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Fracing & Associated Media Composition in Colorado

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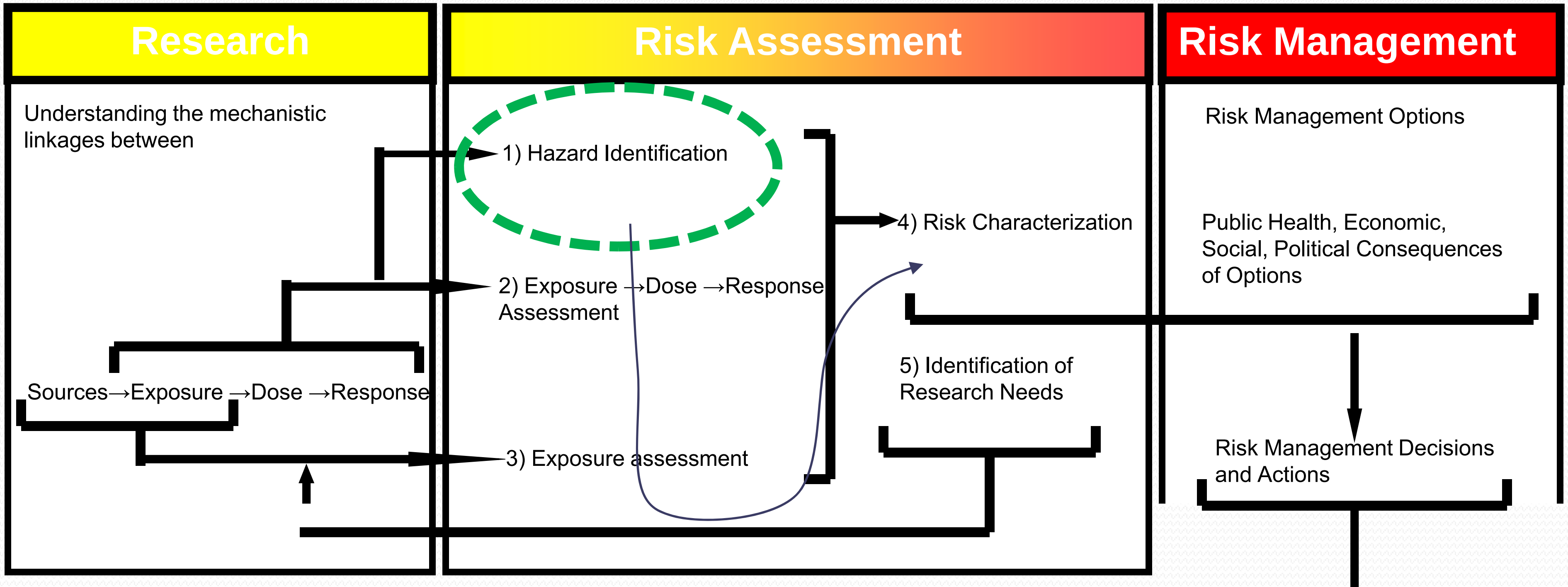
Overview

- Risk Assessment in regards to ID of materials
- Selection of Chemicals for Analysis
- Statistical Considerations
- Media and Sample Collection
- Results for Flowback, Frac Fluids, and Produced Waters
- Narrow Selection for Risk Assessment
- Limitations
- Acknowledgements

NAS/NRC Risk Assessment/Management Paradigm



Research

Understanding the mechanistic linkages between

Sources→Exposure →Dose →Response

Risk Assessment

1) Hazard Identification

2) Exposure →Dose →Response Assessment

3) Exposure assessment

4) Risk Characterization

5) Identification of Research Needs

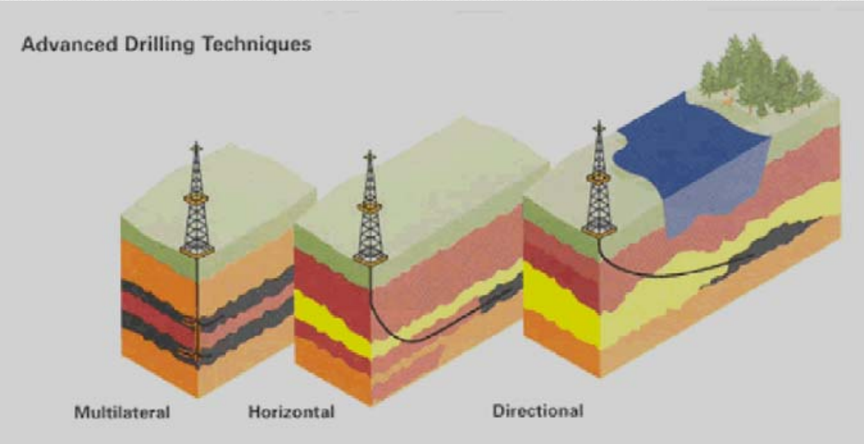
Risk Management

Risk Management Options

Public Health, Economic, Social, Political Consequences of Options

Risk Management Decisions and Actions

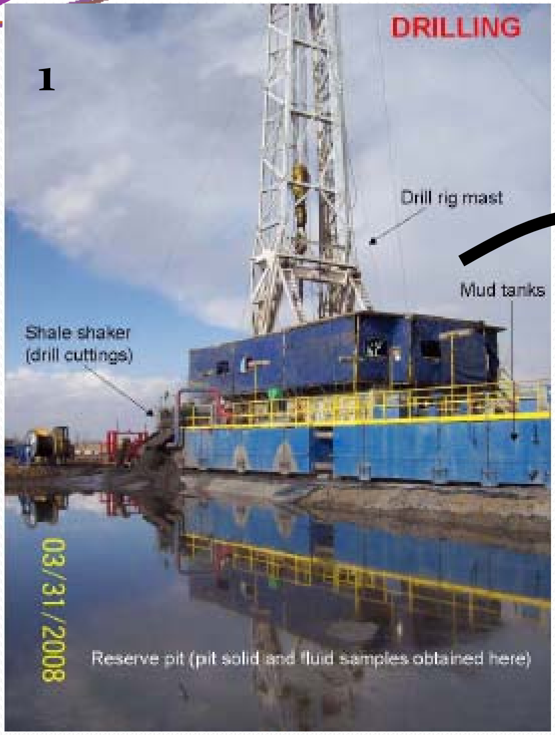
Source: Adapted from NRC, 1983.



Argonne, Trip Report for Field Visit to Fayetteville Shale Gas Wells, ANL-EVS_R07-4, DOE, August, 2007

