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Anja Schmidt[1,*], Richard A. Skeffington[2], Thorvaldur Thordarson[3,4], Stephen Self[5], Piers M. Forster[1], Alexandru Rap[1], Andy Ridgwell[6,9], David Fowler[7], Marjorie Wilson[1], Graham W. Mann[8], Paul B. Wignall[1], and Kenneth S. Carslaw[1]

[1]School of Earth and Environment, University of Leeds, Leeds, UK
[2]Department of Geography and Environmental Science, University of Reading, UK
[3]Faculty of Earth Sciences, University of Iceland, Askja, Sturlugata 7, IS101 Reykjavik, Iceland
[4]School of GeoSciences, Grant Institute, University of Edinburgh, UK
[5]Department of Earth and Environmental Sciences, The Open University, Milton Keynes, UK
[6]School of Geographical Sciences, University of Bristol, University Road, Bristol BS8 1SS, UK
[7]Natural Environment Research Council (NERC), Centre for Ecology and Hydrology, Penicuik, Midlothian, UK
[8]National Centre for Atmospheric Science, University of Leeds, Leeds, LS2 9JT, UK
[9]Department of Earth Sciences, University of California at Riverside, Riverside, CA, USA

***Corresponding author:**
Anja Schmidt
School of Earth and Environment
University of Leeds
Email: a.schmidt@leeds.ac.uk
Phone: +44(0) 113 34 36429

Abstract

Several biotic crises during the past 300 million years have been linked to episodes of continental flood basalt volcanism, and in particular to the release of massive quantities of magmatic sulphur gas species. Flood basalt provinces were typically formed by numerous individual eruptions, each lasting years to decades. However, the environmental impact of these eruptions may have been limited by the occurrence of quiescent periods that lasted hundreds to thousands of years. Here we use a global aerosol model to quantify the sulphur-induced environmental effects of individual, decade-long flood basalt eruptions representative of the Columbia River Basalt Group, 16.5–14.5 million years ago, and the Deccan Traps, 65 million years ago. For a decade-long eruption of Deccan scale, we calculate a decadal-mean reduction in global surface temperature of 4.5 K, which would recover within 50 years after an eruption ceased unless climate feedbacks were very di_erent in deep-time climates. Acid mists and fogs could have caused immediate damage to vegetation in some regions, but acid-sensitive land and marine ecosystems were well-bu_ered against volcanic sulphur deposition effects even during century-long eruptions. We conclude that magmatic sulphur from flood basalt eruptions would have caused a biotic crisis only if eruption frequencies and lava discharge rates had been high and sustained for several centuries at a time.

Main Text

A CFB province producing total magma volumes of 0.1-4.0 million km^3 is typically formed by hundreds to thousands of individual and volumetrically large (on the order of 1000 km^3) eruptions, each separated by highly uncertain hiatus periods with the overall emplacement taking place on a timescale of 100,000s of years[10,11]. These eruptions far exceed even the largest historic eruptions in terms of lava volume, duration and amount of gases emitted into the atmosphere[6-8]. Intriguingly, the timing of the emplacement of four out of five CFB provinces in the last 300 Myr coincides with periods of high extinction rates of species[1,2,4], leading to a suggestion of a causal link[1-4,7,10]. Yet after more than four decades of research this hypothesis remains equivocal and contested[3,12].

It is well known from observations of historic eruptions that emissions of magmatic sulfur dioxide (SO_2) and its oxidation products, such as sulfuric acid aerosol, are the main agents able to induce profound climatic and environmental change[13,14]. Consequently, climatic cooling and environmental acidification due to the emission and deposition of large quantities of magmatic sulfur are the two most commonly proposed causal agents causing global biotic crises during periods of CFB volcanism[3,5]. However, no previous study took into account the buffering capacities of soils and other environments when assessing the effects of acid rain, hence this causal link remains elusive and unquantified. Similarly, previous studies either relied on extrapolations of the surface cooling caused by explosive volcanism[3,5], or used simple relationships between the mass of sulfuric acid aerosol particles generated from SO_2 and its cooling effects[6]. Both approaches do not account for two key factors that may reduce the aerosol-induced cooling: limited oxidant availability, which affects SO_2 conversion to acidic aerosol, and particle growth to large sizes, which reduces the particle light-scattering efficiency and shortens particle lifetime in the atmosphere due to sedimentation of particles. While the relative importance of these processes has been quantified for short-lived explosive eruptions[15-17], this is not the case for CFB eruptions, which differ fundamentally in terms of eruption style, and height and duration of SO_2 emissions (Extended Data Figure 1).

