Message

From: Strynar, Mark [/O=EXCHANGELABS/OU=EXCHANGE ADMINISTRATIVE GROUP (FYDIBOHF23SPDLT)/CN=RECIPIENTS/CN=5A9910D5B38E471497BD875FD329A20A-STRYNAR, MARK]
Sent: 5/13/2016 12:36:14 PM
To: Weber, Eric [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=f7d8051919254186be0a4d292574c01d-Weber, Eric]; Libelo, Laurence [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=da33642e6438407daf4c35afe870046b-Libelo, Laurence]; Washington, John [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=fdc3e8ce9f1d45c4894881ff420ca104-Washington, John]; Lindstrom, Andrew [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=04bf7cf26aa44ce29763fbc1c1b2338e-Lindstrom, Andrew]; Lynch, David [/o=ExchangeLabs/ou=Exchange Administrative Group (FYDIBOHF23SPDLT)/cn=Recipients/cn=c732d9b0621e4f15a84a62c1af51a809-Lynch, David]
Subject: RE: Total organic fluorine - ethers do not degrade easily..
Attachments: 3-3-14 T0 D7 and D14 U2M3O-hexane deg study extracts.xlsx

I it looks like I did not run the samples on the TOFMS. However after 14days I saw no change what so ever. I will need to replicate this one and a few others for a longer period of time to prove or disprove the biodeg potential of the PFECAs.

Mark

From: Weber, Eric
Sent: Thursday, May 12, 2016 4:13 PM
To: Libelo, Laurence <Libelo.Laurence@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>; Washington, John <Washington.John@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Lynch, David <Lynch.David@epa.gov>
Subject: RE: Total organic fluorine - ethers do not degrade easily..

Laurence,

Attached is a short PPt that captures what I have put together so far concerning the potential degradation pathways for the polyfluorinated ethers. My efforts thus far have focused primarily on the carboxylated polyfluorinated ethers. I ran both GenX and Adona through the EAWAG Pathway Prediction System (PPS) for Aerobic Biodegradation. This system was originally developed at the University of Minnesota. Due to the retirements of key individuals, it was moved last year to EAWAG where Kathrin Fenner is now responsible for the system. She received significant funding from the Swiss Science Foundation to update the system. This includes development of web services, which will allow for the Chemical Transformation Simulator to make seamless calls to the PPS for anyone who is interested in generating potential products resulting from aerobic biodegradation. This capability should be in place by the end of the year.

The pathways summarized in the PPt represent what I think is the most viable pathways for their degradation in aerobic systems. I will not turn my focus to the polyfluorinated ethers.

At some point, it would probably be good for us to have a call to address any questions.

Eric

From: Libelo, Laurence
Sent: Wednesday, May 11, 2016 8:11 AM
To: Weber, Eric <Weber.Eric@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>; Washington, John

<Washington.John@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Lynch, David <Lynch.David@epa.gov>
Subject: RE: Total organic fluorine - ethers do not degrade easily..

Great.

Here is a very draft lit review that gives an idea of what is published already. It does not include the pathways but the citations give a few.

From: Weber, Eric
Sent: Wednesday, May 11, 2016 8:02 AM
To: Libelo, Laurence <Libelo.Laurence@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>; Washington, John <Washington.John@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Lynch, David <Lynch.David@epa.gov>
Subject: RE: Total organic fluorine - ethers do not degrade easily..

Laurence,

Started to give this problem some thought yesterday. I should have a good part of the day to continue to work on potential degredation pathways for the fluorinated ethers.

Eric

From: Libelo, Laurence
Sent: Wednesday, May 11, 2016 7:17 AM
To: Weber, Eric <Weber.Eric@epa.gov>; Strynar, Mark <Strynar.Mark@epa.gov>; Washington, John <Washington.John@epa.gov>; Lindstrom, Andrew <Lindstrom.Andrew@epa.gov>; Lynch, David <Lynch.David@epa.gov>
Subject: FW: Total organic fluorine - ethers do not degrade easily..

Eric and others,

There is a good bit of "chatter" internationally on the ethers. There is little measured data except at elevated temps and higher concentrations of Lewis acids. But – from all of it it seems pretty likely that that the C-O-C can be broken abioticly. The question is what effect adding F or a lot of F has. Kraftt say in the review that we know little about them but should be concerned. Our lit review shows that the mechanisms may be pretty common in the environment. As with the "regular" per and polyfluoro chemicals reactions may be different than expected based on non-F containing organics. (how is that for not being skeptical/cynical?).

