## BIOLOGY LETTERS

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#### Review



**Cite this article:** Kantola IB, Masters MD, Beerling DJ, Long SP, DeLucia EH. 2017 Potential of global croplands and bioenergy crops for climate change mitigation through deployment for enhanced weathering. *Biol. Lett.* **13**: 20160714.

http://dx.doi.org/10.1098/rsbl.2016.0714

Received: 1 September 2016 Accepted: 4 November 2016

#### **Subject Areas:**

ecology, plant science, biochemistry

#### **Keywords:**

basalt, carbon sequestration, agriculture, global climate change, silicate weathering, biofuels

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An invited contribution to the mini-series 'Enhanced rock weathering' edited by David Beerling.

## Global change biology

## Potential of global croplands and bioenergy crops for climate change mitigation through deployment for enhanced weathering

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Conventional row crop agriculture for both food and fuel is a source of carbon dioxide ( $CO_2$ ) and nitrous oxide ( $N_2O$ ) to the atmosphere, and intensifying production on agricultural land increases the potential for soil C loss and soil acidification due to fertilizer use. Enhanced weathering (EW) in agricultural soils—applying crushed silicate rock as a soil amendment—is a method for combating global climate change while increasing nutrient availability to plants. EW uses land that is already producing food and fuel to sequester carbon (C), and reduces  $N_2O$  loss through pH buffering. As biofuel use increases, EW in bioenergy crops offers the opportunity to sequester  $CO_2$  while reducing fossil fuel combustion. Uncertainties remain in the long-term effects and global implications of large-scale efforts to directly manipulate Earth's atmospheric  $CO_2$  composition, but EW in agricultural lands is an opportunity to employ these soils to sequester atmospheric C while benefitting crop production and the global climate.

#### 1. Introduction

Atmospheric CO<sub>2</sub> is regulated on geologic timescales by the natural chemical weathering of silicate rocks, a process that can be accelerated by applying crushed fast-weathering silicate rocks to the land surface as 'enhanced weathering' (EW) [1–4]. Conventional row crop agricultural practices result in a net loss of carbon (C) from the soil to the atmosphere and high requirements for fertilizer and lime [5-8]. EW with basalt, a fast-weathering, Ca- and Mg-rich silicate rock, has the potential to create a net C sink in these systems while reducing N loss, counteracting soil acidification, and supplying nutrients through the by-products of the weathering processes. The 10–15 M km<sup>2</sup> of global cropland [9] offers a host of environments for deployment of EW substrates, with a potential return of 200-800 kg sequestered CO<sub>2</sub> t<sup>-1</sup> basalt [10]. In addition, growing interest in biofuels to reduce fossil fuel consumption has increased the proportion of agricultural land producing annual and perennial bioenergy crops, with the potential to expand into marginal lands [7,11-13]. Perennial crops have longer growing seasons than annuals and extensive root systems supporting large biotic communities [8,11,14], which may be more effective than annuals at weathering. In this review, we examine the potential for basalt EW to sequester CO2 and benefit crop yield in conventional and perennial bioenergy agroecosystems.

### 2. Basalt weathering for C sequestration

The chemical weathering of silicate rock sequesters CO2 as bicarbonate and carbonate minerals in soils and oceans [1,3,15]. Basalt is being explored for EW due to availability and nutrient content. Basalt weathering occurs at slow natural rates over 6.8 M km<sup>2</sup>, or 4.6% of terrestrial land area [16]. EW in agricultural lands expands the potential weathering area by 10-15 M km<sup>2</sup> [3,15], and offers secondary benefits to agriculture from basalt application as a soil amendment [15]. The use of rock fertilizers is not novel: dolomite and limestone are commercially available, and have three major values beyond C sequestration: buffering soil pH, reducing N loss and providing elemental nutrients [17-20]. The various forms of basalt contain 8-20% Ca and Mg oxides by weight, and 1-2% potassium oxides and phosphates, with small quantities of micronutrients, including Cu, Ni, and Zn (e.g. [21-23]). In an agricultural setting, organic acids produced by plants weather the rock surface, liberating nutrients and dissolving silica [24]. Ca<sup>2+</sup> and Mg<sup>2+</sup> are among the most easily weathered base cations of basalt [25,26], and react to form soluble bicarbonate compounds [10]. Consumption of H<sup>+</sup> ions during the weathering process buffers the soil, increasing the availability of existing soil nutrients, particularly P, which form plant-resistant compounds at low pH (figure 1) [20,27].