The Process

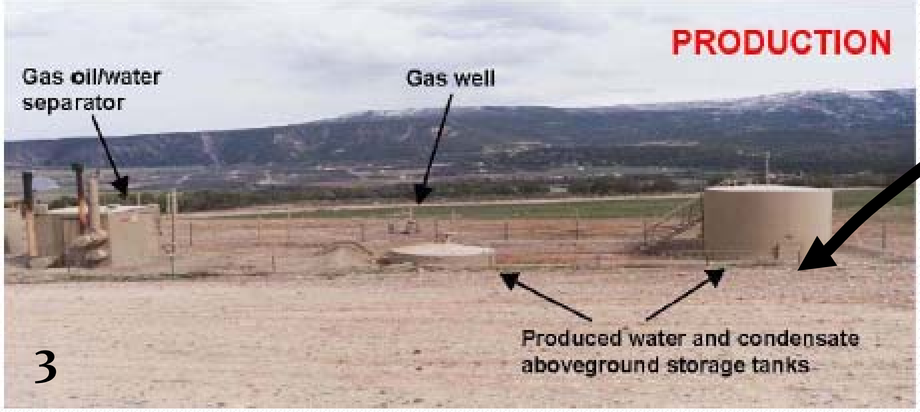
1



2A

2B

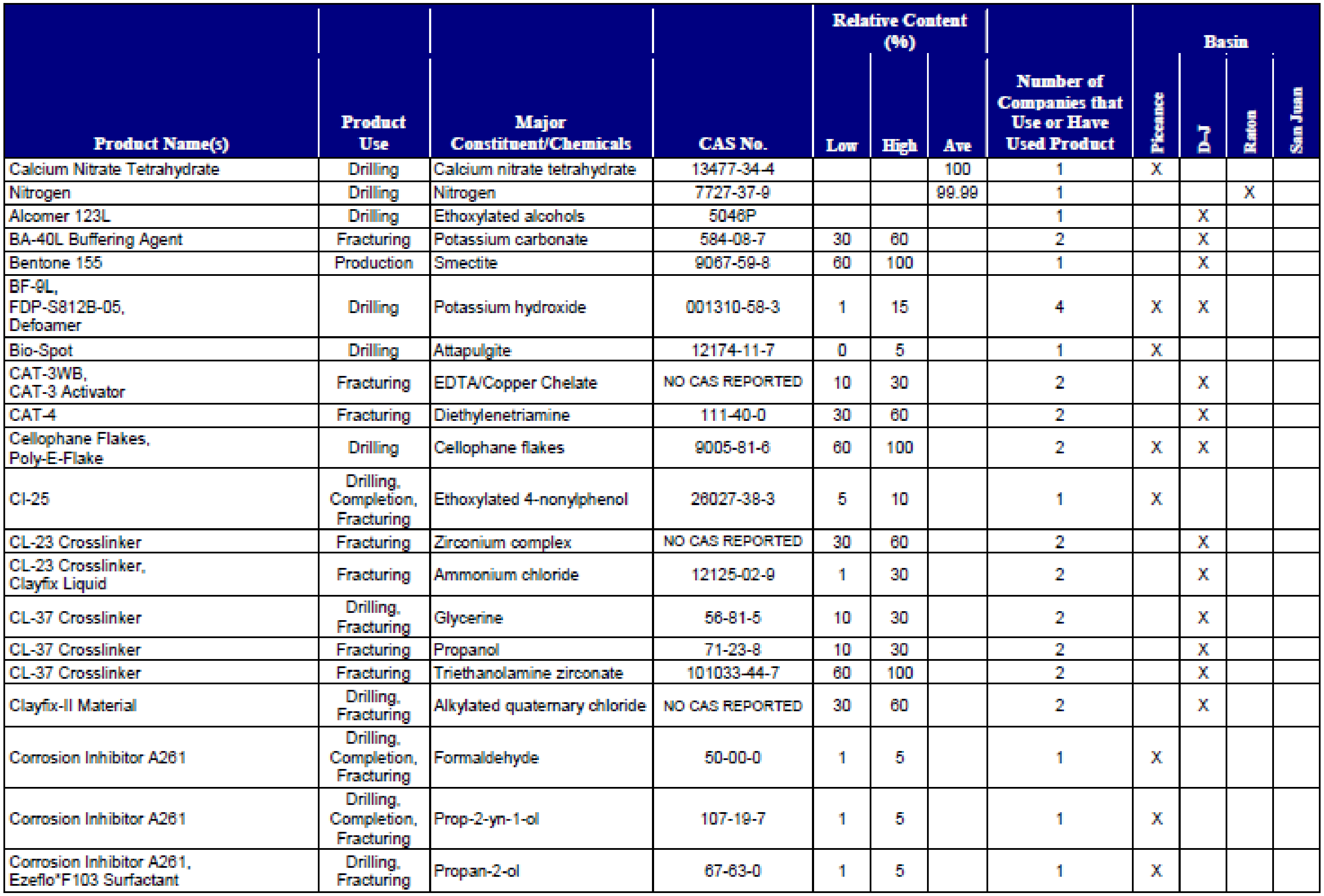
3



Constituents for Analytical Evaluation (CAE)

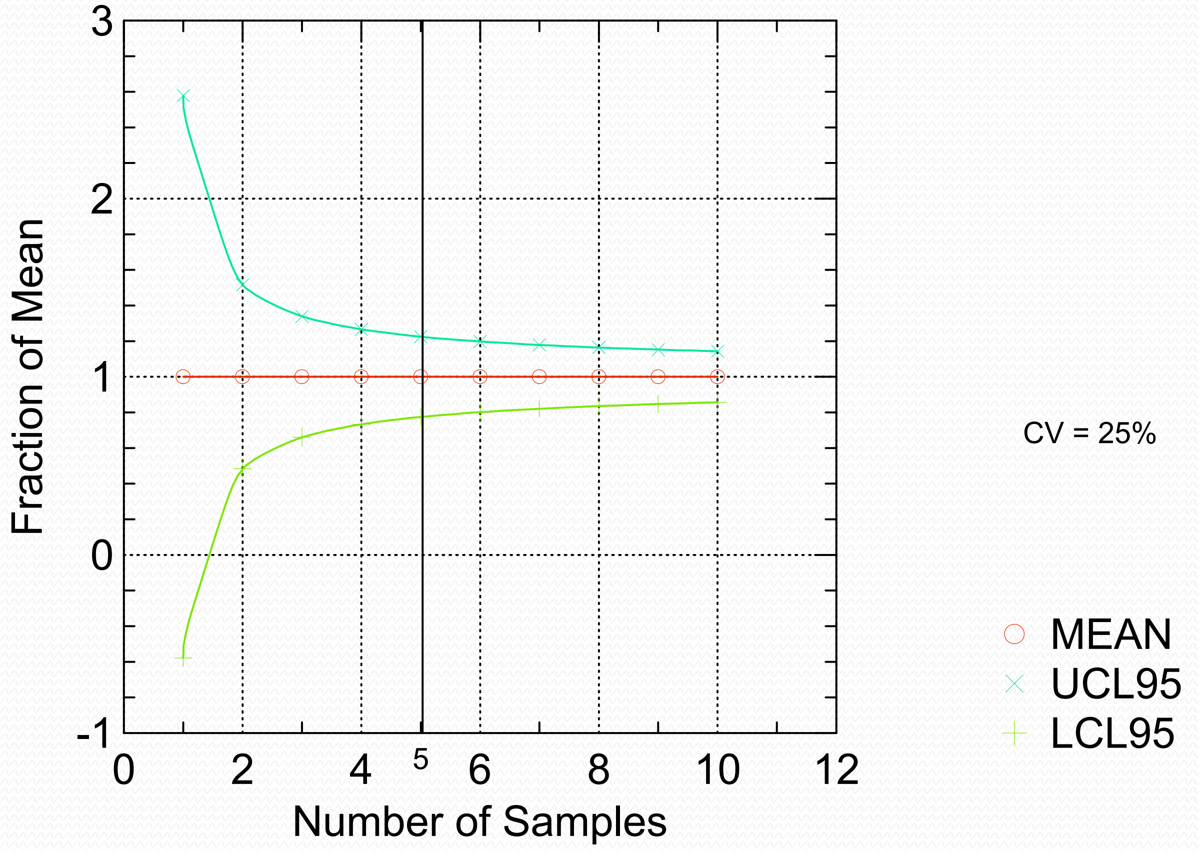
- **Developed from:**
  - MSDS representing the chemicals and materials currently in use by 7 participating COGA companies
  - Chemicals commonly tested for during environmental investigations
  - Chemicals perceived by environmental interest groups as chemicals of health concern
- **More than 100 products**
  - Found to be used in current drilling and completion operations and constituents
  - It is recognized that only a fraction are used at any one time

Example:

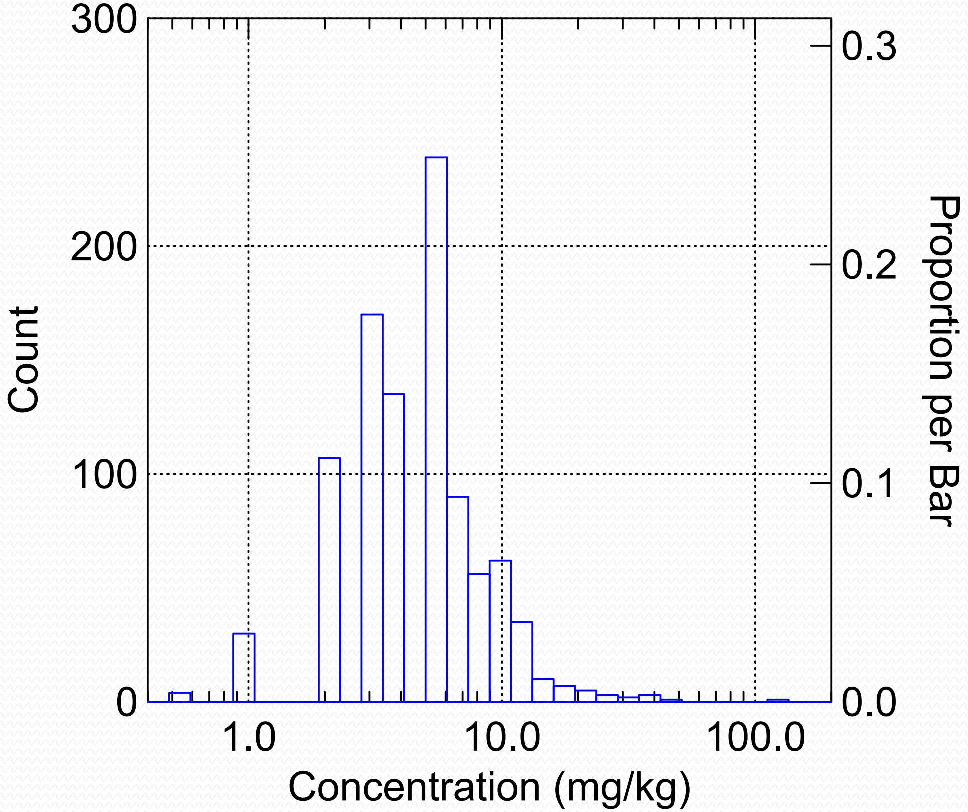


Product Name(s)	Product Use	Major Constituent/Chemicals	CAS No.	Relative Content (%)			Number of Companies that Use or Have Used Product	Basin			
				Low	High	Ave		Piceance	D-J	Raton	San Juan
Calcium Nitrate Tetrahydrate	Drilling	Calcium nitrate tetrahydrate	13477-34-4			100	1	X			
Nitrogen	Drilling	Nitrogen	7727-37-9			99.99	1			X	
Alcomer 123L	Drilling	Ethoxylated alcohols	5046P				1		X		
BA-40L Buffering Agent	Fracturing	Potassium carbonate	584-08-7	30	60		2		X		
Bentone 155	Production	Smectite	9067-59-8	60	100		1		X		
BF-9L, FDP-S812B-05, Defoamer	Drilling	Potassium hydroxide	001310-58-3	1	15		4	X	X		
Bio-Spot	Drilling	Attapulgite	12174-11-7	0	5		1	X			
CAT-3WB, CAT-3 Activator	Fracturing	EDTA/Copper Chelate	NO CAS REPORTED	10	30		2		X		
CAT-4	Fracturing	Diethylenetriamine	111-40-0	30	60		2		X		
Cellophane Flakes, Poly-E-Flake	Drilling	Cellophane flakes	9005-81-6	60	100		2	X	X		
CI-25	Drilling, Completion, Fracturing	Ethoxylated 4-nonylphenol	26027-38-3	5	10		1	X			
CL-23 Crosslinker	Fracturing	Zirconium complex	NO CAS REPORTED	30	60		2		X		
CL-23 Crosslinker, Clayfix Liquid	Fracturing	Ammonium chloride	12125-02-9	1	30		2		X		
CL-37 Crosslinker	Drilling, Fracturing	Glycerine	56-81-5	10	30		2		X		
CL-37 Crosslinker	Fracturing	Propanol	71-23-8	10	30		2		X		
CL-37 Crosslinker	Fracturing	Triethanolamine zirconate	101033-44-7	60	100		2		X		
Clayfix-II Material	Drilling, Fracturing	Alkylated quaternary chloride	NO CAS REPORTED	30	60		2		X		
Corrosion Inhibitor A261	Drilling, Completion, Fracturing	Formaldehyde	50-00-0	1	5		1	X			
Corrosion Inhibitor A261	Drilling, Completion, Fracturing	Prop-2-yn-1-ol	107-19-7	1	5		1	X			
Corrosion Inhibitor A261, Ezeflo*F103 Surfactant	Drilling, Fracturing	Propan-2-ol	67-63-0	1	5		1	X			

Statistical Considerations in Sampling
Number of Samples



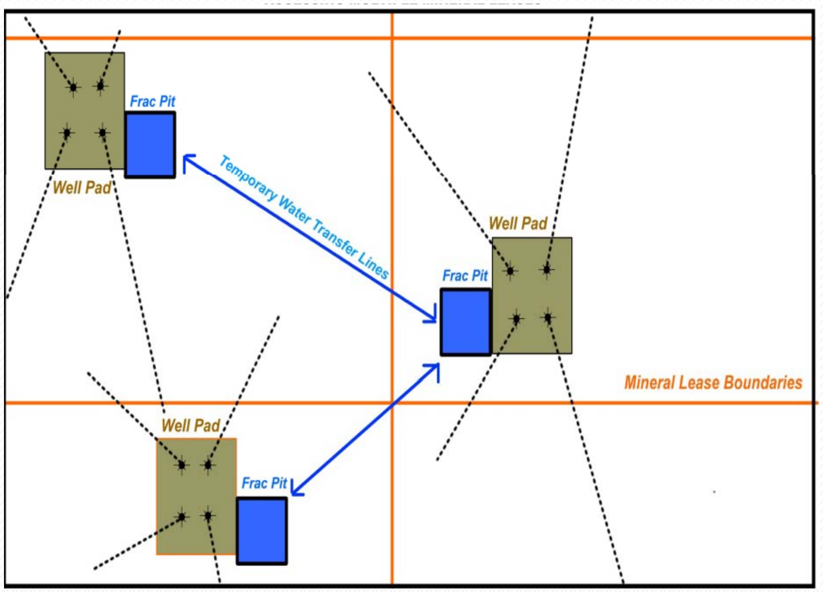
Statistical Considerations in Sampling
Underlying Distributions



Colorado Arsenic Background Samples – n= 960

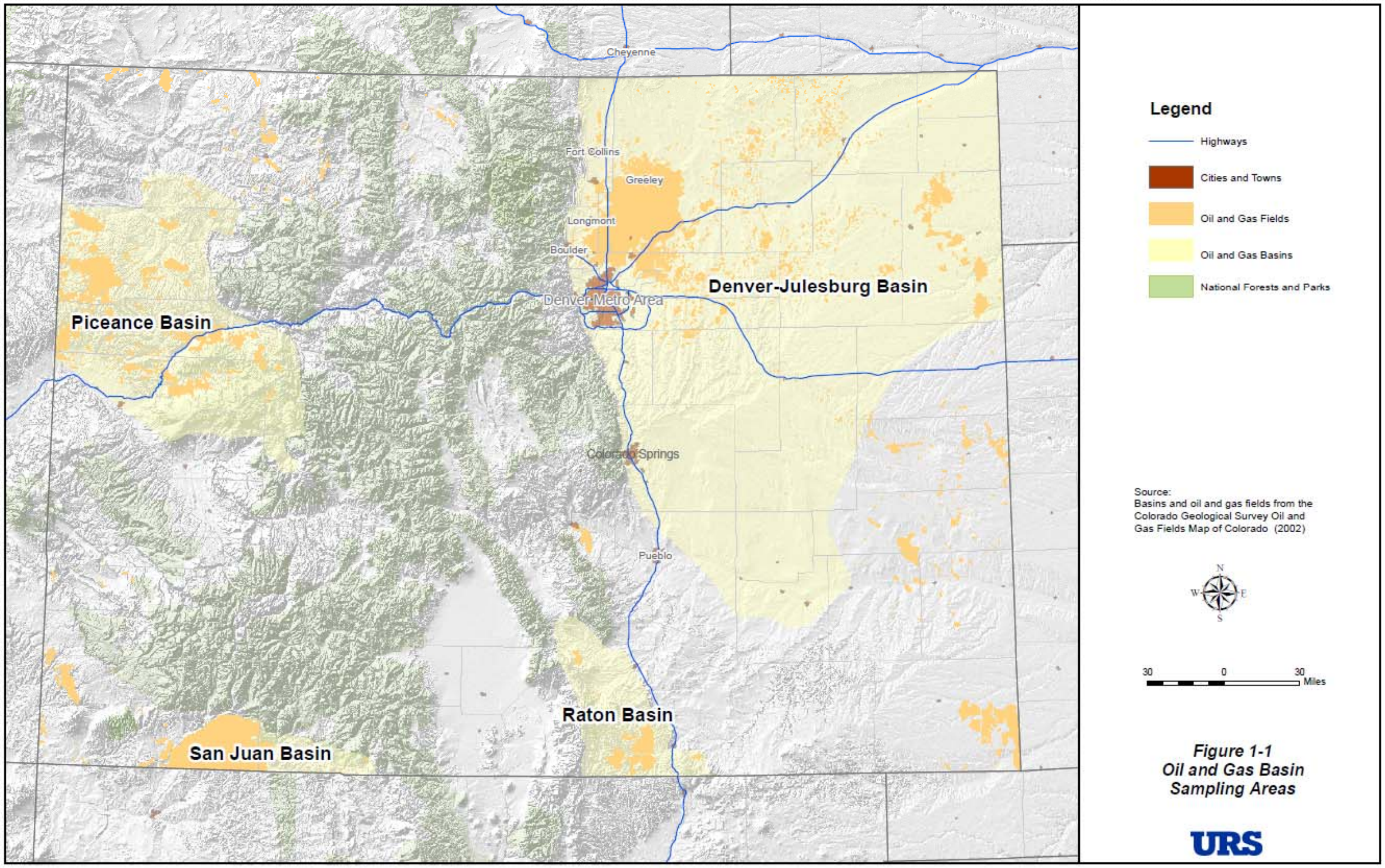
Media Sources

- Media sampled include:
  - Pit solids
  - Pit fluids
  - Frac fluids
  - Drill fluids
  - Flowback fluid (early and late)
  - Produced water
  - Background soil



