# Potential Use of Passive Sampling for Environmental Monitoring of Petroleum E&P Operations

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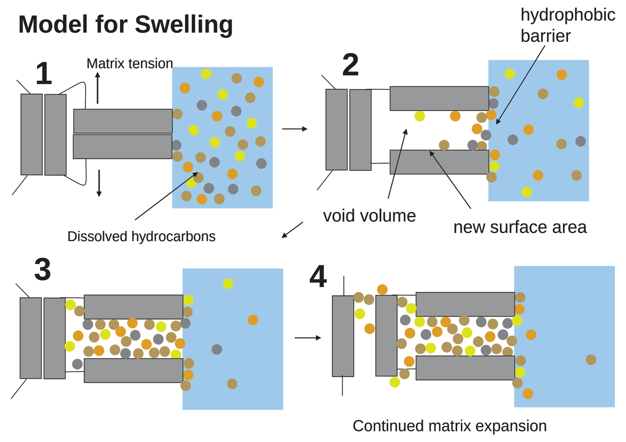
Traditional environmental monitoring relies on water or soil samples being taken at various time increments and sent to offsite laboratories for analysis. Reliance on grab samples generally captures limited "snapshots" of environmental contaminant concentrations, is time intensive, costly, and generates residual waste from excess sample and/or reagents used in the analysis process. As an alternative, we are evaluating swellable organosilica sorbents to create passive sampling systems for monitoring applications. Previous work has focused on absorption and detection of fuels, chlorinated solvents, endocrine disruptors, explosives, pesticides, fluorinated chemicals, and metals including Ba, Sr, Hg, Pb, Fe, Cu, and Zn. The advantages of swellable organosilica are that the material can capture target compounds for an extended periods of time, does not absorb natural organic matter, and resists biofilm formation since the sorbent possesses an animated surface morphology.

### Project Goals:

1. Measure capture affinity for a wide range of chemical species related to oil and gas E&P operations.
2. Develop effective calibration methods for quantitation.

Swellable organosilica capable of absorbing liquid and gaseous compounds. Commercially available as Osorb®.

