Stream Monitoring for Evaluating Groundwater Methane Associated with Shale-Gas Development

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Stream-reach mass balance uses methane in gaining streams to calculate groundwater concentration and potential contamination

- Baseflow of a gaining stream gives a weighted average
- Represents a larger capture area and at lower cost than monitoring wells

Presentation topics:

- History of stream gas tracer studies
- Methane persistence in streams
- Gas transfer (atmospheric loss)
- Bacterial consumption (oxidation)
- Transport modeling to determine methane loads
- Isotopic fingerprinting

Previous stream gas-tracer studies

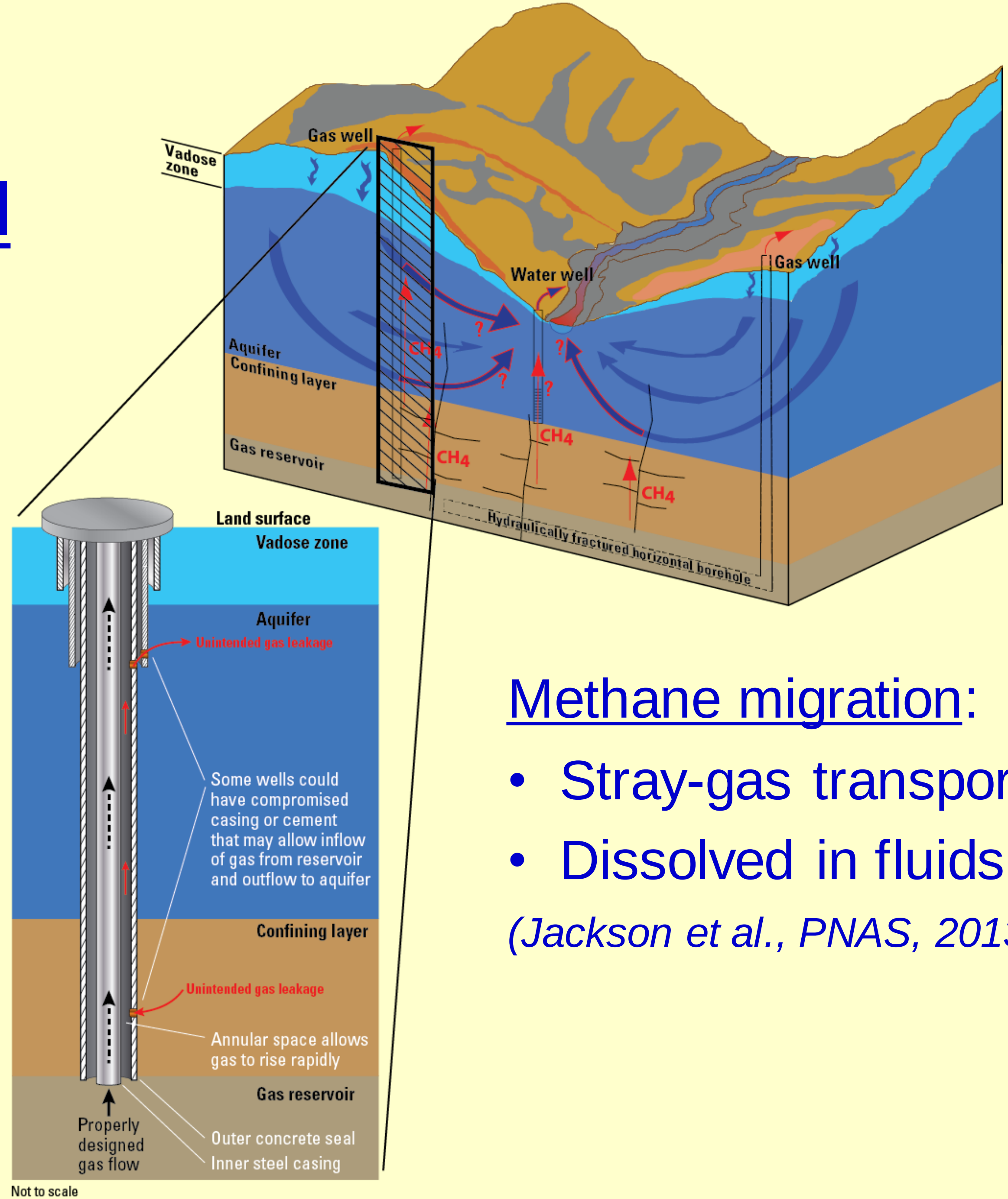
- Initial gas tracer methods development: Kilpatrick and Cobb, 1985)
- Stream re-aeration (^{85}Kr, methyl Cl, propane) (Tsivoglou, 1967; Tsivoglou and Neal, 1976; Wilcock, 1984; Jin et al., 2012)
- Groundwater Inflow (SF_6, propane) (Genereux and Hammond, 1990, 1992; Wanninkhof et al., 1990; Cook et al., 2006)
- Carbon cycling / evasion to atmosphere (propane, CO_2) (Wallin et al., 2011)
- Contaminant (toluene) volatilization versus biodegradation (propane) (Kim et al., 1995)
- Stream nitrogen fluxes / demitrfication (CFCs, NO_3,SF_6) (Duran and Hemond, 1984; Bohlke et al., 2004, Tobias et al., 2009)
- Groundwater dating (He, Kr) (Stolp et al., 2010; Solomon et al., in review)

Our studies document the first stream CH_4 injections, which we use to quantify groundwater CH_4 concentrations and fluxes (Heilweil et al., 2013; Heilweil et al., in review)

Why Care About Groundwater Methane?

- Public concern – increased contamination with proximity to gas wells (Jackson et al., PNAS, 2014)
- Explosive hazard (basements, pump houses)
- Early warning indicator of other contaminants:
  - Fracking fluids
  - Flow-back water with high salinity and radioactivity
- Potent greenhouse gas (IPCC reported greenhouse potency up to 84 x CO_2)

Conceptual Model



Methane pathways:

- Improperly completed well bores
- Fractures

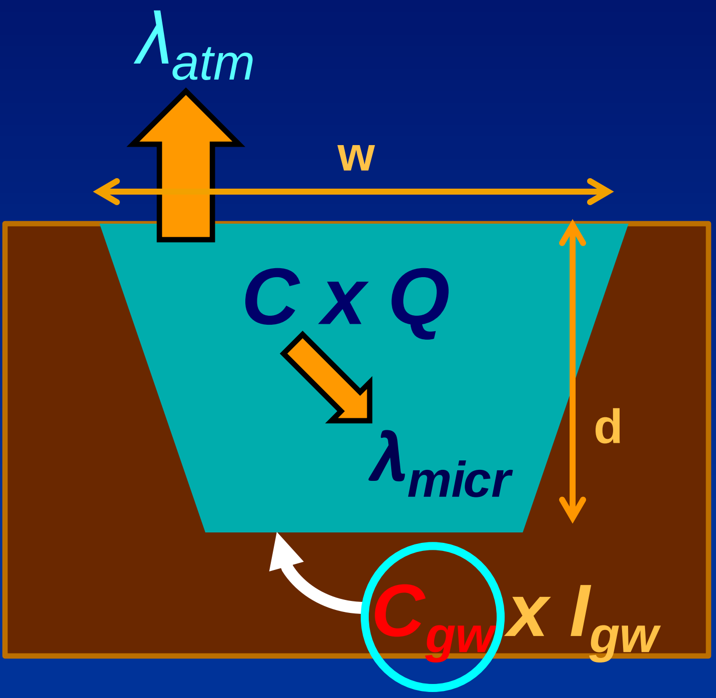
Methane migration:

- Stray-gas transport
- Dissolved in fluids

(Jackson et al., PNAS, 2013)

Stream-Reach Methane Mass Balance

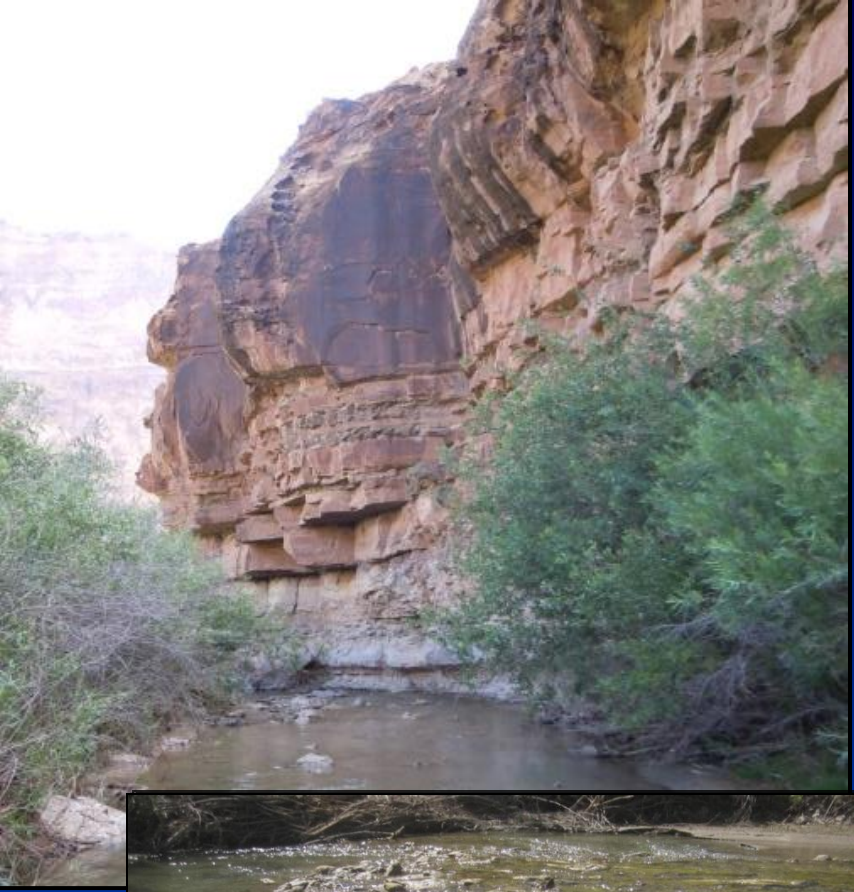
- Stream CH_4 [*C*] and load (C x Q) are function of groundwater concentration (C_{gw}) and influx (I_{gw}), loss to the atmosphere (λ_{atm}) , and microbial oxidation to CO_2 (λ_{micr})
- λ_{atm} varies by stream - function of turbulence, temperature, wind shear, molecular diffusion *(Wanninkhof , WRR,1990)*
- Need to determine *Q*, I_{gw}, *C*, $^*\lambda$ (λ_{atm} + λ_{micr}) to solve for C_{gw}



$$Q\frac{\partial C}{\partial x} = I_{gw}(C_{gw} - C) - {}^*\lambda dwC$$

(Heilweil et al., Groundwater, 2013)

