Characterization of Marcellus and Barnett Shale Flowback Waters and Technology Development for Water Reuse

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Major R&D Efforts on Produced Water Management

- **Industry Water Conservation Consortia**
  - **Barnett Shale (BSWCMC)**
  - **Appalachian Shale (ASWCMC)**
  - **Marcellus Shale Coalition**
- **Individual Developer Company Testing of Available Know-How**
- **RPSEA Program**
- **NETL-DOE Program**
- **NYSERDA Project on Shale Gas Issues**

Components in Flowback Water

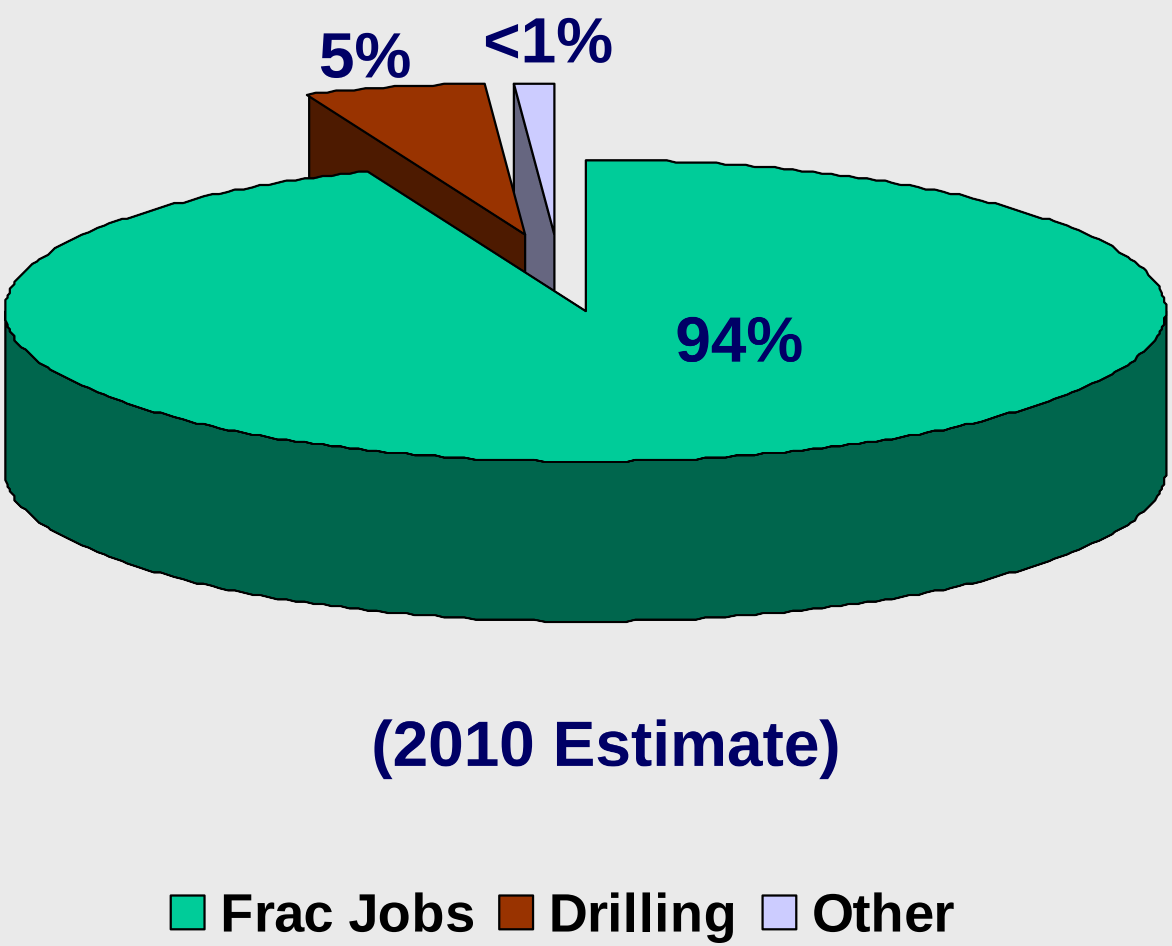
Constituents of Produced Water

+

Frac Job Additives

- Sand
- Friction Reducer
- Oxygen Scavengers
- Corrosion Inhibitors
- Scale Inhibitors
- Biocides

Natural Gas Industry Water Use in the Appalachian and Barnett Shale



(2010 Estimate)

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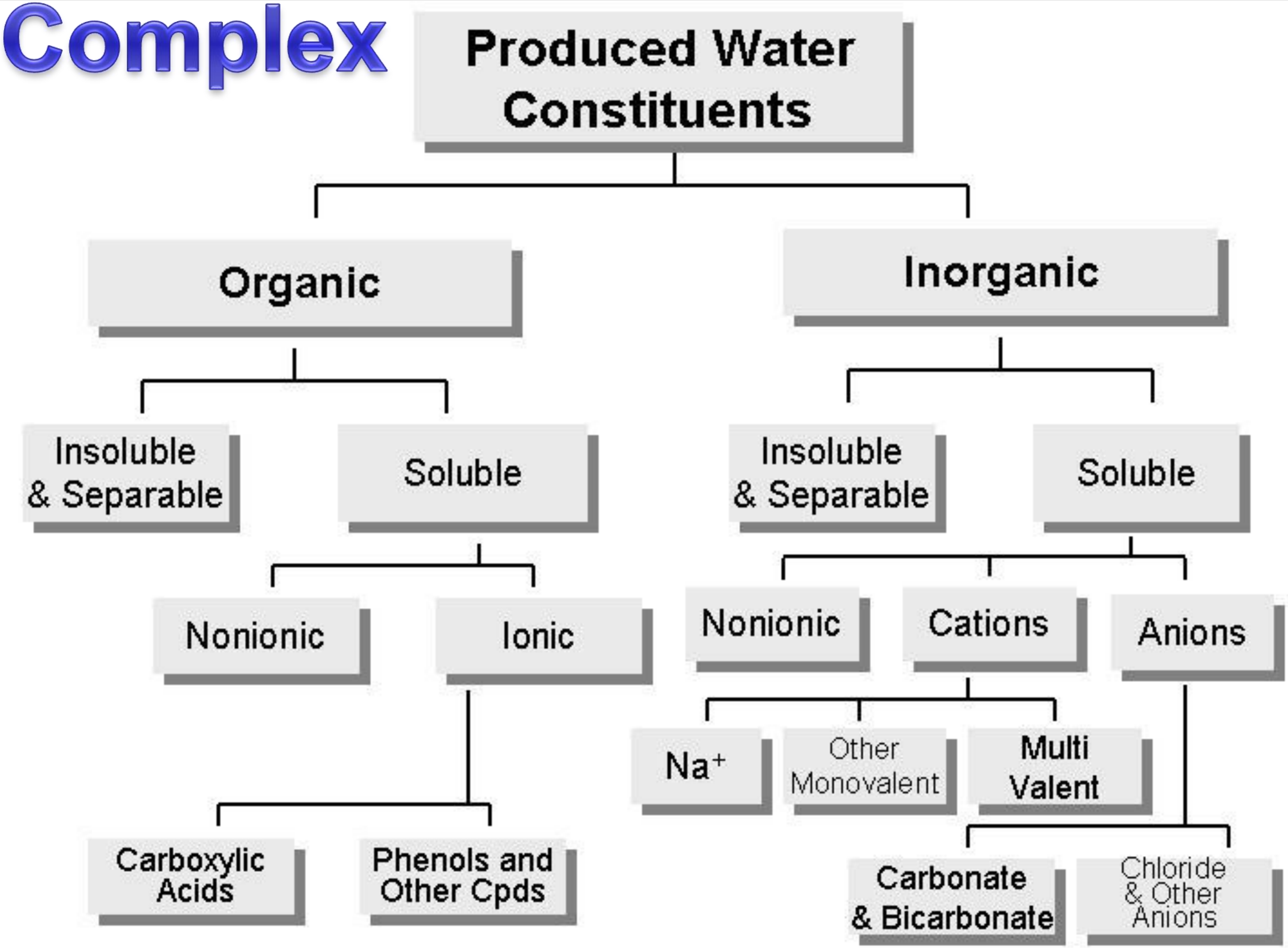
Chemistry and Composition of Flowback Water

