

# Bakken Crude Awareness

## for Responders

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USEPA Environmental Response Team (ERT)



# Unit Train



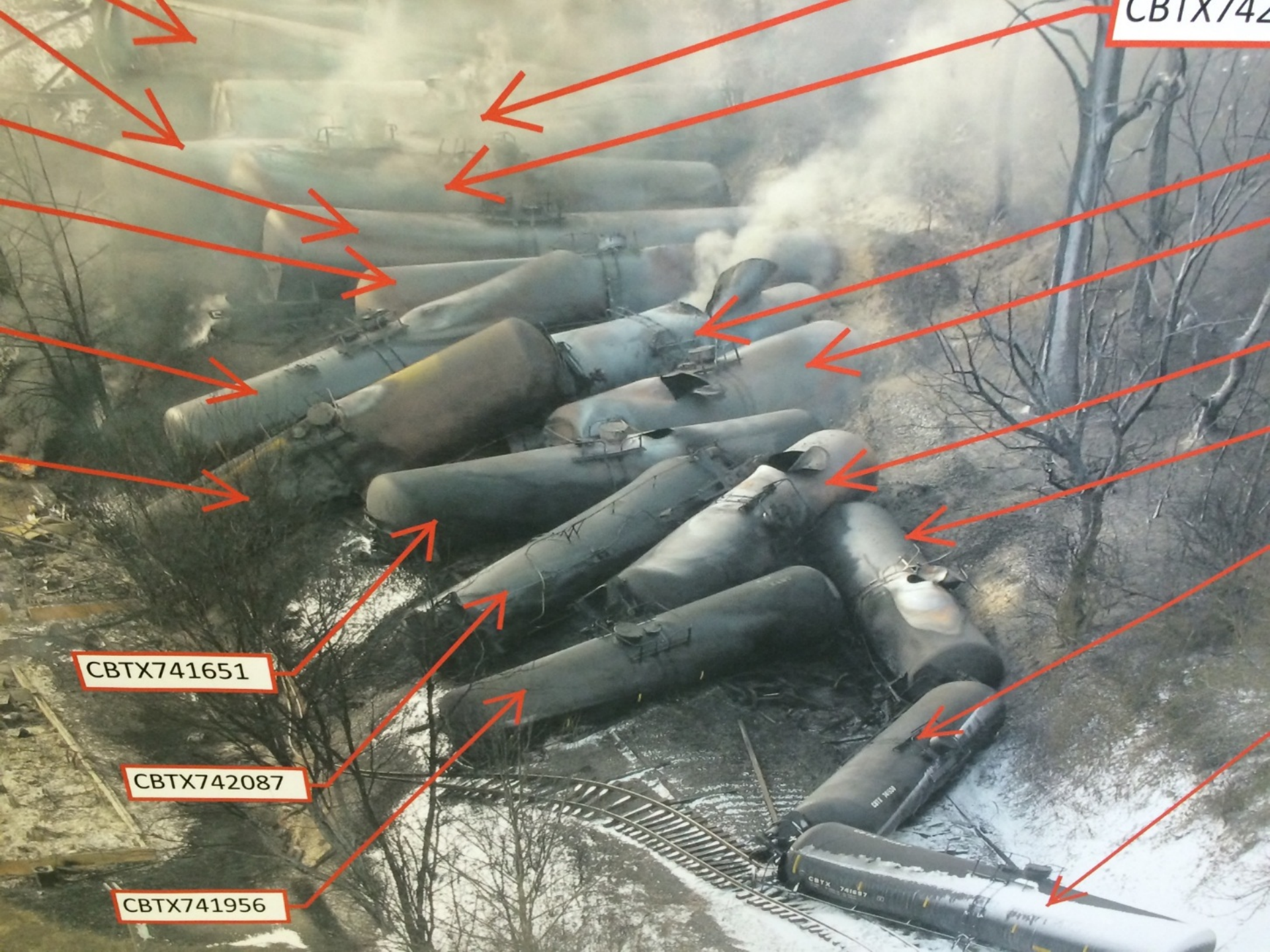


# Mt. Carbon West Virginia





CBTX742



CBTX741651

CBTX742087

CBTX741956

CBTX 741687





# Bakken Crude Oil: Worker H&S Pilot Scale Studies

- ▶ Cold weather
  - Air monitoring/sampling
  - Collection/recovery methods
  - Weathering
- ▶ Warm weather
  - Air monitoring
  - Water sampling
    - Benzene Dissolution Study
  - Weathering
  - Still/Agitated Scenarios



