

Evaluation of Trace Total Organic Carbon in High Purity Sulfuric Acid

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- Problem statement and motivation
- Challenges of trace TOC analysis in concentrated acid
- Method Development for TOC analysis in H_2SO_4
- Proof of Concept Experimental Data
- Practical Application: TOC Leaching from common plastics by sulfuric acid
- Discussion
- Conclusions

Problem Statement

- Organic contamination present at ppm concentrations represents risk to semiconductor fabrication processes
- Total organic carbon analysis widely accepted and implemented on UPW systems
 - Proven tool for general organic purity evaluation
 - Sub ppb TOC levels common for UPW water sources
 - Drive process improvements through input characterization and control
- Focus on greater visibility and control of other key process inputs
- Sulfuric acid is difficult to analyze directly because of corrosive nature
 - Dilutions of 100x or more necessary
 - Sacrifice sensitivity with dilution

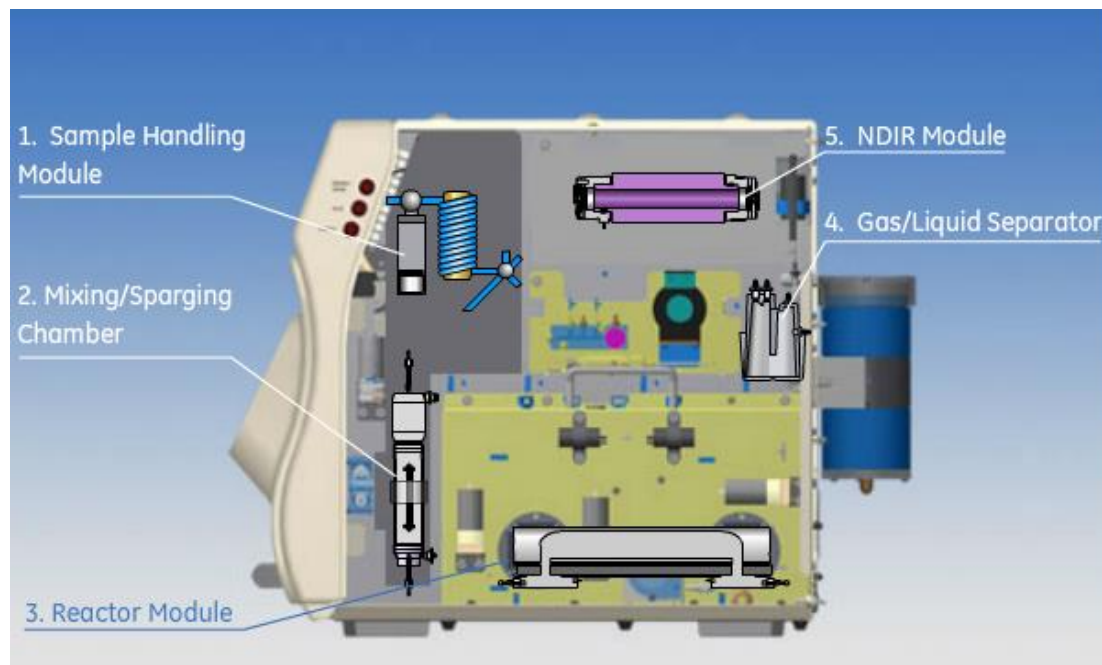
Goal – sub ppm TOC quantitation in H₂SO₄

TOC Analysis Overview

- Sievers InnovOx™ TOC Analyzer – Super Critical Water Oxidation
- Introduce aqueous sample with $\text{Na}(\text{SO}_4)_2$ oxidizer into sealed reactor
- Elevate temperature to reach super critical water conditions
 - Solubilize organic species, insolubilize inorganic interferences
- Efficient organic carbon oxidation to CO_2
- Detection via Near Infrared (NDIR) absorption
- Methods developed for TOC analysis in concentrated acids
 - HCl , HNO_3 , H_3PO_4

TOC measurement in challenging matrices – H_2SO_4 next on list

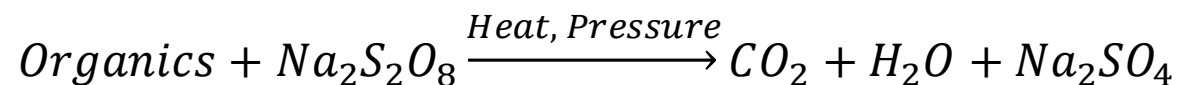
Experimental: Analytical Instrument



1. Sample Handling Module delivers sample and appropriate amounts of acid and oxidizer to Mixing/Sparging Chamber.
2. A sparging gas removes IC and volatile organics liberated by the acid then sent to the Reactor Module.

