Preliminary Assessment of Contaminant Migration Potential from Hydraulic Fracturing Makeup Fluid in the Upper Humboldt River Basin, Nevada

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INTRODUCTION

This report describes the results of the concentration analysis and assessment of migration potential for hydraulic fracturing fluids injected in the upper Humboldt River Basin subsurface. The report highlights chemical constituents that have a high likelihood of migrating toward potential receptors so Noble Energy, Nevada Division of Environmental Protection (NDEP), and the Nevada Division of Minerals (NDOM) can make informed decisions regarding the hydraulic fracturing process.

Noble Energy is beginning exploration activities in three locations within Elko County, NV. The oil play is expected to be in low permeable shale and will require hydraulic fracturing. NDEP and the NDOM have requested a preliminary assessment of the migration potential for any constituents used in the hydraulic fracturing process.

Noble Energy has identified three potential exploration sites within the upper Humboldt River Basin (Figure 1):

- 24 miles south of Elko
- 15 miles east of Elko
- 7 miles northwest of Wells

The purpose of this project is twofold:

1. Determine the concentration of chemical constituents in hydraulic fracturing fluids
2. Develop expected ranges for transport parameters (groundwater velocity, sorption and decay parameters, etc.) for this hydrogeologic regime and use analytic solute transport solutions to determine the likelihood of migration for chemical constituents.

BACKGROUND

The upper Humboldt River Basin consists of several deep structural basins in which basin-fill deposits of Tertiary and Quaternary age and volcanic rocks of Tertiary age have accumulated. The bedrock of each basin and adjacent mountains are composed of carbonate and clastic sedimentary rocks of Paleozoic age, and crystalline rocks of Cambrian, Jurassic, and Tertiary age. Target depths for the exploration wells are in the 6,000 to 12,000 ft bgs. Preliminary investigations suggest that the resource target is aligned with a Paleozoic trap play overlain by a Tertiary resource play. Previous deep oil exploration efforts in the Humboldt River basin suggest that carbonate rocks may be both above and below the resource zone with relatively high permeability (Plume, 2009). Hydraulic fracturing wells in the upper Humboldt Basin are screened vertically (not horizontally) through the shale unit. We assume that fluids injected into the well will disperse radially through the shale unit as fractures are propped. Both injectate, oil, and mobilized gas have potential to migrate into the overlying volcanic/carbonate units. Injectate, oil, and gas may also migrate into the carbonate unit below, but will not be considered explicitly in this report.
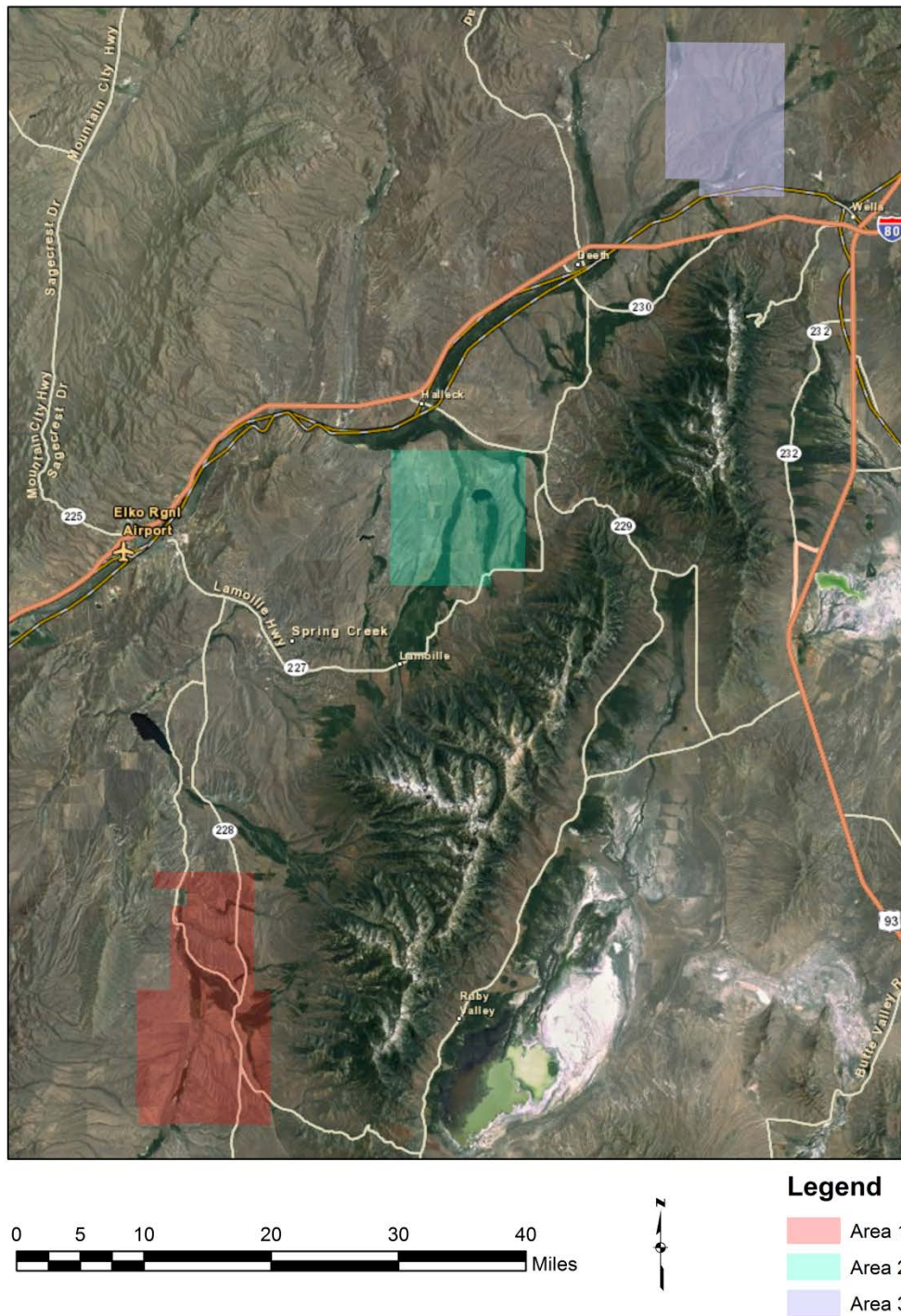
Figure 1.   Location of Noble Energy's three exploration areas.