# Cold Weather: OHMSETT Testing



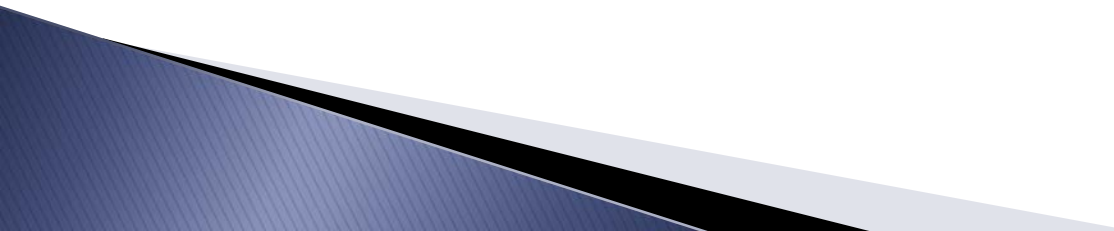


# Release of Bakken Crude

- ▶ Air Monitoring
  - AreaRae's
  - UltraRae 3000 w/Benzene Specific Tubes (RAESep)
  - TAGA Continuous
  - TVA 1000
  - Tedlar Bag GCMS Analysis (sampling)
  - Sampling w/Carbon Tubes (Eight Hour Exposure Evaluation)

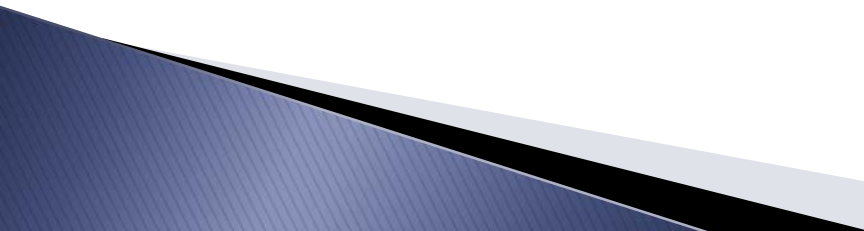


# Bakken Crude Specifics

- ▶ Flash Point = 95 degrees plus
  - ▶ LEL = 0.8%
  - ▶ UEL = 8.0%
  - ▶ API Gravity = 45
  - ▶ Specific Gravity = 0.82
  - ▶ Benzene Concentration = 1700 – 1900 ppm
- 