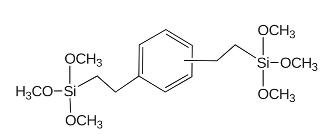

**Above**: Snapshot series of Osorb swelling when acetone is added drop-wise.

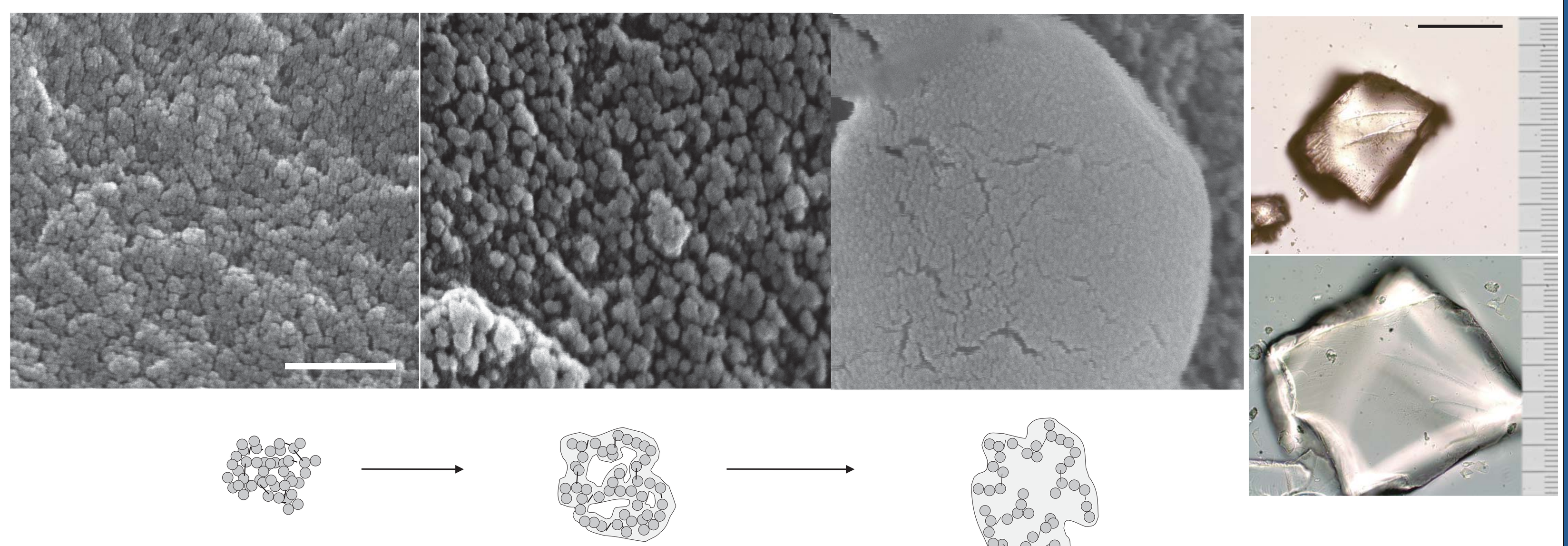



Proposed model for absorption of dissolved organics by swellable organosilica. (1) Initial adsorption to the surface of the material. (2) Sufficient adsorption occurs to trigger matrix expansion leading to absorption across the Osorb-water boundary. (3) Pores fill leading to further percolation into the porous matrix. (4) Further matrix expansion increases available surface area and void volume.

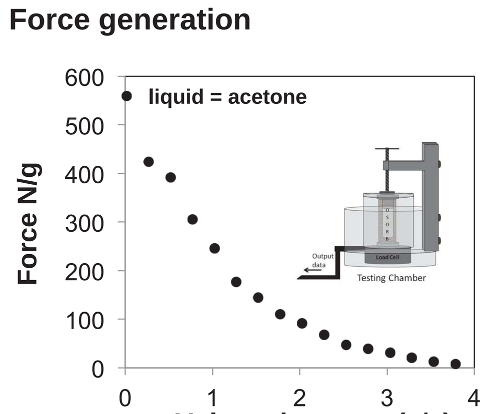
**Properties**

- Osorb silica nanomaterials swell 3x original volume
- Absorbs organic solvents out of water
- Swells rapidly and with generates large forces (100 N/g)
- Swelling is reversible
- Inert matrix





### Force generation




| | |
|---|---|
| Max force | 600 N/g (61,000 *w/w*) |
| Work = | 0.8 ± 0.1 J/g |
| $\Delta H_{swell}$ = | 5.2 ± 1.2 J/g |