Production Pit

4 Energy Basins in Colorado

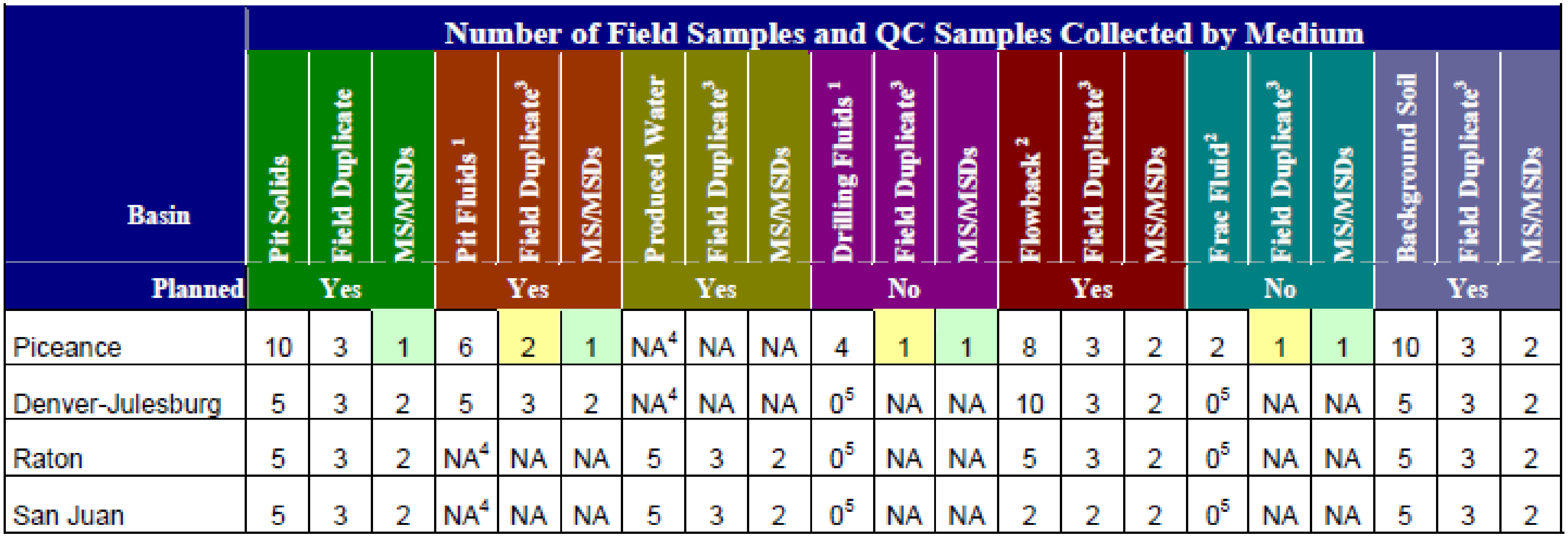


Source:
Basins and oil and gas fields from the Colorado Geological Survey Oil and Gas Fields Map of Colorado (2002)

Figure 1-1
Oil and Gas Basin
Sampling Areas

URS, Field Activities Report for Characterization of Exploration and Production Pit Solids and Fluids in Colorado Energy Basins, June 4, 2008

Sample Collection



Number of Field Samples and QC Samples Collected by Medium

Basin	Pit Solids	Field Duplicate	MS/MSDs	Pit Fluids[1]	Field Duplicate[3]	MS/MSDs	Produced Water	Field Duplicate[3]	MS/MSDs	Drilling Fluids[1]	Field Duplicate[3]	MS/MSDs	Flowback[2]	Field Duplicate[3]	MS/MSDs	Frac Fluid[2]	Field Duplicate[3]	MS/MSDs	Background Soil	Field Duplicate[3]	MS/MSDs
Planned	Yes			Yes			Yes			No			Yes			No			Yes		
Piceance	10	3	1	6	2	1	NA[4]	NA	NA	4	1	1	8	3	2	2	1	1	10	3	2
Denver-Julesburg	5	3	2	5	3	2	NA[4]	NA	NA	0[5]	NA	NA	10	3	2	0[5]	NA	NA	5	3	2
Raton	5	3	2	NA[4]	NA	NA	5	3	2	0[5]	NA	NA	5	3	2	0[5]	NA	NA	5	3	2
San Juan	5	3	2	NA[4]	NA	NA	5	3	2	0[5]	NA	NA	2	2	2	0[5]	NA	NA	5	3	2

[1] Six pit fluid (PF) samples from the Denver-Julesburg Basin were erroneously given the matrix code of DF (drilling fluids); the matrix code was corrected on the datasheets and in the database.

[2] One flowback water sample (FB) from the Raton Basin was erroneously given the matrix code of FF (frac fluid); the matrix code was corrected on the datasheets and in the database.

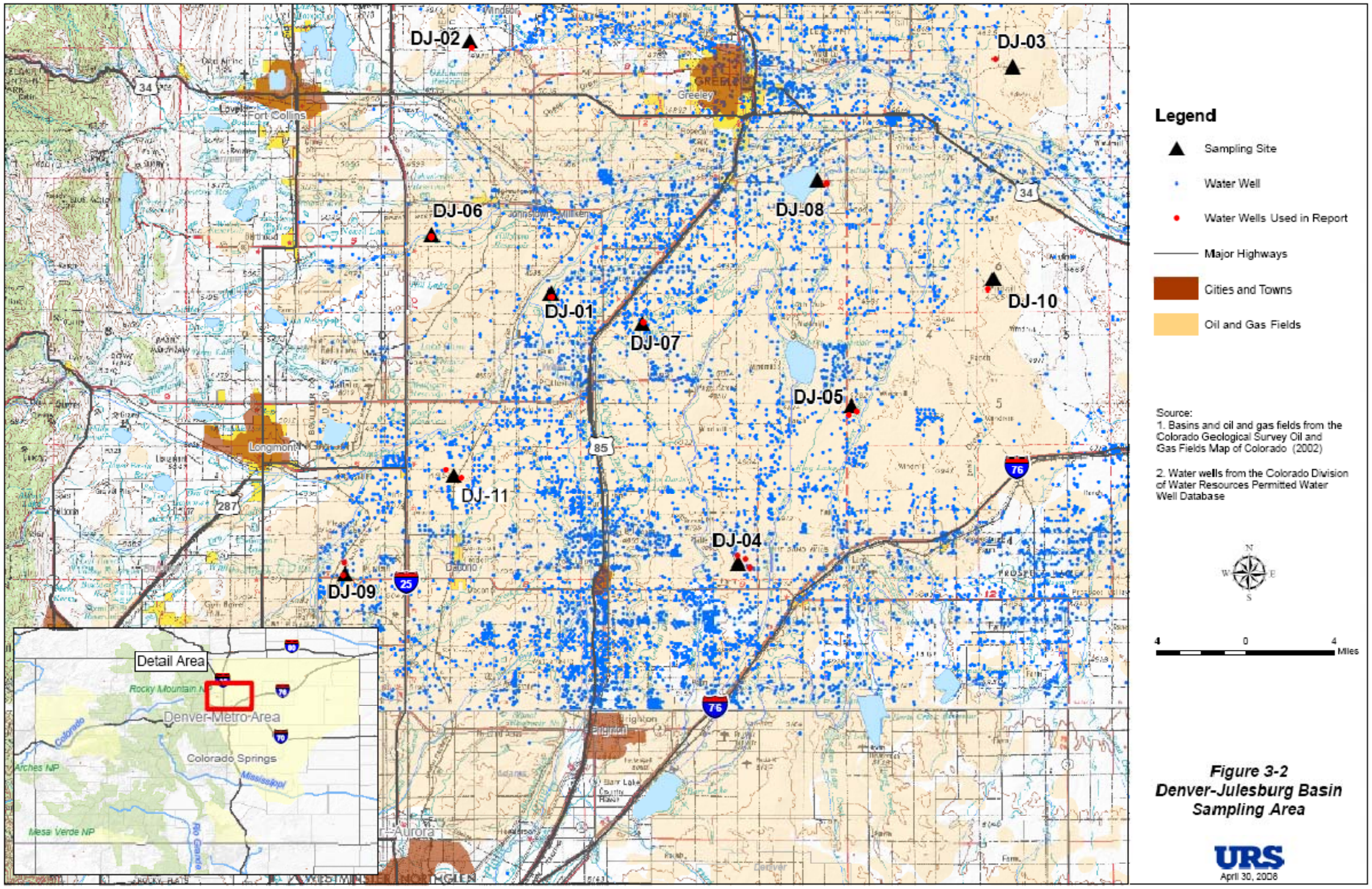
[3] Collocated. Field duplicates were not homogenized.

[4] Due to the difference in geology and fluid management practices between the northern basins and the southern basins, pit fluid samples were collected in the northern basins, and produced water samples were collected in the southern basins.

[5] Collection of drilling fluid and frac fluid was not part of the initial investigation scope; these samples were collected at the request of a single operator in the Piceance Basin.