The fluoro ethers are marketed for everything from space station applications to lubes on hard drives in your computer to kids toys. Given the very widespread use of the fluoro ethers I am really concerned that this PFOA all over again. Not PFOA of 2010 onwards but PFOA of 1998 – 2004. There is a fair amount of work going on in the EU and Asia on them. I expect to see human blood data soon. A little fish data has come from China. We probably should be ready to answer technical questions about them. Given the state of PFASs globally I expect that the ethers will be a big deal to EPA and the U.S. Government and we might want to have a plan in place to deal with the questions we are going to get.

Laurence

From: Seow, Jimmy [mailto:Jimmy.Seow@DER.wa.gov.au]
Sent: Tuesday, May 10, 2016 5:52 AM
To: Xenia Trier <Xenia.Trier@eea.europa.eu>; Libelo, Laurence <Libelo.Laurence@epa.gov>; 'HOLMES Nigel' <Nigel.Holmes@ehp.qld.gov.au>; Toke Winther <towin@mst.dk>; Anna & Arlene (Green Science Policy Institute) <anna@greensciencepolicy.org>
Cc: Graham White <Graham.White@hc-sc.gc.ca>; Balan, Simona@DTSC <Simona.Balan@dtsc.ca.gov>; Lau, Chris <Lau.Christopher@epa.gov>; Laurel Schaider <schaider@silentspring.org>; Vierke, Lena <Lena.Vierke@uba.de>; pgrand@hsph.harvard.edu; Field, Jennifer <jennifer.field@oregonstate.edu>; Bert-Ove.Lund@kemi.se; Roland Weber POPs <roland.weber10@web.de>; 'Scheringer Martin' <martin.scheringer@chem.ethz.ch>; KARHU Elina <Elina.KARHU@echa.europa.eu>
Subject: RE: Total organic fluorine - ethers do not degrade easily..

Hi all

Thanks Xenia

Just a quick one.

Yes I agree that it would be a good idea to invite MP Krafft.

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From: Xenia Trier [mailto:Xenia.Trier@eea.europa.eu]
Sent: Tuesday, 10 May 2016 5:32 PM
To: Libelo, Laurence; 'HOLMES Nigel'; Seow, Jimmy; Toke Winther; Anna & Arlene (Green Science Policy Institute)
Cc: Graham White; Balan, Simona@DTSC; Lau, Chris; Laurel Schaider; Vierke, Lena; pgrand@hsph.harvard.edu; Field, Jennifer; Bert-Ove.Lund@kemi.se; Roland Weber POPs; 'Scheringer Martin'; KARHU Elina
Subject: RE: Total organic fluorine - ethers do not degrade easily..

Dear All

Agree, ester linkages are 'easy', whereas ether linkages likely to be as poorly biodegradable as the PFAAs they replace, according to Krafft and Riess who are some of the very best phys-chem/organofluoro people in their field, cf their recent

physical-chemical review on environmental aspects on PFAS (attached). Some hints on how they react to the TOPA method could be found in the Krafft papers.

Regarding substitution to the alternative ethers:
They almost say straight out: 'Guys– you have not studied the degradation of alternatives enough to claim that they are safer – all points towards they will create the same problems (and they are 'surprised' at the short half life of ADONA). See below excerpts and the markings in blue and yellow.
They list suggested alternatives.

In future literature reviews of chemicals, I would highly suggest also ***to make sure*** to look into the phys-chem and the synthesis literature (e.g. Colloids, Langmuir, Angewandte Chemie, Bio-physicochemical journals etc), since a lot of valuable information on degradation, behaviour in the body, toxicity etc is described there. The reviews are the most easily accessible journals.

In some future study is to be made on biodegradability and/or the TOPA method, how about inviting an organofluoro synthesis/phys-chem expert, such as MP Krafft into it?

