Article:
Schmidt, A, Skeffington, RA, Thordarson, T et al. (9 more authors) (2016) Selective environmental stress from sulphur emitted by continental flood basalt eruptions. Nature Geoscience, 9 (1). pp. 77-82. ISSN 1752-0908

https://doi.org/10.1038/ngeo2588

Selective environmental stress from sulfur emitted by continental flood basalt eruptions

Anja Schmidt[1,*], Richard A. Skeffington[2], Thorvaldur Thordarson[3,4], Stephen Self[5,6], Piers M. Forster[1], Alexandru Rap[1], Andy Ridgwell[7,8], David Fowler[9], Marjorie Wilson[1], Graham W. Mann[10], 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 Environment, Earth and Ecosystems, The Open University, Milton Keynes, MK7 6AA, UK
[6]Department of Earth and Planetary Science, University of California-Berkeley, Berkeley, CA, USA
[7]School of Geographical Sciences, University of Bristol, University Road, Bristol BS8 1SS, UK
[8]Department of Earth Sciences, University of California-Riverside, Riverside, CA, USA
[9]Natural Environment Research Council (NERC), Centre for Ecology and Hydrology, Penicuik, Midlothian, UK
[10]National Centre for Atmospheric Science, University of Leeds, Leeds, LS2 9JT, UK

***Correspondence and data requests should be addressed to:**
Anja Schmidt
School of Earth and Environment
University of Leeds
Email: a.schmidt@leeds.ac.uk
Phone: +44(0) 113 34 36429

Nature Geoscience
Last modified: 19 October 2015

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 sulfur gas species. Flood basalt provinces were typically formed by numerous individual eruptions, each lasting years to decades. However, the environmental impact 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 sulfur-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 different 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-buffered against volcanic sulfur deposition effects even during century-long eruptions. We conclude that magmatic sulfur from flood basalt eruptions would have caused a biotic crisis only if eruption frequencies and lava discharge rates were high and sustained for several centuries at a time.

Main Text

Continental flood basalt (CFB) provinces produced total magma volumes of 0.1-4.0 million km^3 and were typically formed by hundreds to thousands of individual, volumetrically large (on the order of 1000 km^3) eruptions. Eruptions were separated by hiatus periods of uncertain length, with the overall emplacement of a CFB province taking place on a timescale of 100,000s of years[1,2]. Individual eruptions far exceeded even the largest historic eruptions in terms of lava volume, eruption duration and amount of gases emitted into the atmosphere[2-4]. Intriguingly, the emplacement of four out of five CFB provinces during the last 300 Myr coincided with periods of high extinction rates of species[5-8], leading to suggestions of a causal link[1,5-7,9]. Yet, after more than four decades of research, this hypothesis remains equivocal and contested[9,10].

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[11,12]. Consequently, climatic cooling and environmental acidification due to the emission and deposition of large quantities of magmatic sulfur ('acid rain') are two widely proposed causal agents for global biotic crises coinciding with periods of CFB volcanism[9,13-15]. A number of studies have also suggested that multiple volcanic and/or non-volcanic factors resulting in climatic, tectonic and biogeochemical changes contributed synergistically to periods of biodiversity crises[9,13,15-21]. To date there are, however, no estimates of the contributions of magmatic sulfur from decade- to century-long CFB eruptions that account for the buffering capacities of soils and other environments when assessing the effects of acid rain. To constrain the climatic effects, previous studies either relied on

extrapolation of the surface cooling caused by sulfur species emitted during explosive volcanism[9,13,14], or used simple relationships between the mass of sulfuric acid aerosol particles generated from SO_2 and its cooling effects[4]. Neither approach accounts for two key factors that may reduce the aerosol-induced cooling: limited oxidant availability, which affects SO_2 conversion to acidic aerosol, and enhanced particle growth, which reduces the particle light-scattering efficiency and shortens particle lifetimes in the atmosphere. The relative importance of these processes has been quantified for short-lived explosive eruptions[22-24], but not for large-magnitude CFB eruptions, which differ fundamentally in terms of eruption style, and height and duration of SO_2 emissions (Supplementary Figure 1 and Supplementary Table 4).