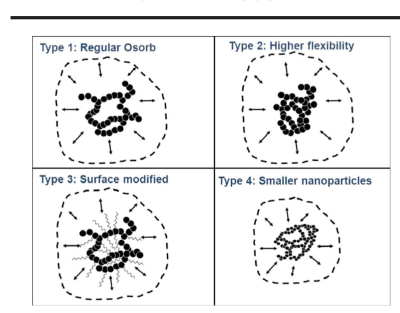
Entropically driven process

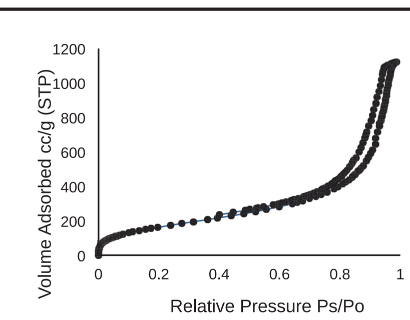
300% $\Delta V$, 650% $\Delta mass$

### Form Factors

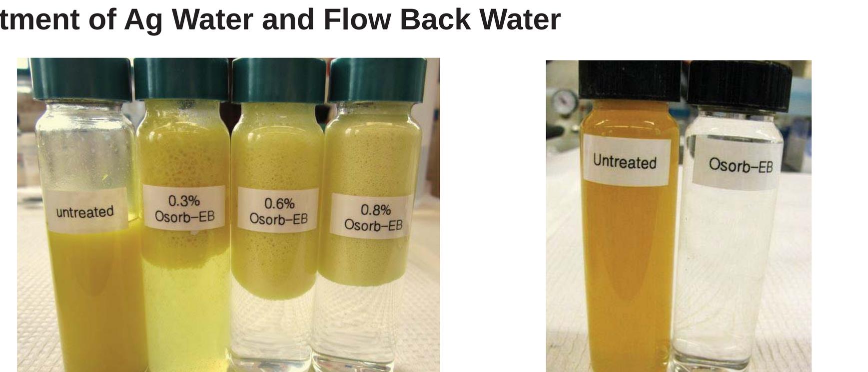
### Surface Area and Pore Volume

| Type | Swell mL/g | Surface Area($m^2$/g) | Pore Volume (mL/g) | Pore Size Distribution (%) under 6 nm | 6-8 nm | 20-80 nm |
|---|---|---|---|---|---|---|
| 1 | 5.2 | 885 | 2.85 | 6 | 8 | 68 |
| 2 | 9.8 | 416 | 0.57 | 48 | 22 | - |
| 3 | 4.6 | 171 | 0.27 | 98 | - | - |
| 4 | 2.5 | 803 | 0.98 | 20 | 15 | 38 |



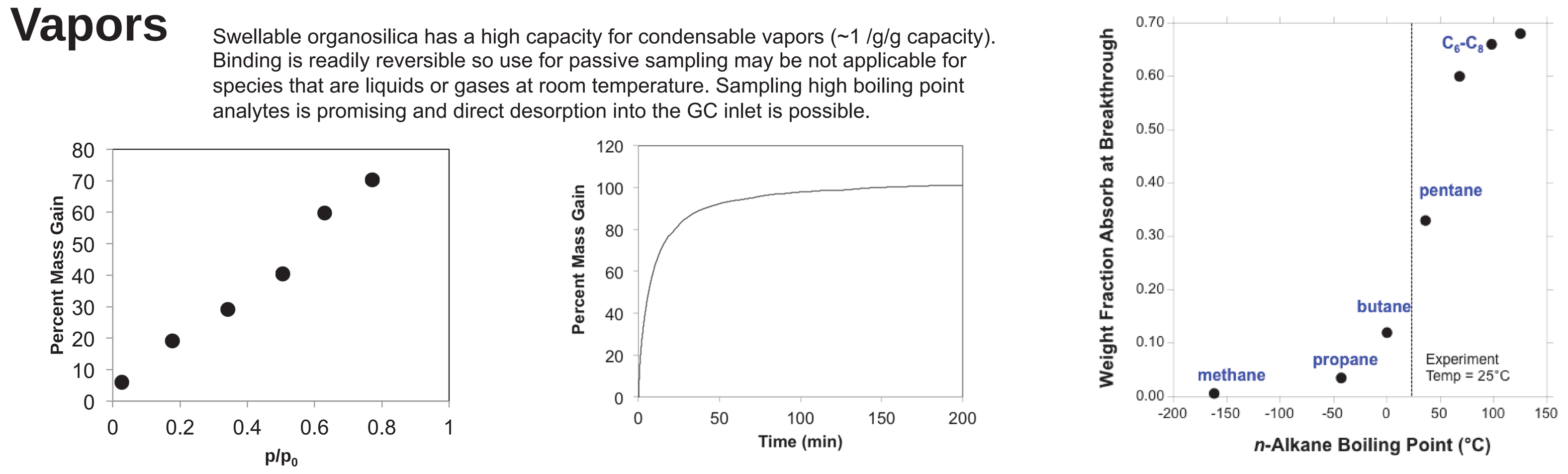

### Treatment of Ag Water and Flow Back Water




(Left) Treatment of crop duster rinse water with 0.3%, 0.5%, and 0.8% swellable organosilica. (Right) Treatment of flow back water with 0.4% swellable organosilica.

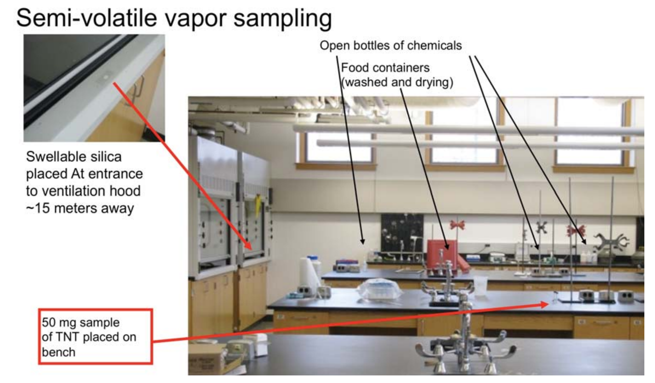
## Vapors

Swellable organosilica has a high capacity for condensable vapors (~1 /g/g capacity). Binding is readily reversible so use for passive sampling may be not applicable for species that are liquids or gases at room temperature. Sampling high boiling point analytes is promising and direct desorption into the GC inlet is possible.

