C. Ricardo Viteri, PhD
Bruce Richman, PhD,
Artyom Vitouchkine, PhD,
Michael A. Armen, PhD,
Anthony Miller, PhD

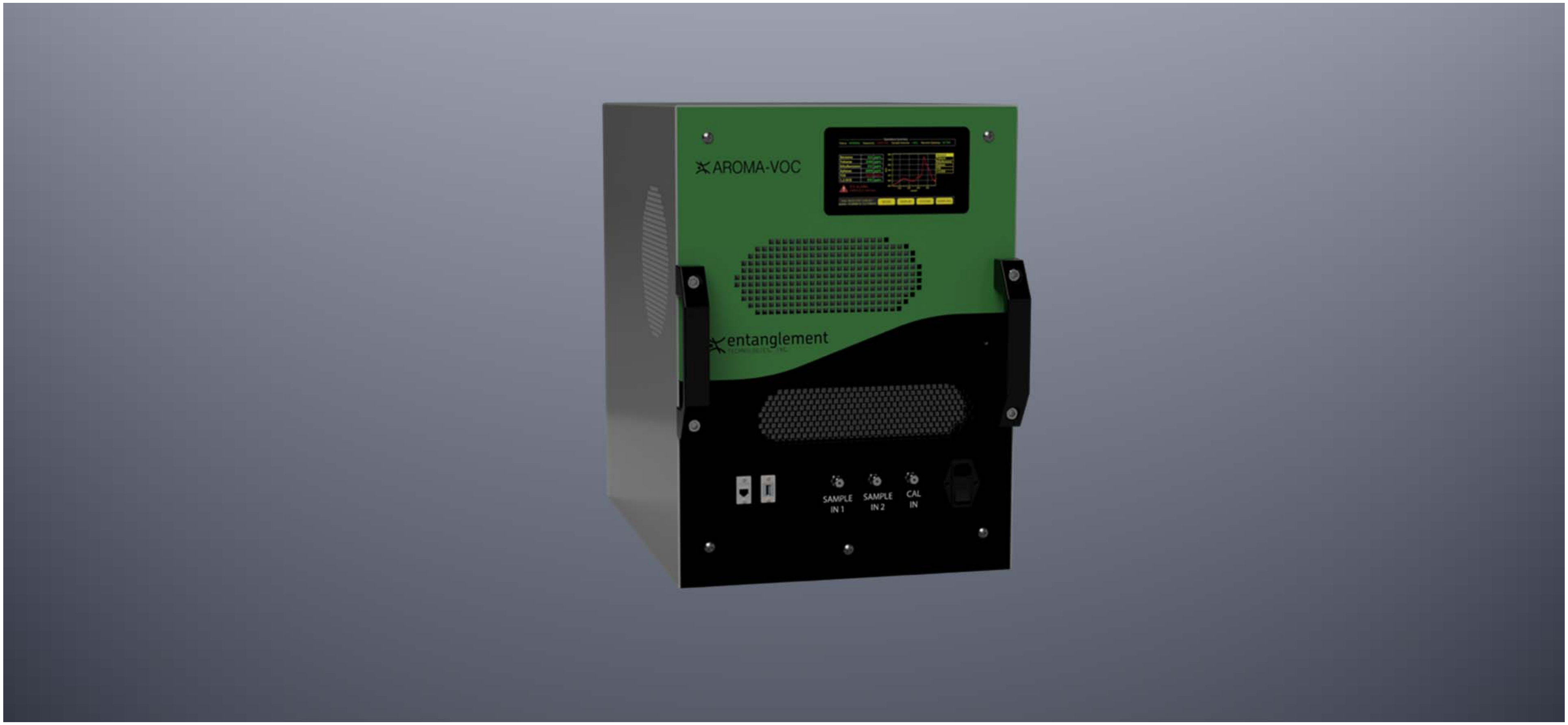
Prevalence and Extent of cVOC Contamination in Sanitary Sewers due to Groundwater Contamination in the San Francisco Bay Area

entanglement
TECHNOLOGIES, INC.

Outline

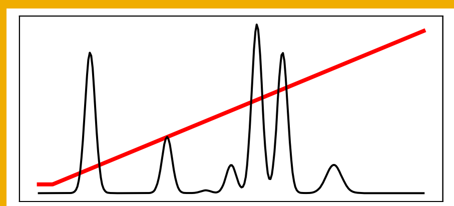
- Introduction to the AROMA analyzer
  - Analyzer mode of operation
  - Analyzer Performance
- Introduction to Sewer Pathway
  - Prevalence, magnitude, challenges and risk
- Measurements of spatial and temporal variability
  - Measurements throughout the SF Bay Area over two years.

The AROMA-TCE/BTEX Trace Vapor Analyzer



Technology

Separation Front End



Ramped thermal desorption chemical concentration and separation: Robust, fast, stable, inert, compact.

- ✓ > 10k cycles
- ✓ Insensitive to O_2, H_2O

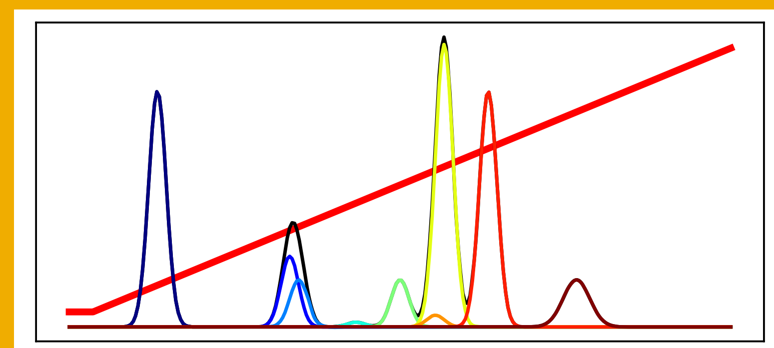
Embedded Instrument Management

- Proprietary FPGA based laser management
- Real-time data acquisition and management
- High precision analog and digital servo systems
- Internal library and automatic result processing

Inlet

- ✓ Direct/Air manifold
- ✓ Direct fluid sampling system

Tunable laser + CRDS Core



Rapid broadband spectroscopy eliminates need for complete separation and allows speciation.

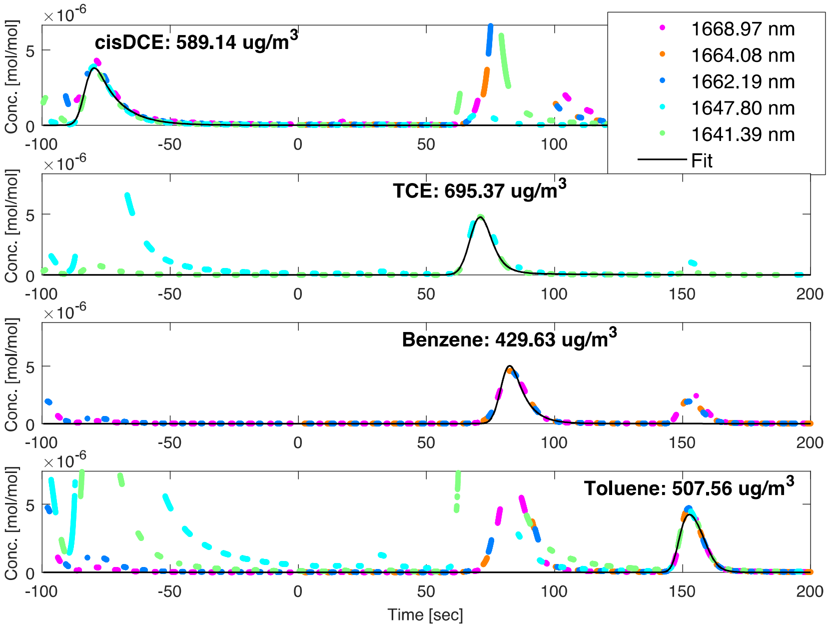
- ✓ > 500 nm/sec tuning over ~100 nm.
- ✓ 50% duty cycle cavity locked CRDS
- ✓ Proprietary electro-optical servos and laser design provide robust performance in harsh vibrational environments
- ✓ MDAL as low as 1.2×10^{-12} $cm^{-1}/\sqrt{Hz}$

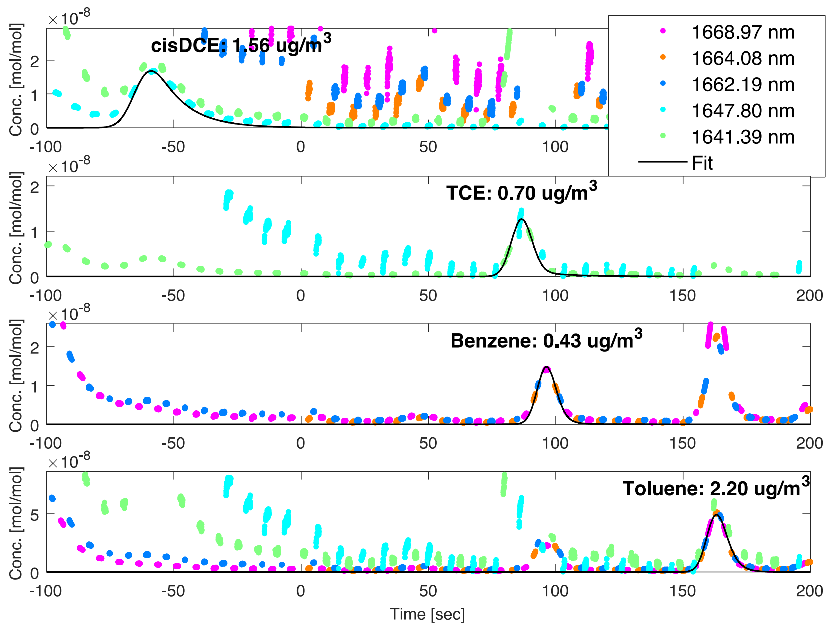
AROMA Principles

Fast, robust analyte separation is analyzed in a high performance CRDS core to provide speciated, high sensitivity chemical analysis. Direct intake to analyzer core allows for Hz level analysis with species classification

Multispecies detection with hopping

Fast hopping CRDS and analyte dispersion measurements at two concentrations. Automated fitting results (black) shown.





