Groundwater monitoring for TPH

A Tale of Two Methods

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Why Monitor for TPH

- Required for Regulatory Compliance
- Required for Permit
- Establish if TPH concentrations rising or falling
- Identify if TPH type is changing
  - New source
  - New pathway
- Assess if seasonal or other external events affect TPH change

QED

Method 6200B

- GC-MS method
- 60 individual compounds
- Detection limits for individual compounds as low as 0.5 ppb
- C6 – C10 only
- 17 of the 60 found in petroleum compounds
- Mainly chlorinated solvents

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Method 6200B

Benzene	ND	ug/L	0.50	1	02/23/15 06:42	71-43-2
Bromobenzene	ND	ug/L	0.50	1	02/23/15 06:42	108-86-1
Bromochloromethane	ND	ug/L	0.50	1	02/23/15 06:42	74-97-5
Bromodichloromethane	ND	ug/L	0.50	1	02/23/15 06:42	75-27-4
Bromoform	ND	ug/L	0.50	1	02/23/15 06:42	75-25-2
Bromomethane	ND	ug/L	5.0	1	02/23/15 06:42	74-83-9
n-Butylbenzene	ND	ug/L	0.50	1	02/23/15 06:42	104-51-8
sec-Butylbenzene	ND	ug/L	0.50	1	02/23/15 06:42	135-98-8
tert-Butylbenzene	ND	ug/L	0.50	1	02/23/15 06:42	98-06-6
Carbon tetrachloride	ND	ug/L	0.50	1	02/23/15 06:42	56-23-5
Chlorobenzene	ND	ug/L	0.50	1	02/23/15 06:42	108-90-7
Chloroethane	ND	ug/L	1.0	1	02/23/15 06:42	75-00-3
Chloroform	ND	ug/L	0.50	1	02/23/15 06:42	67-66-3
Chloromethane	ND	ug/L	1.0	1	02/23/15 06:42	74-87-3
2-Chlorotoluene	ND	ug/L	0.50	1	02/23/15 06:42	95-49-8
4-Chlorotoluene	ND	ug/L	0.50	1	02/23/15 06:42	106-43-4
1,2-Dibromo-3-chloroprop	ND	ug/L	1.0	1	02/23/15 06:42	96-12-8
Dibromochloromethane	ND	ug/L	0.50	1	02/23/15 06:42	124-48-1
1,2-Dibromoethane (EDB)	ND	ug/L	0.50	1	02/23/15 06:42	106-93-4

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Method 6200B

1,2-Dichlorobenzene	ND	ug/L	0.50	1	02/23/15	06:42	95-50-1
1,3-Dichlorobenzene	ND	ug/L	0.50	1	02/23/15	06:42	541-73-1
1,4-Dichlorobenzene	ND	ug/L	0.50	1	02/23/15	06:42	106-46-7
Dichlorodifluoromethane	ND	ug/L	0.50	1	02/23/15	06:42	75-71-8
1,1-Dichloroethane	ND	ug/L	0.50	1	02/23/15	06:42	75-34-3
1,2-Dichloroethane	ND	ug/L	0.50	1	02/23/15	06:42	107-06-2
1,1-Dichloroethene	ND	ug/L	0.50	1	02/23/15	06:42	75-35-4
cis-1,2-Dichloroethene	ND	ug/L	0.50	1	02/23/15	06:42	156-59-2
trans-1,2-Dichloroethene	ND	ug/L	0.50	1	02/23/15	06:42	156-60-5
1,2-Dichloropropane	ND	ug/L	0.50	1	02/23/15	06:42	78-87-5
1,3-Dichloropropane	ND	ug/L	0.50	1	02/23/15	06:42	142-28-9
2,2-Dichloropropane	ND	ug/L	0.50	1	02/23/15	06:42	594-20-7
1,1-Dichloropropene	ND	ug/L	0.50	1	02/23/15	06:42	563-58-6
cis-1,3-Dichloropropene	ND	ug/L	0.50	1	02/23/15	06:42	10061-01-5
trans-1,3-Dichloropropene	ND	ug/L	0.50	1	02/23/15	06:42	10061-02-6
Diisopropyl ether	ND	ug/L	0.50	1	02/23/15	06:42	108-20-3
Ethylbenzene	ND	ug/L	0.50	1	02/23/15	06:42	100-41-4
Hexachloro-1,3-butadiene	ND	ug/L	2.0	1	02/23/15	06:42	87-68-3