KR Xenia

Per- and polyfluorinated substances (PFASs): Environmental challenges
Marie Pierre Krafft a,*, Jean G. Riess b
Current Opinion in Colloid & Interface Science 20 (2015) 192–212
doi:10.1016/j.cocis.2015.07.004

13.2. To which extent are F-alkyl ether PFASs degradable?
The manufacture of polymers with polyfluorinated backbones requires the high level of performance that is presently only attainable with long-F-chain processing aids. In order to circumvent the environmental issues of the historic PFOA/PFNA-type processing aids, ether oxygens or other "weak points" were introduced in the F-chain that would ensure degradability while the acid function and total number of fluorinated carbons remained essentially the same. However, the claimed degradability advantage of these new long-F-chain ethers (PFECAs and PFESAs, Table 1) in environmental conditions is not yet clearly established, and their toxicity profile and that of their degradation products remain uncertain. The still limited public information available about their production, use, environmental exposure, persistence and exposure of biota and humans has recently been discussed [352••, 372].
There is actually little experimental evidence to support the expectation that PFECAs and PFESAs would be rapidly degraded in the environment. The ether oxygens are sterically sheltered and electron-depleted by the bordering electron-withdrawing F-chains, and thus inactivated. An in silico study estimated the basic properties, degradation halflives and transfer efficiency of PFECAs and PFESAs, and concluded that their behavior, including their persistence and mobility in the environment, should not be significantly different from those of the substances they replace [398]. Their thermal stability, resistance to photodecomposition, hydrolysis and reaction with OH radicals under environmentally relevant conditions appear indeed to be similar to those of regular Falkyl chain PFAAs [36••, 352••, 372]. ADONA (Table 1) for example, has been described as stable, not readily biodegradable and non-reactive, and a decomposition temperature of 125–175 °C was reported [250] that is similar to that of NH_4^+ PFOA, 167 °C [399]. Decomposition of PFECAs required combining persulfate $S_2O_8^{2-}$ oxidation and ultrasonic irradiation [400]. There is little or no evidence for lesser bioaccumulation potential for PFECAs/PFESAs as compared to their PFCA/PFSA analogues, or indication of atmospheric degradation, or different biological handling and toxicity mechanisms [352••]. No metabolism has been reported. There is no evidence that their eventual (largely unknown) degradation

products are innocuous. Releases of ADONA and GenX (Table 1) have been identified nearby factories [372]. The toxicity profile of ADONA was deemed superior to that of PFOA, but the two products were evaluated under different conditions [250]. GenX was actually suggested to be classified as having, like PFOA, specific target organ toxicity (STOT) by its producer [352••]. F-53B (Table 1) was found as persistent, similarly toxic in zebra fish and likely as bioaccumulative as PFOS [373].
Human data on ether acids are essentially inexistent. A (surprisingly short) human serum elimination half-life of 559 ± 254 h (3 male workers) has been suggested for ADONA [401].
Assessment of the bioaccumulation potential and toxicity of ADONA and other ether-type alternatives was not considered possible for lack of relevant data [110], but there seems to be little reason why long-Fchain PFECAs/PFESAs should not be classified in the same hazard category as PFOA/PFOS under REACH and other regulations. What has been described as a possible "lock-in" situation may have been created, in which the chemical banished from the market is replaced by other chemicals of essentially the same group with only minor structural changes, without solving the basic problem raised by the former product [372, 402•]. We simply know less about them.

...

The creed that inserting "weak" points into the chain's backbone may facilitate F-chain degradation has been around for a while. If effective, this approach means that one would forsake one of the major assets of F-chemicals, their resistance to harsh conditions. Introduction of ether oxygens,\\$CH_2$-,\\CHF- and other groups, or alternating CF_2 and CH_2 groups in F-chains has been achieved, but degradability in environmental conditions has generally not been established. Several sulfonates (e.g. $C_3F_7OCF_2CF_2CH_2CH_2SO_3H$, $C_6F_{13}CH_2CF_2CH_2CH_2SO_3H$), sulfamido betaine and sulfamido amine oxide surfactants derived from $C_3F_7OCF_2CF_2CH_2CH_2SO_2Cl$ and $C_4F_9(CH_2CF_2)_{(1\ or\ 2)}CH_2CH_2SO_2Cl$ have been synthesized [413, 414], as well as oligo(vinylidene fluoride) telomers $C_nF_{2n+1}(CH_2CF_2)_xCH_2COOH$ (n = 2, 4; x = 2) [415]. Various surfactants that combine an F-isopropyl terminal group with pending CF_3 groups located on alternate carbons along the hydrophobic backbone had surface tensions comparable to that of PFOA [416]. Sequential block copolymerization of vinylidene fluoride, trifluoropropene and vinyl acetate led to surfactants that combine a terminal C_6F_{13} chain, isolated CF_2 groups in the backbone and pending CF_3 groups [417]. Their environmental behavior, degradability, pharmaco- and toxicodynamics remain to be investigated. Identified alternatives to PFOS-related PFASs (with not only short-F-chain homologues) have been listed [3, 363••, 418].
Other approaches may use (innocuous enough) particles, such as silica, laponite clay or polystyrene latex, as dispersion (emulsions, multiple emulsions, foams, etc.) stabilizing agents [419, 420]. For food products, polysaccharides (starch, cellulose) or protein-based particles (casein) or protein/polysaccharide associations are being developed [421]. All these approaches require evaluation of any counter-risk posed by particle use.