To constrain the environmental effects and consequences for habitability induced by magmatic sulfur emissions from individual decade- to century-long CFB eruptions, we use a global aerosol model[25], a soil and freshwater acidification model[26], and an Earth system model for deep time environments[27] (Online Methods and Supplementary Information). The eruption source parameters used in our model experiments are based on the well-constrained 14.7 Ma (mid-Miocene) Roza eruption emplaced in the youngest CFB province, the Columbia River Basalt Group (16.5-14.5 million years ago), 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 lava 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[4]. Lava volumes in excess of 1000 km^3 for individual eruptions in the Deccan Traps have been proposed[3], but individual eruption durations are unknown. Plume rise modelling for basaltic fissure eruptions suggests gas emissions to altitudes of 9-13 km[28,29], 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 eruptions, assuming either greater mean lava discharge rates or that more than one lava flow field was active at any one time (Supplementary Table 1). Uncertainties arising from our model configuration are discussed in the Supplementary Information.

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 aerosol particle concentrations exerts a negative radiative forcing, cooling the climate through increased light scattering by the particles and increases in cloud droplet concentrations. By contrast, any unoxidized SO_2 acts as a greenhouse gas and absorbs ultraviolet radiation, which warms the climate. 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 (Supplementary Table 2). This non-linearity is caused by the combination of limited aerosol production, differences in particle growth with increasing SO_2 emissions, the saturation of the aerosol indirect forcing, and the offset of the negative aerosol forcings by the positive forcing from SO_2. 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 (Supplementary Table 3). The saturation of the aerosol-induced cloud forcing is caused by

the well established mechanism of a decreasing sensitivity of cloud reflectance to changes in droplet concentrations[25]. A previous study on explosive super-eruptions also suggested that the positive greenhouse gas forcing from volcanic SO_2 may offset the aerosol cooling[23]. However, the forcing by SO_2 is not normally considered in climate model simulations of the effects 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}; Supplementary Table 2).

Our simulations show that the frequency and duration of individual CFB eruptions and hiatus periods, strongly affect the severity and longevity of the climatic effects. For an individual Deccan-scale eruption lasting a decade, 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 (Figure 1 and Online Methods). For context, simulations of the effects of the 74 ka Toba eruption suggest peak global mean temperature changes of between -3.5 K and -10 K[24,30]. 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 would 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 reached equilibrium (Figure 1). Our estimates are at the lower end of previous estimates of global mean surface temperature reductions for the Roza case[4]. For the K-Pg, the survival of ectothermic tetrapods at mid-latitudes (but not at high-latitudes and with the exception of lizards)[10], supports our findings of surface temperatures potentially dropping and fluctuating

significantly on decadal timescales, but which are by no means 'catastrophic'.

We find that the chemical and aerosol microphysical processes controlling the magnitude of climatic impacts differ fundamentally between long-lasting CFB eruptions and short-lived explosive eruptions, which significantly influences their relative effects on climate (Supplementary Figure 1 and Supplementary Table 4). 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 and 0.8 μm, depending on the amount of SO_2 emitted. Further growth is limited because the high removal rates in the troposphere limit the particle lifetimes to about two weeks (Supplementary Table 3). Conversely, for large-magnitude explosive eruptions that inject SO_2 into the stratosphere, particles typically have time to grow to diameters much larger than 0.8 μm[22,24] 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 surface 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 (Supplementary Table 4).

