

Prominent role of sulfate reduction in robust sulfur retention in subtropical soil

Qian Yu

Tsinghua University <https://orcid.org/0000-0003-4962-313X>

Jan Mulder

Norwegian University of Life Sciences

Gaoyue Si

Tsinghua University

Longfei Yu

Jinan University

Ronghua Kang

Chinese Academy of Sciences

Kaiyi Liu

Tsinghua University

Jiming Hao

Tsinghua University

Lei Duan (✉ lduan@tsinghua.edu.cn)

Tsinghua University

Article

Keywords: soil, sulfur, subtropical soil, elemental cycles

DOI: <https://doi.org/10.21203/rs.3.rs-311235/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Sulfur budgets in catchments indicated that about 80% of the deposited sulfur was retained in the subtropical soil, it alleviates the historical acidification caused by elevated deposition. The strong sulfur retention was attributed to the reversible sulfate adsorption in previous studies. Here we report that sulfate reduction is a prominent yet thus far overlooked mechanism for sulfur retention, based upon the comprehensive evidence of soil sulfur storage and multi-isotope within entire soil profile along a hydrological continuum in a typical subtropical catchment of China. Using a dual isotopic mass balance model, we determined that annual flux of reduction accounted for approximately 38% of sulfur retention, which was close to the proportion of reduced species in soil. Consequently, the release of sulfur legacy would be less serious with the decreasing sulfur deposition in China, compared to the projections only considering adsorption.

Introduction

Atmospheric sulfur (S) deposition has caused widespread soil and surface water acidification, and led the loss of base cation and nutrient, and the mobilization of harmful metals¹⁻³. Sulfate (SO_4^{2-}) retention in ecosystems has been implicated as a counter effect to the environmental impacts derived from S deposition¹⁻³. It was poor in temperate forests of Europe and North America, manifesting as almost all the deposited sulfur (S) leaching out even with moderate atmospheric input (Fig. 1a). However, significant S retentions (as large as $160 \text{ kg S ha}^{-1} \text{ yr}^{-1}$, accounting about 80% of the total S deposition) have been widely reported in subtropical catchments, even under chronically heavy S deposition (Fig. 1).

The mechanisms for sulfur retention remains unclear in subtropical forest catchments. Sulfate adsorption has usually been reported as the main mechanism for SO_4^{2-} retention in forest catchments⁴⁻⁷, and used as the only factor for modeling and predicting the acidification processes^{8,9}. While a large reservoir of adsorbed SO_4^{2-} was observed due to the strong adsorption capacity, this could not explain the long-term S sink in the deeper soil and before-stream zone in subtropical regions^{10,11}. In addition, S incorporation into soil organic matter might not be the reasonable cause to the strong SO_4^{2-} retention due to the limited organic matter even in the upper soil in subtropical forests, though some studies have emphasized the importance of S incorporation into soil organic matter^{5,12}. Sulfate reduction usually played a minor role or ignored in forested catchments dominated by aerobic soil^{5,6,12,13}, but could be an additional mechanism for attenuating SO_4^{2-} in catchments with a larger area of wetland¹⁴⁻¹⁶. Its contribution to S retention in subtropical must be confirmed.

The S retention mechanisms were difficult to distinguish and quantify merely based on the traditional flux/budget approach. Sulfur isotope is a useful tool to identify the sulfate reduction in ecosystems¹⁴⁻¹⁷, due to the distinctive isotope fractionation effects ($^{34}\epsilon$) between the sulfate reduction (as large as 72‰) and the other processes ($\sim 0\text{‰}$)¹⁸. Furthermore, the isotope approach combined with mass balance could

be used to estimate fluxes of SO_4^{2-} turnover processes¹⁵. In this study, we determined the hydrological SO_4^{2-} fluxes, soil S storage, and $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ within the entire soil profile along a hydrological continuum in a typical subtropical catchment of China (TSP, Fig. 1b & 2). Sulfate reduction was ascertained by the isotopic signal, and the mechanisms for S retention were quantified as using a model involving mass and isotope balance. The results showed that SO_4^{2-} adsorption, reduction, and net incorporation into organic matter, accounting 46%, 30%, and 4% of the total deposited S, respectively. Potential environmental hazards of the legacy S in subtropical soil were further proposed.

