

EPA Analytes and Current Analytical Methods

Technical Workshop on Analytical Chemical Methods

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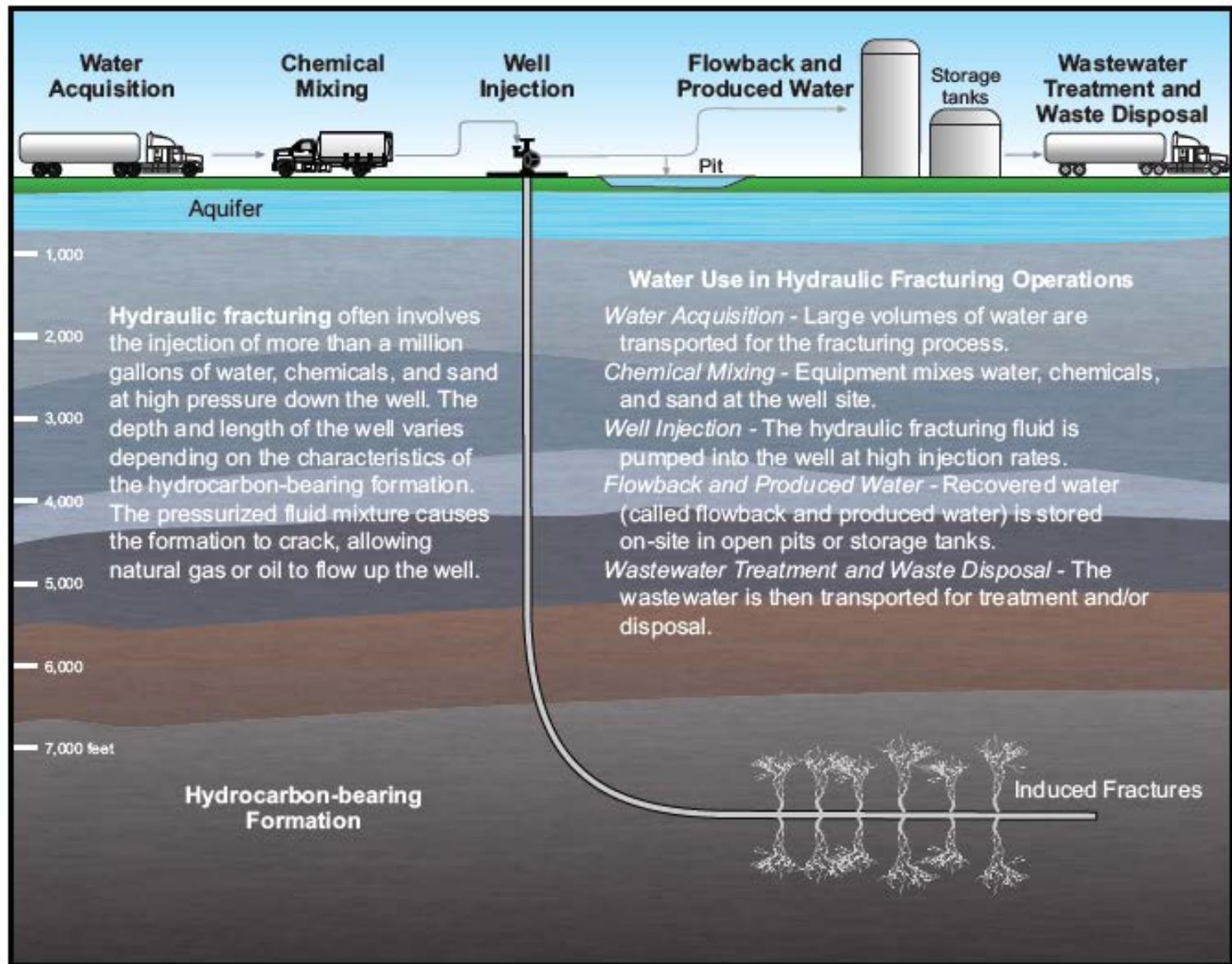
EPA Study of the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources

EPA Study Goals

- To assess the potential impacts of hydraulic fracturing on drinking water resources
- To identify the driving factors that affect the severity and frequency of any impacts



