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Simple Modeling of the Disposition of Fluids On-Site in a Pit

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Overview

1. Chemical Analysis
2. Chemical Selection
3. Fate & Transport
4. Exposure
5. Risk in Reference to PCOCs
6. Take home Points

1. Chemical Analysis

- 173 Analytes
- 3 "liquid" Media – Frac Fluids, Flowback fluid, Produced Water
- Polynuclear Aromatic Hydrocarbons (PAHs)
  - anthracene, chrysene, fluorene, naphthalene, and pyrene
- Volatile Organic Compounds (VOCs)
  - benzene, toluene, ethylbenzene, and xylenes (BTEX), as well as trimethylbenzene, etc.
- Metals (metalloid) & Elements
  - 8 RCRA Metals (As, Ba, Cd, Cr, Pb, Hg, Ag, Se)
  - Secondary (e.g., boron, copper, nickel, zinc, etc.)
- Ethylene and Propylene glycol
- The radioactivity indicators gross alpha and gross beta
- Chlorides, Suflates, pH, sc, etc.
- Total Extractable Petroleum Hydrocarbons (TEPH)
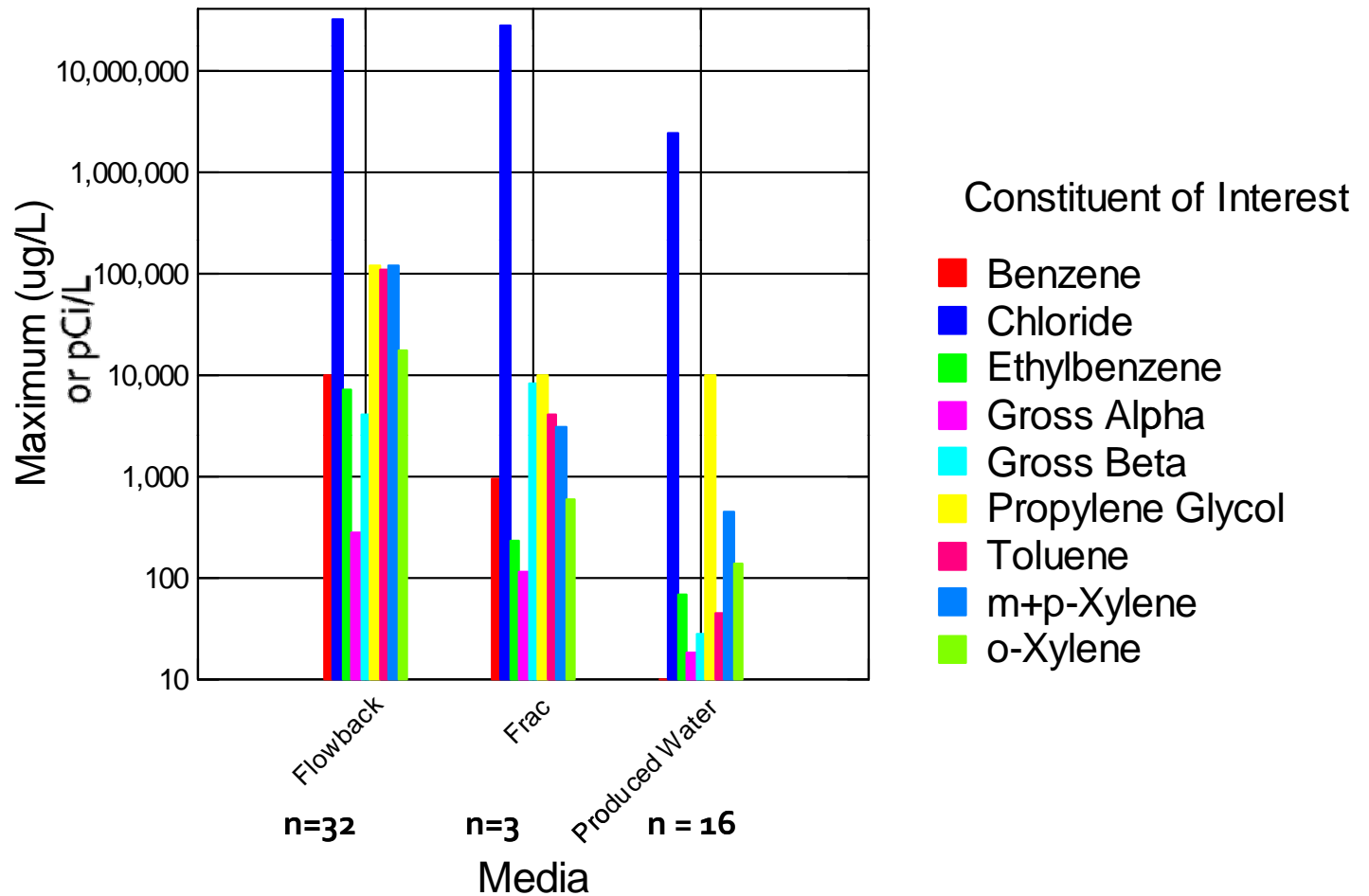
2. Chemical Selection