Results And Discussion

Large S retention in the subtropical soil

TSP catchment had a S retention average of $141 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ during 2001 to 2017, with $177 \pm 41.4 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ input from the throughfall, $36.2 \pm 7.20 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ export by stream water (Fig. 2c), and limited S-gas emissions¹⁹. The chronic S retention in this catchment is attributed to the large S storage in the soil. Soil from 0 to 215 cm deep acts as a large S store of $\sim 14,300 \text{ kg S ha}^{-1}$ (Fig. 3a), which is equivalent to the cumulative S retention in ~ 100 years according to the annual retention flux from 2001 to 2017. Corresponding to stronger S retention, the S reservoir is larger than temperate forest soil even with high S application¹³.

At the hillslope, the S store in the soil was dominated by adsorbed SO_4^{2-} and total reduced S with proportions of 35% and 34%, followed by organic S of 23% (Fig. 3a), it is similar to the S species composition in the entire catchment which mainly composed of hillslope topography (96% of the total area). The reduced S, as trivial species in previous studies, however, have extraordinary large contribution to the total S in the soil in this catchment. The proportion gradually increased with the soil depth, exceeding 70% at the deepest layer (Fig. 3a). In addition, the S store in reduced species had larger proportion in plots at groundwater discharge zone (49%) than those at hillslope (34%). These implies SO_4^{2-} reduction may be an important mechanism for S retention, especially in the deeper soil and the water logged zone before stream.

The large S retention, accounted to $\sim 80\%$ of the S deposition within TSP catchment, was widely found in subtropical (Fig. 1). Subtropical China has one of the highest levels of atmospheric S deposition in the world²⁰. The annual S deposition in subtropical forest (145 million ha, accounting for 61% of the forested land in China and 45% of the total subtropical forests in the world) was averaged at $37.0 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ from 2005 to 2015 (Fig. 1b), which is used to represent the historical S deposition. According to the retention ratio, the total S retention was $4.29 \text{ Tg S yr}^{-1}$, and the S store in soil was calculated as $\sim 429 \text{ Tg}$ in the entire subtropical forest in China. There may be 150, 146, and 98.7 Tg S stored in the subtropical forest soil as adsorbed SO_4^{2-} , reduced S, and organic S, consecutively, when on the basis of the S species composition in TSP catchment with typical soil across subtropical China.

Isotopic evidence for SO_4^{2-} reduction

Evidence for SO_4^{2-} reduction was enhanced by the isotopic signals. The $\delta^{34}\text{S}$ of water soluble SO_4^{2-} had distinct increases with the soil depth after depths of 75 cm at the hillslope and 25 cm at the groundwater discharge zone when the $\delta^{34}\text{S}$ of total S in the soil demonstrated a sharp decline (Fig. 3a). This indicates that there was a process with significant isotopic fractionation in the deeper soil, resulting in an enrichment of ^{34}S in the remaining dissolved SO_4^{2-} and ^{34}S depletion in the bulk soil, as well as increases of reduced S content of the soil profiles. Sulfate reduction may be a reasonable explanation, converting the substrate SO_4^{2-} in soil solution to sulfide fixed on soil. In addition to the behavior of $\delta^{34}\text{S}$ in water soluble SO_4^{2-} and total S with soil depth in the soil cores, the increase in $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ in SO_4^{2-} from throughfall to surface water along the hydrological continuum provides further evidence for the occurrence of sulfate reduction (Fig. 2c).