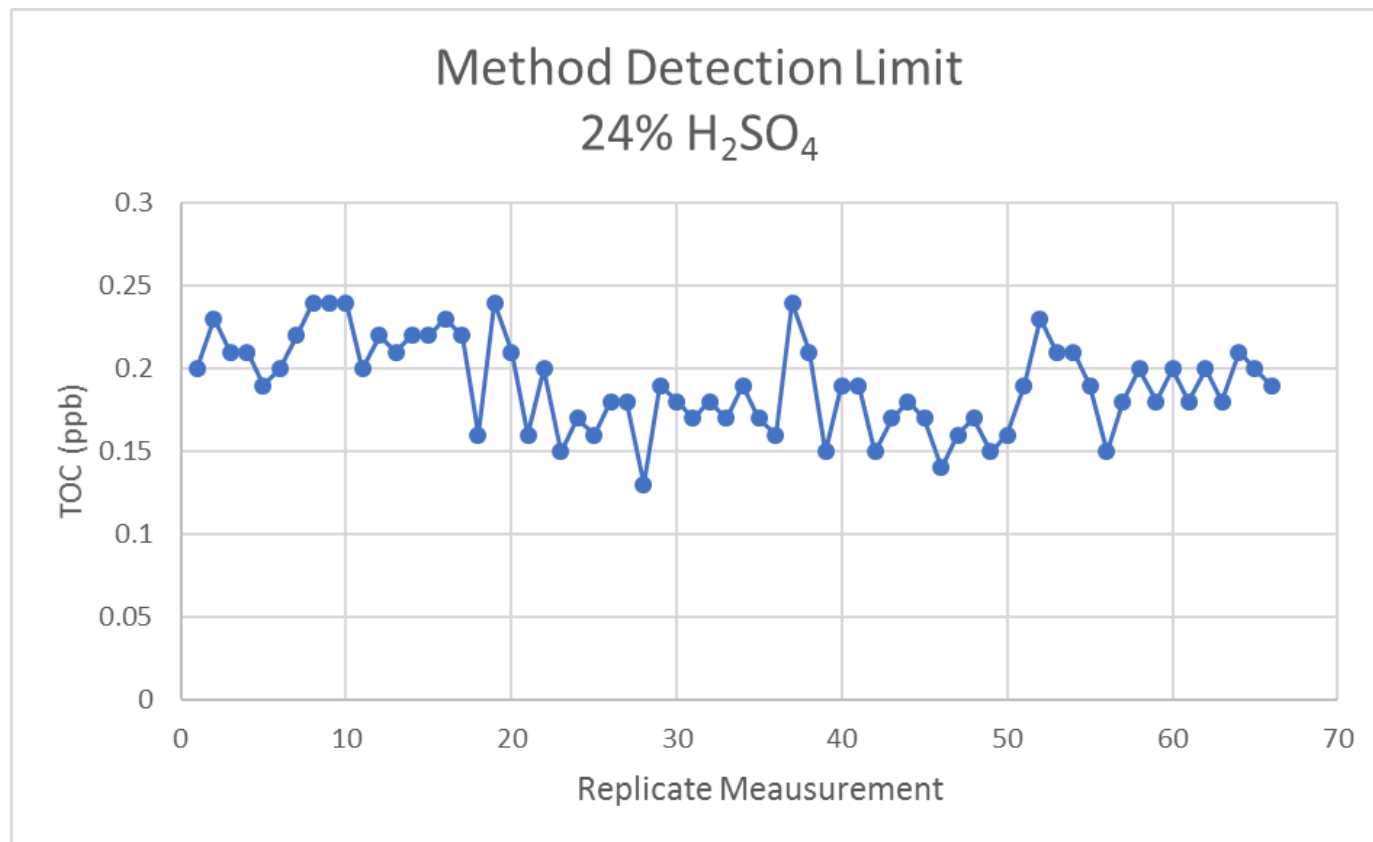


3. Supercritical Water Oxidation (SCWO) brings water to a supercritical state of 375°C and 3200 psi where wet chemical oxidation achieves unprecedented efficiency.
4. Sample enters the NDIR cell where CO₂ molecules absorb IR light coming from the source, reducing total transmittance that reaches the detector.
5. The resulting peak is recorded and a quantifiable concentration is calculated.



