Do Agricultural Inputs Accelerate Pyrite and Carbonate Weathering?

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Pyrite (FeS_2) is a common mineral in the subsurface that is prone to oxidation, which produces sulfuric acid. In lab experiments, it has been shown that nitrate reduction can be coupled to pyrite oxidation by bacteria, which could remove nitrate from the groundwater. This reaction might be important in watersheds with a high proportion of agricultural land use, due to high inputs of nitrate fertilizers. We hypothesize that agricultural land use accelerates pyrite oxidation. Our hypothesis is difficult to test for several reasons. 1) There is currently no clear isotopic signal to distinguish between oxidant sources for pyrite oxidation. 2) Many electron donars can reduce nitrate; thus, not all denitrification is a result of pyrite oxidation. 3) Sulfate in surface waters have many sources, which makes it difficult to determine sulfate derived from pyrite oxidation. To test our hypothesis, we use stream water chemistry, multivariate statistics, bedrock chemistry, and mixing models to delineate sulfate derived from precipitation, pyrite oxidation, and fertilizers across a land use gradient in the Susquehanna Shale Hills Critical Zone Observatory (SSHCZO; Pennsylvania, USA). The pyrite-derived sulfate flux in Shale Hills (subcatchment with no agricultural land use) is 3.0-6.2 x 10^{-3} mol m^{-2} yr^{-1}, which is 8.5-17.3% of the total sulfate flux. We observe seasonal variations in pyrite-derived sulfate ranging from 0.2-99.5% of the total stream sulfate with the highest proportions in the dry summer months. Additionlly, stream chemistry shows increasing carbonate dissolution related to pyrite oxidation. In the larger Shavers Creek watershed, pyrite-derived sulfate concentrations increase as a function of agricultural land use (R^2= 0.88, $p < 0.001$). This supports the hypothesis that nitrate fertilizers increase rates or extents of pyrite oxidation. Nitrate reduction coupled to pyrite oxidation might significantly attenuate groundwater nitrate concentrations. We also observe increases in calcium concentrations with increased agricultural land use. This might be a result of enhanced carbonate disolution via increaced sulfuric acid production.