Accompanied by the fractionation of ^{34}S - SO_4^{2-} , ^{18}O of SO_4^{2-} tend to enrichment during sulfate reduction controlled by kinetic isotope effects and/or equilibrium oxygen exchange with water¹⁷. The kinetic isotope effects suggest the $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ of residual SO_4^{2-} evolves in a linear relationship with a slope of 1:4 in systems with rapid sulfate reduction rates (Trend A, Fig. 3b), based on an assumption of preferential ^{16}O -bond rupture and the stoichiometry of the sulfate molecule. Conversely, the equilibrium oxygen isotope exchange between water regulates the $\delta^{18}\text{O}$ of residual sulfate tend to reveal a curvilinear response with lower rates of sulfate reduction and enhanced recycling of intracellular sulfur (Trend B, Fig. 3b). Paired $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ of water soluble SO_4^{2-} offers an additional support to the sulfate reduction with high rate within the TSP catchment. A near-linear relationship between $\delta^{18}\text{O}$ and $\delta^{34}\text{S}$ was observed in water soluble SO_4^{2-} with a slope of 0.38 (Fig. 3b). This corresponded to the trend with high sulfate reduction rates (Trend A) rather than that with equilibrium isotope exchange (Trend B), indicating rapid sulfate reduction in this catchment. The slope shifts from low values in hillslope (0.36, $R^2 = 0.94$) to higher values in groundwater discharge zone (0.49, $R^2 = 0.91$), conforming to the stronger anaerobic condition and more reduced S store in the groundwater discharge zone.

Mechanisms for S retention quantified with modelling

A model was developed based upon mass and isotope balance estimated the co-occurrence of three S-retention processes in soils in TSP catchment, including SO_4^{2-} adsorption, reduction, and net incorporation into organic matter, accounting 46%, 30%, and 4% of the total deposited S, respectively (Fig. 4). This was based on the assumption that the ^{34}S fractionation effect during the reduction ($^{34}\epsilon_r$) is 16‰ (according to the Rayleigh distillation equation, Supplementary Text 4). The S fluxes calculated by the model is sensitive to the $^{34}\epsilon_r$, and the contributions of adsorption and reduction to total S deposition varied from 37–53% and 23 to 38%, respectively, with $^{34}\epsilon_r$ in the range of 12‰-20‰. The uncertainties of S fluxes from incorporation, adsorption, and reduction were 20%, 49%, and 35% with synthesis consideration of the impact factors.

As the main retention mechanism, sulfate adsorption, having a total flux of $\sim 81.2 \text{ kg S ha}^{-1} \text{ yr}^{-1}$ in this catchment, can explain the increasing adsorbed SO_4^{2-} store in the soil (359, 611, and 3,600 kg S ha^{-1} for 0–50 cm soil in 2004¹⁰, 2011²¹, and 2017, Fig. 3a, respectively). Generally, the old and deeply weathered subtropical soils with low pH (3.7–4.1 in TSP catchment) and large Fe/Al oxides have large adsorption capacity^{4,6,9,22}. In addition, sulfate adsorption is concentration-related^{4,6,8}, whereby high dissolved sulfate concentration in the soil (Fig. 2c) from heavy atmospheric S deposition would stimulate the adsorption in TSP catchment. Previous studies demonstrated the importance of SO_4^{2-} adsorption in S retention based upon SO_4^{2-} pool adsorption measurements or adsorption capacity^{4,6,9}. In this study, the flux of SO_4^{2-} adsorption was quantified using isotopic model, and further clarifying the contribution to S retention. The model results emphasized the importance of sulfate reduction on S retention within TSP catchment, combined with the evidence of S store and isotopic signals. The strong sulfate reduction in the subtropical zone appears to be promoted by sufficient anaerobic conditions due to both the hot and humid climate. And the abundant Fe-oxides (or Fe^{2+}) in the soil²² can fix the sulfide, and form iron sulfide minerals, may subsequently convert to pyrite. In the biogeochemistry of S, subtropical soil might be an important region to capture the reactive S except the extensively studied salt marshes, peatlands, and marine sediments^{23–25}.

It is common to treat the entire forest catchment as one soil type (well-drained forest soils) rather than along the whole soil profile and hydrological gradients¹³. The variations in 3-dimensional retention fluxes account for differences in soil-related depth and water flow path. They are explicitly demonstrated in this study, showing the importance of the deeper soil and the waterlogged zone in S retention, and where sulfate reduction performed prominently. The S flux decreased by 42.3 and 77.1 $\text{kg S ha}^{-1} \text{ yr}^{-1}$ in the upland 40 cm and deeper soil in aerated hillslope, respectively. This attributed to 20% and 44% of the total S deposition in the entire forested catchment of TSP (Fig. 4). The residual 16% of S retention occurred in the waterlogged groundwater discharge zone, although which only accounts for 4% of the total basin area (Fig. 4). The overlook of these regions fed the limited awareness of the role played by sulfate reduction on S retention.