- Anthracene
- *Arsenic*
- Barium
- **Benzene**
- Cadmium
- Chromium(III)
- *Chrysene*
- Copper
- **Ethylbenzene**
- Flourene
- Mercury

- Nickel
- *Naphthalene*
- Phenanthrene
- *Phthalate, bis(2-ethylhexyl)*
- Pyrene
- Selenium
- Silver
- **Toluene**
- **Xylene, - m, - p**
- **Xylene, - o**
- Zinc

Bold = important
Italicized = dismissed (risk, or off-site relevance)

PCOCs

Maximums

Selection

- Flow Back only
  - Higher concentrations compared to produced water
  - Liquid, so more mobile
  - N=32 with duplicates
  - Solids leaching from pits was performed but not discussed here
- Chemicals Selected
  - BTEX
  - Based on max for all samples
  - Model doesn't allow gross alpha, beta (alt. strict dilution)
  - Prelim work on PAHs revealed insig. risk at meas. levels
  - Cl, Bo, glycols* more of an ecorisk

Ballpark – Order of Magnitude Frame of Reference
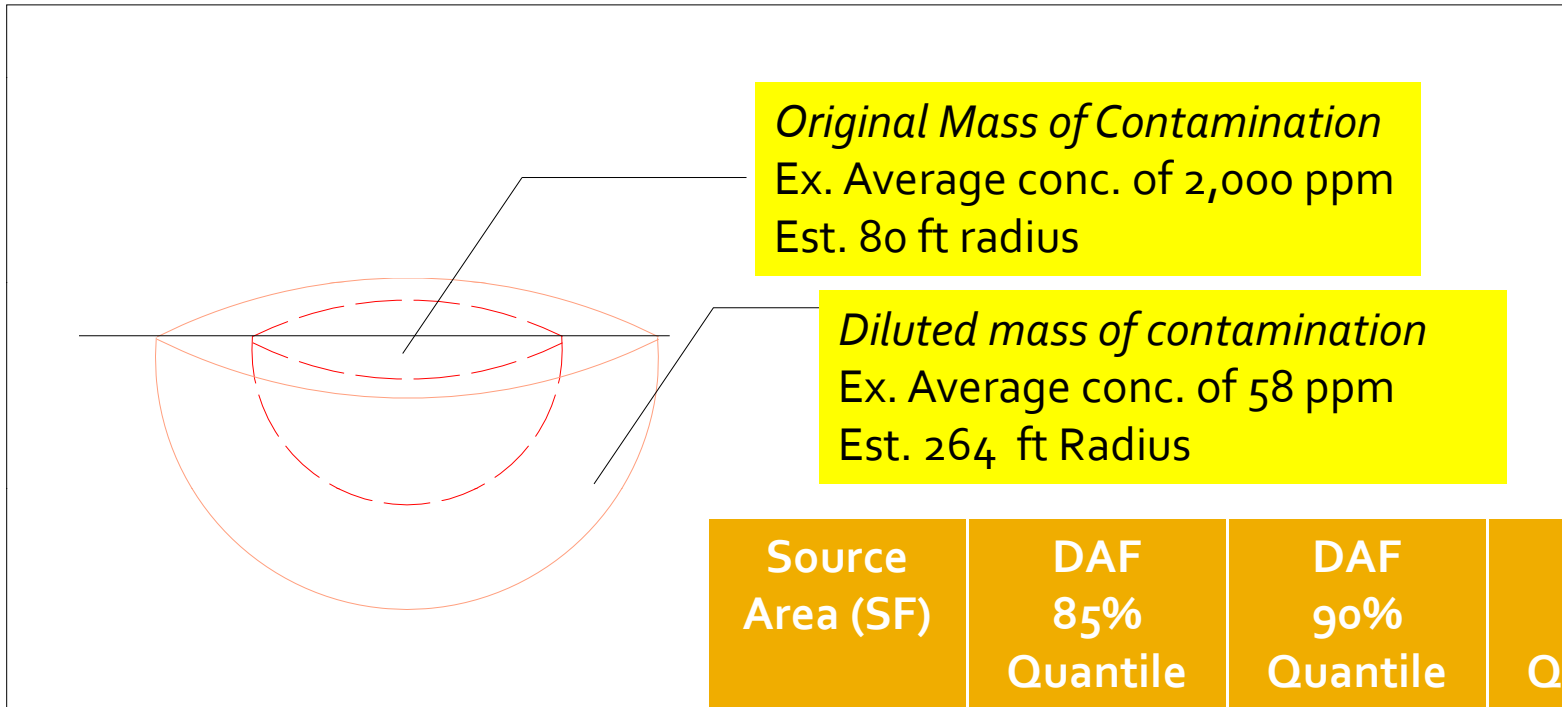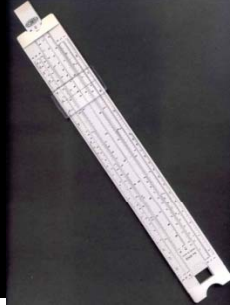
Original Mass of Contamination
Ex. Average conc. of 2,000 ppm
Est. 80 ft radius