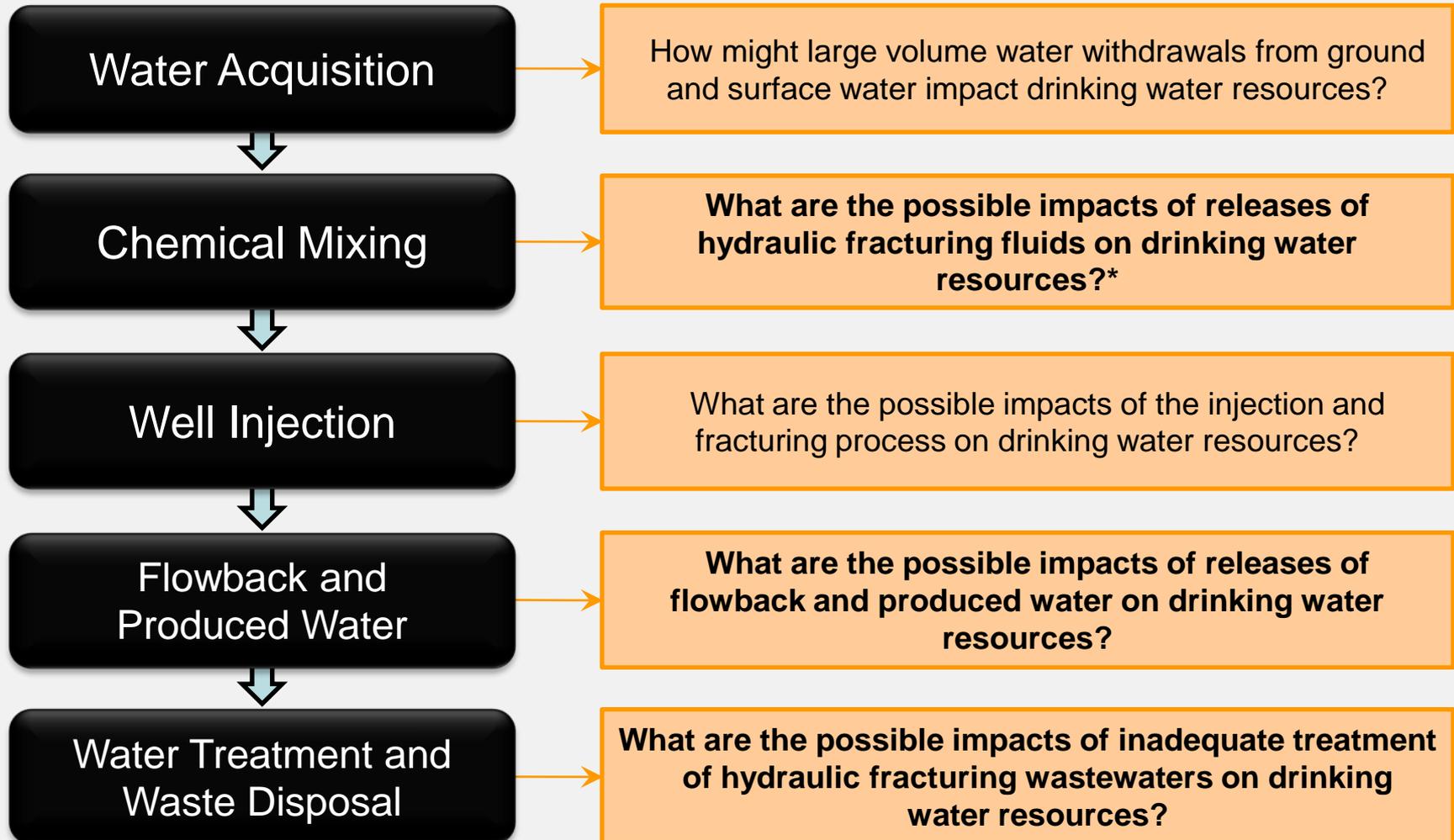
Hydraulic Fracturing



Hydraulic Fracturing Water Cycle

Water Use in Hydraulic Fracturing Operations

Fundamental Research Questions



HF Water Cycle

Water Use in Hydraulic Fracturing Operations

Secondary Research Questions Requiring Analytical Method Development

Chemical Mixing

What are the identities and volumes of chemicals used in hydraulic fracturing fluids, and how might his composition vary at a given site and across the country?