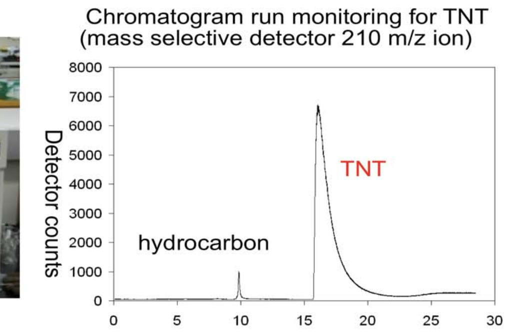



**Left.** Absorption isotherm for acetone vapor as a function of pressure. **Middle.** Absorption isotherm as a function of time at saturated vapor pressure. **Right.** Weight fraction absorbed at 25°C for alkane vapors at saturated vapor pressure and 1 atm.

Semi-volatile vapor sampling

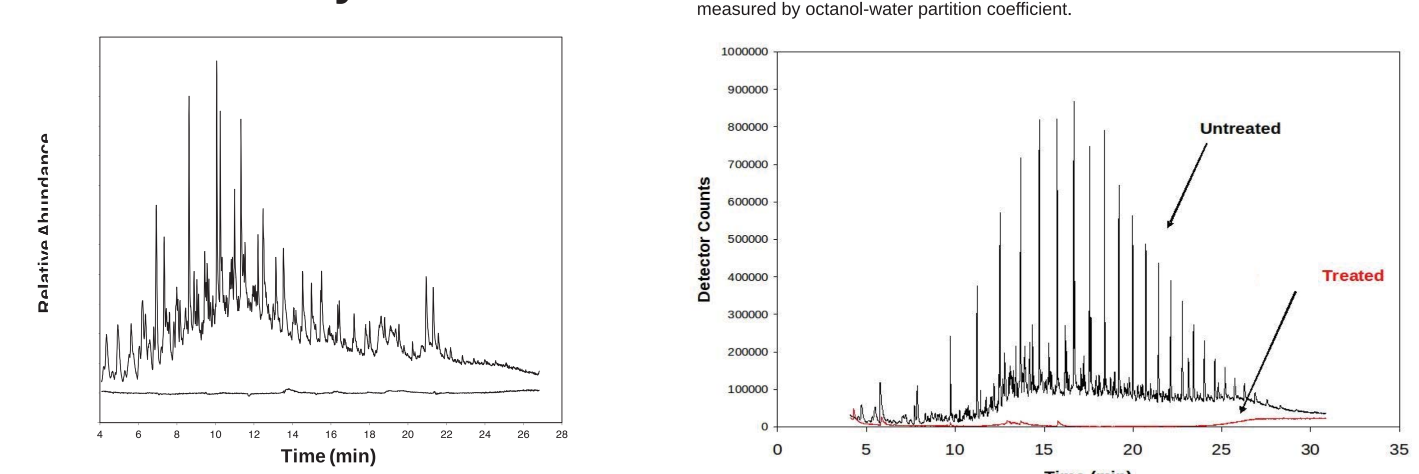


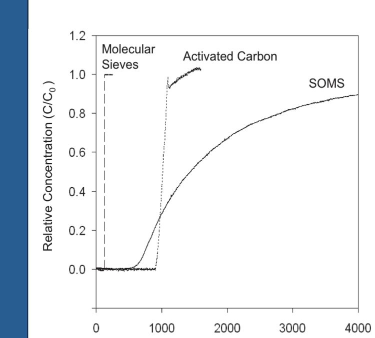

Sampling took place overnight
5 mg of swellable organosilica was placed in injection port of a GC-MS.
Desorbed for 15 s at 225°C