Diluted mass of contamination
Ex. Average conc. of 58 ppm
Est. 264 ft Radius

Note: I'm not advocating dilution as a solution to pollution.

100 ft wide source
Ref: EPA: Soil Screening Technical Guidance, Technical Background Document. EPA/540/R-95/128. May 1996.

Source Area (SF)	DAF 85% Quantile	DAF 90% Quantile	DAF 95% Quantile
1,000	42400	3430	182
5,000	4240	437	27
10,000	1810	204	13
50,000	293	41	3.7

3. Fate & Transport

- ## Phys-Chem properties
  - ### Solubility
  - ### Retardation
  - ### Log K_{ow}
- ## Hydrogeologic Parameters
  - ### Depth to GW
  - ### Porosity, Hydraulic Conductivity
- ## Model Specifics
  - ### Distance to Point of Exposure (POE)
  - ### Options -Decay v. no Decay

SOURCE

EXPOSURE ROUTE

PEOPLE

EXPOSURE POINT

MEDIUM
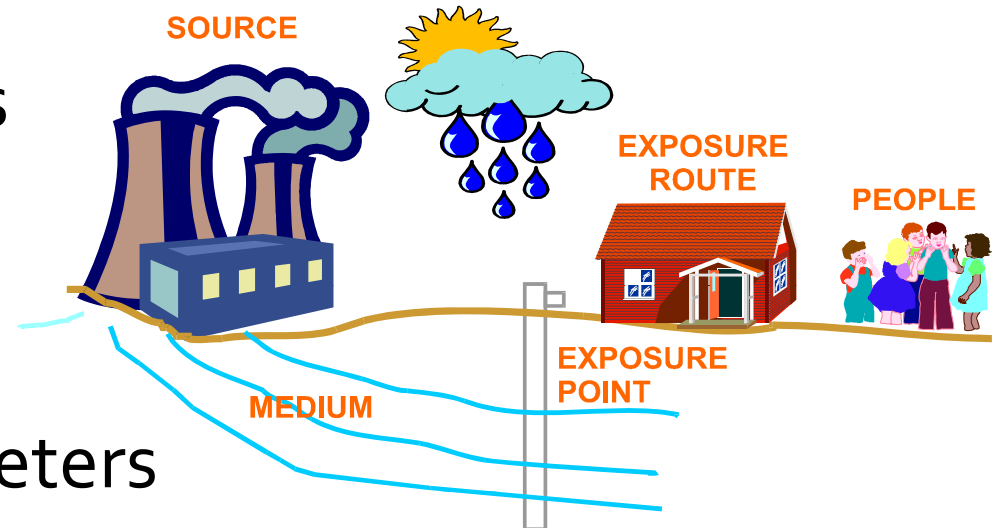
Hydrogeologic Parameters
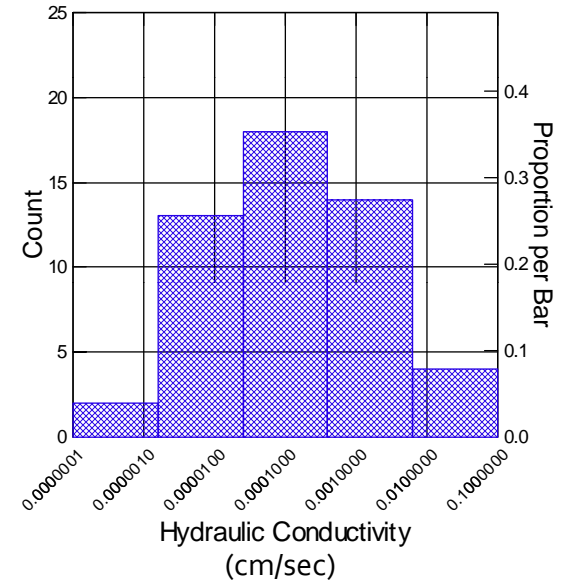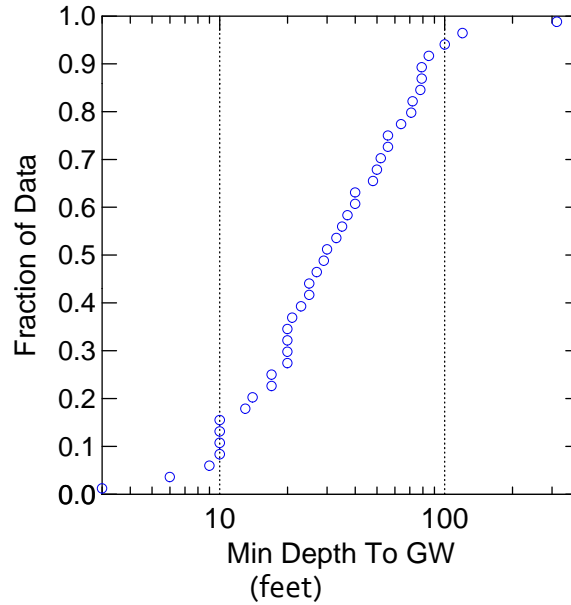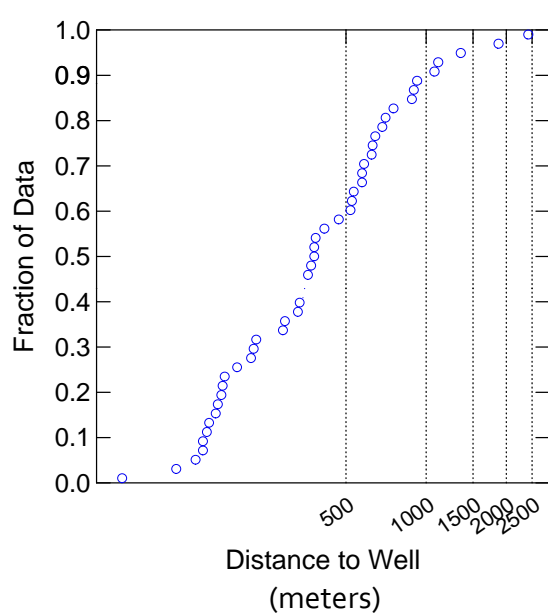
28 Site Locations in DJ & Piceance