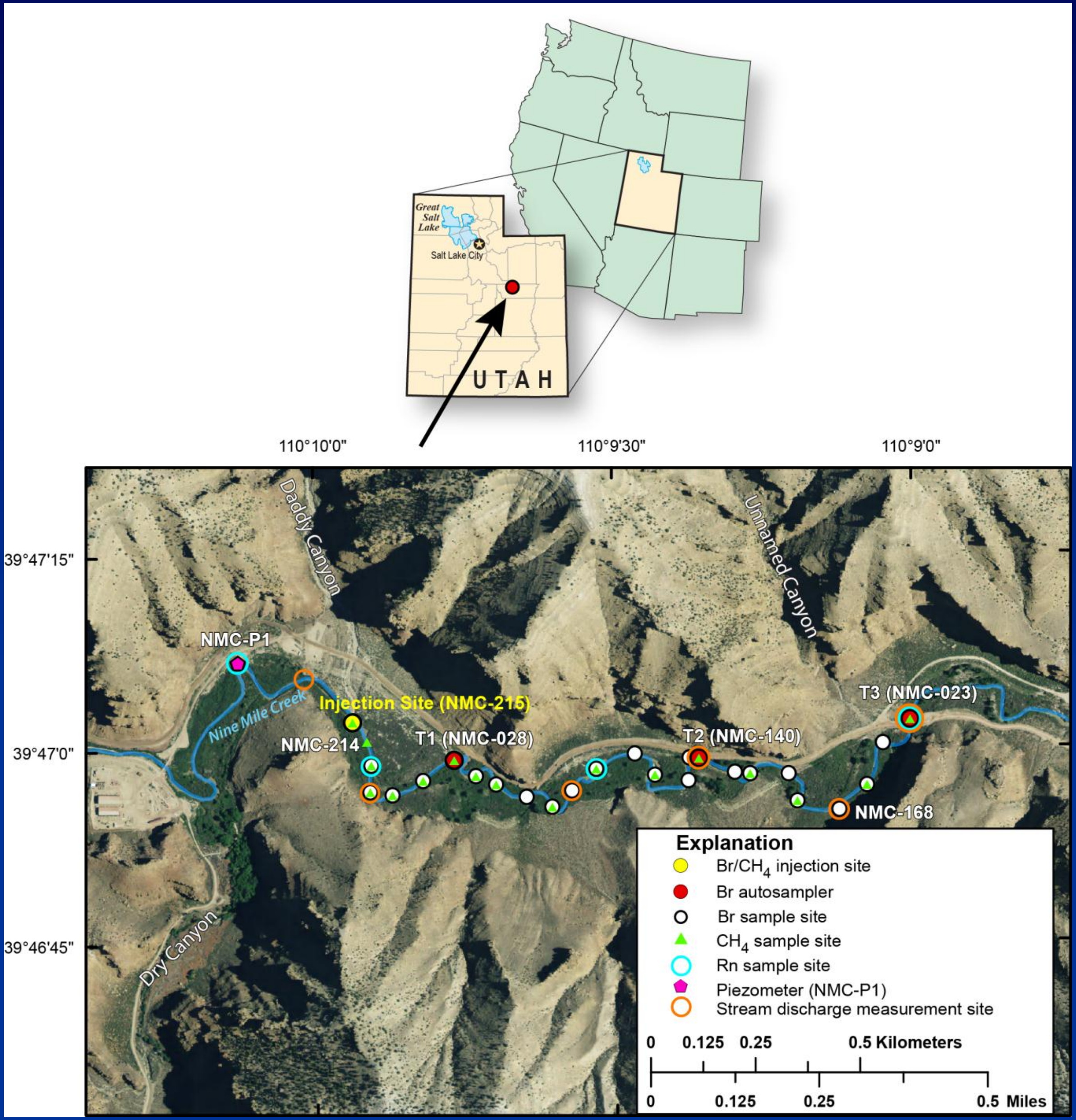
Three study locations

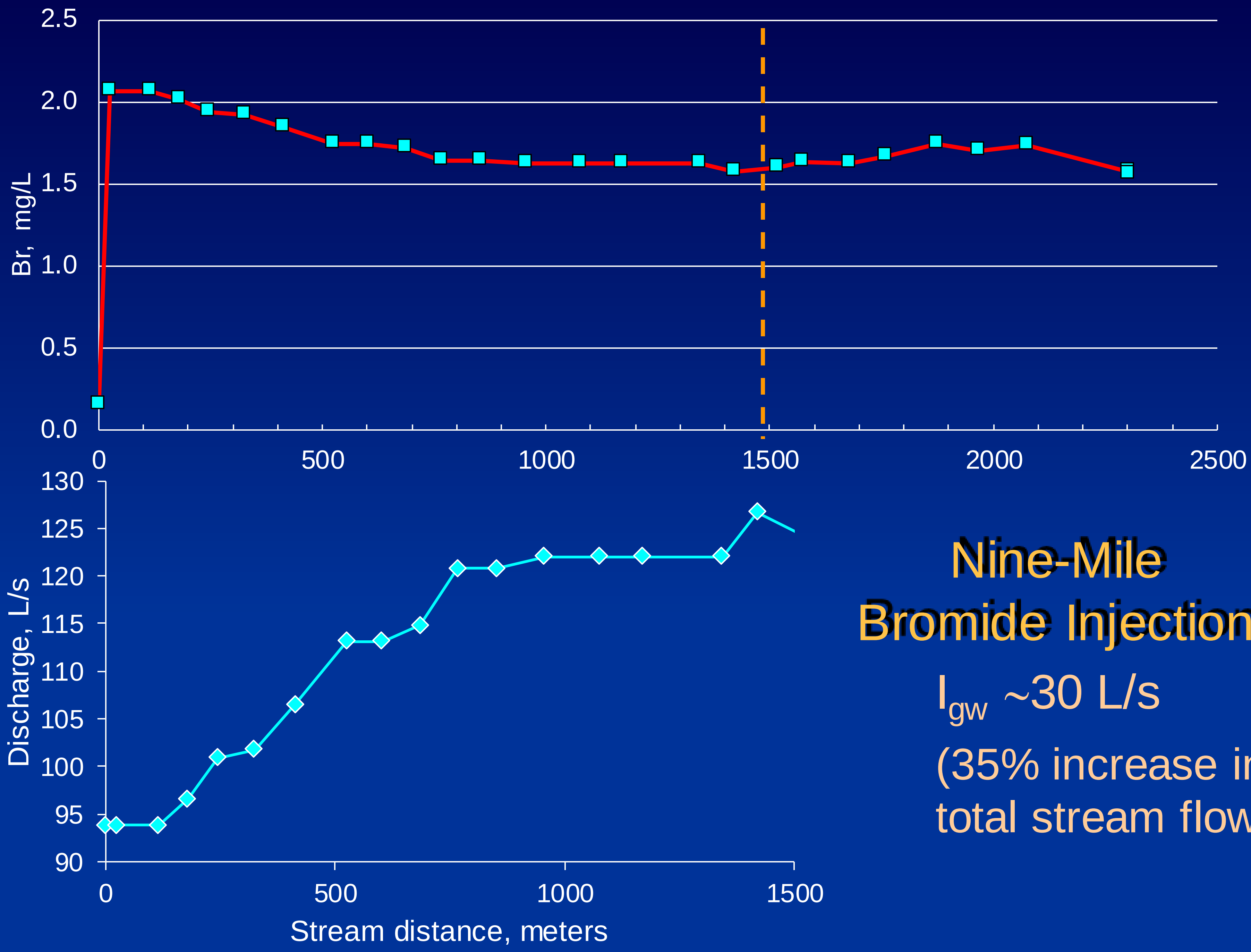


Method Testing at Nine-Mile Creek

- Low-discharge (90 L/s) medium gradient (0.007 m/m) stream
- Main objective: Methane injection to evaluate its downstream persistence and gas transfer velocity

Nine-Mile Creek Location Map



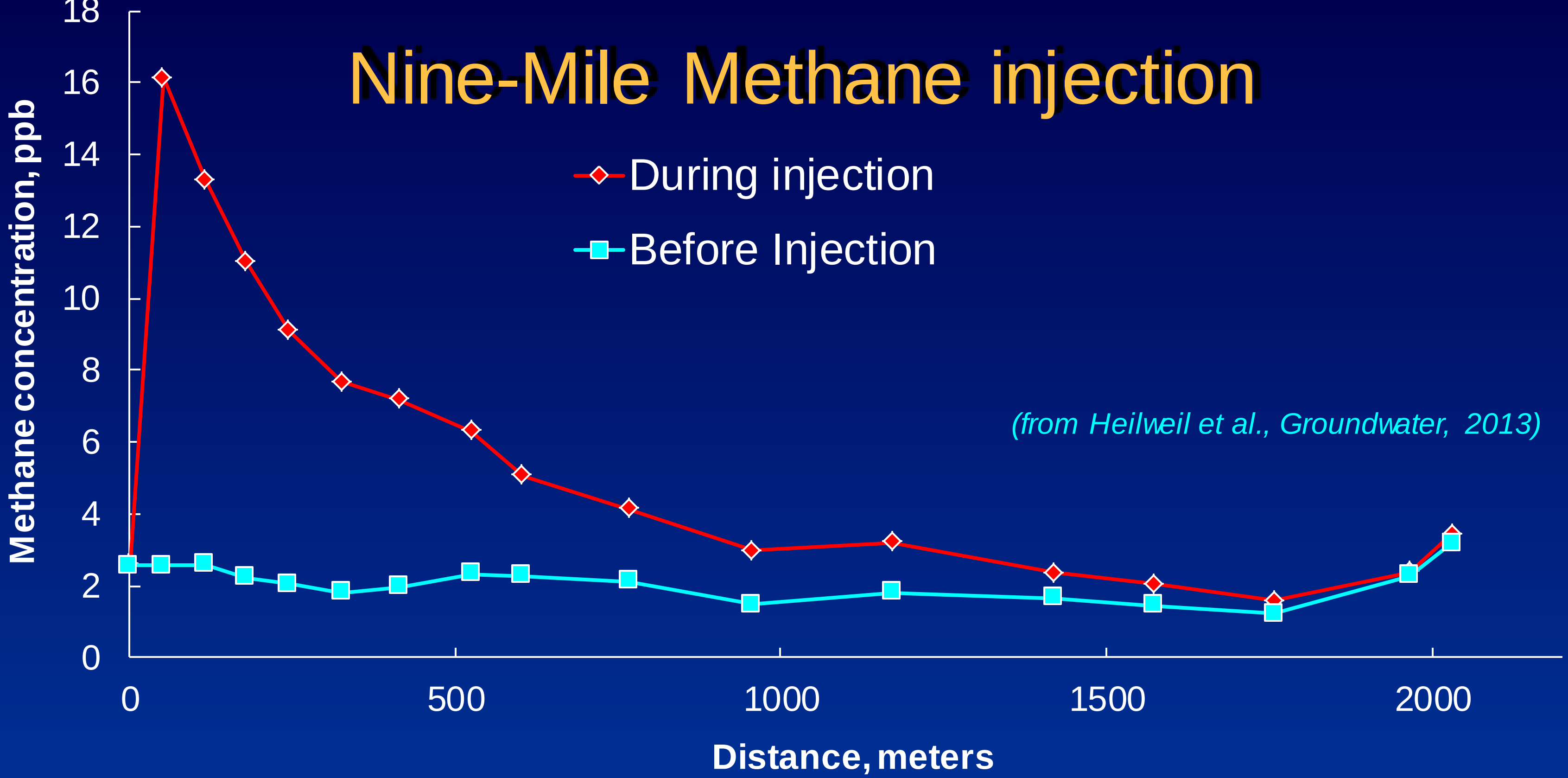


Nine-Mile Bromide Injection

I_{gw} ~30 L/s

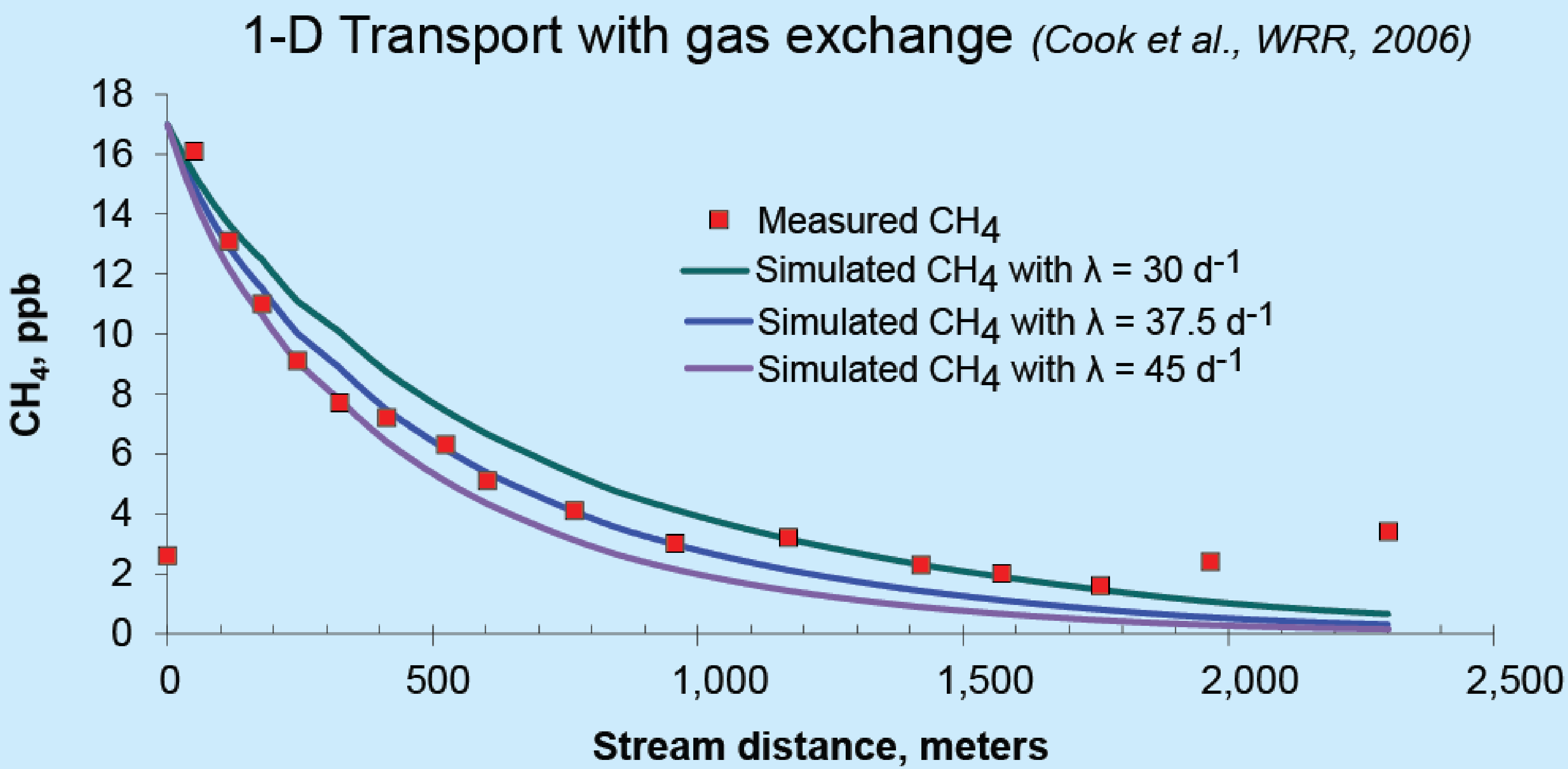
(35% increase in total stream flow)

Nine-Mile Methane injection



- CH_4 dissolved in stream water using Si tubing
- Injected CH_4 persisted for >1,500 m
- Gradual decrease in CH_4 from 5x background

Nine Mile Model Results



(from Heilweil et al., Groundwater, 2013)

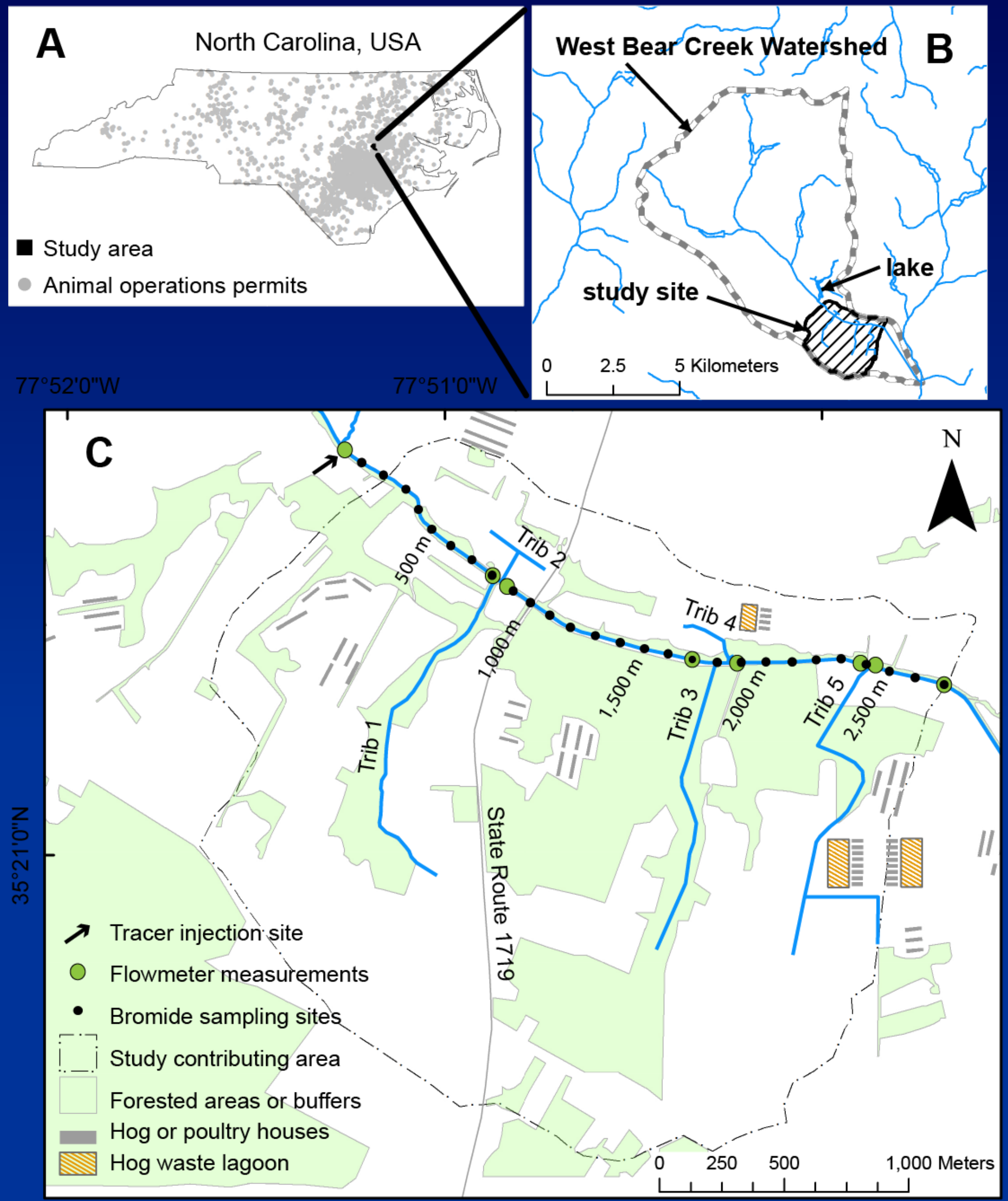
- Apparent gas transfer velocity (*k =*λ x d) of 4.5 ± 1 m/d
- Did not evaluate gas transfer to atmosphere (λ_{atm}) versus bacterial consumption (λ_{micr})

