256

Finally, the exported Figure S1 demonstrates that the calculated from the SOMBA framework (such as  $\tau_j$  and pre-weathering concentrations) are equivalent to the values assumed or calculated *a-priori*. The same is true for the estimate rock powder application amount—in this case it is important to consider potential mismatches between mixing and sampling depth, where the detected rock powder amount is going to be less than the amount assumed *a-priori* if the sampling depth is less than the mixing depth.





1265Figure S1: This figure demonstrates that the soil mass balance framework developed here is internally consistent. The calculated<br/>dissolution fraction  $\tau_j$  (a) and pre-weathering soil concentration (b) are equivalent to the values assumed a-priori. The same is true<br/>for detected rock powder application amounts (c) when taking into account potential mismatches between soil mixing and sampling<br/>depth.

1270	S2 Soil data
1271 1272	
1273 1274	S2.1 Site and sampling information
1275	Elmbrook: This field is classified as loamy-sand, with a mean pH of 7.0, and is on a corn-
1276	yellow pea rotation. The only fertilizer used is chicken litter.
1277	Hawthorne: This field is classified as silt-loam, with a mean pH of 6.4. This field is used as
1278	pastureland, growing native grasses for grazing. There is no tillage, irrigation, fertilizer, or
1279	liming use.
1280	Longleaf Ridge: This field is classified as loamy-sand. This field is used for peanuts, and is
1281	irrigated by a center pivot. There is no tillage, regular nitrogen application, and highly infrequent
1282	liming.
1283	Tower/Ike Lewis: Tower and Ike Lewis fields are managed by the same farmer. The fields are
1284	no-till and are ripped every 3 years. Both fields are on a corn-soy rotation, and receive nitrogen
1285	fertilizer during corn season. There is no irrigation. No pH data is available for this field.
1286	
1287	Elmbrook, Hawthorne, and Longleaf fields were sampled in a grid array across the entire field
1288	region, with 2 cores taken at each sampling location and homogenized. Samples were dried at 60
1289	°C, sieved to 2mm and ground prior to analysis. Tower and Ike Lewis samples were collected by
1290	randomly pooling 12 15-cm drill cores from a 1m radius circle. Samples were dried at 60 °C,
1291	sieved to 2mm and ground prior to analysis.
1292 1293	
1294	S2.2 Analytical information
1295	Powdered seil semples (typically 0.1 g) were leasted in 12 ml of 1M Ammonium Acetate (trace
1290	motel grade) and contributed in 15 ml networkers tubes for 5 minutes at 4000 mm to release
129/	including rade) and centrifuged in 15 ini polypropytene tubes for 5 minutes at 4000 rpm to release
1298	any adsorbed cations (i.e, the exchangeable fraction) and subsequently washed in 2 ml of 2X
1299	with $Q = Q = (18.2)$ and centrifuged again. The soil was then transferred into pre-

1300 acid-cleaned quartz crucibles, dried at 60 °C and ashed at 600 °C to incinerate any organic matter

1301 (and release volatiles). The dried residue was weighed for insoluble content and to estimate the

1302 LOI. The residue was then transferred into pre-acid-cleaned teflon beakers and dissolved

1303 completely using a mixture of 5 ml distilled hydrochloric acid (HCl), 5 ml distilled nitric acid

1304 (HNO3) and 1 ml of trace metal grade hydrofluoric acid (HF), capped, heated at 100 °C for 24

hours. The samples were then uncapped and evaporated to dryness at 90 °C and redissolved in 5ml of 6N HCl.

1307

1308 Splits were taken for elemental concentrations measurements. For analysis on the Agilent 8900

1309 Triple Quadrupole ICP-MS, a split of 15 µl from each sample was evaporated, diluted 1000

1310 times with 1% HNO3 (v/v) and spiked with  $^{26}$ Mg and  $^{49}$ Ti. Indium was introduced externally as

1311 an internal standard. For analysis on the Thermo Scientific Element XR ICP-MS, a split of 10 µl

1312 from each sample was evaporated, diluted 400 times with 5% HNO3 (v/v) and spiked with <sup>26</sup>Mg,

<sup>42</sup>Ca, <sup>49</sup>Ti and 1ppb In. Values were normalized using routine measurements of USGS

1314 geostandards BHVO-2 and SGR-1b (processed with each batch of samples throughout the entire

1315 procedure), whose precision was within 1% of certified values (4% for Al) on the Agilent (LL).

1316 For more information on the analytical procedure see also Reershemius et al. (2023).

1317

1318

### 1319 S2.3 Implementation of soil heterogeneity in Monte Carlo simulations

1320

1321 We use soil composition data from five novel field sites sampled at high spatial densities to 1322 constrain in-field heterogeneity for the Monte Carlo signal-to-noise analysis. The data are 1323 normalized by the field mean concentration (Figure S2) before we fit log-normal distributions to 1324 make sure the population means are 1. The use of log-normal (rather than normal) distributions is 1325 intentional because samples generated from log-normal distributions always have positive values, 1326 preventing the occurrence of non-physical negative soil concentrations in the signal-to-noise 1327 analysis without having to filter some data. For normal distributions, this could be achieved by 1328 simply filtering out negative model occurrences, but this would change the mean of generated 1329 sample distributions and cause a systematic error in calculated dissolution fractions. In addition, 1330 using log-normal compared to normal fits also represents a conservative choice for the signal-to-

- 1331 noise analysis due to the generally higher variance, as well has overall better fits compared to
- 1332 normal distributions ( $R^2$  better for 11 out of 20 elemental field distributions).