Complex



Produced Water Constituents
Organic
Inorganic
Insoluble & Separable
Soluble
Insoluble & Separable
Soluble
Nonionic
Ionic
Nonionic
Cations
Anions
Na+
Other Monovalent
Multi Valent
Carboxylic Acids
Phenols and Other Cpds
Carbonate & Bicarbonate
Chloride & Other Anions

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Components in Flowback Water

Constituents of Produced Water

+

Frac Job Additives

- Sand
- Friction Reducer
- Oxygen Scavengers
- Corrosion Inhibitors
- Scale Inhibitors
- Biocides

Sampling and Analysis of Flowback Water

Data on Sampling and Analysis of Flowback Water

- **Marcellus Shale Water Characterization**
  - Funded by MSC and ASWCMC Consortia
  - Sampling from 19 locations
  - Includes general chemistry and detailed analysis of constituents of interest
  - Lists of Constituents of Interest provided by the WV-DEP and PA-DEP
  - Over 250 determinations performed on samples
- **Barnett Shale Water Characterization**
  - Sampling from 5 locations
  - Same sampling and analysis approach as Marcellus
  - Funded by RPSEA-DOE / Coord w/ BSWCMC

Marcellus Shale Approach

- Samples taken at 0, 1, 5, 14, and 90 days following the frac job at each location
- Sampling at Day 0:
  - Raw Water without additives
  - Raw Water with chemical additives before sand addn.
- Uniformity of sampling and analysis
  - Standardized Plans (FSAP, QAPP)
  - Sampling performed by URS
  - Analyses performed by one lab (Test America)
- Two lists of constituents for analysis
  - Extensive List applied to one sample/location
  - Less extensive list applied to other samples

General Chemistry of Influent and 5-Day Flowback (FB) Water Samples

	Influent		5-Day Flowback		
Parameter	Range	Median	Range	Median	Units
pH	6.7 – 7.4	7.2	5.8 – 7.2	6.6	-
Alkalinity *	6.2 – 88.8	52.5	48.8 - 327	138	mg/l
TDS **	35 – 5,510	334	38,500-238,000	67,300	mg/l
Tot Susp Solids **	<2‡ – 24	9.6	10.8 – 3,220	99	mg/l
Tot Org Carbon **	1.8 – 202	3.8	3.7 - 388	62.8	mg/l
Biochemical Oxygen Demand ¥	<2.0‡ - 110	149	794	2.8	mg/l
Oil & Grease **	19	31	NA	< 5	mg/l

* mg/l as CaCO3

¥ mg/l as O_2

‡ ND = Nondetect

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Comparison of 14-Day FB Water with Conventional Produced Water

	14-Day Flowback		Conv. PW
Parameter	Range	Median	Ranges[₣]
pH	4.9-6.8	6.2	5 – 8
Alkalinity *	26.1-121	85.2	NA
TDS **	3,010 – 261,000	120,000	3,000 - 350,000
Tot Susp Solids **	17 - 1,150	209	0-250
Tot Org Carbon **	1.2 – 509	38.7	NA
Biochemical Oxygen Demand [¥]	2.8 – 2,070	2.8	NA
Oil & Grease **	< 0.5 - 103	7.4 mg/l	3 – 100

* mg/l as CaCO3
** mg/l
¥ mg/l as O_2
‡ ND = Nondetect
NA = Not Available
₣ IPEC, 2004; GRI, '94

Cations and Anions in Influent and FB Water Samples from Two Locations

	Influent Blend		5-Day Flowback	
Parameter **	Range	Median	Range	Median
Sodium (Na^+)	25.7 - 6,190	67.8	10,700 – 65,100	18,000
Calcium (Ca^{2+})	6.7 – 2,990	32.9	1,440 – 23,500	4,950
Magnesium (Mg^{2+})	1.2 - 235	6.7	135 – 1,550	559
Iron (Fe^{2+})	ND – 14.3	1.2	10.8 – 180	39
Barium (Ba^{2+})	0.06 – 87.1	0.4	21.4 – 13,900	686
Chloride (Cl^-)	4.1 – 3,000	42.3	26,400 – 148,000	41,850
Bicarbonate (HCO_3^-)	< 1 – 188	49.9	29.8 - 162	74.4
Ammonia (NH_4^+)	0.58 - 441	5.9	15 - 242	82.4