West Bear Creek, North Carolina

West Bear Creek Injection

- Medium-discharge (500 L/s), low-gradient (0.003 m/m) stream with high nitrate load due to hog & poultry concentrated animal feeding operations (CAFO's) *(Solomon & Genereux, NSF EAR-1045134)*
- Bromide tracer dilution: I_{gw} = 70 L/s (15% streamflow increase over 2.7 km)
- <u>Main objective</u>: quantify fractions of methane loss to atmosphere (λ_{atm}) versus microbial oxidation (λ_{micr})

West Bear Creek Location Map

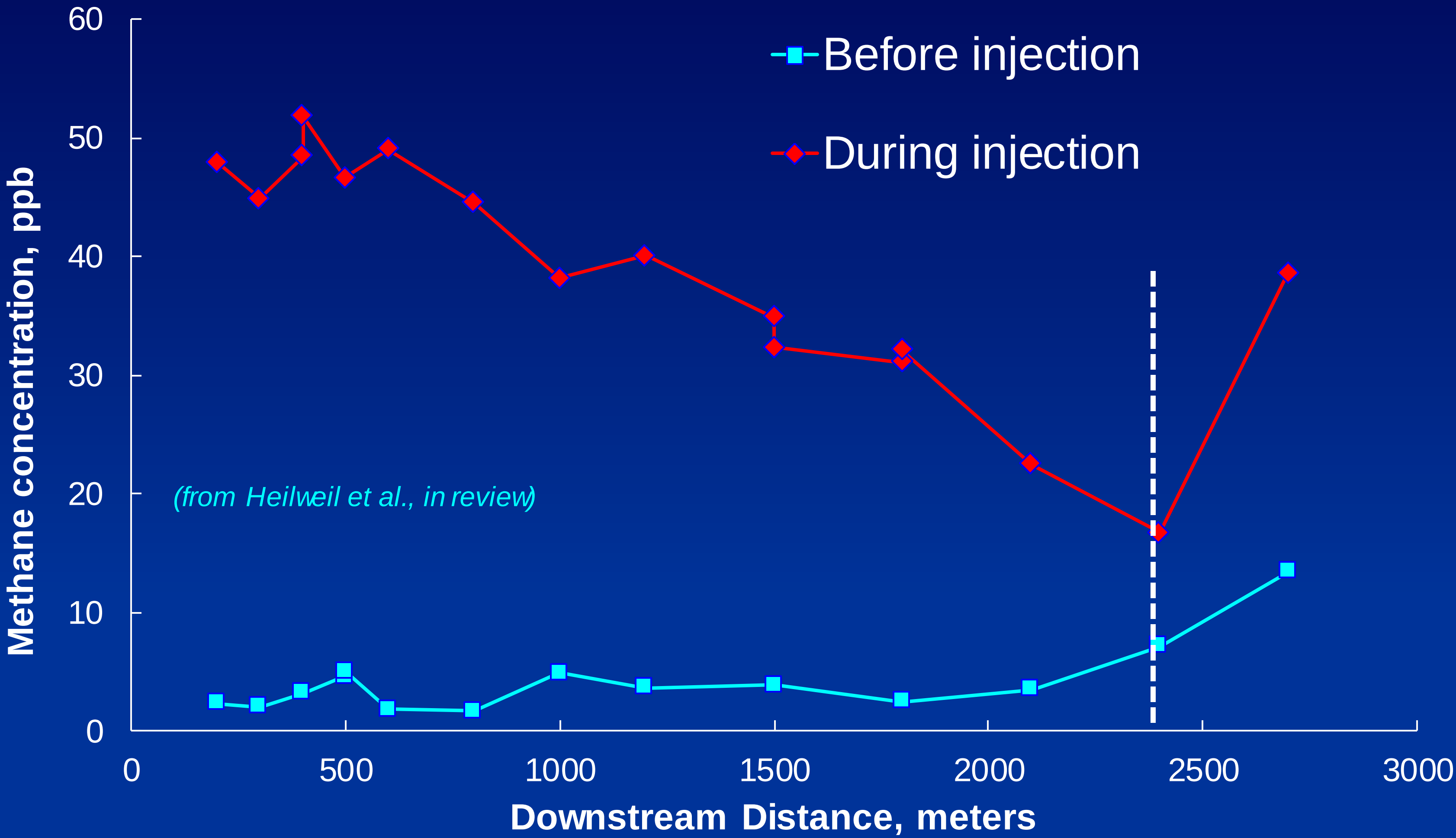


Modified from Gilmore et at., WRR, in review

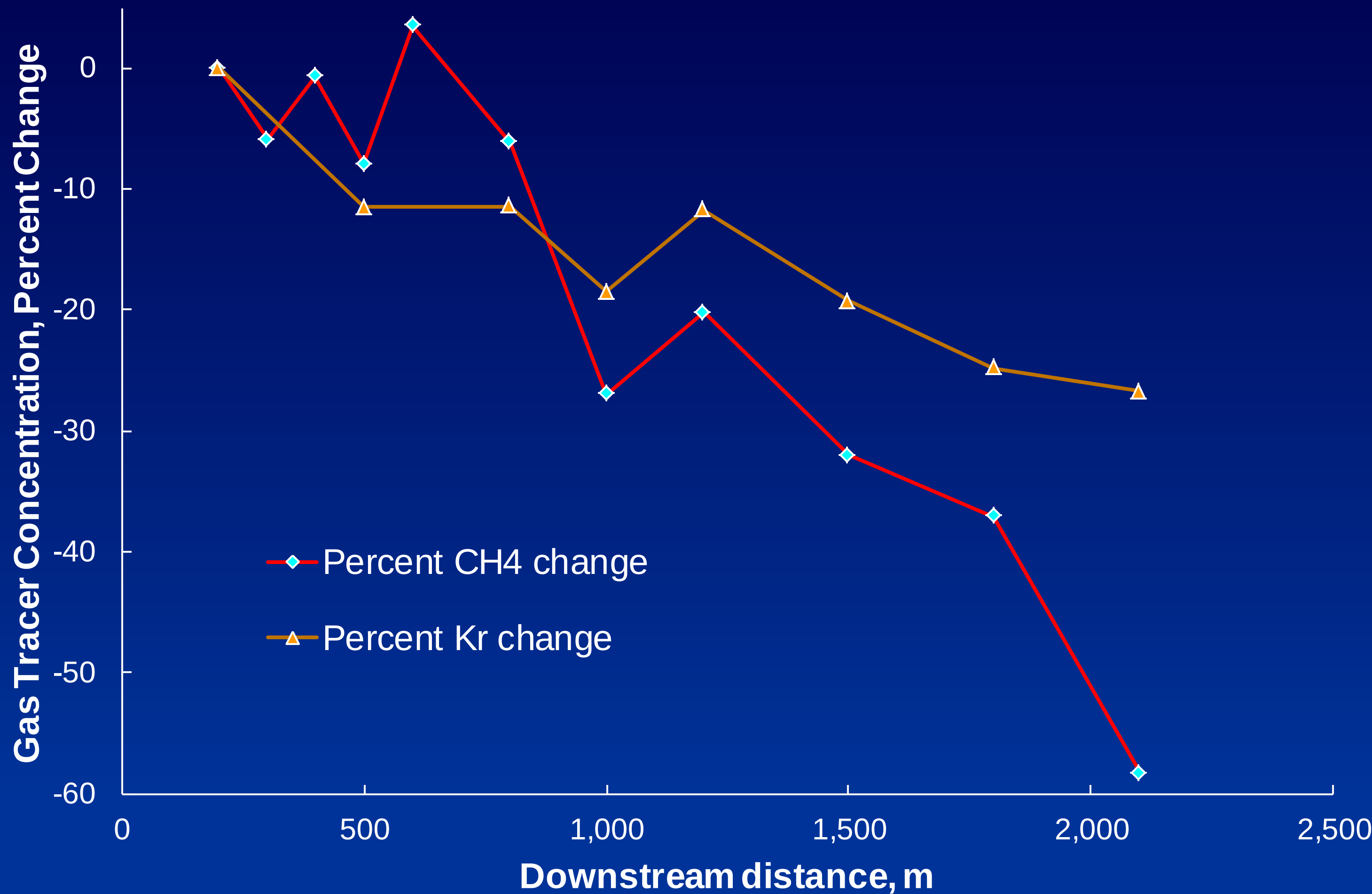
Approach

- Side-by-side gas injection of CH_4 and Kr
- Theoretical K_{CH4} (and λ_{atm}) can be calculated from K_{Kr} based on the ratio of their diffusion coefficients
- More-rapid decline in CH_4 would indicate additional loss due to microbial oxidation (λ_{micr})

West Bear Creek Methane Injection



- Injected methane persisted more than 2,000 m downstream

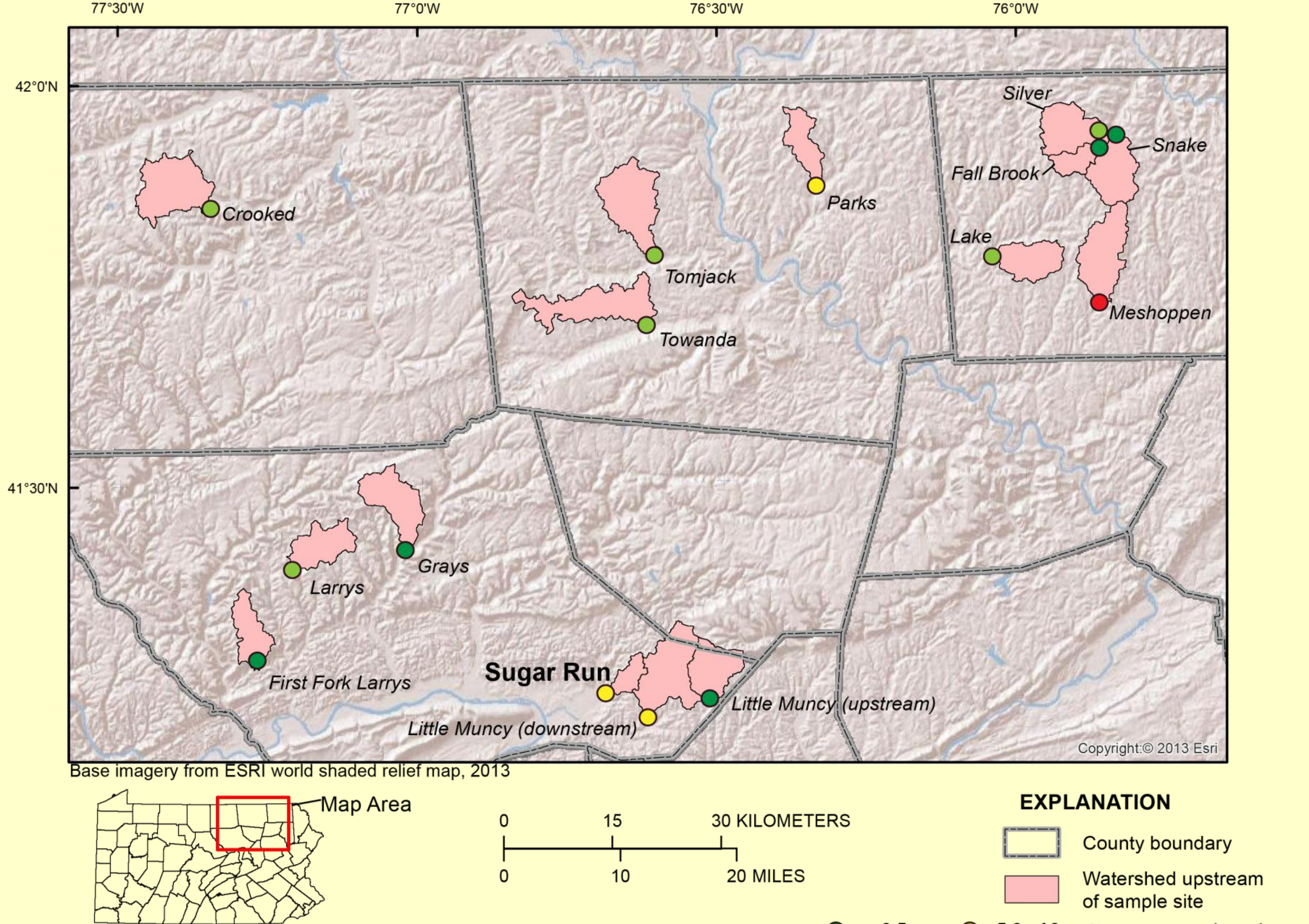


(from Heilweil et al., in review)

