Towards Closing the Mass Balance - PFASs & Paper and Textiles

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Tip of the Iceberg?

- NC State Landfill project (NSF funded) – 70+ PFASs in landfill leachate (Barlaz, Lang, Allred)
- Growing literature on select PFASs on paper & fabric
- Total oxidizable precursor assay applied to urban runoff and AFFF-contaminated groundwater, soil, and sediment
- Few attempts to characterize total fluorine or go beyond PFCAs, PFSAs, select PFASs in materials

1Kotthoff et al. 2015; Vestergrren et al. 2015; Ye et al. 2015; Trier et al. 2011
2 Gruber et al. 2014 (poster at 6th Intl PFAS Workshop, Idstein Germany on water-repellent geotextiles)
3 Houtz et al., 2011
4Houtz et al. 2013
Approach

• Pilot project – 15 papers & 9 textiles
• 70+ individual PFASs by LC-MS/MS
  – 15 (C4-18) PFCAs & 9 (C2-10) PFSAs & 3 FTSAs
  – 8 FT(U)CAs, 5 FTMAPs, 7 diPAPs, 5 PFPis, 15 (C4-8) PFSAAs, SAmPAP
• Total oxidizable precursor (TOP) assay¹
• Total fluorine by particle induced gamma ray emission (PIGE) spectroscopy

¹Houtz et al. 2013; Houtz et al. 2011
Samples & Analysis

- 15 papers\textsuperscript{1} & 9 textiles\textsuperscript{2} samples of convenience
- Ground finely, extract with methanol, freeze, centrifuge, analyze two portions of extract
  - 1\textsuperscript{st} portion, spiked with IS then LC-MS/MS
  - 2\textsuperscript{nd} portion, blown to dryness, react 3 mL 60 mM persulfate/125 mM NaOH at 65\degree C for 6 h; acidify to pH 2, spike with IS, micro liquid-liquid extraction
- LC-MS/MS method described in Allred et al. 2015

\textsuperscript{1} Paper samples donated by NC State and Green Science Policy Institute
\textsuperscript{2} Samples donated by Tom Webster (Boston U)
Total Oxidizable Precursor (TOP) Assay

Hydroxyl radicals degrade precursors to form ‘dead-end’ PFCAs\(^1\) and PFSAs\(^2\)

\[ \text{NaOH} \quad \text{MeOH} \quad \text{pH} > 11 \]

\[ \text{Dried} \quad \text{Extract} \quad \text{pH} > 11 \]

\[ T = 85^\circ C \]

\[ \text{C}_{8} \text{Precursor} \]

\[ \text{C}_{n} \text{F}_{2n+1} \text{COO}^- \quad n = 4 - 7 \]

\(^1\) Houtz et al. 2011; 2013

\(^2\) PFSAs are observed oxidation products in paper and textiles and in environmental samples.
Results

- Not close to closing mass balance
- FtOHs likely to account for some mass
- TOP assay provides conservative estimate
- Net production of perfluoroalkyl sulfonates (PFSAs) but no precursor tested to date known to oxidize to PFSAs
- Fluorinated polymers do not contribute unless extracted by MeOH (unlikely)
- PFASs concentrations above the EU proposed limit of 2 µg/kg for consumer products
Total Fluorine by PIGE

- Particle-Induced Gamma-ray Emission (PIGE)
- Spectroscopic measurement of $^{19}$F nuclei – rapid, non-destructive, quantitative...
- Ion beam analysis technique used in geology, archeology
- Nuclear excitation instead of atomic excitation (XRF, etc.)
Excitation Source

- 1.7 MV tandem Pelletron Accelerator (Van de Graaff design)
- 3.4 MeV protons
- Penetration ~ 100 μm
Gamma-ray Detection

- In air analysis: minimal sample preparation
- Total fluorine measurement – not identification
- High throughput
- Cost effective
Example Spectra

- 180 seconds with 9 nA of beam on target
Next Steps

• 600 additional samples from Alex Stone, Washington State Dept. Ecology, by PIGE for total fluorine
• 10% run by LC-MS/MS and 5% by TOP assay
• GC-MS for FTOHs % other volatiles
• LC & GC HRMS non-target screening
• LC-MS/MS and PIGE results will be posted to Washington Department of Ecology website
Conclusions

- Even the most extensive LC-MS/MS measurements collect <10% of the PFAS present on papers & fabric
- TOP assay provides conservative estimate of total PFAS content on papers/fabric
- Precursors that oxidize to form sulfonates present on paper/fabric
- GC- & LC-HRMS needed to identify missing mass
Collaborators

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- Johnsie Lang

**Hope College**
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- David Lunderberg
- Nick Hubley

**Washington State Dept. Ecology**
- Alex Stone