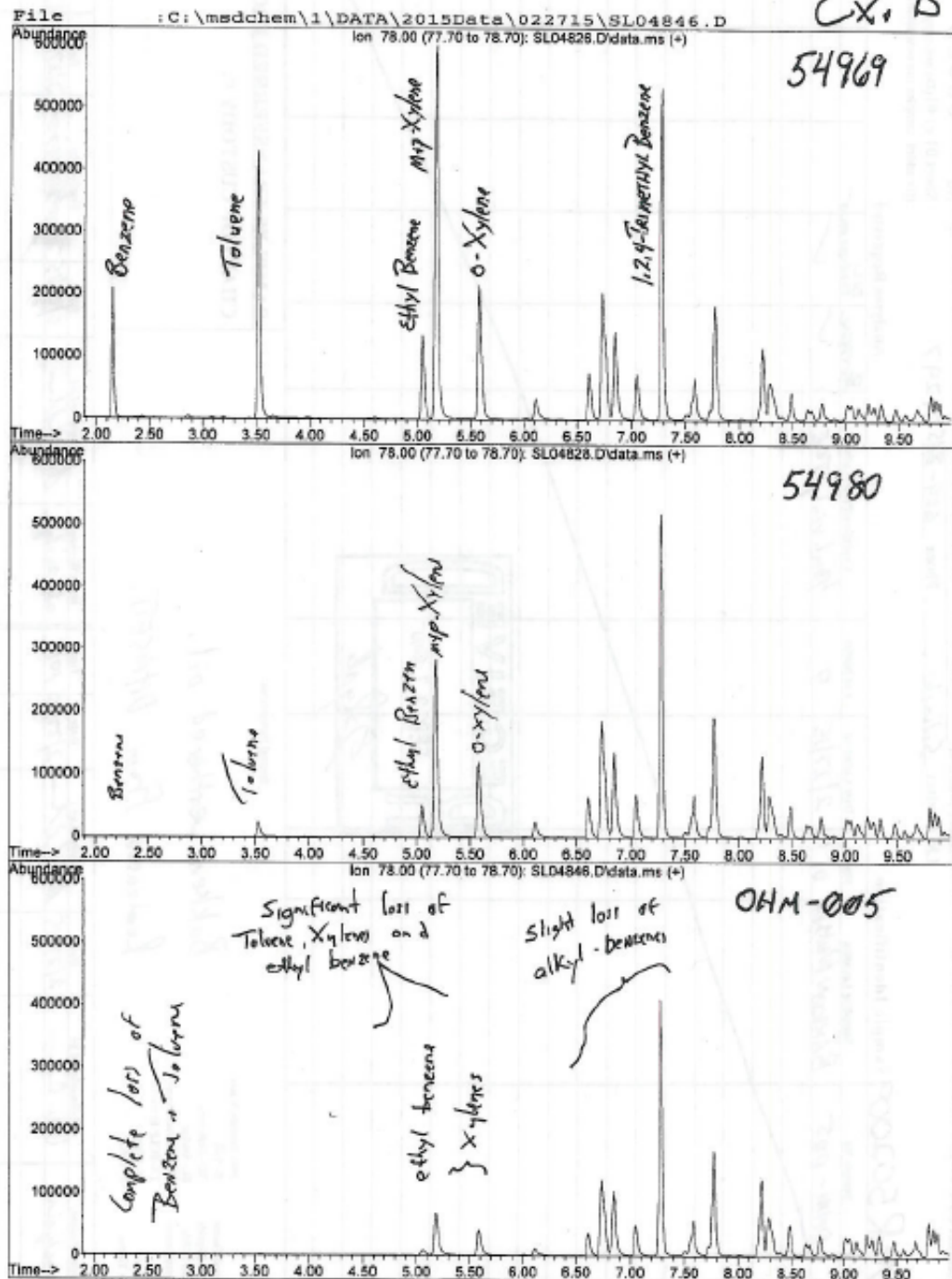
# Volatile Compound Reduction With Weathering: Cold

- ▶ Significant Levels of Light Hydrocarbons in Unweathered sample
  - ▶ After 24 Hours a Significant Loss of Light Hydrocarbons Up to Nonane and BTEX Compounds
  - ▶ After Seven Days a Complete Loss of Benzene and Toluene. Significant loss of Xylenes
- 

# Initial Concentration

# 1 Day Weathering

# 7 Day Weathering





# Benzene Air: Concern Levels

- ▶ TWA (8 hrs.) = 1 ppm
- ▶ STEL = 5 ppm 15 minutes
- ▶ 0.5 ppm Action Level (8-hr TWA additional monitoring, medical surveillance, and additional employee training)
- ▶ NIOSH REL of 0.1 ppm and the ACGIH TLV of 0.5 ppm



# Release and TAGA Monitoring





# ASTM Skimmer Testing



# Additional Skimmer Testing



- ▶ Weathered Oil Recovery Rate
  - 20 gpm
- ▶ Fresh Oil Recovery Rate
  - 5 gpm

Grooved Drum Skimmer



# Air Monitoring



# ULTRA RAE 3000

- ▶ 9.8eV Lamp (IE Benzene 9.25)
- ▶ Benzene from 50 ppb to 200 ppm and other VOCs up to 10,000 ppm
  - With RAESep Tube
  - Only Benzene Specific Handheld available at time of study (now have Lumex BA-15)