Environmental acidification can affect ecosystems either through direct exposure to acidic species, or indirectly through the acidification of soils and stream waters. It has been suggested that acidification contributed to the K-Pg mass extinction[9,13,31] and the end-Permian mass extinction[15]. 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[32] and damage thresholds are represented by the deposition and concentration standards (critical loads and critical levels) used in European policymaking[33-35]. 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[34]. For both eruption scenarios, this critical load is exceeded over an area of about 30 degrees latitude north and south of the eruption site with peak zonal-mean loads of 5.5 $kmol_c\ ha^{-1}\ a^{-1}$ for the Deccan-scale eruption (Figure 2a). However, detailed modelling using MAGIC[25] shows that such high deposition rates would have to be sustained for centuries to cause significant acidification and damage in most cases (Table 1, Online Methods and Supplementary Information). Therefore, we conclude that soil acidification due to volcanic sulfur deposition cannot directly explain global-scale mass extinction events, in contrast to previous studies that neglected the acid buffering capacities of soils and other environments[9,13,15]. 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 (see also Online Methods and Supplementary Information). We find that an acid-sensitive spodosol, 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}. However, 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, but the recovery occurs 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. Although there is evidence that oxisol-like soils were widespread in the late Cretaceous, including the Deccan Traps area (Supplementary Information), they seem unlikely to have been distributed widely enough to allow for global mass extinctions.

Acute effects on fish and amphibians due to acidification of stream waters[36] 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 annual-mean pH of 3.94) and for the 1m deep spodosol after almost 200 years of continued deposition rates of 5 $kmol_c$ ha^{-1} a^{-1} (reaching an equilibrium annual-mean pH of 3.95) (Table 1 and Supplementary 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 diversity at the K-Pg boundary[10], constraining the pH of freshwaters to not less than four[36] (Table 1).

The impact of sulfur deposition on seawater chemistry and acidification from decade-long volcanic eruptions is also predicted to be negligible (Online Methods and Supplementary Information). At Deccan-scale rates, we calculate that volcanic sulfur deposition would have to occur continuously for more than three millennia to drive a surface ocean pH decline comparable

to the current anthropogenic perturbation of ~0.1 pH units (Supplementary Table 5).

For the Deccan-scale scenario, maximum annual-mean SO_2 ground-level concentrations are comparable to those experienced in the 1970s in Central Europe due to anthropogenic pollution. Critical levels[36] for ground-level SO_2 are not exceeded on a scale sufficient to cause global-scale foliar damage (Supplementary Figure 3 and Online Methods). Although the Deccan-scale SO_2 emission rates greatly exceed anthropogenic emission rates, very high ground-level SO_2 concentrations are mitigated by the much higher injection altitude of volcanic SO_2. Our model simulations suggest that the direct effects of acid mists and fogs on vegetation[33,34] 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 (Supplementary Figure 4). 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[33] (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 the effects of magmatic sulfur from decade- to century-long CFB eruptions to environmental acidification were likely selective and localized. Further increases in acidity could be caused by magmatic halogen and carbon dioxide emissions (CO_2). Model simulations of pulsed eruptions in the 251 Ma Siberian Traps[15] suggest that the effects of

magmatic halogens would have been localized. Assuming that HCl is dispersed and deposited like SO_2, our calculated acid deposition rates would be about 25% higher (using a very high SO_2 to HCl ratio[3] of 1:0.29). Volcanic CO_2 emissions and high atmospheric pCO_2 can decrease the pH of precipitation. Today unacidified rain has a pH of about 5.6 and a reasonably precise relationship between pCO_2 and pH of water in equilibrium with it is given by the following formula[37]: $pH = 3.9 – 0.5\log_{10} pCO_2$. For the Late Cretaceous, atmospheric pCO_2 values of 330 ppm to >2300 ppm have been reported[38] and of about 280 ppm for the mid-Miocene[39]. Even at much higher atmospheric pCO_2 of 3550 ppm as estimated for the end-Permian, the pH of rain would decrease to only about 5.1. In contrast to previous work[15], this leads us to conclude that there would be no foliar damage *per se* due to high pCO_2 and/or the release of volcanic CO_2. Cases for severe environmental acidification have been made for CFB provinces where non-magmatic halogen emissions play a role[15,40], but this is not relevant for the Deccan Traps or for 14.7 Ma Roza.

Our model simulations show that the climatic and environmental 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 has not been demonstrated convincingly for any CFB province emplaced during the Phanerozoic. But even if individual CFB eruptions lasted for centuries or longer, the mean magmatic gas release rate may have been lower[41], resulting in lower eruption column heights[29] 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 and

207 contributions of other volcanic and non-volcanic stressors such as ozone depletion resulting from
208 the emissions of halogenated species[15,42] ought to be quantified in concert with the sulfur-induced
209 effects.