..

While regulations are indispensable for pollution control and rational management of PFAS risk, they also have limitations and downsides, including a negative economic impact on growth of development. Enforcement of regulations is further complicated by the multiplication of proprietary variants and the fractionation of use among many, often undisclosed PFASs or mixtures thereof. This practice, by reducing tonnages used in a given location belowanalytical "visibility" or belowcertain regulatory thresholds (e.g. the 100 tons limit that requires data on bioaccumulation for REACH authorization [371]), renders global monitoring, regulation and control of implementation virtually impossible.
This is the case for the F-polyethers that have replaced PFOA and PFNA in F-polymer manufacture [352••, 372] (Point/Section 13). Multiplication of components in a technical product [16–18] also complicates the regulators' task. For lack of information, some PFASs have remained unnoticed while already in use for 30 years [373]. Certain compounds, by formally changing categories (e.g. from polyether to polymer [352••])may also elude regulation. Some rules do not apply to imported finished goods. While direct emissions of regulated substances decrease, emissions of these substances through production and degradation of precursors continue.

From: Libelo, Laurence [mailto:Libelo.Laurence@epa.gov]
Sent: 05 May 2016 14:24
To: 'HOLMES Nigel' <Nigel.Holmes@ehp.qld.gov.au>; Xenia Trier <Xenia.Trier@eea.europa.eu>; Seow, Jimmy <Jimmy.Seow@DER.wa.gov.au>; Toke Winther <towin@mst.dk>; Anna & Arlene (Green Science Policy Institute) <anna@greensciencepolicy.org>
Cc: Graham White <Graham.White@hc-sc.gc.ca>; Balan, Simona@DTSC <Simona.Balan@dtsc.ca.gov>; Lau, Chris <Lau.Christopher@epa.gov>; Laurel Schaider <schaider@silentspring.org>; Vierke, Lena <Lena.Vierke@uba.de>; pgrand@hsph.harvard.edu; Field, Jennifer <jennifer.field@oregonstate.edu>; Bert-Ove.Lund@kemi.se; Roland Weber POPs <roland.weber10@web.de>; 'Scheringer Martin' <martin.scheringer@chem.ethz.ch>
Subject: RE: Total organic fluorine

Nigel,

Thank you. I agree. The CH2CH2 ester linkage should break pretty easily. This needs to be confirmed but there is good reason to think it will happen. I spoke with Erica a few months ago and she said about the same.

The TOP approach should work for most polymer linkages. I am hoping that someone is looking at how other linkages without the ester i.e. – CF2 – C(backbone), C-Sl, C-N -, CF2-O-CF2, etc react. I think there is lot more polymer materials in AFFF, landfill leachate, biosolids, house dust, soils and other media then we know and that these are a very large potential source. Quantifying these is necessary to try to figure out total potential monomers that might form.

My other big question is how these linkages behave in sea water. Washington and Jenkins in ES&T 2015 showed OH-catalyzed hydrolysis for the acrylate linkage. How could the TOPA approach be used to estimate release of acid monomers from polymer materials in the ocean?

Thanks all.