To constrain the environmental effects and consequences for habitability induced by

magmatic sulfur emissions from individual decade- to century-long CFB eruptions we use numerical models including a global aerosol model, GLOMAP[18], a soil and freshwater acidification model, MAGIC[19], and an Earth system model, GENIE[20] (Online Methods). Our model experiments are based on the well-constrained 14.7 Ma (mid-Miocene) Roza eruption emplaced in the youngest CFB province on Earth, the Columbia River Basalt Group, and individual eruptions from the 65 Ma Deccan Traps, which coincided with the Cretaceous-Paleogene (K-Pg) mass extinction. The Roza eruption produced a total volume of 1300 km^3 and is the only individual CFB eruption with a constraint on both duration and emission fluxes of about 1200 Tg of SO_2 per annum for a decade or two[6]. Magma volumes in excess of 1000 km^3 for individual eruptions in the Deccan Traps have been proposed[8], but individual eruption durations are unknown. Plume rise modeling for basaltic fissure eruptions suggests gas emissions to altitudes of 9-13 km[21,22], corresponding to the upper troposphere or lower stratosphere depending on latitude. We simulate a 'Roza-scale' eruption by emitting 1200 Tg of SO_2 per year at 9-13 km altitude at 120°W, 45°N, and a 'Deccan-scale' eruption by emitting 2400 Tg of SO_2 per year at 135°E, 21°S. The latter is considered an upper bound for the SO_2 emitted by individual CFB-scale eruptions, assuming either greater mean lava discharge rates or that more than one flow field was active at any one time (Online Methods, Extended Data Table 1).

We find that the net climate effect of magmatic sulfur emitted by individual CFB eruptions is to reduce surface temperatures (Figure 1), resulting from the combined effects of acidic aerosol particles and SO_2. The increase in the former exerts a negative radiative forcing, cooling the climate via both aerosol direct and indirect forcing (the latter due to changes in cloud reflectance caused by changes in cloud droplet concentrations). By contrast, any unoxidized SO_2 acts as a greenhouse gas and absorbs ultraviolet radiation, which warms the climate (positive forcing). We show that the relationship between the amount of SO_2 emitted and the magnitude of these two opposing climate forcings is highly non-linear. For example, a 20-fold increase in SO_2 release leads to less than a 6-fold increase in negative forcing (Extended Data Table 4). In our model, this non-linearity is caused by the combination of limited aerosol production and differences in particle growth with increasing SO_2 emissions, but also the striking saturation of the aerosol indirect forcing, and the offset of the negative aerosol forcings by the positive forcing from SO_2 (Extended Data Table 4). For instance, we find that for a Roza-scale eruption only 60%

of the emitted SO_2 eventually forms volcanic aerosol (~1490 Tg of sulfuric acid aerosol per year) because of the sustained depletion of atmospheric oxidants in our model, in particular the hydroxyl radical, OH (Extended Data Table 2). The saturation of the indirect forcing is caused by increasing aerosol concentrations, effectively decreasing the sensitivity of cloud reflectance to changes in aerosol loading[18]. A previous study on explosive super-eruptions also suggested that the positive greenhouse gas forcing from volcanic SO_2 may offset the aerosol cooling[16]. However, the forcing by SO_2 is not normally considered in climate model simulations of volcanic eruptions or their geo-engineering analogues. Yet we show that for a Deccan-scale eruption the SO_2 forcing (+1.4 W m^{-2}) offsets about 8% of the global mean aerosol forcing (-17.6 W m^{-2}; Extended Data Table 4).