1334

Figure S2: Distributions of baseline data for the 5 field sites (Table 1) including log-normal fits to the data. The shape parameters, corresponding to the standard deviation of the normal distribution of the logarithm of the data, are plotted in Figure S3.

- 1337
- 1338 Generally, a random variable is log-normally distributed if:
- 1339
- 1340  $X \sim LogNormal(\mu, \sigma)$
- 1341

S48

1342Which means that:13431344
$$ln(X) \sim N(\mu, \sigma^2)$$
S4913451346where  $\mu$  is the mean,  $\sigma$  the standard deviation, and  $\sigma^2$  the variance of the respective distributions,1347with log-normal distributions conventionally defined via the standard deviation of the underlaying1348normal distribution. The expected value (mean) of a log-normal variable X can be calculated as:13491350 $E[X] = e^{\left(\mu + \frac{\sigma^2}{2}\right)}$ S50a1351Hence, when using the parameters of log-normal fits to populations with a given mean (Figure S2)

1353 to generate synthetic data for the Monte Carlo simulations, if generating  $\mu$  and  $\sigma$  independently, 1354 the mean of the resulting populations will not be the same as of the initial distribution (i.e., 1). Or 1355 said differently, if we want the mean of a synthetic distribution to be a specific value,  $\mu$  and  $\sigma$  are 1356 not independent—only one can be randomly generated. We implement this into the Monte Carlo 1357 simulation by randomly generating shape parameters ( $\sigma_{syn}$ ) and then calculating  $\mu_{syn}$  such that E(X)1358 = 1:

1359

1360 
$$E[X] = e^{\left(\mu_{syn} + \frac{\sigma_{syn}^2}{2}\right)} = 1$$
 S50b

1361

1362 Now, taking the natural logarithm:

1363

1364 
$$\ln\left(e^{\left(\mu_{syn}+\frac{\sigma_{syn}^2}{2}\right)}\right) = \ln(1) \Rightarrow \mu_{syn} + \frac{\sigma_{syn}^2}{2} = 0 \Rightarrow \mu_{syn} = -\frac{\sigma_{syn}^2}{2}$$
S51

1365

1366 The empirically constrained simulated  $\mu_{syn}$  and  $\sigma_{syn}$  describe log-normal distributions with a mean 1367 of 1 and  $\sigma$  (shape) parameters constrained from field data (with a mean of 1), and are used to 1368 randomly generate sets of samples by multiplying these in-field variance factors with true "true" 1369 sample compositions.

Because the  $\sigma$  values from the fit to field data (Figure S2) are neither normally nor log-normally distributed (negative R<sup>2</sup>; Figure S3), in the Monte Carlo simulations we generate synthetic  $\sigma_{syn}$ values by randomly pulling from uniform distributions set out by the minimum and maximum observed  $\sigma$  values observed in field data (for Ca, Mg, and Na the used values are 0.072402 and 0.687422, and for Ti 0.119775 and 0.288003).

1376



Figure S3: Histograms as well as normal and log-normal fits to the shape parameters from log-normal fits to soil data. The signal-to-noise analysis and related Monte Carlo simulations use uniform distribution set out by the minimum and maximum Ca, Mg, and Na shape values (b) as well as Ti shape values (c) due to low fit of both normal and log-normal distributions.

# 1382 S3 Impact of feedstock mass loss on base cation and immobile element1383 concentrations

a) Base cation enrichment due to feedstock mass loss, constant feedstock composition



S52

1384<br/>138513851386Figure S4 Change of base cation concentration as a result of feedstock mass/volume loss from the system considering constant<br/>feedstock compositions.

1387

1388 Calculated as:

1389

1390 
$$\Delta j = [j]_{n=t} - [j]_{n=t}^*$$

1391

# 1392 Where $[j]_{n=t}$ is equation from S44, and $[j]_{n=t}^{*}$ calculated from a linear loss of base cations 1393 relative to the dissolution fraction:

1394

1395 
$$[j]_{n=t}^{*} = [j]_{s} + ([j]_{n=0} - [j]_{s})(1 - \tau_{j})$$
 S53

1396

1397 Where  $[j]_{n=0}$  is equation from S36.

1398



[immobile element; i]

 $1400 \\ 1401 \\ 1402$ Figure S5: Sketch of the impact of enrichment of post-weathering soil immobile element concentrations when the feedstock immobile element concentration is lower than in soil.

1403 1404 1405

# 1407 S4 Impact of soil composition on signal-to-noise analysis



Figure S6: Cumulative distribution plot of the ratio of agricultural soil (LandCover2 = "Row Crops" and "Small Grains") composition (Smith et al., 2013) to US-basalt composition (Lehnert et al., 2000). As the ratio increases above the value of 0.2 defined here as a cut off for soils suitable for soil mass balance approaches, the fraction of soils fulfilling this condition quickly increases.



Figure S7: Average errors on detected dissolution fractions for two simulated mass transfer coefficients ( $\tau_j = 0.25$  in a,  $\tau_j = 0.5$  in b). The simulations are based on US soil (Smith et al., 2013) and basalt (Lehnert et al., 2000) compositions considering soils with base cation and Ti concentrations at least 2 times lower than basalt (in contrast to Figure 5, which shows the same for soil concentrations that are at least 5 times lower). The simulated in-field soil heterogeneity is based on the novel dataset presented in Table 1.

