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Viability of greenhouse gas removal via artificial addition of volcanic ash to the ocean



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ABSTRACT

Mitigating human contributions to climate change is a highly debated topic, as it becomes evident that many nations do not adhere to optional reductions in global emission. Substantial research is taking place into negative carbon technologies that actively reduce the amount of atmospheric carbon dioxide (CO_2) via greenhouse gas removal (GGR). Various GGR methods have been proposed, from reforestation to ocean fertilisation. This article discusses advantages of an approach based on enhanced input of tephra to the ocean, to increase the drawdown of atmospheric CO_2 . Natural addition of tephra to the ocean results in preservation of enhanced organic matter in sediment. Hence, augmenting its delivery should raise the level of sequestration. Calculations indicate that offshore tephra addition could sequester 2750 tonnes of CO_2 per 50,000 tonnes of ash delivered (a typical bulk carrier's capacity). The cost is estimated as ~\$55 per tonne of CO_2 sequestered and is an order of magnitude cheaper than many proposed GGR technologies. Further advantages include: tephra addition is simply an augmentation of a natural Earth process, it is a low technology approach that requires few developments, and it may sequester carbon for thousands of years. Hence, offshore tephra addition warrants further investigation to assess its viability.

1. Introduction

Recent proposals to remediate human contributions to climate change through geoengineering have generated considerable discussion of the topic (Royal Society, 2018). Ensuring that the world stays below the Intergovernmental Panel on Climate Change (IPCC) upper limit to "safe" warming (IPCC, 2018) will require additional measures other than non-binding agreements (Haszeldine et al., 2018; Tollefson, 2018). Hence, Greenhouse Gas Removal (GGR), via geoengineering, has been posited to reduce levels of anthropogenic carbon dioxide (CO₂) in the atmosphere. GGR may therefore help avoid large-scale impacts of climate change such as ecosystem collapse and major changes in ocean circulation (Lomax et al., 2015; Steffen et al., 2018).

Proposals have included a variety of GGR methods, from reforestation and habitat restoration (e.g. Bastin et al., 2019) to infrastructural changes, such as low-carbon concrete production

http://dx.doi.org/10.1016/j.ancene.2020.100264 2213-3054/© 2020 Elsevier Ltd. All rights reserved. (Ghouleh et al., 2017), and use of biomass in building materials (e.g. Ramage et al., 2017). Other GGR proposals involve enhancing the rate at which Earth's natural carbon cycle sequesters atmospheric CO₂ in natural sinks (Royal Society, 2018). Examples of manipulating natural cycles include increasing the alkalinity of the ocean (i.e., reversing ocean acidification (Renforth and Henderson, 2017)), enhancing mineral carbonation (i.e., converting silicate rocks into carbonates (Matter et al., 2016)) and ocean fertilization (i.e., enhancing photosynthetic carbon removal (Boyd et al., 2007)).

All proposed GGR interventions have associated risks and face scientific, economic and societal barriers to implementation. For example, repurposing terrestrial biomass for carbon sequestration necessarily requires the utilization of agricultural land currently used to produce food. Manipulation of natural cycles also suffer from an unpalatable image due to perceived meddling with the natural world, and potential impacts on ecosystems (Royal Society, 2018).

Because no single mechanism of emissions reduction or GGR can feasibly halt the rise in atmospheric CO_2 levels (Royal Society, 2018), considering a range of emissions reduction and GGR strategies with lesser risks and implementation barriers, rather than adoption of a single big impact, high-risk strategy is beneficial. Hence, we present a potential GGR mechanism based



Viewpoint



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on enhanced input of the products of explosive volcanism (Fig. 1) into the oceans. This approach builds on the role that natural tephra deposition in the oceans plays in the carbon cycle (Fig. 2) (Longman et al., 2019) and examines the potential enhancement of these natural processes to achieve GGR. Based on real-world data, we calculate the potential of the proposed method to sequester atmospheric carbon, and provide an estimate of likely costs.

2. The approach

The global amount of organic carbon (C_{org}) reaching the seafloor is estimated as equivalent to 8.4 Gt CO₂ a⁻¹, of which ~13% is buried and 87% returned to the ocean-atmosphere (Burdige, 2007). The variety of processes controlling the C_{org} burial efficiency (CBE) lead to wide geographical variations in this value, from >70% to <0.3%; (Dunne et al., 2007). Within these processes four distinct mechanisms are available by which tephra deposition enhances CBE (Longman et al., 2019), outlined below.

2.1. Fertilization

Tephra releases nutrients, such as dissolved Iron (Fe), to surface waters when it falls into the oceans, and may thus stimulate biological productivity where availability of nutrients limits phytoplankton growth (Olgun et al., 2011). This process has been studied extensively (see Olgun et al. (2011) and Duggen et al. (2010) for reviews). For example, phytoplankton blooms occurred



Fig. 1. Schematic image detailing the processes which may occur to enhance carbon sequestration and greenhouse gas removal via the addition of volcanic ash to the ocean. 1) The fertilization of phytoplankton blooms in the upper ocean. 2) The release of Mg^{2+} (and Ca^{2+}) ions to the ocean, via the dissolution of minerals contained in the ash. Here we use the dissolution of olivine as an example. Mg^{2+} is released during this process which consumes H^+ ions, thus increasing alkalinity. 3) The transfer of organic carbon from the upper to lower ocean (the biological pump), enhanced by the association of phytoplankton to ash particles. 4) The remineralization of some organic matter during transport through an oxygenated water column. 5) The formation of a volcanic ash layer at the sediment-water interface. 6) Removal of O_2 from organic-rich sediments and formation of anoxic conditions, reducing organic carbon oxidation and remineralization. 7) The release of reactive species of Fe, Mn and Al, available to bind to organic carbon and reduce oxidation.