Our simulations show that the frequency and duration of individual CFB eruptions as well as hiatus periods strongly affect the severity and longevity of the climatic effects. For a proposed individual eruption duration of a decade[6], the peak global mean surface temperature reduction is 6.6 K (90% confidence interval of -7.7 K to -5.7 K) by the end of year 10 for a Deccan-scale eruption (Figure 1 and Online Methods). For context, simulations of the 74 ka Toba eruption suggest peak global mean temperature changes of between -3.5 K and -10 K[17,23]. Assuming present-day, century-scale climate feedbacks and ignoring potential carbon-cycle feedbacks, the mean temperature changes during the first decade are also substantial: -3.0 K for a Roza-scale eruption and -4.5 K for a Deccan-scale eruption. However, the cooling from decade-long eruptions is short-lived and could have been sustained only if eruptions occurred in quick succession without hiatuses longer than a decade, or if an individual eruption lasted far longer than 150 years so that temperature changes reach equilibrium (Figure 1). Our estimates are at the lower end of previous estimates of global mean surface temperature reductions for 14.7 Ma Roza[6]. For the K-Pg, the survival of ectothermic tetrapods at mid-latitudes (but not at high-latitudes and with the exception of lizards)[12], supports our findings of surface temperatures potentially dropping and fluctuating significantly on decadal timescales, which are, however, by no means ‘catastrophic’.

Markedly, we find that the chemical and microphysical processes controlling the magnitude of climatic impacts differ fundamentally between CFB and explosive eruptions due to

their differences in eruption style (Extended Data Figure 1). In our simulations, a sustained release of SO_2 into the upper troposphere/lower stratosphere during a CFB eruption provides a sustained source of sulfuric acid vapour, albeit limited by oxidant availability. The sulfuric acid nucleates to form many tiny particles less than 10 nm in diameter, which grow by condensation and coagulation to diameters of between 0.3 to 0.8 μm, depending on eruption scale. Further growth is limited because the high removal rates in the troposphere limit the particle lifetimes to about two weeks (Extended Data Table 2). Conversely, for large explosive eruptions that inject SO_2 into the stratosphere, particles typically have time to grow to diameters much larger than 0.8 μm[15,17] due to differences in atmospheric circulation that result in slow removal rates in the stratosphere. Importantly, at particle diameters between 0.4 μm and 0.8 μm sulfuric acid aerosol particles scatter more incoming solar radiation back to space than at larger sizes and particle removal via gravitational settling is insignificant. Bearing in mind that the temperature changes induced by CFB eruptions are limited, we find that, the aerosol optical depth (AOD, a dimensionless measure of the degree to which the transmission of light is reduced due to absorption and scattering by aerosol particles) and therefore climate are perturbed more efficiently for CFB eruptions, even though the generated aerosol burden per unit mass of SO_2 emitted is lower than for explosive eruptions (Extended Data Table 3).

Environmental acidification can affect ecosystems either through direct exposure to acidic species, or indirectly through the acidification of soils and stream waters. Acidification has been suggested to have contributed to the K-Pg mass extinction[3,5,24] and the end-Permian mass extinction at 252 Ma[9]. We can use modern understanding of acidification mechanisms and damage thresholds for ecosystems to evaluate the probability of damage to sensitive soils, vegetation and waters in the past. Acidification mechanisms are encapsulated in the widely-used MAGIC model[25] and damage thresholds are represented by the deposition and concentration standards (critical loads and critical levels) used in European policymaking[26-28]. Ecosystems with an average acid sensitivity have a critical load of 1 $kmol_c\ ha^{-1}\ a^{-1}$, assuming this load is exceeded for at least a century[27]. For both eruption scenarios, this critical load is exceeded in an area of about 30 degrees latitude relative to the eruption site with peak zonal-mean loads of 5.5 $kmol_c\ ha^{-1}\ a^{-1}$ for the Deccan-scale eruption (Figure 2a). At first sight this suggests that soil acidification would be intense and widespread, but detailed modelling using MAGIC[25] shows