** mg/l

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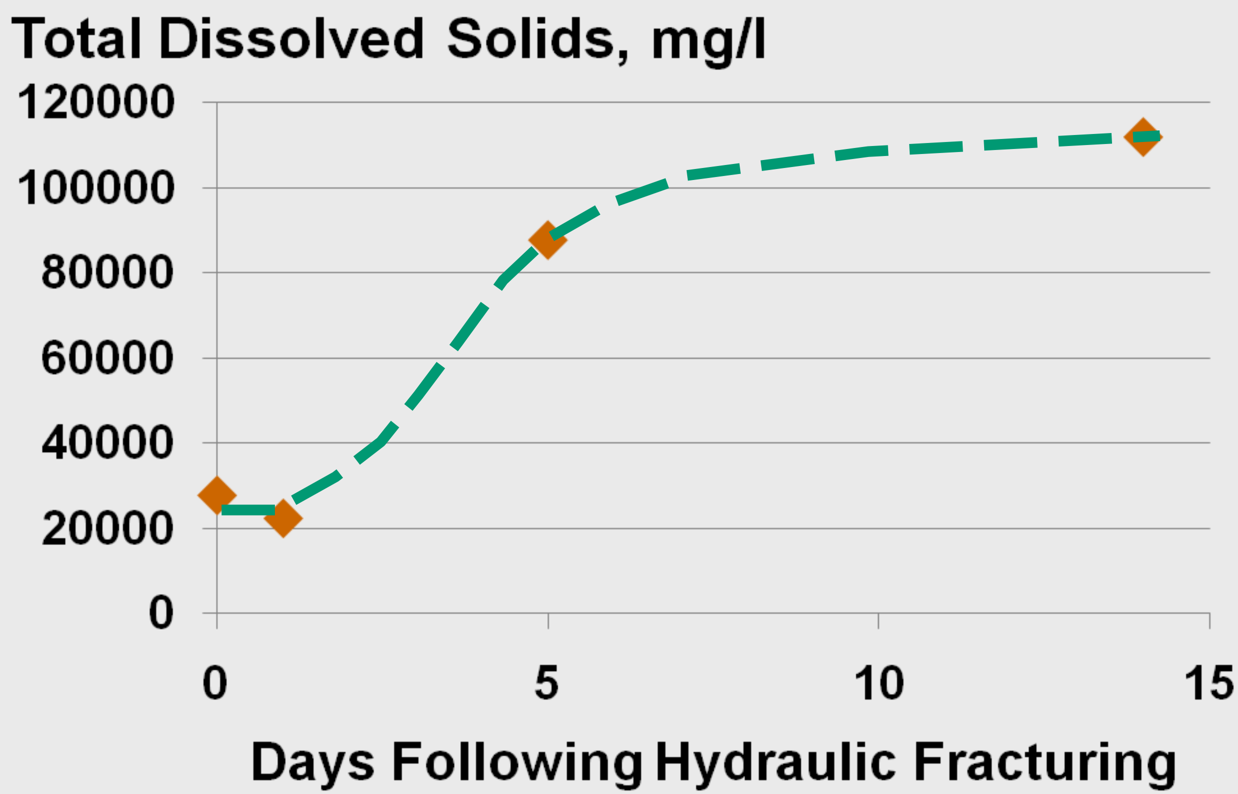
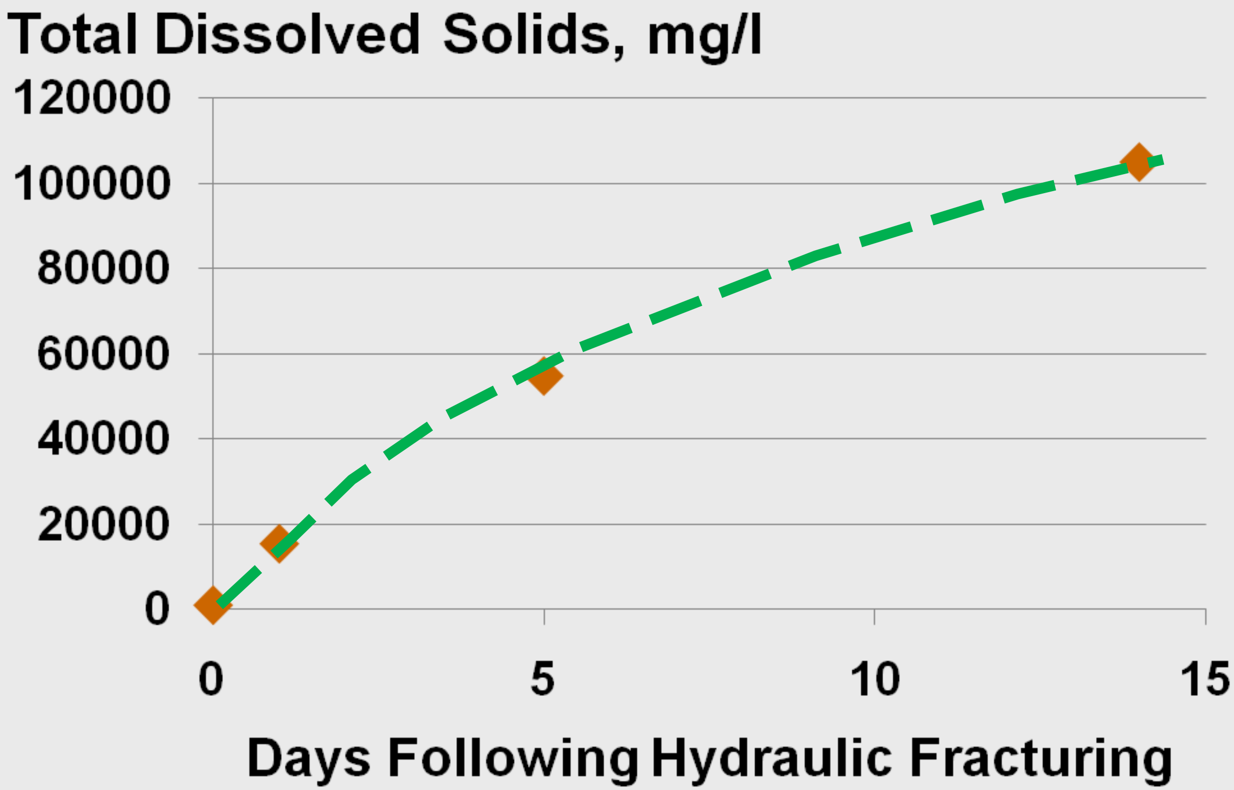
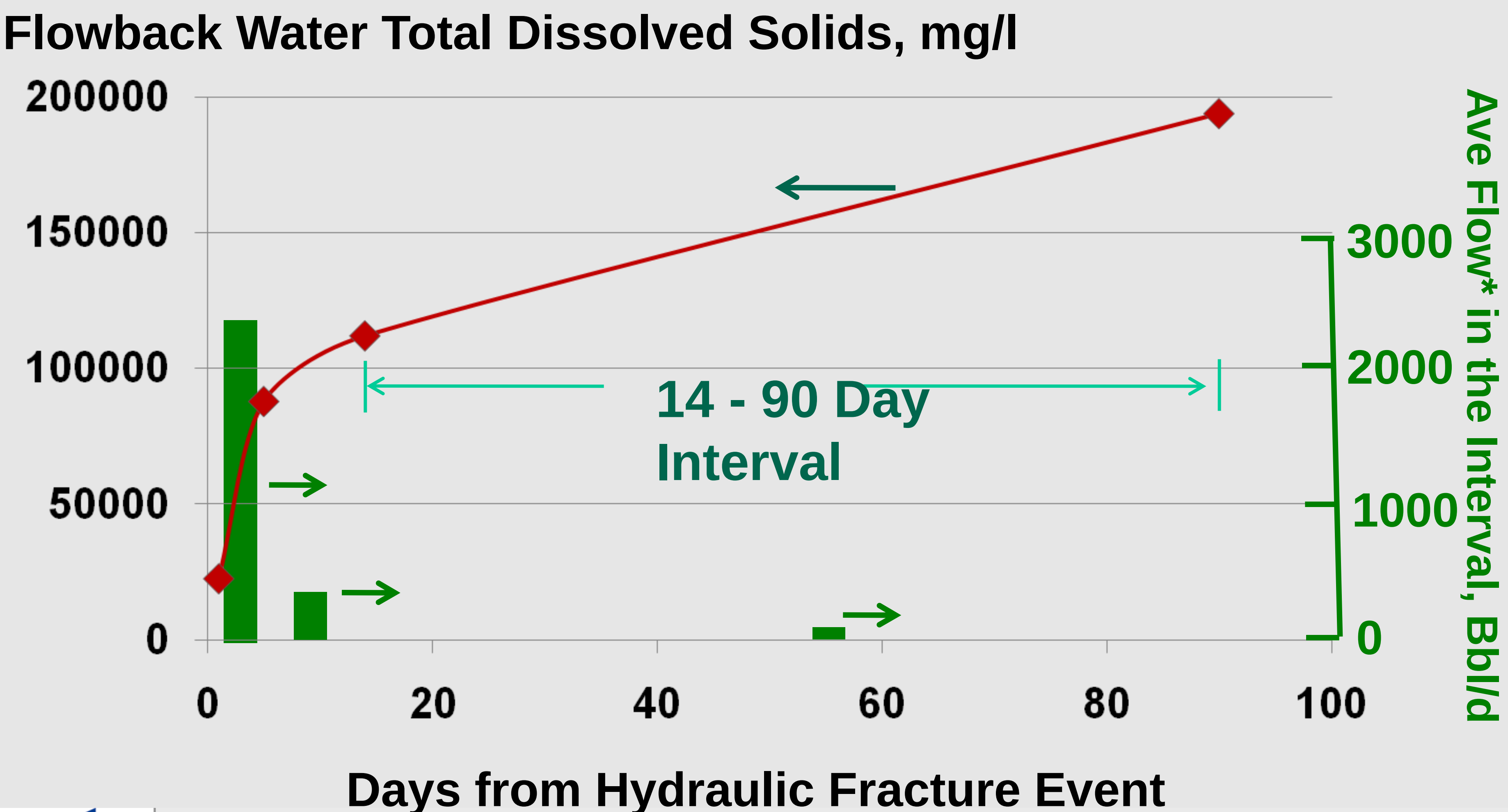
Concentration of TDS in Flowback Water with Time During Well Completion: Location A



Concentration of TDS in Flowback Water with Time During Well Completion: Location B



Typical Profile of Flowback Water Flow and Dissolved Solids Versus Time



•Average Daily Flow of the Flowback Water Output within Each Interval

Categories of Chemicals of Concern

- Volatile Organics
- Semivolatile Organics
- Pesticides
- Organophosphorus Pesticides
- PCBs
- Metals
- Radiological Determinations

