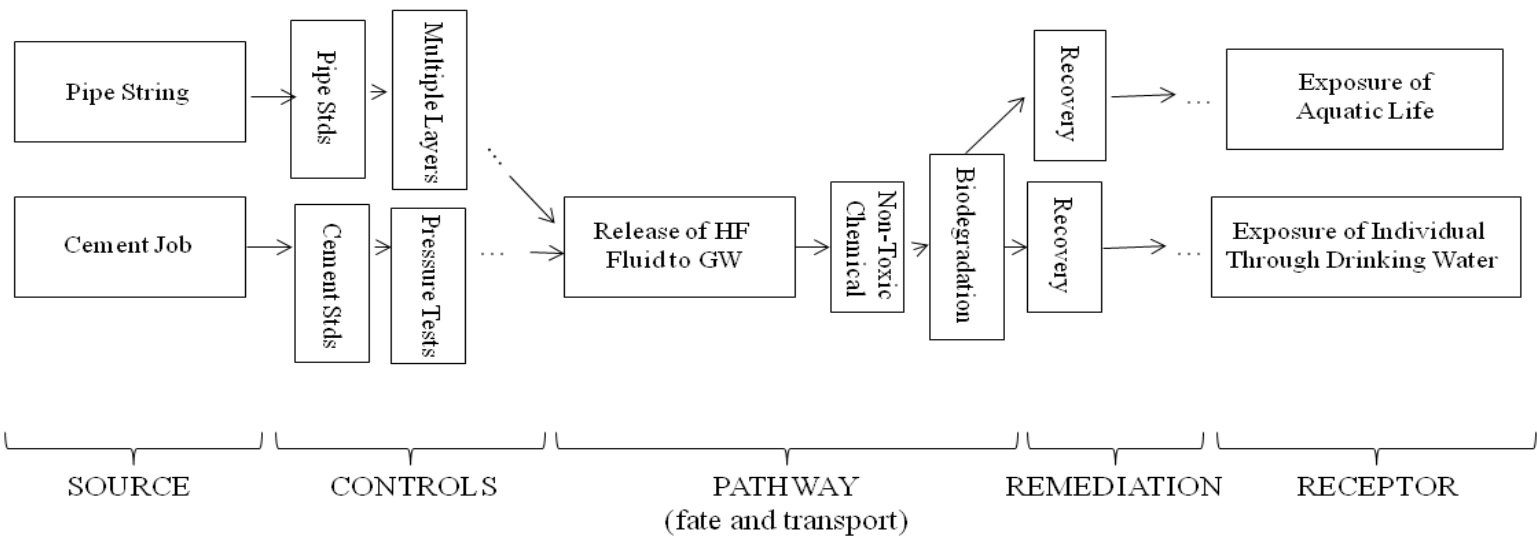
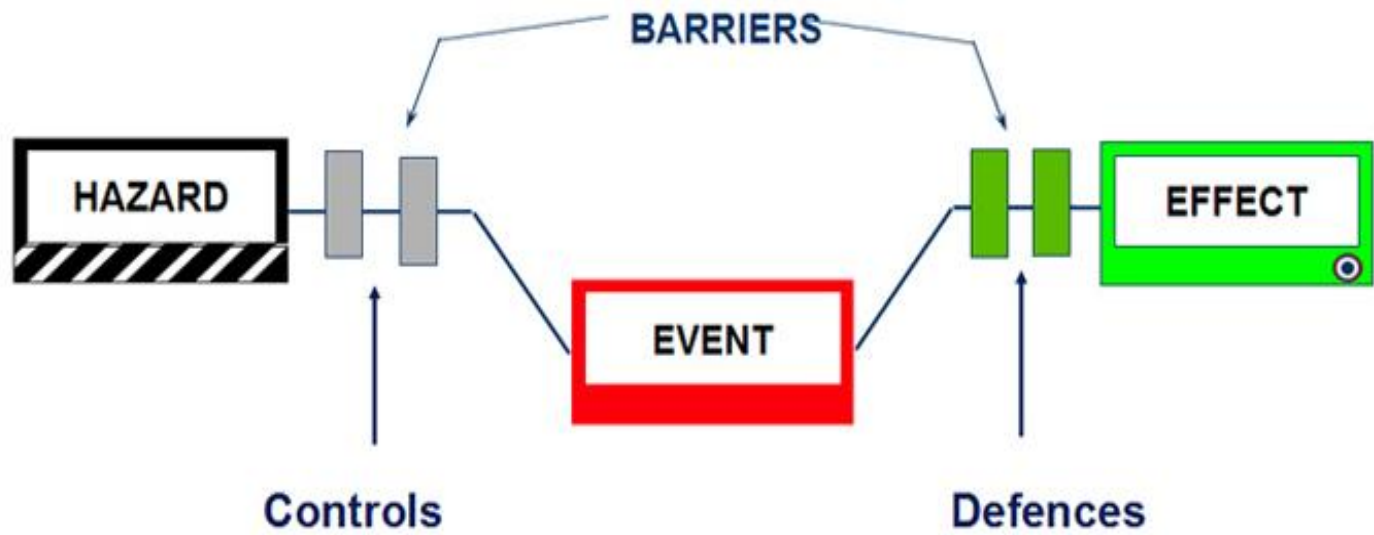


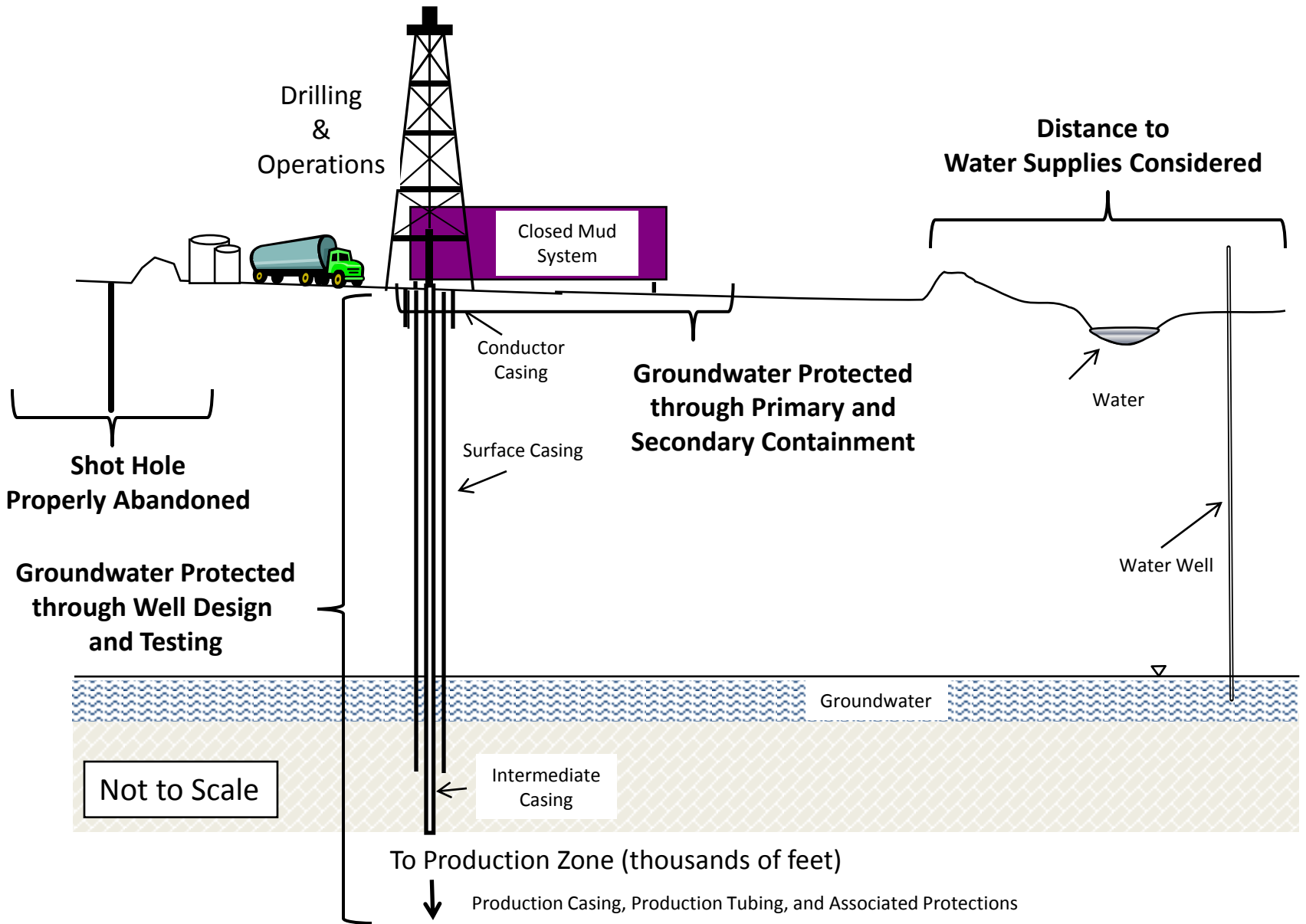
Considerations for Fate and Transport Evaluation Of Potential Release Scenarios during Hydraulic Fracturing Operations