Global rates of rock weathering are directly related to temperature, moisture and interactions with vegetation [4,14,28,29]. Basalts are among the fastest weathered silicate rocks, and in situ weathering of basalt minerals on the Earth's surface currently consumes 179 Mt of CO<sub>2</sub> annually [16], approximately 0.5% of annual fossil fuel emissions [30]. This sequestration is limited by basalt quality (Ca +Mg concentration and degree of previous weathering) [4,10] and weathering conditions, such as low temperatures in Siberia or dry conditions in Ethiopia [16], which slow the rate of chemical reactions. Weathering is enhanced by increasing the reactive surface area and by increasing temperature and moisture: EW will proceed most rapidly in warm, wet environments [15,26,31]. Rates of CO<sub>2</sub> capture by EW are uncertain, but the most Ca- and Mg-rich silicate rocks have the capacity to sequester >1t  $CO_2 t^{-1}$  rock, while basic rocks, including basalts, range from 200-800 kg CO<sub>2</sub> t<sup>-1</sup> rock [4,10,15]. Plants and rhizosphere microbes, particularly mycorrhizal fungi, accelerate weathering while mining the rocks for nutrients, including P and K, through the production of root exudates and acidification [24,32-34]. The rate of mineral dissolution from ground rock increases 1- $5\times$  in the presence of plants [14,18,29,32].

## 3. Agricultural lands as carbon sinks

Global soils represent a C reservoir of up to 1.5 Pg of organic C and 1 Pg of inorganic C [6], but many agricultural soils are CO2 sources due to soil disturbance and heavy cropping, emitting 5-6 Gt CO<sub>2</sub>-eq yr<sup>-1</sup> [6,7,35-37]. To support the growing human population over the next century, global cropland must expand, or agricultural production must intensify on existing arable land [9,11]. Expansion into natural areas such as tropical forest, or increases in management practices such as tillage and fertilizer application can greatly increase soil C disturbance and N loss to volatilization and runoff [11]. EW has potential to mitigate the effects of

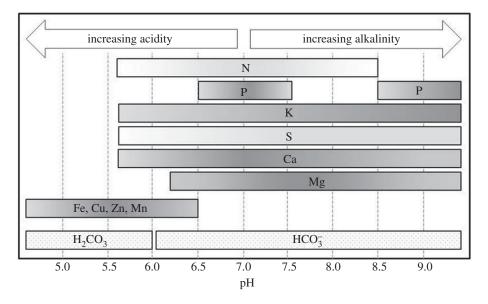
agriculture at a global scale and at global locations, without disrupting food production. Earth's surface supports 10-15 M km<sup>2</sup> of arable land with potential to deploy EW (7-10% of global land area) [3,15], an area that is expected to expand with growing production requirements in the future (tables 1 and 2). The ubiquity of agricultural lands around the world gives a wide range of temperature and moisture regimes at which EW can be explored, and the weathering rate will differ for each, as will the specific soil chemistry that will determine appropriateness of EW [15,39].

Carbon losses from agricultural soils occur due to soil disturbance, crop harvest and microbial activity [6,11]. Crop biomass temporarily sequesters 128-165 Gt of C [6] and contributes roots and litter to slower-turnover organic matter pools in the soil. Liberation of C by tillage, microbial consumption of organic matter and the removal and subsequent destruction of aboveground biomass outweigh C inputs under row crops, and result in a net loss of C [6,12,37]. EW sequesters atmospheric CO<sub>2</sub> as inorganic C in soils, and does not directly counteract the organic C loss from agricultural practices, instead reducing net C loss [15]. Alkaline solutions formed in terrestrial reactions may travel through soil water and groundwater to streams and rivers and ultimately to oceans, where vast quantities of C are stored in the shells of marine organisms and precipitated to the sea floor [40].

### (a) EW effects on the N cycle in agricultural soils

Much of the increase in agricultural productivity in the past century can be traced back to the widespread adoption of N fertilization, but long-term N fertilizer use has negative effects at both global and local scales. N fertilizer production consumes 1.2% of annual energy produced globally, and represents 1.2% of total greenhouse gas emissions [41,42]. Fertilizers are often applied at rates in excess of biological demand, or in excess of neutralizing soil ions, and lost to volatilization or runoff, resulting in eutrophication of aquatic systems [5]. N2O has a global warming potential approximately 300 times higher than CO2 over a 100-year time period [43], and N fertilizers increase rates of nitrification and/or denitrification [44-46]. Conservation of N in agriculture is critical to reducing the rates of N fertilizer production and application, and N emissions from agricultural soils.