URS, Field Activities Report for Characterization of Exploration and Production Pit Solids and Fluids in Colorado Energy Basins, June 4, 2008

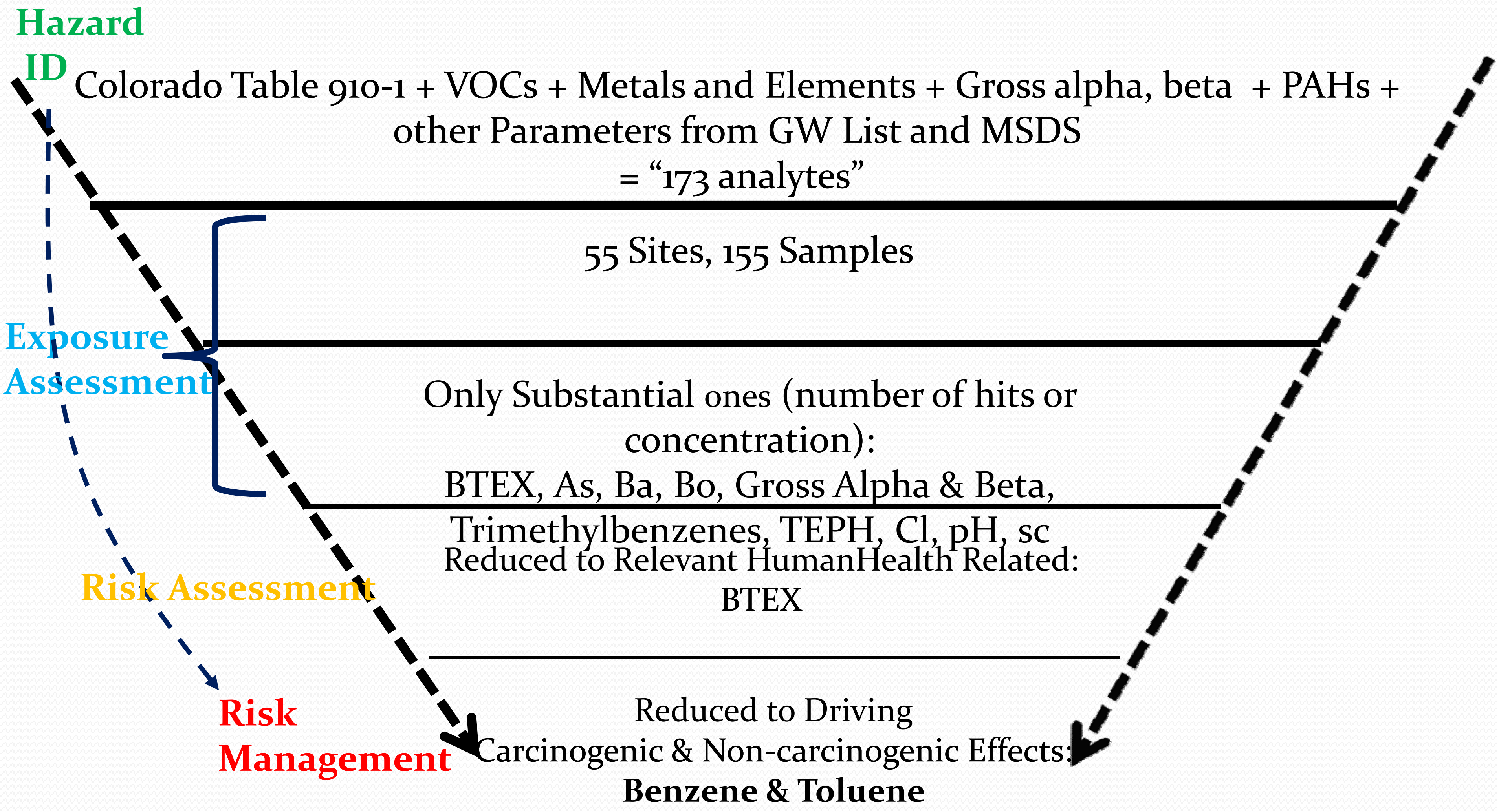
Denver-Julesburg (DJ) Locations



Source:
1. Basins and oil and gas fields from the Colorado Geological Survey Oil and Gas Fields Map of Colorado (2002)
2. Water wells from the Colorado Division of Water Resources Permitted Water Well Database

Figure 3-2
Denver-Julesburg Basin
Sampling Area

Chemical Selection



Hazard ID

Colorado Table 910-1 + VOCs + Metals and Elements + Gross alpha, beta + PAHs + other Parameters from GW List and MSDS
= "173 analytes"

55 Sites, 155 Samples

Exposure Assessment

Only Substantial ones (number of hits or concentration):
BTEX, As, Ba, Bo, Gross Alpha & Beta, Trimethylbenzenes, TEPH, Cl, pH, sc

Risk Assessment

Reduced to Relevant HumanHealth Related:
BTEX

Risk Management

Reduced to Driving
Carcinogenic & Non-carcinogenic Effects:
Benzene & Toluene

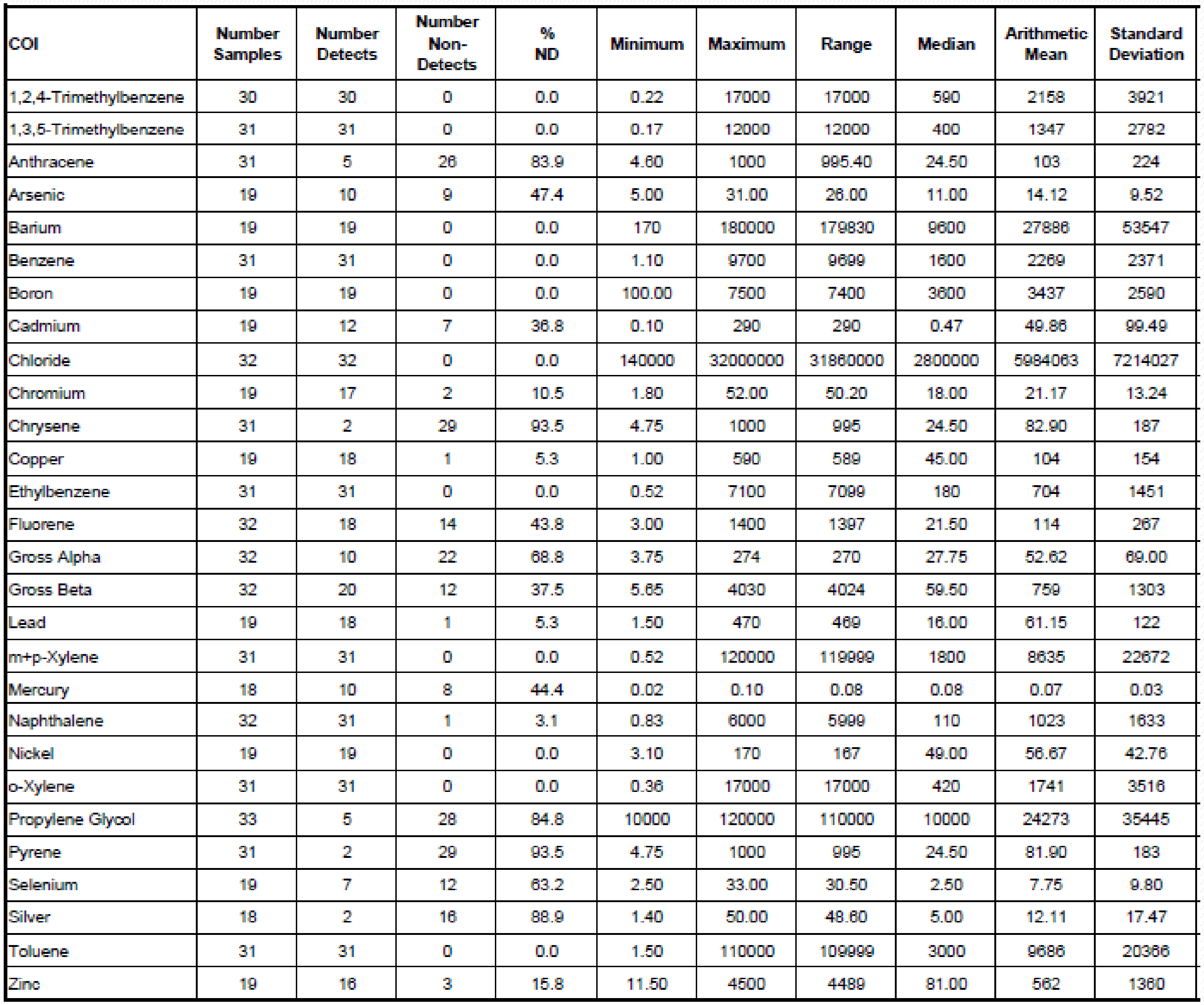
* Does not include GC-MS TICs analyzed, est. 39,882 total

Flowback Fluids


Collecting flowback sample from frac tanks using a bailer

- Samples were collected throughout the four basins (n=24 [plus duplicates])
- One flowback fluid samples collected in the DJ Basin was analyzed as a solid due to the high amount of suspended sediment present in the sample
- Constituents detected in 100 percent of the samples:
  - barium; benzene; boron; chloride; ethylbenzene; naphthalene; nickel; toluene; total xylenes; trimethylbenzene; and TEPH.