EPA Hydraulic Fracturing
Technical Workshop
on Fate and Transport

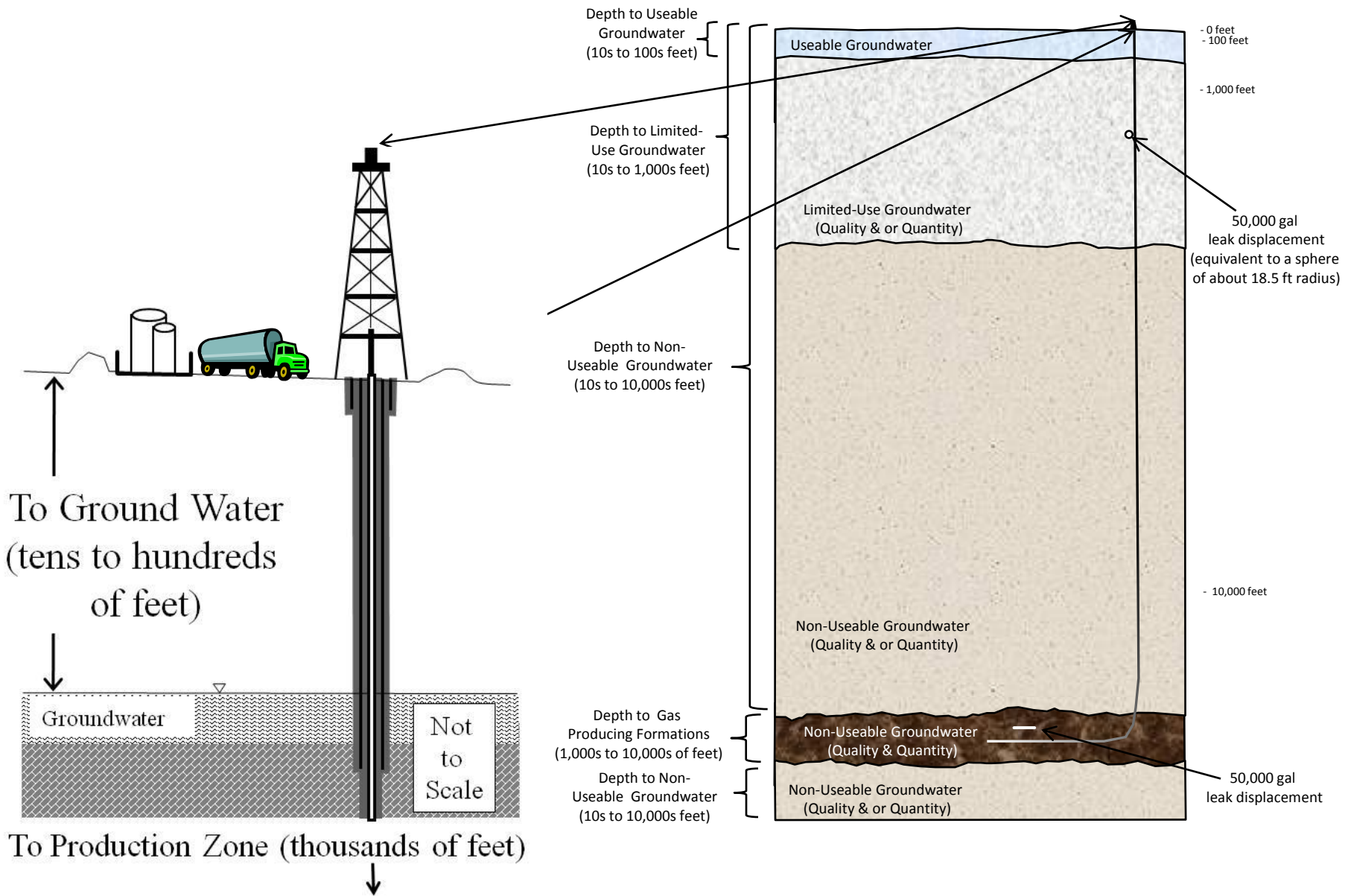
March 28-29, 2011



Set up a Site Conceptual Model



Consider likelihood of Event



Potential Total Volumes from HF are Limited
And Starting Concentrations are Low.

Consider Potential Chemicals of Concern for Hydraulic Fracturing

Additives (Low starting concentrations)

Salts, organics, metals,

Produced water (actually not part of HF process)

Salts, organics, metals,

Methods for Examining Potential Produced Water Impacts are Available

Methodologies for identifying and quantifying potential saline water to ground-water supplies have been in use for years and are well documented, for example:

Richter, B.C. and C.W. Kreitler, December 1991, Identification of Sources of Ground-Water Salinization using Geochemical Techniques, EPA/600/2-91-064, United States Environmental Protection Agency, Ada, Oklahoma, may be accessed on line.

Knuth, M., J.L. Jackson, and D.O. Whittemore, March-April 1990, An Integrated Approach to Identifying the Salinity Source Contaminating A Ground-Water Supply, Ground Water, Vol. 28, No. 2, 207-214.

Lee, R.S., D.T. Adamson, and M. Vanderford, November 5-9, 2007, Visual Methods for Geochemical Screening of Possible Impacts to Groundwater by Oilfield Brines, presented at the 14th Annual International Petroleum Environmental Conference, Houston, TX.

Panno, S.V., K.C. Hackley, H.H. Hwang, S.E. Greenberg, I.G. Krapac, S. Landsberger, and D.J. O'Kelly, March-April 2006, Characterization and Identification of Na-Cl Sources in Groundwater, Groundwater, Vol. 44, No. 2, 176-187.

Uliana, M.M., May 2005, Identifying the Source of Saline Groundwater Contamination Using Geochemical Data and Modeling, Environmental & Engineering Geoscience, Vol. XI, No. 2, 107-123.