Measured Analyzer MDL

Toxic Vapor Analysis				Dynamic Headspace	
Species	**MDL [μg/m³]***	**MDL [pptv]***	**CA RSL [μg/m³]**	**Liquid MDL [ppb]**	**CA MCL [ppb]**
TCE	**0.02**	**6**	**0.478**	**0.011**	**5**
Benzene	0.005	1.4	0.36	0.004	1
Toluene	0.01	2.6	520		
Ethylbenzene	0.01	4.4	1.1		
Xylene (combined)	0.04	10	10		
Matrices (typical)	Soil Gas, Indoor Air, Outdoor Air, Sewer Headspace				

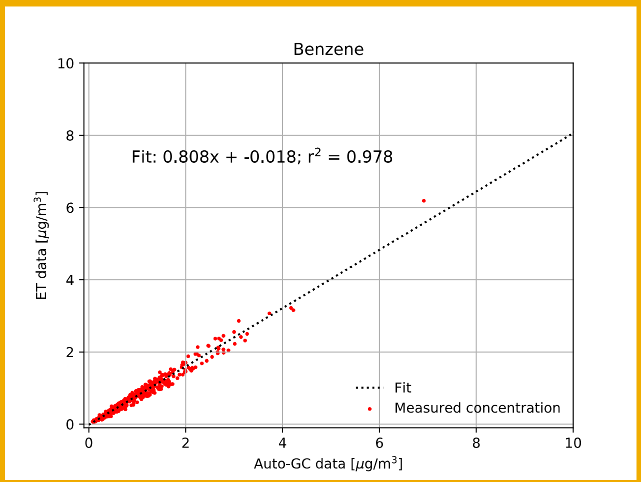
Oil-Field Tracer Analysis (via direct sampling front end)		
Species		**MDL [ppb]***
IPA		6
1-propanol		0.7
1-butanol		0.7
1-pentanol		0.4
Fluoro-alcohol 1		1.5
Fluoro-alcohol 2		1.9
Matrices	Oil-field Produced Brine	

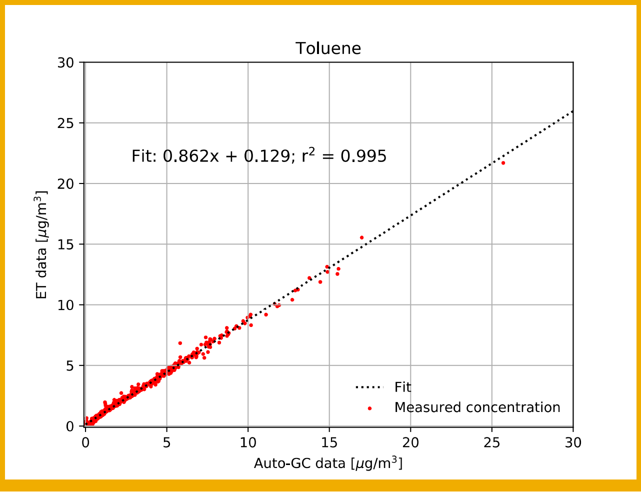
*MDL is 3-sigma, > 7x repeat, @ ~5x MDL delivered as per EPA 301. MDLs recorded simultaneously for all species in grouping.

Performance Validation: BAAQMD, ESTCP, EPA

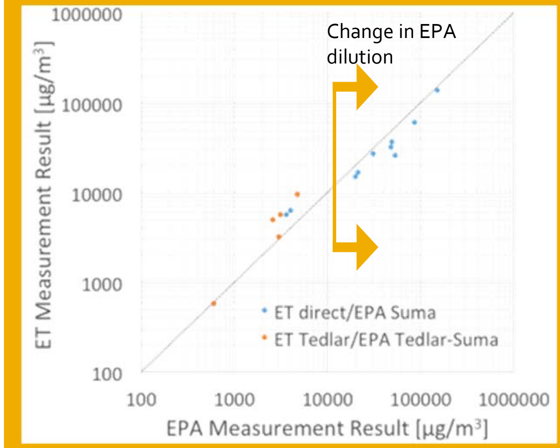
BAAQMD

Month-long, 24/7, unattended, side-by-side with dual column auto-GC



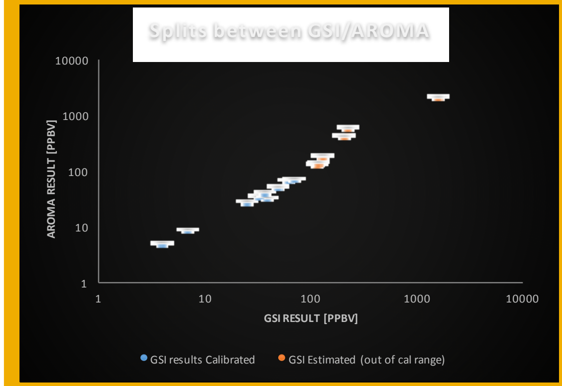


USEPA



- Side-by-side measurements with gold standard (SUMMA canister + GC/MS by TO-15) measurements performed by EPA lab (region 9).
- The dynamic range was so large that EPA used ET results to select dilution for analysis to prevent contamination of their instrument.

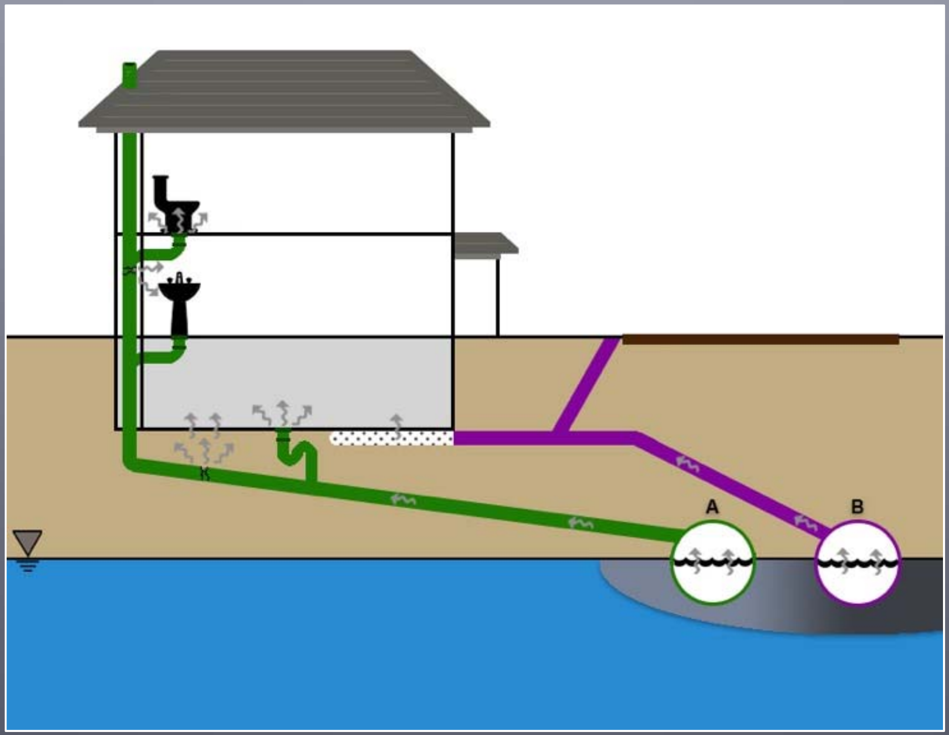
ESTCP



- Tedlar-based co-sampling of sanitary sewer headspace vs GC/MS
- Included in ESTCP sanitary sewer methodology study.

Introduction to Sewer Pathway

Variability complicates the picture



Key Features of the Sewer Pathway

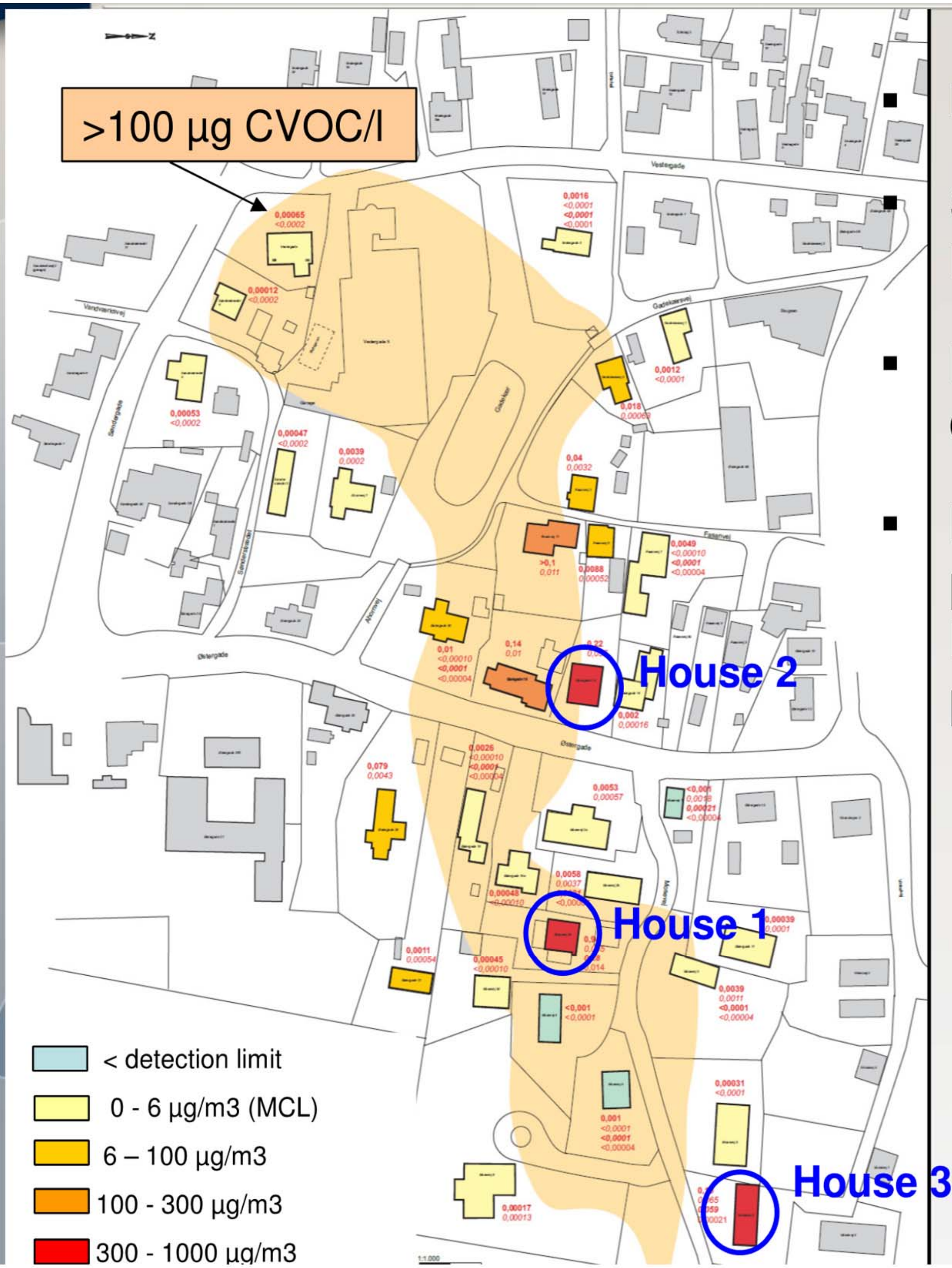
- cVOCs **frequently** migrate into sewer systems, particularly when sewers and groundwater intersect.
- cVOCs in the sewer **often** lead to unacceptable indoor air concentrations (~10%)
- Initial studies show attenuation factors of 0.02 (50x) have been found at multiple sites
- cVOCs in sewer systems pose a threat **that is comparable to direct soil-vapor driven VI**