Method 6200B

Isopropylbenzene	ND	ug/L	0.50	1	02/23/15	06:42	98-82-8
Methylene Chloride	ND	ug/L	2.0	1	02/23/15	06:42	75-09-2
Methyl-tert-butyl ether	ND	ug/L	0.50	1	02/23/15	06:42	1634-04-4
Naphthalene	ND	ug/L	2.0	1	02/23/15	06:42	91-20-3
n-Propylbenzene	ND	ug/L	0.50	1	02/23/15	06:42	103-65-1
Styrene	ND	ug/L	0.50	1	02/23/15	06:42	100-42-5
1,1,1,2-Tetrachloroethane	ND	ug/L	0.50	1	02/23/15	06:42	630-20-6
1,1,2,2-Tetrachloroethane	ND	ug/L	0.50	1	02/23/15	06:42	79-34-5
Tetrachloroethene	ND	ug/L	0.50	1	02/23/15	06:42	127-18-4
Toluene	ND	ug/L	0.50	1	02/23/15	06:42	108-88-3
1,2,3-Trichlorobenzene	ND	ug/L	2.0	1	02/23/15	06:42	87-61-6
1,2,4-Trichlorobenzene	ND	ug/L	2.0	1	02/23/15	06:42	120-82-1
1,1,1-Trichloroethane	ND	ug/L	0.50	1	02/23/15	06:42	71-55-6
1,1,2-Trichloroethane	ND	ug/L	0.50	1	02/23/15	06:42	79-00-5
Trichloroethene	ND	ug/L	0.50	1	02/23/15	06:42	79-01-6
Trichlorofluoromethane	ND	ug/L	1.0	1	02/23/15	06:42	75-69-4
1,2,3-Trichloropropane	ND	ug/L	0.50	1	02/23/15	06:42	96-18-4
1,2,4-Trimethylbenzene	**1.9**	ug/L	0.50	1	02/23/15	06:42	95-63-6

Method 6200B

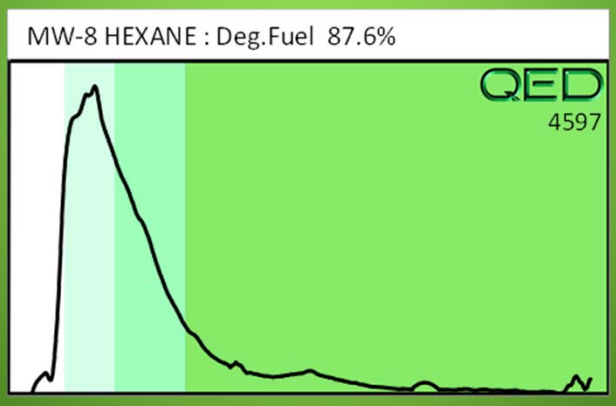
1,3,5-Trimethylbenzene	**2.2**	ug/L	0.50	1 02/23/15	06:42	108-67-8
Vinyl chloride	ND	ug/L	1.0	1 02/23/15	06:42	75-01-4
m&p-Xylene	ND	ug/L	1.0	1 02/23/15	06:42	179601-23-1
o-Xylene	ND	ug/L	0.50	1 02/23/15	06:42	95-47-6