when the eruption of Kasatochi volcano deposited tephra in the nutrient-poor NE Pacific Ocean (Langmann et al., 2010; Olgun et al., 2011), in the vicinity of the Mariana Islands following the 2003 Anatahan eruption (Lin et al., 2011), after the eruption of Miyakejima in 2000 (Uematsu et al., 2004), and potentially in the Southern Pacific after the eruption of Pinatubo in 1991 (Siegenthaler and Sarmiento, 1993). Other research suggested that the deposition of subduction zone-related ash may play a role in controlling productivity (Duggen et al., 2007). In each case, the increased productivity sequestered CO₂ from the ocean-atmosphere. The 2008 eruption of Kasatochi, for example, led to the export of \sim 0.01 Pg carbon from the upper ocean (Hamme et al., 2010). Carbon was removed from the upper oceans when phytoplankton (and their consumers) settled out of the upper ocean and into the deep ocean (the 'biological pump'; Sarmiento and Gruber, 2006). In addition to accelerating the rate of the biological pump (Fig. 2), tephra deposition in the surface oceans also likely enhances the transport of organic carbon (C_{org}) from surface oceans into deeper water, because plankton debris may become physically associated with the negatively buoyant particles (e.g., Rubin et al., 2011). This process leads to the incorporation of dense, Fe-rich dust (and by analogy tephra) in algal colonies, ballasting the tephra and enhancing sinking rates (Pabortsava et al., 2017).

2.2. Dissolved Oxygen (O_2) consumption

Much of the Fe contained within tephra is in the form of Fe^{II} (Maters et al., 2017), which is highly reactive and rapidly oxidized to Fe^{III} through pore water O_2 consumption. This process also occurs during tephra transport through the water column. Due to the fast settling rates of ballasting tephra, this process is insignificant, leading to the export of a large proportion of Fe^{II} to the sediment (Hembury et al., 2012). Once sufficient tephra



Fig. 2. Examples of Holocene-age tephra in the natural environment. Panel a is an aerial image of cinder cone volcanoes in Lanzarote (Canary Islands), displaying both the extensive tephra fields surrounding them and their proximity to the ocean (Source: Google Earth). Panel b is an example of bedded tephra deposits from Tenerife (also Canary Islands).

(i.e., a layer >0.5 cm thick) accumulates on the ocean floor, oxidation of Fe^{II} in the tephra causes dissolved O₂ concentrations to fall to zero within sediment pore waters, reducing the exposure of the newly deposited C_{org} to oxidative processes (Haeckel et al., 2001; Hembury et al., 2012). Because the oxidation of labile C_{org} in marine sediments critically depends on dissolved O₂ levels in pore water (Hartnett et al., 1998), the presence of tephra likely enhances C_{org} preservation in sediments and further sequesters CO₂ from the ocean-atmosphere system (Fig. 2).

2.3. Colloidal association

Tephra contains high concentrations of reactive Fe, Manganese (Mn) and Aluminium (Al) (Homoky et al., 2011). These reactive phases form stable colloids with C_{org} (Lalonde et al., 2012), inhibiting C_{org} oxidation and enhancing preservation (Fig. 2). Notably, the colloid– C_{org} complexes are sufficiently stable to protect C_{org} from oxidation, even if they are transported from shelf environments to the deep sea (Dunne et al., 2007).

2.4. Authigenic carbonate formation

Tephra is also rich in divalent cations released into sediment pore waters during diagenesis (Gieskes, 1983; Murray et al., 2018). One proposed method of GGR is to increase ocean alkalinity through artificial addition of divalent cations to the ocean (Kheshgi, 1995; Renforth and Henderson, 2017). Within marine sediments, cations released from tephra react with the enhanced alkalinity created by C_{org} oxidation, resulting in the precipitation of authigenic calcium carbonate and calciummagnesium carbonate (Ca(Mg)CO₃). Again, this process effectively locks carbon derived from C_{org} into a form that may be stable for millennia (Schrag et al., 2013).

3. Technology readiness

Addition of tephra to the oceans requires no new technology and is proven feasible with ocean fertilization experiments (Boyd et al., 2007). In mesoscale experiments, the addition of artificial Fe enhances phytoplankton productivity in high nutrient, low chlorophyll environments, by alleviating Fe-related nutrient limitation (Martin and Fitzwater, 1988). Observations of phytoplankton blooms as a result of natural tephra addition to High Nutrient, Low Chlorophyll (HNLC) regions have also confirmed the fertilizing potential of tephra in these environments (Langmann et al., 2010; Olgun et al., 2011). The mechanisms relating to the impact of tephra within seafloor sediments indicate that sequestration of plankton-produced C_{org} may occur over millennial timescales. The amount of tephra deposition required to enable significant levels of carbon sequestration, however, needs assessment.

Most active terrestrial volcanoes produce tephra. Except Australia, it is produced on every continent (Fig. 3). Tephra is among the most common components of global oceanic sediments. It is present in ~25% of Pacific Ocean sediments (Scudder et al., 2016), and with an estimated yearly flux of ash to the Pacific Ocean of 0.13 – 0.22×10^{15} g a⁻¹ (Olgun et al., 2011). Quarrying of recent tephra (optimal for this proposed method) provides aggregate for cement works and road surfaces, but supplies are not limiting. Large recent deposits of basaltic tephra are located at active volcanoes across the globe (Fig. 3). In addition, bentonite clay (diagenetically altered tephra) mining is well-established (Eisenhour and Brown, 2009), so novel, energy-intensive, extraction techniques are not required. Most tephra extraction occurs in open pits using bucket loaders. It would only require sorting of the unconsolidated tephra to grain size $<63 \mu m$, the fraction containing most Fe-rich minerals (Homoky et al., 2011).



Fig. 3. Global map displaying the location of all active (and recently active) volcanoes (red triangles), and of global ports (blue circles) Also indicated is regions in which tephra deposition is considered highly likely (yellow), from Olgun et al. (2011). Most volcanoes are located either on, or close to the ocean, and very few are a significant distance from major ports. Also displayed are the extent of coastal and shelf seas (those which are <200 m in depth), which would be the target for offshore tephra addition.