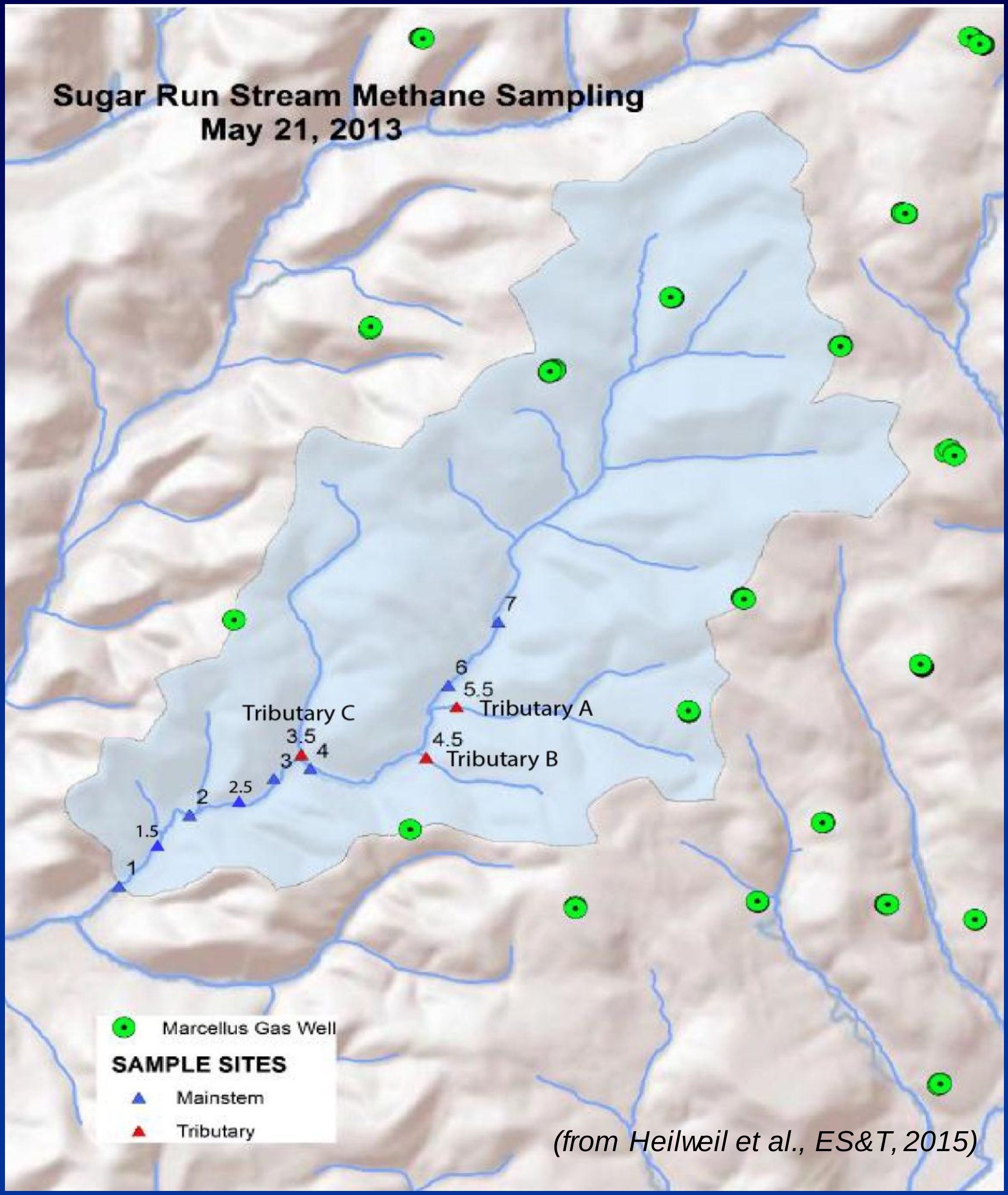
Larger decline in CH_4 indicates non-conservative behavior

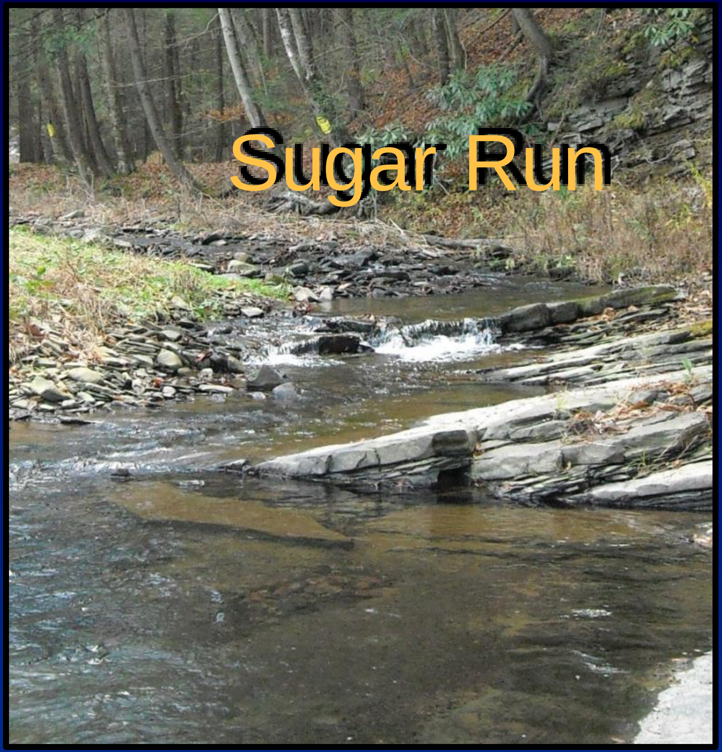
Sugar Run, Pennsylvania

Reconnaissance sampling in northeastern PA



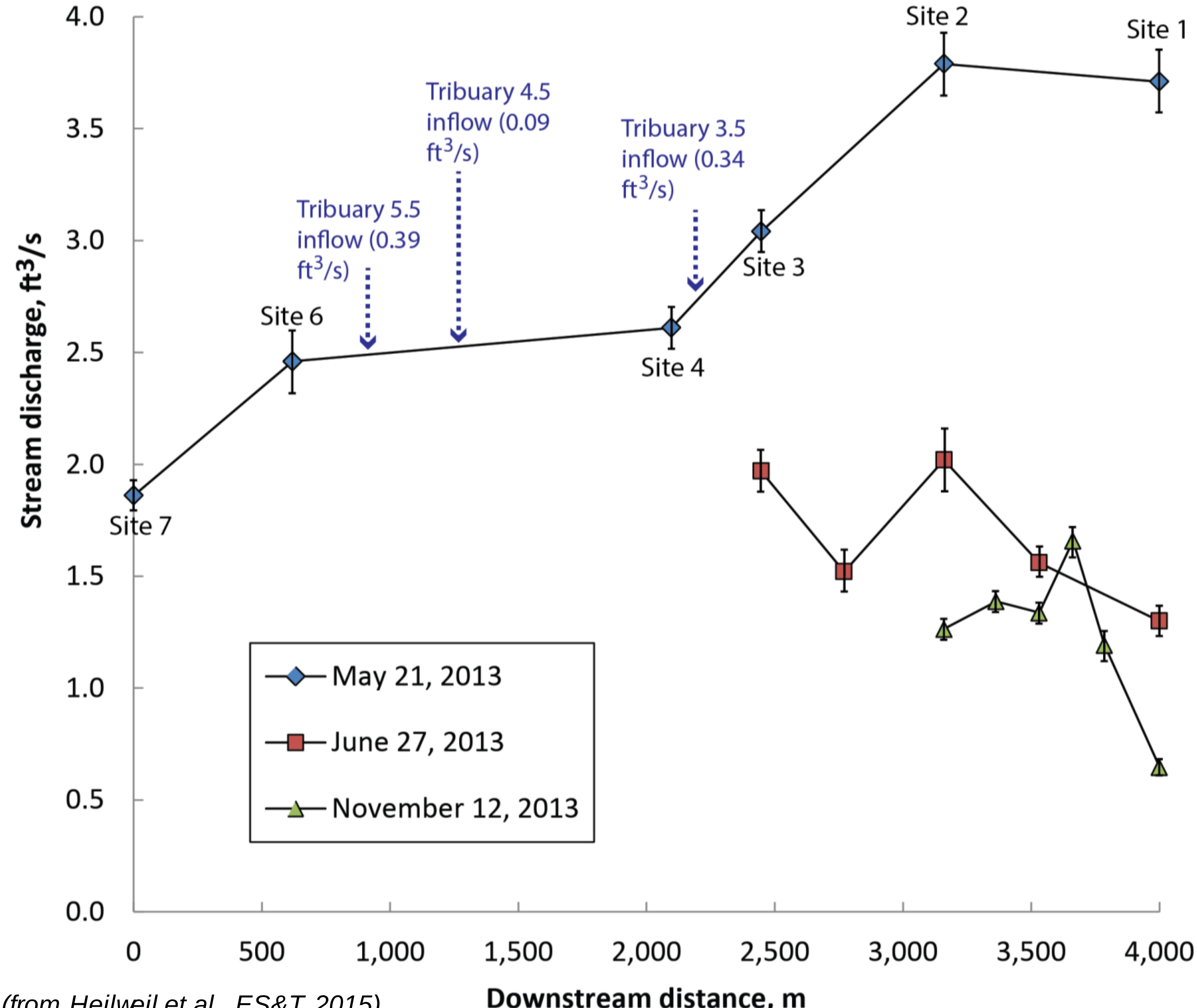
(from Heilweil et al., ES&T, 2015)





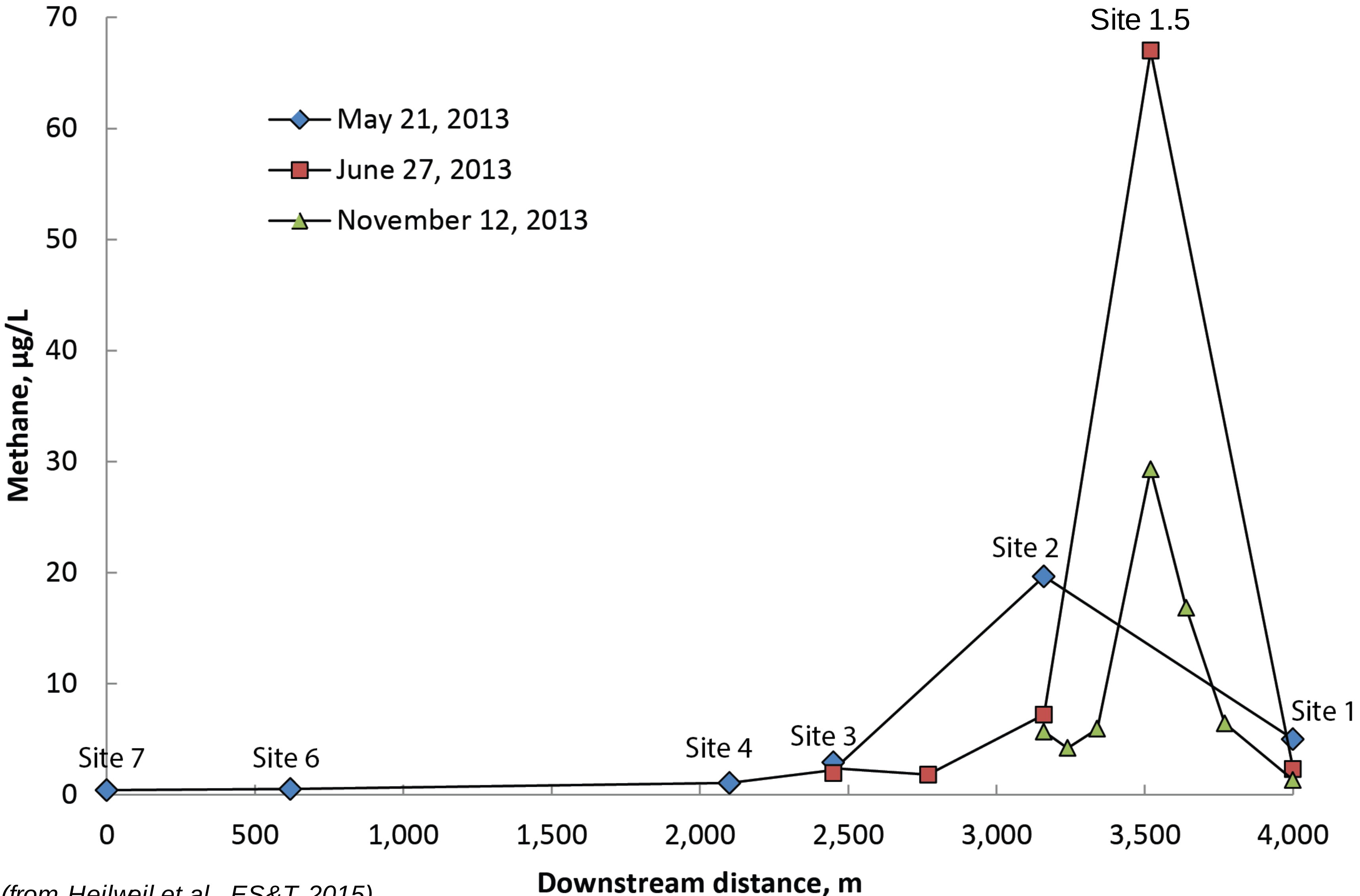
- Small-discharge (40 - 100 L/s), high-gradient (0.04 m/m) stream
- Main objective: quantify groundwater methane load and determine its source

Stream Discharge at Sugar Run

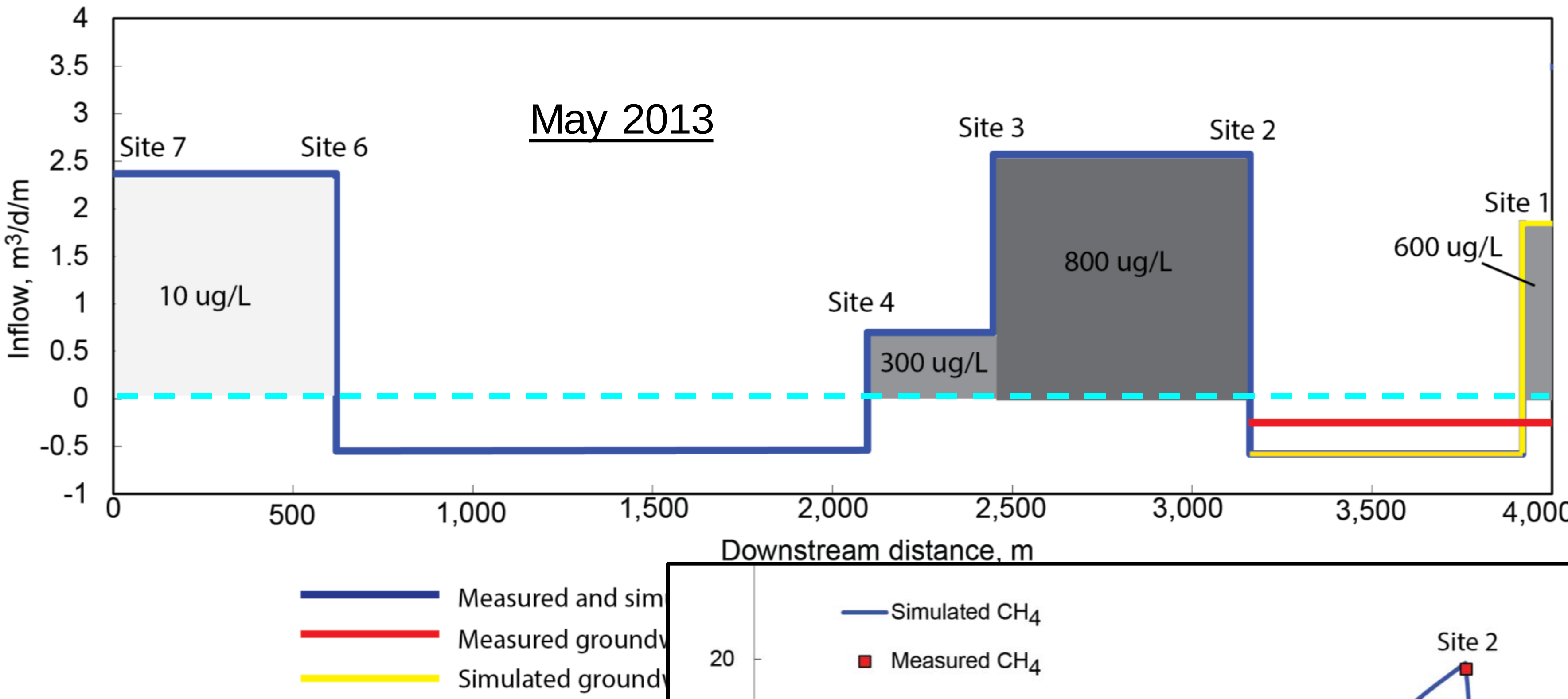


(from Heilweil et al., ES&T, 2015)