Volatile Organics

Volatile Organics

- 71 Species
- A few sought after constituents are often found in conventional produced waters: benzene, toluene, xylenes, ethylbenzene
- Most of the volatiles on the list were man made chemicals not found in conventional produced waters

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Examples

- Chlorinated benzenes
- Chlorinated alkanes
- Chlorinated alkenes
- Ketones
- MTBE
- Brominated benzenes
- Acrolein
- Chloroform
- Methylene chloride
- Styrenes
- Vinyl acetate
- Vinyl chloride
- Ethylbenzene
- Trichloroethylene
- Chloromethane
- Acrylonitrile
- Carbon Disulfide
- Carbon Tetrachloride

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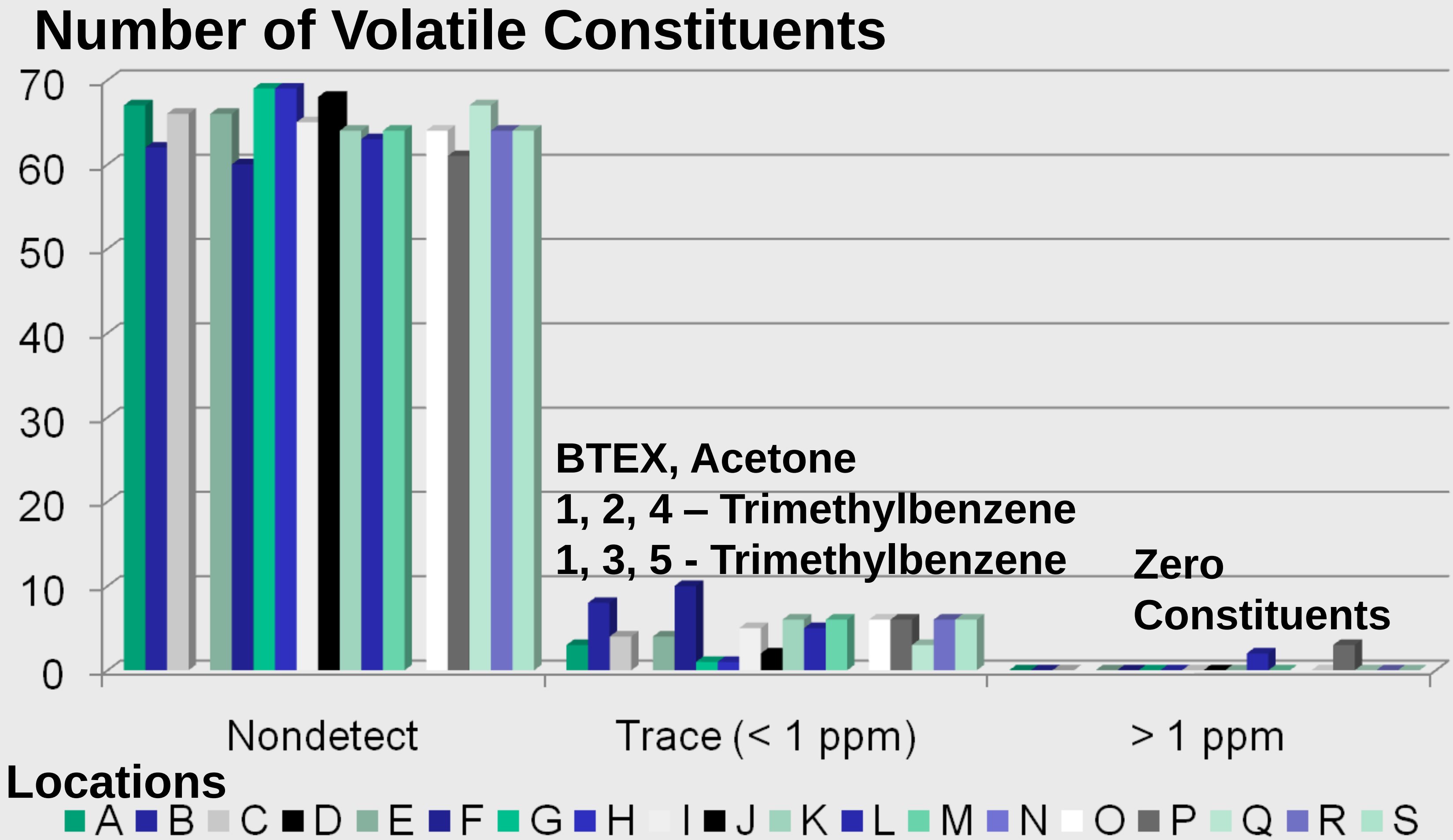
Summary of Results of Volatiles Measurements in 14-Day Samples



Semivolatile Organics

Semivolatile Compounds

- **113 Species**
- **A few sought after constituents are occasionally found in conventional produced waters: naphthalene, 2-methyl naphthalene, phenanthrene, phenol**
- **Many of the semivolatiles on the list were man made chemicals not found in conventional produced waters**
- **Many of the semivolatiles are derived from or constituents of coal or coal tar**

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Examples

- Benzo (a) pyrene
- Chlorinated phenols
- Chrysene
- Chlorinated Benzenes
- Nitrophenols
- Fluorene
- Methylphenols
- Naphthalene
- 1,4 - Naphthoquinone
- Phenol
- Pyrene
- Phthalates
- Fluoranthene
- Diphenylamine
- Acenaphthylene
- Bis (2-Chloroethyl) ether
- Dibenzofuran

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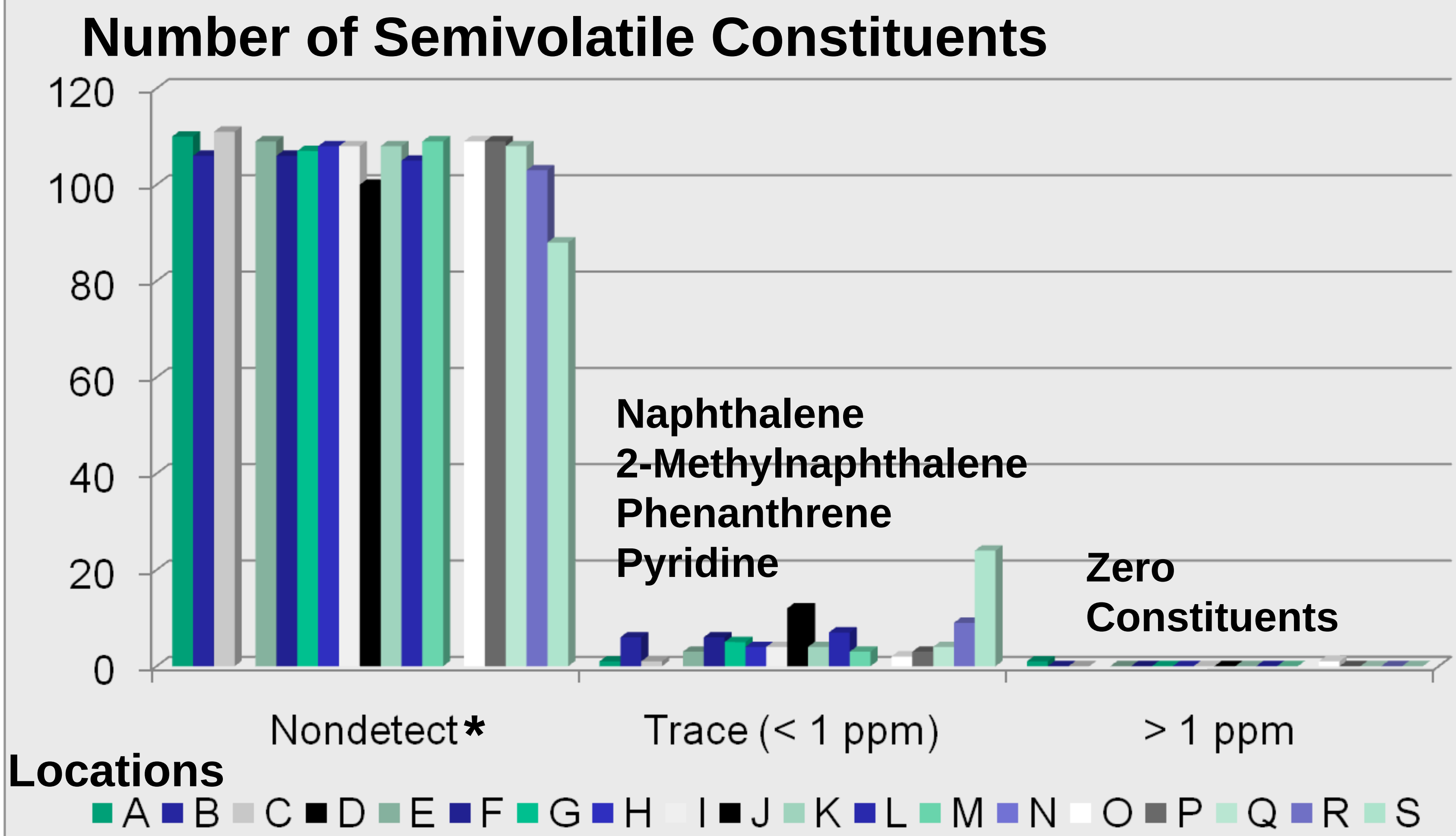
Summary of Results of Semivolatile Measurements in 14-Day Samples