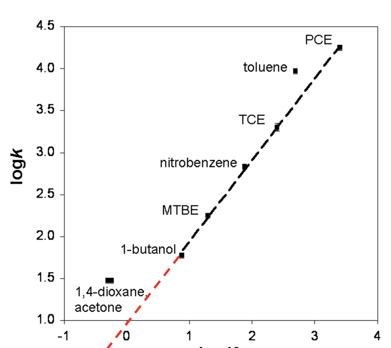

## Solvents and Hydrocarbons

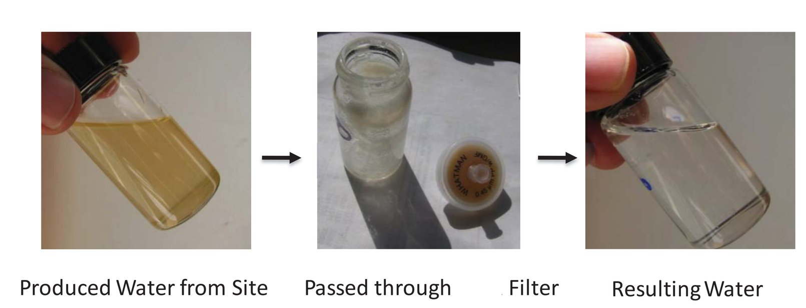
Removal of hydrocarbons from water was tested and found to be excellent, even under high concentrations. Affinity for dissolved organics by swellable organosilica depends on the polarity as measured by octanol-water partition coefficient.



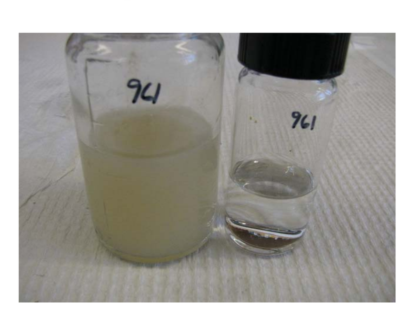

Breakthrough curves for 470 ppm aqueous toluene when applied to columns containing swellable organosilica, activated carbon, or molecular sieves.

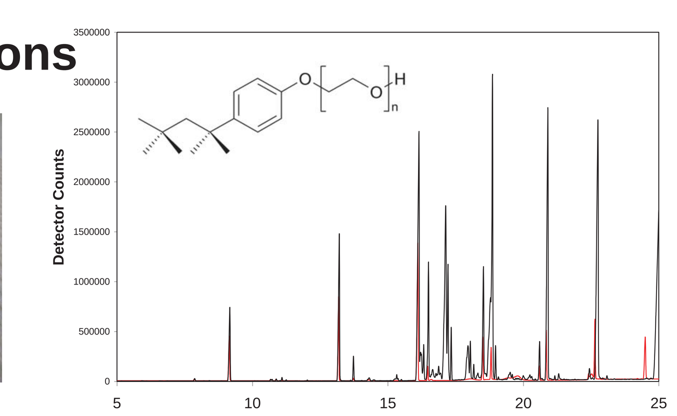



Plot of partition coefficient, log*k*, for binding of various contaminants in water by swellable organosilica vs. $\log K_{ow}$. The fitted linear regression line is: $\log(k)=0.97*\log(K_{ow})+0.96$, $R^2=0.998$. Conditions: contaminant concentration 100 ppm, 0.5% *w/v* swellable organosilica per volume of solution, *T*=25°C. Error bars are less than the symbol depicted unless otherwise displayed.

## Complex Emulsions





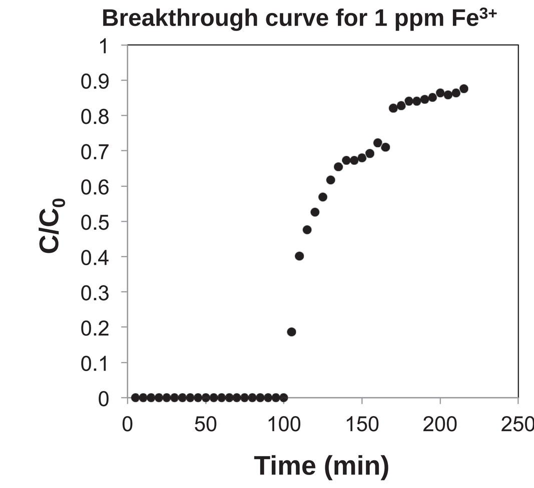

**Far left.** Bench-scale testing showed that swellable organosilica was effective at removing chemical surfactants from seawater. **Left.** GC-FID analysis of water before and after treatment at pilots scale. >99% of the oil is removed and >50% of the surfactants (*) were removed. An example of a surfactant is shown.

