The potential use of Ba/Sr ratios as an indicator of fracking fluid spills

JOHAN SCHIJF* AND CAROLINE G. COULTER

UMCES/Chesapeake Biological Laboratory, P.O. Box 38, Solomons, Maryland 20688, USA.
*correspondence: schijf@cbl.umces.edu

Strontium (Sr) and barium (Ba) are ubiquitous in surface freshwaters at nM to low-μM concentrations but enriched in fracking fluids by up to 4 orders of magnitude. Monitoring of Sr and Ba levels has thus been proposed as a way to detect spills. Our 2-year survey of streams overlying the Marcellus Shale in western Maryland, where a temporary reprieve from fracking activities has been ordered, indicates that baseline Sr and Ba levels are variable in space and time, complicating the early detection of fluid spills depending on location and season. On the other hand, Ba/Sr ratios appear to be constant in individual streams and Ba is often near saturation with respect to barite ($BaSO_4$), while Sr is greatly undersaturated with respect to celestite ($SrSO_4$). Physicochemical models of typical stream waters suggest that a fluid spill would raise Sr concentrations yet that Ba concentrations are constrained by precipitation. Hence, even rather minor spills might trigger a conspicuous decrease of the Ba/Sr ratio. Other common ions, albeit equally variable, are not as enriched in fracking fluids nor subject to such solubility limits. For example, Na and Cl levels are less sensitive to fluid spills and cannot distinguish them from road salt effluent based on the Na/Cl ratio. One exception may be Br, which is virtually absent from surface freshwaters and could signal a spill by its mere presence.

Ongoing experiments in our laboratory are designed to validate this idea by measuring the Ba/Sr ratio in mixtures of stream water and fracking fluid. Filtered water from streams naturally enriched in Ba, enriched in Sr, and with Ba/Sr ~ 1, were spiked (0.2, 0.02 and 0.002% by volume) with filtered produced water, collected from a university test well several weeks after fracking, and continuously agitated on a rotary shaker at 25°C. Analysis by ICP-MS and ion chromatography revealed that the produced water contains about 10 mM each of Ba and Sr, and about 1000 mM chloride. Nevertheless, preliminary data show no deviation of the Ba/Sr ratio from its calculated initial value over a period of 2 weeks. This implies that barite precipitation is kinetically hindered, in spite of pronounced supersaturation, likely due to the absence of particles that promote nucleation. Further experiments are planned in the presence of clean sand (to prevent sorption or contamination), at lower temperatures, and with fluids that have a different composition.