(* < 0.5 µg/l for Most Constituents)

Pesticides

Examples

- Chlordane
- Alpha-BHC
- Beta-BHC
- Delta-BHC
- Gamma-BHC
- Heptachlor
- Aldrin
- Heptachlor epoxide
- Endosulfan I
- Dieldrin
- 4, 4’ - DDE
- Endrin
- Endrin ketone
- Endrin aldehyde
- Endosulfan II
- 4, 4 - DDT
- Endosulfan sulfate
- Toxaphene

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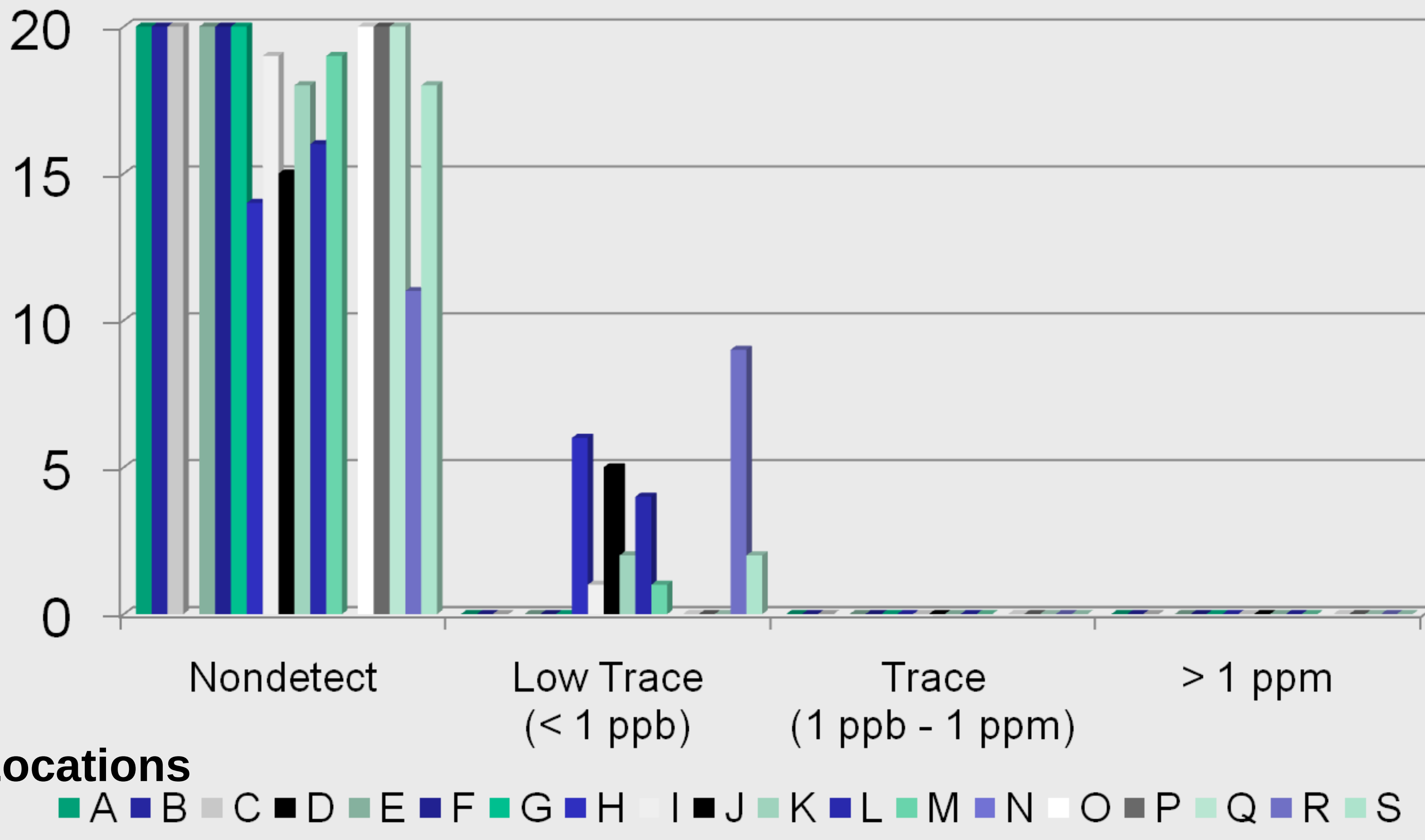
Number of Chlorinated Pesticide Constituents



Organophosphorus Pesticides & PCB's

All Non-Detect

Metals

Examples

- Mercury
- Arsenic
- Boron
- Trivalent Chromium
- Hexavalent Chromium
- Copper
- Nickel
- Zinc
- Lead
- Selenium
- Cobalt
- Iron
- Manganese
- Lithium
- Tin

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Selected Metals in 5-Day Flowback Water Compared to Muni Sludges

	5 – Day Flowback		Muni Sludges**	
Metals *	Range	Median	Median	95th %ile
Chromium (Cr^{3+})	ND – 0.15	0.015	35	314
Copper	ND – 4.15	ND	511	1,382
Nickel	ND – 0.187	ND	22.6	84.5
Zinc	0.068 – 2.93	0.16	705	1,985
Lead	ND – 0.606	ND	65	202
Cadmium	ND – 0.009	ND	2.3	7.4
Mercury	ND - 0.00024	ND	1.5	6.0
Arsenic	ND – 0.124	0.029	3.6	18.7

* mg/l
ND = Non Detect

** Penn State, 2000 (Survey of POTW's)

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Barnett Flowback Water

General Chemistry of Influent and 5-Day Flowback (FB) Water Samples

	Barnett 5-Day FB		Marcellus 5-Day		
Parameter	Range	Median	Range	Median	Units
pH	6.6 – 8.0	7.1	5.8 – 7.2	6.6	-
Alkalinity *	238–1630	610	48.8 - 327	138	mg/l
TDS **	23,600 – 98,900	36,100	38,500-238,000	67,300	mg/l
Tot Susp Solids **	36.8 – 253	133	10.8 – 3,220	99	mg/l
Tot Org Carbon **	9.5 – 99.1	18.1	3.7 - 388	62.8	mg/l
Biochemical Oxygen Demand ¥	92.6 - 1480	319	794	2.8	mg/l
Oil & Grease **	< 4.8-1720	< 5	NA ‡	< 5	mg/l