       The hydraulic fracturing chemicals that Noble anticipates using in Humboldt operations are listed in Table 1. There are three possible mechanisms by which the carbonate, volcanic and alluvial groundwater resources may be impacted by migrating hydraulic fracturing fluids. First, and most unlikely, if high permeability vertical faults extend into an overpressured shale unit,

migration of hydraulic fracturing fluids to the surface may occur over timescales of 100's of years [*Gassiat et al.*, 2013]. The second and third mechanisms, release of hydraulic fracturing fluids through leaky boreholes and spills at the ground surface, result in more immediate contamination risk.

The potential contamination of shallow aquifers from hydraulic fracturing fluids is generally considered to be neglidible as compared to other contamination sources [*Gassiat et al., 2013*]. This type of contamination has been considered as highly unlikely because:

1. No hydraulic fracturing fluid has yet been found in drinking water wells [*Osborn et al., 2011*]
2. The significant distance between the shale unit (at depths up to a few thousand meters) and the shallow aquifers (at less than a few hundred meters depth) would not lead to contaminant migration over short timescales [*Alpha Environmental Consultants, 2009; Zoback et al., 2010; Howarth et al., 2011*]
3. It is very unlikely that hydraulic fractures would propagate over such long distances to directly connect the gas shale and shallow aquifers [*Zoback et al., 2010*];
4. Fault reactivation due to hydraulic fracturing would likely occur on small distances of a few meters [*EPA, 2012*]
5. During production, downwards and horizontal flow to the horizontal shale gas well would be promoted, decreasing the risk of upwards migration [*Howarth et al., 2011*].

METHODS AND ANALYSES

The chemical constituent concentrations in the hydraulic fracturing makeup water were determined by dividing the input mass of each chemical by the total proposed fluid volume (554,000 gallons). The chemical mass and fluid volumes were supplied by Noble Energy as estimated from previous hydraulic fracturing operations (Table 1).

Migration potential is calculated for the shale and alluvial units assuming that the entire hydraulic fracturing fluid and associated chemicals are introduced. Under normal hydraulic fracturing operations the pressure in the resource unit (shale) is relieved by allowing the well to "flowback," thereby capturing some portion of the contaminants. As described above a small potential exists for contaminants to migrate through the subsurface to the shallow alluvium. More likely sources of shallow contamination at fracking (like other industrial sites) are thought to be compromised boreholes or surface spills (Kissinger et al., 2013). Regardless, even if this were to happen, concentrations would be reduced significantly due to degradation and/or transport dilution effects. Therefore, this analysis presents a highly hypothetical case to determine the worst-case scenario and associated impacts.

