Methane from Biofuels

NEIWPCC Webinar

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Methane Hazards

- Methane is a flammable gas
  - Lower explosive limit (LEL) = 5%
  - Upper explosive limit (UEL) = 15%
  - Mixtures containing less than 21% oxygen may become flammable when mixed with air

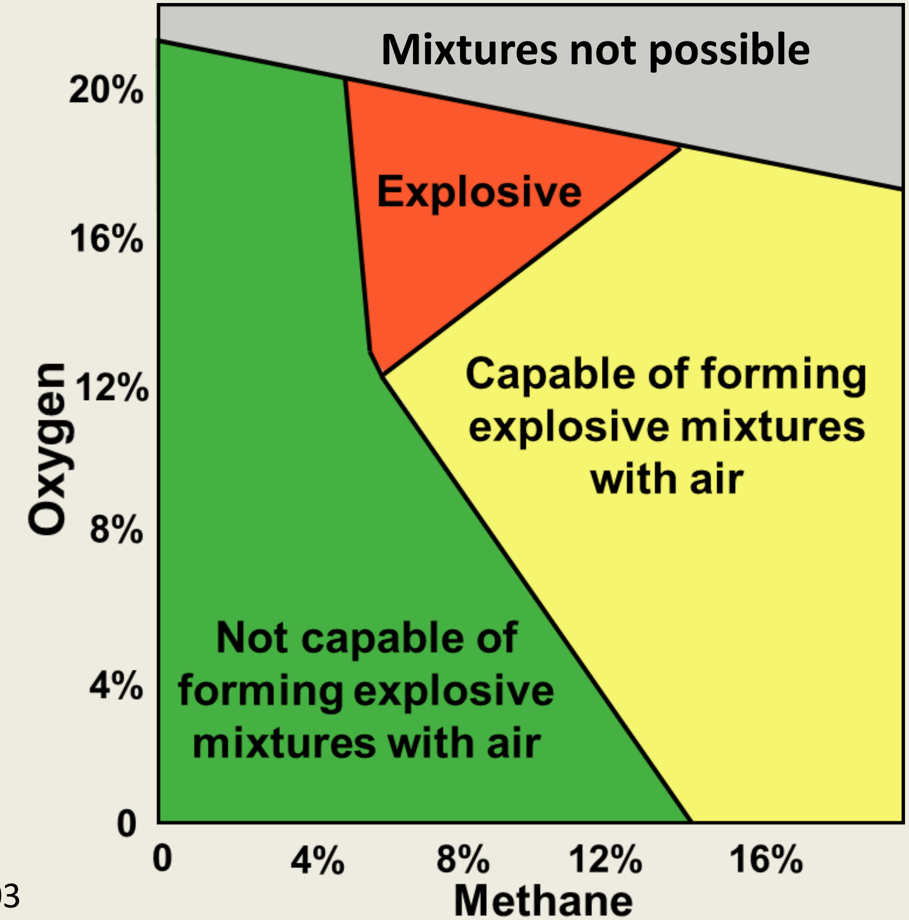


Figure source:
30 CFR 57.22003

Concerns with Biofuels

- Very high methane generation rates observed at ethanol and biodiesel release sites
  - May create immediate hazards (methane has no odor!)
- Different SCM than a petroleum release
  - Different analytical parameters, meters, investigation techniques
  - Longer duration monitoring
  - Additional VI monitoring may be required
- High ethanol concentrations (6% - 10%) may initially inhibit biological degradation
  - Time delay between release and methane generation possible

Findings from Case Studies

- Methane appearance may be delayed, suggesting extended monitoring if receptors are present
  - Low or no initial methane may not mean no future risk
  - May appear without detection of source biofuel
- Have seen >12% methane in a well casing headspace with aqueous-phase methane as low as 7,200 µg/L
  - Sub-saturation levels of dissolved methane can create risks
- Methane flux rates exceeding those of a Municipal Solid Waste Landfill have been observed

Findings from Case Studies

- Methane levels as high as 22% v/v in a closed surface chamber have been observed
- Biogenic gas production can lead to:
  - Stripping of petroleum VOCs from groundwater and advection of petroleum vapor by methane and other biogenic gases
  - Methane exerts a large oxygen demand which can allow petroleum vapors and methane to migrate further
- Methane in soil gas maybe the risk driver for high % biofuel blend releases

Ebullition

Surface and Flux Measurements

Surface sampler (5 gal bucket)

Flux Ring

Monitoring Well Headspace Measurements

Landfill gas meter (GEM)

Tubing

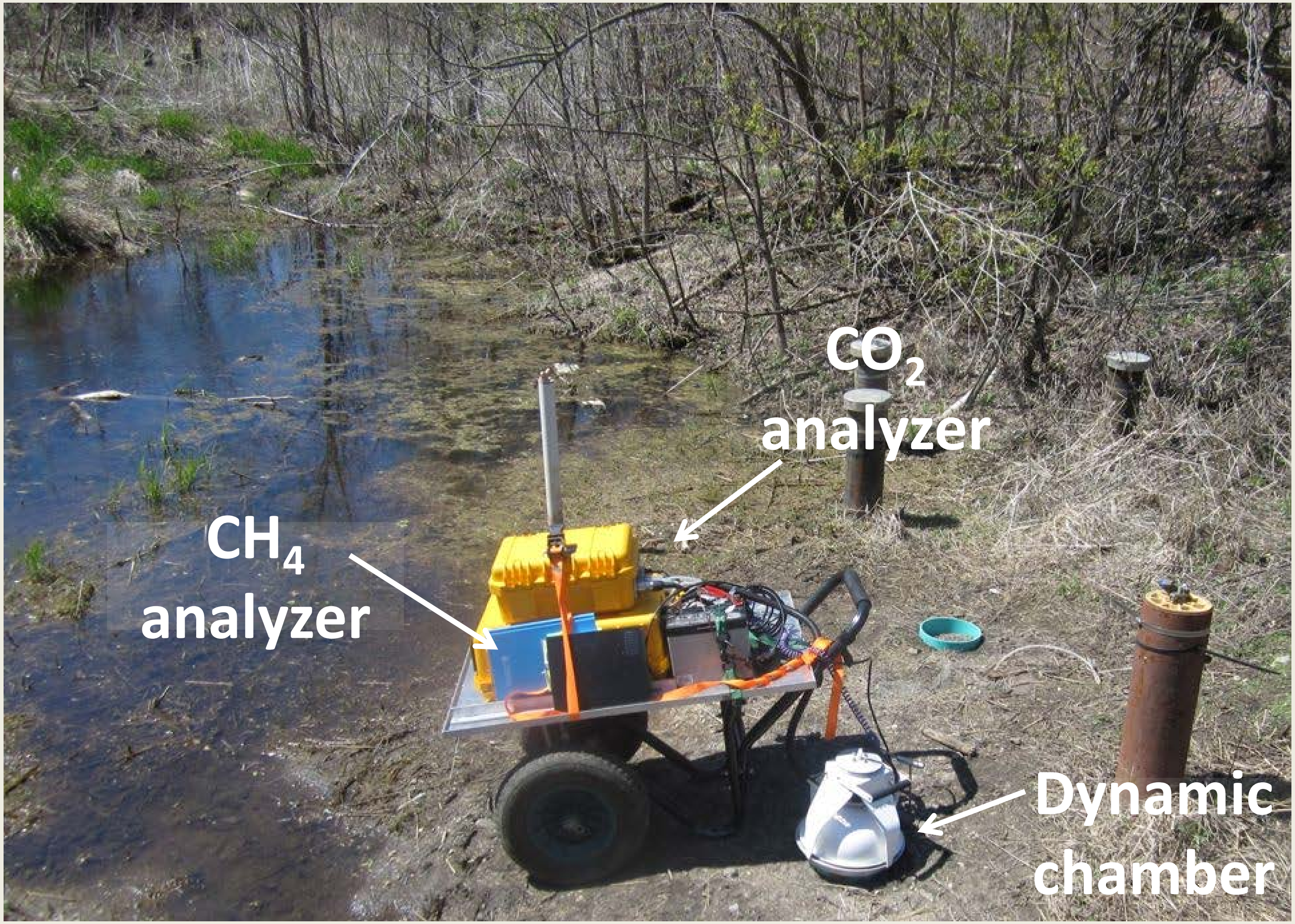
Stopper (toy ball)

