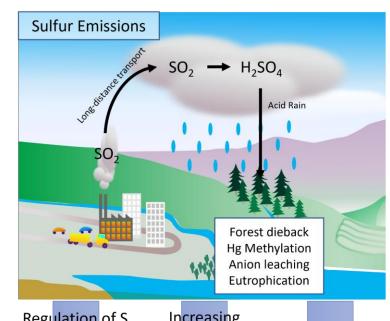
The Changing Sulfur Cycle: Effects and consequences of human-impacted sulfur cycling

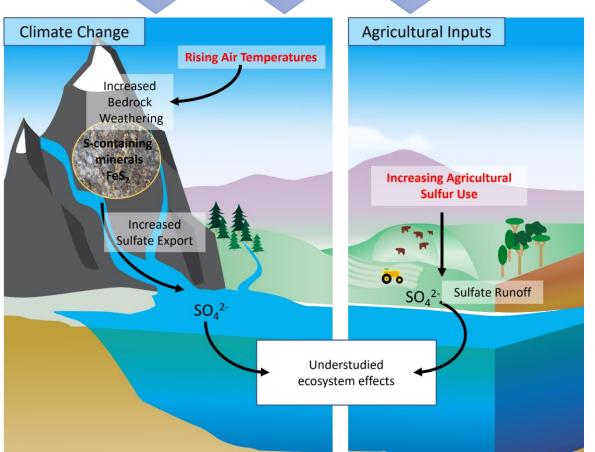
A Changing Sulfur Cycle

The amount of bioavailable sulfur (S) cycling through the biosphere has more than doubled since pre-industrial times¹.

The negative effects of S pollution from fossil fuel emissions have been well-studied. S emissions cause the formation, transport, and deposition of sulfuric acid in rainfall. In the 1970's, acid rain caused the dramatic decline of many ecosystems, which led to regulations on S emissions. These regulations were extremely effective at reducing the negative effects of S pollution from emissions. However, despite this success, human impacts on the S cycle are far from over – instead, they have now shifted to other sources. Factors like climate change and agricultural intensification have produced new and significant sources of excess S in the environment.

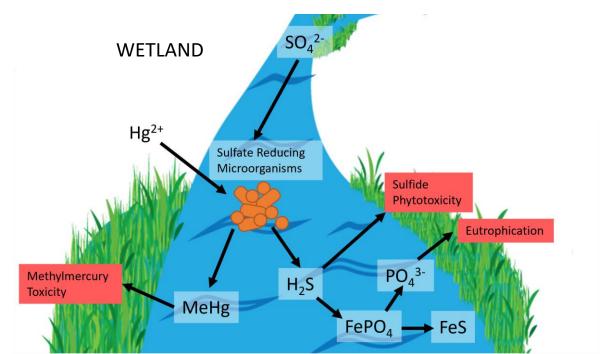


agricultural S use



With less S provided from the atmosphere, farmers have needed to add more S onto their crops to meet growing demands. These amendments are often much larger in magnitude than the peak load of S from acidic deposition², indicating that **agricultural amendments** have overtaken emissions as the primary source of anthropogenic S into the environment. Despite this, the environmental effects of agricultural S use have remained largely understudied.

Alpine areas are key water resources of the world and are extremely vulnerable to a changing climate³. Recent work has shown that warming conditions accelerate geologic weathering, increasing sulfate export from alpine areas¹¹. Biogeochemical cycling within alpine areas can influence water quality in downstream locations, so determining changes in alpine S cycling will be key to adapting to the consequences of a warmer climate.