that such high deposition rates would have had to be maintained continuously for centuries to cause significant acidification and damage in most cases (Table 1 and Online Methods). Therefore, we conclude that soil acidification due to volcanic sulfur deposition cannot directly explain global-scale mass extinction events, which is in contrast to previous studies that neglected the acid buffering capacities of soils and other environments[3,5,9]. In detail, sulfur deposition leads to a set of acidification responses: the soil base saturation and the ratio of Ca^{2+} to Al in the soil solution decline, stream pH drops and toxic inorganic monomeric aluminum (Al^{3+}) concentrations increase. These changes were used as acidification criteria and quantified in Table 1 for different deposition magnitudes (based on Figure 2a) and durations (Online Methods). We find that an acid-sensitive podzol, which we considered a representative sensitive soil type for the mid-Miocene and Late Cretaceous, can tolerate several centuries of continued deposition rates of 3 $kmol_c\ ha^{-1}\ a^{-1}$. Although for continued deposition rates of 5 $kmol_c\ ha^{-1}\ a^{-1}$ the ratio of Ca^{2+} to Al in the soil solution drops below the threshold at which damage may occur after century-long deposition, the recovery is rapid, occurring within decades once volcanic activity has ceased. Only for extreme soil types, such as the acid-sensitive, weathered oxisol, is soil-mediated ecosystem damage possible. These soils were, however, not distributed widely enough during the Late Cretaceous to allow for global mass extinctions.

Acidification of stream waters to a degree that acute effects on fish and amphibians occur[29] only takes place for the shallow oxisol after almost 60 years of continued deposition rates of 3 $kmol_c\ ha^{-1}\ a^{-1}$ (reaching an equilibrium pH of 3.94) and for the 1-m deep podzol after almost 200 years of deposition rates of 5 $kmol_c\ ha^{-1}\ a^{-1}$ (reaching an equilibrium pH of 3.95) (Table 1 and Extended Data Figure 2). Figure 2a shows that these effects would be limited spatially and by the soil type. Our results are generally supported by the vertebrate fossil record and survival patterns of pH-sensitive species such as alligators, turtles and frogs, which experienced only small reductions in their numbers at the K-Pg[12,30], constraining the pH of freshwaters to not less than four[29] (Table 1).

The impact of sulfur deposition on seawater chemistry and ‘ocean acidification’ from decade-long volcanic eruptions is also negligible (Online Methods). At Deccan-scale rates, we calculate that volcanic sulfur deposition would have needed to proceed continuously for almost

three millennia to drive a surface ocean pH decline comparable to the current anthropogenic perturbation of ~0.1 pH units (Extended Data Table 5).

Although for the Deccan-scale scenario peak SO_2 ground-level concentrations are comparable to those experienced in the 1970s in Europe due to anthropogenic pollution, critical levels[29] for ground-level SO_2 are not exceeded on a scale sufficient to cause global-scale foliar damage (Online Methods). However, ground-level SO_2 concentrations strongly depend on the injection height of volcanic SO_2. Our model simulations suggest that the direct effects of acid mists and fogs on vegetation[26,27] may have caused the most lethal and immediate damage to vegetation, with 44% of the land area above the critical level in the Deccan-scale scenario (Online Methods). The fact that there is no soil intermediary or long-term exposure requirement and that the acidity of mists is likely much greater than that of rainfall makes this a potent mechanism where cloud-water is intercepted[26] (Figure 2b). In the present-day climate, the interception of cloud-water by the surface is mostly restricted to upland areas, and the presence of neutralizing species in the cloud-water (such as calcium or ammonia) can reduce the effects. Therefore, persistent and widespread damage from acid mists in deep times seems possible only if the cloud distribution or amount were much greater than at present.