Monitoring well headspace concentrations at a B100 Site

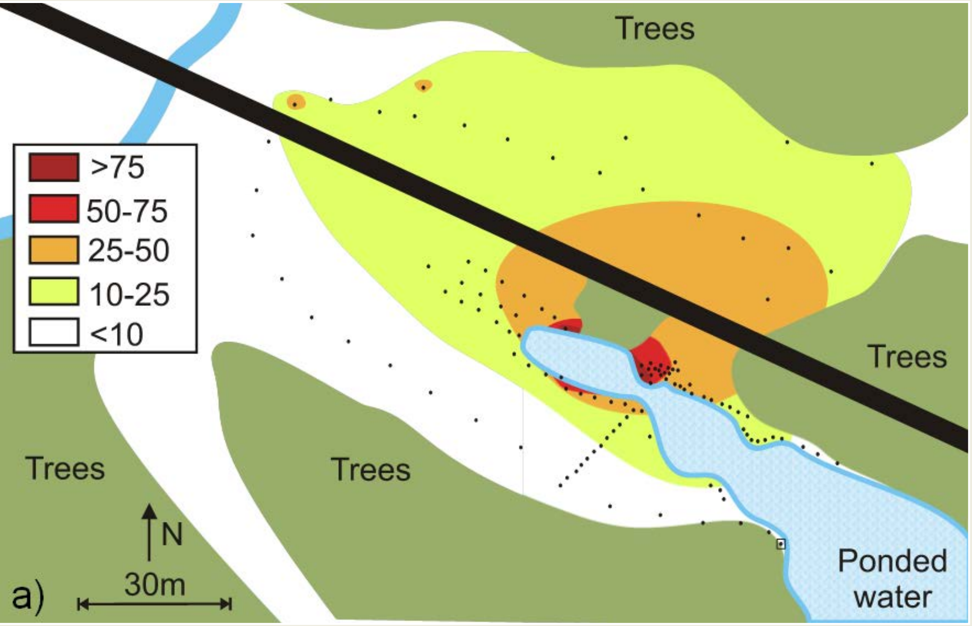
Well	CH_4 %	CO_2 %	O_2 %	PID ppm
MW-1	0	2.9	14.6	2.0
MW-2	67.0	33.0	0	3.2
MW-3	55.3	27.4	0	4.7
MW-4	65.7	34.3	0.1	7.8
MW-5	0	3.5	9.7	1.2
MW-6	0	7.6	2.1	6.8
MW-7	38.4	25.0	0	1.6

November 2006 - Cambria, MN
25,000 gals DFE (E95)

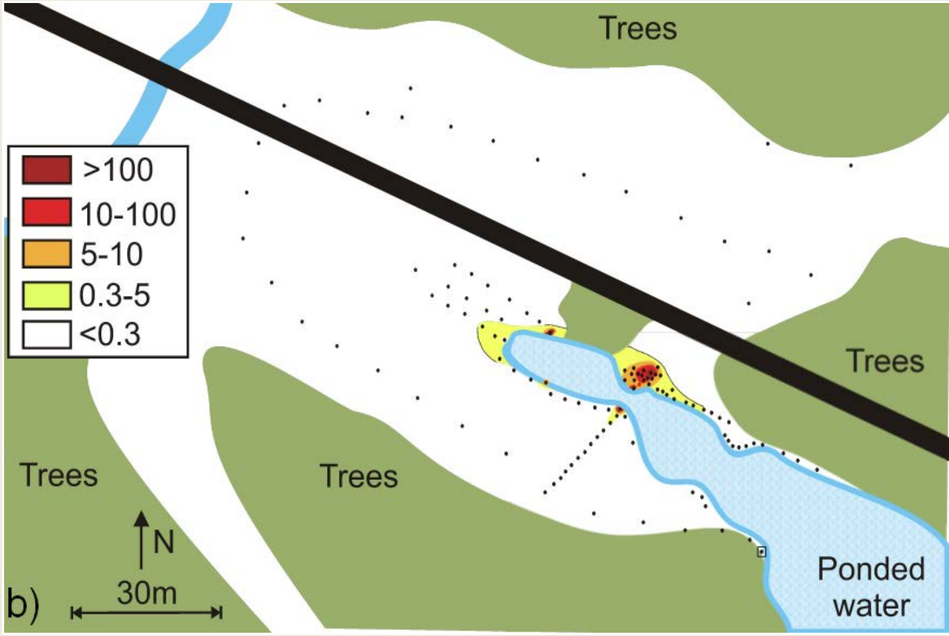
Real-time CO_2 and CH_4 Surficial Flux Measurements