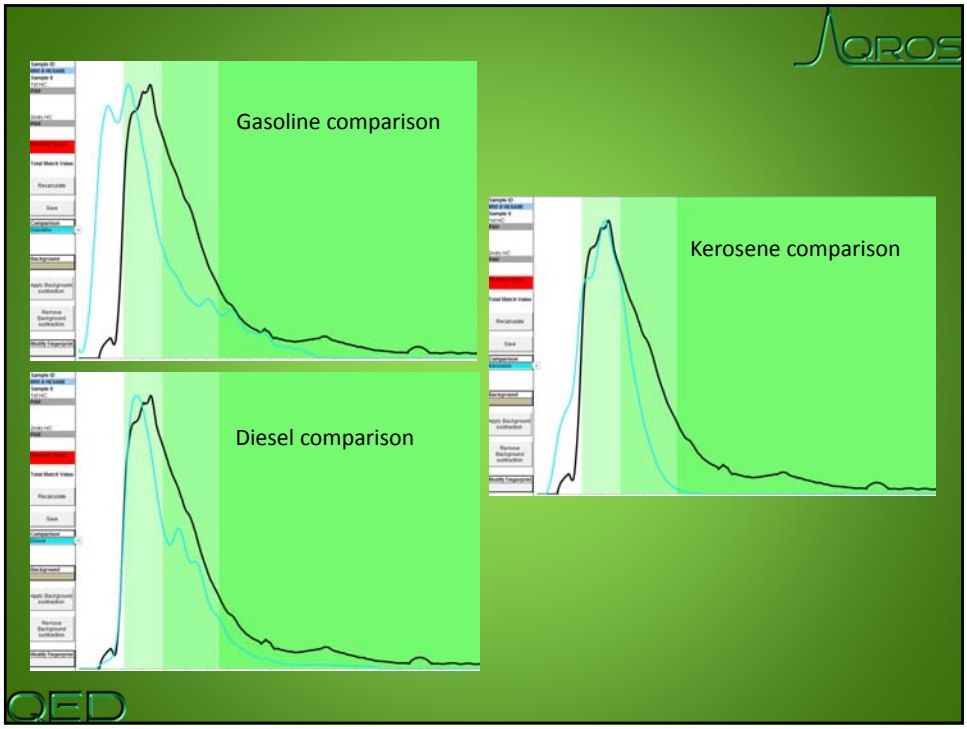
QED Method

- UV Fluorescence method
- Detects hundreds of compounds associated with petroleum compounds
- Detects hydrocarbons in C6 – C35 range
  - Only if soluble in water
- Provides fingerprint that can be used to identify the hydrocarbon type
- Detection limit approximately 10 ppb
- Recommended by DoT for TPH analysis of soil

QED Method

Matrix	Sample ID	Dilution used	BTEX (C6 - C9)	GRO (C5 - C10)	DRO (C10 - C35)	TPH (C5 - C35)	Total Aromatics (C10-C35)	16 EPA PAHs	BaP	Ratios			HC Fingerprint Match
										% light	% mid	% heavy	
h	MW-8 HEXANE	0.8	<0.039	<0.019	5.4	5.4	0.32	0.01	<0	0	94.7	5.3	Deg.Fuel (FCM) 87.6%