cVOC concentrations in the sewer can be highly variable on multiple timescales

Prevalence of Sewer Contamination

Multiple studies across the US and internationally have identified cVOCs in sewer systems that intersect groundwater plumes, NAPL, or are in the vadose zone of groundwater contamination

- Elevated TCE/PCE concentrations have been found at a majority of sites.
- Most tested Sites have sewer @ or near water table.
  - Indiana Site has sewer in vadose zone
- ESTCP Study (Tom McHugh/ Lila Beckley @ GSI)
  - Five sites evaluated for TCE/PCE in sewer (ASU house, Indiana EPA house, Moffett, Houston Dry cleaners, Austin Dry cleaners)
  - In all areas concentrations of > 10x screening were found in >40% of man holes
- Kelly Pennell, ET and EPA
  - Extensive characterization of CA superfund site
- ET Study
  - 6 Bay area sites evaluated
    - TCE detected at 5 of 6 sites
    - TCE > 10x screening at 4 of 6 sites

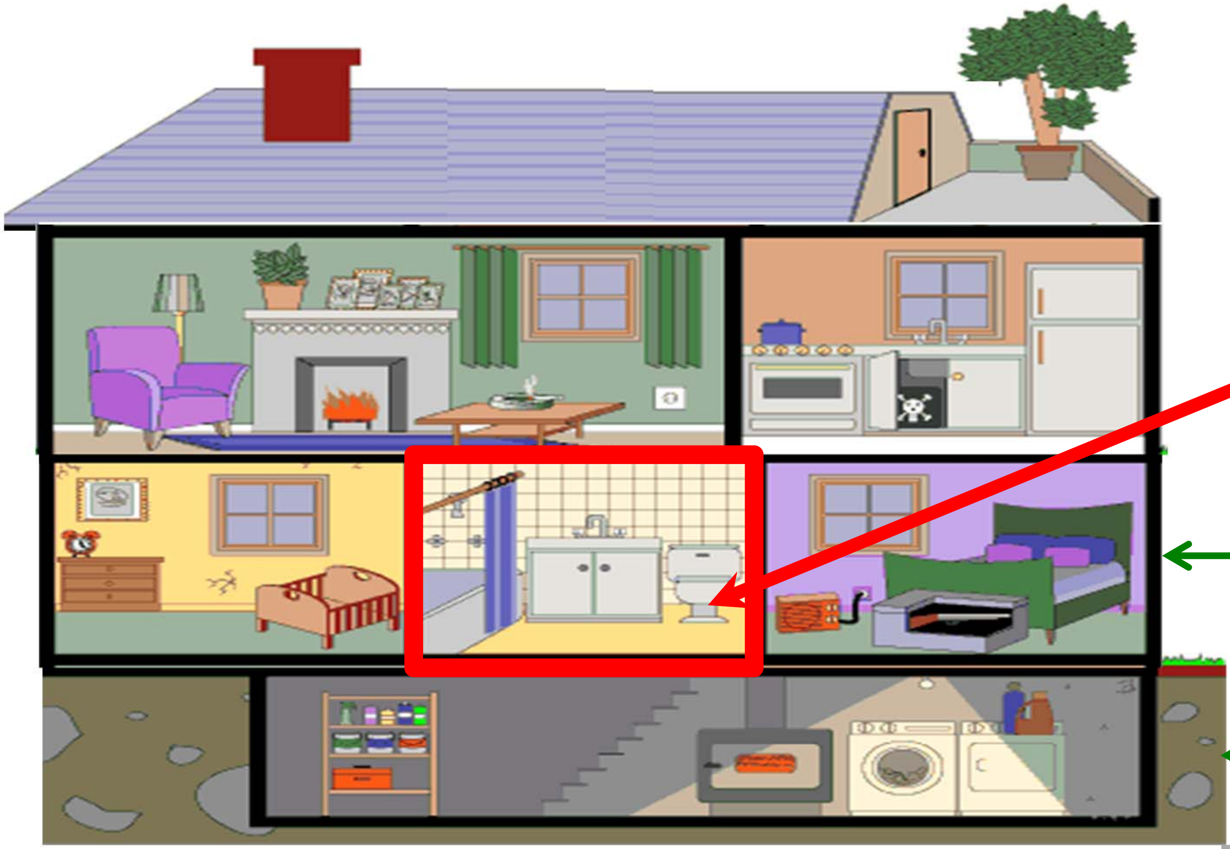


- Measurements in 32 houses
- Semi-annual monitoring in 15 houses
- PCE and degradation products detected in indoor air
- No clear correlation between plume extent and locations of houses with vapor intrusion problems

Results from investigations in 3 houses with significant VI problems

Riis et al., 2010, Vapor Intrusion through Sewer Systems: Migration Pathways of Chlorinated Solvents from Groundwater to Indoor Air, Battelle Conference.

Sewer Gas Confirmed as Source



Measured Indoor Air Concentrations for Tetrachloroethene (PCE)

Toilet Connection 190 ug/m3

First floor with Bathroom closed off 0.64 ug/m^3

Basement 0.36 ug/m^3

10^{-6} Cancer Risk = 11 ug/m^3
Non-Cancer Risk=42 ug/m^3

Pennell, K.G., Scammell, M.K., McClean, M.D., Ames, J., Weldon, B., Friguglietti, L., Suuberg, E.M., Shen, R., Indeglia, P.A., Heiger-Bernays, W.J., 2013. Sewer gas: an indoor air source of PCE to consider during vapor intrusion investigations. *Ground Water Monit. Rem.*:119–126

Do VOCs Move From Sewers Into Buildings?

YES - detected tracer in all buildings tested

Range of Sewer to Building Attenuation?

ASU House:	Land Drain System **20x – 40x**	Sanitary Sewer System **60x – 80x**
Indy Duplex:	Upstream Manhole **160x - >1000x**	Downstream Manhole **50x – 100x**
Moffett:	Sanitary Manhole **1300x - >2500x**	Telephone Manhole **45x – 50x**

Do VOCs Move From Sewers Into Buildings?

<u>YES</u> - detected tracer in all buildings tested

Range of Sewer to Building Attenuation?

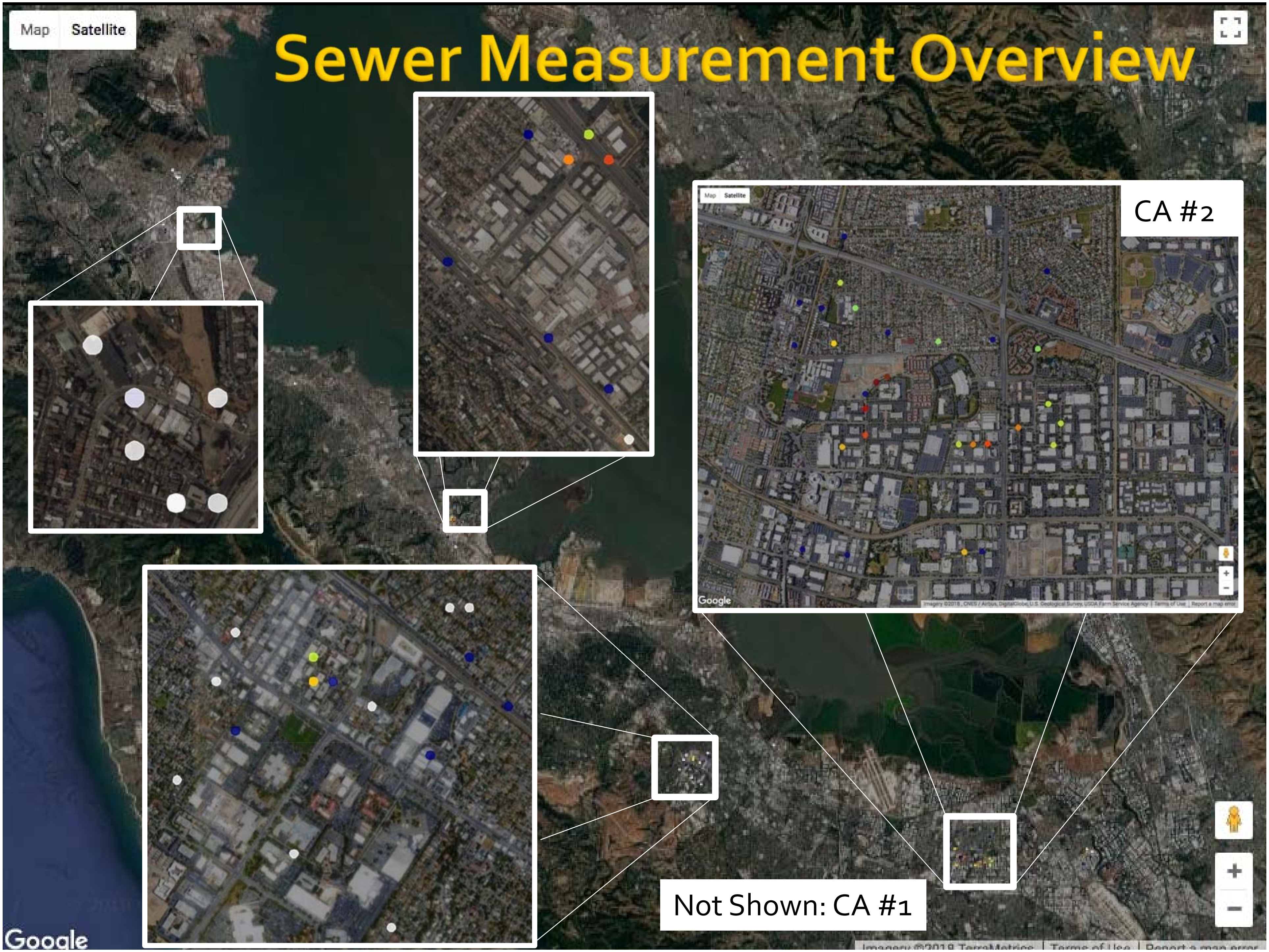
	Land Drain System	Sanitary Sewer System
ASU	20x – 40x	60x – 80x
Moffett:	1300x - >2500x	45x – 50x

cVOCs in sewer systems pose a threat **that is comparable to direct soil-vapor driven VI**