Experimental: Instrument Sensitivity

- Instrument Detection limit
 - 10 Repetitive measurements of UPW
 - IDL = 50 ppb
- Method Detection limit for 24% H_2SO_4
 - 65 Repetitive measurements
 - $\sigma = 27$ ppb
 - MDL = 82 ppb
 - Marginally higher than IDL
 - LOQ = 270 ppb
- Equivalent to 1 ppm in 96% H_2SO_4



Experimental – Instrument Performance

- Linearity over H_2SO_4 concentration range
 - 1 ppm KHP spiked in 1, 5, 10, and 24 % H_2SO_4
 - Spike samples showed near 100 % recovery for 5, 10, and 24% tests
- Sensitivity
 - KHP spiked at 0.2, 0.5, and 2 ppm
 - Results were within 70 ppb of expected values
- 48% H_2SO_4 pH < 1
 - Equilibrium shift to H_2CO_3
 - Difficult to extract CO_2 from solution
 - TOC recovery biased low

Table 1. KHP Spike Recovery from 1-24% H_2SO_4 .

[H ₂ SO ₄] %	Spiked TOC (ppm)	Blank TOC (ppm)	TOC measured (ppm)	Recovered TOC (ppm)	%Recovery
1	1	0.32	1.78	1.45	145%
5	1	0.26	1.28	1.02	102%
10	1	0.26	1.27	1.00	100%
24	1	0.18	1.18	1.00	100%

Table 2. KHP Spike Recovery Data from 0.2 – 2 ppm.

[H ₂ SO ₄] %	Spiked TOC (ppm)	Blank TOC (ppm)	TOC measured (ppm)	Recovered TOC (ppm)	%Recovery
24	0.2	0.18	0.448	0.27	134%
24	0.5	0.18	0.783	0.6	121%
24	2	0.18	2.263	2.08	104%

Sulfuric Acid Chemistry

- ACS certified grade H_2SO_4 (Fisher)
 - 2.5 L glass bottle
 - Baseline TOC data (24%): 160 ppb, 190 ppb, 200 ppb
 - Average = 183 ppb, σ = 21 ppb, 11% RSD
- Detectable organic carbon present in high purity sulfuric acid
 - Electronic grade has comparable TOC
- Sulfuric acid decomposes many organic species
 - Saccharides, cellulose
- Residual organic species stable in room temperature 96% H_2SO_4
 - Increased likelihood of persisting in fabrication process conditions
 - Speciation unknown at present