4. Storage potential and longevity of storage

The gross storage potential is defined here as the increase in CO_2 storage resulting from tephra addition to the oceans. The net storage potential is the gross storage minus the CO_2 requirement of delivering the tephra to the oceans, although the latter value is not included in most methods evaluated in the GGR Royal Society report (Royal Society, 2018).

We provide an estimate of the potential carbon storage using the Peru margin as an example, due to its naturally high primary productivity resulting from upwelling of nutrient-rich Pacific bottom waters (Pennington et al., 2006). The high productivity depletes O_2 in the water column, and an oxygen minimum zone (OMZ) bathing sediment to depths of 400 m (Bohlen et al., 2011). As a result, the sediments contain up to 15% C_{org} below the OMZ (Arthur et al., 1998). CBE increases from 18% on the inner shelf

Table 1

Estimates of gross and net potential carbon dioxide (CO₂) storage.

Gross potential CO ₂ storage	Value	
Typical inner Peru shelf Corg burial rate	79.5 mmol m ⁻² d ^{-1a}	
Yearly Corg flux to sediments	348.52 gC m ⁻² yr ^{-1a}	
CO ₂ equivalent flux to sediments	1277 gCO ₂ m ⁻² yr ^{-1a}	
Typical Peru shelf burial efficiency	18% ^b	
Typical Peru shelf burial efficiency below Oxygen	47 % ^b	
Minimum Zone		
Likely increase in burial efficiency as a result of	29% ^b	
O ₂ depletion		
Resource requirement		
Thickness of tephra applied to sediment	0.5 cm	
Volume of tephra required per square meter	$5 \times 10^3 \text{ cm}^3 \text{ m}^{-2}$	
Mass of tephra (50% porosity)	$6.7 \times 10^3 \text{ g m}^{-2c}$	
Assumed bulk carrier capacity	50,000 t ^d	
Area covered per carrier load	$7.5\times10^{6}~m^{2c}$	
Yearly supply of carbon to this area before	$2.61 \times 10^9 \text{ gC yr}^{-1e}$	
remineralization		
Gross CO ₂ storage per load per year for 29%	2777 t CO ₂ ^f	
reduction of remineralization		
CO ₂ emissions associated		
CO ₂ emitted by 44 tonne truck (per tonne load and	91.2 gCO ₂ t ⁻¹ km ^{-1g}	
km travelled)		
Distance from tephra source to port	30 km ^g	
Number of journeys	$\sim 1140^{g}$	
CO ₂ emitted per 50,000 tonnes tephra transported	136 t CO ₂ ^g	
to port	1. 14	
CO ₂ emitted by carrier (per tonne load and km	$3 \text{ gCO}_2 \text{ t}^{-1} \text{ km}^{-111}$	
travelled)	$150 \dots 10^3 \text{ acc} 1 \text{ Im}^{-1} \text{ h}$	
CO ₂ emitted by 50,000 t bulk carrier	$150 \times 10^{\circ} \text{ gCO}_2 \text{ km}^{\circ}$	
spreading	2000 km ²	
CO ₂ emitted per carrier load	300 t CO ₂ ^h	
Net CO ₂ storage per load	2341 t CO ₂ ^j	

^a Typical CO_2 equivalent fluxes are calculated from the Particulate Organic Carbon (POC) rain rate of Site 1 from the inner Peruvian shelf (Dale et al., 2015).

^b Burial efficiencies are taken from the average carbon burial efficiency of sites 1 and 2 of the inner Peru shelf, with oxygen minimum zone (OMZ) carbon burial efficiencies an average of sites 6-8 (Dale et al., 2015).

 $^{\rm c}$ Mass of tephra with a density of $1400\,kg\,m^3(a$ typical value of tephra; Gudmundsson et al., 2012) and 50 % porosity (Hembury et al., 2012) required per square meter of seafloor.

^d Bulk carrier capacity from (Freese, 2017).

^e Yearly CO₂ equivalent flux to the area covered by tephra.

^f Gross increase in CO₂ preserved in sediment achieved by reducing remineralization by 29%.

^g Estimate of onshore CO₂ emissions, calculated assuming truck size of 44 tonnes (typical articulated lorry load size) an average distance of 30 km from tephra source to port, 1140 journeys necessary to carry 50,000 tonnes of tephra, and using the EDF's green freight calculator (Mathers et al., 2014).

^h Estimate of offshore CO₂ emissions, calculated from values in (Freese, 2017). ^j Net CO₂ storage calculated via subtraction of onshore and offshore CO₂ emissions from gross storage. (with no OMZ) to average of 47% below the OMZ (Dale et al., 2015) due to the reduced oxidant exposure.

Table 1 provides an estimate of the key parameters required to assess gross and net potential storage of C_{org} on the inner shelf through the addition of tephra to these sediments. These calculations assume that reduced oxidant exposure in the sediments resulting from the addition of tephra yields a similar increase in CBE to that resulting from the OMZ. As with all GGR strategies, large uncertainties exist in evaluating these parameters, in particular CBEs. Nevertheless, this exercise is useful for providing a comparison with other GGR strategies with similar uncertainties (Royal Society, 2018) (Table 2).

