



Quantitative Determination of Fluorinated Alkyl Substances in Municipal Wastewater

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Overview

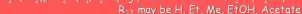
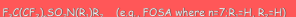
Purpose:
 To develop a method to simultaneously quantify perfluoroalkyl carboxylates, sulfonates, selected sulfonamides, and fluorotelomer sulfonates in municipal wastewater

- Method:**
1. Centrifugation was used for sample clean-up
 2. High-volume-injection (500 μ l) was used for sample concentration
 3. Analysis by LC ESI-MS/MS
 4. Quantitation was based on the ratio of the peak area of the analyte to that of the internal standard

- Results:**
- Methodology applied to municipal wastewater influents and effluents (24 h composites)
 - Each wastewater treatment plant had a different fingerprint of fluorinated alkyl substances
 - In some WWTPs, there were increased concentrations of analytes (perfluoroalkyl carboxylates, 6-8 FTS, PFOSA) in the effluents, suggesting that degradation may be occurring
 - In 5 out of the 6 WWTPs analyzed, the perfluoroalkyl sulfonates were the most abundant class present

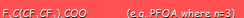
Fluorinated alkyl substances can be synthesized by one of two ways:

★ **Electrochemical Fluorination:** (branched, odd and even numbers of C)



3M Co. announced to phase out production of C₈-based chemistry (May 2000)¹
 Switched to C₇-based chemistry, not toxic and does not accumulate²

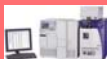
★ **Fluorotelomerization:** (linear, only even numbers of C)



No phase out of any fluorotelomer chemistry

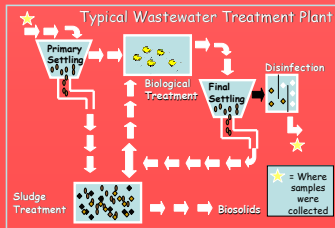
Analytical Details

Sample Clean-up: Centrifugation
Sample Concentration: High-Volume-Injection (500 μ l sample loop)
Separation: Waters 2690 LC
Identification & Quantification: Micromass Quattro micro Triple Quadrupole
Detection limit: ~0.3 ppt **Precision:** 1.8 % RSE (n=5)
Quantitation linear range: ~0.8 ppt - 70 ppt
QA/QC Standards
 • Perfluoroethoxyethane sulfonate (quantitation)
 • $[^{13}C_6]$ PFOA (method recovery standard)
Field Blanks: DI water (n=1) transported to site
 • no background detected
Spike Controls: DI water spiked and transported
 • 91-100 % recovery
Field Active Spikes: Wastewater spiked @ 1 conc.
 • 85-110 % recovery
 • exception PFOS, PFDS, sulfonamides (adsorption?)

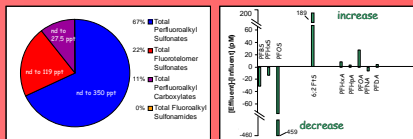


Introduction

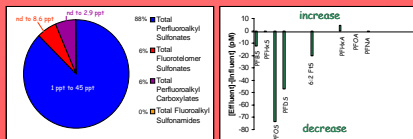
Fluorinated alkyl substances have been quantitated in:
 • in many densely populated and remote regions³
 • in air, surface waters, groundwater, and biota^{4,5}
 Very little is known about fate & transport through a WWTP



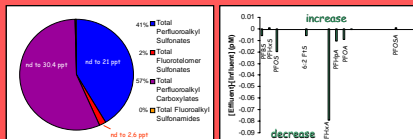
Results



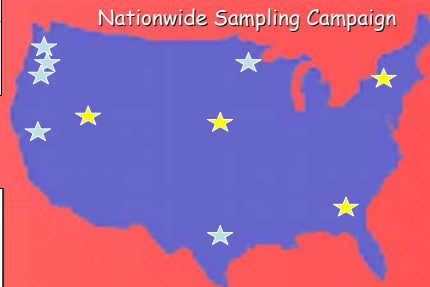
WWTP No. 1¹
 Serving a population of ~600,000



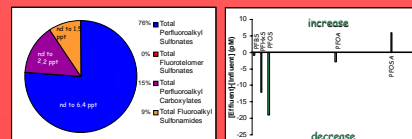
WWTP No. 2¹
 Serving a population of ~135,000



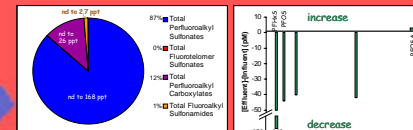
WWTP No. 3¹
 Serving a population of ~50,000



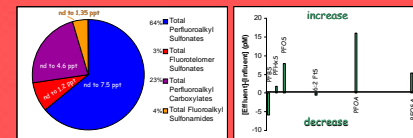
★ = Samples collected and analyzed
 ★ = Samples collected and still need to be analyzed
 *Percent distribution indicative of what was observed at each WWTP in the combined influent and effluent (pM comparison)
 *Individual concentration ranges for each class are given in the pie slices.



WWTP No. 4¹
 Serving population of ~ 200,000



WWTP No. 5¹
 Serving a population of ~90,000



WWTP No. 6¹
 Serving a population of ~65,000

Future Work

- Complete method demonstration with nationwide influent and effluent (24 h composite) samples
- Apply methodology to complete a 10 day mass balance on a WWTP, including aqueous & sludge samples
- Collaboration with Chris Higgins & Dr. Richard Luthy (Stanford)

References:

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