Figures (main text)

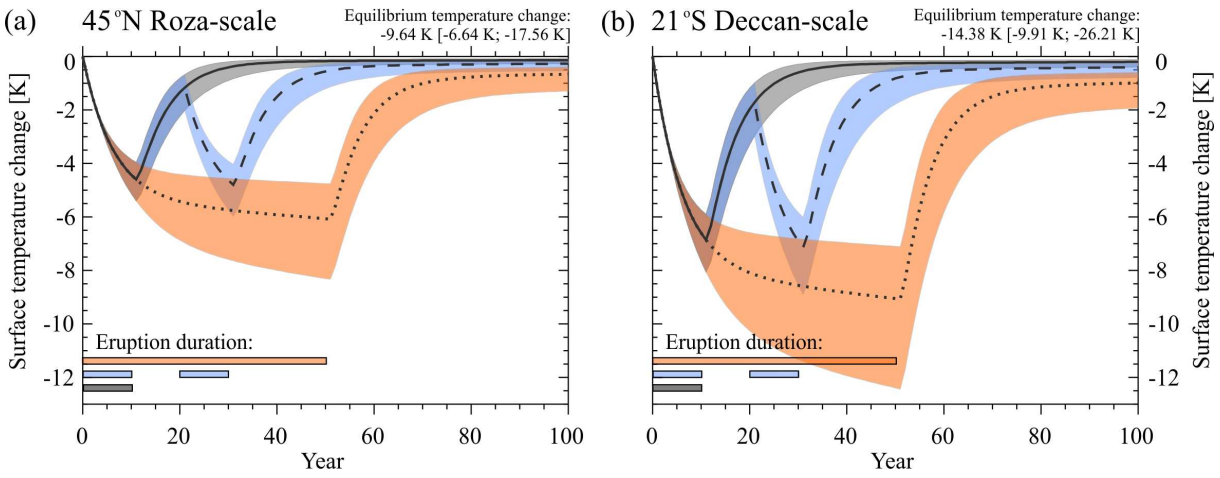

Figure 1. Global mean surface temperature change and its dependence on eruption duration and mass of SO_2 emitted. (a) for a Roza-scale eruption emitting 1,200 Tg of SO_2 per year at 45°N and **(b)** for a Deccan-scale eruption emitting 2,400 Tg of SO_2 per year at 21°S. The eruption duration and hiatuses 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.