Overall migration potential for subsurface solutes is a function of subsurface physical characteristics such as the hydraulic gradient, hydraulic conductivity, and matrix porosity; however, migration potential for individual constituents may vary based on likelihood of 1)

degradation and 2) sorption. Degradation potential for each constituent was determined through a literature review. Of the proposed constituents listed in Table 1, ammonium persulfate, 2,2- Dibromo

Table 1.   Characteristics of chemicals proposed for Humboldt hydraulic fracturing operations.

Chemical	Formula	Purpose	Maximum Ingredient Conc. in HF Fluid (% by mass)	Mass (kg) chemical in 554,000 gal water	Concentration in hydraulic fracturing fluid mg/L	log K_{oc}	Source	Notes
Petroleum Distillate	C10-C14 naphthenes, iso- and n-paraffin	Corrosion Inhibitor, friction reducer	0.50000%	10,466.23	4,991	3.1 (napth)	2	
Ammonium Persulfate	$(NH_4)_2S_2O_8$	Breaker, viscosity breaker, fracturing	**0.02000%**	418.65	200	unknown	3	Decomposed by moisture to form oxygen and ozone
Hydrochloric Acid	HCl	Acid	0.10000%	2,093.25	998	unknown		
Inorganic salts	NaCl	chemical tracer	0.01000%	209.32	100	unknown		
Citric Acid	$C_6H_8O_7$	Iron control	0.03600%	753.57	359	-1.2		
Potassium Chloride	KCl	Clay Stabilizer	1.00000%	20,932.45	9,982	unknown	4	stable
2,2-Dibromo-3-nitrilopropionamide	$C_3H_2Br_2N_2O$	Biocide, fracturing, completion	0.00200%	41.86	20	1.81	5	Observed half-life in soil 4-24 hours through biotic and abiotic degradation.
Triisopropanolamine	$[CH_3CH(OH)CH_2]_3N$	Crosslinker	**0.00200%**	41.86	20	1	6	mixed results from degradation studies
Potassium carbonate	K_2CO_3	pH adjusting agent	0.05000%	1,046.62	499	unknown		
Glycerin	C3H8O3	Non-emulsifier	0.10000%	2,093.25	998	0	6	
Formic Acid	HCOOH	Corrosion Inhibitor	0.00034%	7.12	3	Adsorption nominal	1	May be anaerobically degraded by microorganisms to form hydrogen, nitrogen, hydrogen sulfide, carbon dioxide and methane

Bold values were modified to be consistent with previous hydraulic fracturing operation concentrations from the fracfoucs.org (Frac Focus, 2013).

1   Montgomery, J, 2007, Groundwater Chemicals Desk Reference, Taylor & Francis Group, LLC.
2   http://www.cdc.gov/niosh/ipcsneng/neng1379.html
3   http://hazard.com/msds/mf/baker/baker/files/a6096.htm
4   http://www.chemicalbook.com/ProductChemicalPropertiesCB9137176_EN.htm
5   PubChem Compound. USA: National Center for Biotechnology Information.
6   Hazardous Substances Data Bank; US National Library of Medicine

-3-nitrilopropionamide, and formic acid are known to have the potential to degrade in the subsurface. Sorption potential was determined through review of known octanol-water partition coefficients (log K_{ow}- Table 1), a parameter related to a chemical's tendency to sorb to the organic fraction of the aquifer matrix. Log K_{ow} can range from -3 (low sorption potential) to 7 (high sorption potential). Sorption potential is not understood for many of the constituents in Table 1. Citric acid, 2,2-dibromo-3-nitrilopropionamide, triisopropanolamine, glycerin, and formic acid have low sorption potential, while the naphthalene portion of petroleum distillates is known to have moderate sorption potential.

Estimates of aquifer hydraulic and transport parameters are given in Table 2. Groundwater velocities were estimated from the regionalal hydraulic gradient and, aquifer hydraulic conductivity as defined by Plume (2009) for the regional groundwater system. Effective porosity for various depths were provided by Noble as summarized in Figure 2. Dispersion and matrix diffusion parameters were taken from the literature as appropriate for the hydrogeologic conditions that exist. Given the large uncertainty expected for the transport parameters this analysis is not meant to be predictive but informative of the general transport conditions.