Stream Methane in Sugar Run



(from Heilweil et al., ES&T, 2015)

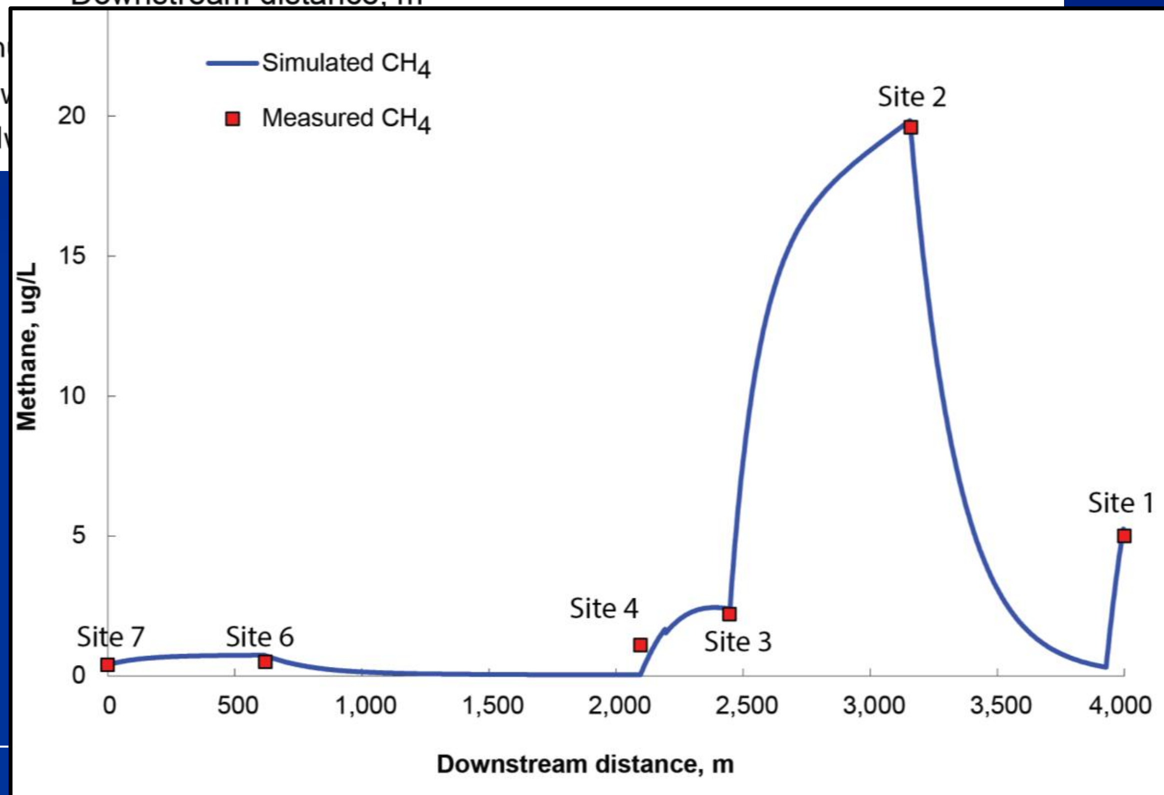


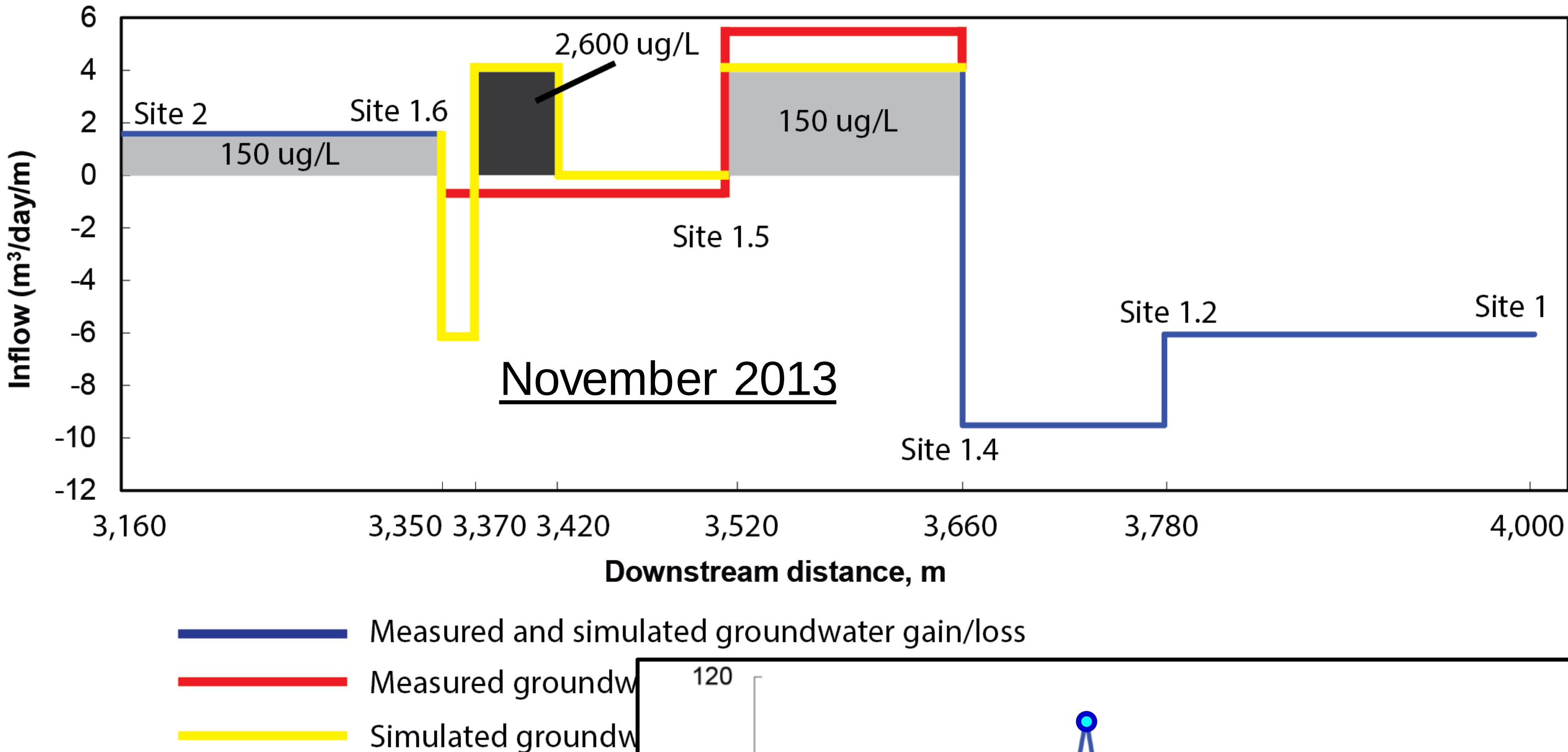
800-m spacing

I_{gw}: 170 L/s (30% of Q)

k_{CH4}: 20 ± 10 m/d

Calculated CH_4 load: 1.8 kg/d



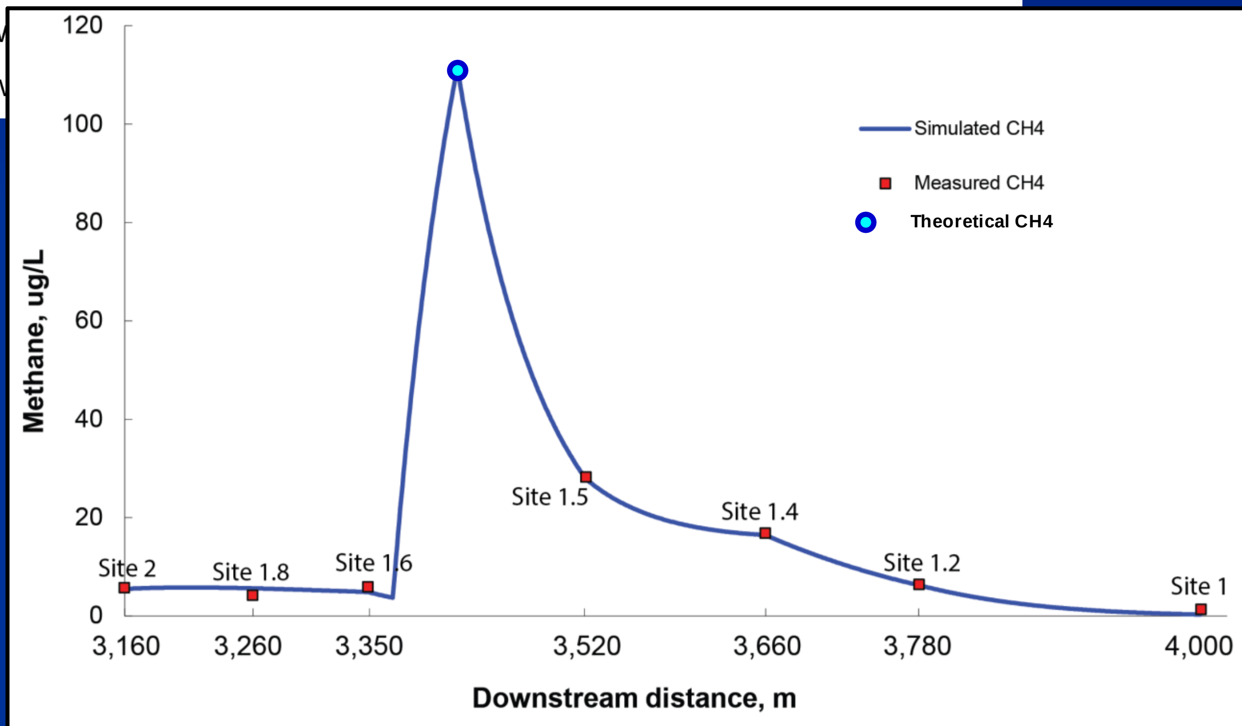


200-m spacing

I_{gw}: 9 L/s (18% of Q)

