Fracture Gel's Possible Synergistic Influence for Chloride's Effects on Vegetation

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Description of Experiment

We made a preliminary investigation into fracture gel's possible effects on a single species of woodland vegetation that is found throughout the state of West Virginia. *Vacccinium vacillans* is one of a group of plants known in this state as huckleberry.[1] The investigation followed the model of applications made in 2010 using chloride only.[2]

Sample applications were made to examine possible effects from land application of fracture waste, or flowback, as allowed under West Virginia Office of Oil and Gas' *General Water Pollution Control* Permit, GP-WV-1-88.

Land application of flowback is allowed, if the parameters of the permit are met, for all wells except those drilled to Marcellus shale formation.[3]

Process

The application fluid was rainwater mixed with fracture gel components. Two of the applications also included the amount of sodium chloride required to make a 5,000 mg/l chloride solution.

The fracture gel was modeled on a typical solution of solvent (in this case kerosene) mixed with guar gum. Water was added to the solution to create the gel. Industry uses varying amounts of the gel with other chemicals and sand, or pure water alone, through the various stages for a fracture process. We used two solutions-to-water ratios for making gel, ratios typical for solution to total water used. One ratio was 3 gallons of solvent to 1,000 gallons of water (about 11 ml per gallon). The other ratio was 6 gallons to 1,000 gallons of water (about 22 ml per gallon). This is more or less comparable to the amount of gel in flowback, except our mixture was more homogenous. In industry applications, flowback can include thick gel clots.

We made four one gallon applications. All were application to the plant's leaf surfaces and ground, covering about 1 square foot each. Application 1 was a 3 gallon to 1,000 gallon gel. Application 2 was a 6 gallon to 1,000 gallon gel. Application 3 was a 3 gallon to 1,000 gallon gel with 5,000 mg/l chloride. Application 4 was a 6 gallon to 1,000 gallon gel with 5,000 mg/l chloride.

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[1] Identification based on P. D. Strausbaugh and Earl Cole, [1978], *Flora of West Virginia.*

[2] George Monk and Molly Schaffnit, 2010, *Chloride Application Study, 2010.*

[3] The General Permit's chloride limitation is 12,500 mg/l with no load factor.

Applications		
1	Approximately 11 mg/l kerosene (plus guar gum) in 1 gallon of water.	Equal to 3 gallons solvent and guar to 1,000 gallons water.
2	Approximately 22 mg/l kerosene (plus guar gum) in 1 gallon of water.	Equal to 6 gallons solvent and guar to 1,000 gallons water.
3	Approximately 11 mg/l kerosene (plus guar gum) in 1 gallon of water plus 5,000 mg/l chloride.	
4	Approximately 22 mg/l kerosene (plus guar gum) in 1 gallon of water plus 5,000 mg/l chloride.	

Results of Applications

There were no visible signs of damage to vegetation from the gel-only applications. A distinct hydrocarbon odor remained for a week after, even after rain showers, to the leaf duff layer under the plants.

Leaf duff was scraped away from around the plant base for gel and chloride applications. Plants receiving gel and 5,000 mg/l chloride mixture showed signs of leaf scorch/chlorosis within 2 days. Application 4 (6 gallons of solvent to 1,000 gallons of water, plus chloride) showed more extreme signs of damage, with plants eventually losing almost all of their leaves.

Timeline for gel and chloride applications	
30 July	1 gallon applications made.
1 August	Visible scorching/chlorosis.
5 August	Scorching and chlorosis increasing in severity.
6 August	Fallen leaves at bases of plants.
10 August	Most leaves fallen from application 4 plants.

The plant receiving application 3 showed comparable (or slightly more extreme) results to a plant receiving 5,000 mg/l chloride alone.[4] The plants receiving application 4 showed much more severe results, comparable to either higher concentration or load of chloride.

Discussion

The LGC series of Halliburton gel products include guar gum or similar starches and diesel or other simple or complex hydrocarbon solvents, alone or in combination.[5] LGC-35 CBM, known to be used in West Virginia, contains non-specific "paraffinic solvent" and "polysaccharide" starch according to the Material Safety Data Sheet.[6] We modeled our gel formula on LGC-IV with Kerosene which uses kerosene and guar gum. None of the Material Safety Data Sheets we examined gave actual mixtures. The EPA's 2004 *Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs* states that diesel and guar gum were of roughly comparable volumes.[7] We found a 66% solvent and 33% guar mixture by volume created a clot-free gel. The EPA's fracture study states that 6 gallons of solvent to 1,000 gallons of water was an intermediate amount. That's approximately what was used to fracture a non-shale resource in West Virginia.[8]

The gel has two contrasting qualities. It is slippery while at the same time being adhesive. The fluid sticks to surfaces. Leaves when dry show a barely visible sheen/residue. The hydrocarbon element is readily noticed by its odor and the rainbow sheen on the gel fluid mixture.

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[4] Monk and Schaffnit, 2010, *Chloride Application Study, 2010.* See photograph 6, page 11, for comparison.

[5] The solvents used in Halliburton's LGC series of products are (listed according to their frequency in Material Data Safety Sheets): diesel (CAS 68476-34-6); hydrotreated light petroleum distillate (CAS 64742-47-8); paraffinic solvent; petroleum distillate (CAS 64741-44-2); mineral oil (CAS 8042-47-5); naphtha, hydrotreated heavy (CAS 64742-48-9); methanol (CAS 67-56-1); dipropylene glycol monomethyl ether (CAS 34590-94-8); glycol ether; gas oils, petroleum, straight-run (CAS 64741-43-1); gas oils, petroleum, straight-run, high-boiling (CAS 68915-97-9); polypropylene glycol (CAS 25322-69-4); and kerosene (CAS 8008-20-6). Ethylene glycol monobutyl ether (CAS 111-76-2), also called 2-Butoxyethanol or 2-BE, appears alone, without guar or other starch, in LGC-MI. This and most of the other solvents are known toxics for humans.