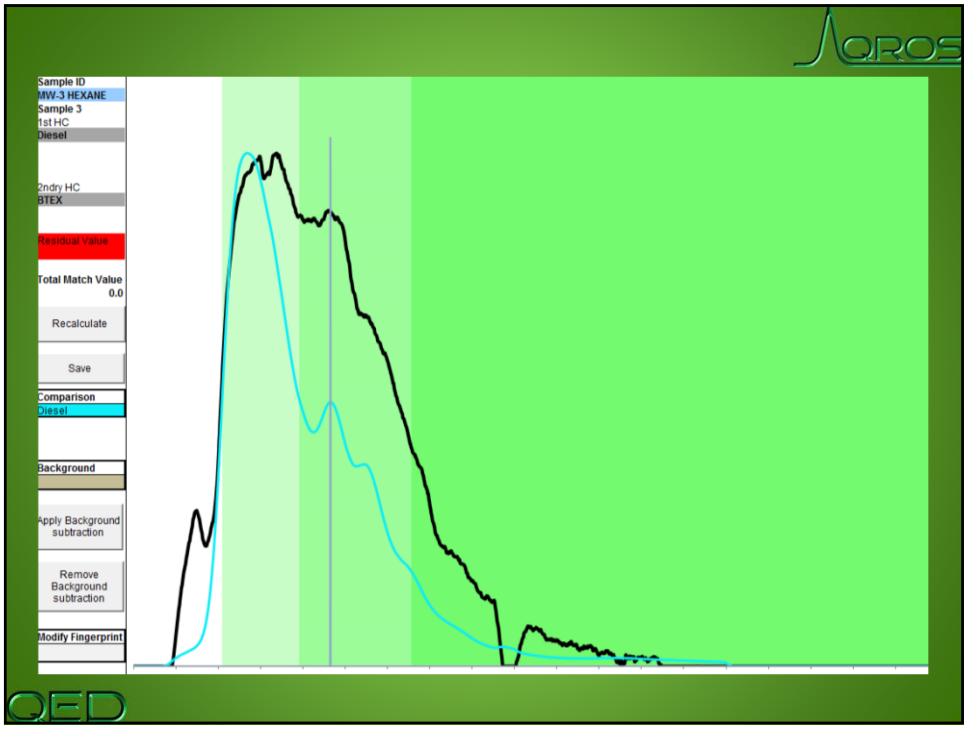



Gasoline comparison
Diesel comparison
Kerosene comparison
QED


QED

QED v 6200B - Site 1

	QED	mg/L		6200B	mg/L
	GRO	DRO	Identification	GRO	DRO
MW-1	<0.019	0.06	Deg.Fuel (FCM) 69.7%	ND	ND
MW-2	<0.019	0.22	Deg.Fuel Residue (FCM) 48.9%	ND	ND
MW-3	<0.019	0.1	Deg.Diesel (FCM) 66.4%	ND	ND
MW-4	0.079	2.3	Deg.Fuel (FCM) 62%	0.0147	0.0041
MW-5	<0.019	0.04	Deg.Fuel Residue (FCM) 45.9%	ND	ND
MW-6	0.076	0.11	Deg.Fuel Residue (FCM) 74.9%	ND	ND
MW-7	<0.019	0.06	V.Deg.Diesel (FCM) 81.5%	ND	ND
MW-8	<0.019	5.4	Deg.Fuel (FCM) 87.6%	0.0041	ND



QED v 6200B - Site 2

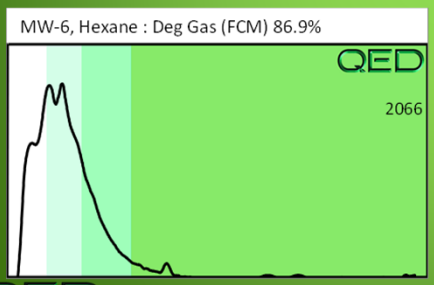
	QED	mg/L		6200B	mg/L
	GRO	DRO	Identification	GRO	DRO
MW-3	<0.036	0.05	V.Deg.PHC (FCM)	ND	ND
MW-5A	<0.036	0.05	V.Deg.PHC (FCM)	0.003	0.002
MW-6	0.81	2.1	Deg Gas (FCM) 86.9%	1.94	0.134
MW-7	<0.036	<0.01	Pet.Hyd not Detected	ND	ND
MW-11	<0.036	0.01	Background Organics (FCM)	ND	ND
MW-13	<0.036	0.01	Background Organics (FCM)	0.015	ND
MW-14	<0.036	<0.01	Pet.Hyd not Detected (FCM)	ND	ND
MW-15	1.8	4.1	Deg Gas (FCM) 88%	4.26	0.289
MW-16	<0.036	0.05	Deg.Diesel (FCM) 56%	ND	ND
MW-18	<0.036	<0.01	Pet.Hyd not Detected	ND	ND

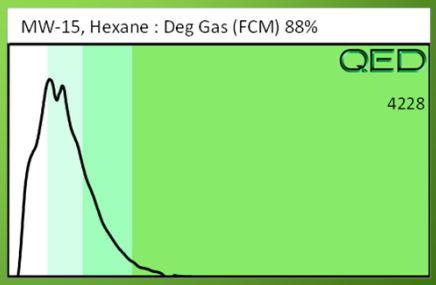
A method with a low detection limit for a limited number of compounds may not give a better overall detection limit than a method with higher individual detection limits that detects many more compounds

Comparison of Monitoring Wells

Both wells from Site 2

mg/L	MW-6	MW-15
Benzene	0.818	0.402
Ethyl Benzene	0.422	0.724
IsoPropylbenzene	0.0222	0.0453
n-propylbenzene	0.0438	0.119
toluene	0.043	ND
1,2,4-Trimethylbenzene	0.204	0.88
1,3,5-trimethylbenzene	0.0836	0.249
m&p xylene	0.215	1.7
o xylene	0.0892	0.145
naphthalene	0.135	0.289
MTBE	0.0678	0.0277