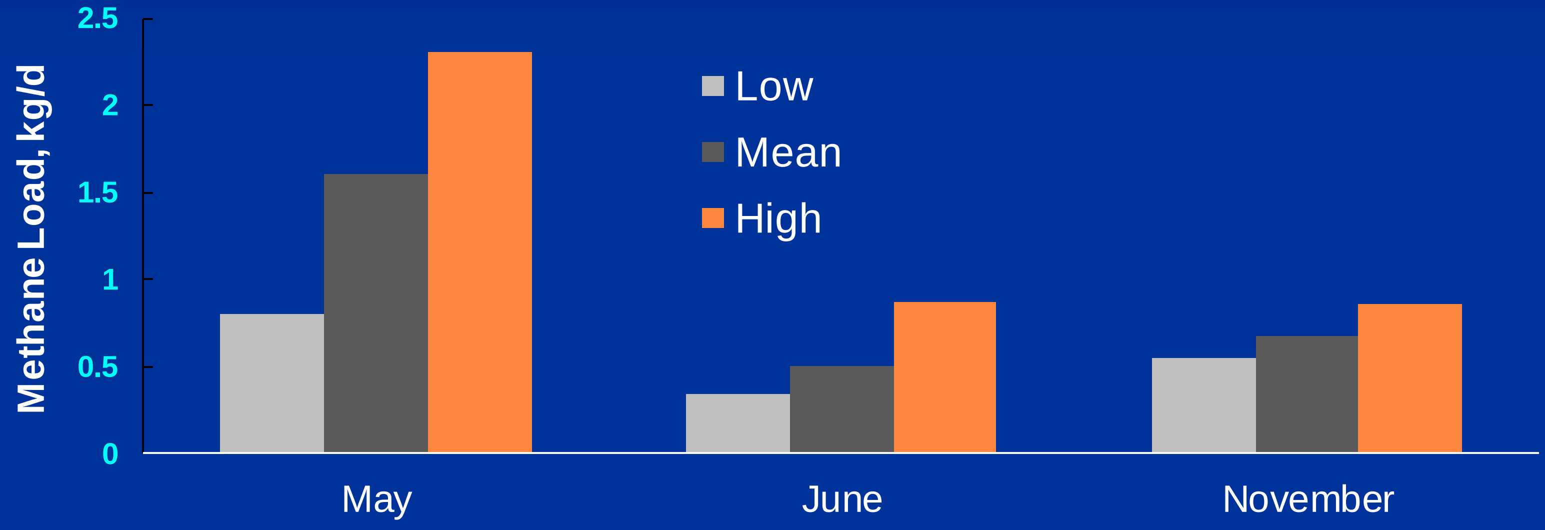
K_{CH4}: 10 ± 5 m/d

Calculated CH_4 load: 0.7 ± 0.2 kg/d

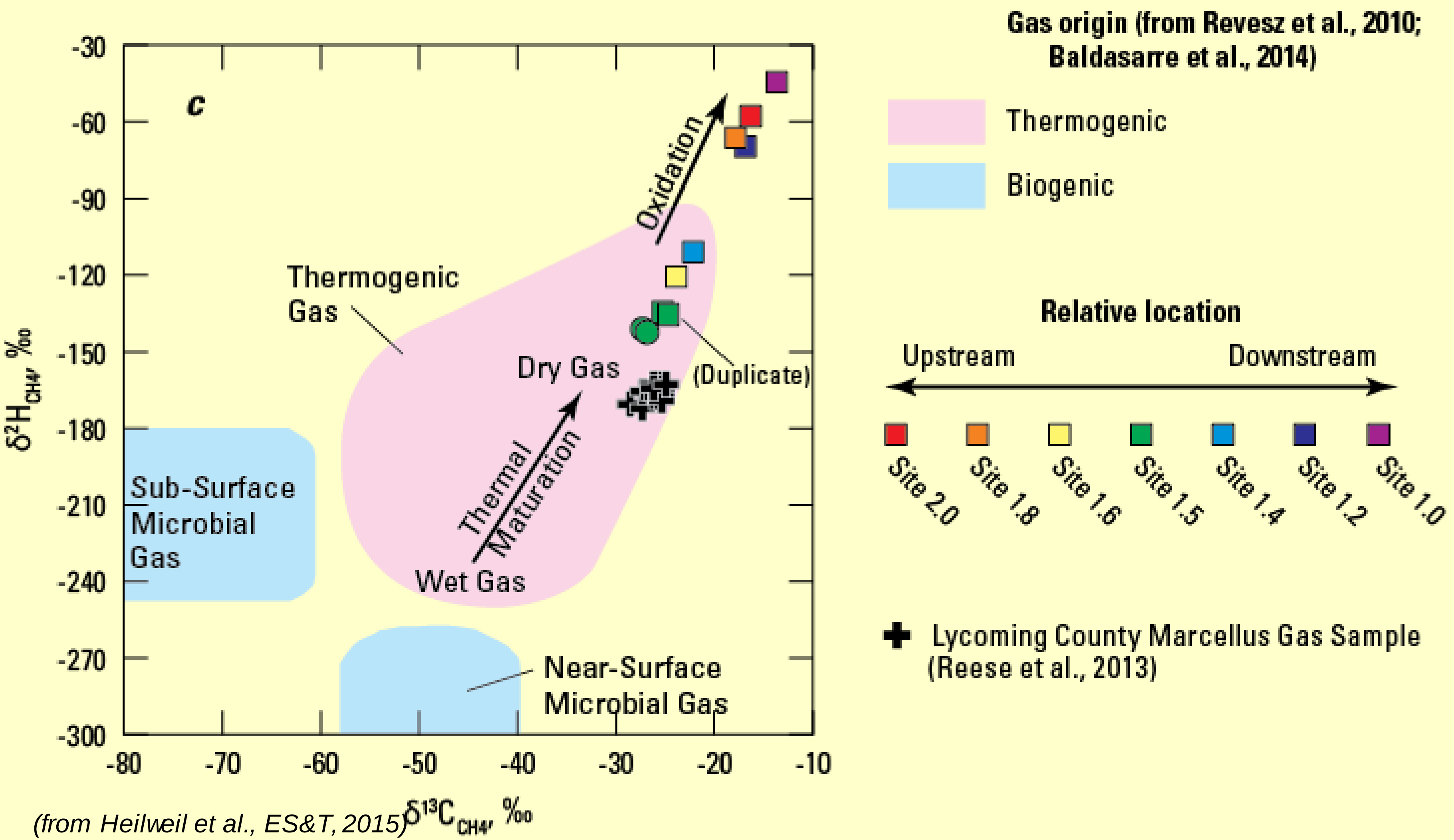


Modeling Insights

- Uncertainty in K_{CH4} and I_{GW} are largest sources of error
- Gas and conservative-ion stream injections could improve these parameter values
- Refined sampling resolution (decreasing spacing between stream sites) reduces uncertainty in methane load
- Groundwater methane discharge may vary seasonally

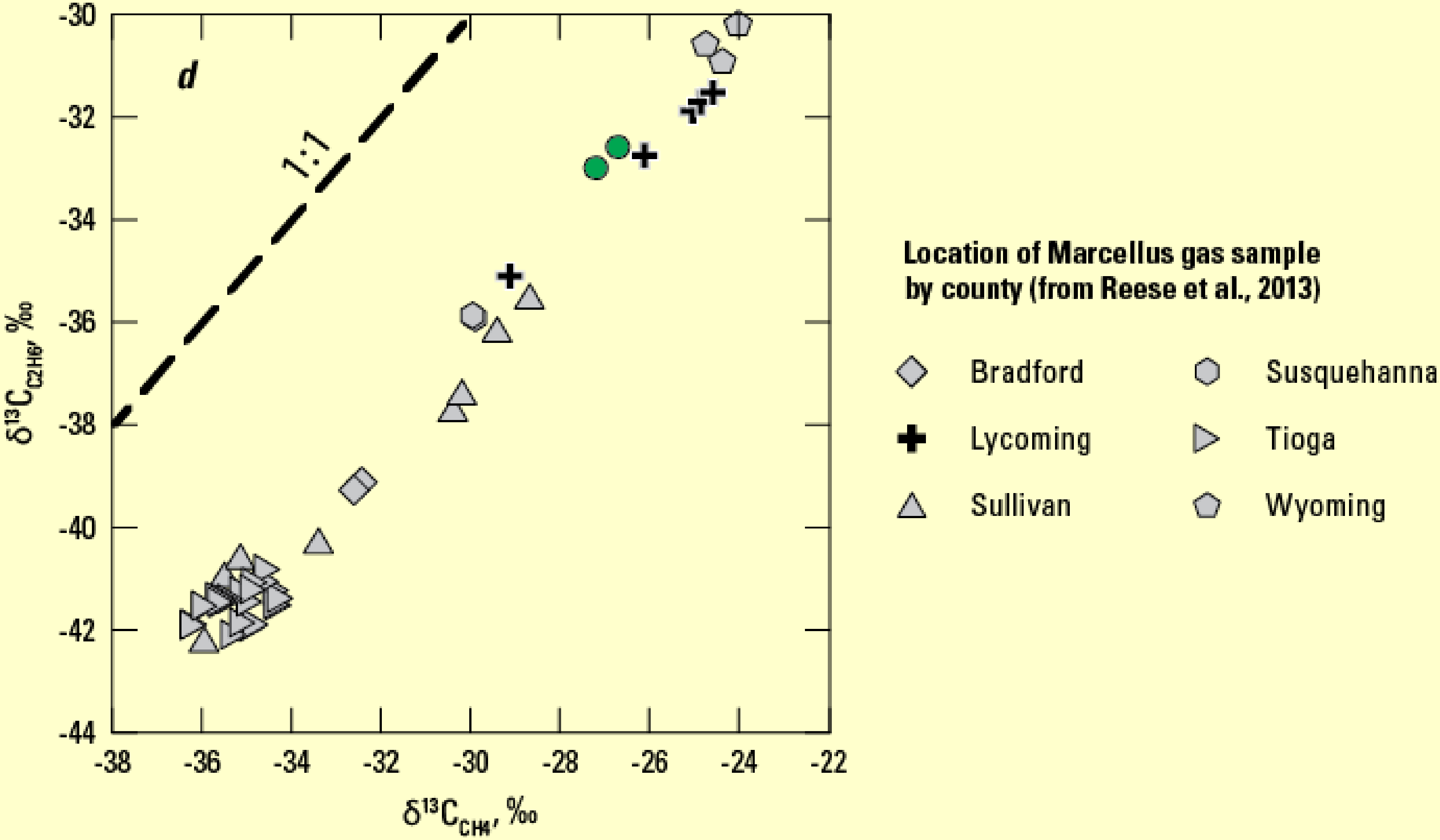


Sugar Run Isotopic Fingerprinting: $\delta^{13}C_{CH4}$ versus $\delta^{2}H_{CH4}$



(from Heilweil et al., ES&T, 2015)

$\delta^{13}C_{CH4}$ versus $\delta^{13}C_{C2H6}$

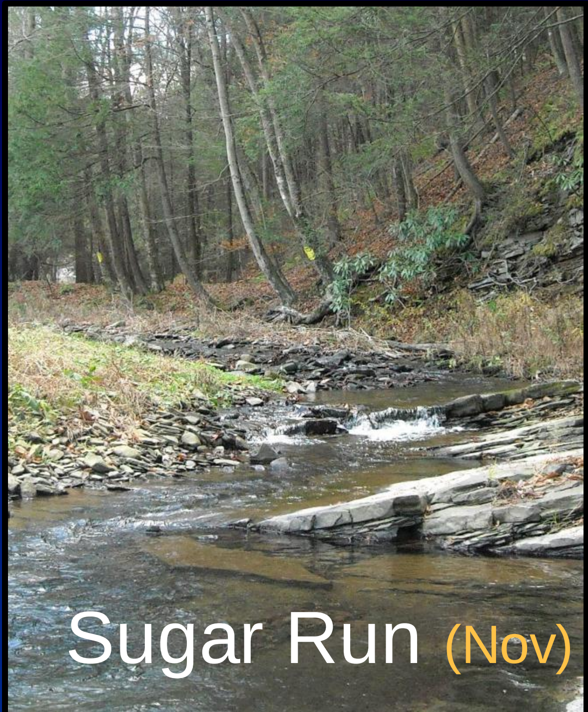


(from Heilweil et al., ES&T, 2015)

Sugar Run Study Epilogue

- September 2013: PA DEP Violation letter stating 5 water wells were impacted by stray gas migration from a leaky horizontal gas well drilled beneath Sugar Run assumed to have defective casing or cement: *"the gas well had caused or allowed gas from lower formations to enter fresh groundwater…"*
- June 2015: With increasing public pressure, partly due to press coverage of our ES&T paper, PA DEP assessed $9 million civil penalty "*for failure to repair leaking gas well*" under the *Clean Streams Law*
- *---*

Extrapolating Sugar Run CH_4 flux of 1 kg/d per 6 mi^2 to entire Marcellus (95,000 mi^2) yields estimates up to 100's of thousands of metric tons of CO_2 equivalent per year



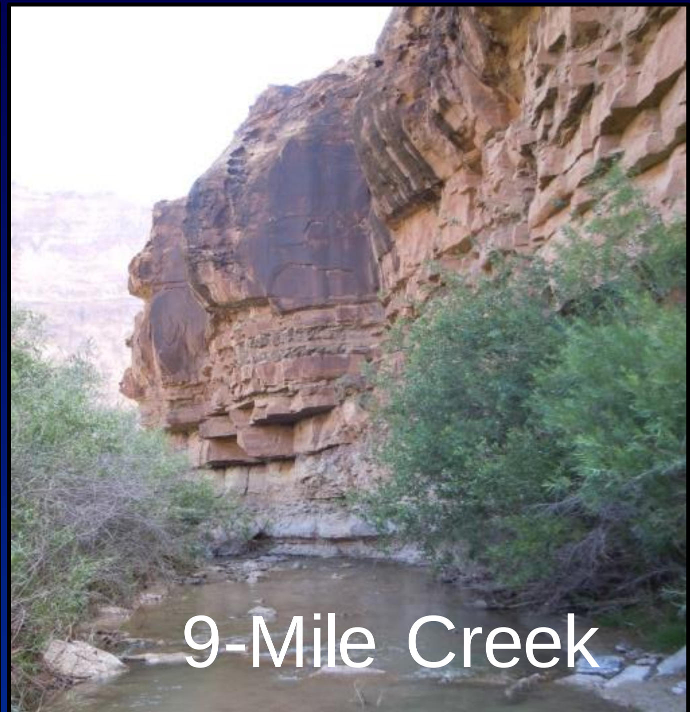
K_{CH4}: 10 m/d

I_{gw}: 780 m^3/d)

Length: 800 m

q_{gw}: 1.0 m^3/d /m

K_{ch4}/q_{gw}: 10.3 /m



K_{CH4}: 4.5 m/d

I_{gw}: 2600 m^3/d

Length: 1500 m

q_{gw}: 1.7 m^3/d /m

K_{ch4}/q_{gw}: 2.6 /m

K_{CH4}: 1.2 m/d

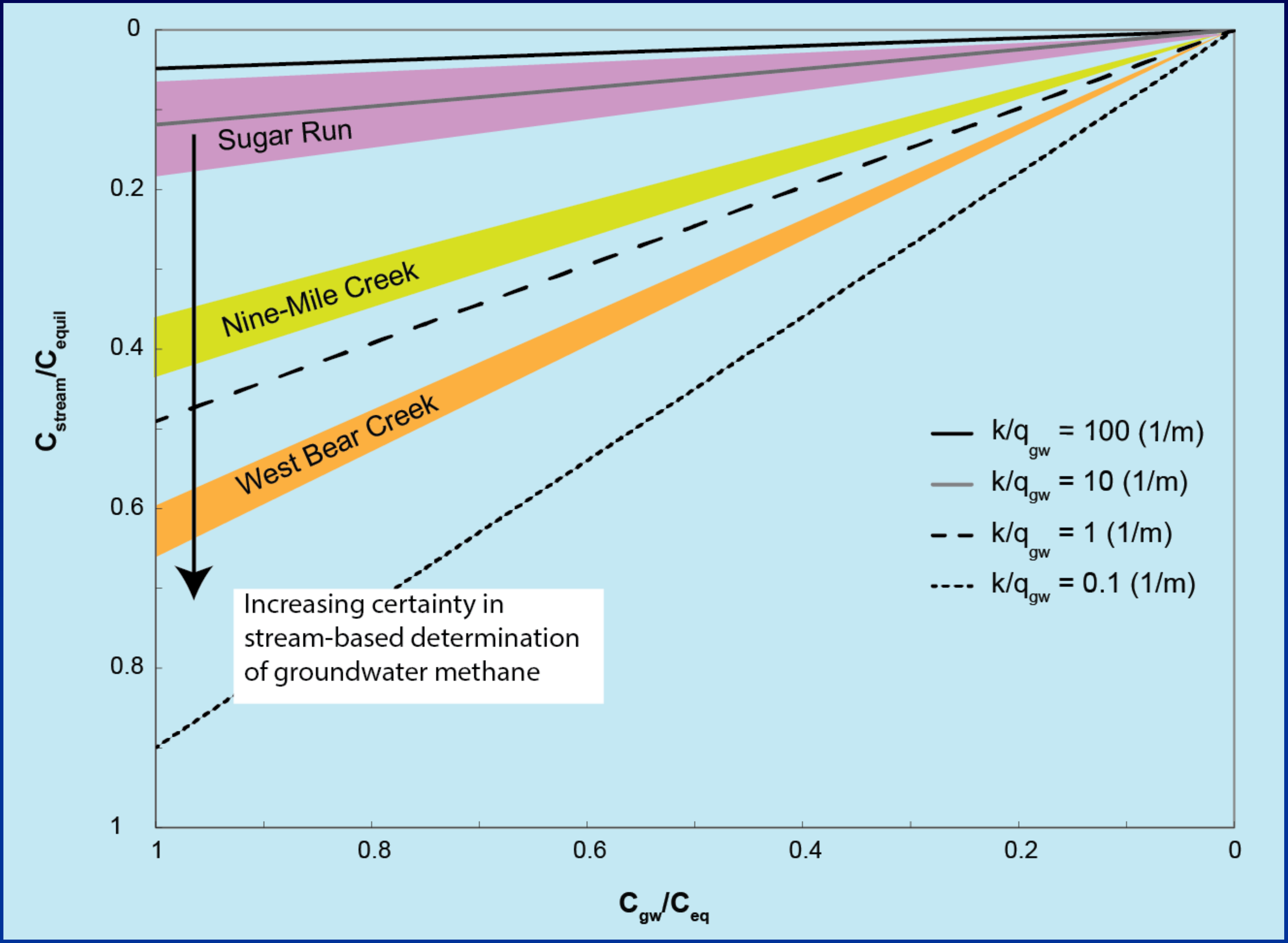
I_{gw}: 6050 m^3/d)

