Identifying sources of streamwater sulfate after a summer drought in the Sleepers River watershed (Vermont, USA) using hydrological, chemical, and isotope approaches

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In many forested headwater catchments, peak sulfate concentrations in stream water occur in the fall during re-wetting of the watershed resulting in episodic stream acidification. We investigated the sources of highly elevated stream water sulfate concentrations in a first order stream at the Sleepers River watershed (Vermont, USA) after the particularly dry summer of 2001 using a combination of hydrological, chemical and isotopic approaches. Throughout the summer of 2001 sulfate (SO$_4^{2-}$) concentrations in stream water doubled from 6 to 12 mg/L while flows decreased. Simultaneously increasing Na$^+$ and Ca$^{2+}$ concentrations and $\delta^{34}$S values increasing from $+7\%$ towards those of bedrock sulfur ($+8$ to $+13\%$) indicated that chemical weathering involving the oxidation of sulfides in schists and phyllites was responsible for the initial increase in sulfate concentrations. During re-wetting of the watershed in late September and early October of 2001, increasing stream flows were accompanied by decreasing Na$^+$ and Ca$^{2+}$ concentrations, but sulfate concentrations continued to increase to peak concentrations of more than 25 mg/L, indicating that bedrock weathering was not the sole source responsible for peak sulfate concentrations. The further increase in sulfate concentrations coincided with an abrupt decrease of $\delta^{34}$S values in stream water sulfate from maximum values near $+10\%$ to minimum values near $-3\%$. Soil investigations revealed that some C horizons in the spodosols of the watershed contained sulfide minerals with $\delta^{34}$S values of $-22\%$. Our data indicate that soil sulfides were
oxidized to sulfate during the particularly dry summer of 2001, and the newly formed sulfate was transported to the streams during re-wetting of the watershed contributing ~50% of the sulfate during peak concentrations in the stream water. The current study provides evidence that a quantitative assessment of the sources of stream water sulfate in forested watersheds is possible by combining hydrological, chemical and isotopic techniques, provided that the isotopic compositions of all potential sulfate sources are known. This approach is suitable for obtaining a better understanding of the causes of episodic stream water acidification.