Richter, B.C. and C.W. Kreitler, Fall 1987, Sources of Ground Water Salinization in Parts of West Texas, Ground Water Monitoring Review, 75-84.

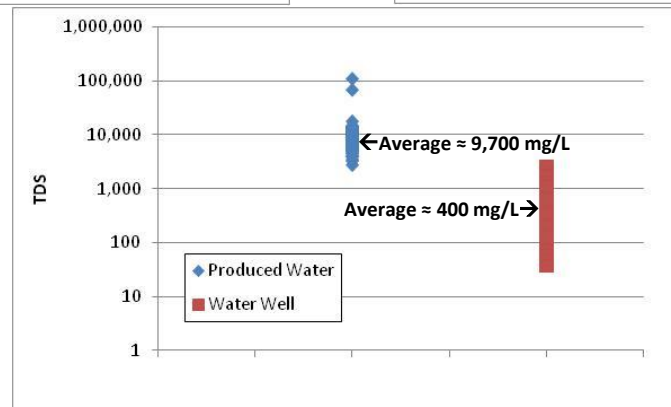
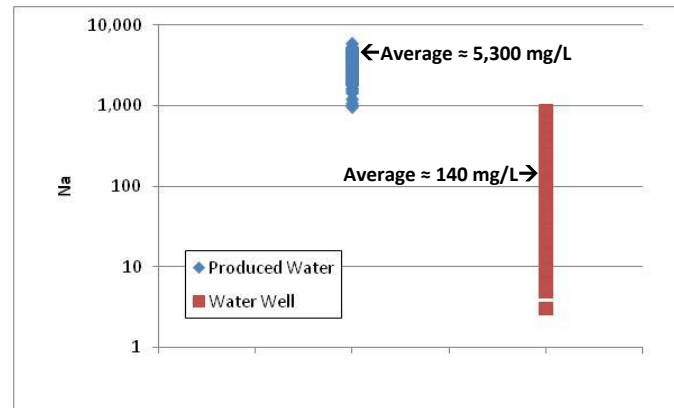
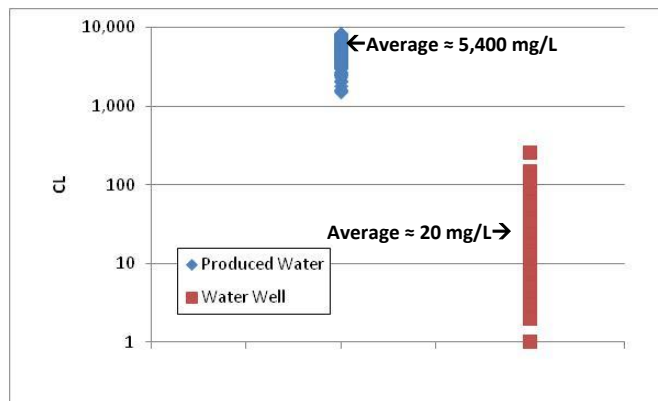
Richter, B.C. and C.W. Kreitler, January 1982, Identification of Sources of Ground-Water Salinization Using Geochemical Techniques, EPA/600/S2-91/064, United States Environmental Protection Agency, Ada, Oklahoma, may be accessed on line.

McNellis, J.M. C.O. Morgan, and B.H. Lowell, 1969, Computer-Produced Tables, Maps, and Diagrams as Tools in the Interpretation of Brine Data from Southeastern Kansas (U.S.A.), Chem. Geol, Vol. 4, 303-324.

Geochemical methods use common water chemistry parameters to identify mixing of saline and potable water.

Parameters of interest may include: Na, K, Ca, Mg, Cl, SO₄, Co₃, HCO₃, TDS, Br, I, etc. , and take advantage of potentially great differences between the makeup of saline and potable water.

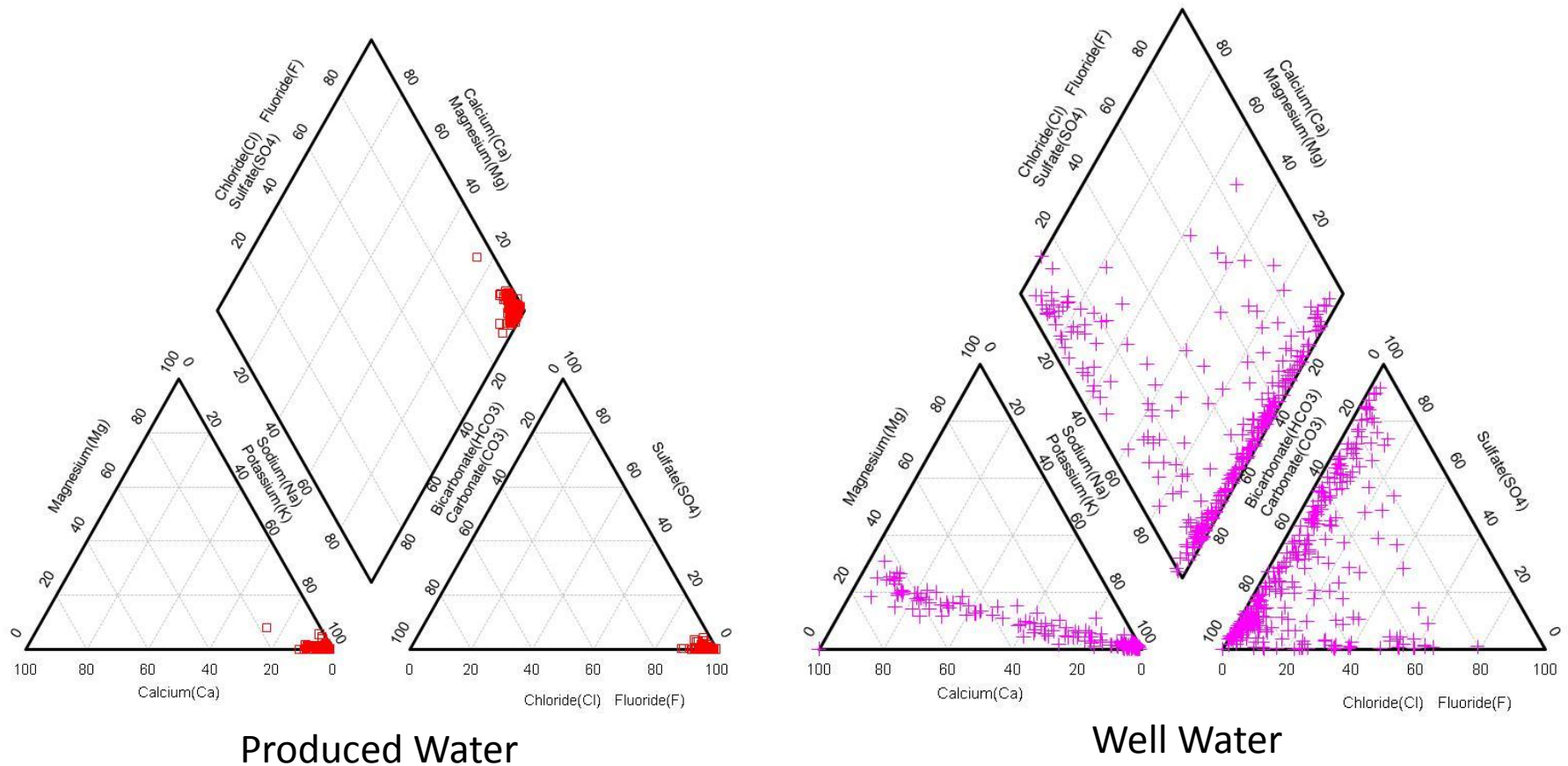
For example, a large database of produced water (fractionation water base) and well waters from an area show their distinct character when comparing various parameters. (Note: These plots show data from hundreds of samples from throughout a large area. Focusing on specific locations, depths, etc. may likely show more separation of the produced water and well water.)