Length: 1800 m

q_{gw}: 3.4 m^3/d /m

K_{ch4}/q_{gw}: 0.4 /m

Relation of gas transfer rate to groundwater inflow



Approach for Stream Methane Studies

Scaled approach:

- Reconnaissance stream CH_4 sampling
- Higher resolution stream & shallow groundwater sampling
- Hydrocarbon isotopes to identify source
- Gas & bromide stream injections to determine I_{GW} and K_{CH4}
- Seasonal/annual sampling to establish baseline variability in CH_4 load and evaluate trends caused development

Conclusions

- Km-scale persistence of stream CH_4 supports feasibility of method
- Transport modeling can quantify [CH_4] and loads
- Most CH_4 escapes to atmosphere
- CH_4-laden groundwater discharge to streams CH_4 is likely an important greenhouse gas source but more work is needed to quantify it globally
- Pilot-scale application of stream methane method in the Marcellus shale-gas play shows the utility of a scaled approach
- But seasonal/annual data collection needed for temporal variability in CH_4 load and evaluating trends **prior to** shale-gas extraction to clearly evaluate impacts of development

Future Efforts

- Sampling and analysis improvements:
  - Simplified stream-tracer injection methods
  - Flow-integrated CH_4 sampling methods
  - Lower-cost CH_4 analysis
- Evaluate prevalence of thermogenic CH_4 groundwater contamination in the Appalachian Basin (eastern U.S.) and other shale-gas plays through regional reconnaissance stream methane studies
- Further investigate carbon cycling in stream
  - Ultimate fate of microbially oxidized methane (CO_2)
  - Impacts of increased pCO_2 (acidification)

Acknowledgements

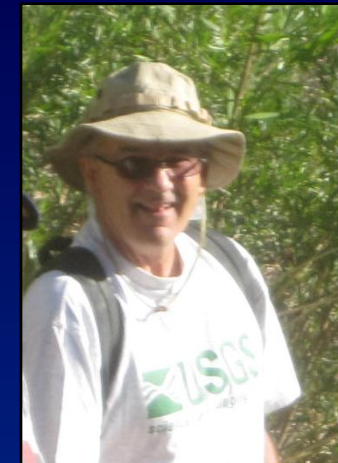
Todd Sowers *Pennsylvania State University*

Peter Cook *CSIRO, Australia*

Erik Pollack *University of Arkansas*

Troy Gilmore and David Genereux
North Carolina State University

David Susong, Briant Kimball, John Solder,
Ryan Rowland, Tom Marston, Phil Gardner,
Pat Lambert, Randy Conger and Jamie Marlow
U.S. Geological Survey



More Information:

http://ut.water.usgs.gov/projects/methanestream/

Vic Heilweil: heilweil@usgs.gov

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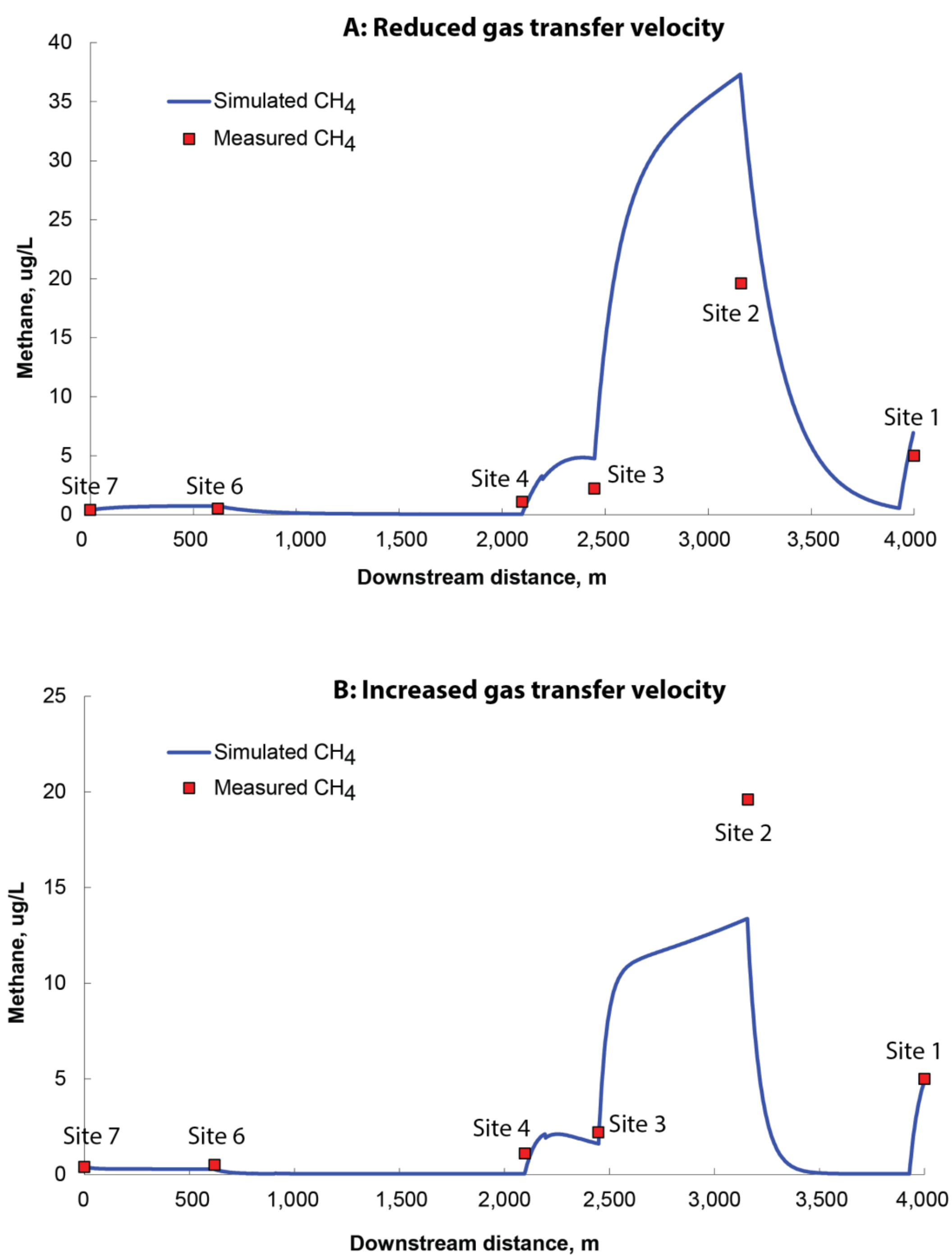
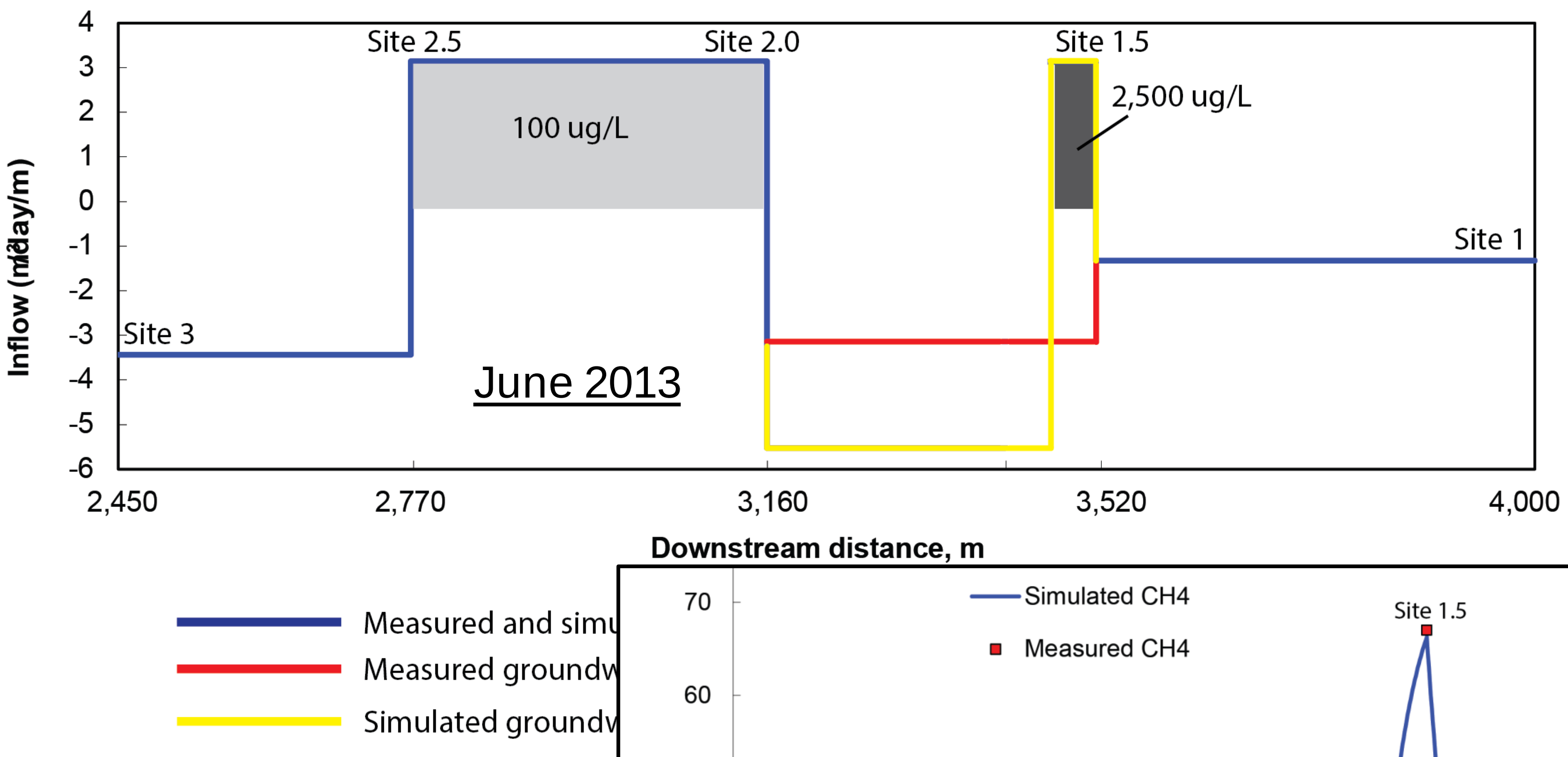
Model sensitivity to gas transfer velocity (k_{CH4})

- k_{CH4} ~10 to 30 m/d
- Coarse sample spacing (800 m) and I_{GW} estimated with flowmeter rather than Br injection
- Combined impact is large uncertainty (~50%) in methane load (1.8 ± 0.8 kg/d)