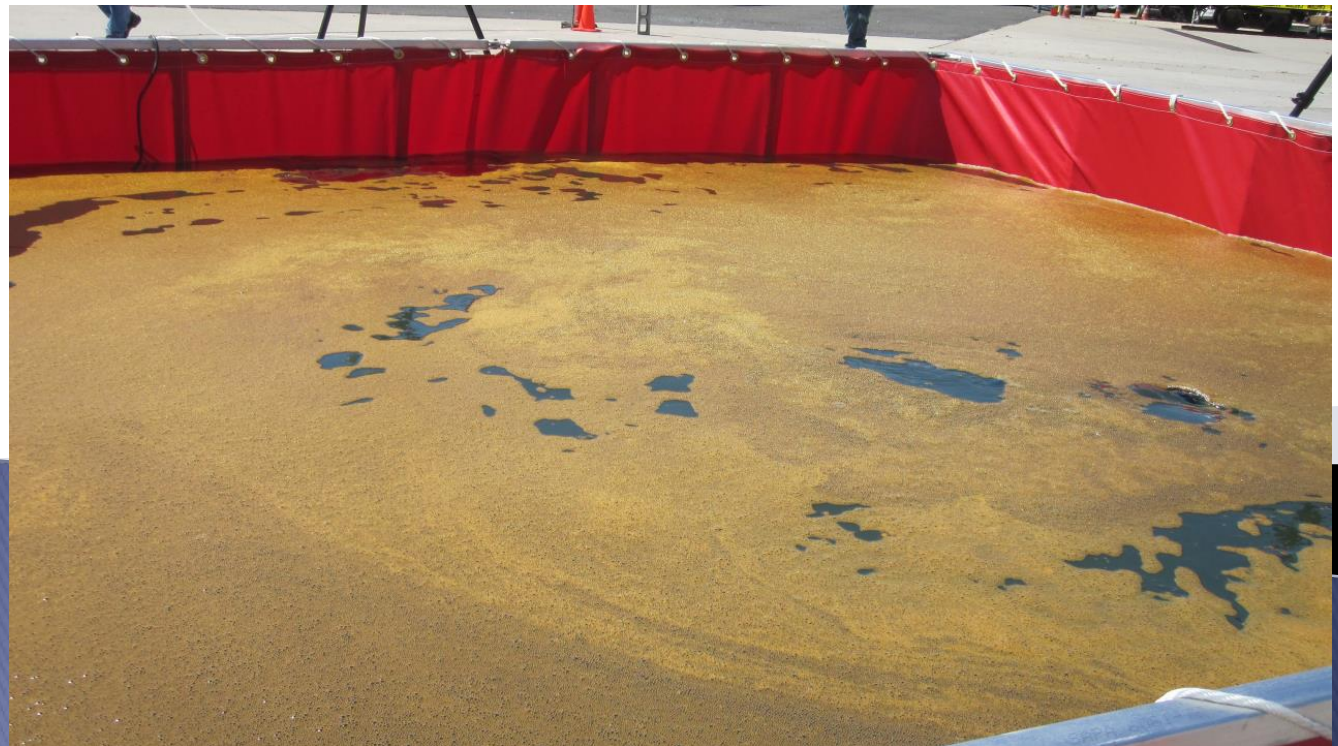


# OPEN CUP FLASH POINT

- ▶ Fresh Oil-Too volatile and was lost prior to determination
- ▶ Oil Weathered One Day-132.0 Degrees Fahrenheit
- ▶ Oil Weathered Seven Days-165 Degrees Fahrenheit