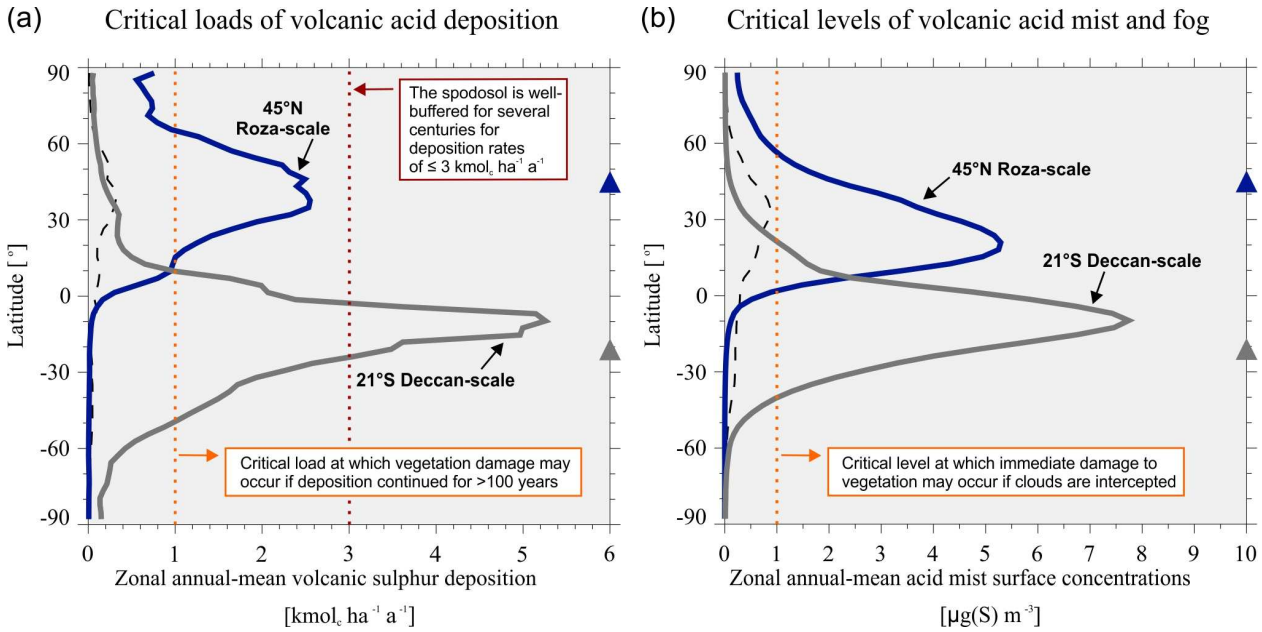

Figure 2. Annual latitudinal-mean volcanic acid deposition rates and acid mist concentrations for CFB-scale eruptions compared with standards to protect soils, vegetation and waters from the effects of acid deposition ('critical loads') and direct exposure to pollutants ('critical levels')[36]. (a) Critical loads [kmol$_c$ ha^{-1} a^{-1}] for a Roza-scale eruption at 45°N (blue line with the blue triangle indicating the eruption's location), a Deccan-scale eruption at 21°S (grey line with the grey triangle indicating the eruption's location) and a model simulation without volcanic emissions but 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[33] 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				Stream water acidification				
			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 para-meters**	**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])**
Spodosol 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)
Spodosol Depth: 0.25 m		**3**	6.2	791 (606)	1.1	-	4.1	75 (200)	-	73	-
Spodosol 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 that there are no threshold exceedances. The effects are explored for a range of different deposition rates based on the results shown in Figure 2a, soil parameters and soil types with initial values of soil and water variables shown in the second column (see also Online Methods and Supplementary Information). If deposition is continued indefinitely, these variables reach a new equilibrium. For instance, the initial base saturation (BS) for the spodosol 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[36], which for the spodosol 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 $\mu eq\ L^{-1}$ harmful effects on freshwater fish and other species occur if the pH drops below 4.5 (increasing the solubility of Al^{3+}).

References

1 Schoene, B. *et al.* U-Pb geochronology of the Deccan Traps and relation to the end-Cretaceous mass extinction. *Science* **347**, 182-184 (2015).

2 Self, S., Widdowson, M., Thordarson, T. & Jay, A. E. Volatile fluxes during flood basalt eruptions and potential effects on the global environment: A Deccan perspective. *Earth Planet. Sci. Lett.* **248**, 518-532 (2006).

3 Self, S., Blake, S., Sharma, K., Widdowson, M. & Sephton, S. Sulfur and chlorine in Late Cretaceous Deccan magmas and eruptive gas release. *Science* **319**, 1654-1657 (2008).

4 Thordarson, T. & Self, S. Sulfur, chlorine and fluorine degassing and atmospheric loading by the Roza eruption, Columbia River Basalt Group, Washington, USA. *Journal of Volcanology and Geothermal Research* **74**, 49-73 (1996).

5 Rampino, M. R. & Stothers, R. B. Flood Basalt Volcanism During the Past 250 Million Years. *Science* **241**, 663-668, doi:10.1126/science.241.4866.663 (1988).

6 Stothers, R. B. Flood Basalts and Extinction Events. *Geophys. Res. Lett.* **20**, 1399-1402 (1993).

7 Courtillot, V. E. & Renne, P. R. On the ages of flood basalt events. *Comptes Rendus Geoscience* **335**, 113-140 (2003).

8 Raup, D. M. & Sepkoski, J. J. Mass Extinctions in the Marine Fossil Record. *Science* **215**, 1501-1503, doi:10.1126/science.215.4539.1501 (1982).