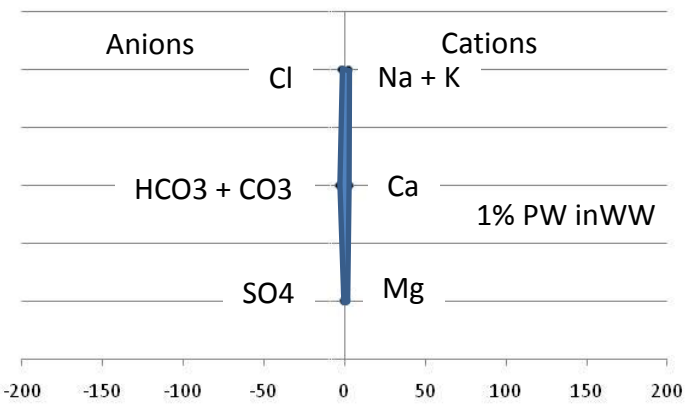
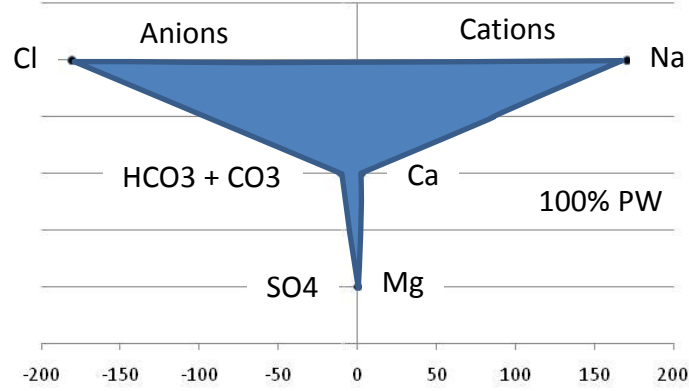
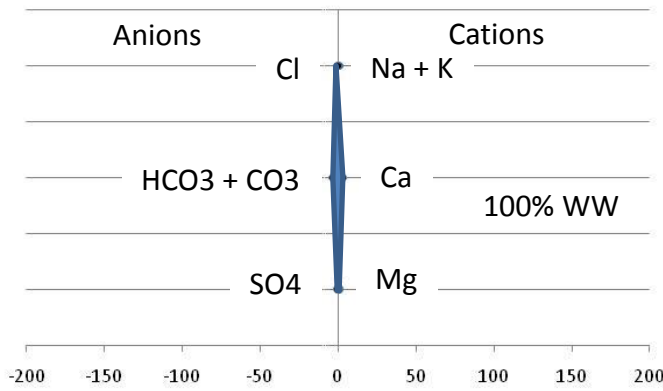
By evaluating the differences between waters, appropriate parameters or combinations may be selected for evaluation of potential mixing.

Piper plots of major ions is another way of showing distinct chemical types of water.

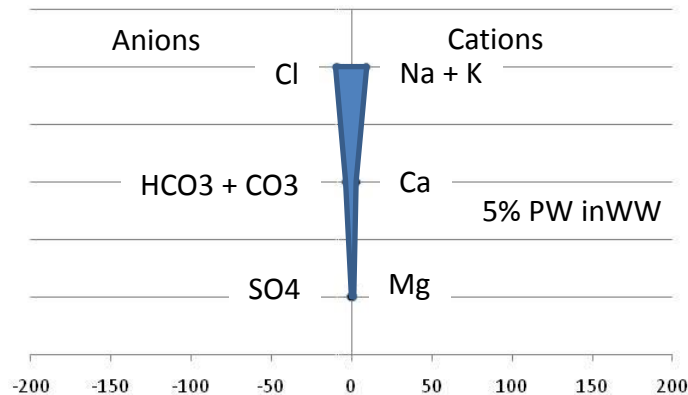
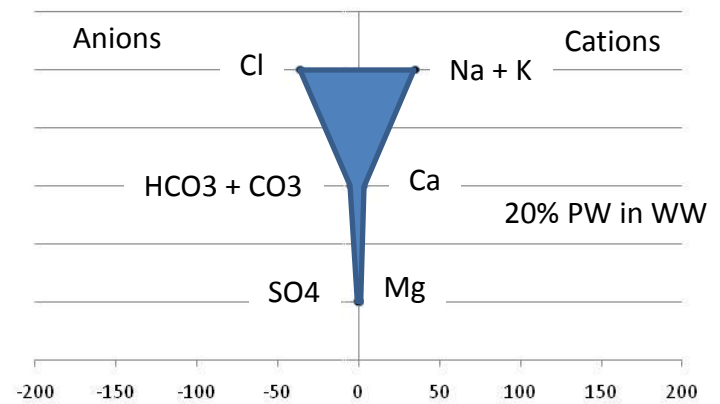
Produced waters (used to makeup fractionation water) have a fairly tight geochemical fingerprint, while well waters are generally different than produced water and variable in composition. Note that these diagrams represent water type, not concentrations.



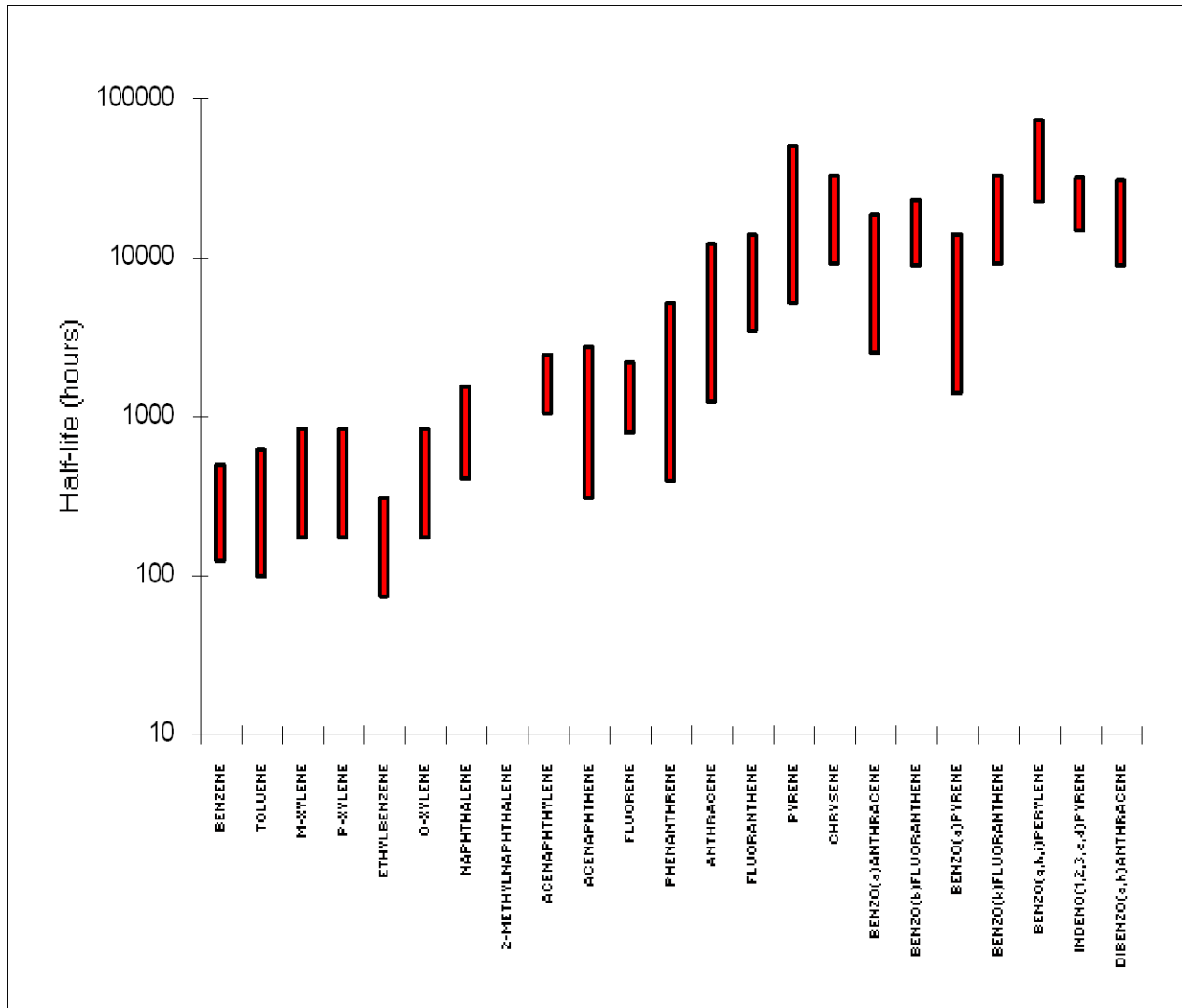
Stiff Diagrams of major ions indicated the general chemistry of waters and mixtures. These may be used to indicate water type visually and relative concentrations.