Organic carbon present in process chemical but not measured

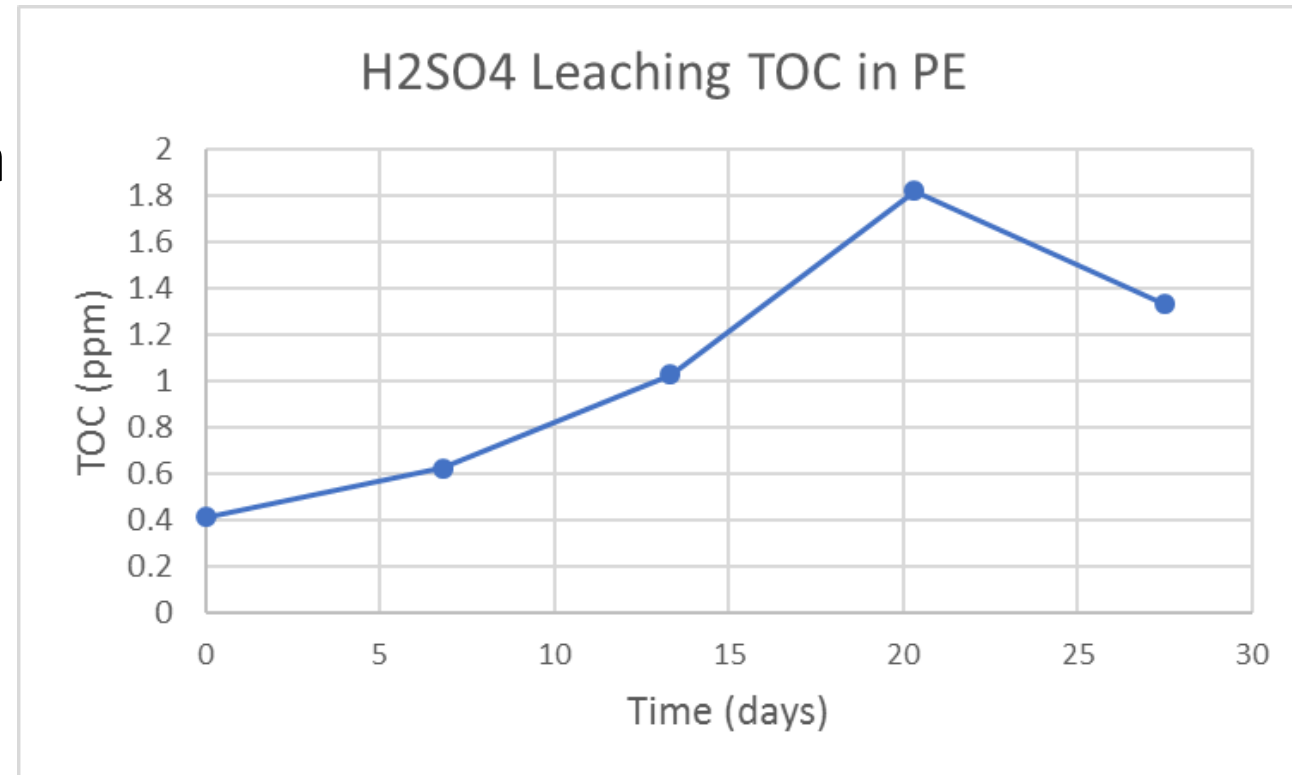
Organic Leaching into H₂SO₄

- Leaching of organic components into UPW well established
 - BPOG, USP 661.2 evaluating TOC leaching into medical plastics
- Sulfuric acid leaching organics from plastics explored
- Glass/plastic containment is necessary
 - Corrosive to common metal containment
- Transport and/or storage in plastic containment industry best practice
- Possible TOC concentrations change when in contact with plastic surfaces

Experiment to assess TOC profiles versus time in sulfuric acid

Initial observation - HDPE

- 96% H₂SO₄ in HDPE bottle
- Diluted to 24% and analyzed over a 4 week period
- Only measuring bulk TOC
- Significant change in TOC concentrations over time
- Initially at ~ 1.2 ppm
- Maximum of ~ 7.2 ppm at 3 weeks