* mg/l as CaCO3

¥ mg/l as O_2

‡ ND = Nondetect

Summary of Results

- **Flowback water characteristics are consistent with ranges observed with conventional produced water**
- **Low suspended solids and TOC**
- **Man-made chemicals of concern are at non-detect levels.**
- **BTEX and PAHs are at trace levels.**
- **Oils and greases are at non-problem levels, but some control may be needed**
- **Soluble organics are highly biodegradable**
- **Heavy metals are lower than in Mun Sludge**

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Possible Treatment Needs

- Brine Volume Reduction with Water Recovery (for reuse in future frac jobs)
- Removal of Polymers (Friction Reducer Compounds)
- Scale Control (Including NORM Scale)
- Oil and Grease Control
- Soluble Organics: Decrease Total Organic Carbon
- Control of suspended solids
- Microbial Control

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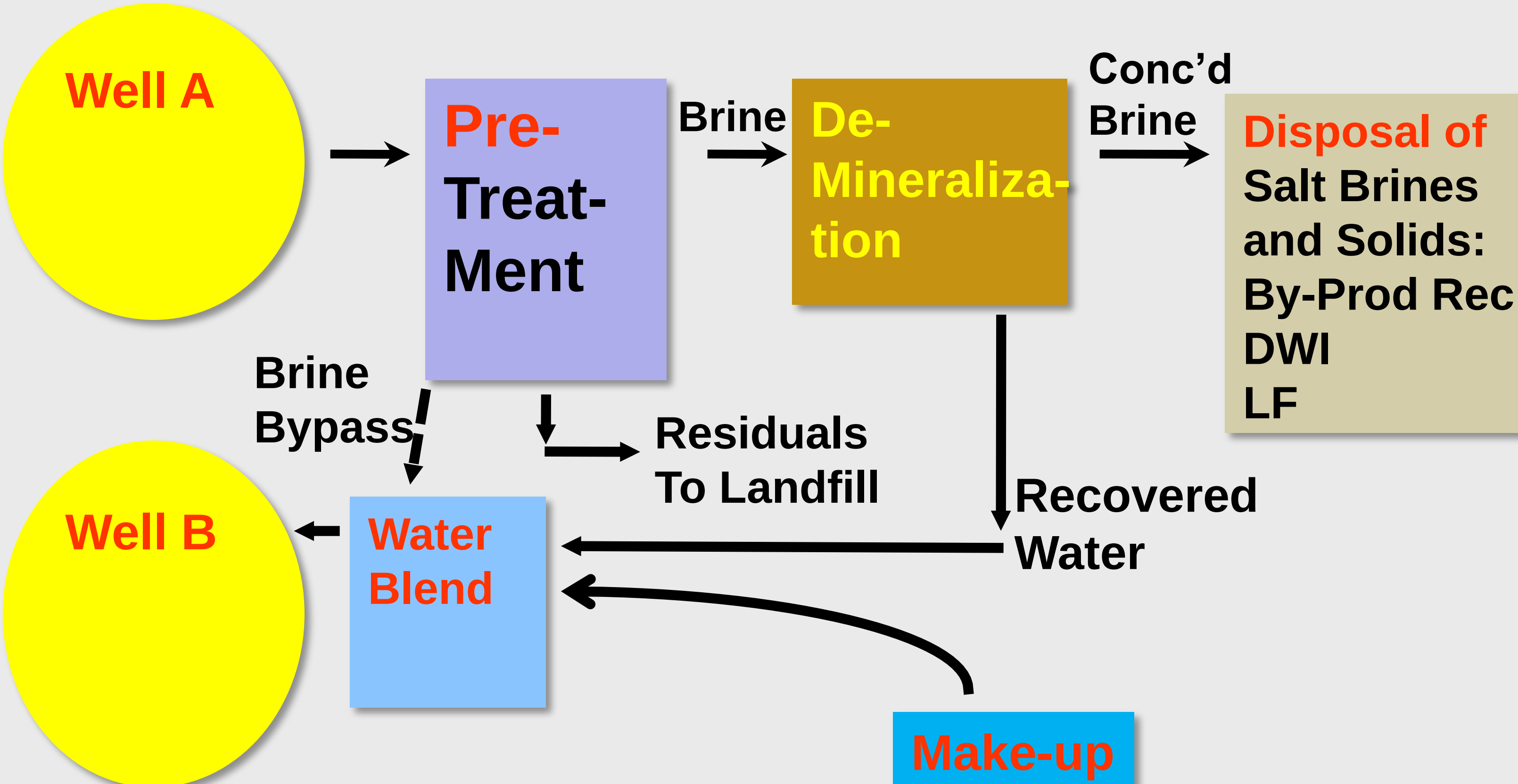
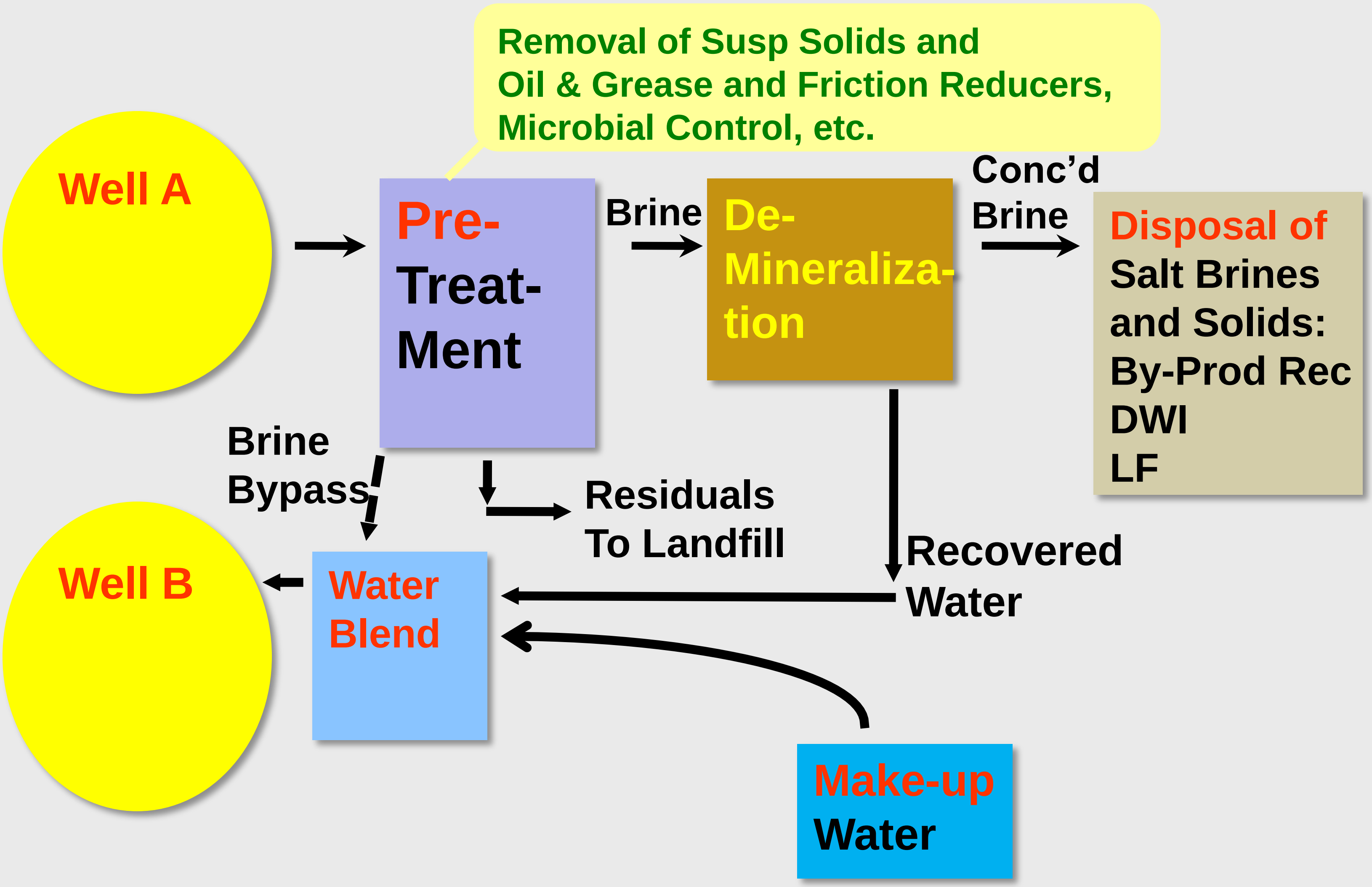
Water Reuse