## Metals and Emerging Contaminants

**Sampling and Recovery of Pharmaceutical Compounds from Natural Waters**

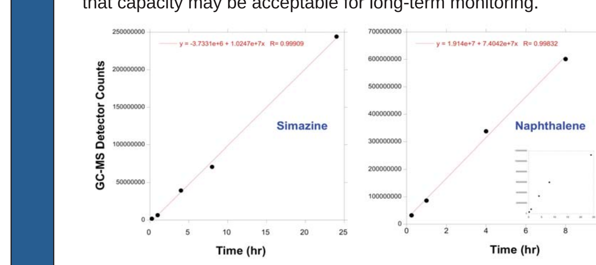
| Sorbent | Percent Recovery from Humic Acid Laden Water* Acetaminophen | Atrazine | Caffeine | Carbamazepine | Coumatetralyl | Diphenhydramine | Trimethoprim | Sulframethoxazole |
|---|---|---|---|---|---|---|---|---|
| RP-18 | 0.007±0.001 | 0.03±0.03 | 0.7±0.2 | 1.2±0.4 | 6±4 | | 2.7±0.4 | 0.11±0.02 |
| Oasis HLB | ND | 15.9±4 | | 17±7 | 19±7 | 20±6 | 34±24 | 5±2 |
| Osorb | ND | 85±10 | 9±5 | 26±7 | | 27±21 | | |
| Osorb-PEI | | | | | 116±30 | 7±2 | 8±4 | 22±8 |

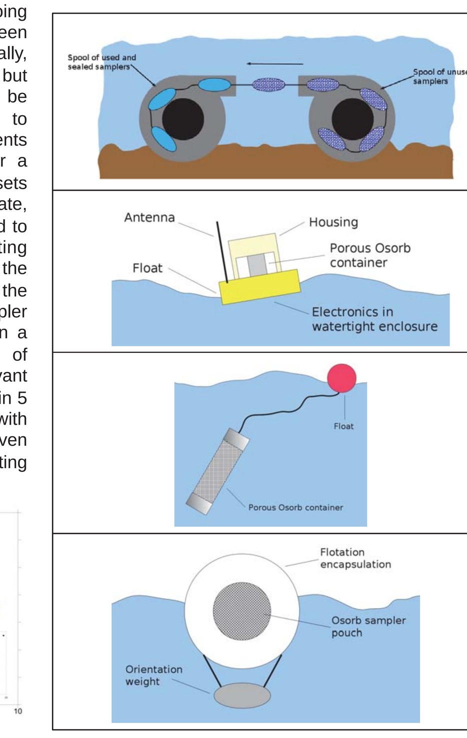
*Matrix: deionized water spiked with 10 ppm humic acid (Aldrich).
Concentration of each analyte was 10 ppb.
Shading indicates best performing material. Samples were run in triplicate. Osorb outperforms for 6/9 analytes.
Method: HPLC-MS/MS, Agilent 1200HPLC-6410 triple quad using both quantitative and confirmatory ions.
A separate calibration curve was run for each analyte.




1.Humic acid in organic solvent extracts: >200 μg of humic acid was present in RP-18 and Oasis HLB extracts. Osorb extracts had <0.1 μg humic acid in eluents used for LC-MS/MS.
2.Oasis HLB SPE cartridges appear to have variable recoveries based on flow rate through the cartridge of packed material. Regular Osorb the least sensitive to variable flow rates through a cartridge.
3.Beds of Osorb appear useful in extracting all but the most polar species (ex. acetaminophen). The inability to extract highly polar species is also reflected in the lack of absorption of natural organic matter.
4.Other species found to be absorbed by Osorb: perfluorooctanoic acid, PCBs, BTEX, hydrocarbons, nitroaromatics, PAHs, estradiol, and 2,4-D.