Real Time Gas Flux Results at Cambria



- **Locally high** CO_2 and CH_4 fluxes
- Related to existing EtOH in capillary fringe



a) CO_2 effluxes

b) CH_4 effluxes

[μmol m^{-2} s^{-1}]

Sihota et al., J. Contam. Hydrol. 2013

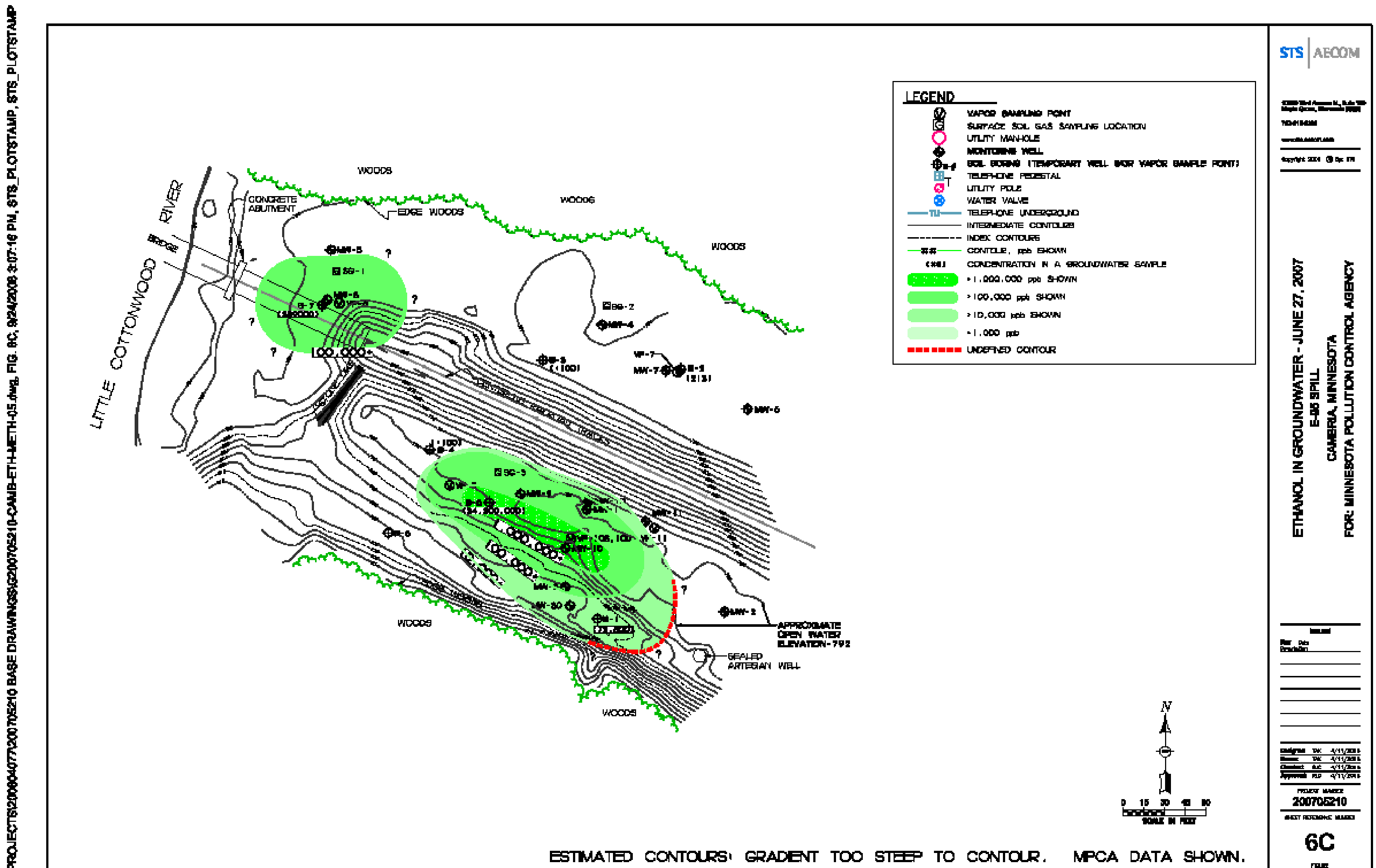
Table 2
Real time CO_2 and CH_4 effluxes measured at Balaton and Cambria sites in 2012.

		Balaton	Cambria
CO_2 efflux [μmol m^{-2} s^{-1}]	Minimum	0.6	0.5
	Maximum	178.4	174.7
CH_4 Efflux [μmol m^{-2} s^{-1}]	Minimum	ND	ND
	Maximum	9.1	392.9
Approximate background CO_2 efflux[a] (±SE, n) [μmol m^{-2} s^{-1}]		5 (1, 2)	6 (0.8, 2)
Average CO_2 efflux attributable of DFE degradation in the source zone (±SE, n) [μmol m^{-2} s^{-1}]		21 (4, 55)	26 (2, 128)
Average CH_4 efflux attributable of DFE degradation in the source zone (±SE, n) [μmol m^{-2} s^{-1}]		1.4 (0.5,19)	24 (9, 46)
Total carbon flux from DFE degradation in the source zone [μmol m^{-2} s^{-1}]	Average (±SE, n)	22 (4, 55)	32 (5, 128)
	Minimum	5	6
	Maximum	174	500
Source Zone CH_4:CO_2 ratio[b]	Average (±SE, n)	0.04 (0.01, 19)	0.5 (0.1, 46)
	Minimum	0.003	0.005
	Maximum	0.12	3.4[c]
Depth-integrated DFE degradation rate in the source zone [mgEtOH m^{-2} s^{-1}]	Average (±SE, n)	0.3 (0.06, 55)	0.5 (0.07, 128)
	Minimum	0.07	0.1
	Maximum	3	8