- Two Schools of Thought
  1. Condition brines to control SS, O&G, scale-forming potential, microbes, etc. --- without demineralization --- and blend for reuse
  2. Employ Demineralization to generate a low TDS water that can be recovered for reuse
     - ✓ Demineralization can be achieved with thermal systems or with membranes.
     - ✓ Pretreatment is used to protect the demineralization processing stage.
     - ✓ Prevention of fouling of heat exchangers and membranes is important.
- Each of the above options has advantages and disadvantages

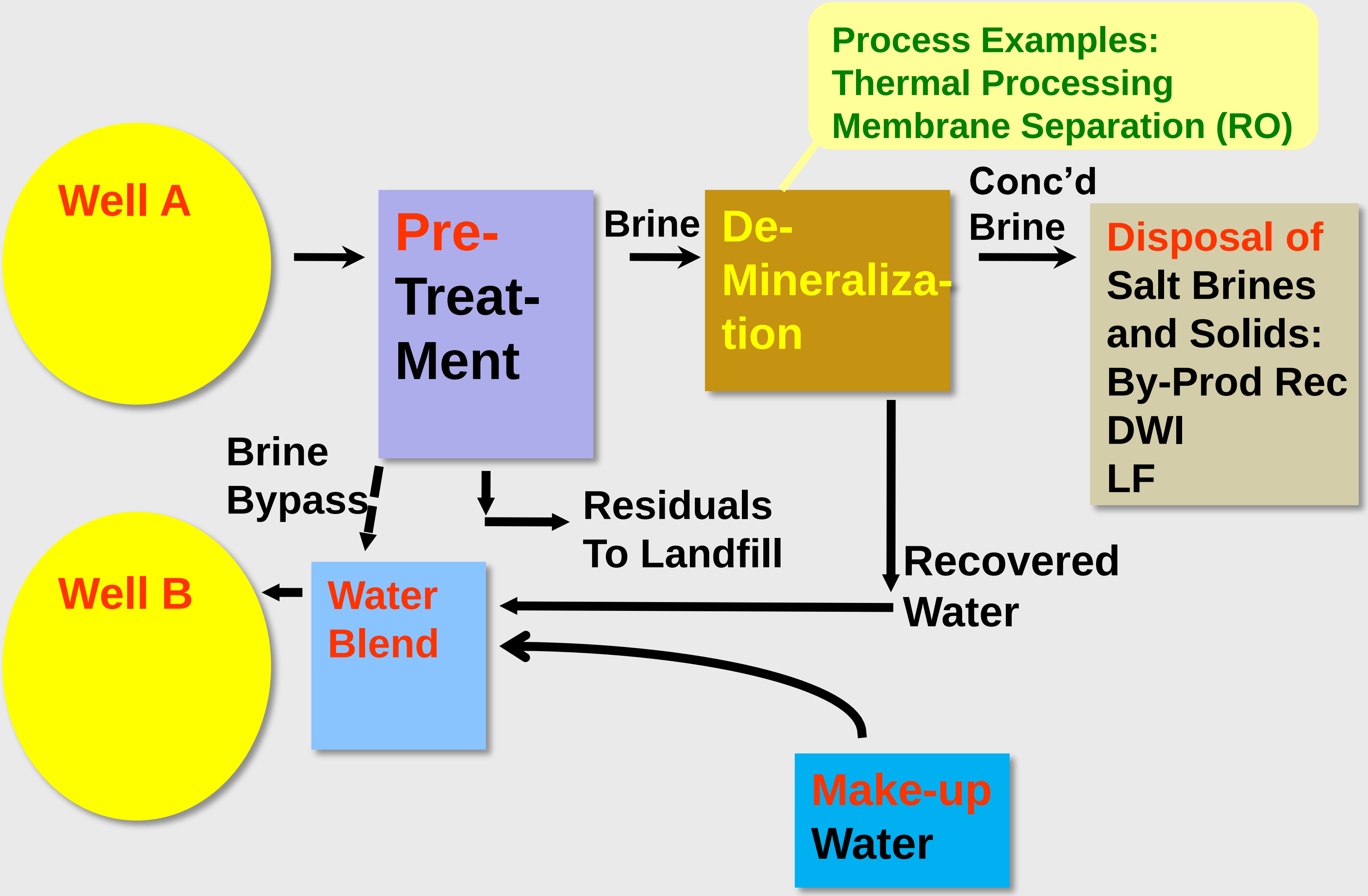
Water Reuse Options Flowsheet



Water Reuse Options Flowsheet



Water Reuse Options Flowsheet



Fountain Quail Mechanical Vapor Recompression Unit for Flowback Water Treatment and Reuse

- **At Devon Sites**
- **> 6,000 bbls/d/site**
- **AquaPure Mfgr**
- **Operated by Fountain Quail**
- **Obtaining field Performance Information**
- **Over 70% Water Recovery**
- **Handles wide feed variations**

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Reverse Osmosis Trials in the Barnett

Examples of Currently Available Innovative Brine Management Technology Options

- Fountain Quail (Thermal Processing for Water Recovery)
- 212 Resources (Thermal Processing for Water Recovery)
- GE Thermal Processing (Thermal Processing for Water Recovery)
- Intevras (Heat Recovery from Compressor Engines for Brine Evap)
- GeoPure (UF / Reverse Osmosis)
- Ecosphere Technologies (Ozonation and Reverse Osmosis)

Rapidly Moving Shale Gas Industry Solutions

- Evolving Methods for Improved Shale Gas Completions and Operations Impact Water Demands and Treatment Needs
- Improved Understanding of the Water Life Cycle of Development Areas is Important
- No Single Silver Bullet
- Field Experience and Relevance is Critical
  - Solution Providers / Service Companies
  - Developers
  - Technologists
- Need to Avoid Prescriptive Remedies

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Thank You

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Characterization of Marcellus Shale and Barnett Shale Flowback Waters and Technology Development for Water Reuse

Tom Hayes
Gas Technology Institute

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 Barnett and Appalachian Shales are among the largest and most active natural gas plays in the U.S. that geographically covers all or part of 20 counties in North Texas and large areas of Pennsylvania and West Virginia. The Barnett area is proven to have approximately 2.5 trillion cubic feet (59 km^3) of natural gas reserves and is widely estimated to contain up to 27 trillion cubic feet (700 km^3) of technically recoverable natural gas (USGS, 2004; Clouser, 2006). The Marcellus Play of the Appalachian Shale Region is considered to be larger in size and capacity in comparison to the Barnett. Both shale plays are considered to be unconventional gas formations; each of these plays depend upon the economical utilization and environmentally-responsible management of large volumes of water for continued sustainable development.