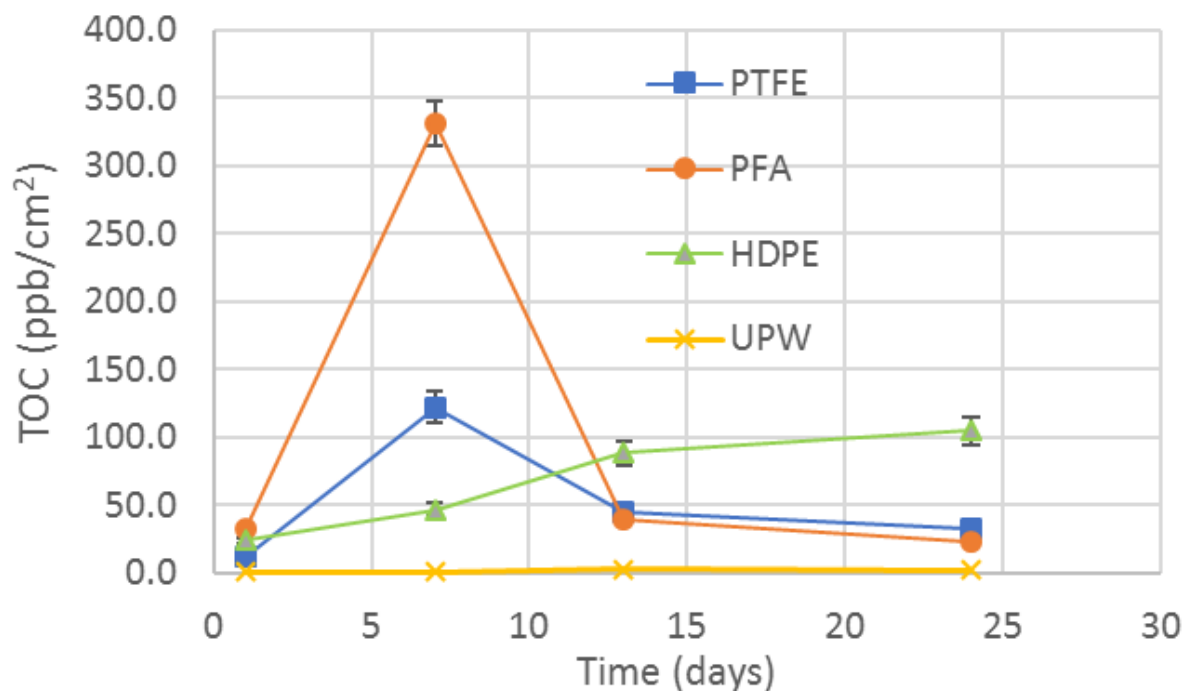
TOC concentrations in HDPE change significantly over time

Experimental Design

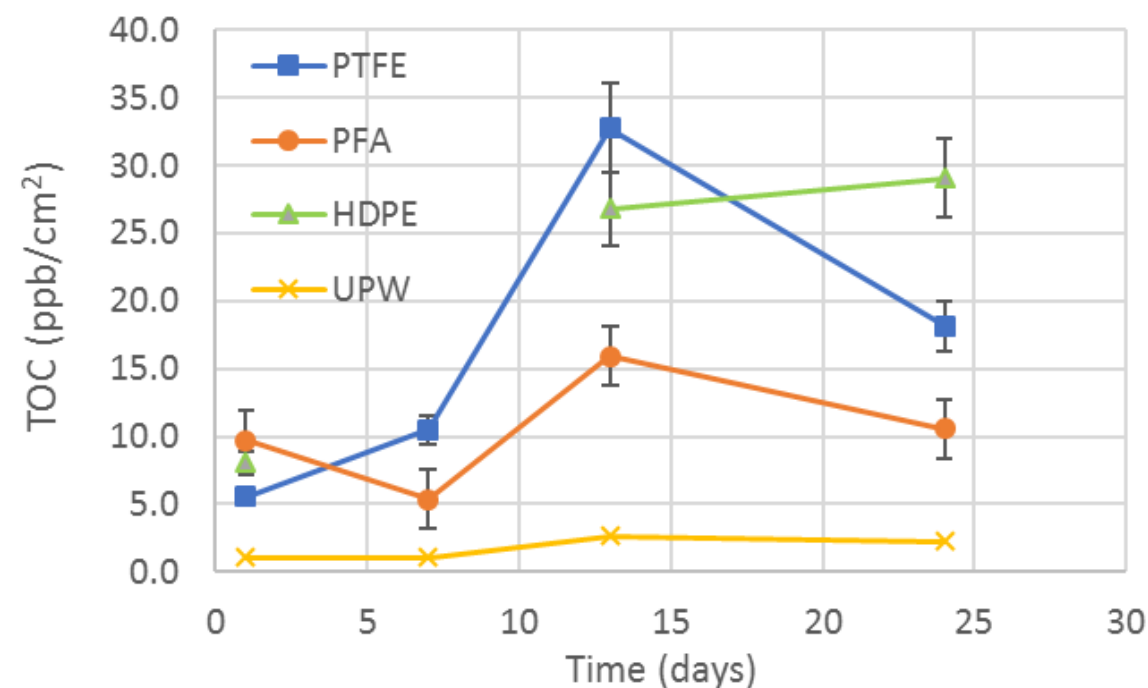
- Plastics evaluated: PTFE, PFA, HDPE
 - New from supplier
 - UPW Rinse 7x
- Solvents : UPW, 96%, 48%, 24 % H₂SO₄
- Introduced solvents into containers
- Measure periodically for TOC concentrations
 - Normalizing for surface area contact: ppb·cm⁻²
- Experiments conducted at room temperature
- Analysis parameters:
 - All tests run at 24% acid (i.e. 96% diluted 4x)
 - 25% Na(SO₄)₂ oxidizer, 0 Acid
 - Zero Sparge time – No dissolved CO₂ in matrix at low pH
- Evaluate vs UPW control