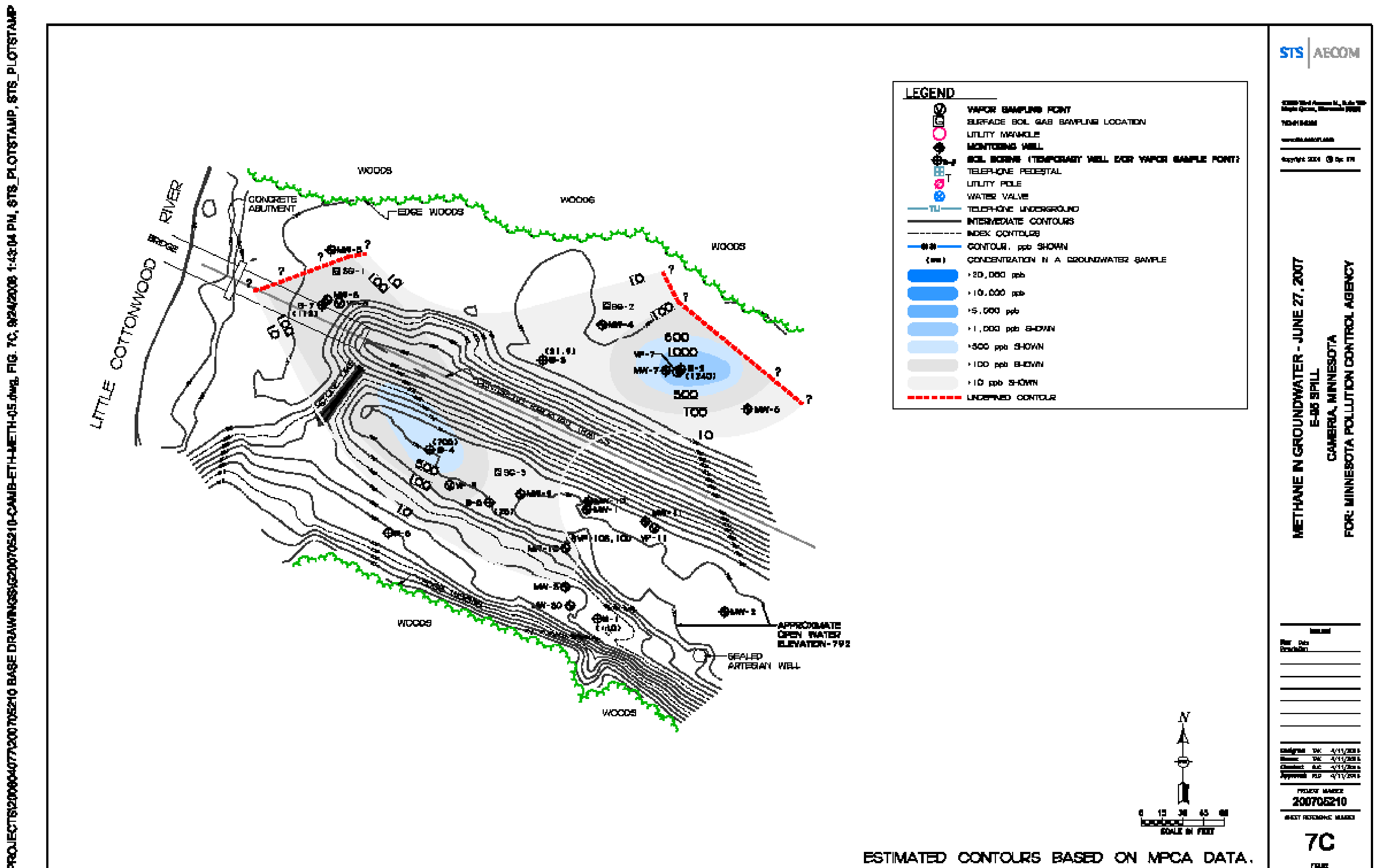
[a] Within the area defined as the source zone and CH_4 fluxes were detected.
[b] Assumed (geometric mean of replicate measurements). ND: non-detect. BG: background CO_2 efflux correction used. SE = standard error, n = number of measurements.
[c] Based on an ebullition flux.

- Published active MSW landfill CH_4 flux rates: **37-94** µmol m-^{2} s-^{1}
- Cambria source zone: ave **24**, max **393** µmol m-^{2} s-^{1}
- **24 µmol m-^{2} s-^{1} = 50 L of methane gas per m^2 per day!**