Table 2.   Aquifer hydraulic and transport parameters

| Aquifer Parameters	Value	Source
Shallow alluvium		
Hydraulic Conductivity	10^{-3} cm/s	Fetter, 1994
Porosity	0.35	Representative value from Noble borehole data
Hydraulic Gradient	0.004	Plume, 2009 - Humboldt River Floodplain
Longitudinal Dispersivity	1.5-3 m	Gelhar, 1986
Average Linear Velocity	4 m/yr	Darcy's Law
Volcanics overlying shale		
Hydraulic Conductivity	10^{-5} cm/s	Domenico and Schwartz, 1990
Porosity	0.2	Representative value from Noble borehole data
Hydraulic Gradient	<0.004	Expert judgement
Longitudinal Dispersivity	1.5-3 m	Gelhar, 1986
Average Linear Velocity	10^{-1} m/yr	Darcy's Law
Shale		
Hydraulic Conductivity	10^{12}-10^{9} cm/s	Domenico and Schwartz, 1990
Porosity	0.04	Representative value from Noble borehole data
Hydraulic Gradient	<0.004	Expert judgement
Longitudinal Dispersivity	1.5-3 m	Gelhar, 1986
Average Linear Velocity	10^{-5} m/yr	Darcy's Law
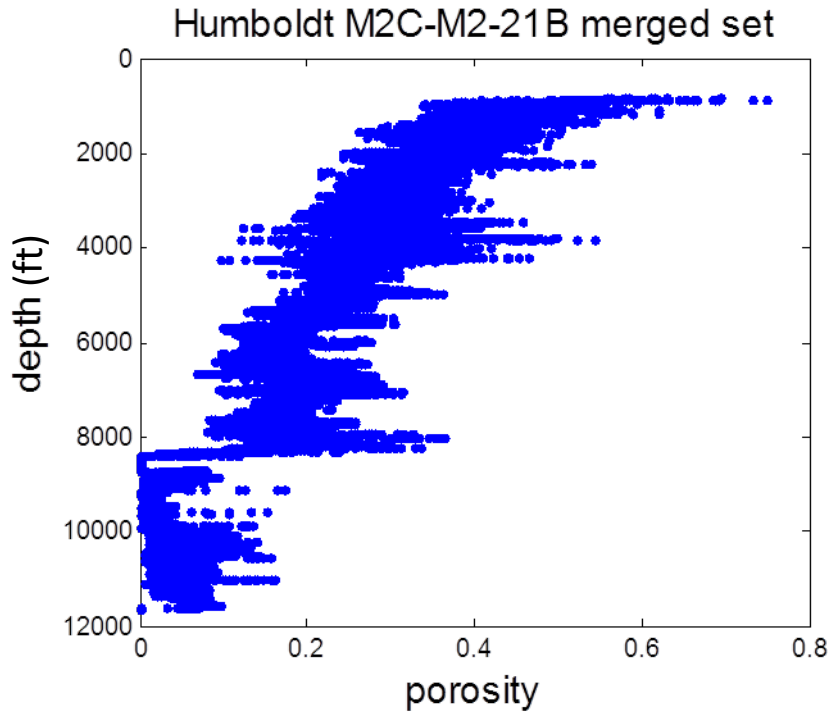
Figure 2.   Porosity with depth (ft) from Humboldt M2C-M2-21B borehole.

Given the estimates of chemical and subsurface characteristics listed above, estimates of travel distance and time are calculated using the advection-dispersion equation for the change in concentration, *C*, in space, *x*, and time, *t*, for a solute subject to retardation as it is transported in a porous medium:

$$R\frac{\partial C}{\partial t} = -v\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2},$$
(1)

where, *R*, the retardation coefficient is solute specific; the average linear velocity, *v*, is a function of the formation and the hydraulic gradient; and the dispersion coefficient, *D*, representing expected spread of solute around particles moving at the average velocity is a function of the formation. Estimates of the average linear velocity, *v*, are obtained by applying Darcy's Law:

$$v = -\frac{K}{n}\frac{dh}{dx}$$
(2)

where *K* is the formation hydraulic conductivity, *n* is the porosity of the formation, and dh/dx is the hydraulic gradient.   The retardation coefficient is related to a chemical's tendency to sorb to the organic fraction of the aquifer matrix (approximated by the octanol-water partition

coefficient log K_{ow}), the bulk density (ρ_B) and the porosity of the aquifer, for example with a relationship such as:

$$R = 1 + \frac{\rho_B}{n} K_d,$$ (3)

where bulk density can be approximated from porosity and grain density (ρ) using $\rho_B = \rho(n-1)$, typically, $\rho = 2.65$ g/cm^3, and K_d is calculated from K_{oc} and the fraction of organic carbon.