Selected parameters for Modeling

Depth to GW	1 or 3 m
Hydraulic Conductivity	3.63E-3 cm/sec
Point of Exposure (POE)	10 m or 72 m

Attribute/Parameter	Units	N	Min	Max	Average	LCL$_{2.95\%}$	5% Quantile
Distance to Nearest Well	Meters	49	72	2,420	512	373	135
Distance to Surface Water	Meters	49	15	2,350	515	385	59
Minimum Depth to GW*	Feet	42	3	315	45	29	8

Hydrogeologic Parameters

- Hydraulic gradient   0.008
- Dispersivity   100 cm
- Porosity   0.25
- Source   direct into GW
- pH   set at 6.3

- Basis:
  - Field data
  - Model response - faster travel
  - Model response – > max concentrations at POE

Fate

- Decay vs. non-decay
- Chlorides ignored
- Lowest decay rates from ASTM 1739 used
- Domenico, 1st Order decay

Scenario	Depth to GW (meters)	Hydraulic Conductivity (cm/s)	POE (meters)	Decay of Organic Constituents
9	1	3.63E-3	10	No
10	3	3.63E-3	72	Yes
11	1	3.63E-3	72	No
12	3	3.63E-3	10	Yes

Model for Transport

- S_w = source width (cm)
- S_d = source depth (cm)
- αx = Long GW dispersivity (cm)
- αy = Vert GW dispersivity (cm)
- V = GW velocity (cm/day)
- x = distance downgradient from source
- R_i = Constituent Retardation factor
- $C_i(x)$ = Conc. of constituent i at x (cm)
- $C_s(x)$ = Conc. of constituent i at source (cm)
- λ_i = first Order decay rate for constituent I (day^{-1})
- K = hydraulic conductivity (cm/sec)
- I = Hydraulic gradient [head] (cm/cm)
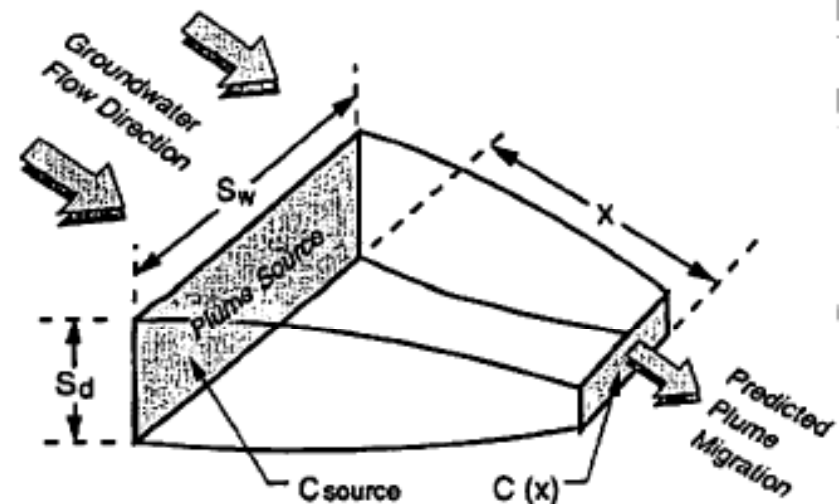
- λ_i = o for no decay
- DAF = $C_s(x)$/ $C_i(x)$