Potential consequences of large S retention

S retention is of crucial importance for resisting cationic nutrient transport and aluminium mobilization^{1–3,26}. Although China received chronically elevated atmospheric S deposition with the increase of SO_2 from 6.8 in the 1980s to 34 Tg yr^{-1} in 2006²⁷, the robust S retention in subtropical China ($\sim 80\%$ of total S deposition) alleviated the acidification in the past decades¹¹. Relatively light surface water acidification in China was observed as a result, even under heavy deposition compared to that in temperate forests²⁸. However, the S retention in soil ultimately would act as a delayed risk of concern in environment and human health²⁹. Potential hazard depends on the stability of the legacy S in response to the changes in environmental conditions. The consistency or discrepancy of contributions between calculated fluxes and reservoirs indicated the difference in stability of S species. For instance, the annual flux of reduction was estimated to be 38% of the retention, using a dual isotopic mass balance model, it was close to the

proportion of reduced species in soil. However, the proportion of adsorbed S store in the soil (35%) was significantly lower than the ratio of sulfate adsorption flux to total S retention (58%). This indicates that the reduced S reservoir is relatively stable, and the historical reduction was well accumulated in soil profile. In contrast, the adsorption of sulfate is highly reversible, and the previously adsorbed S in soil might be released in some periods. Numerous studies have documented that desorption of adsorbed S would occur in light of continuous decline in atmospheric S deposition, and it reported to delay the recovery of soil and water acidification in America and Europe^{1,3,9,30}. The results derived from monitoring and modelling showed a sharp decline in S deposition in China when the national SO₂ emissions decreased by 72% after 2006²⁷. Consequently, sulfate desorption from the watersheds could be predicted in consideration of the large adsorbed SO₄²⁻ storage (~ 150 Tg S) in subtropical China.

Fortunately, a large proportion of S was stored as relatively irreversible reduced S in contrast to reversibly adsorbed SO₄²⁻. Re-mobilization of reduced S only occurs in response to the decreased watershed wetness or water table related to climate changes. Nonetheless, as with peatlands and saline marshlands, the re-oxidation of reduced S is considered to be a serious environmental problem in a drier climate under scenarios of predicted increased climate warming in northern hemisphere^{31,32}. This would cause an intense acid pulse from the large accumulation of reduced S, and thus the transient acidification of soils and adjacent water bodies. At the same time, it would promote the emission of biogenic sulfur gases, which has important impacts on atmospheric acid deposition, aerosol formation, and global climate change. In addition, the large sulfate reduction in subtropical accelerated decomposition of soil organic matter, resulting the extra emission of CO₂²⁹. It will be necessary to pay attention to the impacts of sulfate reduction on carbon cycling and climate change.

Methods

Study site, sampling and chemical analyses

This study was conducted in Tieshanping (TSP), a 4.6 ha headwater catchment located in the center of the subtropical China (Fig. 1b). It has a typical and widespread soil type (Haplic Acrisol) and vegetation type (*Pinus massoniana*). A relatively steep northeast-facing hillslope and a hydrologically connected terraced groundwater discharge zone were selected to dominant landscape in this study (Fig. 2). Throughfall (TF), soil water at 5 and 40 cm depths (S₁ and S₂), and stream water (SW) were collected weekly from 2001 to 2017. Soil cores were sampled in triplicate in hillslope (H1, H2, and H3), groundwater discharge zone (G1, G2, and G3), and nearby the weir (W) in October 2017. Soil water in 60 cm were sampled in May, August, and October 2017 at H3, G1, G2, and G3, labeled S_{H3}, S_{G1}, S_{G2}, and S_{G3}, respectively. Subsamples of soil cores in different depths were measured for total S, organic S, and δ³⁴S of the total S. They were extracted by DI-water and 0.01 M Ca(H₂PO₄)₂ for water soluble SO₄²⁻ and adsorbed SO₄²⁻. The total reduced S was determined by the total S minus the organic S, water soluble SO₄²⁻, and adsorbed SO₄²⁻. Water samples and soil extracts were analyzed for SO₄²⁻ concentration, δ³⁴S

and $\delta^{18}\text{O}$ of SO_4^{2-} , and $\delta^{18}\text{O}_{\text{H}_2\text{O}}$. S inputs and leaching losses were determined by multiplying SO_4^{2-} concentrations by water fluxes. Additional details can be found in Supplementary Text 4. A density rock layer in about 2 m impedes the exchange between the soil water and groundwater.