Temporal and Spatial Analysis of Sewer Head Space TCE concentartion in the SF Bay Area

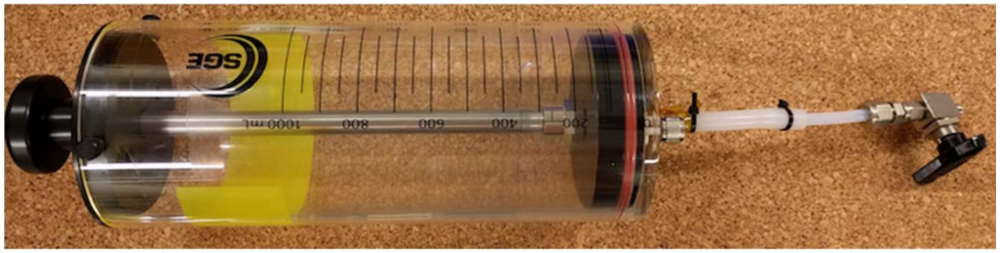
Variability complicates the picture

Sewer Measurement Overview



Sewer Sampling Methodology

- Direct Sampling to instrument
  - Sampled within one foot from bottom of manhole (as per McHugh *et. al.*)
- Syringe extraction with immediate analysis
  - Measurements performed ~6" below manhole cover vent
- Some manholes became inaccessible during the course of the study
- Daily QA/QC performed
- **Sampling Bias:** Several sewers were selected based on groundwater but through-cover access was impossible.

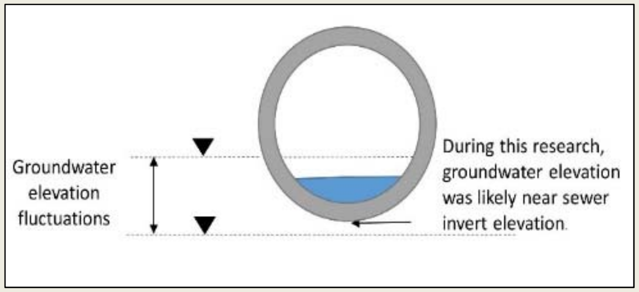


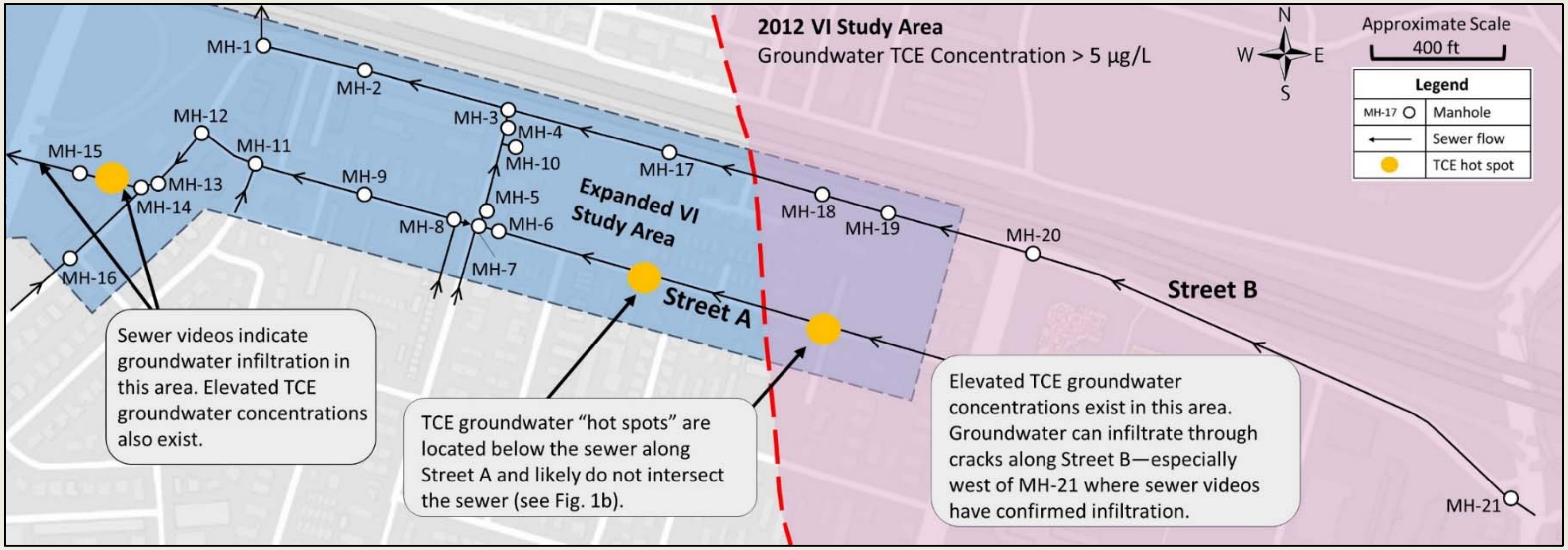
University of Kentucky (and others) conducted sewer gas sampling (Roghani *et al.* (2018))

Important information:

- Extents of contamination plumes
- Plume VOC concentrations
- Pipe failure locations (from CCTV sewer videos & reports)
- Plume and pipe intersection locations

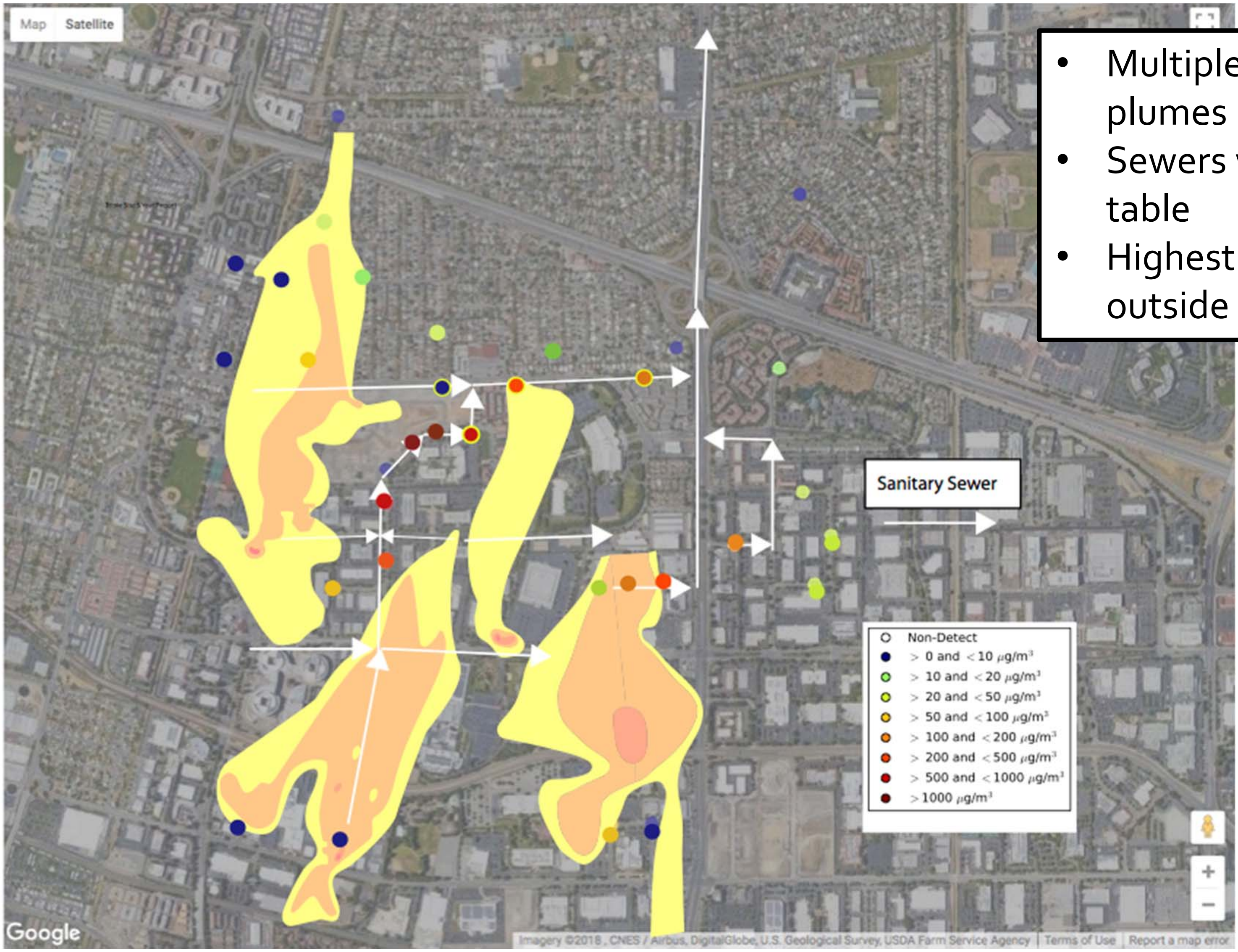
Groundwater was "near" the sewer invert:





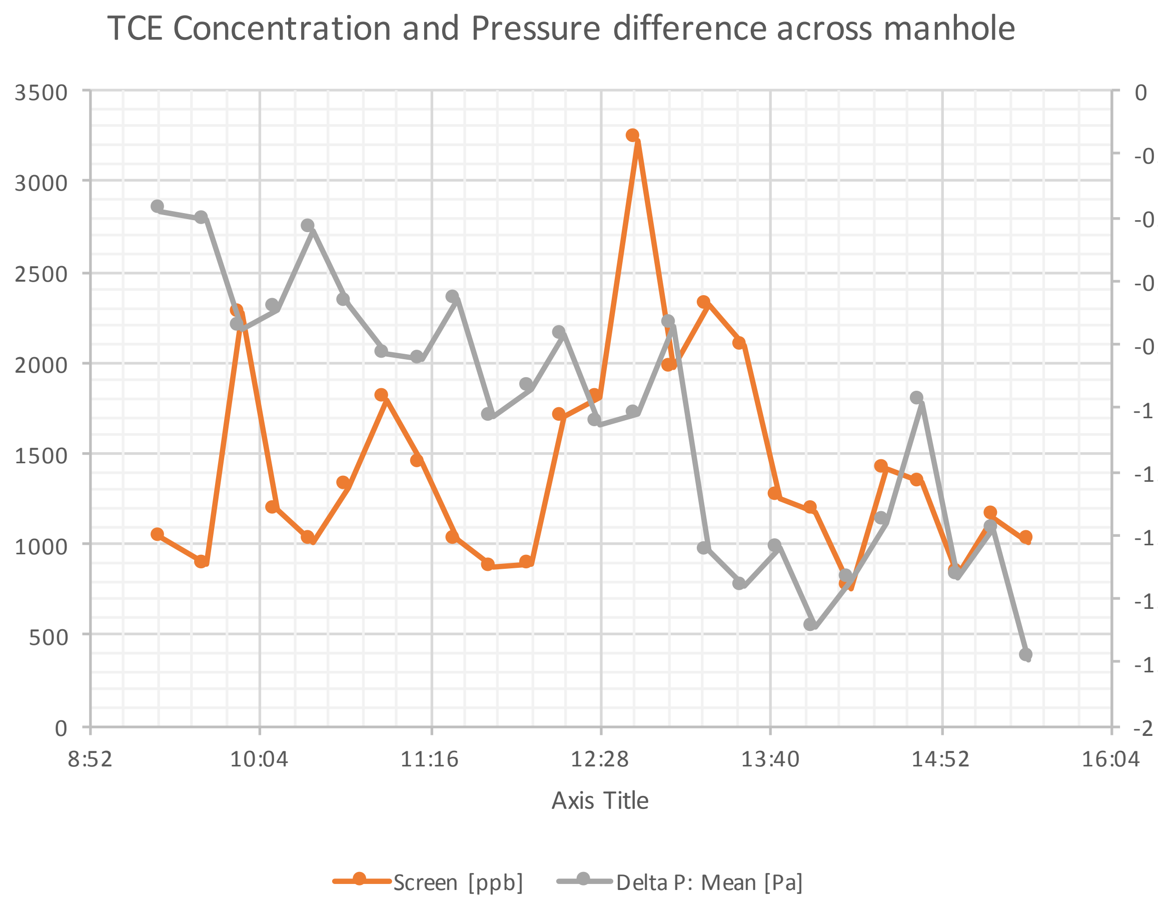
College of Engineering
Department of Civil Engineering

CA Site #2



- Multiple groundwater plumes
- Sewers within 3′ of water table
- Highest Concentrations outside of plumes

Short Term Temporal Variability



Moffett Field

- No correlations other than liquid concentration observed.
- Limited data collected (windspeed, temperature, across-manhole pressure)

Short Term Temporal Variability And Correlation

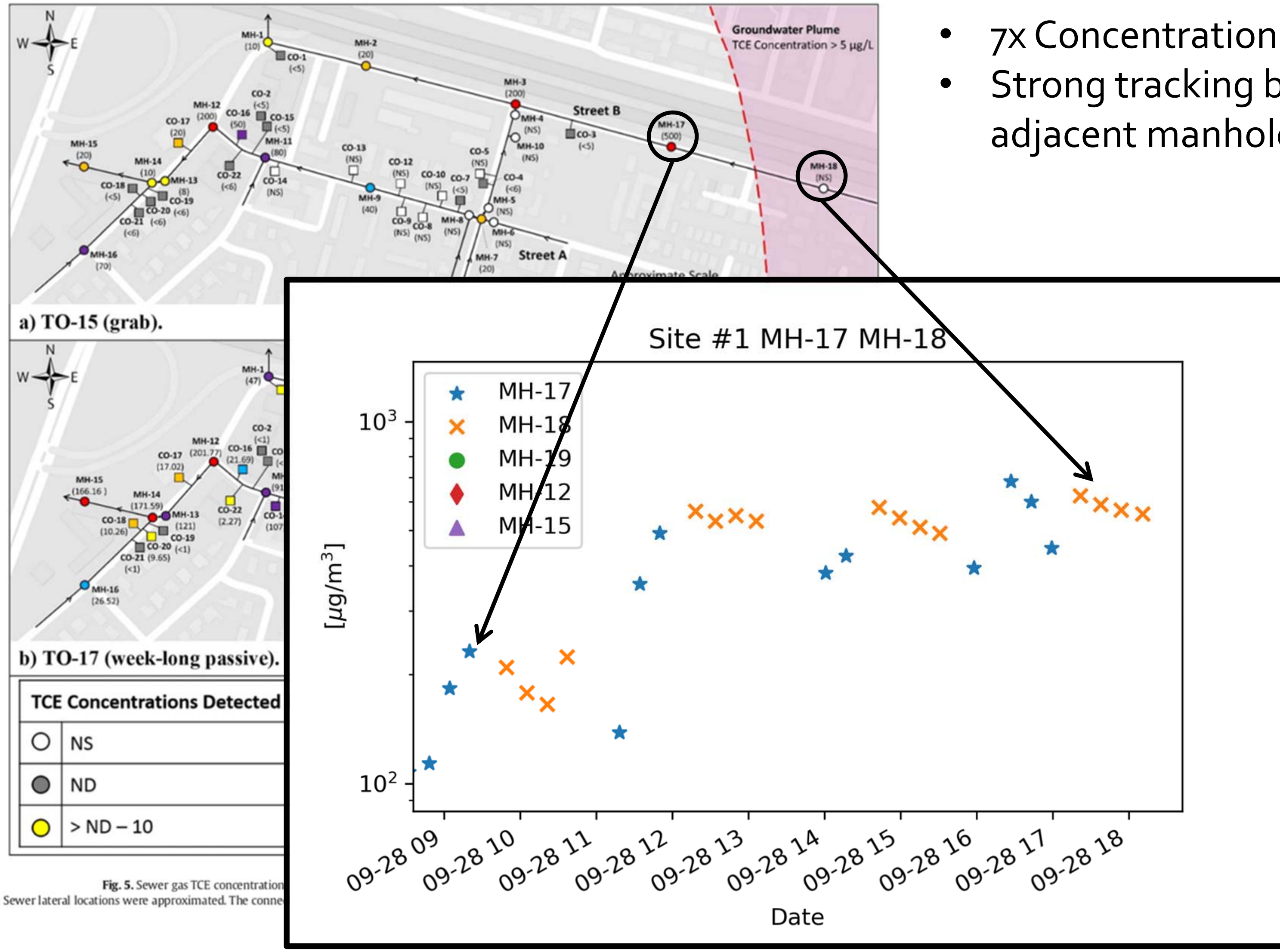
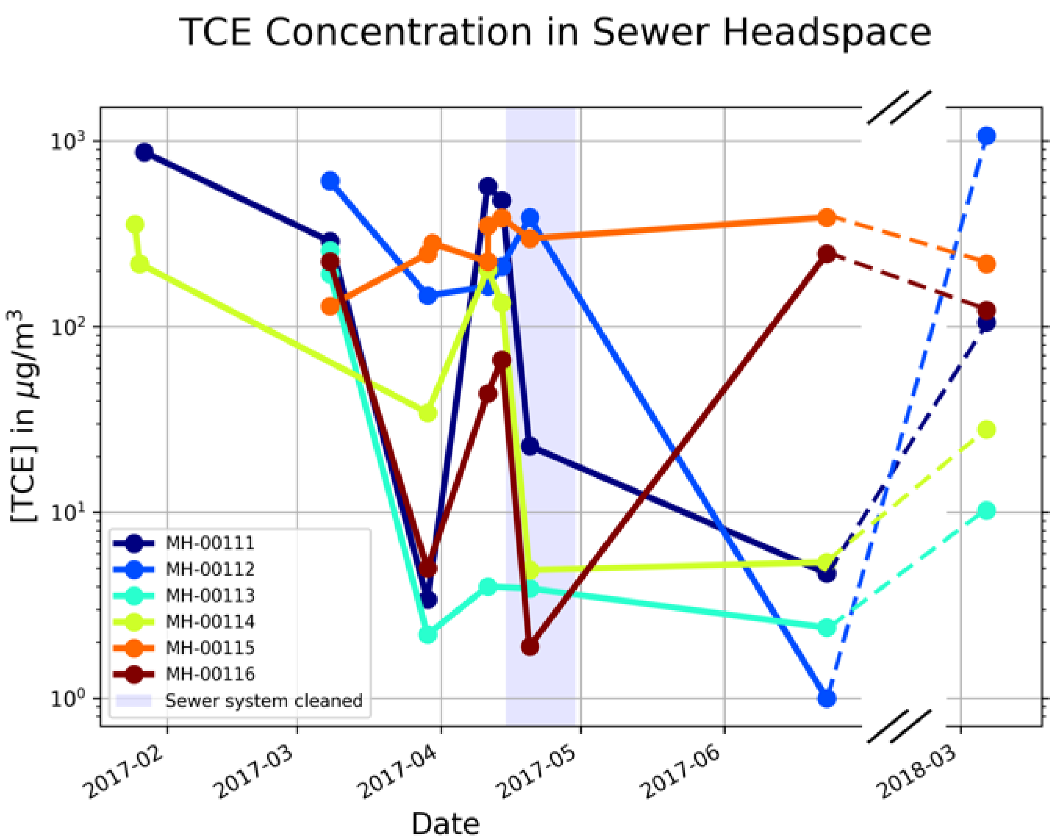