9 Wignall, P. B. Large igneous provinces and mass extinctions. *Earth-Science Reviews* **53**, 1-33 (2001).

10 Archibald, J. D. *Dinosaur extinction and the end of an era: what the fossils say*. (Columbia University Press, 1996).

11 Robock, A. Volcanic eruptions and climate. *Rev. Geophys.* **38**, 191-219, doi:10.1029/1998RG000054 (2000).

12 Delmelle, P. Environmental impacts of tropospheric volcanic gas plumes. *Geological Society, London, Special Publications* **213**, 381-399 (2003).

13 Officer, C. B., Hallam, A., Drake, C. L. & Devine, J. D. Late Cretaceous and paroxysmal Cretaceous/Tertiary extinctions. *Nature* **326**, 143-149 (1987).

14 Campbell, I. H., Czamanske, G. K., Fedorenko, V. A., Hill, R. I. & Stepanov, V. Synchronism of the Siberian Traps and the Permian-Triassic Boundary. *Science* **258**, 1760-1763, doi:10.1126/science.258.5089.1760 (1992).

15 Black, B. A., Lamarque, J.-F., Shields, C. A., Elkins-Tanton, L. T. & Kiehl, J. T. Acid rain and ozone depletion from pulsed Siberian Traps magmatism. *Geology*, doi:10.1130/g34875.1 (2013).

16 Erwin, D. H. The Permo-Triassic extinction. *Nature* **367**, 231-236 (1994).

17 Erwin, D. H., Bowring, S. A. & Yugan, J. End-Permian mass extinctions: A review. *Geological Society of America Special Papers* **356**, 363-383, doi:10.1130/0-8137-2356-6.363 (2002).

18 Knoll, A. H., Barnbach, R. K., Payne, J. L., Pruss, S. & Fischer, W. W. Paleophysiology and end-Permian mass extinction. *Earth Planet. Sci. Lett.* **256**, 295-313 (2007).

19 D'Hondt, S., Pilson, M. E. Q., Sigurdsson, H., Hanson , A. K. & Carey, S. Surface-water acidification and extinction at the Cretaceous-Tertiary boundary. *Geology* **22**, 983-986 (1994).

20 Hallam, A. & Wignall, P. B. Mass extinctions and sea-level changes. *Earth-Science Reviews* **48**, 217-250, doi:http://dx.doi.org/10.1016/S0012-8252(99)00055-0 (1999).

21 McLean, D. M. Deccan traps mantle degassing in the terminal Cretaceous marine extinctions. *Cretaceous Research* **6**, 235-259 (1985).

22 Pinto, J. P., Turco, R. P. & Toon, O. B. Self-limiting Physical and Chemical Effects in Volcanic Eruption Clouds. *J. Geophys. Res.* **94(D8)**, 11165-11174 (1989).

23 Bekki, S. Oxidation of Volcanic SO_2 - a Sink for Stratospheric OH and H_2O. *Geophys. Res. Lett.* **22**, 913-916 (1995).

24 Timmreck, C. *et al.* Aerosol size confines climate response to volcanic super-eruptions. *Geophys. Res. Lett.* **37**, L24705 (2010).

25 Schmidt, A. *et al.* Importance of tropospheric volcanic aerosol for indirect radiative forcing of climate. *Atmos. Chem. Phys.* **12**, 7321-7339, doi:10.5194/acp-12-7321-2012 (2012).

26 Cosby, B. J., Hornberger, G. M., Galloway, J. N. & Wright, R. F. Modelling the Effects of Acid Deposition: Assessment of a Lumped Parameter Model of Soil Water and Streamwater Chemistry. *Water Resources Research* **21**, 51-63, doi:10.1029/WR021i001p00051 (1985).

27 Ridgwell, A. & Schmidt, D. N. Past constraints on the vulnerability of marine calcifiers to massive carbon dioxide release. *Nature Geosci* **3**, 196-200, doi:http://www.nature.com/ngeo/journal/v3/n3/suppinfo/ngeo755_S1.html (2010).