The calculated net potential removal is \sim 2300 t of CO₂ per 50,000 t of tephra delivered to the oceans per year. The impact of Fe fertilization has a limited duration, but each addition of tephra to the seafloor will impact C_{org} storage for hundreds to thousands of years. Table 1 assumes a tephra layer of 5 mm is required to achieve the calculated increase in CBE. Microelectrode studies of tephra deposited on the seafloor reveal, however, that pore water dissolved O₂ concentrations can fall to <50% of bottom water levels within 1 mm of the sediment-water interface (Hembury et al., 2012). Thus, the dependence of CBE on dissolved O₂ exposure times (Hartnett et al., 1998) would likely lead to enhanced CO₂ storage even under minimal tephra loading. Note also, that the natural CBEs observed on the Peru margin are not typical of shelf sediments. The average CBE in sandy sediments that represent 70% of the global area of continental shelves with water depths <200 m is $\sim 1\%$ (Burdige, 2007). Hence, selection of optimal seafloor sites for large increases in gross potential storage (i.e. large Corg fluxes, but low CBE, delivery of optimum amounts of tephra to achieve maximum increase in Corg preservation), and net potential storage (i.e. close to readily accessible tephra deposits) may yield potential CO₂ storage rates similar to those described in Table 1. In addition, timing tephra loading to coincide with the maximum rate of C_{org} deposition at the sediment surface (e.g. following phytoplankton blooms) would further enhance the scale of C_{org} preservation. During seasonal upwelling, Corg production in surface waters and fluxes to the seafloor are high, but they are largely remineralised in

Table 2

Comparison of removal potential and costs, alongside technology readiness levels (TRLs) of other proposed GGR methods, and enhanced tephra loading. Table adapted from Royal Society (2018), with additional data from this study.

GGR Method	Global CO ₂ removal potential (Gt CO ₂ a ⁻¹)	Cost per tCO ₂ (US\$)	Technology readiness level (TRL)
Afforestation, reforestation and forest management	Afforestation/ reforestation: 3-20, forest management: 1-2	3-30	8-9
Wetland, peatland and coastal habitat restoration	0.4-20	10-100	5-6
Soil carbon sequestration	1-10	10 profit, 3 cost	8-9
Biochar	2-5	0-200	3-6
Ocean fertilization	1-3	10-500	1-5
Enhanced terrestrial weathering	0.5-4	50-500	1-5
Mineral carbonation	-	50-300 (ex situ), 20 (in situ)	3-8
Ocean Alkalinity	40	70-200	2-4
Offshore tephra loading	0.88 ^a	~55	2-4

^a Estimates of global potential for CO₂ removal from tephra loading taken from Longman et al. (2019). There are 9 TRLs describing maturity of technology: TRL1 basic principles, TRL2 invention and research, TRL3 proof of concept, TRL4 bench scale research, TRL5 pilot scale, TRL6 large scale, TRL7 inactive commissioning, TRL8 active commissioning and TRL9 operations.

oxygenated bottom waters, yielding low CBEs (Dale et al., 2015). Timing the delivery of tephra to just after the upwelling period may result in large absolute carbon burial.

5. Resources required

The only processing of the tephra before its use would be light crushing and sorting. Spreading tephra over the ocean would require infrastructure, including loading terminals and adapted ships (i.e. with mechanisms for tephra release), but land transport costs would be low because most volcanoes are located close to the oceans (Fig. 3). Marine vessels require an energy source, but the use of redundant coal barges could reduce CO₂ emissions. Freshly deposited tephra is unconsolidated and can be removed and loaded into transport using conventional excavators and trucks. Compared to other proposed GGR methods, this approach is uncomplicated (Table 2). Ocean fertilization, for example, requires the processing of Fe^{II}-rich solution (Boyd et al., 2000). Other proposals require entirely new approaches to infrastructural development (e.g. carbon capture and storage; Royal Society, 2018). In contrast, offshore tephra addition would require: i) loading of ash onto barges; ii) travel to site of optimal loading as determined via study of seafloor environment and ocean currents (see Boyd et al., 2000); and iii) release of ash in a steady manner along prescribed paths.

6. Environmental benefits and challenges

Studies have invoked ocean-wide changes in bottom water and deep-sea oxygenation levels as cause of benthic foraminiferal extinction at the Cretaceous-Tertiary boundary (e.g., Coccioni and Galeotti, 1994). Hence, it has been suggested that tephra deposition on the seafloor may have a similar impact on benthic communities. Ash fall associated with the 1991 Mt. Pinatubo eruption, for example, caused mass mortality of benthic foraminifers over a large area of the South China Sea (Hess and Kuhnt, 1996), with mortality of all benthic foraminifers at sites receiving 6-8 cm of tephra. In addition, species diversity reduced at sites receiving ~ 2 cm of tephra (Hess et al., 2001; Hess and Kuhnt, 1996). Whereas recovery of the benthic community from the K-T extinction took several thousand years (Coccioni and Galeotti, 1994), recovery of South China Sea sediments was largely complete less than 10 years after tephra deposition, even in the areas that received the thickest deposits (Hess et al., 2001; Kuhnt et al., 2005). Tephra may leach some toxic elements into the water column (Jones and Gislason, 2008). In some circumstances, a drop in the pH of seawater can occur as acids are released (Frogner Kockum et al., 2006; Frogner et al., 2001). Other impacts of tephra deposition are unknown, including potential impacts on planktic, and larger organisms. While large-scale input of tephra to surface waters in the immediate vicinity of volcanoes may be harmful, no evidence exists that the initial mortality is long-lasting or widespread (Hoffmann et al., 2012; Jones and Gislason, 2008; Wall-Palmer et al., 2011). Examples from the geologic record are also available showing that predeposition benthic ostracod species survived deposition of at least 6 cm of tephra (Perrier et al., 2012). Nevertheless, environmental impact assessments would be required to dynamically examine ecosystem responses to enhanced tephra loading.

Extraction of tephra will lead to environmental impacts onshore, but most types of tephra are of low toxicity. Standard procedures can also mitigate the risks, such as cast-back mining adopted during industrial bentonite extraction (Eisenhour and Brown, 2009).