Our results demonstrate that environmental acidification due to magmatic sulfur emissions is unlikely to have directly caused catastrophic global-scale extinctions. Further increases in acidity and toxicity could be caused by magmatic halogen emissions, however, model simulations of pulsed eruptions in the 250 Ma Siberian Traps[9] suggest that their effects are localized. Even when assuming that magmatic HCl is dispersed and deposited like SO_2, our calculated acid deposition rates would increase by 30-50% only (using a very high SO_2 to HCl ratio[8] of 1:0.29; Online Methods). Cases for severe environmental acidification have been made for CFB provinces where non-magmatic halogen emissions play a role[9,31], but this is not relevant for the Deccan Traps or for 14.7 Ma Roza.

Our model simulations show that the climatic effects of episodic magmatic sulfur emissions could have been large enough to impair habitability only if individual eruption frequencies and lava discharge rates were high and sustained for centuries or longer without

hiatuses. Such a longevity and intensity of individual eruptions, and hence cooling of climate, has not been demonstrated convincingly for any CFB province emplaced during the Phanerozoic. In fact, if individual CFB eruptions lasted for centuries or longer, then the mean magmatic gas release rate may have been lower[32], resulting in lower eruption column heights[22] and lower acid deposition rates. This in turn would suggest a reduced effect from magmatic sulfur on climate and spatially even more confined, and perhaps, subdued environmental effects. In future, the effects of other volcanic and non-volcanic stressors such as ozone depletion resulting from the emissions of halogenated species[9] ought to be quantified in concert with the sulfur-induced effects.

Figures (main text)

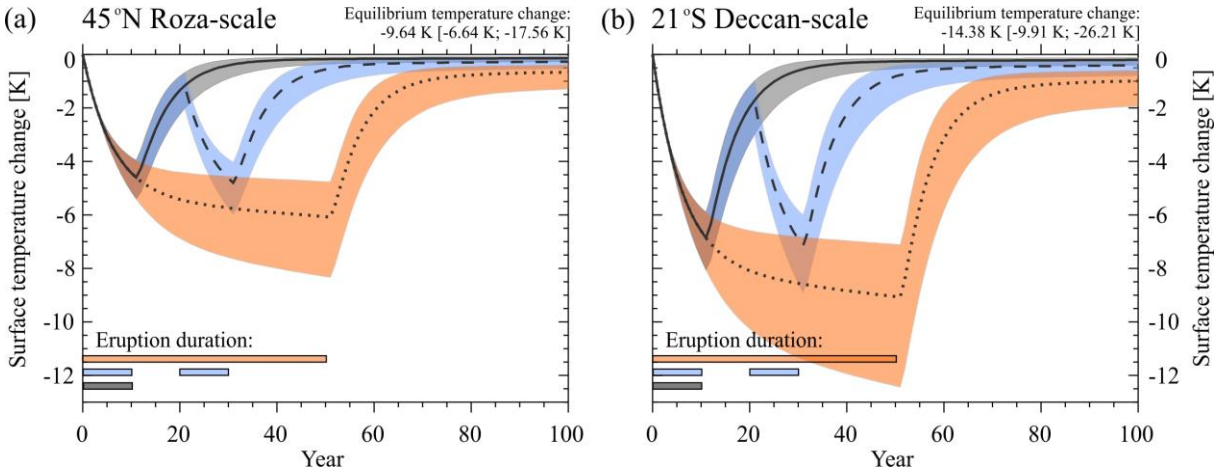

Figure 1. Global mean surface temperature change and its dependence on eruption duration and emission magnitude. (a) for a Roza-scale eruption emitting 1,200 Tg of SO_2 per year at 45°N and **(b)** for a Deccan-scale eruption emitting 2,400 Tg of SO_2 per year at 21°S. The eruption duration and hiatuses considered for each case are indicated by the colored bars (grey = 10 years of continuous eruption; blue = 10 years of continuous eruption followed by a 10-year hiatus followed by another 10 years of continuous eruption; and orange = 50 years of continuous eruption). The shading refers to uncertainty in surface temperature change based on 90% uncertainty range of the climate feedback parameter (Online Methods). The equilibrium temperature change including the 90% confidence interval is in the top-right corners and would require continuous SO_2 emissions for more than 150 years.