LT-1a: Solute Transport with First-Order Decay:

$$\frac{C(x)_i}{Csi} = \exp\left(\frac{x}{2\alpha_x}\left[1 - \sqrt{1 + \frac{4\lambda_i \alpha_x R_i}{v}}\right]\right) erf\left(\frac{S_w}{4\sqrt{\alpha_y x}}\right) erf\left(\frac{S_d}{2\sqrt{\alpha_z x}}\right)$$

where:

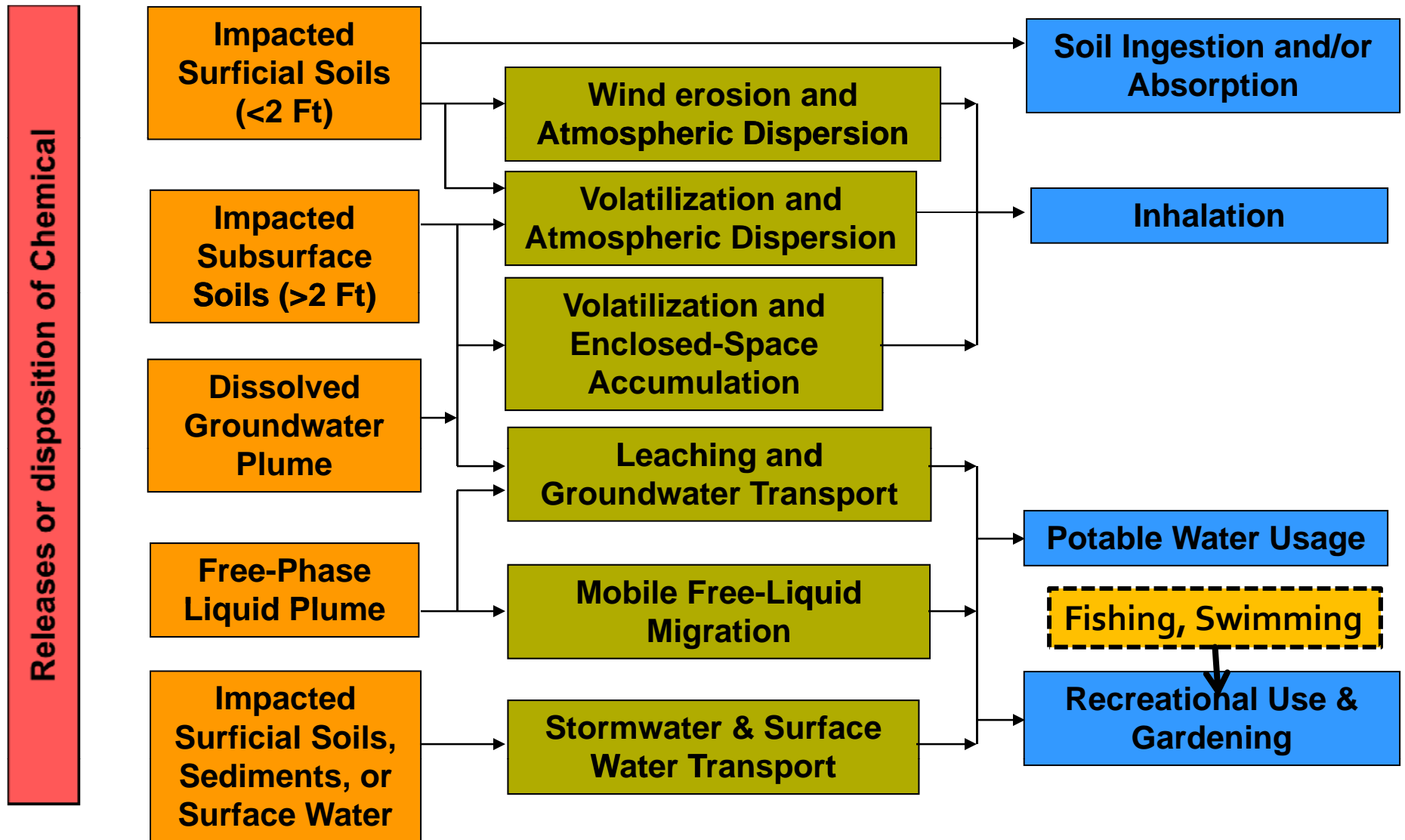$$v = \frac{K \cdot i}{\theta_e}$$

5. Exposure

- Scenarios
  - Fishing (SW)
  - Swimming (SW)
  - Well water consumption (DW)
  - Volatilization & inhalation *
  - On-site Commercial & Construction Worker*
- Multiple Routes & Chemicals
  - Each calculated separately & combined

* Not discussed here but available in RA by QEPA, 2008

Exposure Pathways

Releases or disposition of Chemical

Impacted Surficial Soils (<2 Ft)	**Wind erosion and Atmospheric Dispersion**	**Soil Ingestion and/or Absorption**
Impacted Subsurface Soils (>2 Ft)	**Volatilization and Atmospheric Dispersion**	**Inhalation**
	Volatilization and Enclosed-Space Accumulation	
Dissolved Groundwater Plume	**Leaching and Groundwater Transport**	
Free-Phase Liquid Plume	**Mobile Free-Liquid Migration**	**Potable Water Usage**
		Fishing, Swimming
Impacted Surficial Soils, Sediments, or Surface Water	**Stormwater & Surface Water Transport**	**Recreational Use & Gardening**

ASTM E 1739, Standard Guide For Risk-Based Corrective Action Applied At Petroleum Release Sites. American Society for Testing and Materials, Chonshohoken, PA. . November 1995; ASTM*: ASTM E 1739-95 (2002), Standard Guide For Risk-Based Corrective Action Applied At Petroleum Release Sites*. American Society for Testing and Materials, Chonshohocken, PA. 2002.

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6. Risk in Reference to PCOCs

Ground Water Pathway