Flowback Fluid Detail



COI	Number Samples	Number Detects	Number Non-Detects	% ND	Minimum	Maximum	Range	Median	Arithmetic Mean	Standard Deviation
1,2,4-Trimethylbenzene	30	30	0	0.0	0.22	17000	17000	590	2158	3921
1,3,5-Trimethylbenzene	31	31	0	0.0	0.17	12000	12000	400	1347	2782
Anthracene	31	5	26	83.9	4.60	1000	995.40	24.50	103	224
Arsenic	19	10	9	47.4	5.00	31.00	26.00	11.00	14.12	9.52
Barium	19	19	0	0.0	170	180000	179830	9600	27886	53547
Benzene	31	31	0	0.0	1.10	9700	9699	1600	2269	2371
Boron	19	19	0	0.0	100.00	7500	7400	3600	3437	2590
Cadmium	19	12	7	36.8	0.10	290	290	0.47	49.86	99.49
Chloride	32	32	0	0.0	140000	32000000	31860000	2800000	5984063	7214027
Chromium	19	17	2	10.5	1.80	52.00	50.20	18.00	21.17	13.24
Chrysene	31	2	29	93.5	4.75	1000	995	24.50	82.90	187
Copper	19	18	1	5.3	1.00	590	589	45.00	104	154
Ethylbenzene	31	31	0	0.0	0.52	7100	7099	180	704	1451
Fluorene	32	18	14	43.8	3.00	1400	1397	21.50	114	267
Gross Alpha	32	10	22	68.8	3.75	274	270	27.75	52.62	69.00
Gross Beta	32	20	12	37.5	5.65	4030	4024	59.50	759	1303
Lead	19	18	1	5.3	1.50	470	469	16.00	61.15	122
m+p-Xylene	31	31	0	0.0	0.52	120000	119999	1800	8635	22672
Mercury	18	10	8	44.4	0.02	0.10	0.08	0.08	0.07	0.03
Naphthalene	32	31	1	3.1	0.83	6000	5999	110	1023	1633
Nickel	19	19	0	0.0	3.10	170	167	49.00	56.67	42.76
o-Xylene	31	31	0	0.0	0.36	17000	17000	420	1741	3516
Propylene Glycol	33	5	28	84.8	10000	120000	110000	10000	24273	35445
Pyrene	31	2	29	93.5	4.75	1000	995	24.50	81.90	183
Selenium	19	7	12	63.2	2.50	33.00	30.50	2.50	7.75	9.80
Silver	18	2	16	88.9	1.40	50.00	48.60	5.00	12.11	17.47
Toluene	31	31	0	0.0	1.50	110000	109999	3000	9686	20366
Zinc	19	16	3	15.8	11.50	4500	4489	81.00	562	1360

Concentration (ug/L or pCi/L)

ND set at ½ DL for stats

Frac Fluids

- Frac fluid samples collected in the Piceance Basin (n=2)
- One of the frac fluid samples collected was analyzed as a solid due to the high amount of suspended sediment present in the sample.
- Constituents detected in 100 percent of the frac fluid samples:
  - barium; benzene; boron; chloride; ethylbenzene; gross beta; naphthalene; nickel; sulfate; toluene; total xylenes; trimethylbenzene; and TEPH.

Frac Fluids (as Solids) Detail

COI	Number Samples	Number Detects	Number Non-Detects	% ND	Minimum	Maximum	Range	Median	Arithmetic Mean	Standard Deviation
1,2,4-Trimethylbenzene	2	2	0	0.0	3	6.1	3.1	4.550	4.550	2.192
1,3,5-Trimethylbenzene	2	2	0	0.0	1.4	2.7	1.3	2.050	2.050	0.919
Anthracene	2	0	2	100.0	0.46	0.49	0.0	0.475	0.475	0.021
Arsenic	2	2	0	0.0	0.1	0.1	0.0	0.100	0.100	0.000
Barium	2	2	0	0.0	260	270	10	265	265	7
Benzene	2	2	0	0.0	1.4	1.5	0.1	1.450	1.450	0.071
Boron	2	2	0	0.0	3.4	3.4	0.0	3.400	3.400	0.000
Cadmium	2	2	0	0.0	0.015	0.015	0.0	0.015	0.015	0.000
Chloride	2	2	0	0.0	22000	22000	0.0	22000	22000	0.000
Chromium	2	1	1	50.0	0.5	0.5	0.0	0.500	0.500	0.000
Chrysene	2	0	2	100.0	0.46	0.49	0.0	0.475	0.475	0.021
Copper	2	0	2	100.0	0.5	0.5	0.0	0.500	0.500	0.000
Ethylbenzene	2	2	0	0.0	0.45	0.57	0.1	0.510	0.510	0.085
Fluorene	2	0	2	100.0	0.46	0.49	0.0	0.475	0.475	0.021
Gross Alpha	2	0	2	100.0	0.44	0.47	0.0	0.455	0.455	0.021
Gross Beta	2	0	2	100.0	3.4	4.2	0.8	3.800	3.800	0.566
Lead	2	0	2	100.0	0.16	0.16	0.0	0.160	0.160	0.000
m+p-Xylene	2	2	0	0.0	6.5	9.2	2.7	7.850	7.850	1.909
Mercury	2	0	2	100.0	0.016	0.016	0.0	0.016	0.016	0.000
Naphthalene	2	2	0	0.0	3.5	7.1	3.6	5.300	5.300	2.546
Nickel	2	2	0	0.0	0.13	1	0.9	0.565	0.565	0.615
o-Xylene	2	2	0	0.0	1.1	1.5	0.4	1.300	1.300	0.283
Propylene Glycol	2	0	2	100.0	10.5	10.5	0.0	10.500	10.500	0.000
Pyrene	2	0	2	100.0	0.46	0.49	0.0	0.475	0.475	0.021
Selenium	2	0	2	100.0	0.049	0.049	0.0	0.049	0.049	0.000
Silver	2	0	2	100.0	0.5	0.5	0.0	0.500	0.500	0.000
Toluene	2	2	0	0.0	6.3	6.4	0.1	6.350	6.350	0.071
Zinc	2	0	2	100.0	1	1	0.0	1.000	1.000	0.000

ND set at ½ DL

Produced Water

Collection of produced water sample at Site.

- Collected in the Raton, DJ, San Juan Basins (n=10)
- Constituents detected in 100 percent samples:
  - Barium; Boron; Chloride; and Nickel
  - Occur naturally in formation waters
  - At least a portion of the detected concentration for each constituent is likely due to natural background.
- Detected PCOCs
  - Benzene in 5
  - Ethylbenzene in 3
  - Naphthalene in 4
  - Toluene in 4
  - Xylenes in 4
  - Trimethylbenzene in 4
  - TEPH in 4
- In general, the PCOCs were detected at a higher frequency in produced water from the San Juan Basin than from the Raton Basin

Produced Water (Total + Dissolved) Detail

COI	Number Samples	Number Detects	Number Non-Detects	% ND	Minimum	Maximum	Range	Median	Arithmetic Mean	Standard Deviation
1,2,4-Trimethylbenzene	16	5	11	68.8	0.45	17	16.6	0.500	3.297	5.493
1,3,5-Trimethylbenzene	16	6	10	62.5	0.5	6.3	5.8	0.500	1.761	2.065
Anthracene	16	0	16	100.0	4.7	10	5.3	4.800	5.163	1.292
Arsenic	16	1	15	93.8	5	20	15.0	5.000	5.938	3.750
Barium	16	16	0	0.0	9	9900	9891	2800	2960	2609
Benzene	16	8	8	50.0	0.24	10	9.8	0.500	2.474	3.583
Boron	16	16	0	0.0	30	2900	2870	970	920	741
Cadmium	16	7	9	56.3	0.027	0.5	0.5	0.150	0.162	0.099
Chloride	16	16	0	0.0	17000	2400000	2383000	365000	688813	839648
Chromium	16	12	4	25.0	0.52	11	10.5	1.100	2.822	2.897
Chrysene	16	0	16	100.0	4.7	10	5.3	4.800	5.163	1.292
Copper	16	8	8	50.0	1.9	57	55.1	5.000	12.525	16.362
Ethylbenzene	16	5	11	68.8	0.2	67	66.8	0.500	7.400	19.093
Fluorene	16	0	16	100.0	4.7	10	5.3	4.800	5.163	1.292
Gross Alpha	16	0	16	100.0	0.88	18	17.1	10.450	9.029	5.437
Gross Beta	16	1	15	93.8	1.3	28.5	27.2	22.250	16.994	9.895
Lead	16	1	15	93.8	1.5	9.3	7.8	1.500	2.050	1.949
m+p-Xylene	16	6	10	62.5	0.35	440	439.6	0.500	56.078	146.091
Mercury	16	1	15	93.8	0.0093	0.1	0.1	0.100	0.094	0.023
Naphthalene	16	6	10	62.5	0.5	7.1	6.6	0.500	1.484	2.077
Nickel	16	16	0	0.0	0.79	18	17.2	2.450	3.374	4.051
o-Xylene	16	6	10	62.5	0.5	140	139.5	0.500	18.339	47.501
Propylene Glycol	16	0	16	100.0	10000	10000	0.0	10000	10000	0.000
Pyrene	16	0	16	100.0	4.7	10	5.3	4.800	5.163	1.292
Selenium	16	0	16	100.0	2.5	2.5	0.0	2.500	2.500	0.000
Silver	16	1	15	93.8	1.6	5	3.4	5.000	4.788	0.850
Toluene	16	6	10	62.5	0.18	44	43.8	0.500	7.711	14.575
Zinc	16	6	10	62.5	4.7	140	135.3	11.000	24.938	33.669