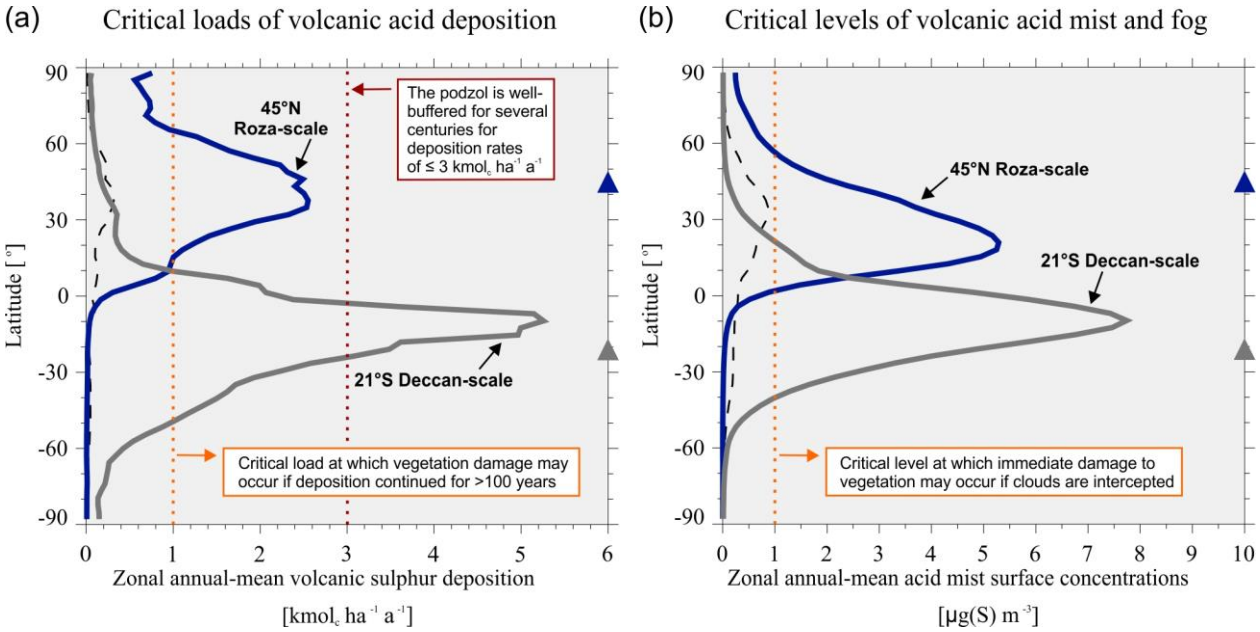

Figure 2. Annual latitudinal-mean volcanic acid deposition rates and acid mist concentrations for CFB-scale eruptions compared with standards to protect soils, vegetation and waters from the effects of acid deposition ('critical loads') and direct exposure to pollutants ('critical levels')[29]. (a) Critical loads [kmol$_c$ ha^{-1} a^{-1}] for a Roza-scale eruption at 45°N (blue line), a Deccan-scale eruption at 21°S (gray line) and a model simulation with only year 2000 anthropogenic emissions for context (dashed black line). **(b)** Critical levels [µg(S) m^{-3}] of acid mist concentrations for the same model experiments. The critical level of 1 µg(S) m^{-3} at which immediate damage to vegetation occurs if low-level clouds are intercepted[26] is exceeded on hemispheric scales for both eruption scenarios, making this a lethal mechanism to cause vegetation damage in some but not all parts of the world.