Scenario	Scenario 9	Scenario 10	Scenario 11	Scenario 12	Acceptable Range
Depth to GW (meters)	1	3	1	3	☒
Point of Exposure (POE) (meters)	**10**	72	72	10	☒
Decay of Organic Constituents	No	Yes	No	Yes	☒
Benzene Risk	**3.5E-4**	*3.3E-103*	7.9E-6	3.3E-103	1E-4 to 1E-6
Toluene HQ	**1.6E+0**	1.6E-99	3.6E-2	1.5E-99	<1
Ethyl Benzene HQ	2.0E-1	2.1E-100	4.6E-3	1.9E-100	<1
Xylenes HQ	4.0E-1	*3.8E-100*	9.0E-3	3.8E-100	<1
TOTAL Risk*	**3.5E-4**	3.3E-103	7.9E-6	3.3E-103	1E-4 to 1E-6
TOTAL HQ	**1.2E+1**	7.6E-1	2.6E-1	1.1E-98	<1

* Ignores Arsenic

Risk in Reference to PCOCs

Surface Water Pathway

Scenario	Scenario 9	Scenario 10	Scenario 11	Scenario 12	Acceptable Range
Depth to GW (meters)	1	3	1	3	☒
Point of Exposure (POE) (meters)	10	72	72	10	☒
Decay of Organic Constituents	No	Yes	No	Yes	☒
Benzene Risk	8.1E-8	7.7E-107	8.1E-8	7.7E-107	1E-4 to 1E-6
Toluene HQ	6.7E-4	6.6E-103	6.7E-4	6.3E-103	<1
Ethyl Benzene HQ	1.1E-4	1.1E-103	1.1E-4	1.0E-103	<1
Xylenes HQ	1.5E-4	1.4E-103	1.5E-4	1.4E-103	<1
TOTAL Risk	8.1E-8	1.2E-7*	8.1E-8	7.7E-107	1E-4 to 1E-6
TOTAL HQ	3.1E-3	4.0E-3**	3.1E-3	2.9E-102	<1

* Arsenic at 1.2E-7   ** Barium at 3.12E-3
Arsenic at 5.4E-4

7. Points

- For Colorado, the fluids for potential disposition did not contain significant PAHs with respect to risk
- Under reasonable to most likely conditions, BTEX was not a significant risk either
- Local & regional hydrogeologic and geologic conditions should be looked at closely
- Conservatism is easier to explain and digest
- Limitations
  - Not directly injected into surface water
  - Regulatory restrictions
  - Not all products accounted for
  - RA not done directly for ecosystem effects
  - Geology-Hydrogeo Specific to CO

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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.

