
From: Fletcher, Steven G CIV NAVSEA HQ, SEA 05
To: Berkoski, Daniel T CIV NAVSEA, SEA 05; Hunstad, Mary P CIV NAVSEA HQ, SEA 05
Sent: 3/15/2017 12:50:17 PM
Subject: FW: Newly Discovered PFASs

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From: Corl III, William E CIV Chemist, LQAO, C1198
Sent: Wednesday, March 15, 2017 8:49 AM
To: Fletcher, Steven G CIV NAVSEA HQ, SEA 05; Willey, Janice L CIV SEA04X, LQAO
Cc: Adelson, Jordan M CIV SEA04X, LQAO; Brown, Kim P CIV NAVFAC HQ, EV; Corack, Jennifer M CIV NAVFAC Atlantic, EV
Subject: RE: Newly Discovered PFASs

Steven,

More typical Jennifer Fields work to identify other compounds present. The paper uses a method of monitoring mass defect (Kendrick mass analysis) to infer degree of saturation or heteroatom content composition using a highly sensitive (TOF) mass spectrometer. In short, picture flipping a puzzle over so that you have no color patterns to help you resolve where the pieces match. Now break off "clusters" of pieces and weigh them. Assuming certain puzzle clusters of certain weight always connect at certain points, we can estimate how the original puzzle might have looked. The method works backwards in a similar fashion by measuring the masses of the fragment losses and then "guessing" the different ways those pieces can go back together (which is why the study identifies classes). Note that the results cannot be confirmed because there are no standards to reproduce the inferred presence. And, stated confidence decreases for higher or lower homologues because the potential fragmentation possibilities get messy. Like any good researcher, her conclusions set herself up for further funding.

Although as a chemist I admire the method, the paper further complicates the AFFF story.

My key take-aways:

1. " In the AFFFs, 75% of the new PFASs were discovered in 3M AFFFs and CPs produced using ECF, whereas the remaining 25% are fluorotelomer-based PFASs. The wide variety of ECF-derived PFASs discovered, most of which share the same base structure of Class 13, is consistent with ECF synthesis that creates many unintended byproducts in the production of ECF-derived PFASs.^{30,33} On the other hand, the limited number of newly discovered fluorotelomer-derived PFASs is evidence telomerization produces few unintentional products."
2. "Novel PFAS Classes Found Only in Groundwater. Eleven of the 13 classes (Table 3) found only in groundwater are ECF-derived. The presence of the 11 ECF-derived classes may be attributed to either degradation of PFASs found in 3M AFFF or parent compounds in AFFFs prior to 1988, for which the composition is unknown. The two fluorotelomer classes (Classes 39–40; Table 3) are likely degradation products of a parent compound in fluorotelomer AFFFs, although no biodegradation studies to date have observed these two classes."
3. " The limited number of fluorotelomer-based PFASs in AFFFs and groundwater identified in this study suggest that (a) previous AFFF characterization efforts were successful,^{21,23} and/or (b) degradation of fluorotelomer-based PFASs to PFCAs may occur more readily than ECF-derived PFASs."
4. " Little is known about the newly discovered PFASs with regards to subsurface remediation strategies, transport, and toxicity. The (presumed) wide range of solubilities for the newly discovered PFASs may pose challenges for using ex situ remediation techniques, such as granulated active carbon, because shorter-chained compounds are likely to break through

systems designed to capture PFOS and PFOA.^{85,86} Shorter chained anionic and zwitterionic PFASs are expected to migrate downstream of source areas faster than their longer-chained counterparts in a manner analogous to their elution order on analytical C18 columns.⁸⁷ To the best of our knowledge, no toxicity studies exist for any of the novel PFASs identified.

Nonfluorinated cationic surfactants exhibit greater toxicity.

By analogy, cationic and zwitterionic PFASs, which also have cationic moieties, may be more toxic than the newly discovered anionic PFASs. However, conclusions about potential toxicity regarding the newly discovered PFASs cannot be determined from mere detection."

And finally my favorite: "... over 240 individual PFASs that can now be associated with AFFF."

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From: Fletcher, Steven G CIV NAVSEA HQ, SEA 05

Sent: Wednesday, March 15, 2017 7:13 AM

To: Willey, Janice L CIV SEA04X, LQAO; Corl III, William E CIV Chemist, LQAO, C1198

Cc: Adelson, Jordan M CIV SEA04X, LQAO

Subject: Newly Discovered PFASs

New Jennifer Fields article. This is way over our heads. Hope you understand it better than we do.

v/r,

Steve Fletcher, P.E.

Fire Protection Engineer

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