7. Scalability and engineering challenges

As with ocean fertilization through iron addition, tephra fertilization should be scalable without significant cost increases. The financial cost/benefit ratio depends on the scale of operations and the site selection. Typical charter rates for 50,000 t bulk carriers are \sim \$10,000 d⁻¹. A 2000 km deployment at 20 km hr⁻¹ and 2 days loading (UNCTAD, 2018) yields a cost of \sim \$70,000 per deployment. Terrestrial transport costs will increase this estimate. Assuming \sim \$600 d⁻¹ to hire a 44-tonne truck, and ten 60-km round journeys are possible per day, then \sim \$68,000 will be necessary per deployment. Even so, the estimated cost of \$55 per tCO₂ deployed, based on the estimates in Table 1, is an order of magnitude lower than many GGR technologies (Table 2, Royal Society, 2018).

8. Monitoring and evaluation

Laboratory studies can investigate many of the risks to implementation and optimization of tephra dispersal. Both natural (e.g. Hamme et al., 2010; Langmann et al., 2010; Olgun et al., 2011) and laboratory studies (e.g. Hoffmann et al., 2012; Mélançon et al., 2014) have shown that ash fertilizes phytoplankton productivity, so the primary risk is that the approach does not sufficiently raise CBEs. This question may be tackled by undertaking experiments to measure C_{org} degradation rates under various conditions of tephra loading and over a range of sediment types. Laboratory studies can also investigate the responses of benthic biota to tephra loading (cf. Brown et al., 2017). Once laboratory tests are completed, small-scale *in situ* studies would be necessary to test the concept, with several years of monitoring.

9. Social factors

Natural volcanic processes transport millions of tonnes of tephra to the oceans every year, with an estimated 2.2×10^8 t yr deposited in the Pacific Ocean alone (Olgun et al., 2011). Hence, unlike most other proposed GGR interventions, the mechanism outlined here augments a naturally occurring process. Moreover, the addition of tephra to the ocean does not require changes to land use, such as reforestation of agricultural land. Freshly deposited tephra frequently creates a barren landscape in volcanic areas, and following eruptions, governments may have to invest funds to clear tephra from local infrastructure. Hence, tephra deposits are a problem that requires a solution. Nevertheless, public opinion regarding GGR initiatives is likely mixed (Royal Society, 2018). Public engagement to communicate the positive aspects of the approach would be important.

10. Policy factors

'Dumping' material in international waters is currently banned under the London Convention and Protocol. The restriction of tephra loading to shallow waters within territorial waters of individual nations, however, is less clear. Further clarification is required on this issue.

11. Conclusions

In summary, this article has outlined how artificial addition of tephra to the ocean may lead to C_{org} sequestration and GGR, and its positive and negative aspects. The advantages of tephra dispersal in this regard are:

- tephra addition to the oceans is a natural process.
- tephra is widely distributed around the world.
- the technology is simple and readily available.

- no repurposing of valuable land resources is required.
- tephra is not a scarce resource.

The key factors required to transform this hypothesis into a potentially viable GGR method are:

- optimization to achieve maximum GGR for minimal tephra loading.
- identification of optimal oceanic sites.
- determination of potential ecological impacts.
- assessment of prime locations for sourcing tephra and optimal approaches for transporting tephra to the ocean.
- assessment of the scalability, economics and policy issues are required for GGR to have a significant impact.

This analysis therefore suggests that the addition of tephra to the oceans deserves further study, as part of the palette of strategies to remove greenhouse gases.

Declaration of Competing Interest

The authors report no declarations of interest.

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References

- Arthur, M.A., Dean, W.E., Laarkamp, K., 1998. Organic carbon accumulation and preservation in surface sediments on the Peru margin. Chem. Geol. 152, 273– 286. doi:http://dx.doi.org/10.1016/S0009-2541(98)00120-X.
- Bastin, J.-F., Finegold, Y., Garcia, C., Mollicone, D., Rezende, M., Routh, D., Zohner, C. M., Crowther, T.W., 2019. The global tree restoration potential. Science 365, 76– 79. doi:http://dx.doi.org/10.1126/SCIENCE.AAX0848.
- Bohlen, L., Dale, A.W., Sommer, S., Mosch, T., Hensen, C., Noffke, A., Scholz, F., Wallmann, K., 2011. Benthic nitrogen cycling traversing the Peruvian oxygen minimum zone. Geochim. Cosmochim. Acta 75, 6094–6111. doi:http://dx.doi. org/10.1016/j.gca.2011.08.010.
- Boyd, P.W., Jickells, T., Law, C.S., Blain, S., Boyle, E.A., Buesseler, K.O., Coale, K.H., Cullen, J.J., de Baar, H.J.W., Follows, M., Harvey, M., Lancelot, C., Levasseur, M., Owens, N.P.J., Pollard, R., Rivkin, R.B., Sarmiento, J., Schoemann, V., Smetacek, V., Takeda, S., Tsuda, A., Turner, S., Watson, A.J., 2007. Mesoscale iron enrichment experiments 1993-2005: synthesis and future directions. Science 315, 612–617. doi:http://dx.doi.org/10.1126/science.1131669.
- Boyd, P.W., Watson, A.J., Law, C.S., Abraham, E.R., Trull, T., Murdoch, R., Bakker, D.C.E., Bowie, A.R., Buesseler, K.O., Chang, H., Charette, M., Croot, P., Downing, K., Frew, R., Gall, M., Hadfield, M., Hall, J., Harvey, M., Jameson, G., LaRoche, J., Liddicoat, M., Ling, R., Maldonado, M.T., McKay, R.M., Nodder, S., Pickmere, S., Pridmore, R., Rintoul, S., Safi, K., Sutton, P., Strzepek, R., Tanneberger, K., Turner, S., Waite, A., Zeldis, J., 2000. A mesoscale phytoplankton bloom in the polar Southern Ocean stimulated by iron fertilization. Nature 407, 695–702. doi:http://dx.doi.org/ 10.1038/35037500.
- Brown, A., Thatje, S., Hauton, C., 2017. The Effects of Temperature and Hydrostatic Pressure on Metal Toxicity: Insights into Toxicity in the Deep Sea. Environ. Sci. Technol. 51, 10222–10231. doi:http://dx.doi.org/10.1021/acs.est.7b02988.
- Burdige, D.J., 2007. Preservation of organic matter in marine sediments: Controls, mechanisms, and an imbalance in sediment organic carbon budgets? Chem. Rev. 107, 467–485. doi:http://dx.doi.org/10.1021/cr050347q.
- Coccioni, R., Galeotti, S., 1994. K-T boundary extinction: geologically instantaneous or gradual event? Evidence from deep-sea benthic foraminifera. Geology 22, 779–782. doi:http://dx.doi.org/10.1130/0091-7613(1994)022<0779: KTBEGI>2.3.CO;2.
- Dale, A.W., Sommer, S., Lomnitz, U., Montes, I., Treude, T., Liebetrau, V., Gier, J., Hensen, C., Dengler, M., Stolpovsky, K., Bryant, L.D., Wallmann, K., 2015. Organic carbon production, mineralisation and preservation on the Peruvian margin. Biogeosciences 12, 1537–1559. doi:http://dx.doi.org/10.5194/bg-12-1537-2015.
- Duggen, S., Croot, P., Schacht, U., Hoffmann, L., 2007. Subduction zone volcanic ash can fertilize the surface ocean and stimulate phytoplankton growth: Evidence from biogeochemical experiments and satellite data. Geophys. Res. Lett. 34, L01612 doi:http://dx.doi.org/10.1029/2006GL027522.