Water Well (WW)
Produced Water (PW)



BIODEGRADATION HALF LIFE IN SOIL

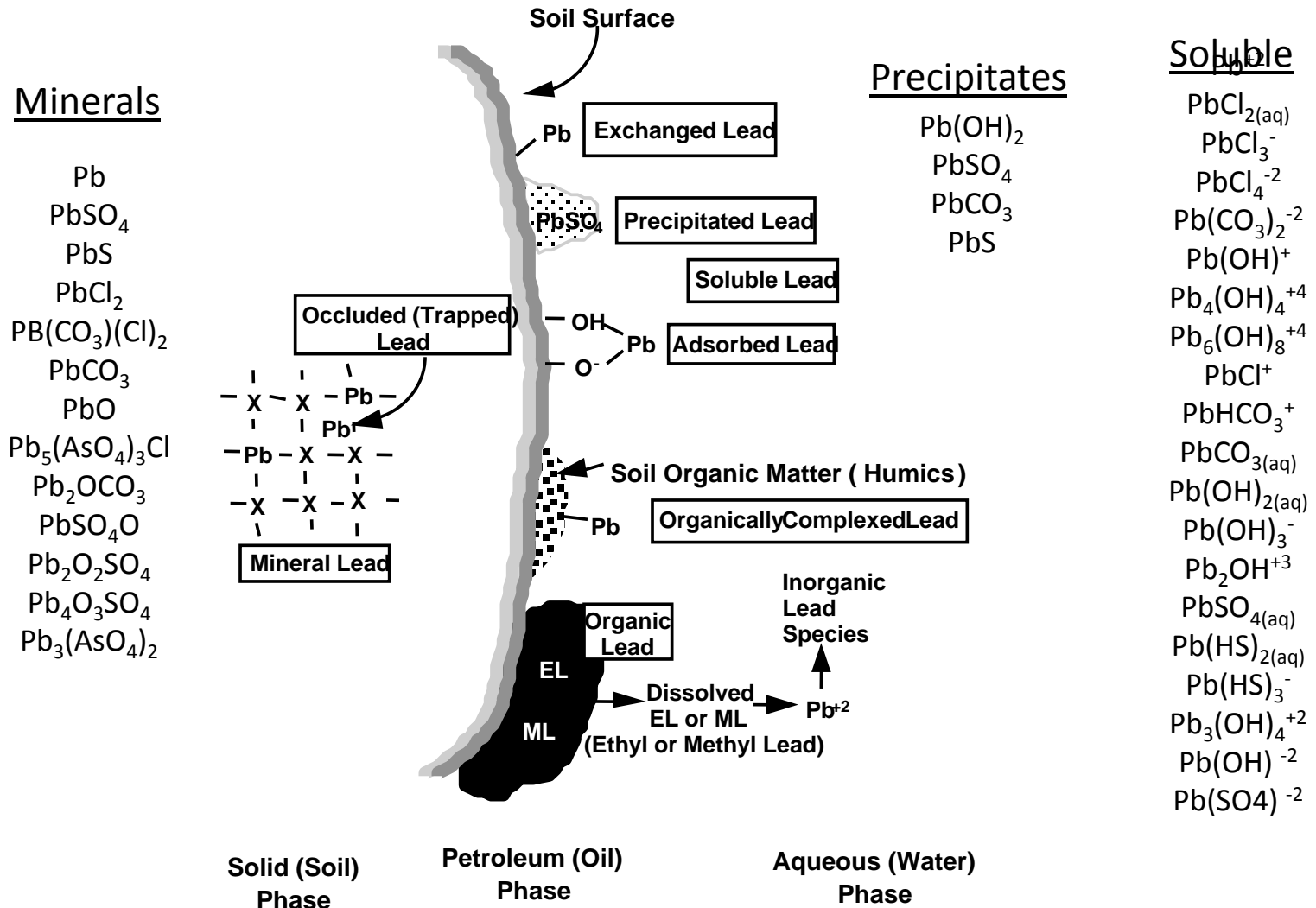


Half Life Increases with Molecular Weight and Complexity

Half Lives for BTEX compounds are on the order of one month

METALS

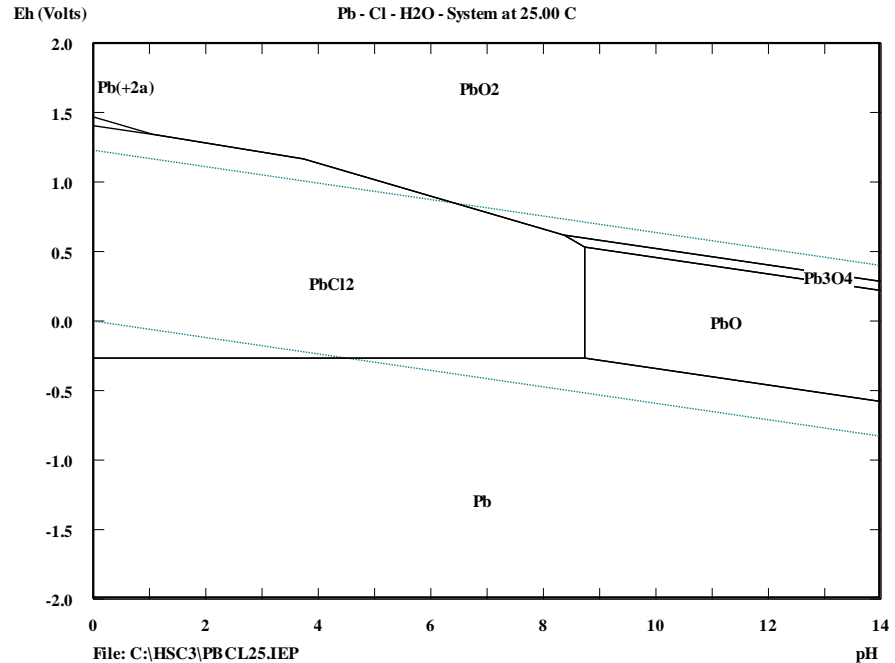
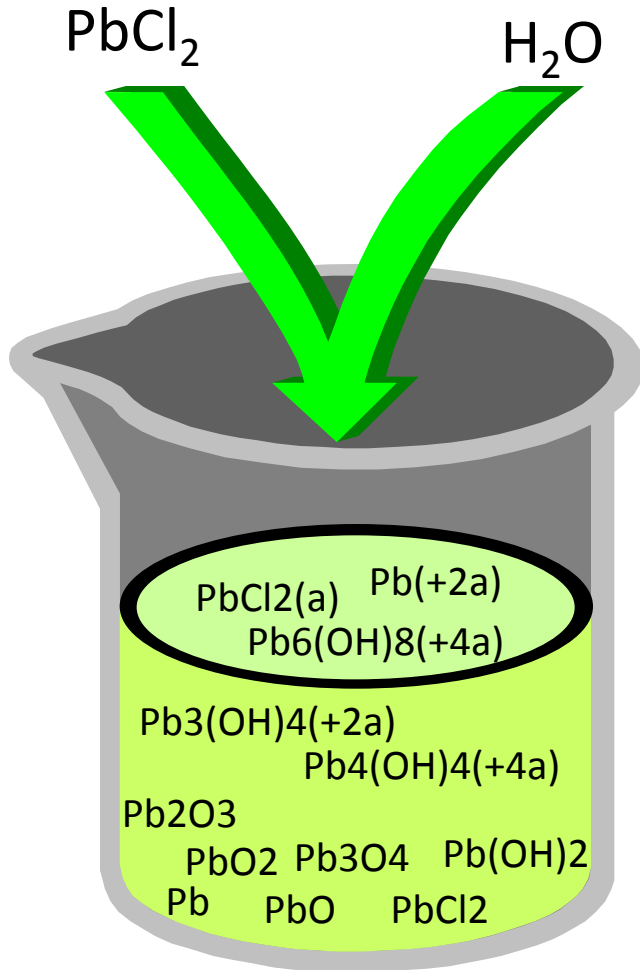
Species and Interactions



Previous Work indicate that Metals from O&G Materials are Immobile if Released to Soil.

METALS

MINTEQA2, HSC3



- Useful for forward modeling (Tier 2).
- Data limited for reverse modeling.
- May be linked to transport model.
- May incorporate sorption.
- **Use to establish system boundaries.**

Natural parameters are preferable to frac fluid additives for evaluating potential salt water influences because of variety of additives, variety of analytical procedures, natural presence of some constituents, and detection limit constraints.

For example, an www.energyindepth.org reference summarizes a typical frac fluid (<http://www.energyindepth.org/frac-fluid.pdf>).