28 Stothers, R. B., Wolff, J. A., Self, S. & Rampino, M. R. Basaltic Fissure Eruptions, Plume Heights, and Atmospheric Aerosols. *Geophys. Res. Lett.* **13**, 725-728, doi:10.1029/GL013i008p00725 (1986).

29 Woods, A. W. A model of the plumes above basaltic fissure eruptions. *Geophys. Res. Lett.* **20**, 1115-1118, doi:10.1029/93GL01215 (1993).

30 Robock, A. *et al.* Did the Toba volcanic eruption of ~74 ka B.P. produce widespread glaciation? *Journal of Geophysical Research: Atmospheres* **114**, D10107, doi:10.1029/2008jd011652 (2009).

31 Retallack, G. J. Acid trauma at the Cretaceous-Tertiary (K/T) boundary in eastern Montana. *GSA Today* **6** (1996).

32 Cosby, B. J., Ferrier, R. C., Jenkins, A. & Wright, R. F. Modelling the effects of acid deposition: refinements, adjustments and inclusion of nitrogen dynamics in the MAGIC model. *Hydrol. Earth Syst. Sci.* **5**, 499-518, doi:10.5194/hess-5-499-2001 (1999).

33 Cape, J. N. Direct damage to vegetation caused by acid rain and polluted cloud: Definition of critical levels for forest trees. *Environmental Pollution* **82**, 167-180 (1993).

34 Fowler, D. *et al.* The Global Exposure of Forests to Air Pollutants. *Water, Air, & Soil Pollution* **116**, 5-32, doi:10.1023/a:1005249231882 (1999).

35 Umweltbundesamt. Manual on methodologies and Criteria for Modelling and Mapping Critical Loads and Levels. (Umweltbundesamt, 2004).

36 Howells, G. P. *Acid rain and acid waters*. 215 (Ellis Horwood, 1990).

37 Stumm, W. & Morgan, J. J. *Aquatic chemistry : chemical equilibria and rates in natural waters*. 3rd edn, 1022 (John Wiley & Sons, Inc, 1996).

38 Beerling, D. J., Lomax, B. H., Royer, D. L., Upchurch, G. R. & Kump, L. R. An atmospheric pCO(2) reconstruction across the Cretaceous-Tertiary boundary from leaf megafossils. *Proceedings of the National Academy of Sciences of the United States of America* **99**, 7836-7840, doi:10.1073/pnas.122573099 (2002).

39 Kürschner, W. M., Kvaček, Z. & Dilcher, D. L. The impact of Miocene atmospheric carbon dioxide fluctuations on climate and the evolution of terrestrial ecosystems. *Proceedings of the National Academy of Sciences of the United States of America* **105**, 449-453, doi:10.1073/pnas.0708588105 (2008).

40 Ganino, C. & Arndt, N. T. Climate changes caused by degassing of sediments during the emplacement of large igneous provinces. *Geology* **37**, 323-326, doi:10.1130/g25325a.1 (2009).

41 Dodd, S. C., Mac Niocaill, C. & Muxworthy, A. R. Long duration (~4 Ma) and steady-state volcanic activity in the early Cretaceous Paraná–Etendeka Large Igneous Province: New palaeomagnetic data from Namibia. *Earth and Planetary Science Letters* **414**, 16-29, doi:http://dx.doi.org/10.1016/j.epsl.2015.01.009 (2015).

42 Black, B. A., Weiss, B. P., Elkins-Tanton, L. T., Veselovskiy, R. V. & Latyshev, A. Siberian Traps volcaniclastic rocks and the role of magma-water interactions. *Geological Society of America Bulletin*, doi:10.1130/b31108.1 (2015).

Acknowledgements:

We thank three anonymous reviewers for their constructive comments that helped to improve this manuscript. We thank A. Haywood for providing Miocene and Late Cretaceous surface albedo fields. A.S. was supported by an Academic Research Fellowship from the School of Earth and Environment, University of Leeds. P.M.F. and K.S.C. were supported by a Royal Society Wolfson Merit Award. SS was supported by an award from the Larsen Funds, University of California-Berkeley.

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. Ridgwell 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.