- Duggen, S., Olgun, N., Croot, P., Hoffmann, L., Dietze, H., Delmelle, P., Teschner, C., Skolen, A.P.M., 2010. The role of airborne volcanic ash for the surface ocean biogeochemical iron-cycle: a review. Biogeosciences .
- Dunne, J.P., Sarmiento, J.L., Gnanadesikan, A., 2007. A synthesis of global particle export from the surface ocean and cycling through the ocean interior and on the seafloor. Global Biogeochem. Cycles 21. doi:http://dx.doi.org/10.1029/ 2006GB002907 n/a-n/a.
- Eisenhour, D.D., Brown, R.K., 2009. Bentonite and its impact on modern life. Elements doi:http://dx.doi.org/10.2113/gselements.5.2.83.
- Frogner Kockum, P.C., Herbert, R.D., Gislason, S.R., 2006. A diverse ecosystem response to volcanic aerosols. Chem. Geol. 231, 57–66. doi:http://dx.doi.org/ 10.1016/j.chemgeo.2005.12.008.
- Frogner, P., Reynir Gíslason, S., Óskarsson, N., 2001. Fertilizing potential of volcanic ash in ocean surface water. Geology 29, 487. doi:http://dx.doi.org/10.1130/ 0091-7613(2001)029<0487:FPOVAI>2.0.CO;2.
- Ghouleh, Z., Guthrie, R.I.L., Shao, Y., 2017. Production of carbonate aggregates using steel slag and carbon dioxide for carbon-negative concrete. J. CO2 Util. 18, 125–138. doi:http://dx.doi.org/10.1016/j.jcou.2017.01.009.
- Gieskes, J.M., 1983. The chemistry of interstitial waters of deep sea sediments: interpretation of deep sea drilling data. In: Riley, J.P., Chester, R. (Eds.), Chemical Oceanography. Academic Press, London, pp. 221–269.
- Gudmundsson, M.T., Thordarson, T., Höskuldsson, Á., Larsen, G., Björnsson, H., Prata, F.J., Oddsson, B., Magnússon, E., Högnadóttir, T., Petersen, G.N., Hayward, C.L., Stevenson, J.A., Jónsdóttir, I., 2012. Ash generation and distribution from the April-May 2010 eruption of Eyjafjallajökull. Iceland. Sci. Rep. 2, 572. doi:http:// dx.doi.org/10.1038/srep00572.
- Haeckel, M., van Beusekom, J., Wiesner, M.G., König, I., 2001. The impact of the 1991 Mount Pinatubo tephra fallout on the geochemical environment of the deep-sea sediments in the South China Sea. Earth Planet. Sci. Lett. 193, 151–166. doi: http://dx.doi.org/10.1016/S0012-821X(01)00496-4.
- Hamme, R.C., Webley, P.W., Crawford, W.R., Whitney, F.A., DeGrandpre, M.D., Emerson, S.R., Eriksen, C.C., Giesbrecht, K.E., Gower, J.F.R., Kavanaugh, M.T., Peña, M.A., Sabine, C.L., Batten, S.D., Coogan, L.A., Grundle, D.S., Lockwood, D., 2010. Volcanic ash fuels anomalous plankton bloom in subarctic northeast Pacific. Geophys. Res. Lett. 37 doi:http://dx.doi.org/10.1029/2010GL044629 n/a-n/a.
- Hartnett, H.E., Keil, R.G., Hedges, J.I., Devol, A.H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature 391, 572–575. doi:http://dx.doi.org/10.1038/35351.
- Haszeldine, R.S., Flude, S., Johnson, G., Scott, V., 2018. Negative emissions technologies and carbon capture and storage to achieve the Paris Agreement Commitments. Philos. Trans. R. Soc. A Math. Eng. Sci. 376, 20160447 doi:http://dx.doi.org/10.1098/rsta.2016.0447.
- Hembury, D.J., Palmer, M.R., Fones, G.R., Mills, R.A., Marsh, R., Jones, M.T., 2012. Uptake of dissolved oxygen during marine diagenesis of fresh volcanic material. Geochim. Cosmochim. Acta 84, 353–368. doi:http://dx.doi.org/10.1016/J. GCA.2012.01.017.
- Hess, S., Kuhnt, W., 1996. Deep-sea benthic foraminiferal recolonization of the 1991 Mt. Pinatubo ash layer in the South China Sea. Mar. Micropaleontol. 28, 171–197. doi:http://dx.doi.org/10.1016/0377-8398(95)00080-1.
- Hess, S., Kuhnt, W., Hill, S., Kaminski, M.A., Holbourn, A., de Leon, M., 2001. Monitoring the recolonization of the Mt Pinatubo 1991 ash layer by benthic foraminifera. Mar. Micropaleontol. 43, 119–142. doi:http://dx.doi.org/10.1016/ S0377-8398(01)00025-1.
- Hoffmann, L.J., Breitbarth, E., Ardelan, M.V., Duggen, S., Olgun, N., Hassellöv, M., Wängberg, S.-Å., 2012. Influence of trace metal release from volcanic ash on growth of Thalassiosira pseudonana and Emiliania huxleyi. Mar. Chem. 132– 133, 28–33. doi:http://dx.doi.org/10.1016/J.MARCHEM.2012.02.003.
- Homoky, W.B., Hembury, D.J., Hepburn, L.E., Mills, R.A., Statham, P.J., Fones, G.R., Palmer, M.R., 2011. Iron and manganese diagenesis in deep sea volcanogenic sediments and the origins of pore water colloids. Geochim. Cosmochim. Acta 75, 5032–5048. doi:http://dx.doi.org/10.1016/J.GCA.2011.06.019.
- IPCC, 2018. Summary for Policymakers. In: Masson-Delmotte, V., Zhai, P., Pörtner, H. O., Roberts, D., Skea, J., Shukla, P.R., Pirani, A., Chen, Y., Connors, S., Gomis, M., Lonnoy, E., Matthews, J.B.R., Moufouma-Okia, W., Péan, C., Pidcock, R., Reay, N., Tignor, M., Waterfield, T., Zhou, X. (Eds.), Global Warming of 1.5°C. An IPCC Special Report on the Impacts of Global Warming of 1.5°C above Pre-Industrial Levels and Related Global Greenhouse Gas Emission Pathways, in the Context of Strengthening the Global Response to the Threat of Climate Change. World Meteorological Organization, Geneva doi:http://dx.doi.org/10.1017/CB09781107415324 p. 32.
- Jones, M.T., Gislason, S.R., 2008. Rapid releases of metal salts and nutrients following the deposition of volcanic ash into aqueous environments. Geochim. Cosmochim. Acta 72, 3661–3680. doi:http://dx.doi.org/10.1016/j. gca.2008.05.030.
- Kheshgi, H.S., 1995. Sequestering atmospheric carbon dioxide by increasing ocean alkalinity. Energy 20, 915–922. doi:http://dx.doi.org/10.1016/0360-5442(95) 00035-F.
- Kuhnt, W., Hess, S., Holbourn, A., Paulsen, H., Salomon, B., 2005. The impact of the 1991 Mt. Pinatubo eruption on deep-sea foraminiferal communities: a model for the Cretaceous–Tertiary (K/T) boundary? Palaeogeogr. Palaeoclimatol. Palaeoecol. 224, 83–107. doi:http://dx.doi.org/10.1016/J.PALAEO.2005.03.042.
- Lalonde, K., Mucci, A., Ouellet, A., Gélinas, Y., 2012. Preservation of organic matter in sediments promoted by iron. Nature 483, 198–200. doi:http://dx.doi.org/ 10.1038/nature10855.
- Langmann, B., Zakšek, K., Hort, M., Duggen, S., 2010. Volcanic ash as fertiliser for the surface ocean. Atmos. Chem. Phys..

