Biodegradation of N-ethyl Perfluorooctane Sulfonamido Ethanol-based Phosphate Diester (SAmPAP diester) in Marine Sediments

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SAmPAP Production and Use

- Major use of SAmPAP esters from 1970s-2002 as grease-proofing agents in food contact paper and packaging.
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• Formulations (e.g. FC-807) typically consisted of 10% mono-, 85% di-, and 5% tri-esters.
Why study SAmPAPs?

1) Potential PFOS-precursors

- SAmPAP esters are among numerous potential perfluorooctane sulfonate (PFOS)-precursors.

- PFOS is persistent, bioaccumulative, globally distributed in the environment. Developmental toxicant in lab animals. (refs: Giesy and Kannan 2001, Conder et al. 2012, Lau et al. 2004, others)
Why study SAmPAPs?

2) High production volume substances

• SamPAP mono- and diesters among predictions of 610 commercially relevant, persistent and bioaccumulative organics (Howard and Muir 2010).

• In 1997, sales of commercial SAmPAP formulation (FC-807) represented the highest quantity of PFOS-equivalents sold by 3M out of all PFOS-precursor or PFOS-containing commercial substances (EPA doc AR226-0681).
3) Stability unclear

- Limited data on stability of high-molecular weight (M.W.) PFOS-precursor candidates (phosphate-based surfactants and polymers).

Why study SAmPAPs?

- SAmPAP diester (high M.W. PFOS-precursor candidate)
- Intermediates (low M.W. PFOS-precursor candidates)
- PFOS
3) Stability unclear

- Limited data on stability of high-molecular weight (M.W.) PFOS-precursor candidates (phosphate-based surfactants and polymers).

- Even for low molecular weight substances, biodegradation studies limited to N-ethyl perfluorooctane sulfonamido ethanol (EtFOSE) in sludge.

**Why study SAmPAPs?**

![Chemical structures of SAmPAP diester, Sludge, EtFOSE, and PFOS]
Hypothesis and Objectives

Objective:
Investigate biodegradation of SAmPAP diester and EtFOSE in sediments.
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Higgins et al. 2005 \([\Sigma \text{PFOS-precursors}] > [\text{PFOS}]\) in sediments from Tokyo Bay, San Francisco Bay, Baltimore Harbour.

Ahrens et al. 2009 \([\Sigma \text{PFOS-precursors}] > [\text{PFOS}]\) in sediments from Tokyo Bay, San Francisco Bay, Baltimore Harbour.

**PFOS and PFOS-precursors in sediments from Vancouver, B.C.**

Source: Benskin et al. 2012
Hypotheses:
1) Occurrence of low-molecular weight perfluorooctane sulfonamides in sediments arises from biodegradation of high-molecular weight precursors.
2) low-molecular weight perfluorooctane sulfonamides are a source of PFOS in sediment.
Experimental Design

• Sediments pooled from locations around False Creek (Vancouver, BC, Canada).
• Half of sediment autoclaved and treated with 1% mercuric chloride.
• 4 g of sediment (inactive or active) placed into 15mL centrifuge tube.
Experimental Design

- 120 d
- 107 d
- 53 d
- 26 d
- 13 d
- 6 d
- 3 d
- 18 h
- 2 h
- 0

4°C, 25°C

- 150ng SAmPAP diester
- 250ng EtFOSE

x3 x3 x1
Experimental Design

Internal Controls:

• 5ng internal negative control-perfluorodecanoate (PFDA)

\[
\begin{align*}
\text{F}_3\text{C} & \text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_2\text{O}^- 
\end{align*}
\]

• 350ng internal positive control \(^{13}\)C-monoisononyl phthalate (\(^{13}\)C-MNoP)

\[
\begin{align*}
\text{O} & \text{C}^{13}\text{C} \text{H}_3 \text{C}^{13}\text{C} \text{H}_3 \text{O}^- 
\end{align*}
\]

• Half life of \(^{13}\)C-MNoP~1 day at 25C, 6-10 days @ 6C. (Otton et al. 2008)
Sample Treatment

• Reactions terminated by addition of 5mL MeOH+vortexing.