ND set at ½ DL

Primary Rad Sources

Media	Rad Agent	Max Conc. (pCi/L)	IR (L/day)	EF (Days/ yr)	1 Year Dose (pCi)	EPA Limit w/o Isotope info (pCi/L)	Ratio of Concentration to Limit
FB	Alpha	274	2	350	191800	15	18
FB	Beta	4030	2	350	2821000	30	134
PF	Alpha	17	2	350	11900	15	1.1
PF	Beta	174	2	350	121800	30	6

FB = Flowback Fluids
PF = Pit Fluids

Chemicals Matching Materials Used

- 7 Companies with >100 products were found as possible sources
- Only 8 of these chemicals were identified at detectable levels in any media:
  - Propanol, 2-butoxyethanol, ethylene glycol, n-heptane, isopropanol, naphthalene, 1,2,4-trimethylbenzene, and ethanol
  - Constituents detected in most of the media are 1,2,4-trimethylbenzene and naphthalene
- Most of these were already included in the desired sampling list and a couple other chemicals were added to the list of those to be reviewed

Constituents listed in Table 2-1 that were found in samples	Constituent Function	CAS No.	Product Name(s)	Product Use
Propan-2-ol (Isopropanol)	▪Cleaner ▪Solvent ▪Gasoline Additive for dissolving water or ice on fuel lines ▪Solubilizes water in Gas	67-63-0	Corrosion Inhibitor A261, Ezeflo*F103 Surfactant	Drilling, Completion, Fracturing
			GasPerm 1000, MA-844W, NE-940, Losurf-259 Surfactant, Losurf-300 Nonionic Surfactant, MA-844W, CI-25, SandWedge® WF, Advantage Foamer HD, D-D Sandwedge	Drilling, Completion, Fracturing
Propanol N-propanol	▪Solvent ▪Solubilizes water	71-23-8	CL-37 Crosslinker	Fracturing
			XLW-14	Fracturing
2-butoxyethanol Ethylene glycol monbutyl ether	▪Oil spill dispersant ▪Cooling agent	111-76-2	Ezeflo* F103 Surfactant	Drilling, Completion, Fracturing
			SSO-21M	Fracturing
Ethylene glycol	▪Cooling agent ▪Deicing Solution ▪Natural gas clathrate inhibitor ▪Removing water and salt	107-21-1	Inflo-150, Breaker 503L, XLD-1	Drilling, Fracturing
1,2,4 Trimethylbenzene	▪Liquid scintillator ▪Gasoline additive ▪Mineral Oil	95-63-6	Losurf-300M	Drilling, Completion, Fracturing
Ethanol	▪Fuel additive ▪Homogenizes water	64-17-5	Losurf-300M	
Naphthalene	▪Decreases rust production ▪Surfactant	91-20-3	NE-940, Losurf-300M, Non-emulsifying Agent W54, CI-25	Drilling, Completion, Fracturing
n-Heptane	▪Solvent	142-82-5	Soltex® Additive	Drilling

NOTES:

CAS No. = Chemical Abstracts Service registry number

Potential Chemicals of Concern (PCOCs)

- From the analyzed constituents, a select group of those meeting at least one of the following characteristics were selected for assessment of risk:
  - present in significant amounts (near the proposed Table 910-1 values for instance),
  - those with a significant frequency of presence (e.g., Trimethylbenzenes, BTEX, most metals), or
  - those with a concern because of significant usage (e.g., glycols, barium, chloride), or
  - those thought to be of concern but having little prior test data (e.g., PAHs),
  - gross alpha and beta

Fate Considerations

- Solids placed in Pits
- Liquids in Subsurface Pits
- Fracing Fluid placed in pits
- Fracing Fluid placed in containers
- Produced Water placed in containers
- Produced Water placed in pits
- Drilling fluids in drilling
- Drilling fluids in pits

Basic Limitations

- Limited number of air samples and they were only collected seasonally in April.
- The following are data gaps for this study:
  - Only produced water data in 3 basins
  - Have Limited Drilling Fluid & Frac Fluid

  - *No verification of actual depth to GW on-site*
  - *No verification of actual hydrogeologic properties (hydraulic conductivity, head difference)*
  - *Limited air data from one season, all estimated exposure doses for base risk are based on conservative modeling*

Points

- Many media Sources in the process
- Important to Consider
  - ID and evaluation of chemicals to support comments of concern or lack thereof
  - Geology /Formation specific constituents
  - Confounders & Limitations (background, lab anal)
  - High quality data for decision making purposes
- A lot of "possible" chemicals, but less present in detectable amounts with good frequency, and even less that drive human health risk concerns

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Fracing & Associated Media Composition in Colorado

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The fracing process begins with wellpad siting, proceeds through completion and ends with production (and the eventual decommissioning or abandonment). The steps in the process include: site selection, well pad development, drilling, fracing, and production. The chemical composition of media during the fracing as well as naturally occurring constituents present in the natural resources all add to the constraints and characteristics of fate, transport, exposure and projected risk. The classical risk assessment process can be divided roughly into: 1) Hazard Identification, 2) Dose-Response Determination, 3) Exposure Assessment, and 4) Risk Characterization, followed by Risk Management (including policy development) and preceded as well as intermingled with research (NRC, 1983, 1994). Within the Exposure Assessment aspect is the fate and transport of chemicals and subsequent exposure. In terms of this risk framework, chemical composition plays a strong initial role in Hazard Identification but is also relevant in terms of dose-response, exposure pathway determination, fate and transport property selection, and risk assessment. The process and consideration of chemical selection are presented with regard to the investigation of fracing impact in four energy basins in Colorado completed in the spring of 2008. The focus will be on three media, flowback material, frac fluids, and produced waters, although other media and subsequent pathways were considered and are discussed in part here.

Risk Assessment in Regards to the Identification of Constituents for Analytical Evaluation

As just mentioned, the identification and eventual selection of chemicals for consideration in risk assessment is part of the classic risk assessment (RA) process (NRC 1983, 1994). Although the identification and selection of chemicals seems limited in scope and limited in interaction to hazard identification, it can be driven by regulatory requirements or public concerns. It can also impact the cost, eventual selection of exposure pathways, and bring to light underlying issues in the RA process and the interweaving of policy with the science.

The steps in the process of drilling and fracing produce a variety of media (frac fluids, produced water, waste pit solids, etc.), all of which should be considered in a holistic approach to both understanding and managing risk in the Oil & Gas (O&G) Industry.

Selection of Chemicals for Analysis

In 2008, in a project funding 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 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). The Material Safety Data Sheets (MSDS) were gathered by requesting input from 7 of the COGA member companies and reviewing the submissions. More than 100 products were looked at and broken into reported relative sub-quantities (%) by Chemical Abstract Service (CAS) number. MSDS are required to report any standard listed chemicals that make up more than 1% of the chemical composition, or >0.01% if the chemical is carcinogenic (OSHA, 2008). From this, the beginnings of a CAE list was produced, which included glycols and pH as a surrogate for acids and bases. A list of standard chemicals of interest in the O&G industry (BTEX, PAHs, Boron, Chloride, etc.) were also added (CDPHE, 2007; COGCC, 2008). Because of a lack of clarity with regard to total extractable petroleum hydrocarbons (TEPH), these were analyzed for both Diesel Range Organics (DRO) and Motor Oil Range Organics (MRO) to allow relative hydrocarbon grouping if desired. Primary metals (and metalloid) included were the eight Resource Conservation and Recovery Act (RCRA) metals consisting of arsenic, barium, cadmium, chromium, lead, mercury, silver, and selenium. An additional fifteen target analyte list (TAL) metals were also added from the EPA Method 6020A Method list and 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. Analysis for specific isotopes at this phase was considered unwarranted by the risk assessor. Consideration for chemicals recommended by local environmental groups was also undertaken; this was also accounted for post-sampling in terms of reviewing tentatively identified compounds (TICs) for relevance and comparing to groups of chemicals used, and the MSDS product list. Basin usage for the products was also recorded in the event that significant findings relevant to geologic formation(s) was(were) discovered. A small subset of samples was analyzed by EPA's Toxic Characteristic Leaching Procedure (TCLP) for eight RCRA metals, plus pH, reactive sulfides, and reactive cyanides to evaluate waste disposal considerations.

Statistical Considerations

In any sampling plan, several consideration with regard to chemicals should be made, including, but not limited to: a) number of samples for the intended use, b) minimum limit of detection (LOD) and limit of quantification (LOQ) for a constituent, c) background levels, d) level of quality of sampling and analysis, e) statistical application, and f) appropriate selection of a method. One should never take a sample before knowing what one will communicate once the results are in. The desire would be to collect multiple samples from each media and ones that are representative of a typical media by energy basin and type of drilling or fracing operation. For example, one should collect both early and late flowback samples and one should consider the regulatory impact of required oil-water separation in certain basins, etc. In terms of return on statistical data, five to six samples (base on a normal distribution) place the mean as reasonably estimated. However, to reasonably estimate the standard deviation more than twenty samples would be necessary. In the case of RA, much of the decision making is driven in orders of magnitude (QEPA, 2008). Therefore, five to six samples per media setting provides a good basis to work from, even in consideration of right-skewed distribution (e.g., lognormal). The subsequent quasi-policy and quasi-science decision of selecting an appropriate estimator (mean, max, upper confidence limit one sided at 95% [UCL1,95]) can then be utilized by a risk manager. In terms of LOD and LOQ for analytical method selection, regulatory levels in Colorado (COGCC, 2008; CDPHE, 2007) were reviewed along with risk assessor pre-estimates of effective dilution-attenuation factors to determine relevant methodologies. Thus, by recognizing end risk calculation relevancy, PAH detection levels were set at standard levels, which are higher than that achievable by more sophisticated (and costly) methods.