Laurence

From: HOLMES Nigel [mailto:Nigel.Holmes@ehp.qld.gov.au]
Sent: Wednesday, May 04, 2016 10:17 PM
To: Libelo, Laurence <Libelo.Laurence@epa.gov>; 'Xenia Trier' <Xenia.Trier@eea.europa.eu>; Seow, Jimmy <Jimmy.Seow@DER.wa.gov.au>; Toke Winther <towin@mst.dk>; Anna & Arlene (Green Science Policy Institute) <anna@greensciencepolicy.org>
Cc: Graham White <Graham.White@hc-sc.gc.ca>; Balan, Simona@DTSC <Simona.Balan@dtsc.ca.gov>; Lau, Chris <Lau.Christopher@epa.gov>; Laurel Schaider <schaider@silentspring.org>; Vierke, Lena <Lena.Vierke@uba.de>; pgrand@hsph.harvard.edu; Field, Jennifer <jennifer.field@oregonstate.edu>; Bert-Ove.Lund@kemi.se; Roland Weber POPs <roland.weber10@web.de>; 'Scheringer Martin' <martin.scheringer@chem.ethz.ch>
Subject: RE: Total organic fluorine

Laurence

Erica Houtz mentions fluoropolymers in her 2013 PhD thesis to the extent that biotransformation is slow and the TOPA method could be used to tests their susceptibility to hydroxyl radical attack in the long term. But it seems this needs to be tested further. Where a fluorotelomer dimethylene (-CH2-CH2- spacer) group is involved in the side chain I think the perfluorinated chain would be more readily cleaved off the polymer backbone (as well as at ester linkages) by TOPA to result in PFCAs.

Fluoropolymers are now in use in firefighting foams with the added dimension of fluoropolymer-siloxane composites.

Queensland Government

Erika says (p96) - The precursor assay could also be tested on polymerized products to rapidly determine their susceptibility to hydroxyl radical deterioration. If polymerized products yield PFAAs upon exposure to hydroxyl radical, their long-term ability to serve as a source of PFAAs would seem more likely.

Erika's PhD is 8Mb in size so I won't attach it to fill up your inboxes. I happy to send it individually or you can find it via the Berkley site:
http://www.berkeley.edu/search?q=Oxidative+Measurement+of+Perfluoroalkyl+Acid+Precursors%3A
2013 - Oxidative Measurement of Perfluoroalkyl Acid Precursors: Implications for urban runoff management and remediation of AFFF-contaminated groundwater and soil

Regards

Nigel Holmes
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From: Libelo, Laurence [mailto:Libelo.Laurence@epa.gov]
Sent: Wednesday, 4 May 2016 9:41 PM
To: 'Xenia Trier'; Seow, Jimmy; Toke Winther; Anna & Arlene (Green Science Policy Institute)
Cc: Graham White; Balan, Simona@DTSC; Lau, Chris; Laurel Schaider; HOLMES Nigel; Vierke, Lena; pgrand@hsph.harvard.edu; Field, Jennifer; Bert-Ove.Lund@kemi.se; Roland Weber POPs; 'Scheringer Martin'
Subject: RE: Total organic fluorine

Sorry to jump in at the end of the email chain but –

Do you know how the TOP oxidation effects polymers? Will if quantify sidechain polymers or polyethers that degrade to FOTHs and further to acids?

Thanks.

Laurence

==========

E. Laurence Libelo, Ph.D.
Senior Environmental Engineer
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From: Xenia Trier [mailto:Xenia.Trier@eea.europa.eu]
Sent: Wednesday, May 04, 2016 7:35 AM
To: Seow, Jimmy <Jimmy.Seow@DER.wa.gov.au>; Toke Winther <towin@mst.dk>; Anna & Arlene (Green Science Policy Institute) <anna@greensciencepolicy.org>
Cc: Graham White <Graham.White@hc-sc.gc.ca>; Balan, Simona@DTSC <Simona.Balan@dtsc.ca.gov>; Lau, Chris

<Lau.Christopher@epa.gov>; Laurel Schaider <schaider@silentspring.org>; HOLMES Nigel (Nigel.Holmes@ehp.qld.gov.au) <Nigel.Holmes@ehp.qld.gov.au>; Vierke, Lena <Lena.Vierke@uba.de>; pgrand@hsph.harvard.edu; Libelo, Laurence <Libelo.Laurence@epa.gov>; Field, Jennifer <jennifer.field@oregonstate.edu>; Bert-Ove.Lund@kemi.se; Roland Weber POPs <roland.weber10@web.de>; 'Scheringer Martin' <martin.scheringer@chem.ethz.ch>
Subject: RE: Total organic fluorine

Dear Jimmy

Yes, the TOP analysis is also interesting, and last year we (PFAS analysis calls) were involved in getting Eurofins to set it up with a lower LOD, and getting it made into a standard method, in support of the EU restriction on PFOA and PFOA precursors. In Colorado last year after the Fluoros conference we also had a session where it was discussed.