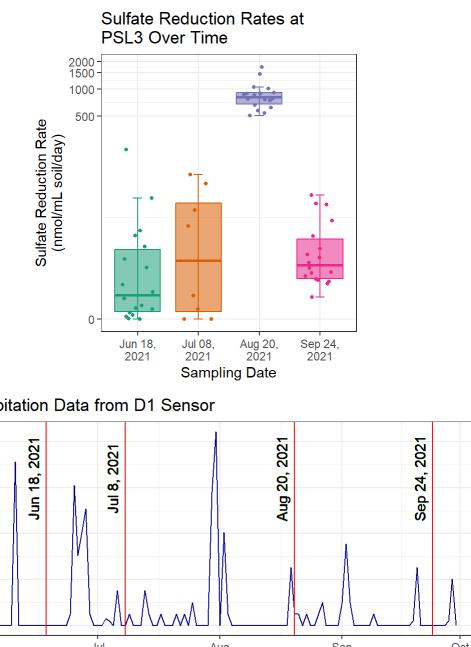
Excess sulfate in the environment can stimulate the activity of **sulfate** reducing microorganisms, leading to a variety of environmental consequences.

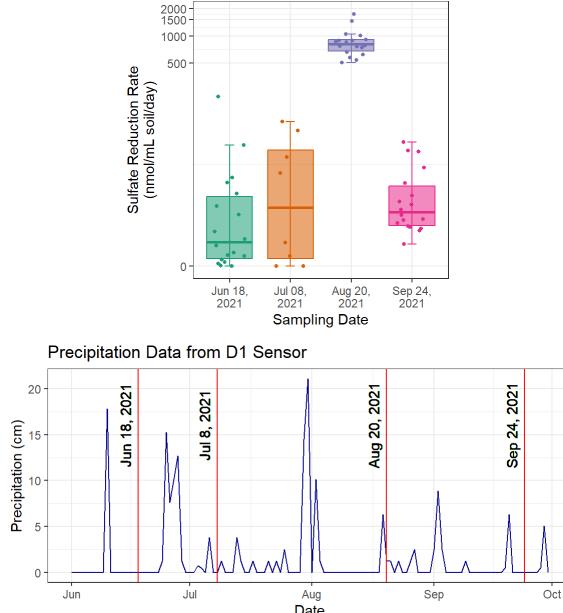
Alpine Wetlands are Key Areas of Sulfate Reduction

sulfate and high rates of sulfate reduction.

Although the Niwot landscape is remote and unpolluted, sulfate concentrations in periglacial solifluction lobe 3 (PSL3) pools even exceeded concentrations found in S-polluted systems (fig 2). This data suggests that PSL3, a hydrologically isolated wetland, is capturing sulfate runoff from bedrock weathering at Niwot Ridge.

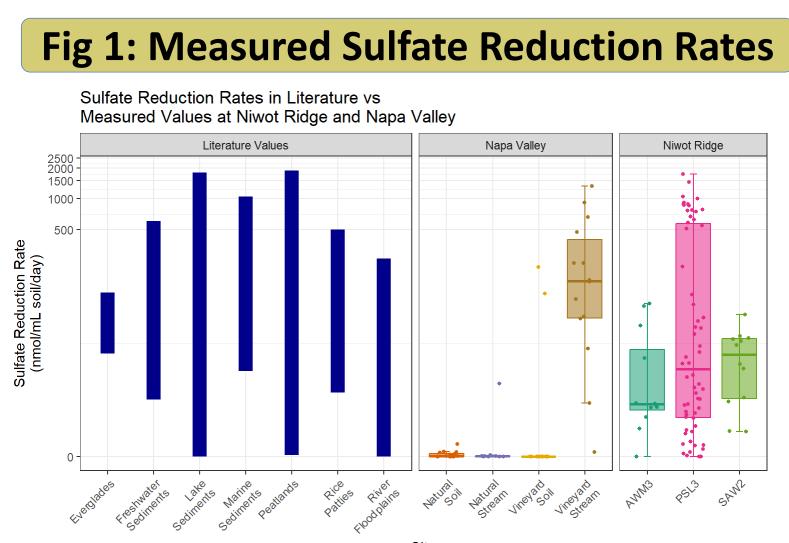
We also observed **high rates of sulfate reduction** in Niwot alpine wetlands (fig 1). The rates measured in these small wetlands were comparable to systems that are considered key areas of sulfate reduction.