EW of basalt shares some similarities to liming, a practice that alters soil pH with CaCO3 to improve nutrient availability in crops, but liming emits CO<sub>2</sub> to the atmosphere as carbonates weather [44]. This CO2 loss is compensated for by reduction of N2O, a more potent greenhouse gas [43], and increased C sequestration in biomass. Logic indicates that increasing soil pH will increase N2O emissions due to increases in microbial N mineralization and nitrification; however, multiple studies have shown a decline in N<sub>2</sub>O emissions following lime applications [44-46]. The mechanism of N<sub>2</sub>O reduction through liming is not well understood, but may be a result of increased microbial production of enzymes reducing N<sub>2</sub>O to N<sub>2</sub> at neutral pH [46,47]. Though a representative basalt (approx. 20% CaO+MgO) has half the buffering capacity of limestone (40% CaO by weight), proposed rates of basalt application  $(2-25\times$  the rate of limestone) [3,48] are adequate to substitute for agricultural lime.



**Figure 1.** Optimal soil pH ranges for plant-essential nutrient availability, with nutrients supplied by basalt weathering (in grey), and dominant species of dissolved carbonate. Darker shading indicates greater availability. Adapted from Truog [27].

#### (b) Effects of EW on soil pH and plant nutrition

Approximately 30% of global soils are acidic (pH < 5.5), and continued overuse of ammonia-based N fertilizers adds free protons and lowers soil pH, resulting in the formation of insoluble nutrient compounds that are unusable by plants, nutrient deficiencies, reduced crop yield and water quality degradation [5,49-51]. Plant uptake of base cations further lowers soil pH, and essential nutrients including P, K and S form compounds unavailable to plants as pH decreases. Conversely, plantavailability of Fe, Mn, Cu and Zn increases at low pH, creating potential for metal toxicity (figure 1) [5,50]. EW consumes free protons in the formation of bicarbonate and raises soil pH, and may increase plant-availability of existing nutrients in the soil while adding micronutrients and Si [51,52]. Although EW does not directly sequester organic C from plants, increases in nutrient availability could support greater biomass production, and subsequently lead to increased organic C inputs to the soil system from roots and litter.

Root exudates chemically weather rocks and minerals, and the reactions are enhanced by mycorrhizal acidification of the rhizosphere [14,29,32–34,53]. Root-associating mycorrhizal fungi provide the link between the inorganic C fixation of EW and the organic C cycle of agricultural soils. Mycorrhizal fungi are critical for developing soil structure, which preserves organic matter and resists water erosion [54]. Increases in soil organic matter benefit agriculture by increasing soil water retention and crop yields, both of which amplify weathering by increasing mineral-water contact times and demand for inorganic nutrients, respectively [32].

# (c) Potential for increased carbonate formation: a global, millennial effect

Carbonate precipitates from the soil solution when soils are saturated with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  cations, and alkaline soils are a significant terrestrial sink of  $\text{CO}_2$  [10,55]. Like their acidic counterparts, alkaline soils suffer from nutrient limitations and loss of productivity, and may benefit from the additions of Fe from EW (figure 1) [51]. Alkalinity resulting from EW may travel through the vadose zone to surface and ground

waters (figure 2), and eventually to rivers and oceans [10,15,16]. Ocean inputs of base cations are desirable to combat ocean acidification, an effect of the continuing rise of atmospheric CO<sub>2</sub> [2,3,37]. Surface coastal oceans provide a major sink for an influx of bicarbonate ions liberated by weathering which, in the presence of adequate Ca<sup>2+</sup> or Mg<sup>2+</sup> cations, can precipitate biologically (e.g. corals and forams) and on longer timescales abiotically (limestone) [40]. The reaction producing carbonate from bicarbonate liberates CO<sub>2</sub> (1 kg kg<sup>-1</sup> sequestered); however, the resulting mineral is highly stable and will persist for millions of years in oceans [3,15,40].