Flowback and Produced Water

What is the composition of hydraulic fracturing wastewaters, and what factors might influence this composition?

Water Treatment and Waste Disposal

What are the potential impacts from surface water disposal of treated hydraulic fracturing wastewater on drinking water treatment facilities?

HF Water Cycle

Water Use in Hydraulic Fracturing Operations

Chemical Mixing

Glycols, Ethoxylated Alcohols, Alcohols, Alcohol amines, Amides, Aldehydes, Aromatic Hydrocarbons, Inorganic Elements, Halogens

Flowback and Produced Water

Glycols, Ethoxylated Alcohols, Alcohols, Alcohol amines, Amides, Aldehydes, Aromatic Hydrocarbons, Inorganic Elements, Radionuclides, Halogens

Water Treatment and Waste Disposal

Disinfection Byproducts, Inorganic Elements, Radionuclides

Analytical Methods Research

- Base Methods
 - SW-846
 - SDWA
 - CWA
 - ASTM
- Analytes
 - Glycols and related compounds
 - Acrylamide
 - Ethoxylated alcohols
 - Disinfection by-products
 - Radionuclides
 - Inorganics

Note methods are available for the majority of analytes. Goal of EPA research is to improve accuracy, precision and sensitivity of methods for hydraulic fracturing related matrices

Analytical Methods Challenges

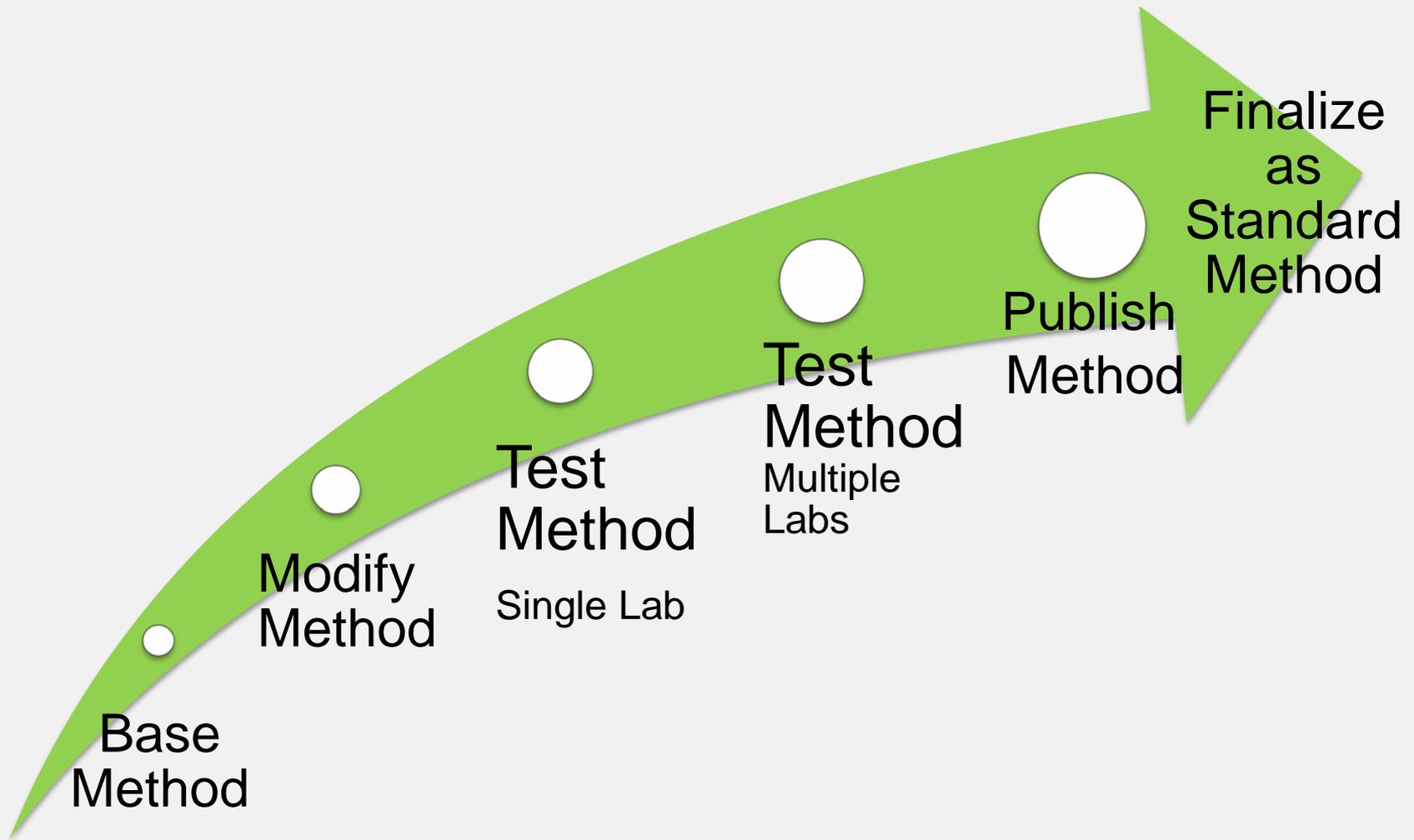
Chemical Name	Base Method	Challenge
Glycols & related compound	SW-846 Methods 8000C and 8321B + ASTM D7731-11	No standard method available to cover all compounds; detection limits too high
Ethoxylated Alcohols	ASTM D7485-09	No standard method available to cover all compounds
Alcohols	SW-846 Method 5030 and 8260C	Confirmation in hydraulic fracturing related matrices
Alcohols, amine (diethanolamine)	No Standard Method	No standard method available
Amides (acrylamide)	SW-846 Method 8032A	Matrix interferences, and poor extractability
Disinfection Byproducts (bromide, bromate and haloacetic acids)	SDWA Methods 521, 551, and 552	Matrix interferences