Although the development of passive sampling has been ongoing for some time, widespread use of solid sampling systems has been limited due to the inherent challenges of calibration. Specifically, sorbents are currently able to collect analytes during sampling, but accurately relating sampling data to concentrations in situ can be problematic. The typical approach currently employed is to compare data from passive sampling to laboratory experiments that measure the kinetics and equilibrium of binding under a standard set of conditions. Reliance on comparative data sets may be prone to error if field conditions (temperature, flow rate, presence of mixed contaminants) differ from the protocols used to calibrate in the laboratory. Preliminary experiments testing swellable organosilica passive sampling devices both in the laboratory and in the field. Bench-scale work has involved the capture of naphthalene and simazine (a pesticide) by a sampler containing standard granular swellable organosilica housed in a stainless steel mesh pouch (1cm³). Various concentrations of natural creek water were spiked with environmentally relevant concentrations of both compounds. The samplers were placed in 5 gallon buckets of spiked creek water which was slowly mixed with a stirbar. The amount of captured targets was linear with time even when exposed to relatively high concentrations (1 ppm) indicating that capacity may be acceptable for long-term monitoring.

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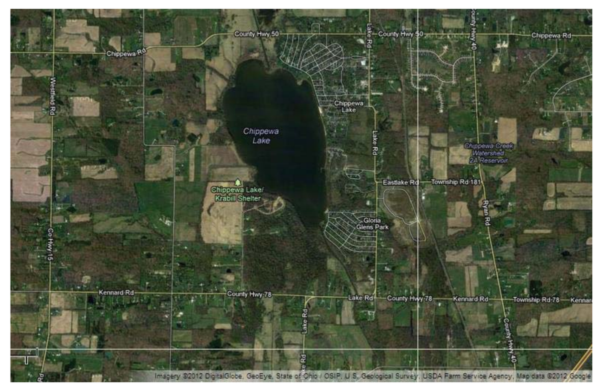
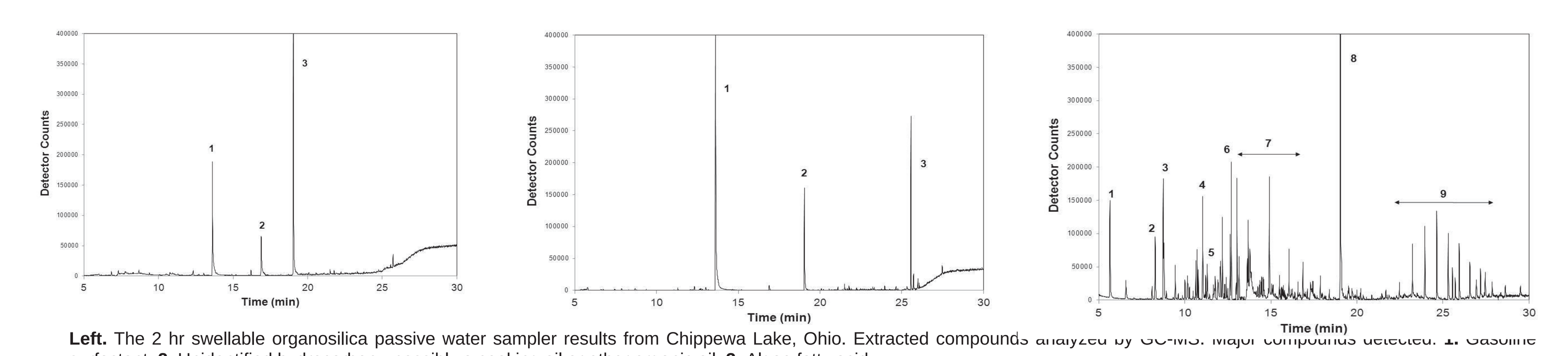
|---|---|
| | **Reel-to-Reel** Application: Long-term monitoring with temporal sampling capability. Requires power. Rivers and other flowing streams with variable water quality. |
| | **Alarm Type** Application: Oceanic sensor for spill detection. Uses Osorb's ability to swell to actuate an alarm switch. Power-off mode until spill detected. |
| | **Standard Passive Sampler** Application: Environmental monitoring. Power free. Some temporal data may be achieved by depth of penetration into Osorb. |
| | **Surface Passive Sampler** Application: Surface sampling. Power free. Monitoring sheens or surfactant slicks. Can be used for below surface sampling. |

At 324 surface acres, Chippewa Lake is Ohio's largest natural inland lake, located in Medina County in Northeast Ohio. The lake is at the headwaters of Chippewa Creek, and has historically been bordered by large areas of wetland on the north and south. However, these wetlands have largely been eliminated today, which may be a contributing factor to increased flooding and poor water quality. The Chippewa Lake watershed, largely located within Lafayette Township, is mostly rural and contains woodlands, farmland, residential areas, and limited urban development.