The worst-case scenario for contaminant migration from hydraulic fracturing wells is a continuous long-term source from a leaky borehole of a chemical with little to no retardation. Since one or more components of all proposed hydraulic fracturing constituents have small or unknown retardation properties, transport estimates will assume no retardation. In this case, the solution to the advection-dispersion equation is:

$$C = \frac{C_0}{2}\left[erfc\left(\frac{x-vt}{2\sqrt{Dt}}\right) - \exp\left(\frac{vx}{D}\right) erfc\left(\frac{x+vt}{2\sqrt{Dt}}\right)\right]$$ (4)

where *erfc* is the complementary error function. For example, the concentration with distance of petroleum distillate assuming an injection concentration of 4,991 mg/L after 1 year and 10 years in shallow Humboldt alluvium using parameters listed in Tables 2 is shown in Figure 3. Table 3 provides an overview of migration distance and dilution factor for a long-term source of solutes released from a leaky borehole, our worst-case migration scenario for this site. Dilution factors can be applied to any initial solute concentration thought to be leaving a borehole. Although hydraulic conductivities and gradients are fairly high in shallow alluvium in the Humboldt basin, high porosity contributes to limited migration with time.

Table 3.   Dilution factors for conservative contaminant migration with distance and time in shallow alluvium.

Shallow alluvium, dispersivity = 1.5 m				
Travel time	10 m	50 m	100 m	500 m
1 year	2%	-	-	-
10 years	100%	9%	-	-
20 years	100%	93%	2%	-

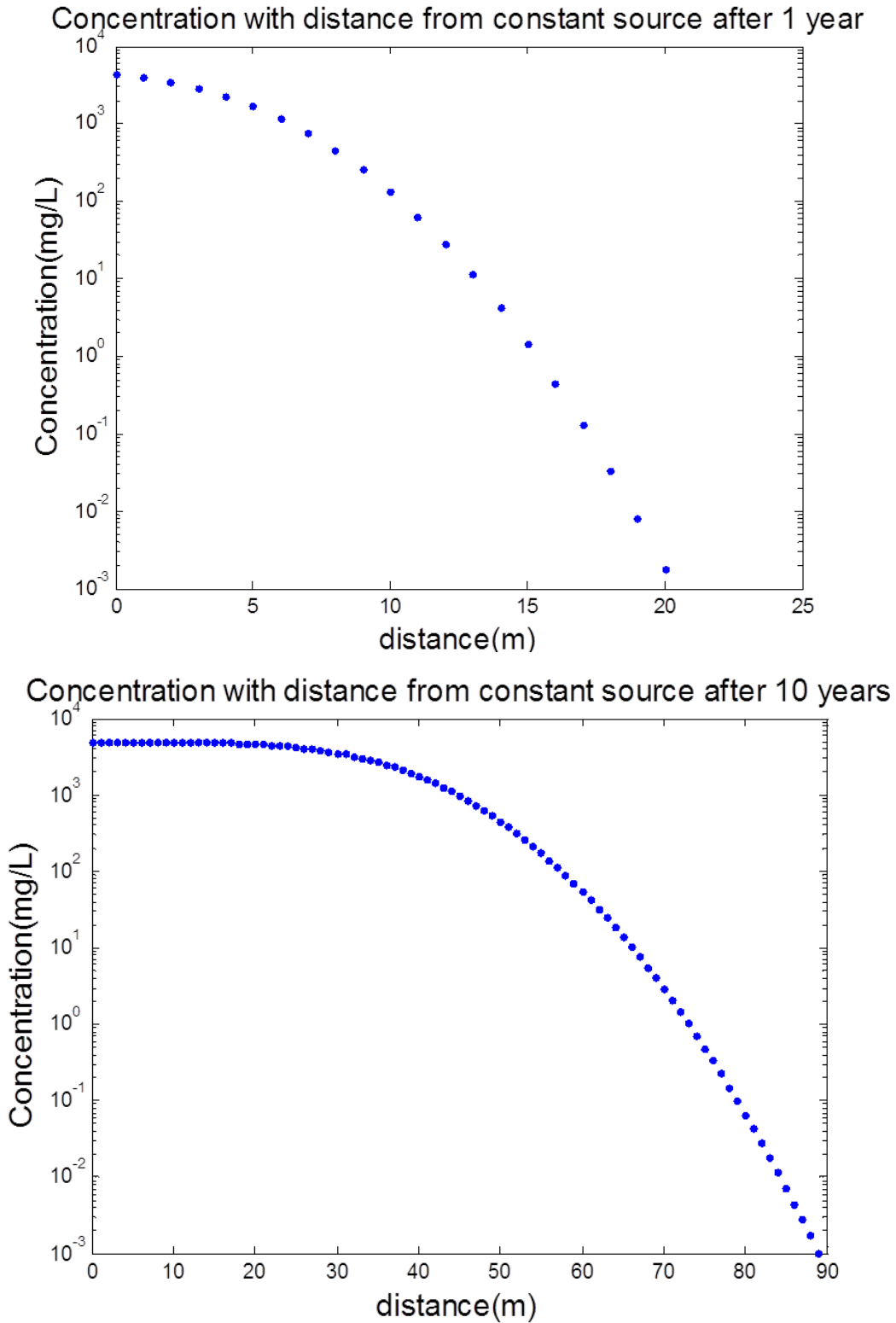| Shallow alluvium, dispersivity = 3 m				
Travel time	10 m	50 m	100 m	500 m
1 year	8%	-	-	-
10 years	96%	17%	-	-
20 years	100%	86%	9%	-