Sulfate reduction rates also showed large variation due to soil heterogeneity and temporal variation. PSL3 was sampled at four different timepoints throughout the summer, each timepoint showing very different rates (above). A comparison with precipitation data showed that this high timepoint was taken right after a rain event, indicating that **sulfate reduction activity may be stimulated by** events like rainfall.

Unpublished data by Miller (*Miller, unpublished work*) also suggests that the high sulfate reduction activity in these areas **could be contributing to methylmercury production.** Miller found high concentrations of methylmercury in subalpine wetland 2 (SAW2), where I observed elevated rates of sulfate reduction.

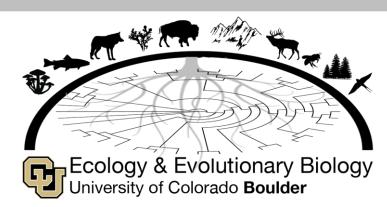




Environmental Biogeochemistry Group UNIVERSITY OF COLORADO BOULDER

^{1,2}Laura Rea and ^{1,2}Eve-Lyn S. Hinckley ¹Dept. of Ecology and Evolutionary Biology, University of Colorado, Boulder ²Cooperative Institute for Research in Environmental Sciences

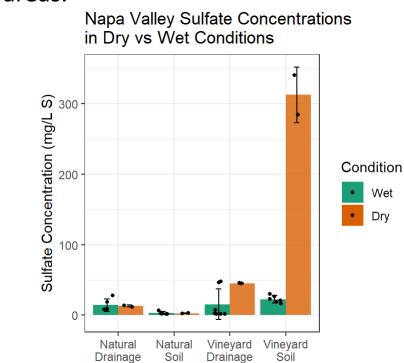
We found that alpine wetlands have very high concentrations of





Evidence of Sulfate Reduction In and Downstream of CA Vineyards

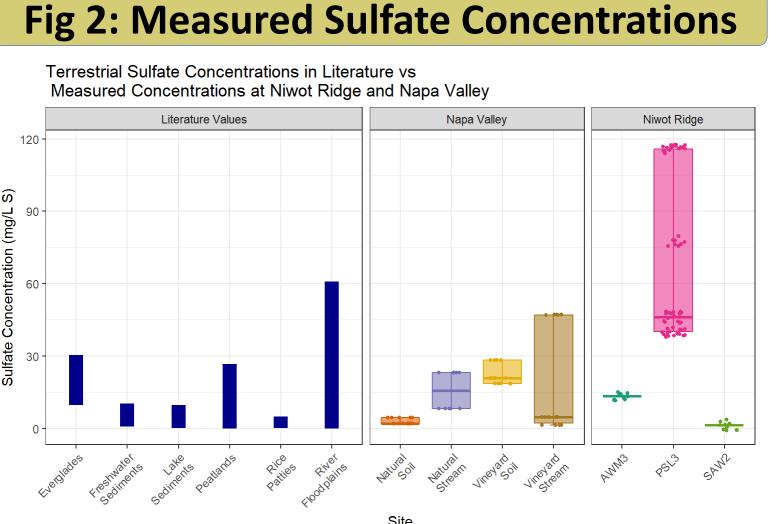
My measurements in Napa Valley show high rates of sulfate reduction in a stream receiving vineyard runoff (figure 1). Additionally, vineyards and vineyard streams showed higher concentrations of sulfate than natural sites. This suggests that sulfate runoff from vineyards may be stimulating sulfate reduction activity in downstream areas.



Although vineyard soils showed a low average sulfate reduction rate, other evidence suggests that these areas may be key areas of sulfate **reduction.** Temporal data (*above*) shows that sulfate concentrations dramatically increased between a wet sampling date and a dry sampling date. This suggests that during a wet period, sulfate reduction transforms sulfate into reduced species which are immobilized in the soil. When the soils dry out, these reduced species are re-oxidized into sulfate, causing the high concentrations observed.