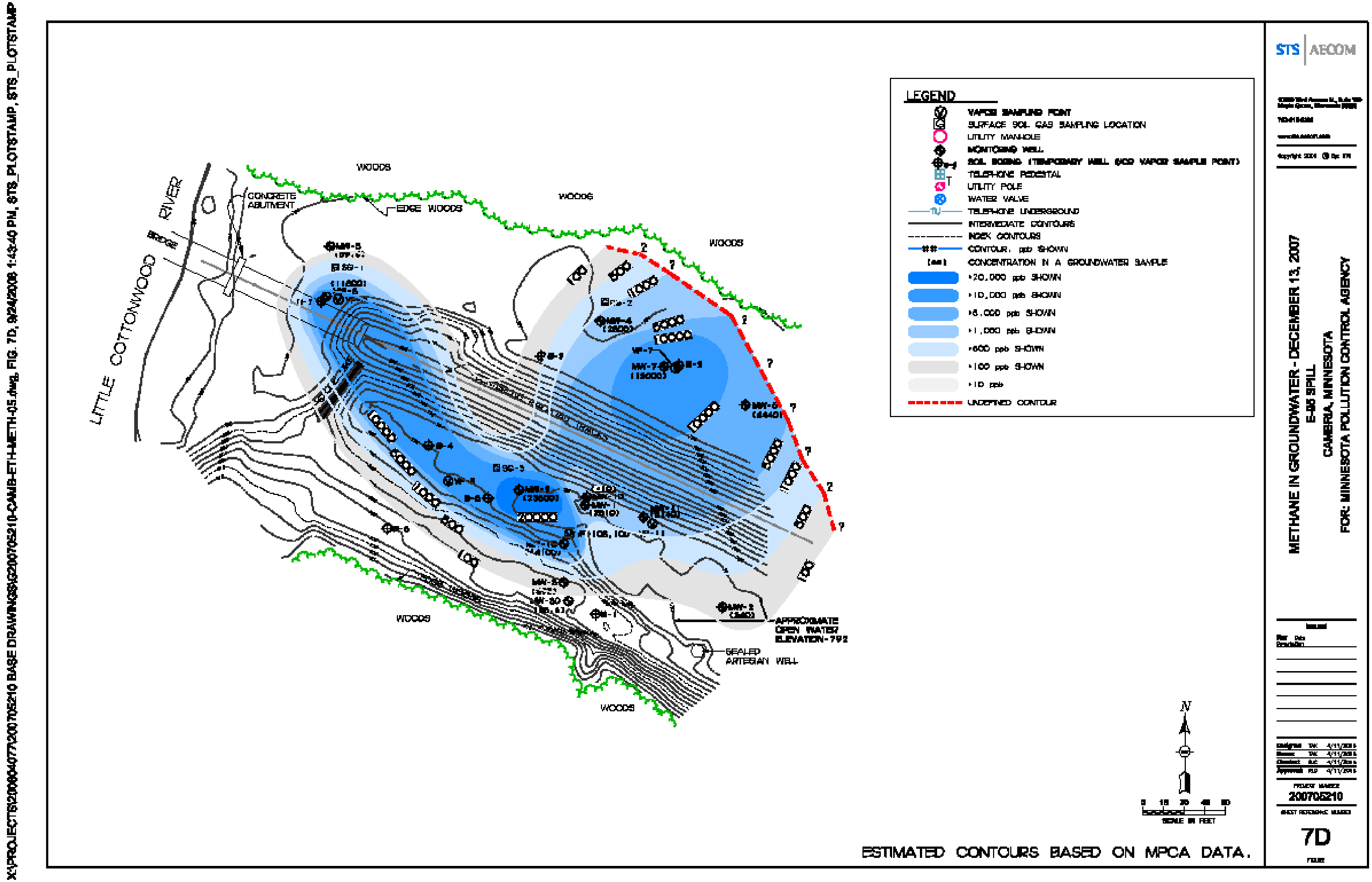
Cambria: Ethanol in Ground Water 6/07



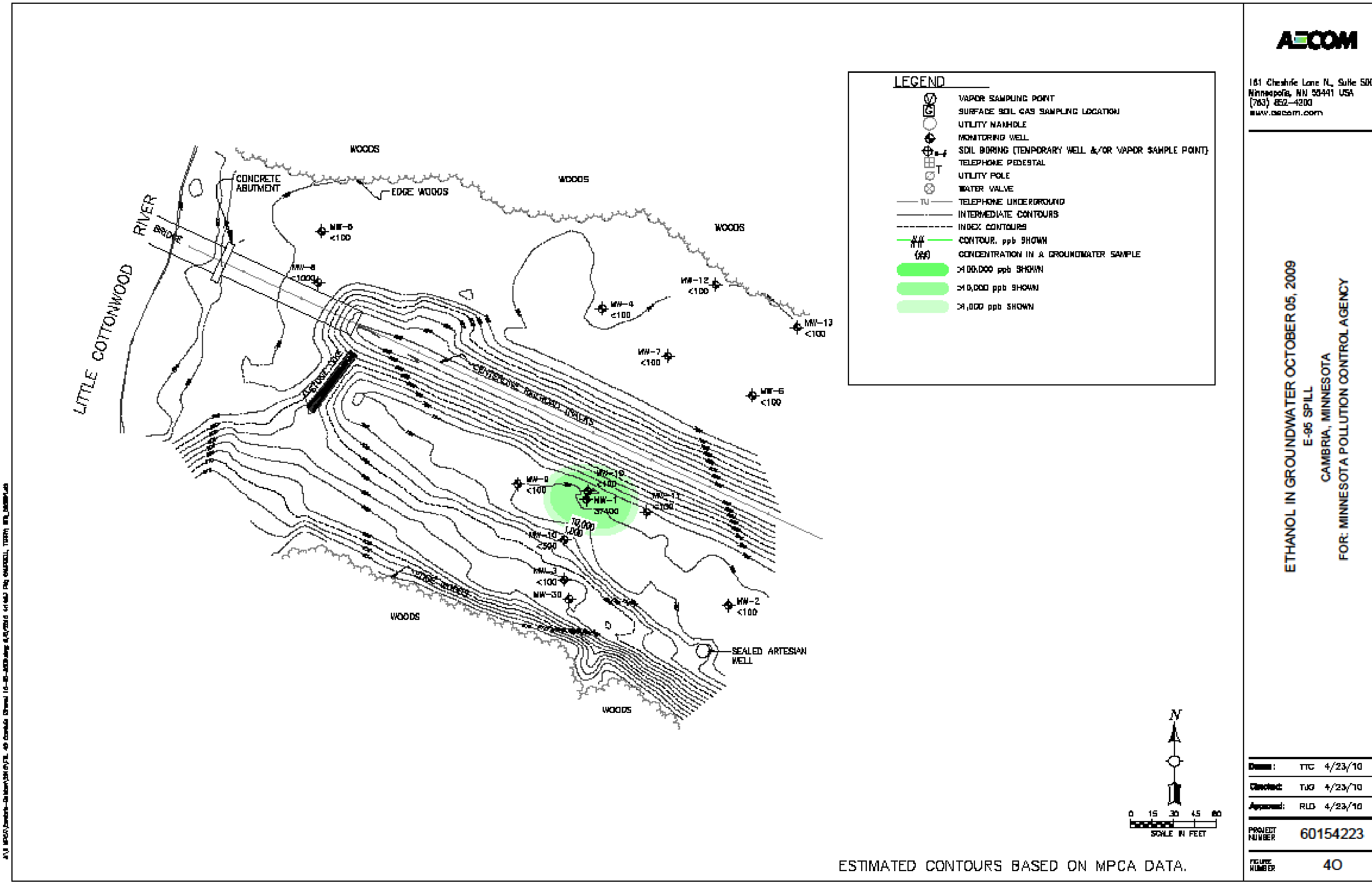
Cambria: Methane in Ground Water 6/07



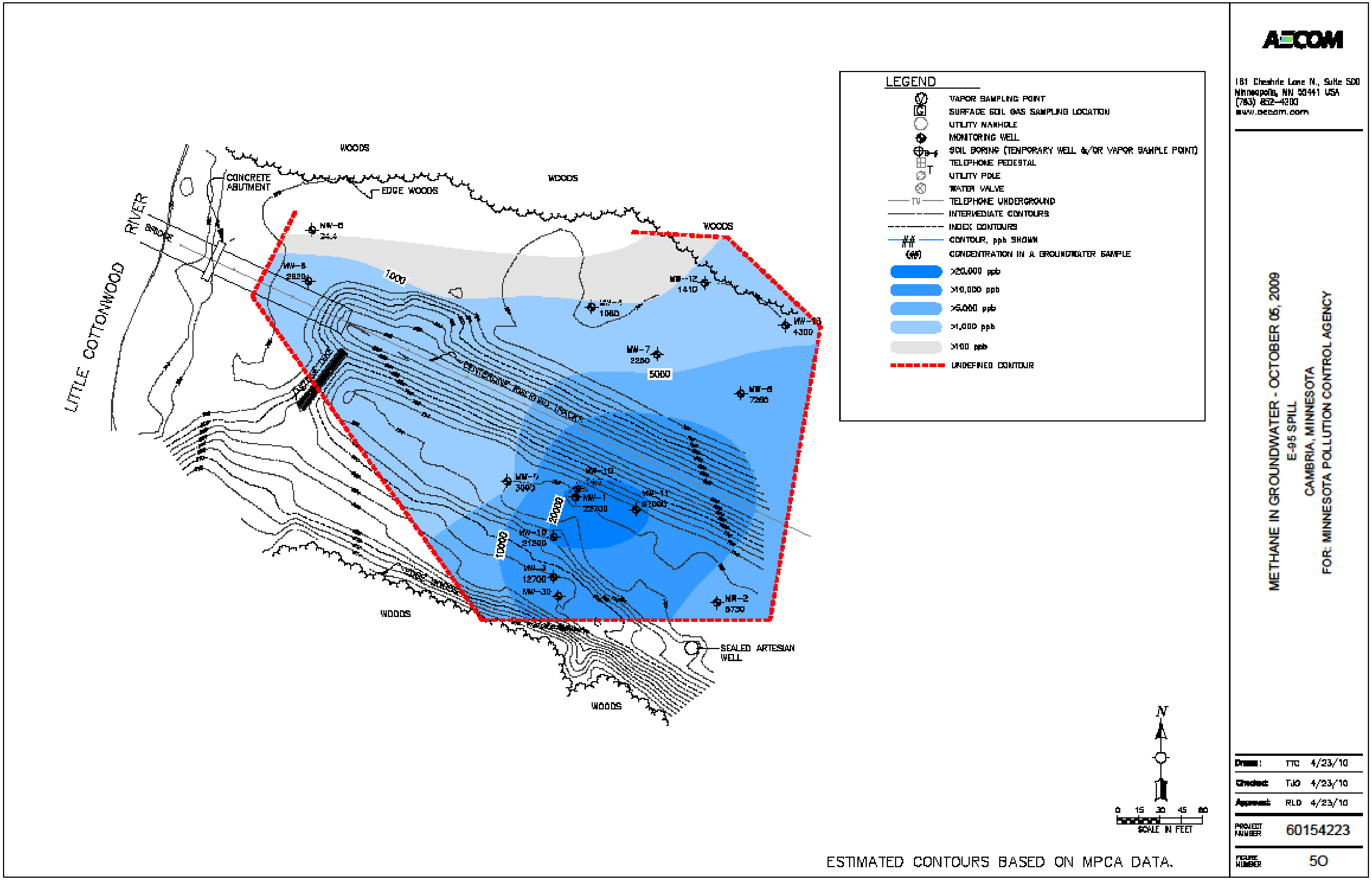
Cambria: Methane in Ground Water 12/07



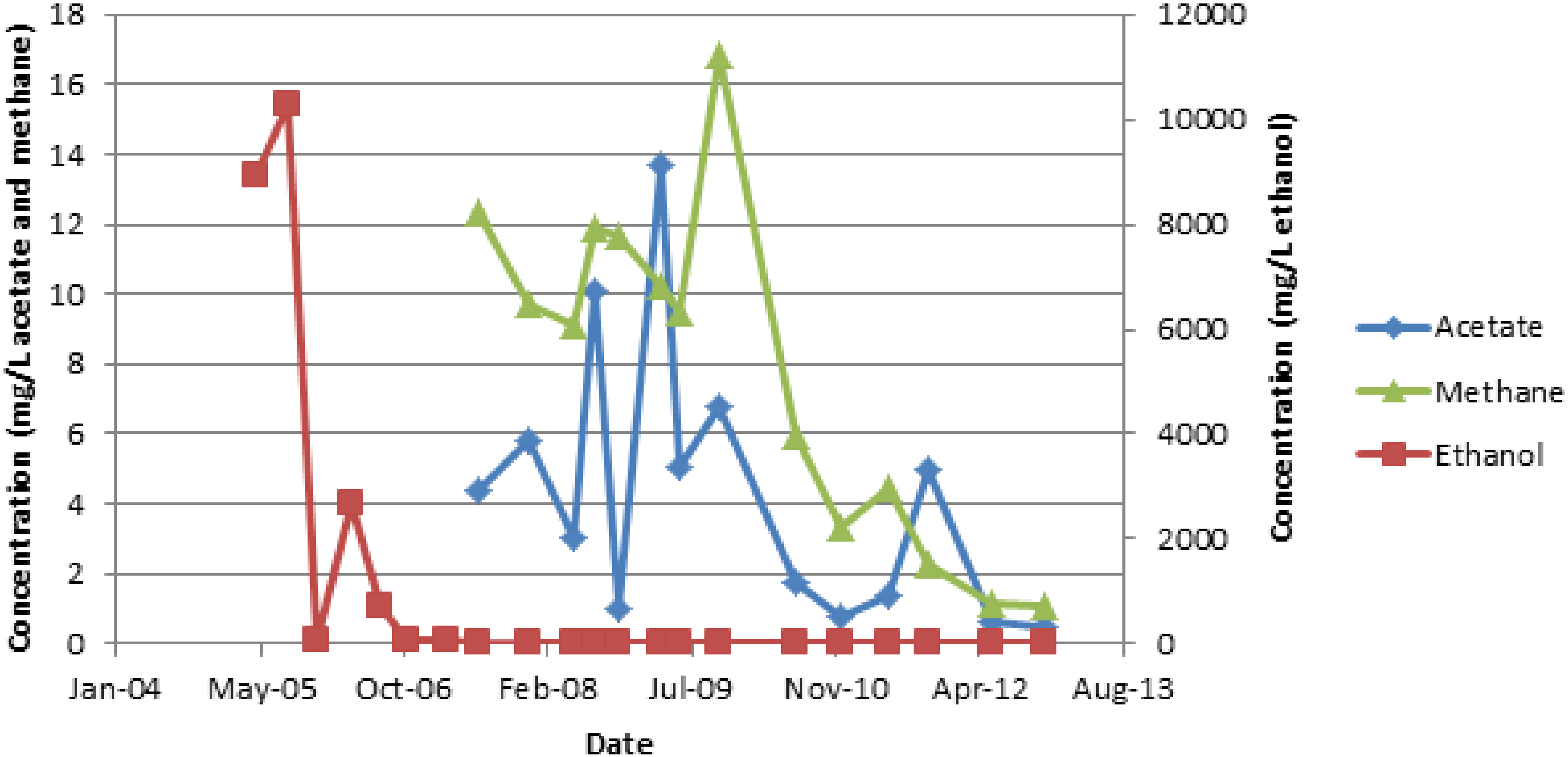
Cambria: Ethanol in Ground Water 10/09