From that data, estimate possible levels of some components at a 0.5% produced water mixture with well water:

Component	mg/L at 0.5% PW in WW	mg/L Detection Limit for component	Detectable
citric acid	0.2	1	No
ethylene glycol	2.2	10	No
n,n-dimethyl formamide	0.1	0.1	Maybe
gluteraldehyde	0.05	1	No
isopropanol	4.3	0.01	Yes
petroleum distillate	4.4	0.001 (xylene)	Yes (at 0.2% Xyl)

Note that in this case two of the chemicals are potentially detectable at a level equivalent to standard inorganic parameters. Of these isopropanol is a natural component and may degrade prior to sampling and analysis or be present in background, while petroleum components are already commonly analyzed. Such evaluation must be done for each component considered.

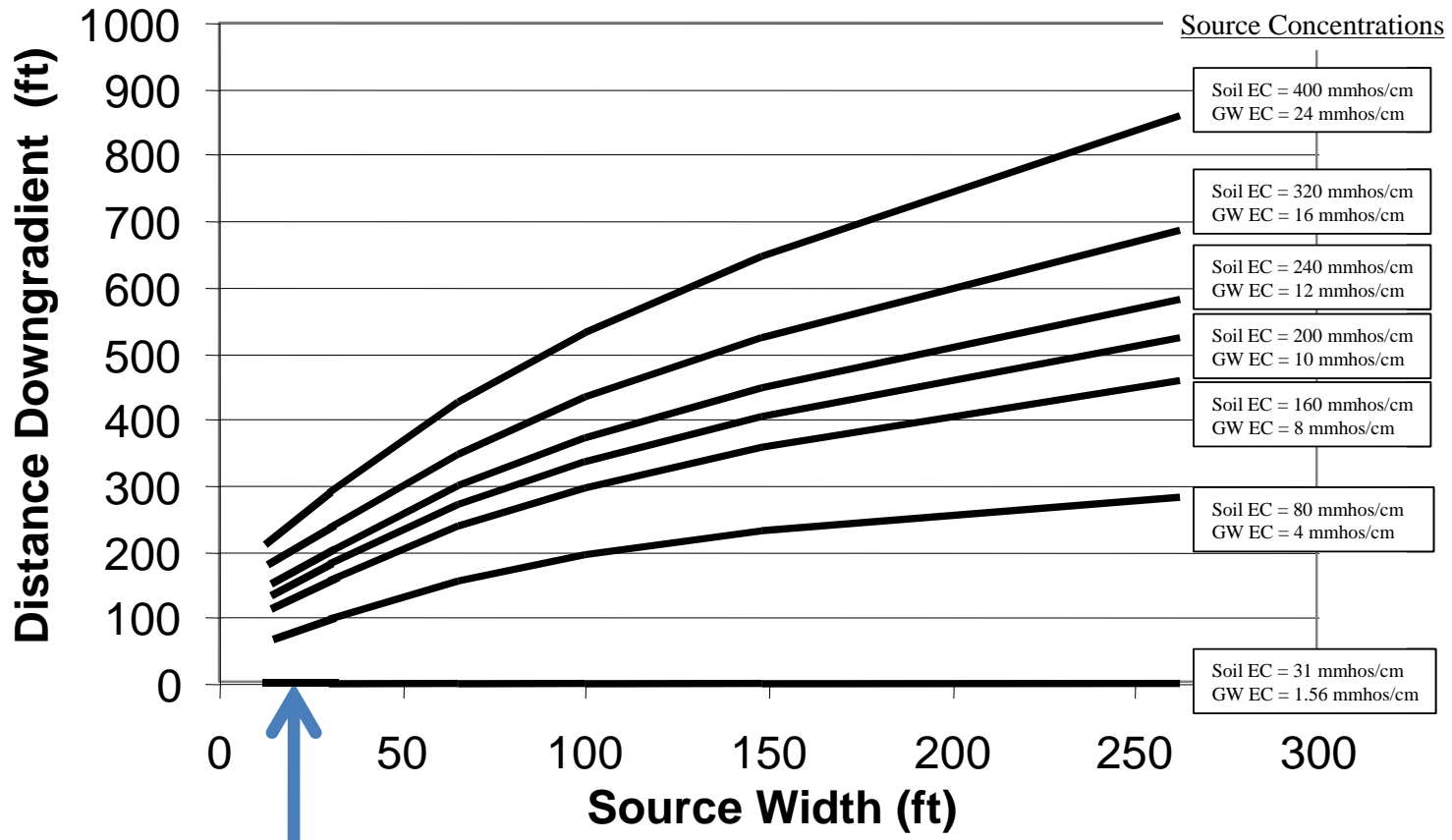
Domenico Equation

$$\frac{C_s}{C_x} = DF_{sat} = \left(\exp \left\{ \frac{x}{2\alpha_x} \left[1 - \sqrt{1 + \frac{4\lambda\alpha_x R}{v}} \right] \right\} \times \left(\operatorname{erf} \left[\frac{S_w}{4\sqrt{\alpha_y x}} \right] \right) \left(\operatorname{erf} \left[\frac{S_d}{2\sqrt{\alpha_z x}} \right] \right) \right)$$

where:

- C_x = dissolved component at a distance x from the source (mg/L)
- x = horizontal distance to point of extraction (cm)
- λ = *first-order degradation constant (day⁻¹)*
- R = *constituent retardation factor (dimensionless)*
- v = *specific discharge (cm/day)*
- α_x = *longitudinal dispersivity (cm)*
- α_y = *transverse dispersivity (cm)*
- α_z = *vertical dispersivity (cm)*
- S_w = *source width (cm)*
- S_d = *source depth (cm)*

Distance to 1.56 mmhos/cm (1,000 mg TDS/L) with Various Source Concentrations



18.5 ft – Approx. soil volume of 50,000 gal release.

Domenico Equation Applied to Salt Transport

Tools are available for evaluating the fate and transport of selected reasonable release scenarios in hydraulic fracturing operations.

These methodologies consider controls in the hydraulic fracturing process as reflected in existing regulations and best management practices before selecting scenarios.

This process will allow focusing on realistic release scenarios, chemicals, pathways, and receptors.

Background chemicals, both anthropogenic and natural, must be considered in any analysis.

Tools must be used that are appropriate for uncertainty in available data and analytical techniques.

Consider previous work that showed oil field waste to be high volume and low toxicity, i.e. produced water, drilling mud.

Fate and Transport Evaluation of Potential Release Scenarios during Hydraulic Fracturing Operations

George Deeley
Shell Upstream Americas

The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

Introduction

Fate and transport includes the processes that control the behavior of chemicals if they are released from some source by escaping existing natural or manmade barriers. Therefore, the mechanism and chance of release must be determined before prioritizing any potential release scenarios. Determination of potential receptors must then be determined for the realistic potential release scenarios. With realistic sources and receptors identified, fate and transport analysis may proceed. Fate and transport analysis will then require input data on appropriate chemicals, hydrogeological data, and geochemical data within a proper modeling framework. Fate and transport results are used to determine appropriate collection of data to fill gaps, validate models, or eliminate pathway from further consideration.

Scope

While focusing on fate and transport of chemicals (exposure pathways) and processes related to potential impacts of hydraulic fracturing on drinking water, there will also be some description of the selection of reasonable release scenarios and receptors. The fate and transport processes will, in general, be similar to those found with other potential chemical releases to soil and groundwater such as surface spills, impoundment leaks, and leaks from underground storage tanks. The major differences will be in some potential release scenarios such as cement jobs, pipe strings, and fractures, which are normally prevented with engineered and natural controls. This process demands the evaluation of these controls before proceeding to further evaluation steps. Also, the chemical nature of potentially released material in upstream operations has been characterized as high volume and low toxicity.¹ Therefore, upstream materials such as produced water are of low potential risk when managed appropriately.

Conceptual Model

A conceptual site model (CSM) is a "...written or pictorial representation of an environmental system and the biological, physical, and chemical processes that determine the transport of contaminants from sources through environmental media to environmental receptors with the system."² Barriers (controls or defenses) may also be part of the system (Figure 1). Whatever the form used, a CSM is critical for determining prioritizing reasonable release scenarios for fate and transport evaluation.

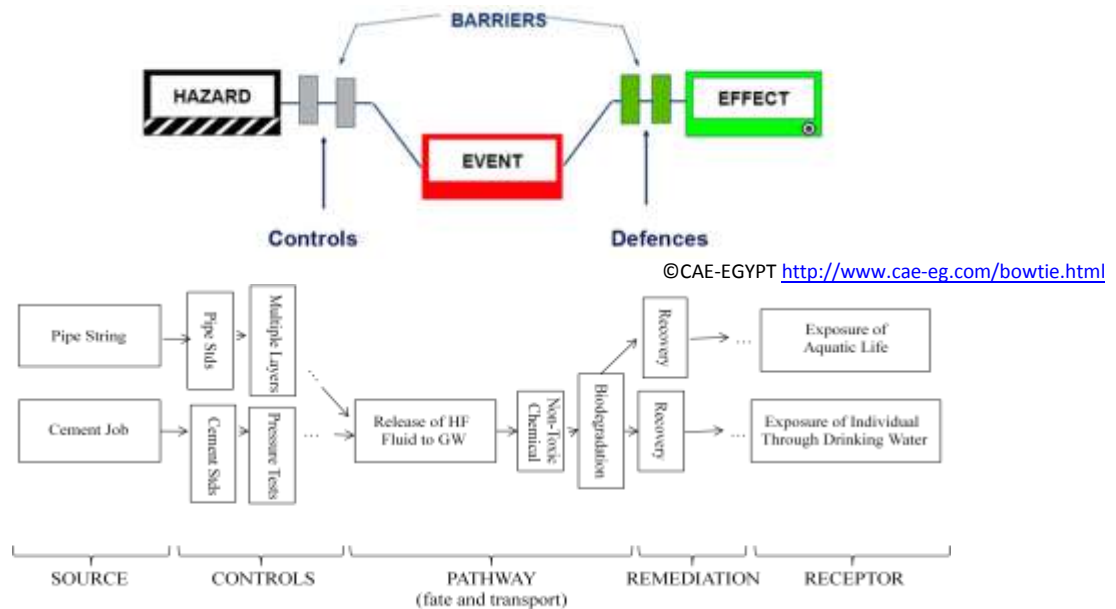


Figure 1. A generalized and a specific form of conceptual site model.

Realistic Potential Release Scenarios

The example CSM in Figure 1 shows a potential pathway from a cement job. There would be no need to evaluate further if the controls for the cement job are adequate to prevent release. Controls may include cement standards, and pressure tests. However, proceeding with development of a potential release scenario may be necessary if controls were considered weak and simple modifications are not sufficient to provide confidence in the controls.

Identify the potential release scenarios by examining the hydraulic fracturing processes that could potentially release material in a manner that could impact drinking water resources. Gather information critical to this potential scenario. These data might include process information and controls, identification of volume and type of additives used in the process, and total volumes of hydraulic fracturing fluids that might be released if controls could fail.

Returning to the potential for a failed cement job, there are numerous standards through regulation or guidance in the industry to prevent such an occurrence.^{3,4} In this case then, it may be determined that existing standards and regulations mitigate cement jobs as a reasonable release scenario. No further analysis is required in this case.

For the sake of discussion, assume that there is found to be potential for a release to surface soil somewhere in hydraulic fracturing process from a control failure. Also assume that it was not due to noncompliance to any applicable regulations. If about 50,000 gallons of hydraulic fracturing fluids⁵ were released, this would represent a maximum volume from one hydraulic fracturing treatment substage.