Analytical Methods Challenges

Chemical Name	Base Method	Concerns
Aldehydes	SW-846 Method 8315	Complex method, confirmation in hydraulic fracturing matrices; detection limits too high
Aromatic Hydrocarbons	SW-846 Methods 5030 and 8260C	Confirmation in hydraulic fracturing related matrices
Inorganic Elements	SW-846 Methods 6010C and 6020A or CWA 200.7	Matrix interferences
Radionuclides (gross alpha & beta)	SW-846 Method 9310	Matrix interferences
Halogens	SW-846 Method 9056A	Matrix interferences

† - DWA methods may be found at <http://water.epa.gov/scitech/methods/cwa/index.cfm>). CWA methods may be found at <http://water.epa.gov/scitech/methods/cwa/index.cfm>. SW-846 Methods may be found at <http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm>. ASTM – American Society for Testing and Materials, International.

Analytical Method Verification Process



Analytical Methods Status

Modify/Develop Method	Test Method Single Lab	Test Method Multiple Labs	Publish Method	Finalize Standard Method
Aldehydes	Radionuclides	Glycols	Ethoxylated alcohols	
Inorganic elements	Ethoxylated alcohols		Acrylamide	
Halogens	Acrylamide			
DBPs (bromide, bromate and haloacetic acids)				

Future research will focus on alcohols, diethanolamine, and aromatic hydrocarbons

Analytical Method Development: Glycols as an Example[†]

- Glycols in drinking water wells
 - Di-, tri-, and tetraethylene glycol + 2-methoxyethanol and 2-butoxyethanol
- EPA SW-846 Method 8015C lists diethylene glycol but no others and not sensitive enough
- EPA Method 8321B, 8000C, and ASTM D7731-11 used in combination to create new method
 - Direct inject LC/MS/MS method

[†] - participating laboratories include: EPA Regions 3 and 5; EPA ORD Laboratories in Cincinnati and Las Vegas; Metropolitan Water District of Southern California; Philadelphia Water District; Eurofins Lancaster Laboratories; and TestAmerica, Inc.

Analytical Method Development: Radionuclides – Gross α and β

- Radionuclides in produced waters and wastewaters
 - Gross α and β as a screening technique
 - Radium, Uranium, Thorium
- SW-846 Method 9310 is for gross α and β
 - Not sensitive enough and subject to high interferences from total dissolved solids and salts
- National Air and Radiation Environmental Laboratory in Montgomery, AL
 - Goal is method with minimum detectable activity of 30 and 50 with a method uncertainty of 30%

Discussion

- What other methods or modifications should EPA consider?
- What has been your experience in addressing analytical challenges?