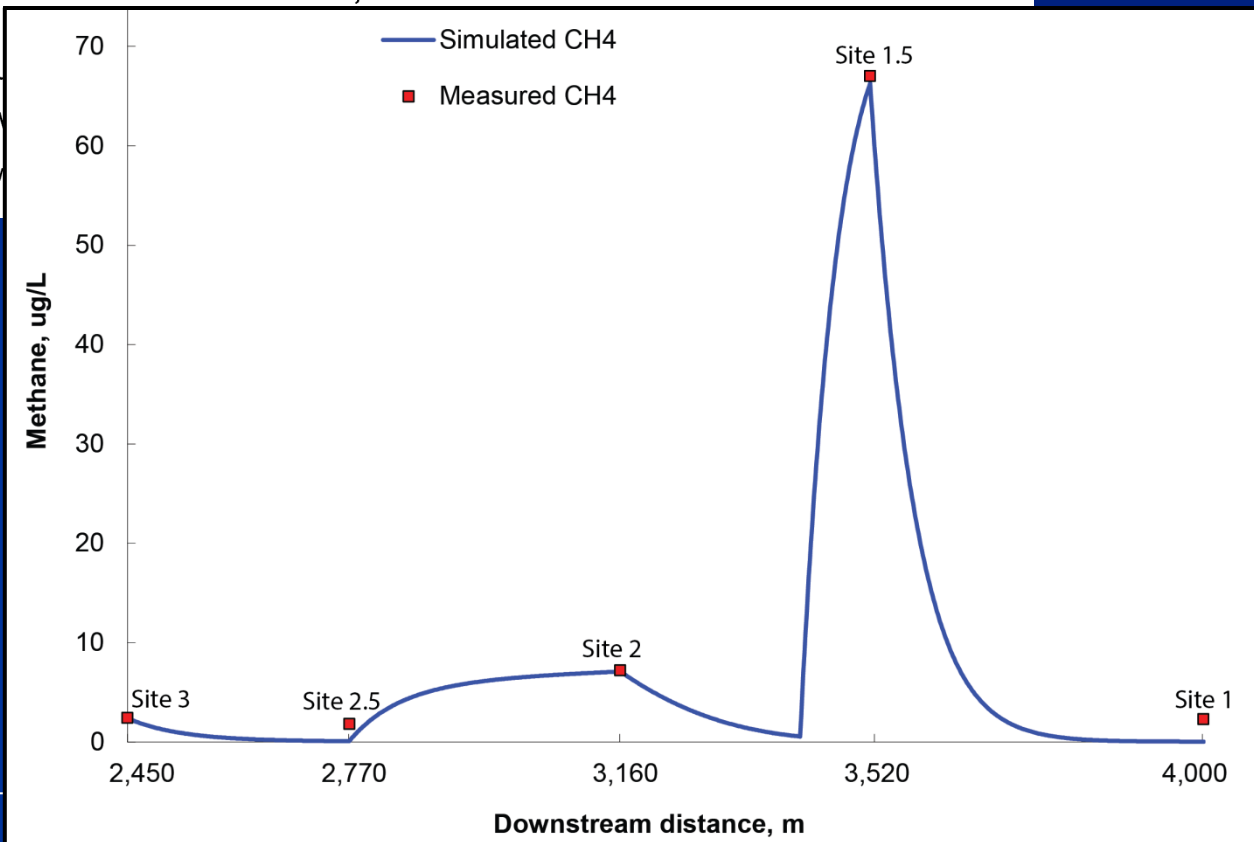




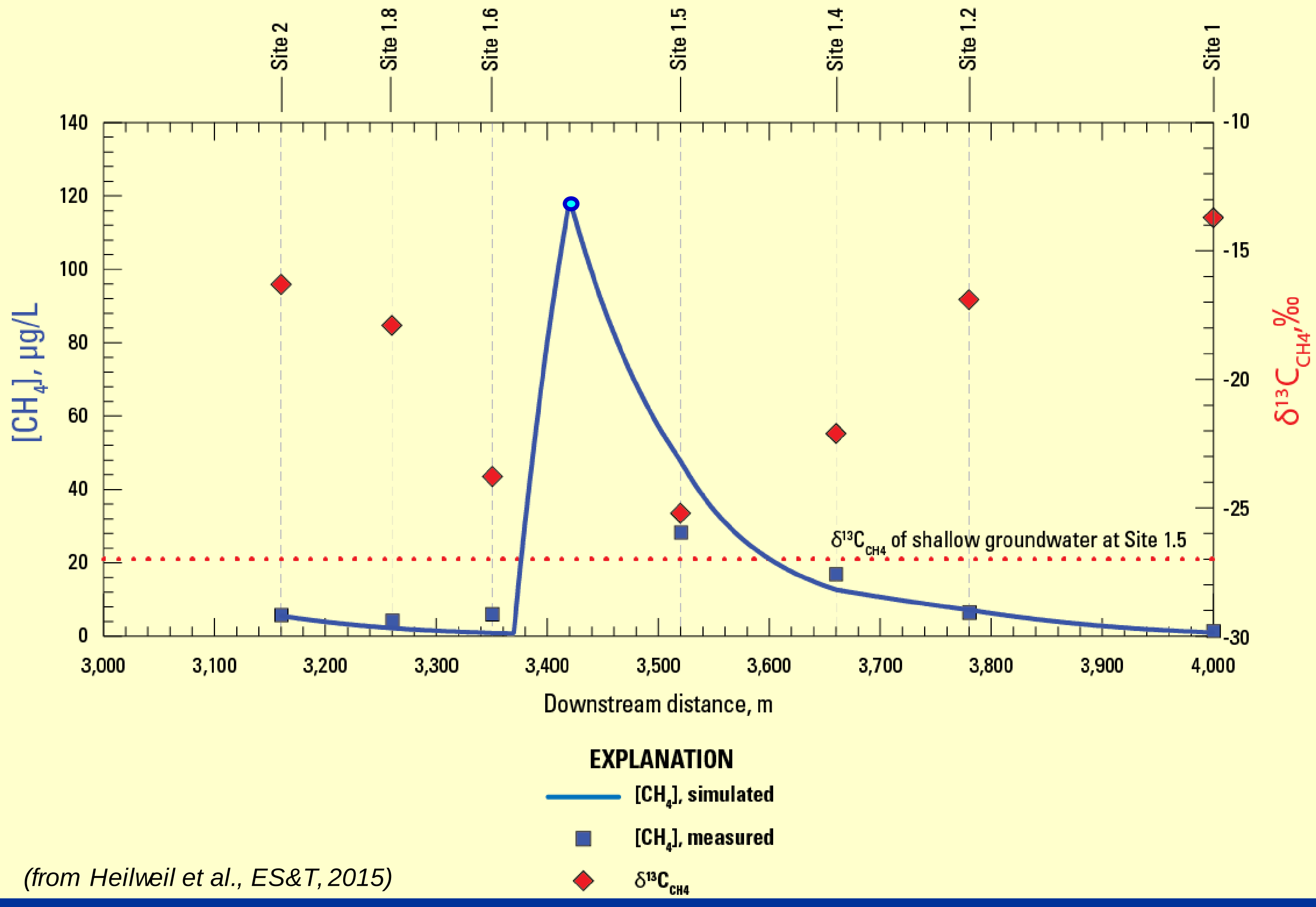
400-m spacing

K_{CH4}: 8 to 22 m/d

CH_4 load: 0.7 ± 0.3 kg/d



Sugar Run Isotopic Fingerprinting



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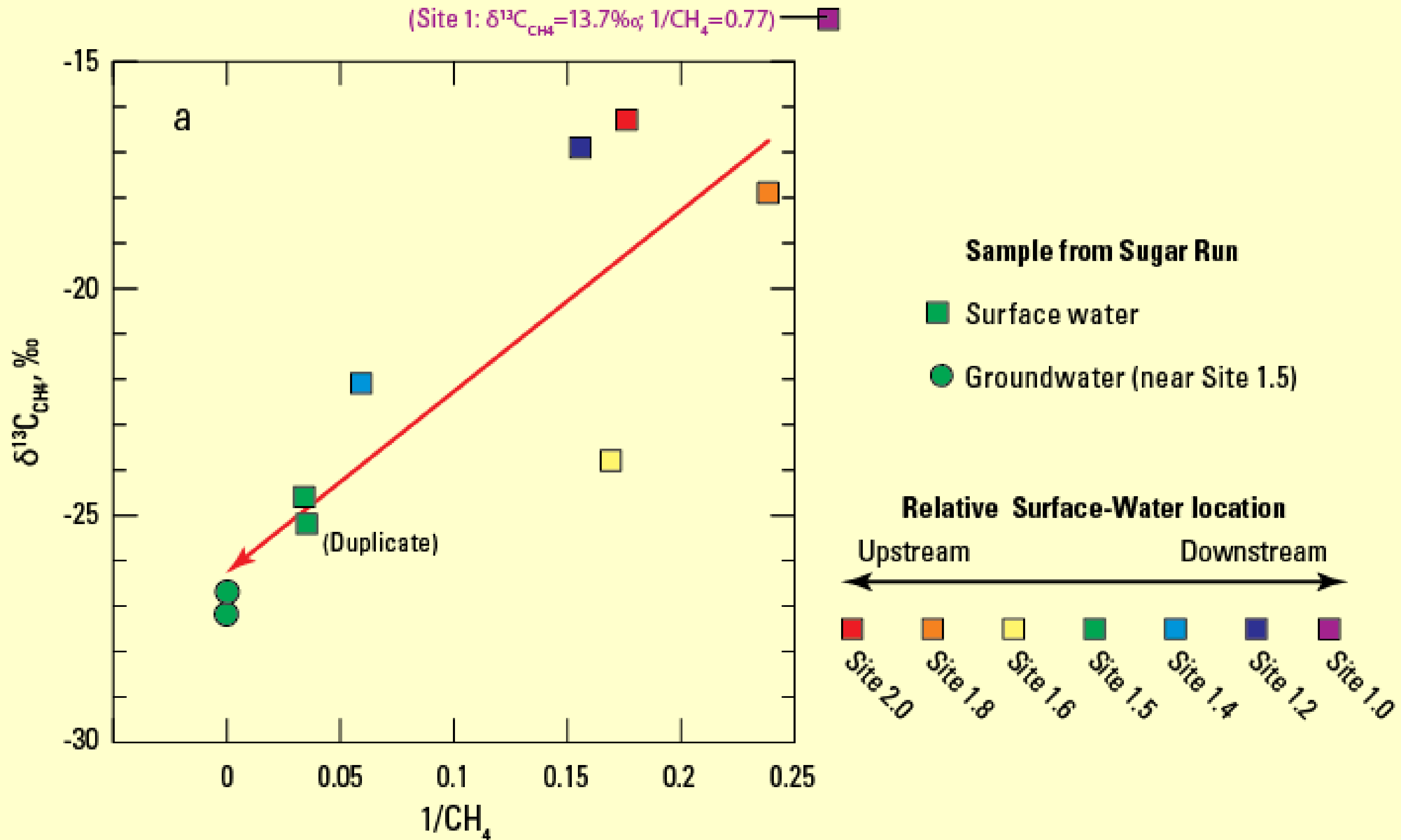
$\delta^{13}C_{CH4}$ versus [CH4]



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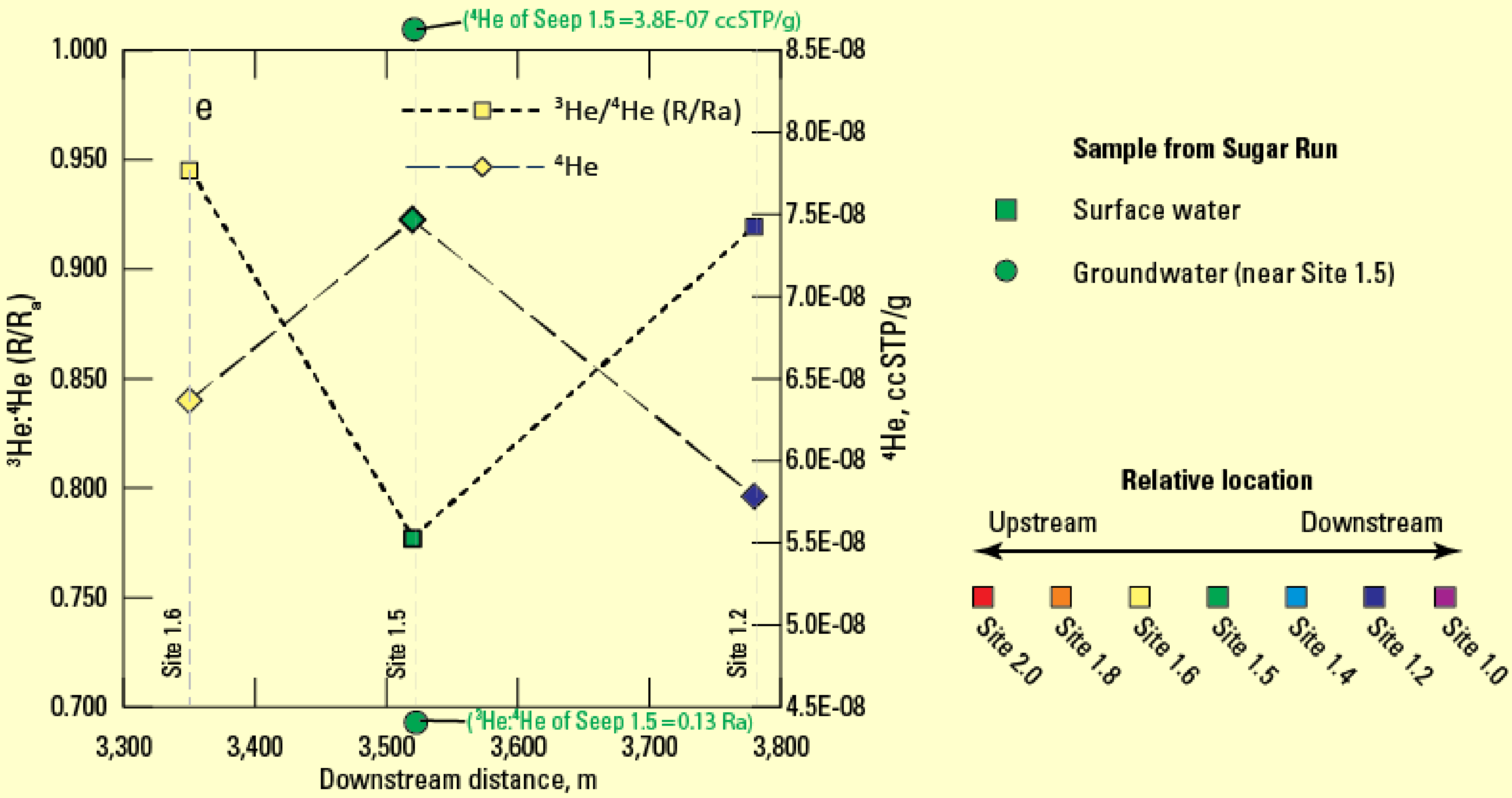
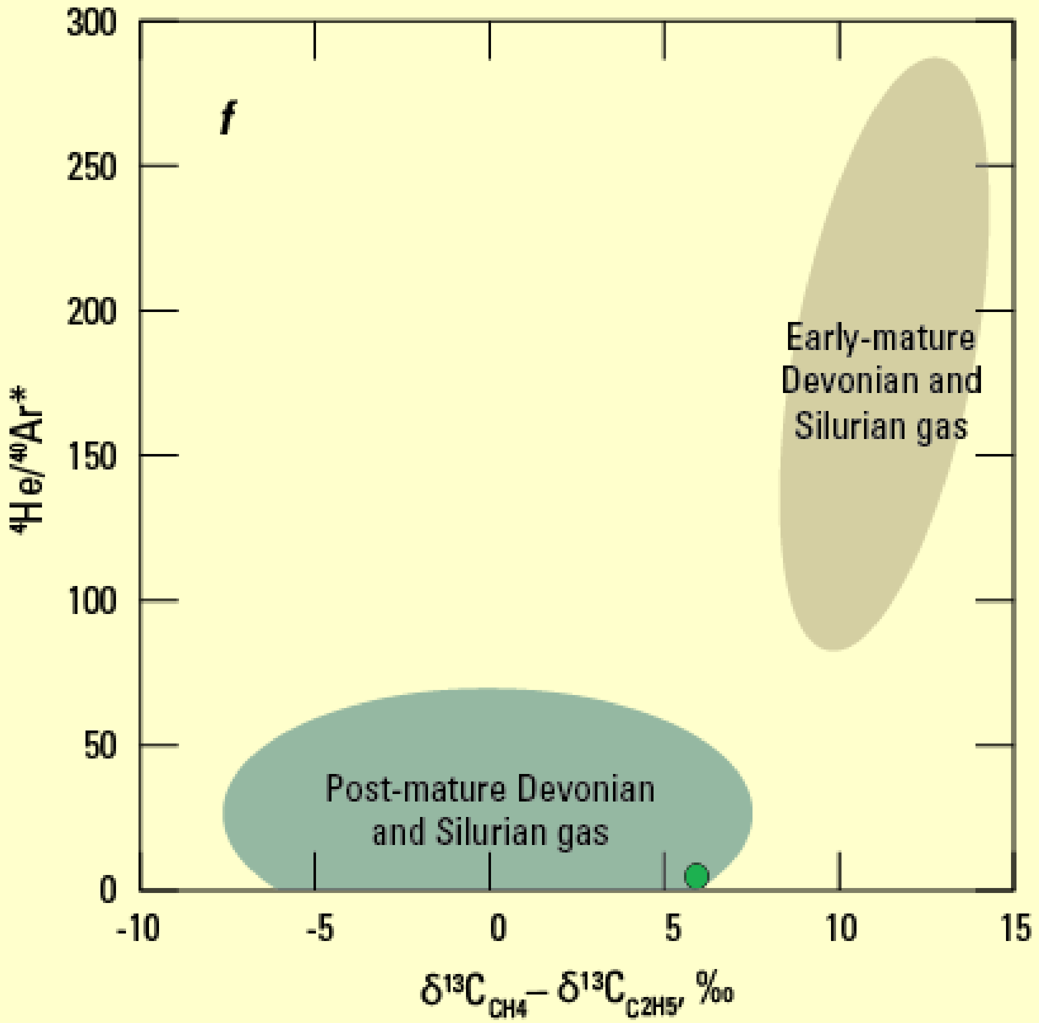
^3He and ^4He



(from Heilweil et al., ES&T, 2015)

$^{3}He/^{40}Ar$ versus ($\delta^{13}C_{CH4}$ - $\delta^{13}C_{C2H6}$)



(modified from Hunt et al., AAPG Bulletin, 2012)

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