Stefan or Jenifer: What is the update on the status of the TOP method – has Eurofins lowered the limits, and is there ongoing work to make it into a CEN/ISO method?

It is true that the TOP will give you the PFAA chain length, assuming the TOP degradation yield is 100%, which it does in some cases but not all. You would then need standards to determine the 'recovery' or degradation yield in various matrices – and often you do not have such standards.

To my knowledge the TOP method does not capture perfluorpolyethers (PFPEs), or fluorinated aromatics.. which are poorly evaluated toxicologically and have interesting (persistent) properties as well. The TOrF method has the advantage that it detects incremental substitution to other organofluorine compounds.

That said, if you only/mainly are interested in PFAA precursors, the TOP method is a very good option to be used for risk assessment.

KR Xenia

From: Seow, Jimmy [mailto:Jimmy.Seow@DER.wa.gov.au]
Sent: 04 May 2016 10:31
To: Xenia Trier <Xenia.Trier@eea.europa.eu>; Toke Winther <towin@mst.dk>; Anna & Arlene (Green Science Policy Institute) <anna@greensciencepolicy.org>
Cc: Graham White <Graham.White@hc-sc.gc.ca>; Arlene Blum ? <arlene@arleneblum.com>; Balan, Simona@DTSC <Simona.Balan@dtsc.ca.gov>; Lau, Chris <Lau.Christopher@epa.gov>; Laurel Schaider <schaider@silentspring.org>; HOLMES Nigel (Nigel.Holmes@ehp.qld.gov.au) <Nigel.Holmes@ehp.qld.gov.au>; Vierke, Lena <Lena.Vierke@uba.de>; pgrand@hsph.harvard.edu; Libelo, Laurence (Libelo.Laurence@epa.gov) (Libelo.Laurence@epa.gov) <Libelo.Laurence@epa.gov>; Field, Jennifer <jennifer.field@oregonstate.edu>; Bert-Ove.Lund@kemi.se; Roland Weber POPs <roland.weber10@web.de>; 'Scheringer Martin' <martin.scheringer@chem.ethz.ch>
Subject: RE: Total organic fluorine

Hi Xenia

Me again.

After I replied to you Nigel emailed this as Toke email has provoked rekindled dialogue on the matter between Nigel and me. I added comments to it which are highlighted in yellow.

Jimmy

The value in the TOPA C4-C14 method (Houtz, Sedlak, Barzen-Hansen & Field) is that we not only get a reliable surrogate for TOF (as the sum of TOPA C4-C14 + C4-C8 sulfonates) but we ALSO get a detailed breakdown according to precursor perfluorinated chain length which we can relate in general terms to PBT. TOrF is of limited value as it does not give any clues about chain length/PBT. Agree as it is the chain length which is of concern such as the long chain length of C6 and above hence the Canadians make moves to limit it (Charles White from Canada can elucidate better of their Regulation on the long chain PFC enforce in 2014).

The paper by Washington *et al* illustrates the problem nicely in terms of an example of a **single compound** (8:2 fluorotelomer alcohol) having **19 potential transformation products** including ketones, alcohols and carboxylics, most with completely unknown effects including 5 end-point perfluorinated carboxylics.

Translate this to practicalities:
- We don't know what is in foam formulations (multiple compounds to C15) – as mentioned Place and Field attempted to find out for the US military foams – see the paper I attached in my last email
- Users don't know what foam purity/compositions they might possess (mixed/contaminated formulations, PFOS, etc) – the SDS do not say whatsoever or worst some foam SDS don't even say it has fluorosurfactants.
- We don't know and can't analyse for most transformation products on their way to end-point perfluorinateds.
- The non-standard functional groups and the odd-chain/unsaturated X:Y poly-fluorinateds hide most compounds from analyses.
- A long list of complex compounds is not useful even if we could do it as we don't know what each does.

However TOPA can reveal the PFC content by perfluorinated chain lengths and we can generally relate that to PBT.