Chippewa Lake was selected because it the proximity to campus and because the water body has a very limited number of inflow sources. Other agencies profile the lake for comparison. Although hydrofracking operations have been done in Medina County (Utica Shale), the number of wells has been limited to date.

Three swellable organosilica passive water samplers were suspended from the sailing dock at the Chippewa Sailing Club with permission. The sailing dock is used solely by club members who race non-motorized racing sailboats. The three samplers were suspended by a cord 3' below the surface of the water and approximately 4' from the bottom about 50' from the shoreline. This depth was selected to ensure that only fully soluble species would be captured and prevent sheens or surface events from blinding or skewing the results. Sampler #1 was removed after two hours, providing the equivalent of a snapshot sample (Figure 8). Sampler #2 was removed after two days (50 hours), providing a short profile of the site (Figure 9). Sampler #3 was removed after 16 days, providing an extremely detailed portrait of the lake organic contaminants (Figure 10).






**Left.** The 2 hr swellable organosilica passive water sampler results from Chippewa Lake, Ohio. Extracted compounds analyzed by GC-MS. Major compounds detected: **1.** Gasoline surfactant; **2.** Unidentified hydrocarbon - possibly a cooking oil or other organic oil; **3.** Algae fatty acid.
**Middle.** The two day swellable organosilica passive water sampler results from Chippewa Lake, Ohio. Extracted compounds analyzed by GC/MS. Major compounds detected: **1.** Gasoline surfactant. **2.** Algae fatty acids. **3.** High molecular weight polycyclic organic of unknown origin (synthetic oil).
**Right.** The 16 day swellable organosilica passive water sampler results from Chippewa Lake, Ohio. Extracted compounds analyzed by GC-MS. Major compounds detected: **1.** toluene; **2.** p-xylene; **3.** styrene; **4.** p-dichlorobenzene; **5.** limonene; **6.** methyl-ethyl-benzene; **7.** BTEX and gasoline hydrocarbons; **8.** algae-derived fatty acid; **9.** several common motor oil hydrocarbons from both 2 stroke and 4 stroke engines.

The 2hr snapshot, taken on a Sunday afternoon with moderate boating in the lake and two jet skis passing back and forth within 100' of the sampling site, indicates a relatively healthy boating lake. The largest peak during the two hour window is a fatty acid generated by lake algae. This naturally occurring fatty acid is at least three times more common than human activity spillage of hydrocarbons. There are also many very small, difficult to fully profile peaks in the low detector count ranges. A probable motor oil peak at approximately 25 minutes on the GC-MS detection process is already apparent, but still only at a trace level.

Based on the two day sample, additional chemical compounds are being detected including aromatic hydrocarbons. The gasoline-surfactant spike and motor oil spike is so pronounced they are at least three times greater than the naturally occurring algae fatty acids. As it is autumn, many people were likely beginning to pull boats from the lake for the winter, and it would appear there has been a substantial fuel-motor oil incident on or in the lake. The 16-day swellable organosilica passive water sample indicates the lake water continues to be contaminated with both gasoline and motor oils associated with boating activity. The chromatogram indicates numerous hydrocarbons associated with gasoline engines, and three new spills (peaks 1-2, 4 and 6) indicate the lake has other substantial and biologically dangerous impacts during this period. The presence of limonene indicates that a boater may have rinsed out their engine compartment with a consumer soap product.

Initial work studying the use of swellable organosilica for passive sampling applications has shown that the materials have the ability to absorb a wide number of chemical species. Extraction of organic compounds is most pronounced due to the hydrophobic expandable matrix. The silica matrix can be functionalized with ligands that bind metals or be tailor to bind fluorinated compounds. Preliminary field testing shows sampling can be done for at least 16 days with minimal biofilm formation.

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