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Rapid, Real-Time TCE Measurements of Sewer Headspace: Characterizing Spatial and Temporal Variability
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 O₂, H₂O

**Inlet**
- Direct/Air manifold
- Direct fluid sampling system

**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

**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 x 10⁻¹² cm⁻³/√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

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

| Matrices (typical) | Soil Gas, Indoor Air, Outdoor Air, Sewer Headspace |

#### Dynamic Headspace

- **Matrices (typical):** Soil Gas, Indoor Air, Outdoor Air, Sewer Headspace

#### Oil-Field Tracer Analysis (via direct sampling front end)

<table>
<thead>
<tr>
<th>Species</th>
<th>MDL [ppb]*</th>
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<tbody>
<tr>
<td>IPA</td>
<td>6</td>
</tr>
<tr>
<td>1-propanol</td>
<td>0.7</td>
</tr>
<tr>
<td>1-butanol</td>
<td>0.7</td>
</tr>
<tr>
<td>1-pentanol</td>
<td>0.4</td>
</tr>
<tr>
<td>Fluoro-alcohol 1</td>
<td>1.5</td>
</tr>
<tr>
<td>Fluoro-alcohol 2</td>
<td>1.9</td>
</tr>
<tr>
<td>Matrices</td>
<td>Oil-field Produced Brine</td>
</tr>
</tbody>
</table>

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*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**
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
VI Off Plume

- 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/m³
- Basement: 0.36 ug/m³

10⁻⁶ Cancer Risk = 11 ug/m³
Non-Cancer Risk = 42 ug/m³

Do VOCs Move From Sewers Into Buildings?

**YES** - detected tracer in all buildings tested

### Range of Sewer to Building Attenuation?

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<tr>
<th>Location</th>
<th>Land Drain System</th>
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<td>20x – 40x</td>
<td>60x – 80x</td>
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<tr>
<td>Indy Duplex:</td>
<td>160x - &gt;1000x</td>
<td>50x – 100x</td>
</tr>
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<td>Moffett:</td>
<td>1300x - &gt;2500x</td>
<td>45x – 50x</td>
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Preliminary Results from ESTCP Project ER-201505
Do VOCs Move From Sewers Into Buildings?

YES - detected tracer in all buildings tested

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

Preliminary Results from ESTCP Project ER-201505
Temporal and Spatial Analysis of Sewer Head Space TCE concentration 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
CA Site #1

CA Site #2
Short Term Temporal Variability

Sequential Measurement at Two Adjacent Manholes

TCE Concentration and Pressure difference across manhole

CA Site #1

Moffett Field
One Year Variability (CA Site #2)

- 1000x variability in week-time scales
- Moderate correlation between sewer headspace concentrations
- Impact of sewer maintenance observed
- No source attribution
- Individual sites fluctuated from well above to well below TCE screening criteria
Multi-year Variability (CA #1)
Multi-year Variability (CA #1)
CA Site #2

Map of Sanitary Sewer and data points

MH-00112

MH-00113

MH-00111

MH-00116

MH-00114

-3 mile
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
Figure D.4. 24-h average indoor air TCE concentrations for the four building operation conditions: a) natural condition with lateral pipe connected; b) CPM condition with lateral pipe connected; c) CPM condition with lateral valve closed and d) natural condition with lateral pipe closed. Error bars indicate the daily minimum and maximum values.
Figure D.4: 24-h average indoor air TCE concentrations for the four building operation conditions: a) natural condition with lateral pipe connected; b) CPM condition with lateral pipe connected; c) CPM condition with lateral valve closed and d) natural condition with lateral pipe closed. Error bars indicate the daily minimum and maximum values.

- 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
**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.
ET science and engineering team

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Ricardo Viteri
Gunnar Skulason
Anthony Miller

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.

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