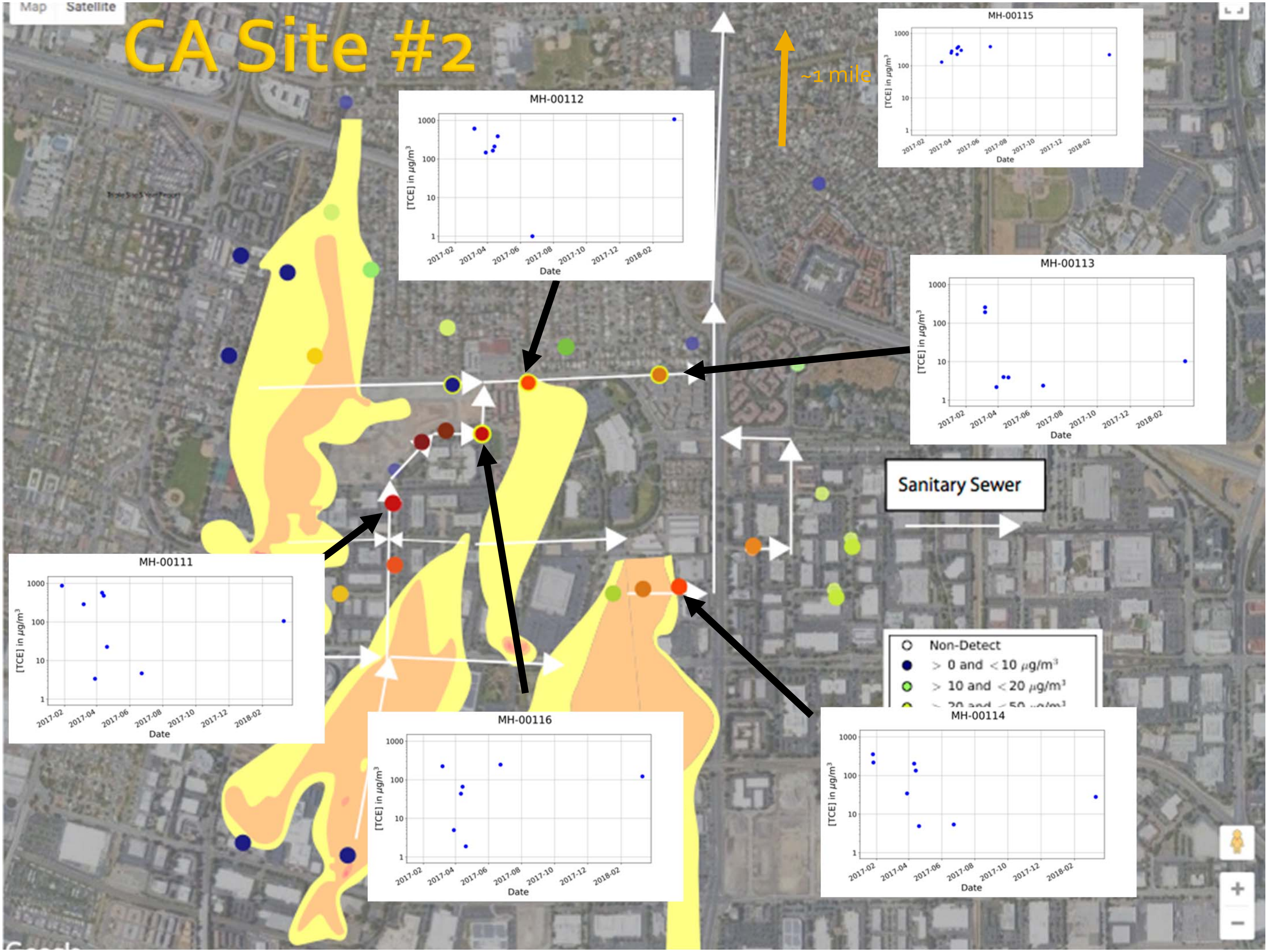
Fig. 5. Sewer gas TCE concentration
Note: Sewer lateral locations were approximated. The conne

- 7x Concentration change in 12 h
- Strong tracking between adjacent manholes.

One Year Variability (CA Site #2)

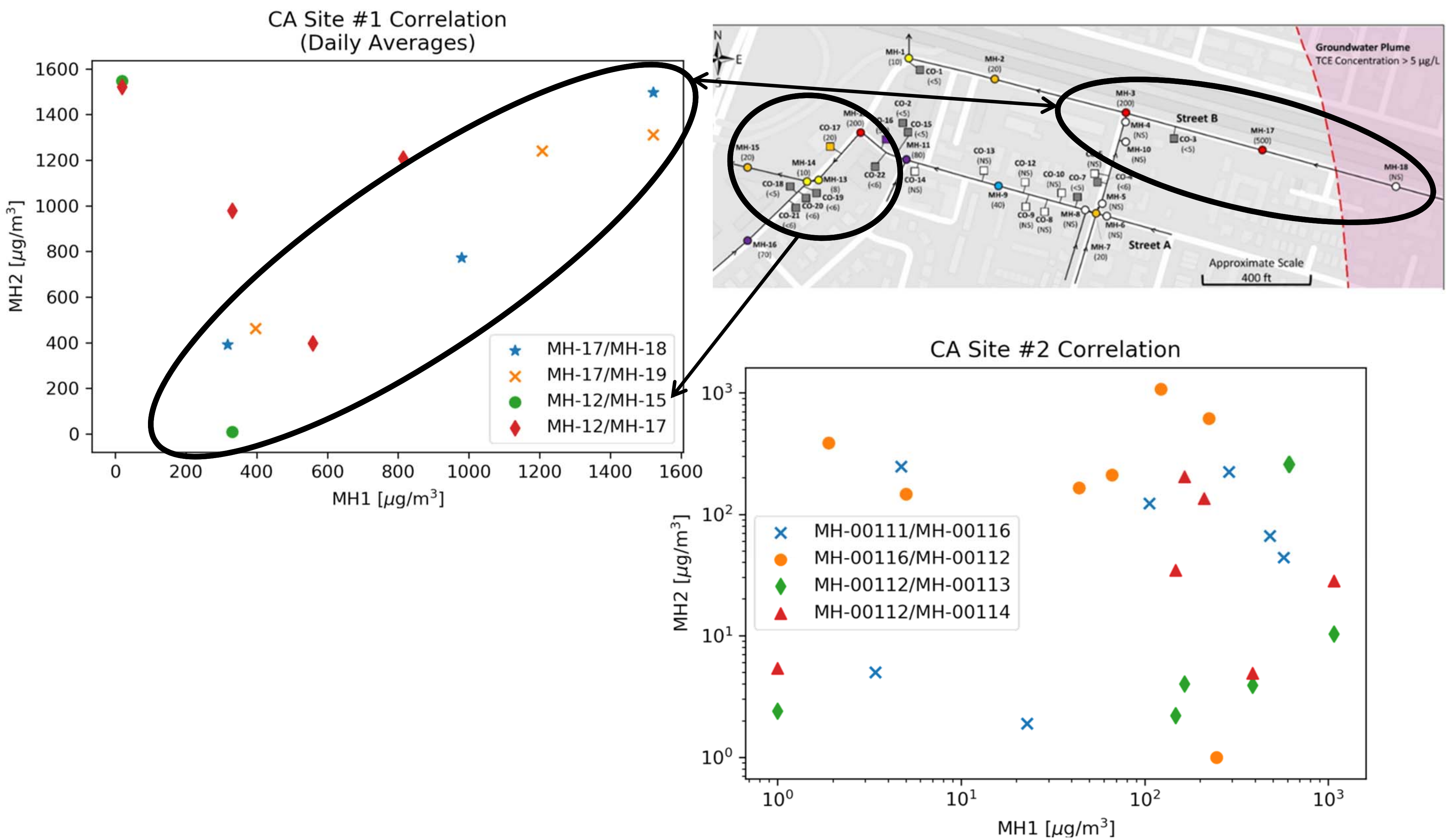


- 1000x variability in week-time scales
- Impact of sewer maintenance observed
- No source attribution
- Individual sites fluctuated from well above to well below TCE screening criteria