Table (main text)

			Soil acidification parameters				**Stream water acidification parameters**				
			Soil- and vegetation-dependent, but BS ≤5% could be considered harmful		*Ca^{2+}:Al≤1 forest vegetation at risk of reduced growth, freezing injuries and dysfunction of fine roots*				*Acute effects on freshwater fish and amphibians*		*Acute effects on tolerant species if exceeded and pH<4.5*
Soil-type	**Initial soil & stream properties**	**Volcanic S deposition [$kmol_c \cdot ha^{-1} \cdot a^{-1}$]**	**Eq. BS [%]**	**Time to Eq. [yr] / (Time to recover [yr])**	**Eq. Ca^{2+}: Al**	**Time to fall below 1.0 [yr] / (Time to recover to 1.0 [yr])**	**Eq. stream pH**	**Time to Eq. [yr] / (Time for full recovery [yr])**	**Time to reduce to pH<4.0 [yr] / (Time to recover to pH>4.0 [yr])**	**Eq. stream Al^{3+} [$\mu eq\ L^{-1}$]**	**Time to increase to 100 $\mu eq\ L^{-1}$ [yr] / (Time to recover to 100 $\mu eq\ L^{-1}$ [yr])**
Podzol Depth: 1.0 m	BS = 12.4 % Ca^{2+}/Al = 5.6 Stream Al^{3+} = 0.0 $\mu eq\ L^{-1}$ Stream pH = 6.85	**3**	6.2	1621 (2430)	1.1	-	4.1	300 (804)	-	73	-
		5	5.2	1014 (2590)	0.7	100 (16)	3.95	197 (865)	83 (4)	214	38 (8)
Podzol Depth: 0.25 m		**3**	6.2	791 (606)	1.1	-	4.1	75 (200)	-	73	-
Podzol 1.0m + Low S adsorp.		**3**	6.2	1592 (2384)	1.1	-	4.1	98 (978)	-	73	-
Oxisol Depth: 1.0 m	BS = 6.7 % Ca^{2+}/Al = 0.54 Stream Al^{3+} = 0.0 $\mu eq\ L^{-1}$ Stream pH = 5.39	**3**	3.2	550 (1360)	0.12	-	3.94	220 (1470)	68 (10)	222	48 (19)
Oxisol Depth: 0.25 m		**3**	3.2	138 (345)	0.12	-	3.94	55 (415)	16 (2)	222	13 (7)

Table 1. Indirect effects of volcanic sulfur deposition on soils and streams including damage threshold exceedances, timescales to reach equilibrium and recovery timescales. Orange shading indicates that thresholds to protect ecosystems are exceeded to a degree that harmful effects may occur. Green shading indicates the there are no threshold exceedances. The effects

are explored for a range of different soil parameters and soil types with initial values of soil and water variables shown in the second column. If deposition is continued indefinitely, these variables reach a new equilibrium., For instance, the initial base saturation (BS) for the podzol is 12.4%. At deposition rates of 3 $kmol_c$ ha^{-1} a^{-1}, the equilibrium BS (Eq. BS) is 6.2%, taking 1621 years to reach this value, which is still above the damage threshold[29]. If deposition rates are then reduced to background values, recovery takes 2430 years. A calcium (Ca^{2+}) to aluminum (Al) ratio of less than 1 puts forest vegetation at risk of reduced growth, freezing injuries and dysfunction of fine roots[29], which for the podzols is only exceeded for deposition rates of 5 $kmol_c$ ha^{-1} a^{-1} applied for a century or longer, and recovery timescales are comparatively fast. For stream waters, an equilibrium pH below 5.0 can affect sensitive freshwater species such as molluscs, and acute effects on fish and amphibians occur at pH below 4. If toxic inorganic monomeric aluminum (Al^{3+}) concentrations exceed 100 μeq L^{-1} harmful effects on freshwater fish and other species occur if the pH drops below 4.5 (increasing the solubility of Al^{3+}).

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Author contributions:

A.S. and K.S.C. devised the study. A.S. ran and analyzed the model simulations and led the interpretation. A.S., T.T., S.S., M.W., R.A.S. and A. Ridgwell designed model experiments. R.A.S. ran the soil and water acidification model simulations and interpreted the results together with A.S., and D.F. advised on the critical load calculations. A. Ridgewell ran the GENIE model and interpreted the results. A.S. and P.M.F. calculated the SO_2 radiative forcing and ran the energy budget model. A. Rap ran the radiative transfer code. AS led the writing and all authors contributed to the editing of the manuscript and approved the final version.

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