Self-Sustaining Active Remediation (STAR) for Contaminated Soils or Liquid Waste

Advances in Quantitative Passive Sampling for Vapour Intrusion Assessments

Brownfields: The Next Generation
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STAR and STARx are based on the process of smoldering combustion:

Exothermic reaction converting carbon compounds to $\text{CO}_2 + \text{H}_2\text{O}$

smoldering possible due to large surface area of organic liquids (e.g., NAPL) within the presence of a porous matrix (e.g., aquifer)
**Modes of Application**

**STAR**

- **In situ (below water table)**
  - Applied via wells in portable in-well heaters
- **Range of contaminants:**
  - Petroleum Hydrocarbons
  - Coal tar
  - Creosote
- **High volatility compounds require fuel surrogate**

**STARx**

- **Ex situ (above ground)**
  - Soil piles placed on “Hottpad” system
- **Highly effective and controlled applications**
- **Ideal for:**
  - Excavated contaminated soils and sediments
  - Waste oils / tank bottom residuals
  - Lagoon sludge
STARx – “Hottpad” Systems

- Contaminated Soil
- Vapor Conveyance Piping
- Vapor Extraction Piping, Cover, and Deployment System
- Loading of Contaminated Soil
- Active Treatment Cell
- Engineered Base for Ignition and Air Injection
- Clean Treated Soil
- Unloading of Clean Treated Soil
• 37-acre former manufacturing facility in Newark, New Jersey
• Coal tar associated with former waste lagoons (now in-filled)
• 55,000 CY impacted soils:
  • Shallow fill (0-10 ft bgs)
  • Deep Sand (~10-40 ft bgs)
STAR Case Study

- Two target layers:
  - Shallow Fill
  - Deep Sand

- Shallow Fill:
  - 1700 wells
  - 20-well Cells
  - 10’ separation

- Deep Sand:
  - 300 wells
  - 6-well Cells
  - 20’ separation

- Operation organized by:
  - Well
  - Cell (groups of Wells operated simultaneously)
  - Node (groups of Cells serviced by single system deployment)
Recuperative Thermal Oxidizer

In well Heater

Well head connection

Extracted Vapors to RTO

Vacuum Extraction

Air Injection for Well Points

Treatment Trailer

Full-scale System
Example Cell: 3-D-03
~10,000kg of coal tar destroyed (via 6 wells) in approximately 10 days

100,000 Safe Working Hours
Full-scale Hottpad – Field Deployment
• Designed for 3,500 m³ of API separator sludge
• Petroleum hydrocarbon-impacted soils
## Full-scale Hottpad - Results

<table>
<thead>
<tr>
<th>Compound</th>
<th>&quot;Before&quot; Concentration (mg/kg)</th>
<th>&quot;After&quot; Concentration (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTEX</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>TPH C$_6$-C$_9$</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>TPH C$<em>{10}$-C$</em>{14}$</td>
<td>356</td>
<td>ND</td>
</tr>
<tr>
<td>TPH C$<em>{15}$-C$</em>{28}$</td>
<td>25,400</td>
<td>ND</td>
</tr>
<tr>
<td>TPH C$<em>{29}$-C$</em>{36}$</td>
<td>9,750</td>
<td>ND</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>35,506</strong></td>
<td><strong>ND</strong></td>
</tr>
</tbody>
</table>
Conventional Active Soil Gas Sampling
Passive Sampling

The mass (M) and time (t) are measured accurately. The key is to know the uptake rate (UR).

\[ C_0 = \frac{M}{UR \times t} \]

UR has units of mL/min
Starvation

In soil and under building slabs, air flow is low, and may produce the “starvation effect” when collecting passive samples, leading to negative bias.

Starvation occurs when the uptake rate of the sampler is higher than the delivery rate of analytes to the sampler; the sampler will “scrub” its environment, causing a low concentration bias.
Mathematical Modeling

What would we expect for the diffusive delivery rate (DDR)?
Steady-State Model

![Graph showing diffusive delivery rate vs. water-filled porosity with different delta values. The graph is semi-logarithmic. Total porosity is 37.5%.]
Lower the Uptake Rate

- Decrease area of sampling surface
- Increase membrane thickness
Concentration in Waterloo Membrane Sampler (µg/m³)

Concentration in Active Sampler (µg/m³)

- Uptake rate about 1 mL/min
- Uptake rate about 0.2 mL/min
Another Use for Passive Samplers: **Long-term Indoor Air Sampling**
Results

![Graph showing measured vs. theoretical uptake rate](image)

- **1:1 line**
- **50% RPD**
Draft Technical Guidance:
Soil Vapour Intrusion Assessment
September 2013

Ministry of the Environment

PIBS # 8477

4) Waterloo Membrane Samplers™. This sampler is composed of a 1.8 mL standard crimp-top chromatographic autosampler vial partially filled with a known amount of adsorbent medium and closed with a polydimethylsiloxane (PDMS) membrane (Zabiegała, et. al., 2006, Gorecki and Namiesnik, 2002). The cross-sectional area and thickness of the membrane are controlled and the partitioning into and permeation across the membrane has been experimentally determined at different temperatures for 40 different compounds ranging from n-alkanes and aromatic hydrocarbons to alcohols and chlorinated organic compounds containing one to three carbon atoms.

PDMS is used as a stationary phase on capillary columns used in gas chromatography and the rate of uptake through the membrane is correlated to the gas chromatographic linear temperature-programmed retention indices (LTFRI) of the analytes. Thus, the calibration constants can be easily estimated from the chromatographic retention times of the analytes. This makes it possible to estimate the concentrations of VOCs whose identity is unknown at the time of sampling and to quantify complex mixtures of analytes (e.g. petroleum fractions). The membrane is also non-porous and very hydrophobic, which avoids concerns for sampling in high wind-speed or high moisture environments.
Summary

- Passive sampling for soil gas sampling has many advantages over active sampling
  - ease of use
  - reproducibility (simple protocols, less inter-operator error)
  - time-weighted average smooths temporal variability

- Starvation can be mathematically described, and passive samplers designed to minimize the starvation effect
  - This innovation was awarded a US patent (#9399912) in 2016

- Waterloo Membrane Samplers can be used for
  - quantitative passive soil vapour sampling
  - long-term indoor air sampling

- Passive sampling is accepted in the MOECC vapour intrusion guidance