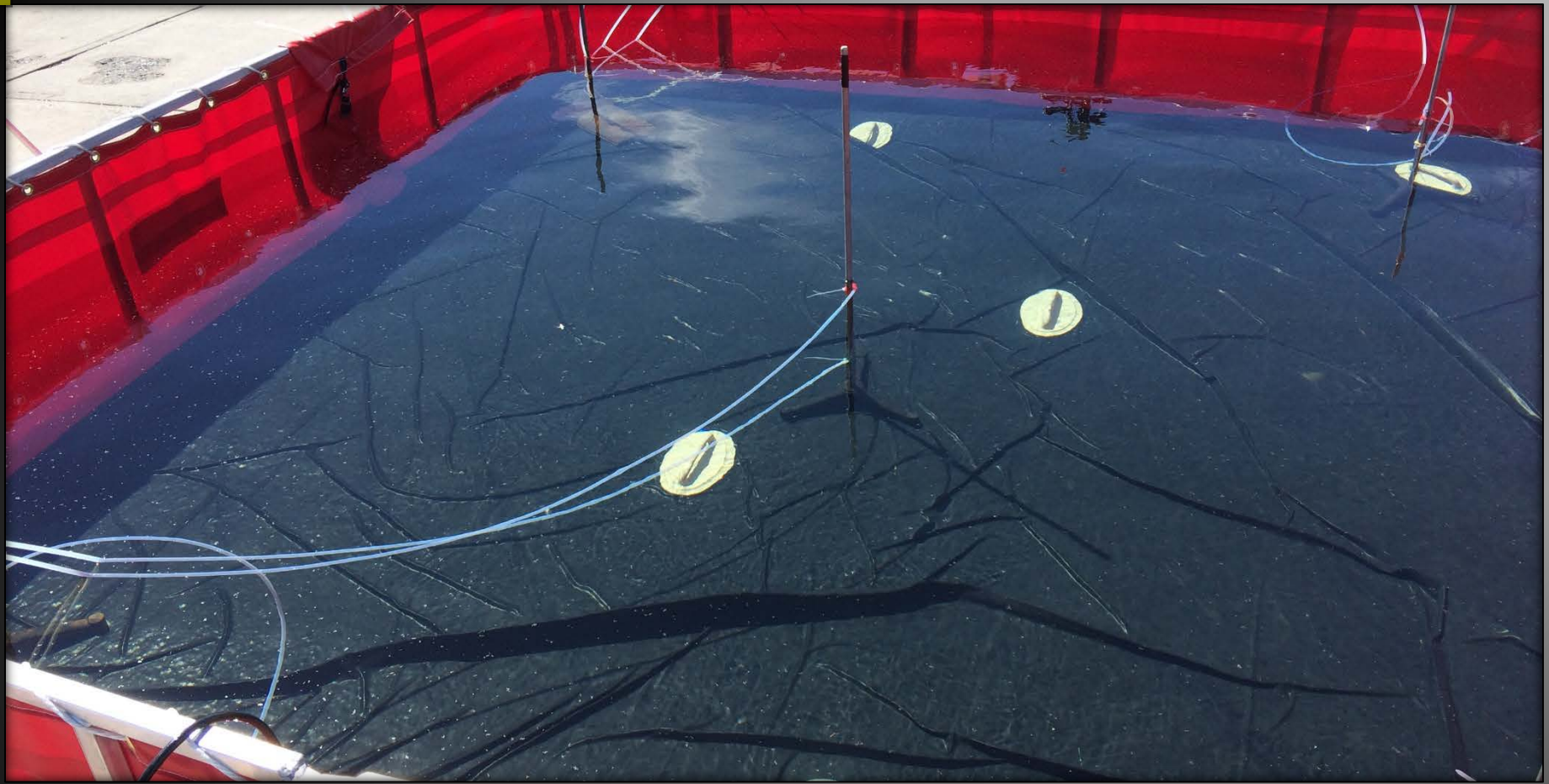
# PHASE II Warm Weather Testing



# Testing Area Layout







## Quiescent Pool Prior To Release >>

Location of Water Sampling Ports

# AreaRae Setup







# Water Sampling Collection Configuration >>

Siphon Flow

# Bakken Oil Release







# Flash Point Data

- ▶ Time Zero  $\leq 23^{\circ}\text{F}$
- ▶ Time 25:30 Still Pool  $168^{\circ}\text{F}$
- ▶ Time 21:28 Agitated Pool  $161^{\circ}\text{F}$
- ▶ After 24 hours most of the C4 thru C10 hydrocarbons had volatilized.

**Table 2**  
**Oil Sampling and Flash Point Results**  
**Bakken Crude Oil: Worker Health and Safety Pilot Scale Study**

	Cold Weather Oil Samples		Warm Weather Oil Samples	
Initial Conditions	at Eddystone, PA	Arrival OHMSETT	From Tote 3	
Collected	2/4/2015 8:48	2/4/2015 10:30	5/17/2016	
Concentration (µg/g)	1720	1720	1200	
Percent Lost	--	0.0	--	
Flashpoint (°F)	32*	32*	--	
Immediately prior to release		Prior to Release	Start of still water event (1)	Start of turbulent event (1)
Collected		2/11/2015 10:09	6/14/2016 11:45	6/15/2016 10:30
Concentration (µg/g)		1700	1200	1300
Percent Lost		1.2	--	--
Flashpoint (°F)		83	< 23	< 23
Approximately 1 day after release		From pool after ~22.5 hours	From pool after 25.5 hours	From pool after ~21.5 hours
Collected		2/12/2015 8:31	6/15/2016 13:15	6/16/2016 7:58
Concentration (µg/g)		13.8 U	170 U	170 U
Percent Lost		99.2	> 85.8	> 86.9
Flashpoint (°F)		132	168.8	161.6
Extended		7 Day weathering		
Collected		2/18/2015 8:00		
Concentration (µg/g)		U		
Percent Lost		100		
Flashpoint (°F)		155 to 165		

(1) Drum sample from OHMSETT Tote 3, delivered to Somerset County Emergency Services Training Academy 6/14/16.