- Lin, I.I., Hu, C., Li, Y.H., Ho, T.Y., Fischer, T.P., Wong, G.T.F., Wu, J., Huang, C.W., Chu, D. A., Ko, D.S., Chen, J.P., 2011. Fertilization potential of volcanic dust in the lownutrient low-chlorophyll western North Pacific subtropical gyre: Satellite evidence and laboratory study. Global Biogeochem. Cycles 25. doi:http://dx.doi. org/10.1029/2009GB003758.
- Lomax, G., Workman, M., Lenton, T., Shah, N., 2015. Reframing the policy approach to greenhouse gas removal technologies. Energy Policy 78, 125–136. doi:http://dx. doi.org/10.1016/j.enpol.2014.10.002.
- Longman, J., Palmer, M.R., Gernon, T.M., Manners, H.R., 2019. The role of tephra in enhancing organic carbon preservation in marine sediments. Earth-Sci. Rev. doi: http://dx.doi.org/10.1016/J.EARSCIREV.2019.03.018.
- Martin, J.H., Fitzwater, S.E., 1988. Iron deficiency limits phytoplankton growth in the north-east pacific subarctic. Nature 331, 341–343. doi:http://dx.doi.org/ 10.1038/331341a0.
- Maters, E.C., Delmelle, P., Gunnlaugsson, H.P., 2017. Controls on iron mobilisation from volcanic ash at low pH: insights from dissolution experiments and Mössbauer spectroscopy. Chem. Geol. 449, 73–81. doi:http://dx.doi.org/ 10.1016/J.CHEMGEO.2016.11.036.
- Mathers, J., Craft, E., Norsworthy, M., Wolfe, C., 2014. Green Freight Handbook. Enironmental Defense Fund, New York.
- Matter, J.M., Stute, M., Snæbjörnsdottir, S.Ó., Oelkers, E.H., Gislason, S.R., Aradottir, E. S., Sigfusson, B., Gunnarsson, I., Sigurdardottir, H., Gunnlaugsson, E., Axelsson, G., Alfredsson, H.A., Wolff-Boenisch, D., Mesfin, K., Fernandez de la, Reguera, Taya, D., Hall, J., Dideriksen, K., Broecker, W.S., 2016. Rapid carbon mineralization for permanent disposal of anthropogenic carbon dioxide emissions. Science 352, 1312–1314. doi:http://dx.doi.org/10.1126/science. aad8132.
- Mélançon, J., Levasseur, M., Lizotte, M., Delmelle, P., Cullen, J., Hamme, R.C., Peña, A., Simpson, K.G., Scarratt, M., Tremblay, J.-É.É., Zhou, J., Johnson, K., Sutherland, N., Arychuk, M., Nemcek, N., Robert, M., 2014. Early response of the northeast subarctic Pacific plankton assemblage to volcanic ash fertilization. Limnol. Oceanogr. 59, 55–67. doi:http://dx.doi.org/10.4319/ lo.2014.59.1.0055.
- Murray, N.A., McManus, J., Palmer, M.R., Haley, B., Manners, H., 2018. Diagenesis in tephra-rich sediments from the Lesser Antilles Volcanic Arc: pore fluid constraints. Geochim. Cosmochim. Acta 228, 119–135. doi:http://dx.doi.org/ 10.1016/J.GCA.2018.02.039.
- Olgun, N., Duggen, S., Croot, P.L., Delmelle, P., Dietze, H., Schacht, U., Óskarsson, N., Siebe, C., Auer, A., Garbe-Schönberg, D., 2011. Surface ocean iron fertilization: The role of airborne volcanic ash from subduction zone and hot spot volcanoes and related iron fluxes into the Pacific Ocean. Global Biogeochem. Cycles 25 doi: http://dx.doi.org/10.1029/2009GB003761 n/a-n/a.
- Pabortsava, K., Lampitt, R.S., Benson, J., Crowe, C., McLachlan, R., Le Moigne, F.A.C., Mark Moore, C., Pebody, C., Provost, P., Rees, A.P., Tilstone, G.H., Woodward, E.M. S., 2017. Carbon sequestration in the deep Atlantic enhanced by Saharan dust. Nat. Geosci. 10, 189–194. doi:http://dx.doi.org/10.1038/ngeo2899.