Media and Sample Collection

Sample quality is important, particularly if the analysis has broader policy implications. In the 2008 project in Colorado, URS personnel collected the samples independent from the risk assessors (QEPA & pH2) and independent from the labs used for analysis. Statistical analyses were performed by both URS and pH2/QEPA with pH2 directing the parameters. Samples were collected at a variety of sites--55 in all--to represent four energy basins in Colorado; these basins are the Denver-Julesburg (DJ), Piceance, Raton, and San Juan. The media types selected were in consideration of the RA and included: pit solids, pit fluids, drill fluids, frac fluids, flowback fluids, produced water and background soils. It should be noted that some of the materials are co-mingled with other fluids and moved between pits as multiple-pads or sites are developed. Sample analysis for both solids and liquids were separated, and sets of dissolved and total constituent analyses were performed in most cases. Decisions for sample media categorization (fluid/solid) were ultimately determined by the risk assessor after input from URS and the lab.

Samples were collected at points representative of current drilling and fracing operations, both near and away from residences and within differing hydrogeologic and geologic conditions. Multi-point composite samples were collected to achieve better representation (except for VOCs due to potential constituent loss). There was a high frequency of co-located field duplicates (45%) and MS/MSDs (30%) QC samples collected. In addition, rigorous paper, photo, and video documentation were also performed to incorporate with the Level IV Quality Control (QC) data packages and analysis by an NELAC certified laboratory. Also, samples were analyzed for >170 constituents using EPA-approved methods (e.g., VOCs by 8260, SVOCs by 8270, Glycols by 8015). Thorough data validation was performed resulting in >99% data usability. Other Precision, Accuracy, Representativeness, Completeness, and Comparability (PARCC) parameters were satisfactory (URS, 2008).

Analytical Results for Flowback Materials, Frac Fluids, and Produced Waters

Analytical sampling results from the COGA study completed in 2008 represented more than 52,000 data points for pit solids, liquids, fracing fluid, flowback, and drilling fluids. Analytical data included BTEX, PAHs, metals (primary eight RCRA plus secondary), gross alpha, gross beta, boron, and glycols.

Chemicals not Detected

For the solid media, 43 VOCs were reported as Not Detected (ND) in every solid sample, as were 57 semivolatile compounds (SVOCs). In addition, reactive cyanide and reactive sulfide were not detected for reactivity, corrosivity, and ignitability (RCI) analyses performed on solid samples.

The list of non-detect (ND) constituents for liquid media was not as extensive as the list for solids. A total of 39 VOCs and 48 SVOCs were reported as ND in every sample that was analyzed as a liquid. Although the liquids list is shorter, not every constituent that was reported as ND for liquid samples was also reported as ND for solids. In total, the two lists share 81 common constituents, including 35 VOCs and 46 SVOCs. Reactive sulfide and cyanide are not included in this figure because RCI analyses were not performed for liquid samples.

Flowback

A total of twenty four base samples (plus duplicates) of flowback fluids were collected and analyzed throughout the four basins. One of the flowback fluid samples collected in the DJ Basin was analyzed as a solid due to the high amount of suspended sediment present in the sample. The following constituents were detected in 100 percent of the flowback fluid samples: barium, benzene, boron, chloride, ethylbenzene, naphthalene, nickel, toluene, total xylenes, trimethylbenzene (TMB), and TEPH. A few constituents of significance were often below detectable levels, for example: 37% of gross beta, 69% of gross alpha, and 84% of anthracene were ND, whereas ones like BTEX, 1,2,4-TMB, and 1,3,5-TMB, boron, and chloride were always detected. Although the max concentrations for flowback fluids were 270 and 4,030 pCi/L for gross alpha and beta, respectively, the comparable pit fluids were only 17 and 174 pCi/L, respectively

Frac Fluids

Two frac fluid samples (plus a duplicate) were collected and analyzed in the Piceance Basin. One of the frac fluid samples collected was analyzed as a solid due to the high amount of suspended sediment present in the sample. The following constituents were detected in 100 percent of the frac fluid samples: barium, benzene, boron, chloride, ethylbenzene, gross beta, naphthalene, nickel, sulfate, toluene, total xylenes, TMB, and TEPH.

Produced Water

Produced water samples were collected in the Raton and San Juan Basins. Altogether, 10 produced water samples (plus duplicates) were collected between the two basins. The following constituents were detected in 100 percent of produced water samples: barium, boron, chloride, and nickel. These constituents occur naturally in formation waters, and at least a portion of the detected concentration for each constituent is likely due to natural background.

In regard to other PCOCs, benzene was detected in 5 produced water samples; ethyl benzene was detected in 3 produced water samples; naphthalene, toluene, total xylenes, TMB, and

TEPH were detected in 4 produced water samples. In general, the PCOCs were detected at a higher frequency in produced water from the San Juan Basin than from the Raton Basin.

Chemicals Matching MSDS Constituents

Only 8 constituents out of more than 100 found to be present in MSDS reviewed. The constituents found include: propanol, 2-butoxyethanol, ethylene glycol, n-heptane, isopropanol, naphthalene, 1,2,4-TMB, and ethanol. The constituents detected in most of the media are 1,2,4-TMB and naphthalene. Solvents and fracing agents were the most common use of these 8 constituents in the O&G industry in CO.

As a caveat, the detection of a chemical listed in an MSDS for a product in a particular media does not necessarily mean that it came from that product. It only means it could have come from it, but for some it just as easily could have come from a natural occurring deposit. Also, a chemical's presence does not mean that it is a significant risk either.

Narrowing the Selection for Risk Assessment Purposes

From the CAE, a select group of those chemicals meeting one of the following characteristics were selected for assessment of risk: a) present in either significant amounts (near the proposed COGCC Table 910-1 values for instance), b) or those with a significant frequency of presence (e.g, TMBs, BTEX, most metals), or c) those with a concern because of significant usage (e.g., glycols, barium, chloride) , or those thought to be of concern but having little prior test data (e.g., PAHs, gross alpha and gross beta).

These were then considered as constituents in the following media scenarios:

Solids placed in Pits
Liquids in Subsurface Pits
Fracing Fluid placed in pits
Fracing Fluid placed in containers
Produced Water placed in containers
Produced Water placed in pits
Drilling fluids in drilling
Drilling fluids in pits

Details of the RA are provided in QEPA, 2008.

Limitations

As with any assessment there are a number of gaps or limitations imposed or resulting from the manner in which this RA was commissioned. The first is that groundwater as a resource was the prime focus, thus air was not considered in as great as detail; nor is it relevant for the scope this workshop. Secondly, samples were from operations in place in Spring of 2008, not prior, nor post. Other seasons may result in different concentrations, e.g., VOCs. Some practices from the past (diesel fuel in the drilling) or more common today (treatment or recycling of produced waters) were not accounted for. Also, only produced water data from 3 energy basins was collected and there was limited drilling fluid & frac fluid samples compared to that desired by the risk assessor.

In terms of other RA fate & transport aspects, there was no verification of actual depth to groundwater on-site, no verification of actual hydrogeologic properties (hydraulic conductivity, head difference), although neighboring data was gathered and evaluated. All estimated exposure doses for base risk were therefore modeled using conservative parameters for the potential chemicals of concern (PCOCs), i.e, maximum or $UCL_{1,95\%}$.

There are other limitations created by classical risk assessment guidance (ASTM, 2002; EPA 1989a, 1989b, 1991a, 1991b), which includes failure to consider background concentrations (e.g., arsenic), basic solubility under site-specific situations, and toxicological constraints. One of the toxicology constraints is that barium sulfate, normally used as a drilling fluid, is expected as the primary source of the barium, yet it is neither very soluble in many instances, nor very toxic compared the $BaCl_2$ upon which the Reference Dose (RfD) for the element is based (EPA, 2005). In RA it is also important to gauge the general level of influence of one parameter versus another in a RA. For chemicals, the RfDs, Reference Concentrations (RfCs), Benchmark Dose Levels (BMDL), Minimal Risk Levels (MRLs), and Slope Factors (SFs) drive the primary order of magnitude of risk, and generally use safety-uncertainty margins in the range of 10-100 already. For instance $BaCl_2$ uses a safety-uncertainty factor of 300 (EPA, 2005). If is useful to consider this in ranking the value of chemicals and their health hazards in scenarios like the one presented here. In the cases where there is no relevant acceptable value for toxicity, other means, such as a control banding approach, could be applied (Nelson, et al., 2011).

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