Model for flux estimation

The SO_4^{2-} pool in soil solution is conceptualized as an open, continuous flow-through system with competing plant-soil-microbe pools. Previous studies in TSP reveal no net accumulation of SO_4^{2-} on an annual basis in the soil solution even under chronically heavy S deposition¹¹. For the SO_4^{2-} pool in soil solution, the input and net mineralization (mineralization minus gross assimilation of plants and bacterias) of soil SO_4^{2-} is equivalent to the fates: adsorption, reduction, and output, because there is no geologic S source within the catchment. We derive the following mass balance equation accordingly (1):

$$\frac{dc}{dt} \times Q = F_i + F_n - (F_a + F_r + F_o) = 0 \quad (1)$$

where Q is water flux, F_i , F_n , F_a , F_r and F_o represent annual S fluxes of input (atmospheric deposition for the upper layer, and leaching from the first layer for the deeper layer), net mineralization, adsorption, reduction, and output, respectively.

F_i and F_o were directly derived from the measurements (more details in Supplementary Text 5). However, F_a , F_r and F_n were difficult to monitor in the field. $\delta^{34}\text{S}$ and the corresponding isotope effects of the S transformation processes on $^{34}\text{S}/^{32}\text{S}$ were applied to set up the ^{34}S balance, expressed in the equation (2):

$$F_i \times \delta^{34}\text{S}_i + F_n \times \delta^{34}\text{S}_{\text{org}} = F_r \times (\delta^{34}\text{S}_o - {}^{34}\epsilon_r) + (F_a + F_o) \times \delta^{34}\text{S}_o \quad (2)$$

where $\delta^{34}\text{S}_i$ is the $\delta^{34}\text{S}$ of input SO_4^{2-} , $\delta^{34}\text{S}_{\text{org}}$ is the $\delta^{34}\text{S}$ of organic S (= $\delta^{34}\text{S}$ of total S in surface soil, where total S is dominated by organic forms, Fig. 3a). $\delta^{34}\text{S}_o$ denotes the $\delta^{34}\text{S}$ of SO_4^{2-} in the soil water. ${}^{34}\epsilon_r$ refers to the isotope effect ($\epsilon = \text{light}k/\text{heavy}k - 1$, reported in ‰, with k being the rate constant) by reduction. The ${}^{34}\epsilon_r$ was assumed as 16‰, with a range of 12-20‰ in this study, according to the Rayleigh distillation equation (Supplementary Text 5). While during other SO_4^{2-} loss processes, the isotope effects are negligible (Supplementary Text 5).

Similarly, the ^{18}O balance was conceptualized in equation (3):

$$F_i \times \delta^{18}\text{O}_i + F_r \times \delta^{18}\text{O}_{\text{H}_2\text{O}} = F_r \times (\delta^{18}\text{O}_o - {}^{18}\epsilon_r) + (F_a + F_o) \times \delta^{18}\text{O}_o \quad (3)$$

where $\delta^{18}\text{O}_i$ and $\delta^{18}\text{O}_o$ are the $\delta^{18}\text{O}$ of SO_4^{2-} input and output. $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ is the $\delta^{18}\text{O}$ of H_2O (0.5‰). ${}^{18}\epsilon_r$ is the O isotope effect by reduction, having a value of 38% of ${}^{34}\epsilon_r$. More details were added in Supplementary Text 5. Fluxes of net mineralization, reduction, and adsorption were calculated according equation (1), (2), and (3) (Supplementary Text 5). The impacts of the uncertainty of ${}^{34}\epsilon_r$ on our estimates are demonstrated in the Supplementary Text 5.

Declarations

Data availability

The data that support the finding of this study are available from the corresponding author (D.L.) upon request.

Acknowledgements

We are grateful to the National Key Research and Development Project (2019YFC0214800) and National Natural Science Foundation of China (41877329) for supporting this research. Qian Yu is supported by the Shuimu Tsinghua Scholar and China Postdoctoral Science Foundation (2020M670353).