How is sulfate reduction occurring in well-drained, aerated, vineyard soils? Soil heterogeneity may be key. Note in *fig 1* that most vineyard soil subsamples show no sulfate reduction activity. Two subsamples, however, have very high rates. This pattern suggests that **sulfate** reduction could be happening in anoxic microsites within vineyard **soils.** Furthermore, I used a method modified from Fike et al (2017)⁵ to map the spatial distribution of sulfate reduction activity in the soil (above). These results confirmed that sulfate reduction is occurring in small aggregates within vineyard soils.

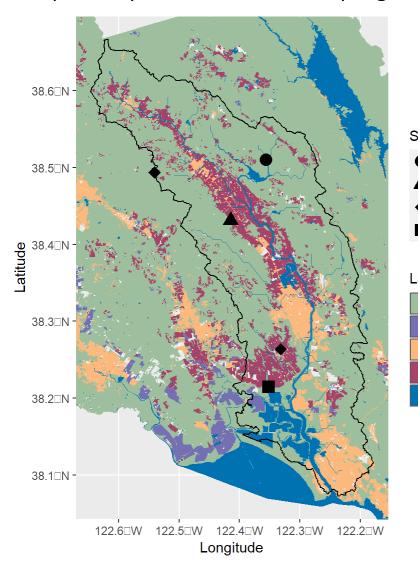






Mapping Sulfate Reduction and **Microbial Communities Across the Napa Valley Watershed**

Could sulfate runoff from vineyards be increasing sulfate reduction on a landscape scale, and could these sulfate inputs be affecting the soil microbial community? My ongoing work is sampling across the Napa Valley watershed to determine this. Samples are currently being measured for sulfate reduction rates and 16S rRNA marker gene sequencing will be used to determine microbial community structure. Napa Valley Watershed and Sampling Sites



Vineyard and Wetlan Land Use

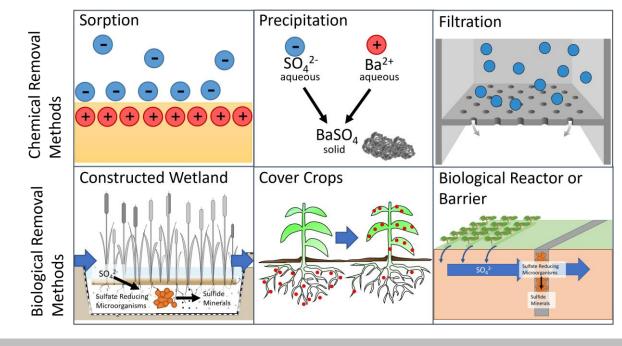
Other Agricultur

Comparing California, U.S. with **New Zealand Vineyard Sites**

Do our findings in Napa Valley apply to other vineyard sites across the world? My upcoming work will compare sulfate runoff and soil microbial communities between Napa Valley and the Marlborough wine region in New Zealand. This information will tell whether soil and climate type affect the fate of S pollution and will allow us to adapt our model to address different environments.

Can We Mitigate S Pollution?

Is there a way to capture sulfate in vineyard runoff? My future work will look at modifying existing sulfate capture methods for use in vineyards.



References

1 Lamarque, J. F. et al. Multi-model mean nitrogen and sulfur deposition from the atmospheric chemistry and climate model intercomparison project (ACCMIP): Evaluation of historical and projected future changes. Atmos Chem Phys (2013). 2 Hinckley, E. L. S., Crawford, J. T., Fakhraei, H. & Driscoll, C. T. A shift in sulfur-cycle manipulation from atmospheric emissions to agricultural additions. Nat Geosci (2020).

3 Immerzeel, W. W. et al. Importance and vulnerability of the world's water towers. Nature (2019). **4** Crawford, J. T., Hinckley, E. L. S., Litaor, M. I., Brahney, J. & Neff, J. C. Evidence for accelerated weathering and sulfate

export in high alpine environments. *Environmental Research Letters* (2019). **5** Fike, D. A. *et al.* Spatially resolved capture of hydrogen sulfide from the water column and sedimentary pore waters for abundance and stable isotopic analysis. Mar Chem (2017).





Faculty Early Career Development Program (CAREER) Award