## 4. Bioenergy crops and the carbon balance

Bioenergy crops have been investigated in both temperate and tropical regions as a means of partially mitigating CO<sub>2</sub> emissions from burning fossil fuels. Combustion of bioethanol and biodiesel produces less net CO2 than fossil fuels because bioenergy feedstocks sequester CO<sub>2</sub> as biomass and belowground in soil as they grow, recycling C between the atmosphere and the terrestrial C pool [7,12,37]. Crops used to produce first generation biofuels (1G) from sugars and oils including maize, soya beans, and sugar crops, are grown on over 9 M km<sup>2</sup> of agricultural land globally, currently with a 90/10 split between food and fuel. In the past 20 years, fuel production from 1G bioenergy crops has increased from near zero in 1990 to 85 million tons of bioethanol and biodiesel in 2010, and the number is expected to grow as countries follow the models of Brazil, the EU and the USA, with subsidies and mandates for fossil fuel reductions (table 2) [38]. 1G bioenergy crops compete with food crops for land area and would benefit from EW in the same manner as those grown for food.

Second generation bioenergy crops (2G), including perennial grasses and woody plants, are grown for cellulose and require additional processing for bioethanol production. 2G crops are intended to spare prime agricultural land and to separate the food and fuel production streams in agriculture [8,11,12,38,56]. Perennial crops have the combined benefits of negative C balance [7,8,12] and high biomass production on

**Table 1.** Global population projections and projections of agricultural production of edible crops for fuel through 2050.

	<u>year</u>			
	2005	2030	2050	% increase
population [9]	6.6B	8.3B	9.1B	37%
global arable land [38]	15 M km²	18.5 M km <sup>2</sup>	21 M km <sup>2</sup>	40%
cereals [9]	2.0 Bt	2.7 Bt	3.0 Bt	46%
bioenergy/non-food cereals	65 Mt	182 Mt	182 Mt	180%
oils	139 Mt	230 Mt	252 Mt	81%
bioenergy/non-food oils	7 Mt	29 Mt	29 Mt	314%
sugar	185 Mt	295 Mt	333 Mt	80%
bioenergy/non-food sugars	28 Mt	81 Mt	81 Mt	189%

Table 2. Projections of global biodiesel/bioethanol production and 1G bioenergy crop land use.

	year ————————————————————————————————————			
	2006	2010	2020	% increase
bioethanol production [38]	31 Mt	67 Mt	125 Mt	303%
biodiesel production	6 Mt	17 Mt	50 Mt	733%
bioenergy land use	1.05 M km <sup>2</sup>	2.2 M km <sup>2</sup>	4.8 M km <sup>2</sup>	357%

marginal land [11,57]. While 2G bioenergy crops have lower nutrient requirements than 1G crops (perennial grasses in the USA range from unfertilized to half the rate of maize) [12], plant-induced weathering of basalt could supply nutrients that improve marginal soils, increasing yields and promoting further organic C sequestration.

# 5. Limits of agricultural benefits from basalt weathering, questions and uncertainties

Global opportunities to deploy EW are widespread, while feasibility at specific locations is more limited. Basalts account for 6.8 M km<sup>2</sup> of Earth's surface, and significantly more beneath the surface and under the oceans [16,58], but mining, processing, and transportation of large amounts of basalt to agricultural areas present financial and logistic challenges to farmers [3,10]. Over 80% of agricultural commodities are consumed locally [9], and areas with limited exports may lack transportation infrastructure needed to import basalt. Remote sources of basalt that do not overlap with arable land, such as outcrops in Siberia or Ethiopia [16], add to the expense of producing the material. In addition to the capital investment in purchasing and transporting basalt, there is a C cost. Fuel consumption and subsequent CO2 release during mining, processing, and transportation reduce gains made by enhanced weathering by an estimated 5-30% of potential C sequestered [15]. Proposed application rates of 10-50 t ha<sup>-1</sup> in agricultural soils [3] exceed typical limestone application rates for maize/soya bean in the USA 5to 25-fold [48], requiring heavy machinery for distribution and restricting deployment of EW in remote or pastoral areas. However, EW in only a portion of global agricultural land area has the potential to offset a significant amount of CO2 production [10,16]. In the USA, with approximately 70 M ha of maize and soya beans planted annually [59], deployment of basalt (10% CaO and 10% MgO,  $R_{\rm CO2} = 0.32$  [10]) at rates between 10 and 50 t ha<sup>-1</sup> represents a theoretical maximum  $\rm CO_2$  capture of 0.2–1.1 Gt  $\rm CO_2$ , up to 13% of the global annual agricultural emissions over the weathering lifespan of the material. This value exceeds the US annual contribution to agricultural emissions (approx. 10% of global) [30,60] before accounting for additional reductions in  $\rm N_2O$  emissions or fertilizer use. However, the rate of weathering in these soils is unknown, creating uncertainly in predicting how quickly  $\rm CO_2$ -capture capacity will be reached. Initial deployment to areas of high-intensity agriculture where basalt, road access and heavy machinery are available, such as North America [22] or the UK [10], will be the first test of weathering potential in farmlands.