Author contributions

Q. Y., L. D., and J. M. conceived the work. Q. Y. designed and conducted field work. Q. Y., G. S., and K. L. carried out analyses. Q. Y. and L. D. analyzed data and wrote the paper. J. M. and L. Y. contributed the discussion, manuscript revision and English revision. All authors discussed the interpretation of the results and contributed to the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at Correspondence and requests for materials should be addressed to L.D.

References

1 Likens, G. E., Driscoll, C. T. & Buso, D. C. Long-term effects of acid rain: Response and recovery of a forest ecosystem. *Science* **272**, 244-246, doi:10.1126/science.272.5259.244 (1996).

- 2 Neary, B. P. & Dillon, P. J. Effects of sulfur deposition on lake-water chemistry in Ontario, Canada. *Nature* **333**, 340-343, doi:10.1038/333340a0 (1988).
- 3 Stoddard, J. L. *et al.* Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* **401**, 575-578, doi:10.1038/44114 (1999).
- 4 Johnson, D. W., Cole, D. W. & Gessel, S. P. Acid precipitation and soil sulfate adsorption properties in a tropical and in a temperate forest soil. *Biotropica* **11**, 38-42, doi:10.2307/2388169 (1979).
- 5 Johnson, D. W., Richter, D. D., Vanmiegroet, H. & Kelly, J. M. Sulfur cycling in 5 forest ecosystems. *Water Air Soil Pollut.* **30**, 965-979, doi:10.1007/bf00303360 (1986).
- 6 Johnson, D. W. Sulfur cycling in forests. *Biogeochemistry* **1**, 29-43, doi:10.1007/bf02181119 (1984).
- 7 Liu, M. & Thomas, G. W. Nature of sulphate retention by acid soils. *Nature* **192**, 384-&, doi:10.1038/192384a0 (1961).
- 8 Cosby, B. J., Hornberger, G. M., Wright, R. F. & Galloway, J. N. Modeling the effects of acid deposition - control of long-term sulfate dynamics by soil sulfate adsorption. *Water Resour. Res.* **22**, 1283-1291, doi:10.1029/WR022i008p01283 (1986).
- 9 Rice, K. C., Scanlon, T. M., Lynch, J. A. & Cosby, B. J. Decreased Atmospheric Sulfur Deposition across the Southeastern US: When Will Watersheds Release Stored Sulfate? *Environ. Sci. Technol.* **48**, 10071-10078, doi:10.1021/es501579s (2014).
- 10 Larssen, T., Duan, L. & Mulder, J. Deposition and leaching of sulfur, nitrogen and calcium in four forested catchments in China: implications for acidification. *Environ. Sci. Technol.* **45**, 1192-1198, doi:10.1021/es103426p (2011).
- 11 Yu, Q. *et al.* Monitoring Effect of SO₂ Emission Abatement on Recovery of Acidified Soil and Streamwater in Southwest China. *Environ. Sci. Technol.* **51**, 9498-9506, doi:10.1021/acs.est.7b01147 (2017).
- 12 Bern, C. R. & Townsend, A. R. Accumulation of atmospheric sulfur in some Costa Rican soils. *J. Geophys. Res.-Biogeosci.* **113**, doi:10.1029/2008jg000692 (2008).
- 13 Mayer, B., Prietzel, J. & Krouse, H. R. The influence of sulfur deposition rates on sulfate retention patterns and mechanisms in aerated forest soils. *Appl. Geochem.* **16**, 1003-1019, doi:10.1016/s0883-2927(01)00010-5 (2001).
- 14 Alewell, C. & Gehre, M. Patterns of stable S isotopes in a forested catchment as indicators for biological S turnover. *Biogeochemistry* **47**, 319-333, doi:10.1007/bf00992912 (1999).