The fracing process begins with wellpad siting, proceeds through completion and ends with production (and the eventually decommissioning or abandonment). The steps in the process include: site selection, well pad development, drilling, fracing, and production. Using the term *waste* to mean any disposal, whether in use or afterwards, one realizes that there are a number of *waste* materials produced during these steps including: drilling fluids, pit solids, pit liquids, frac fluids, flowback fluids, and produced water. An investigation involving sampling and analysis of these materials was conducted along with a followup risk assessment (RA) to assess the impact of fracing in four energy basins in Colorado which was completed in the spring of 2008 [URS, 2008; QEPA, 2008]. The focus of this presentation will be on three media: flowback fluids, frac fluids, and produced waters, although other media (e.g., pit solids as waste) and subsequent pathways were considered and were evaluated in both the sampling and analysis [URS, 2008] and in the RA [QEPA, 2008].

Chemical Analysis

In 2008, in a project funded by the Colorado Oil and Gas Association (COGA), QEPA, pH2 through QEPA, and URS were contracted to devise a sampling and analytical plan as part of a risk assessment for proposed changes in the Oil & Gas (O&G) regulations in Colorado [COGCC, 2008]. This first necessitated the identification of chemicals for analytical evaluation (CAE) and eventual selection of the chemicals [URS, 2008]. A list of chemicals was prepared that included data suggested by a review of Material Safety Data Sheets (MSDS) from COGA member companies. It also included standard chemicals of interest in the O&G industry such as Benzene, Toluene, Ethyl Benzene, Xylenes (BTEX), Polnuclear Aromatic Hydrocarbons (PAHs), Boron, Chloride, Total Extractable Petroleum Hydrocarbons (TEPH), etc. [CDPHE, 2007; COGCC, 2008]. Primary metals (and metalloid) included were the 8 Resource Conservation and Recovery Act (RCRA) metals consisting of arsenic, barium, cadmium, chromium, lead, mercury, silver, and selenium; and an additional 15 target analyte list (TAL) metals were added from EPA Method 6020A which included Aluminum, Antimony, Beryllium, Calcium, Cobalt, Copper, Iron, Magnesium, Manganese, Nickel, Potassium, Sodium, Thallium, Vanadium & Zinc. Based on a review of potential agents associated with raw material derived from subsurface deposits, gross alpha and gross beta were selected for analysis. A small subset of samples from pit wastes was analyzed by EPA's Toxic Characteristic Leaching Procedure (TCLP) for 8 RCRA metals in addition to pH, reactive sulfides, and reactive cyanides to evaluate waste disposal considerations. However, this presentation will only cover flowback fluids, frac fluids, and produced waters, of which there are 32, 3, and 16 sample data points, respectively, including duplicates.

Chemical Selection for Disposition Modeling

Based on the analytical results, measurable values of the 173 analytes were narrowed. Although a number of PAHs were present, their fate-transport and subsequent risk were not shown to be significant human health risks; however, some were modeled. A few chemicals were removed from the modeling of liquid waste disposition based on previous modeling of solid wastes (our scenarios 1 to 8) indicating minimal opportunity for significant risk given basic maximum concentration as well as subsequent fate and transport. Chloride and boron were not selected for modeling as these had Colorado regulatory limits not tied to human health and these limits were not expected to be exceeded in these materials once accounting for dilution, fate, and transport. For instance, the boron maximum was 7.6 mg/L versus a limit of 2 mg/L limit, not including any dilution from transport.

The glycols were initially considered but dismissed based on the risk assessor's qualitative order-of-magnitude assessment with regard to having a *defacto* dilution attenuation factor (DAF) under the modeled circumstances of an initial 4-100 dilution before significant transport. This *diluted* value when compared to drinking water standards and in consideration of fate and transport resulted in their de-selection from the liquid disposition modeling. For instance, only 5 of 33 data points in the flowback fluids and none of the produced water samples detected glycols. The maximum in any medium was 120,000 ug/L, and with a 100 fold dilution (DAF) the result would be 1,200 ug/L. Using a 300-fold safety factor to calculate an acceptable limit based on the more toxic of the glycols (ethylene) [Blood, 1965] would result in 0.14 mg/kg/day acceptable exposure rate. For a 70 kg man consuming 2 L/day, that would be a drinking water limit of 4,900 u/L, higher than any suspect concentration at the point of exposure (POE). Similarly, data for 2-butoxyethanol (2-BE) revealed several detects in pit solids (as solids), pit fluids, flowback fluids, and drilling fluids. The highest of these was 7.1 mg/L in flowback flow fluids. A total of 5 additional hits were noted as tentatively identified compounds (TICs) with suspect validity, the highest estimated concentration from these was 20 mg/L. The ATSDR MRLS for 2-BE are 0.4 mg/kg/day and 0.07 mg/kg/day for intermediate and chronic exposure [ATSDR, 1998]. These were converted to surrogate drinking water limits assuming 55-70 kg female or male humans and using a reasonable maximum likelihood estimate of water intake of 2 liters per day [EPA, 1989]. This results in intermediate surrogate drinking water limits of 11-14 mg/L, and chronic limits of 1.925-2.45 mg/L. One also notes that these limits have uncertainty/safety factors of 90 and 1000, respectively. Using the 20 mg/L and presuming typical DAFs of 100+, 2-BE would not present a significant risk.