Hydraulic fracturing (fracing) is a necessary step for initiating economical well performance, requiring between 1 and 4 million gallons of water for successful well completion. Vertical wells require approximately 1 million gallons and horizontal wells require 3-4 million gallons according to Barnett Shale Producers. These per-well levels of water production also apply to the wells installed and completed in the Marcellus Shale. In both plays, horizontal wells comprise more than 90% of the total wells that are constructed. Of the total water used by the industry, completions using hydraulic fracturing represent more than 94% and drilling represents 5% as see in Slide 6 (Galusky, 2007). During years when more than 2,000 wells are constructed in a shale gas play, approximately 2 billion gallons will be used for new completions. This level of water demand poses a number of challenges for industry in the course of developing the Barnett and Appalachian Shales for natural gas production. In recognition of this need, the natural gas industry has supported efforts to characterize flowback water and evaluate water reuse approaches that significantly reduce freshwater demand while providing environmentally acceptable options for flowback water management.

Flowback Water Characteristics

Effective management of flowback water requires some level of knowledge of the characteristics of the water; a breakdown of categories of constituents found in many flowback and produced waters is depicted in Slide 8. Flowback water contains salts, metals and organic compounds from the formation as well as many of the compounds that were introduced as additives to the influent stream. Discussions between the industry and regulatory agencies of Pennsylvania and West Virginia have pointed to the need for an information base on the composition and properties of flowback water and on the influent water streams that are used

to perform frac jobs. The objective of this effort was to conduct the initial sampling and analysis of water streams associated with shale gas development in the Marcellus Shale.
In recognition of the importance of this effort, 17 member companies of the Marcellus Shale Coalition (MSC) volunteered 19 locations where shale gas wells were scheduled to be hydraulically fractured. The Field Sampling and Analysis Plan and the Quality Assurance Project Plan were developed, reviewed, and finalized for the effort by the companies of the Appalachian Shale Water Conservation and Management Committee (ASWCMC), PA-DEP and WV-DEP. At each of the host sites, samples of influent water streams at Day 0 and the flowback water streams at 1, 5, 14, and 90 days following the frac job event were collected by a single engineering subcontractor, URS. All samples were sent to Test America (a PA-DEP certified environmental testing laboratory) for analysis. The list of constituents recommended for the characterization study was developed from comments received from the PADEP, the WVDEP and members of the Appalachian Shale Water Conservation and Management Committee (ASWCMC). Categories of determinations that were conducted included: 1) General Chemistry, 2) Organic Compounds, and, 3) Metals. Once reviewed and qualified, data from these analyses were organized and tabulated in a source blind manner into an Excel spreadsheet that currently represents the information base.

Results from this effort indicate that values for pH, alkalinity, total dissolved solids, total organic carbon, oils and greases and other parameters from general water characterization are within the normal ranges reported for conventional produced waters by the USGS. General characteristics of Marcellus Shale waters (influent and 5-day flowback) are shown in Slide 13. Comparisons of characteristics of 14-day flowback waters with conventional produced waters are shown in Slide 14. Flowback water concentrations of total dissolved solids ranged from 3,000 to 260,000 mg/l; typical profiles show an increase in total dissolved solids in flowback water with time following a frac job event (as shown in Slides 16-18). Anions and cations of influent and 5-day flowback water are shown in Slide 15; as with conventional produced water, shale gas flowback water cations are dominated by sodium and calcium; the main anion is chloride.

Metals normally seen in conventional produced waters, such as iron, calcium, magnesium, and boron, are at levels in flowback waters that are well within known ranges for normal produced waters. Heavy metals that are of concern in urban industrial wastewaters and POTW sludges --- such as chromium, copper, nickel, zinc, cadmium, lead, arsenic and mercury --- are at very low levels in flowback and produced waters (as shown in Slide 34).

Among volatile organic constituents, more than 93% of all constituent determinations were at non-detectable levels and less than 1% of the determinations (mainly volatile constituents that are a natural part of formation waters) were above 1 ppm (as shown in Slide 23). Virtually all man-made halogenated solvents were at non-detect levels; volatile constituents that are measureable, are those that are normally found in conventional produced waters.

Regarding semivolatile organic constituents, more than 96% of all determinations were at nondetectable levels and less than 0.1% of all constituents were above 1 ppm; the remainder of constituents were at low trace levels – usually below 10 ppb (as seen in Slide 27). All chlorinated pesticides, organophosphorus pesticides and polychlorinated biphenyls in all samples were determined to be at non-detect levels. The results of this shale gas water characterization effort indicate that all pesticides, PCBs, and a large fraction of the volatile and semivolatile constituents should be considered to be unnecessary for the sampling and analysis of flowback waters in the future.

Recently, characterization of shale gas waters has been completed for five locations in the Barnett using the same procedures employed in the Marcellus Shale Project; general characteristics of the 5-day flowback waters are compared between the two plays. For the limited number of sites sampled, the Barnett Shale waters appear to be significantly lower in total dissolved solids -- about half of the TDS levels of the Marcellus Shale waters that range from 38,000 to 238,000 mg/l TDS. Alkalinities of the Barnett waters at 238 to 1630 mg/l (as $CaCO_3$) are relatively higher than the Marcellus waters -- perhaps four times higher -- due to the greater presence of bicarbonate concentrations in the Barnett waters. Marcellus shale water, however, showed significantly higher levels of TOC than Barnett waters though most samples from both plays had TOC levels below 70 mg/l (modest TOC levels).

Water Reuse Technology Evaluations and Development

Information on water flows in the shale gas industry indicate that although each well completion represents a potential significant flowback water output equivalent to 5-35% of the influent water, it is also true that future hydraulic fractures represent substantial opportunities for the reuse of these waters, especially during the growth phase of each shale gas development area. The median flowback water volume collected from 19 locations in the Marcellus Shale was approximately 24 percent of the influent water volumes used for each completion operation.

Predominantly, the industry prefers to dispose of flowback and produced waters using Class II deep well injection if such disposal capacity is locally available and economically accessible. In areas of the U.S. where Class II wells are sparse (the Marcellus Shale has only 7 Class II wells which represents a very low capacity to accept produced waters and flowback), water reuse has been a logical alternative to pursue as is done in the Pennsylvania portion of the Marcellus Shale. In areas of the U.S. where severe limitations of water availability can arise from frequent occurrences of drought, shale gas developers have considered water reuse as a means of significantly reducing demands on sources of fresh water that compete with community water supplies.

Where flowback and produced water reuse are being pursued aggressively, there are mainly two schools of thought that exist in the shale gas industry. Approach A is comprised of conditioning the brines for the removal of suspended solids, oils and greases, bacteria, and scale forming ions (i.e. constituents that potentially interfere with equipment and infrastructure maintenance) with no demineralization (desalination) prior to reuse. Currently, this approach is being used within the Marcellus Shale as the predominant shale gas water management practice. A more rigorous treatment ("Approach B") is comprised of treating shale gas water all the way to the recovery of distilled or demineralized water with the concomitant generation of a small volume of concentrated brine; this rigorous treatment approach is usually capable of recovering demineralized water equivalent to 70-80% of the original flowback/produced water stream. A general flowsheet that encompasses water reuse options available to the industry are shown in Slides 40-42.

Since 2005, the shale gas developers have evaluated a number of processes capable of demineralization and brine volume reductions. The most capable demineralization approach that has been demonstrated in the treatment of shale gas waters -- in terms of reliability and performance -- is the mechanical vapor recompression thermal distillation (MVR) process. This process is capable of handling a very wide range of brines (from less than 10,000 mg/l to more than 120,000 mg/l TDS) while achieving over 70 percent efficiencies in water recovery. This process is commercially applied to shale gas water stream management in the Barnett and in some shale gas fields of the Western U.S. Another demineralization process that has been tested on shale gas waters in the field is reverse osmosis (RO), though to a much lesser extent than the MVR process. Tests with RO on shale gas waters have verified the ability of the process to recover about 60% of highly demineralized water as long as the influent water did not exceed 40,000 mg/l of TDS. Photos of MVR and RO field demonstration units (located in the Barnett Shale) are shown in Slides 43 and 44. Demineralization with either process comes with a significant cost that must be evaluated and understood to achieve effective deployment. In the shale gas industry, demonstrations involving both processes are continuing.