Figure 3. Spatial distribution of petroleum distillate leaking from a borehole (that acts as a continuous source) in shallow alluvium with injection concentration of 4991 mg/L after one year (top) and ten years (bottom) under a natural hydraulic gradient.

Hydraulic conductivities in the deep shale and overlying volcanic units are expected to be orders of magnitude smaller than that of the alluvium (Table 2). When applying the advection-dispersion equation using parameters assumed in Table 2, even at hydraulic gradients up to 0.004, there is insignificant migration of solutes up to 20 years into the future.

CONCLUSIONS

1. While many of the constituents listed in Table 1 are known to be irritants or toxic to humans and the environment, no environmental regulatory standards exist for maximum acceptable levels in drinking water.

2. Although unlikely, there are three mechanisms by which shallow groundwater resources may be impacted by migrating hydraulic fracturing fluids. First, if high permeability vertical faults extend into an overpressured shale unit, migration of hydraulic fracturing fluids to the higher permeability alluvial and/or carbonate units may occur over timescales of 100's of years [Gassiat *et al.*, 2013]. The second and third mechanisms, release of hydraulic fracturing fluids through leaky boreholes and spills at the ground surface, result in more immediate contamination risk [Kissinger *et al.*, 2013].

3. The expected concentration of hydraulic fracturing chemicals in borehole fluids ranges from 20 mg/L to almost 5,000 mg/L (Table 1). Petroleum distillate and other constituents such as potassium chloride, glycerin, potassium carbonate will exist at a release site at high concentrations. A literature review suggests that ammonium persulfate, 2,2-Dibromo-3-nitrilopropionamide, and formic acid will degrade in the subsurface with time. The characteristics and fate of their daughter products is not known. Studies on the degradation potential of triisopropanolamine have produced mixed results. Napthalenes, found in petroleum distillates, are known to have moderate sorption characteristics in the presence of dissolved organic carbon. The remainder of proposed hydraulic fracturing constituents have either unknown or very low sorption potential and are considered conservative for transport estimates.

4. The advection dispersion equation was used to determine dilution factors for persistent and conservative solutes given a long-term source. These calculations are considered "worst-case" transport scenarios by assuming rapid movement of contaminants from the shale to either the alluvial or carbonate via one of the three mechanisms described above.

5. The potential for transport under a natural hydraulic gradient is very small in the deep volcanic and shale units in the absence of significant fractures or long-term enhancement of hydraulic conductivity after cessation of hydraulic fracturing operations.

6. Using estimates of natural hydraulic conditions in shallow alluvium from Plume (2009), porosity from geophysical measurements, and representative estimates of dispersivity, concentrations of up to 10 percent of initial values may be found 100 meters from the source. Detectable concentrations are not expected beyond 500 meters in twenty years.

7. Given their sorption and degradation characteristics, hydrochloric acid, inorganic salts, potassium chloride, potassium carbonate, and some constituents in petroleum distillate are the only chemicals expected to migrate distances of 100-500 meters in 20 years.

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