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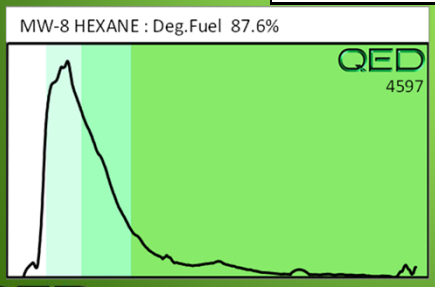
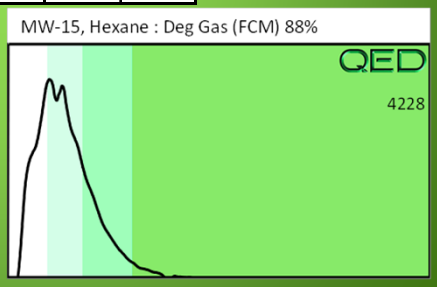
Comparison of Monitoring Wells

MW-8 from Site 1

MW-15 from Site 2

mg/L	MW-8	MW-15
Benzene	ND	0.402
Ethyl Benzene	ND	0.724
IsoPropylbenzene	ND	0.0453
n-propylbenzene	ND	0.119
toluene	ND	ND
1,2,4-Trimethylbenzene	ND	0.88
1,3,5-trimethylbenzene	ND	0.249
m&p xylene	0.0019	1.7
o xylene	0.0022	0.145
naphthalene	ND	0.289
MTBE	ND	0.0277





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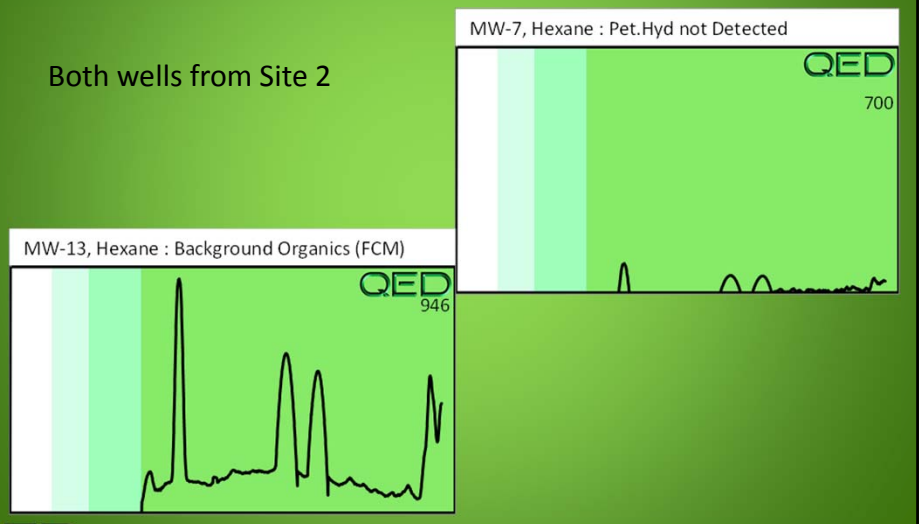
No Detect and Background Organic

Both wells from Site 2



Cost of Analysis

- QED from $25/sample if sampler does analysis on site and runs 10 samples
  - It takes <5 minutes to prepare and analyse a sample
- 6200B from $45/sample
  - 1 to 2 week turnaround

Why Monitor for TPH

	6200B	QED
• Compliance	✓	X
• Permit	✓	X
• TPH concentrations changing	X	✓
• TPH type changing	X	✓
– New source		
– New pathway		
• External influences	X	✓

Regulations v Technology

- New technology brings improvements in the way we do things
- New methods that reduce cost or are measurably better should be used
- Long time frame to change approved methods
- Stakeholders disadvantaged
- Liability issues

How can change be made

- Should Stakeholders lobby regulators ?
- Do consultants have a duty of care to inform stakeholders of new technologies ?
- Should regulators initiate change independently ?
- Should regulators set up the approval process to allow for better or alternative methods to automatically replace older methods ?