Widespread adoption of EW will require demonstration of the effectiveness of EW for the global benefit of C sequestration and local benefits of N loss reduction, base cation buffering and nutrient addition that will benefit farmers directly. While C sequestration is of global importance, few farmers will be willing to expend the cost of basalt additions without commensurate improvements in yield or soil fertility, and assurances that basalt application will not negatively influence long-term productivity, crop value, or the health of farm workers, neighbouring landowners, or consumers. Field trials are needed to quantify C capture and demonstrate agricultural benefits of weathering by-products. Additional uncertainties surrounding EW include long-term effects of climate manipulation, varied rates of weathering at different global locations, availability (logistic and financial) of basalt to landowners, both government and landowner perception of the value of C sequestration, and the unforeseen risks and benefits of rock fertilizers.

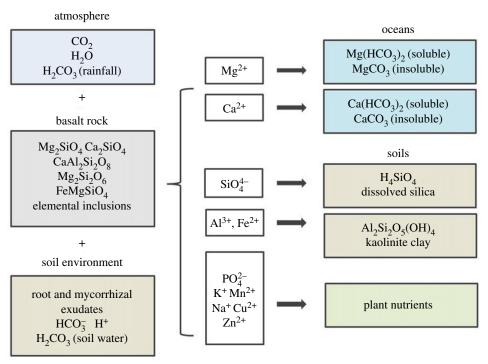


Figure 2. Weathering of basalt minerals by carbonic acid-containing rainfall, soil water, and root and mycorrhizal exudates liberates base cations, metals, and plantessential nutrients. Basalt components ultimately contribute to plant growth, soil formation and oceanic carbonate storage. (Online version in colour.)

## 6. Future of agricultural and bioenergy lands: looking toward 2050

According to FAO estimates [9], the global population will increase to 9.1B by 2050 and world energy demand will rise between 20 and 100% (table 1) [61]. Currently, 37% of global land area is used for agriculture, including both cropland and pasture, and agricultural production is expected to grow at approximately 1% per year through 2050 [9]. By 2050, cereal grain production for food and fuel is expected to increase 46% from 2005 yields, and oils 81% (tables 1 and 2) [9]. Higher productivity requires increased retention and effectiveness of N fertilizers, with consumption expected to increase 1.4% per year between 2012 and 2030 [9]. Biofuel predictions for 2020 (table 2) indicate an increasing demand for biomass for energy production. Bioenergy and non-food crop production are predicted to increase between 71 and 200% by 2050 (table 1) [9,13,62,63], potentially tripling land area in energy crop production. While the development of bioenergy crops and EW were both conceived to combat greenhouse gases and climate change, a shifting climate will exert feedbacks on both. Higher temperatures and rising CO2 concentrations may increase arable land area and crop yields in high latitude regions, but may accelerate organic C decomposition in soils or create desert conditions unfit for agriculture in drier regions [63,64]. Rates of EW may be increased by higher temperatures, but limited by reduced rainfall. The optimal

locations for deploying EW will shift, as will agricultural production, in response to climate variability.

#### 7. Conclusion

Strategies for mitigating the effects of atmospheric CO<sub>2</sub> in the Earth system as the human population increases are required and our review indicates that EW with basalt has the potential to harness a natural process for C sequestration at globally relevant scales in agroecosystems while benefitting food and fuel production. EW on agricultural lands could combat soil acidification and N loss while providing plant-essential nutrients, two major issues associated with intensive cropland farming. However, caution is required before large-scale deployment can be considered. We need better understanding of potential positive and negative impacts on crop production and feedbacks on soil biogeochemistry and unforeseen consequences. Small scale pilot studies that provide empirical data and build public trust and support are essential next steps.

Data accessibility. This work does not contain any new experimental or observational data.

Competing interests. We have no significant competing financial, professional or personal interest that might have influenced the materials presented in this manuscript.

Funding. This paper is a product of the Leverhulme Centre for Climate Change Mitigation, funded by the Leverhulme Trust through a Research Centre award (RC-2015-029).

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