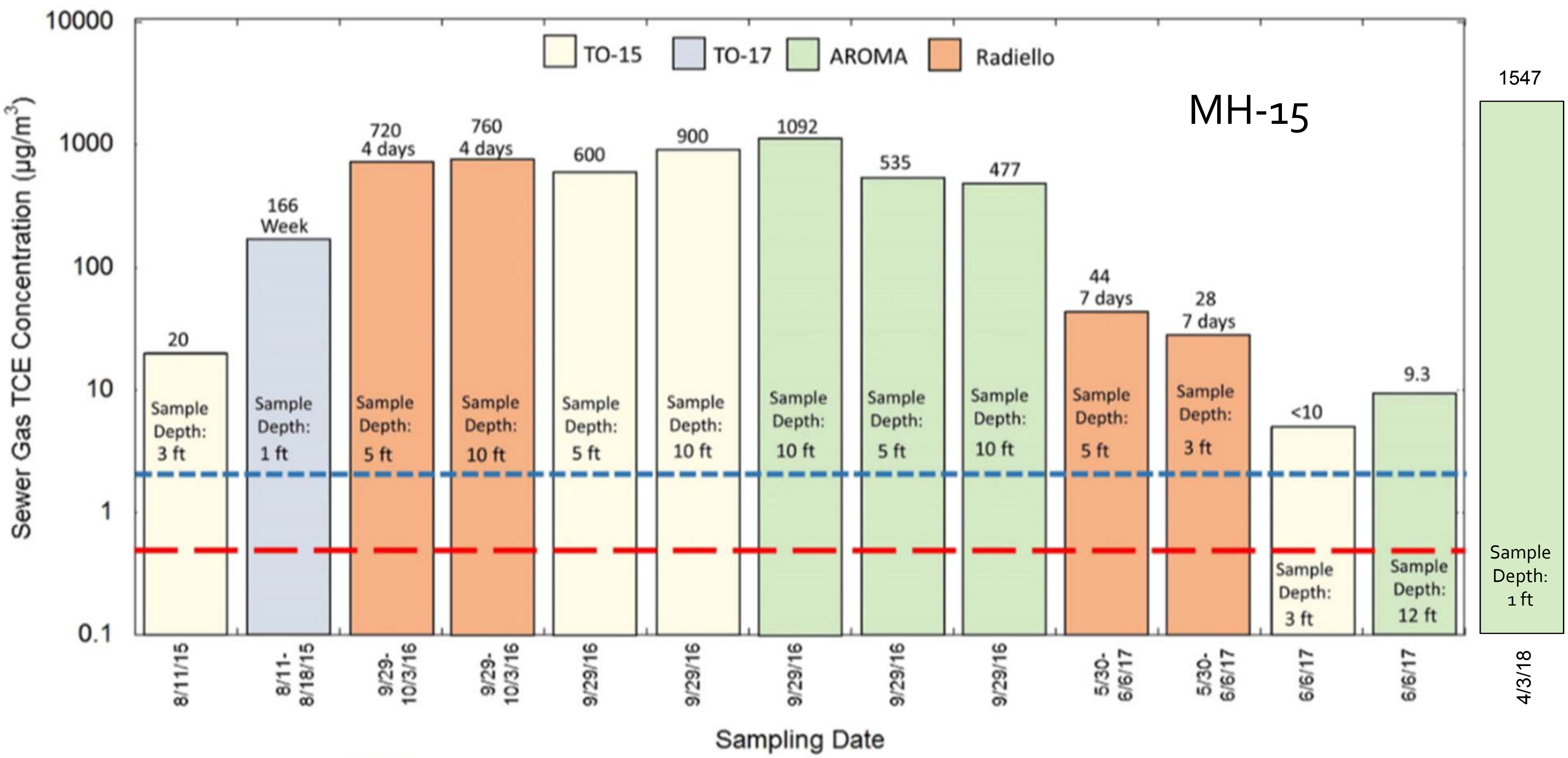


Map
Satellite
CA Site #2
~1 mile
MH-00112
MH-00115
MH-00113
MH-00111
MH-00116
MH-00114
[TCE] in μg/m³
Date
Sanitary Sewer
Non-Detect
> 0 and < 10 μg/m³
> 10 and < 20 μg/m³

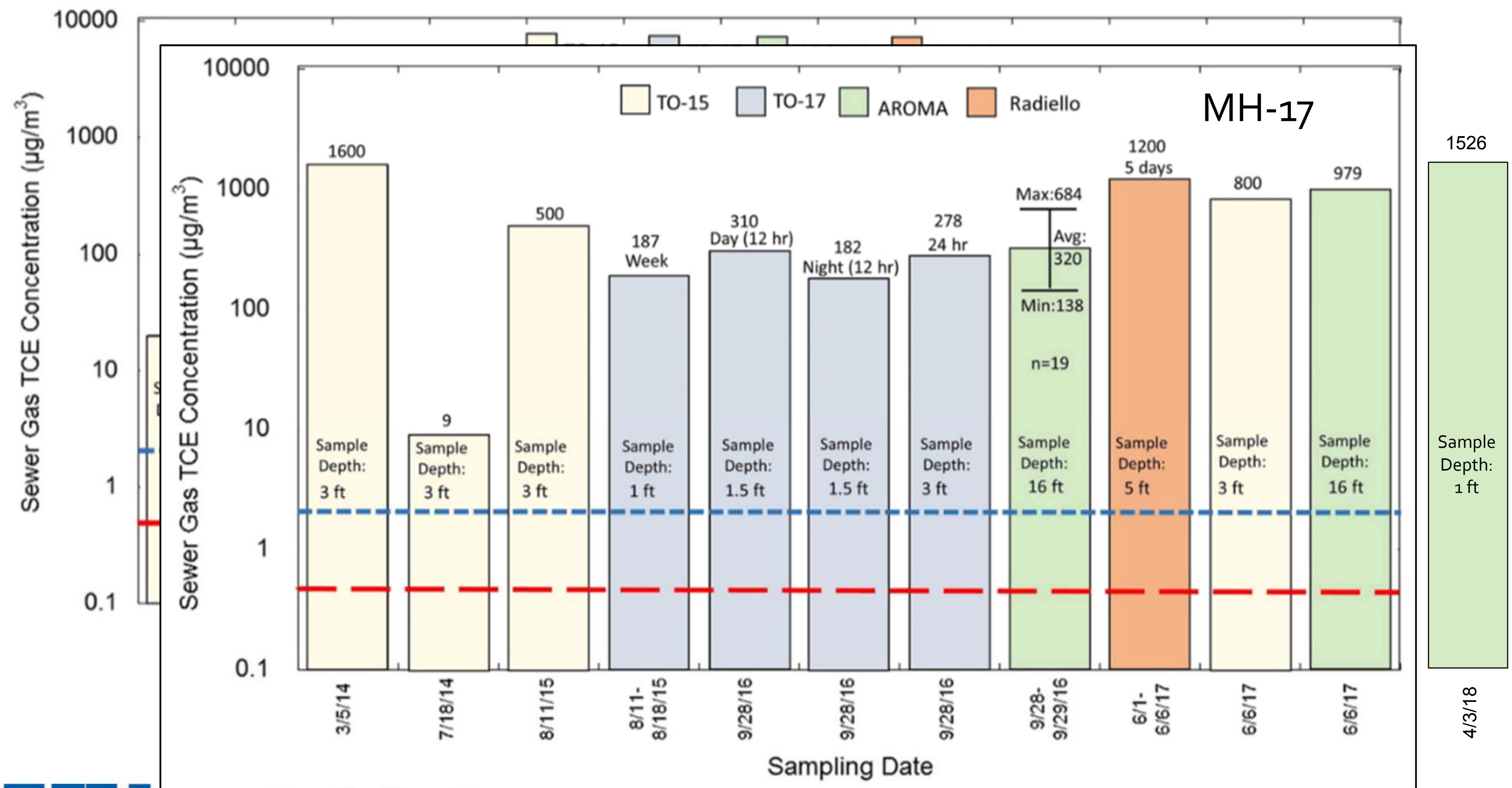
Long Term Correlation



Measurement Correlation (CA #1)

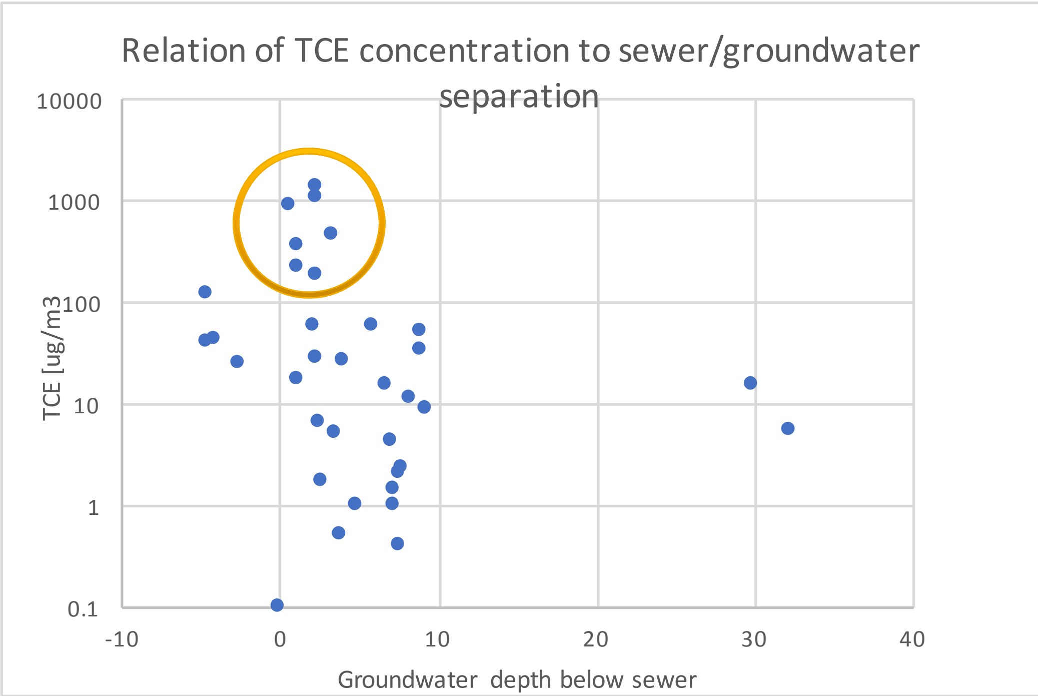


Measurement Correlation (CA #1)