[6] Pamela J. Edwards, 2011, *Chloride Concentration Gradients in Tank-Stored Hydraulic Fracturing Fluids Following Flowback*, see Table 2. Halliburton's LGC-35 CBM and other MSDS information is available at http://www.halliburton.com/toolsresources/default.aspx?navid=1061&pageid=2.

[7] EPA, 2004, *Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs*, Chapter 4.

[8] Pamela J. Edwards, 2011, *Chloride Concentration Gradients in Tank-Stored Hydraulic Fracturing Fluids Following Flowback*, see Table 2

We believe, based on these trials, that fracture gel increases the period of solution contact with leaves and that alone may account for the effects we noted: the thicker the gel, the more profoundly negative effects of chloride on the plant. It is also possible that the gel helped retain chloride in the soil, preventing washout due to rain.[9] The gel by itself seems to have no effect on plants.

We are developing a set of application tests to better examine the possibly synergy of gel and chloride in land application in producing negative effects.

Side Note

Many of the solvents used in Halliburton's LGC products have been studied by the EPA for their use as carriers/inerts for pesticides and herbicides.[10] Other solvents, such as diesel, have known adverse environmental effects. In most cases these solvents readily pass through soils or break down in soil, shedding toxic substances to ground water.

While the amounts of solvent used per gallon of water are relatively small, in fracture jobs requiring 100,000 gallons or more of water, the quantities become large, more than 500 gallons. The volume of these solvents returned to surface as flowback is only a percentage of the amount used, but the quantities of solvent returned to surface can be large.

The state allows the land application of flowback without examination of solvents used or hydrocarbon analysis of fluid before land spraying. The possibility of application of hundreds of gallons of a solvent to a relatively small area would not be considered safe if the application were of the solvent alone. We do not see that an admixture of water, other possibly toxic products, and possible toxic materials from underground make it any safer.

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[9] Fracture gels like what we used are not permanent. Industry adds what they call "crosslinkers" to create a stable and permanent gel. The gel is later treated with "breakers" in the fracture process.

[10] Solvents studied by the EPA as carriers/inerts include dipropylene glycol monomethyl ether (CAS 34590-94-8); distillates (petroleum), hydrotreated light (CAS 64742-47-8); naphtha (petroleum), hydrotreated heavy (CAS 64742-48-9); and mineral oil (CAS 8042-47-5). The EPA memo for dipropylene glycol monomethyl ether notes that toxicity is not likely at application rates of 1 lb/acre for humans and for other terrestrial species at 10 lb/acre. See http://www.epa.gov/opprd001/inerts/dipropylene.pdf. Fluid with this chemical should not be a candidate for land application.

Conclusion

The possible synergistic effects of fracture gel and chloride on vegetation were noted in trial applications to a single species of vegetation. The gel seemed to enhance the negative effects of chloride, causing severe leaf scorching and chlorosis.

Sources

Edwards, Pamela J. 2011. *Chloride Concentration Gradients in Tank-Stored Hydraulic Fracturing Fluids Following Flowback.* U.S. Department of Agriculture, Forest Service, Northern Research Station, Research Paper-NRS-14. http://www.nrs.fs.fed.us/pubs/rp/rp_nrs14.pdf

EPA. 2004. *Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs*. Washington, D.C.: US Environmental Protection Agency, Office of Water, Office of Ground Water and Drinking Water, Drinking Water Protection Division, Prevention Branch, EPA 816-R-04-003. http://www.epa.gov/safewater/uic/pdfs/completestudy.zip for whole document or http://www.epa.gov/safewater/uic/pdfs/cbmstudy_attach_uic_ch04_hyd_frac_fluids.pdf for just chapter 4.

Monk, George and Schaffnit, Molly. 2010. *Chloride Application Study*. http://members.citynet.net/sootypaws/Woods/gaswell/docs/chlorideapplistudy.pdf

Strausbaugh, P. D. and Core, Earl L. [1978]. *Flora of West Virginia*. Grantsville, WV: Seneca Books, Inc.

West Virginia Office of Oil and Gas. *General Water Pollution Control Permit*. GP-WV-1-88. http://www.dep.wv.gov/oil-and-gas/GI/Documents/General%20Water%20Pollution%20Control%20Permit%20.pdf

Photograph 1. The single plant receiving application 3 on 30 July. Application 3 was 1 gallon of gel (comparable to 3 gallons of solvent to 1,000 gallons of water) with 5,000 mg/l chloride.

Photograph 2. The cluster of plants in application 4 on 30 July. Application 4 was 1 gallon of gel (comparable to 6 gallons of solvent to 1,000 gallons of water) with 5,000 mg/l chloride.

Photograph 3. Application 3 plant leaves showing first signs of chlorosis on 1 August. The gel residue is visible as white patches on the leaves.

Photograph 4. Application 4 plant leaves showing first signs of chlorosis on 1 August.

Photograph 5. Detail of application 4 leaves showing chlorosis on 1 August.

Photograph 6. Application 3 plant on 6 August showing severe chlorosis.

Photograph 7. Application 4 plant leaves showing severe chlorosis on 6 August.

Photograph 8. Fallen leaf from application 4 plant on 6 August.

Photograph 9. Application 3 plant on 10 August. A number of leaves have fallen and leaves remaining on plant show severe damage and curling.

Photograph 10. Application 4 plants on 10 August. Most of leaves in application area have fallen. Remaining leaves show severe chlorosis.