As much information as possible on the release liquid is now required. With a hydraulic fracturing fluid this would include its make-up. It is primarily water, sand, and about 0.5% (5,000 ppm) of up to about 8 additives.⁶ These additives may include a gellant (guar), buffer (sodium hydroxide), breaker (NaCl), friction reducer (mineral oil), antimicrobial (gluteraldehyde), acid (HCl), and surfactant (citrus terpenes and isopropanol). If this were flowback solution, there might be salt (NaCl), hydrocarbons, and ions from formation water. Composition of the hydraulic fracturing fluid and formation water may vary greatly depending upon reservoir requirements and properties.

At this point, the source release scenario, release volume, and release composition will be known to some extent. In this case: A surface release of 50,000 gallons of hydraulic fracturing fluid containing 50% original hydraulic fracturing fluid and 50% formation water to surface soil. There would of course be changes to the original hydraulic fracturing fluid such as a loss of proppant to the producing formation.

Assume a roughly estimated composition of spilled material (fluid and formation water) as shown in Table 3.

Table 3. Hypothetical release concentrations (my rough estimates)

Water (from fluid and formation water)	97.8%	
Guar (from fluid)	0.02%	200 ppm
Sodium Hydroxide (from fluid)	0.005%	50 ppm
Sodium Chloride (from fluid and formation water)	2.0%	20,000 ppm
Mineral Oil (from fluid)	0.04%	400 ppm
Gluteraldehyde (from fluid)	0.0005%	5 ppm
Hydrochloric Acid (from fluid)	0.06%	600 ppm
Hydrocarbon (from formation water)	0.05%	500 ppm
Citrus Terpenes (from fluid)	0.005%	50 ppm
Isopropanol (from fluid)	0.005%	50 ppm
NORM (from formation water)	Managed if present	

Fate and Transport

Data are now required on hydrogeology, geochemistry, and chemical properties. This also must include background chemical information (naturally occurring or anthropogenic) for potentially impacted drinking water sources that might interfere with fate and transport evaluation. Typical background chemical constituents and parameters are salts, pH, metals, naturally occurring hydrocarbons, and anthropogenic hydrocarbons.

For each component, available chemical and physical property data are required for subsequent evaluation. These data may include dissolution, precipitation, degradation rates, volatility, sorption, and dispersivity data.

At this point modeling may be performed based on site parameters. In the absence of the detail required for sophisticated modeling, screening models may be used to conservatively estimate fate and transport. For reactive inorganic compounds, a mineral equilibrium model such as mnteqa2 may provide information on the behavior of chemicals such as barium, strontium, etc.⁷ Most of these metals will fall out of solution due to solid precipitation or adsorption at the levels found in the source material. Soluble salts can be conservatively treated as remaining in solution. All chemicals in solution will be subject to potential transport through the unsaturated zone and movement with groundwater. Concentrations in Groundwater will tend to decrease with distance downgradient from the source due to mechanical mixing (dispersion) and biodegradation. This decrease over distance can be defined as a dilution attenuation factor for the saturated zone. This dilution factor is site specific and dependent on horizontal distance to the point of extraction, biodegradation rate, retardation, groundwater flow velocity, dispersivity, and source size. This relation between groundwater concentration in the source area and downgradient from the source can be described by the following steady-state solution for groundwater⁸:

$$\frac{C_x}{C_s} = DF_{sat} = \left(\exp \left\{ \frac{x}{2\alpha_x} \left[1 - \sqrt{1 + \frac{4\lambda\alpha_x R}{v}} \right] \right\} \times \left(\operatorname{erf} \left[\frac{S_w}{4\sqrt{\alpha_y x}} \right] \right) \left(\operatorname{erf} \left[\frac{S_d}{2\sqrt{\alpha_z x}} \right] \right) \right)$$

where:

- C_x = dissolved salt at a distance x from the source (mg/L)
- x = horizontal distance to point of extraction (cm)
- λ = first-order degradation constant – salt does not degrade (day^{-1})
- R = constituent retardation factor (dimensionless)
- v = specific discharge (cm/day)
- α_x = longitudinal dispersivity (cm)
- α_y = transverse dispersivity (cm)
- α_z = vertical dispersivity (cm)
- S_w = source width (cm)
- S_d = source depth (cm)

Validation

Once any modeling is completed, it cannot be considered representative of a system until it is validated, especially where there is uncertainty on any model factors. Uncertainty has to be addressed through data gap analysis and appropriate data gathering to fill those gaps. Also, field sampling and analysis will be required to test the model.

Chemicals must be selected for analysis based on their predicted ability to reach sampling points. Chemicals that are biodegraded readily (benzene, citrus terpenes, isopropanol), precipitated out of solution (barium), adsorbed to soils (polymers), or reacted (HCl) will not move a significant distance. Therefore, they may not be measureable downgradient. Upstream

fate and transport modeling and monitoring exercises have been most successful when performed on salts and divalent ions. Potential impacts may also be evaluated using ion ratios, isotopic methods, and trilinear diagrams.

Remember that any spill from a hydraulic fracturing operation will be of limited mass and volume so one cannot assume an infinite source, i.e., the source is finite and will disappear with time. Immobile chemicals will stay near the release area to be left in place or readily removed.

Risk Assessment

Knowing the distance to a receptor, an exposure rate can be determined. This can be evaluated with accepted risk exposure models for various drinking water receptors.

Conclusions

Processes are available for evaluating the fate and transport of selected reasonable release scenarios in hydraulic fracturing operations. These methodologies consider all controls in the hydraulic fracturing process as reflected in existing regulations and best management practices before selecting scenarios. Background chemicals, both anthropogenic and natural, must be considered in any analysis. Tools must be used that are appropriate for uncertainty in available data and analytical techniques.

References

¹USEPA, October 2002, Exemption of Oil and Gas Exploration and Production Wastes from Federal Hazardous Waste Regulations, United States Environmental Protection Agency, Washington, D.C., accessed at: <http://www.epa.gov/osw/nonhaz/industrial/special/oil/oil-gas.pdf>

²ASTM International, 2008, Standard Guide for Developing Conceptual Site Models for Contaminated Sites, E 1689-95 (Reapproved 2008), ASTM International, 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959.

³DOE, May 2009, State Oil and Natural Gas Regulations Designed to Protect Water Resources, prepared by Ground Water Protection Council for U.S. Department of Energy, accessed at: http://www.gwpc.org/home/GWPC_Home.dwt.

⁴API, October 2009, Hydraulic Fracturing Operations – Well Construction and Integrity Guidelines, Guidance Document HF1, First Edition, American Petroleum Institute, Washington, D.C., accessed at: <http://www.api.org/>.

⁵DOE, April 2009, Modern Shale Gas Development in the United States – A Primer, prepared by Ground Water Protection Council for U.S. Department of Energy, accessed at: http://fossil.energy.gov/news/techlines/2009/09024-Shale_Gas_Primer_Released.html.

⁶Energy in Depth, 2009, A Fluid Situation: Typical Solution Used in Hydraulic Fracturing, accessed at: <http://www.energyindepth.org/frac-fluid.pdf>.

⁷USEPA, March 1991, Minteqa2/Prodefa2 – A Geochemical Assessment Model for Environmental Systems: Version 3.0 User's Manual, United States Environmental Protection Agency, Athens, GA, accessed at: <http://www.epa.gov/ceampubl/mmedia/minteq/USERMANU.PDF>

⁸Domenico, P. A., 1987, An analytical model for the multidimensional transport of a decaying contaminant species, J. of Hydrology, 91, 49-58.