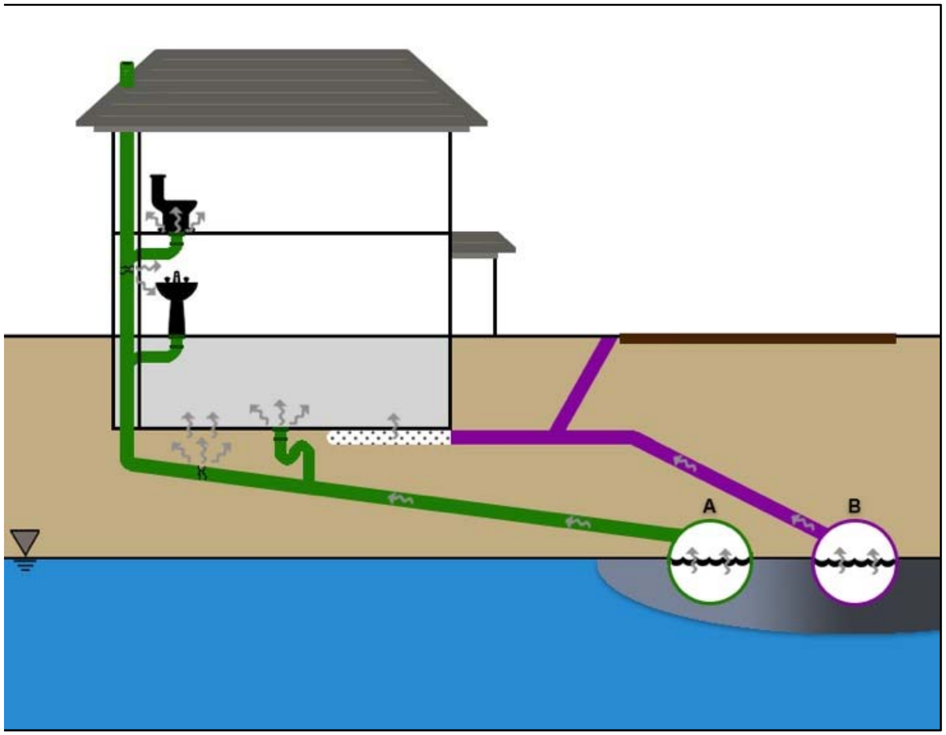


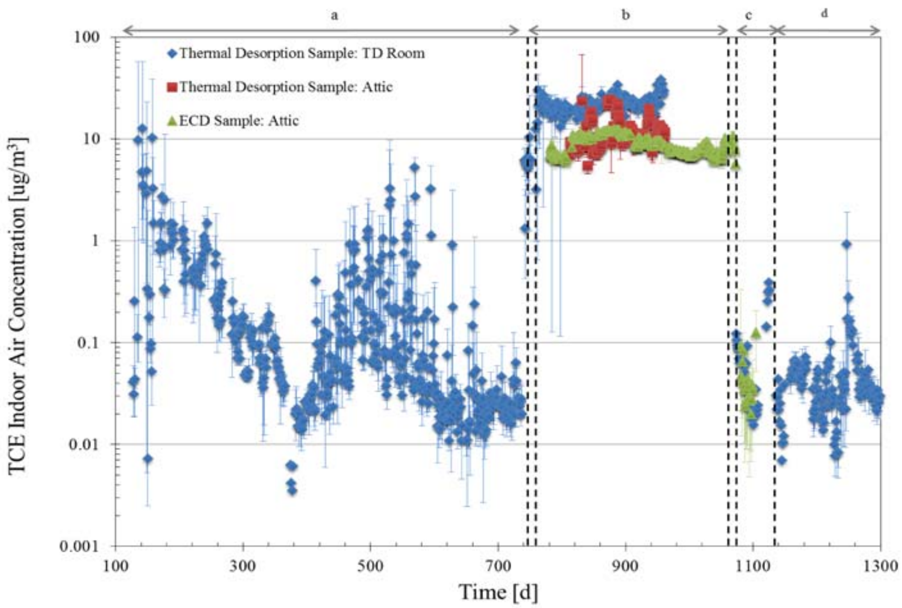
Relationship of TCE concentration to groundwater/sewer separation

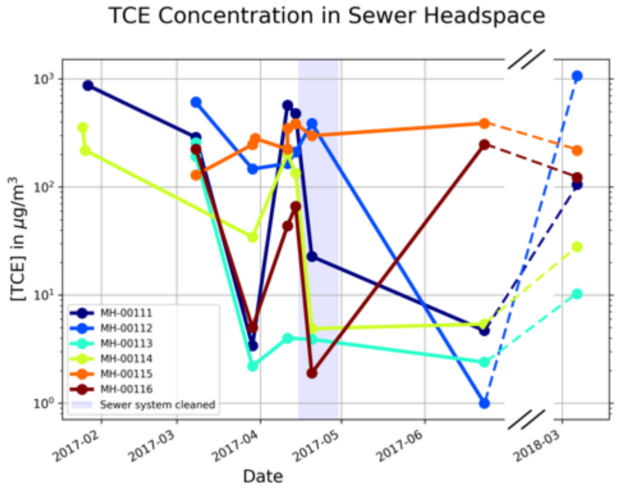
- Highest TCE concentrations observed when first groundwater and sewer are at same depth
- Groundwater depth extracted from monitoring well data
- Only a limited subset of all data has sewer depth and groundwater



Screening with Source and Pathway Variability





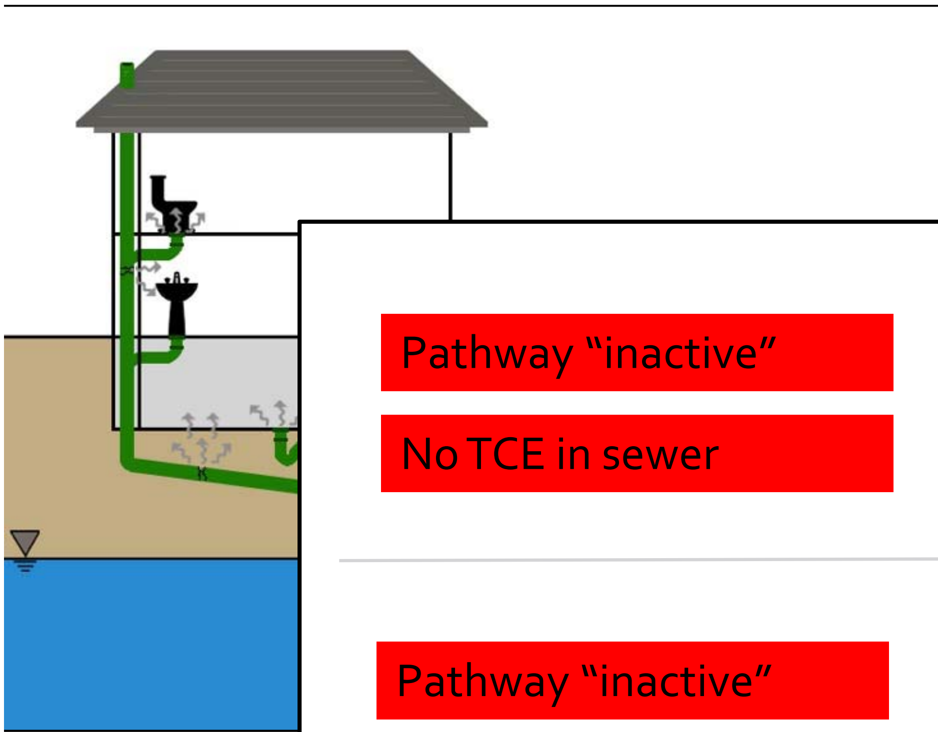


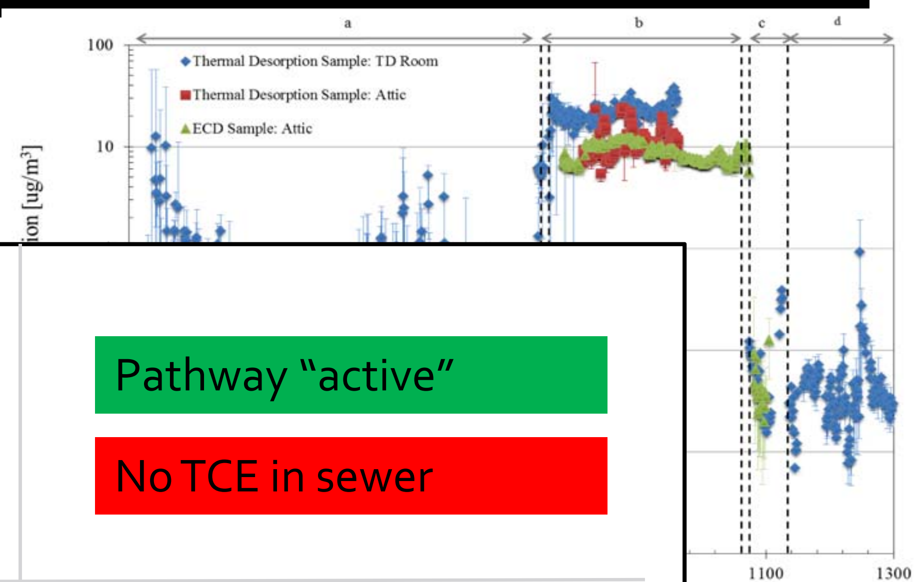
Yuanming Guo, *PhD Thesis*

GSI ENVIRONMENTAL

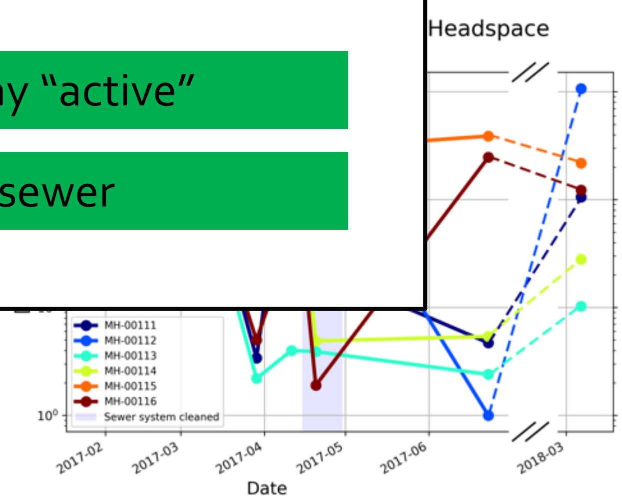
ASU ARIZONA STATE UNIVERSITY

Screening with Source and Pathway Variability





Pathway “inactive” No TCE in sewer	Pathway “active” No TCE in sewer
Pathway “inactive” TCE in sewer	Pathway “active” TCE in sewer



Yuanming Guo, *PhD Thesis*

GSI ENVIRONMENTAL

ASU ARIZONA STATE UNIVERSITY

Early Conclusions

- Significant cVOC concentration in sanitary sewers is *common*
- Elevated cVOC concentrations frequently extend well beyond plume boundaries
- Temporal and spatial variability observed in sewer gas over various scales
- More studies needed to understand sewer concentrations variability and transport to indoor air
- Understanding all variables at play is critical when designing VI mitigation strategies

Acknowledgements

Not Pictured: Mike Armen, Ari Kushner
Special thanks to Kelly G. Pennell, Tom McHugh, Lila Beckley, Yuanming Guo, Blayne Hartman, and Alana Lee for support and advice during this work.
This work was supported by the NIH under Grant No. 1R43ES022538-02 and the NSF under Grant No. IIP-1330903.

entanglement
TECHNOLOGIES, INC.

Tony Miller, CEO
amiller@entanglementtech.com
(650) 204-7875