µg/g = micrograms per gram.

U = Not detected.

-- = Not applicable or not analyzed.

\* - From the MSDS which lists the flash point at 32 degrees Fahrenheit (°F).

**Note: High post RL on June 2016 does not allow for comparison to Feb 2015 samples**



## Initial Release Air Monitoring >>

AreaRaes, TVA PID/FID, UltraRae 3000, Tedlar bags for GC/MS Analysis, and Continuous TAGA Monitoring



# Significant Effervescence



# Total Coverage of Off Gas Foaming





# COMPARISON DATA

Table 2  
 Comparison of Benzene Air Monitoring and Air Sampling Results from 14 June 2016  
 Bakken Crude Oil: Worker Health and Safety Pilot Scale Study  
 Somerset Fire Training Academy, Hillsborough, NJ  
 September 2016

Sample ID	Location	Description	Start Time	Tedlar Bag GC/MS Benzene Concentration (ppmv)	UltraRAE 3000 Benzene Concentration (ppmv)
--	Southside of Pool	Background	9:41	--	0
55612	Southside of Pool	T+1	11:55	5.9 J	3.75
55613	Southside of Pool	T+5	11:59	4.8 J	--
55614	Southside of Pool	T+10	12:04	3.3 J	1.45
55615	Southside of Pool	T+15	12:08	3.1 J	2.75
55616	Southside of Pool	T+30	12:24	5.7 J	69.35
55617	Southside of Pool	T+45	12:39	6.2 J	23.45
55618	Southside of Pool	T+60	12:54	2.2 J	11.6
55619	Southside of Pool	T+75	13:09	4.0 J	28.45
55620	Southside of Pool	T+90	13:24	1.6 J	1.85
55621	Southside of Pool	T+120	13:54	0.8 J	55
55622	Southside of Pool	T+150	14:24	0.58 J	2.95
55623	Southside of Pool	T+180	14:54	0.19 J	0.25
55624	Southside of Pool	T+240	15:54	0.072 J	4.05
55625	Southside of Pool	T+300	16:54	0.042 J	16.25
55626	Southside of Pool	T+1257*	8:51	0.00061	0.15

GC/MS = gas chromatography/mass spectrometry







# OXYGEN DEPLETION DOWNWIND

- ▶ MultiRae & TVA Data:
- ▶ Oxygen levels depressed (~Release T+45-T+150)
- ▶ Oxygen levels dropped to a low of 18.4 %
  - Persisted 2hrs Turbulent & 3 hours in Still
- ▶ IDLH Oxygen atmospheres considered to be less than 19.5% oxygen by volume- SCBA required
- ▶ Maximum FID VOC concentration 7300 ppm (Still), 9400ppm (Turbulent)
- ▶ Maximum PID VOC concentration 545 ppm (Still), 200 ppm (Turbulent)
  - Note: “Downwind” is immediately adjacent to release, not fence line.

**Table 8A Mobile Air Sampling and Monitoring Results from June 14, 2016**  
**Bakken Crude Oil: Worker Health and Safety Pilot Scale Study, Still Water Condition**