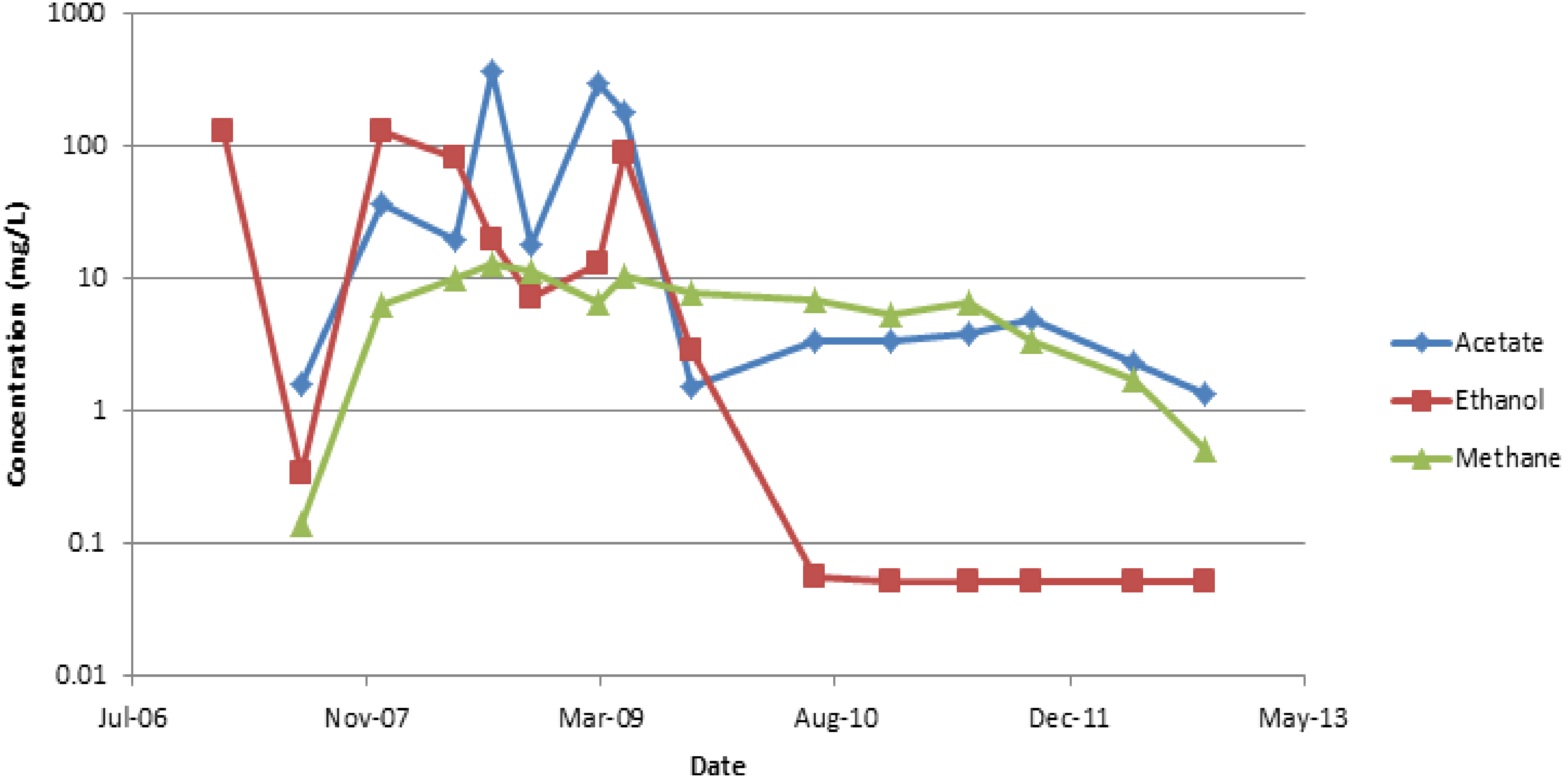
Cambria: Methane in Ground Water 10/09



Balaton Parameter Concentrations Over Time

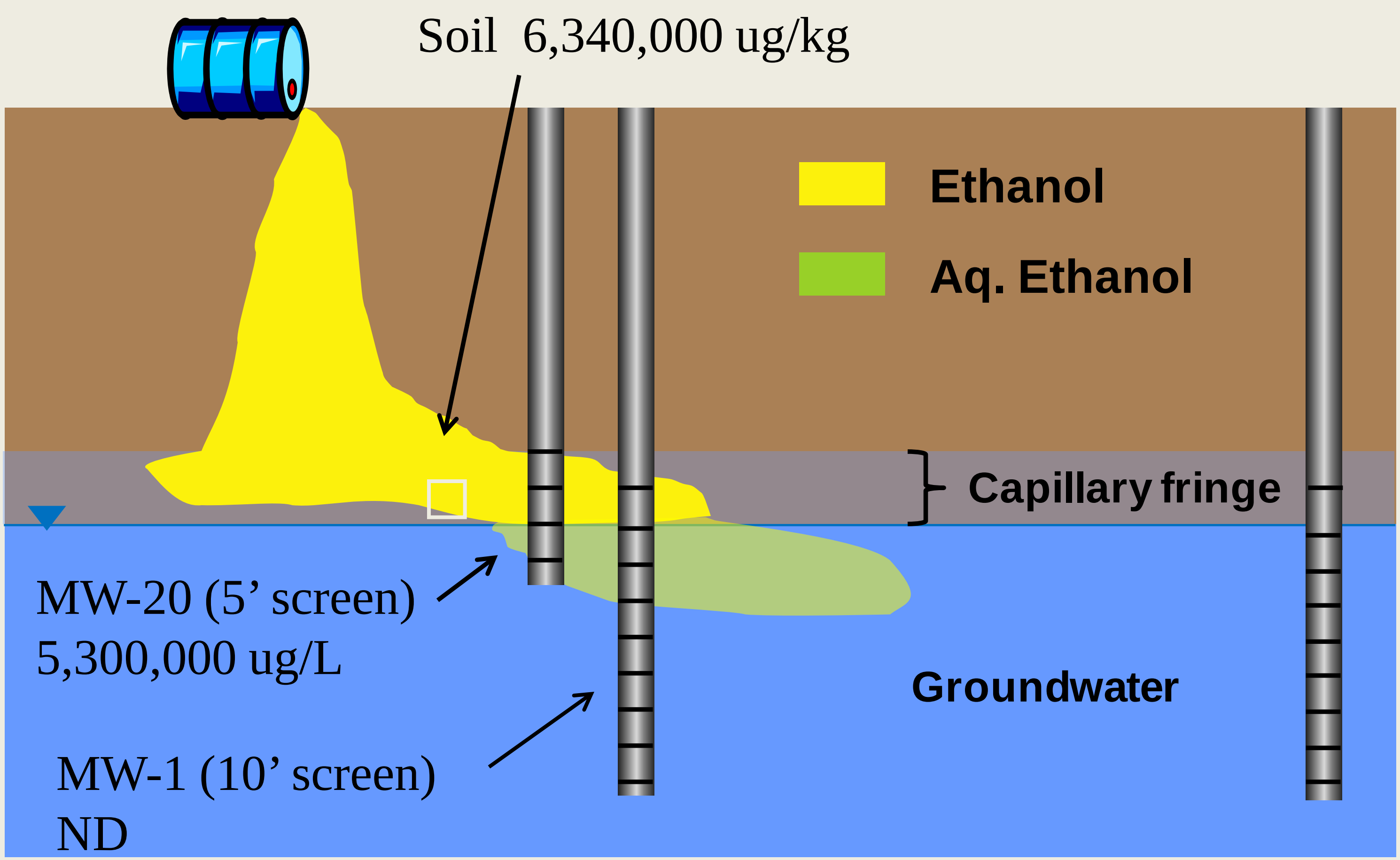


Cambria Parameter Concentrations Over Time



Cambria, MN

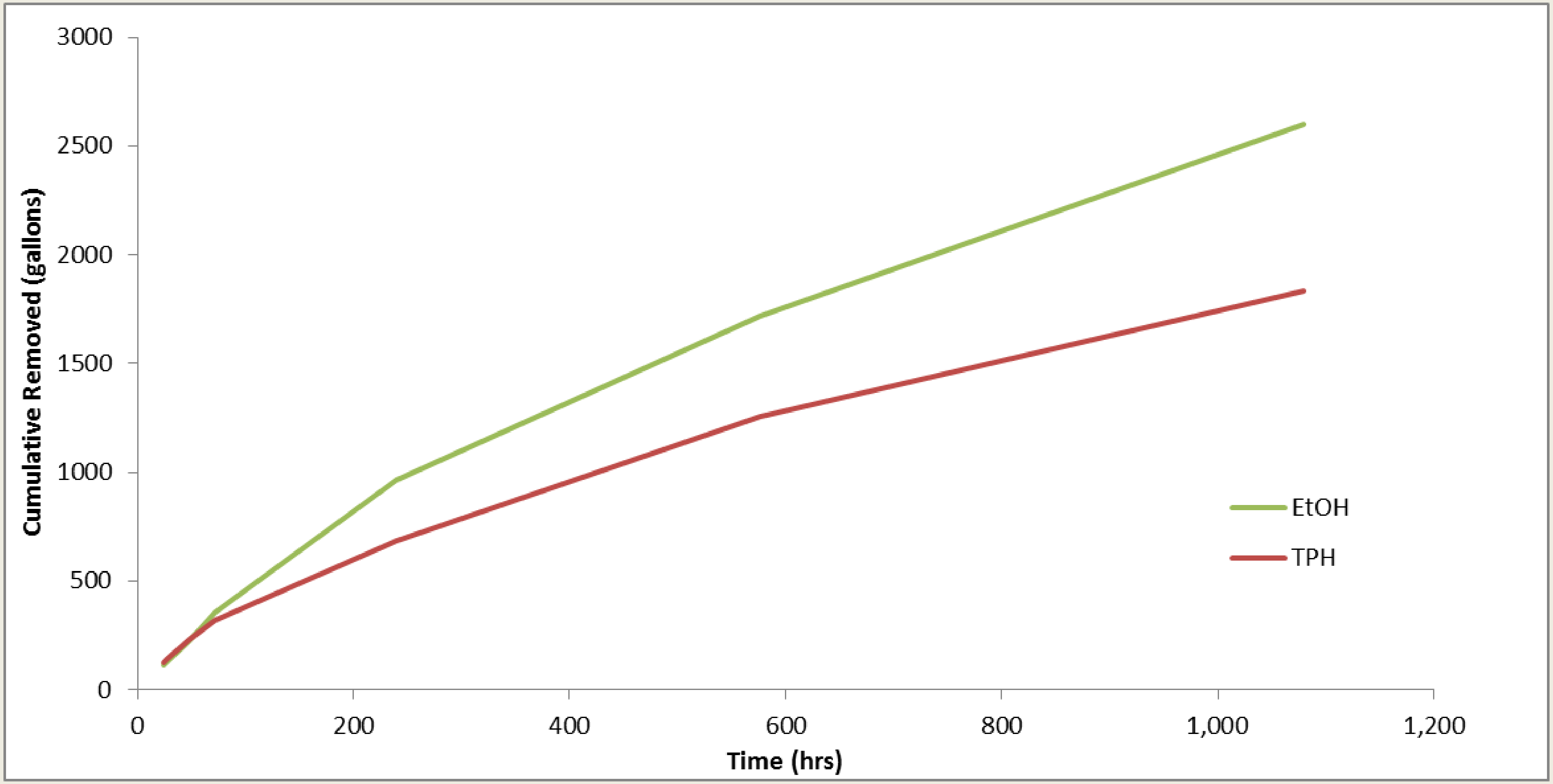
Oct 2011 Results



Remediation

- Simple - Just add (a lot) of oxygen!
  - Very few real world case studies
  - SVE, AS, Bioventing should work
- Methane risks can be remedied just like any other PVI issue
  - Sub-slab depressurization (radon) systems
- Groundwater recovery (PnT) can remove significant mass of ethanol if started immediately
  - Remove source, no ethanol, no methane

SVE Results, E85 Release



July 2008 – Lanesboro, MN
3,000 gals E95

References

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Questions?

August 2014

430,000 gal DFE (E95) AST

~ 7000 gals released

Cause: Thin film epoxy coating failure, followed by stress corrosion cracking of steel floor plate