Data – 96% and 48% H₂SO₄

96% H₂SO₄ TOC Leaching



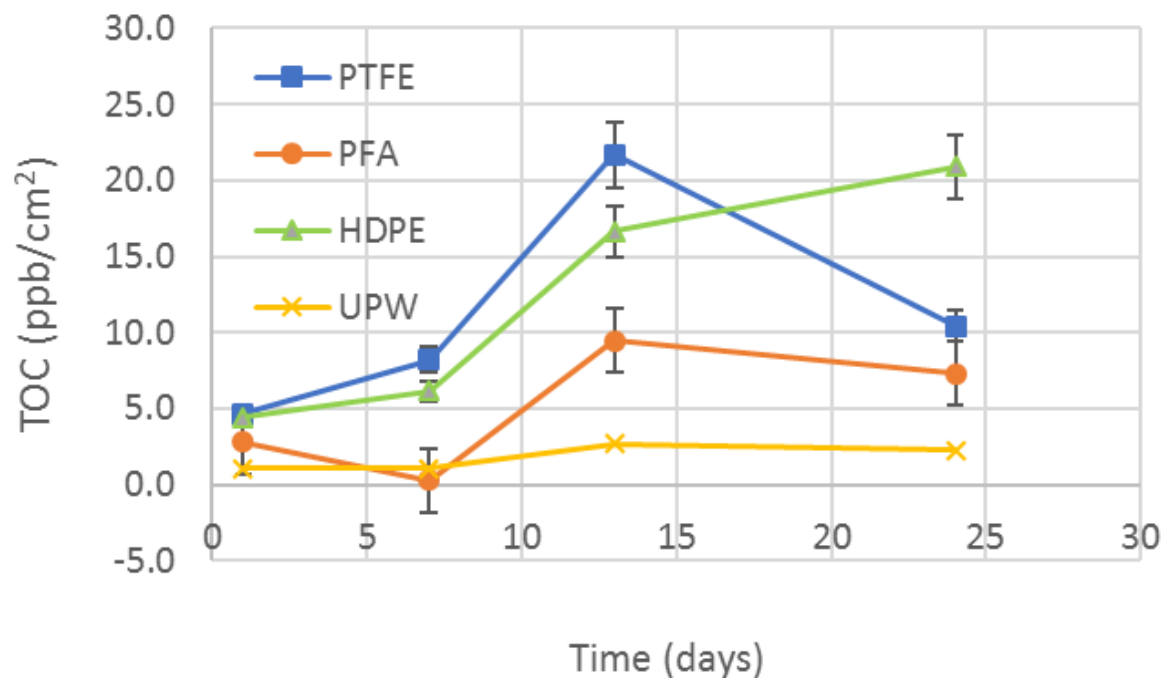
48% H₂SO₄ TOC Leaching



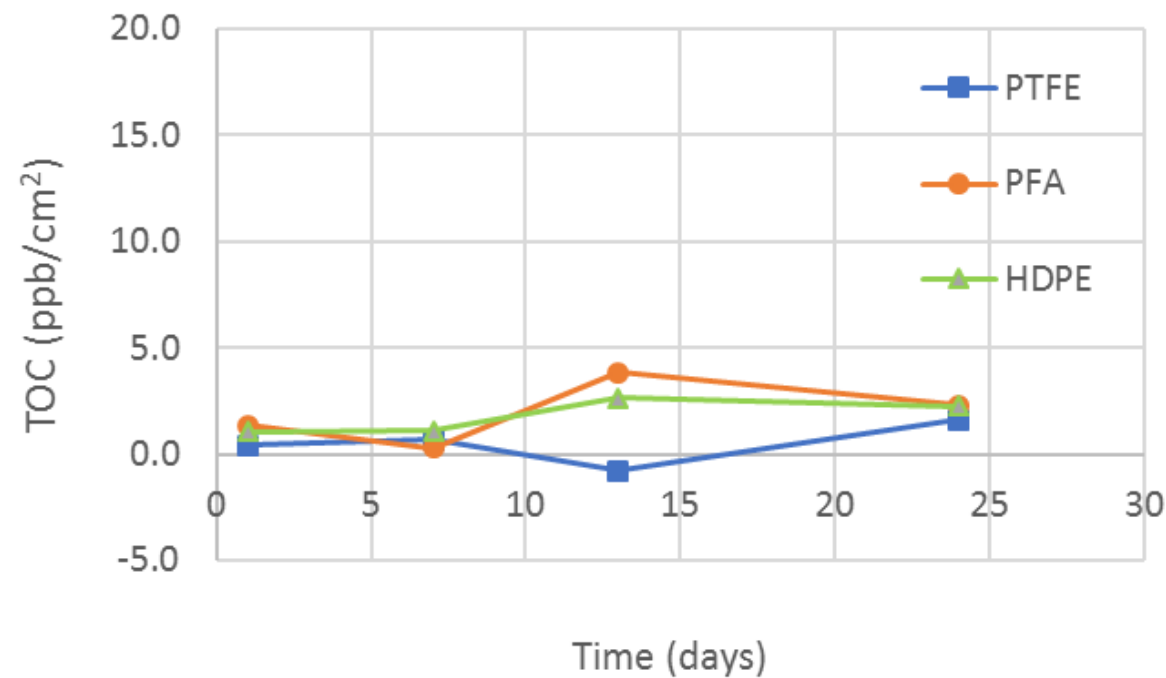
96% H₂SO₄ more aggressive leaching solvent versus 48% both in time and ppb/cm²

Data – 24% and UPW

24% H₂SO₄ TOC Leaching



UPW TOC Leaching



Extraction into H₂SO₄: 96% >> 48% > 24% > UPW

Discussion and Observations

- TOC extraction strength is proportional to H_2SO_4 concentration
 - Both 48% and 24% show a ~6 day lag in peak TOC extracted
- Short term TOC extractability 96%: PFA>>PTFE>HDPE
- Short term TOC extractability 24-48%: PTFE>PFA>HDPE
 - 24%-48% show similar extraction over time
- PFA and PTFE extracted compounds have relatively short lifetime in concentrated H_2SO_4
 - Decomposition to volatile products within 6 days
- Mid term TOC extractability: HDPE>PFA=PTFE
- HDPE extracted compounds resist decomposition versus PFA/PTFE
- UPW comparatively weak extraction solvent

Significant differences in extraction dynamics between plastics

Discussion – Implication of Relative Rates

- Two rate system: rate of extraction vs rate of decomposition
 - Relative rates will vary depending on plastic and organic compounds

$$TOC(t) = rate_{extraction} \cdot surface\ area \cdot TOC_{Ex} - rate_{decomposition} \cdot TOC_{(aq)}$$

- PFA and PTFE organics easily extracted and not persistent
 - Finite amount of organics can be extracted over 4 week time period
 - Easily conditioned surfaces do not contribute additional TOC short term
- HDPE organic extraction/decomposition on longer cycle
 - Deconvolute extraction rate and decomposition rate?

Extend Experimental Timing to Examine Long Term TOC Leaching

Conclusions

- TOC measurement in 24% H₂SO₄ demonstrated
 - Quantitation at 1 ppm TOC in 96% H₂SO₄ achieved
- Latent trace organic carbon present in high purity H₂SO₄
- Organic compound leaching into sulfuric acid is significant relative to UPW over days and weeks
 - PFA, PTFE, and HDPE contribute significant carbon
 - Variation in lifetime of extracted carbon compounds in H₂SO₄ observed
 - PFA and PTFE return to baseline after 2 weeks of initial exposure
 - HDPE extracted TOC persists longer relative to PFA and PTFE
- Additional experimental data of value
 - Establish long term profiles over several months
 - Determine variability between different lots of the same material
 - Evaluate temperature dependence on leaching and decomposition rates
 - Compare TOC leaching: reused containers versus new containers

Thank You!
&
Questions?