• Samples spiked with internal standards and stored in freezer until extraction.

• Extraction using method adapted from Powley et al. (2005) (MeOH+EnviCarb cleanup).

• LC-MS/MS analysis.
Evidence for volatilization of EtFOSE in 25°C inactive sediments
• Formation of products not observed
• No microbial activity (based on $^{13}$C-MnP and microbial test strips)
• No depletion of negative control.
Results - EtFOSE incubations

\[
\text{EtFOSE} \xrightarrow{\text{incubations}} \text{EtFOSAA} \to \text{EtFOSA} \to \text{FOSAA}
\]

![Diagram showing the transformation of EtFOSE to EtFOSA and FOSAA](image)

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**Graphs**

**EtFOSA**
- **Graph** showing the concentration of EtFOSA over time.
- **Axes**:
  - X-axis: Time (days)
  - Y-axis: Concentration (ng/g)
- **Data points**:
  - 4°C inactive sediments
  - 25°C inactive sediments
  - 4°C active sediments
  - 25°C active sediments

**FOSAA**
- **Graph** showing the concentration of FOSAA over time.
- **Axes**:
  - X-axis: Time (days)
  - Y-axis: Concentration (ng/g)
- **Data points**:
  - 4°C inactive sediments
  - 25°C inactive sediments
  - 4°C active sediments
  - 25°C active sediments
Results-EtFOSE incubations

\[ \text{EtFOSE} \rightarrow \text{EtFOSAA} \rightarrow \text{EtFOSA} \]

\[ \text{PFOA (minor)} \rightarrow \text{PFOS} \rightarrow \text{FOSA} \rightarrow \text{FOSAA} \]

Graphs showing concentration of PFOS and FOSA over time at different temperatures.
Summary-EtFOSE incubations

• Biodegradation pathway in sediment consistent that observed in sludge by Lange (2000), Boulanger et al. (2005), Rhoads (2008).

• **EtFOSE biodegradation:** EtFOSAA, PFOS, EtFOSA major products.

% of dose at T=120 days

- **25°C EtFOSE experiment:**
  - EtFOSE: 28%, EtFOSAA: 39%, PFOS: 12%, EtFOSA: 6.4%, FOSAA: <3%

- **4°C EtFOSE experiment:**
  - EtFOSE: 13%, EtFOSAA: 53%, PFOS: 31%, EtFOSA: 1.7%, <1%
Take home messages—EtFOSE biodegradation sediment

• EtFOSE Biodegradation half life in sediment was ~4× greater at 4°C compared to 25°C (160 versus 44 days, respectively).

• Biodegradation half life of EtFOSE in sediment much greater than in sludge (1-4 days @ 25-30°C).

Comparison of EtFOSE biodegradation half life in sediment versus sludge
Results-SAmPAP diester incubations

$\text{SAmPAP diester}$

Concentration (ng/g)

Time (days)
Results - SAmPAP diester incubations

SAmPAP diester

SAmPAP monoester

EtFOSE

PFOS

Concentration (ng/g)

Time (days)

△ 4°C inactive sediments □ 25°C inactive sediments ▲ 4°C active sediments □ 25°C active sediments
Results-SAmPAP diester incubations

• Half life of SAmPAP diester estimated from lower bounds 95% confidence interval of the slope.

• SAmPAP sediment $t_{1/2}$ @ 25°C = >1 year
• SAmPAP sediment $t_{1/2}$ @ 4°C = ~10 years
Summary

1) EtFOSE biodegraded to PFOS in sediment but half life considerably longer than in sludge (t\(_{1/2}\)=44 days in sediments versus ~1-4 days in sludge at ~25°C).

2) No significant biodegradation observed for SAmPAP diester over 120 days (t\(_{1/2}\) > 1 year in sediments at 25°C).
Implications

PFOS-precursors are sufficiently long-lived in sediments to be a potentially significant source of PFOS for benthic organisms (consistent with hypotheses of Martin et al. 2004, Loi et al. 2011, Asher et al. 2012).
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Questions?

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