Although gross alpha and gross beta were present, a set of appropriate phys-chem properties is not available for modeling their fate and transport within the model chosen for the other components. Furthermore, the effect of the anticipated DAF (100+) of disposing of a liquid in a waste pit on-site [where reserve pits at closure tend to be about 75x20 ft to 100x50 ft at depths of 8-10 ft], suggests that in these geologic settings, gross alpha and beta (maximums 274 and 4,030 pCi/L, respectively) would not result in exceedances of 15 and 30 pCi/L EPA suggested levels in absence of isotope data at the anticipated conservatively estimated POE of 72 meters.

The flowback fluids in general produced the highest levels of constituents of concern. The

produced water at the highest levels, for conservatism, were used in the modeling. Maximum values for each constituent were used as opposed to means or upper confidence limits (UCLs). Soil leaching was run simultaneously with the liquid and thus results include both, but are driven by the liquids in the off-site scenarios.

Fate & Transport

In the study in Colorado, the hypothetical practice of releasing flowback or produced water back into waste pits was modeled using a standard fate & transport model used in the ASTM RBCA standard [ASTM, 2002]. The modeling performed assumed a standard pit had an infinite source of flowback fluid and assumed no liner was present. We chose characteristics of the chemicals based on data from the two basins qualitatively considered more risky in setting, and the hydrogeologic characteristics for these basins as well. The model for transport is a standard Domenico model [Domenico, 1985, 1987] for solute transport with a modification for decay-based attenuation. For no decay, the decay constant in the equation, λ, was set to zero. Other parameters were set to limit errors, and apply a certain level of conservancy while still using more regional/local maximum likelihood estimators (MLEs) for hydrogeologic parameters. The hydraulic conductivity (K_{ha}) was selected as 3.63E-3 cm/sec, driven by regulatory concerns [CDPHE, 2007], although the range tends to be lower. The depth to groundwater was varied from 1-3 meters (3.3-9.8 feet) in the 4 scenarios modeled, two with 1 meter and two with 3 meters. The lower range of constituent retardation values from ASTM [ASTM, 2002] was used in the model. The POE for ground water was set at 10-72 meters (33-236 feet), where 72 meters was the nearest well in a survey of 28 sites from the two basins (out the 55 sites from which the full study was conducted). The POE for surface water was also set at 10-72 meters, recognizing that the minimum and 5% quantile values for surface water distance to drilling well at the 28 sites investigated were 15 and 59 meters (49 & 194 feet), respectively. Of the 4 scenarios modeled, two used 10 meters and two used 72 meters; and two assumed decay and two did not. Decay rates were set by chemical by selecting on the lower end of published data.

Exposure

Several assumptions go into the exposure assessment process and a number of limitations also arise from this. In the study in Colorado the fluids released back into waste pits was modeled using a standard fate & transport model used in the ASTM RBCA standard [ASTM, 2002]. As part of this ASTM process, pathways from soils, groundwater and vaporization were considered. Scenarios that were accounted for included fishing, swimming, well water consumption, inhalation of air and dust downwind, etc. Exposures for commercial building occupancy and a construction worker scenario were modeled and are in the RA (QEPA, 2008), but are not presented here. Because multiple pathways, and thus exposures and doses, were modeled on the same population (e.g., person), an overestimate of real exposure is likely to arise. The RA was completed using a variety of assumptions, details of which are provided in the RA [QEPA, 2008].

The results indicate that benzene is driving the carcinogenic risk with all other agents (e.g., PAHs, phthalates, etc.) having little influence. There was an effect from arsenic, but this would already be seen from background levels present in soils already. The results also indicate that

the non-cancer risk is driven by toluene, followed by xylenes and then ethylbenzene, with all other agents having little influence. The groundwater pathway is clearly more important. Based on the 4 scenarios, with scenarios 10 & 11 the most likely, it does not appear that the fluids present the significant risk that might have been anticipated had the fate, transport, and RA not been performed.

Acknowledgments

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