- 15 Alewell, C. & Giesemann, A. Sulfate reduction in a forested catchment as indicated by delta S-34 values of sulfate in soil solutions end runoff. *Isotopes in Environmental and Health Studies* **32**, 203-210, doi:10.1080/10256019608036312 (1996).
- 16 Morth, C. M., Torssander, P., Kusakabe, M. & Hultberg, H. Sulfur isotope values in a forested catchment over four years: Evidence for oxidation and reduction processes. *Biogeochemistry* **44**, 51-71 (1999).
- 17 Antler, G., Turchyn, A. V., Rennie, V., Herut, B. & Sivan, O. Coupled sulfur and oxygen isotope insight into bacterial sulfate reduction in the natural environment. *Geochimica Et Cosmochimica Acta* **118**, 98-117, doi:10.1016/j.gca.2013.05.005 (2013).
- 18 Sim, M. S., Bosak, T. & Ono, S. Large Sulfur Isotope Fractionation Does Not Require Disproportionation. *Science* **333**, 74-77, doi:10.1126/science.1205103 (2011).
- 19 Yu, Q., Si, G., Zong, T., Mulder, J. & Duan, L. High hydrogen sulfide emissions from subtropical forest soils based on field measurements in south China. *Sci. Total Environ.* **651**, 1302-1309, doi:10.1016/j.scitotenv.2018.09.301 (2019).
- 20 Vet, R. *et al.* A global assessment of precipitation chemistry and deposition of sulfur, nitrogen, sea salt, base cations, organic acids, acidity and pH, and phosphorus. *Atmos. Environ.* **93**, 3-100, doi:10.1016/j.atmosenv.2013.10.060 (2014).
- 21 Huang, Y. M., Kang, R. H., Mulder, J., Zhang, T. & Duan, L. Nitrogen saturation, soil acidification, and ecological effects in a subtropical pine forest on acid soil in southwest China. *J. Geophys. Res.-Biogeosci.* **120**, 2457-2472, doi:10.1002/2015jg003048 (2015).
- 22 Wang, Z., Zhang, X., Zhang, Y., Wang, Z. & Mulder, J. Accumulation of different sulfur fractions in Chinese forest soil under acid deposition. *Journal of Environmental Monitoring* **13**, 2463-2470, doi:10.1039/c1em10313j (2011).
- 23 Derry, L. A. & Murray, R. W. Continental margins and the sulfur cycle. *Science* **303**, 1981-1982 (2004).
- 24 Mayer, B., Feger, K. H., Giesemann, A. & Jager, H. J. Interpretation of sulfur cycling in 2 catchments in the black-forest (germany) using stable sulfur and oxygen-isotope data. *Biogeochemistry* **30**, 31-58, doi:10.1007/bf02181039 (1995).
- 25 Novak, M. *et al.* Isotope systematics of sulfate-oxygen and sulfate-sulfur in six European peatlands. *Biogeochemistry* **76**, 187-213, doi:10.1007/s10533-005-4433-7 (2005).
- 26 Mulder, J., Vanbreemen, N. & Eijck, H. C. Depletion of soil aluminum by acid deposition and implications for acid neutralization. *Nature* **337**, 247-249, doi:10.1038/337247a0 (1989).

- 27 Yu, Q. & Duan, L. *Contribution of Atmospheric Reactive Nitrogen to Acid Deposition in China*. (2020).
- 28 Yu, Q. *et al.* Is surface water acidification a serious regional issue in China? *Sci. Total Environ.* **584**, 783-790, doi:10.1016/j.scitotenv.2017.01.116 (2017).
- 29 Hinckley, E.-L. S., Crawford, J. T., Fakhraei, H. & Driscoll, C. T. A shift in sulfur-cycle manipulation from atmospheric emissions to agricultural additions. *Nature Geoscience*, doi:10.1038/s41561-020-0620-3 (2020).
- 30 Wright, R. F., Lotse, E. & Semb, A. Reversibility of acidification shown by whole-catchment experiments. *Nature* **334**, 670-675, doi:10.1038/334670a0 (1988).
- 31 Mitchell, M. J., Driscoll, C. T., McHale, P. J., Roy, K. M. & Dong, Z. Lake/watershed sulfur budgets and their response to decreases in atmospheric sulfur deposition: watershed and climate controls. *Hydrological Processes* **27**, 710-720, doi:10.1002/hyp.9670 (2013).
- 32 Mitchell, M. J. & Likens, G. E. Watershed sulfur biogeochemistry: shift from atmospheric deposition dominance to climatic regulation. *Environ. Sci. Technol.* **45**, 5267-5271, doi:10.1021/es200844n (2011).