Time	Description	Sample ID	Location	Benzene	Benzene	VOCs	VOCs	VOCs	CO	H2S	LEL Methane	LEL Pentane	%O2
				SOP #1741	UltraRAE 3000	MultiRAE	TVA FID	TVA PID	MultiRAE	MultiRAE	MultiRAE	MultiRAE	MultiRAE
				GC/MS	B09924	B09921	13199	13199	B09921	B09921	B09921	B09922	B09921
				ppmv	ppm	ppm	ppm	ppm	ppm	ppm	%	%	%
9:41	Background	--	South of Pool	--	0	0	--	--	0	0	0	0	20.6
11:55	T+1	55612	South of Pool	5.9 J	3.75	123.42	1100	70	0	0	0	4	19.4
11:59	T+5	55613	South of Pool	4.8 J	--	48.9	700	34	0	0	0	0	19.4
11:59	T+10	55614	South of Pool	3.3 J	1.45	312	2700	72	0	0	0	0	19.4
12:04	T+15	55615	South of Pool	3.1 J	2.75	79	3370	173	0	0	0	0	19.4
12:24	T+35	55616	South of Pool	5.7 J	69.35	15.25	7300	545	0	0	0	0	19.1
12:39	T+45	55617	South of Pool	6.2 J	23.45	97	1200	152	0	0	0	0	18.9
12:54	T+60	55618	South of Pool	2.2 J	11.6	113.9	3200	372	0	0	0	0	18.9
13:09	T+75	55619	South of Pool	4.0 J	28.45	60.35	2900	296	0	0	0	0	18.4
13:24	T+90	55620	South of Pool	1.6 J	1.85	49.98	1940	235	0	0	0	0	18.5
13:54	T+120	55621	South of Pool	0.8 J	55	18.7	790	179	0	0	0	0	18.4
14:24	T+150	55622	South of Pool	0.58 J	2.95	4.938	1700	296	0	0	0	0	18.6
14:54	T+180	55623	South of Pool	0.19 J	0.25	41.66	1100	218	3	0	0	0	19.6
15:54	T+240	55624	South of Pool	0.072 J	4.05	45.8	370	89	0	0	0	0	20.6
16:54	T+300	55625	South of Pool	0.042 J	16.25	27.6	380	67	0	0	0	0	20.9
8:51	T+1257	55626*	South of Pool	0.00061	0.15	4.56	32	17	0	0	0	3	20.9

VOCs - volatile organic compounds, FID - Flame Ionization Detector, PID - Photoionization Detector CO - Carbon Monoxide, H2S - Hydrogen Sulfide, LEL - Lower explosive level, %O2 - Percent oxygen, ppmv - Parts per million by volume, T = End time of initial release (11:54), T+value = initial release time plus defined minutes, J = concentration is estimated, \* = Collected June 15, 2016, -- Not Collected

# Monitoring notes:

- ▶ Total VOC concentrations measured along the perimeter of the tanks on both the PID and FID remained above the benzene NIOSH REL of 0.1 ppm and the ACGIH TLV of 0.5 ppm after nearly 24 hours of the initial release for both the still water and turbulent water scenarios.
- ▶ Benzene Concentrations are an issue, Total VOCs persist
  - If no benzene specific readings may require prolonged upgrades
- ▶ Oxygen depleted environments present = Level B



# Some Take Homes

- ▶ There were large discrepancies between the FID and PID readings with the FID readings higher for VOCs than the PID readings.
  - Know what you are using (monitor), what it can/can't see, what actions you are taking based on these readings
  - On June 15, 2016 the highest instantaneous benzene concentration of 2,200 ppbv was observed along the TAGA monitoring path #2 located to the southeast of the turbulent tank approximately 30 minutes after the release of the oil. All TAGA monitoring results for this scenario were below 500 ppbv approximately 135 minutes after the release and below 100 ppbv approximately 270 minutes after the release.
    - If you don't have a TAGA or field GC/MS you have to go with what you have!