- Pennington, J.T., Mahoney, K.L., Kuwahara, V.S., Kolber, D.D., Calienes, R., Chavez, F.P., 2006. Primary production in the eastern tropical Pacific: a review. Prog. Oceanogr. 69, 285–317. doi:http://dx.doi.org/10.1016/j.pocean.2006.03.012.
- Perrier, V., Meidla, T., Tinn, O., Ainsaar, L., 2012. Biotic response to explosive volcanism: Ostracod recovery after Ordovician ash-falls. Palaeogeogr. Palaeoclimatol. Palaeoecol 365–366, 166–183. doi:http://dx.doi.org/10.1016/j. palaeo.2012.09.024.
- Ramage, M.H., Burridge, H., Busse-Wicher, M., Fereday, G., Reynolds, T., Shah, D.U., Wu, G., Yu, L., Fleming, P., Densley-Tingley, D., Allwood, J., Dupree, P., Linden, P.F., Scherman, O., 2017. The wood from the trees: The use of timber in construction. Renew. Sustain. Energy Rev. doi:http://dx.doi.org/10.1016/j.rser.2016.09.107.
- Renforth, P., Henderson, G., 2017. Assessing ocean alkalinity for carbon sequestration. Rev. Geophys. 55, 636–674. doi:http://dx.doi.org/10.1002/ 2016RG000533.
- Royal Society, T., 2018. Greenhouse gas removal. R.Soc. Lond..
- Rubin, M., Berman-Frank, I., Shaked, Y., 2011. Dust- and mineral-iron utilization by the marine dinitrogen-fixer trichodesmium. Nat. Geosci. 4, 529–534. doi:http:// dx.doi.org/10.1038/ngeo1181.
- Sarmiento, J.L., Gruber, N., 2006. Ocean biogeochemical dynamics. Princeton University Press.
- Schrag, D.P., Higgins, J.A., Macdonald, F.A., Johnston, D.T., 2013. Authigenic carbonate and the history of the global carbon cycle. Science 339, 540–543. doi:http://dx. doi.org/10.1126/science.1229578.
- Scudder, R.P., Murray, R.W., Schindlbeck, J.C., Kutterolf, S., Hauff, F., Underwood, M. B., Gwizd, S., Lauzon, R., McKinley, C.C., 2016. Geochemical approaches to the quantification of dispersed volcanic ash in marine sediment. Prog. Earth Planet. Sci. 3, 1. doi:http://dx.doi.org/10.1186/s40645-015-0077-y.
- Siegenthaler, U., Sarmiento, J.L., 1993. Atmospheric carbon dioxide and the ocean. Nature doi:http://dx.doi.org/10.1038/365119a0.
- Steffen, W., Rockström, J., Richardson, K., Lenton, T.M., Folke, C., Liverman, D., Summerhayes, C.P., Barnosky, A.D., Cornell, S.E., Crucifix, M., Donges, J.F., Fetzer, I., Lade, S.J., Scheffer, M., Winkelmann, R., Schellnhuber, H.J., 2018. Trajectories of the Earth System in the Anthropocene. Proc. Natl. Acad. Sci. 115, 8252–8259. doi:http://dx.doi.org/10.1073/pnas.1810141115.
- Tollefson, J., 2018. IPCC says limiting global warming to 1.5 °C will require drastic action. Nature 562, 172–173. doi:http://dx.doi.org/10.1038/d41586-018-06876-2.
- Uematsu, M., Toratani, M., Kajino, M., Narita, Y., Senga, Y., Kimoto, T., 2004. Enhancement of primary productivity in the western North Pacific caused by the eruption of the Miyake-jima Volcano. Geophys. Res. Lett. 31 doi:http://dx. doi.org/10.1029/2003gl018790 n/a-n/a.
- UNCTAD, 2018. Review of Maritime Transport. United Nations, New York and Geneva.
- Wall-Palmer, D., Jones, M.T., Hart, M.B., Fisher, J.K., Smart, C.W., Hembury, D.J., Palmer, M.R., Fones, G.R., 2011. Explosive volcanism as a cause for mass mortality of pteropods. Mar. Geol. 282, 231–239. doi:http://dx.doi.org/10.1016/J. MARGE0.2011.03.001.