# TAGA Monitoring





# Water Sample Collection

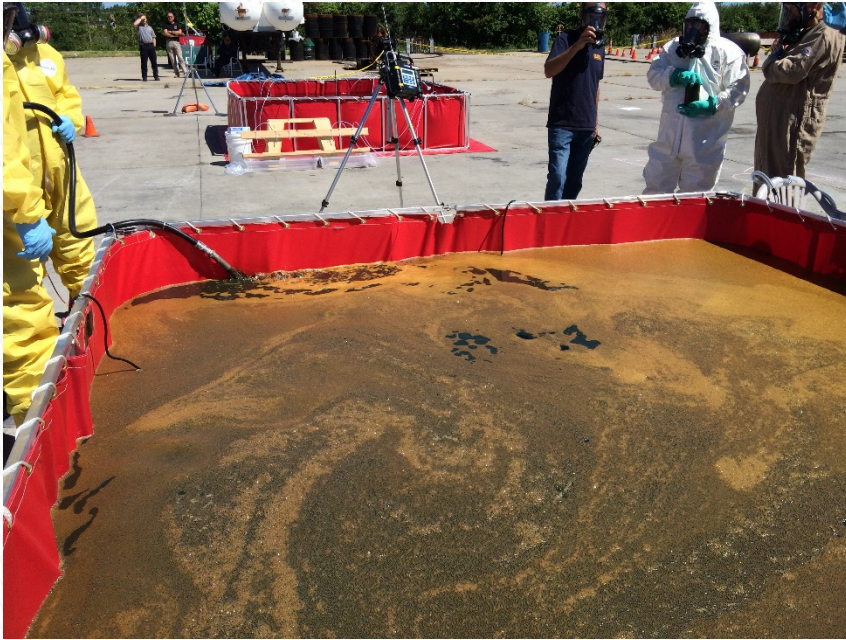




# BENZENE IN WATER

- ▶ Time Zero (Release) - Non-detect
- ▶ Sample 1: Release T+25 minutes 315 ug/l
- ▶ Benzene detected throughout the water column
  - In all samples (shallow/mid/deep and it persisted through final ~24-hr sample, 218 ug/l)
- ▶ Rapid dissolution
- ▶ MCL for Benzene is 5 ug/l

# Oil Characteristics



Initial Release



After Off Gassing



# Rudimentary Oil Thickness Gauging





# New Tool@ERT: BA-15 Lumex Benzene Analyzer

Advantage: Continuous measurement in air (gas) flow

Measurement range  
0.1 – 500  
mg/m<sup>3</sup>  
(31ppb–156ppm)

Averaging interval  
1 s – 5 min

Zero drift correction  
Automatic

Air flow rate 7–10 lpm



# Detection/Quantitation

TABLE 1

APPROXIMATE DETECTION AND QUANTITATION LIMITS

Instrument	Approximate Detection Limit (ppbv)	Approximate Quantitation Limit (ppbv)
Lumex BA-15	50	160
UltraRAE 3000 #1 (ERT-New)	50-75	160-250
UltraRAE 3000 #2 (ERT-Old)	100	330
UltraRAE 3000 #3 (KC-Old)	500-1,500	1,670-5,000

Notes:

EPA U.S. Environmental Protection Agency

ERT Environmental Response Team

PID Photoionization detector

ppbv Parts per billion by volume

ERT-New refers to an UltraRAE 3000 owned by EPA ERT that contained a PID lamp manufactured in August 2017.

ERT-Old refers to an UltraRAE 3000 owned by EPA ERT that contained a PID lamp manufactured in October 2014.

KC-Old refers to an UltraRAE 3000 owned by EPA in Kansas City, Missouri, that contained a PID lamp manufactured in October 2014.

# Benzene Test: Gasoline/Bakken

TABLE 3

COMPARISON OF READINGS FROM BENZENE IN PETROLEUM MIXTURES


Tested Material	GC/MS Value (ppbv)	Field Instruments, Readings (ppbv), and Percent Errors Compared to GC/MS Values					
		UltraRAE 3000 #1 (ERT-New)		UltraRAE 3000 #2 (ERT-Old)		Lumex BA-15	
		Reading	% Error	Reading	% Error	Reading	% Error
Gasoline	205	50.0	75.6	50.0	75.6	226	10.2
Bakken crude oil	338	200	40.9	250	26.1	329	2.7
Gasoline	4,100 <sup>a</sup>	3,600	NC	16,600	NC	4,070	NC
Bakken crude oil	6,760 <sup>a</sup>	7,450	NC	43,300	NC	6,700	NC



# Where is the Report?

- ▶ <https://response.epa.gov/ohmsett>
  - Report is “public”, no login required


Secure | [https://response.epa.gov/site/site\\_profile.aspx?site\\_id=9733](https://response.epa.gov/site/site_profile.aspx?site_id=9733) ☆


 United States Environmental Protection Agency

OSC ON-SCENE COORDINATOR

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## BAKKEN OIL-OHMSETT PILOT STUDY

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**Michael Hoppe**  
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 **Final Bakken Crude Oil: Worker Health and Safety Pilot Scale Studies (April 30, 2018 Rev 0.1)**

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Documents

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[Second Time is a charm version...](#)