Table 5.2 A
Suite of precursor carboxylate-equivalent compounds reported under the TOPA C4-C14 method

C-chain	Compound	Abbreviation	C-chain	Compound	Abbreviation
C4	Perfluorobutanoate	(PFBA)	C10	Perfluorodecanoate	(PFDA)
C5	Perfluoropenatnoate	(PFPeA)	C11	Perfluoroundecanoate	(PFUnA)
C6	Perfluorohexanoate	(PFHxA)	C12	Perfluorododecanoate	(PFDoA)
C7	Perfluoroheptanoate	(PFHpA)	C13	Perfluorotridecanoate	(PFTriA)
C8	Perfluorooctanoate	(PFOA)	C14	Perfluorotetradecanoate	(PFTeA)
C9	Perfluorononanoate	(PFNA)			

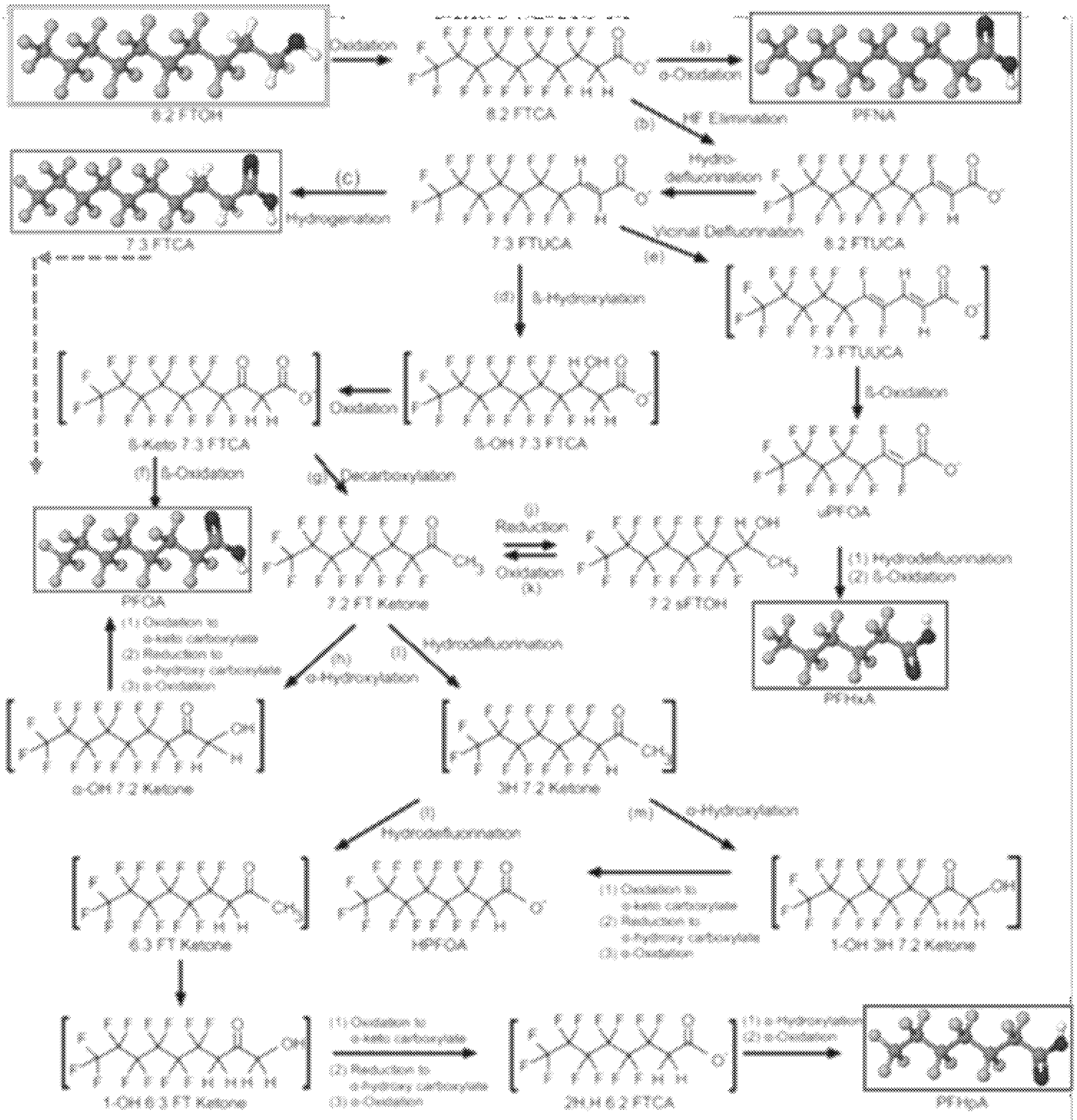

Figure 2.5.2 B – Possible biotransformation pathways for 8:2 fluorotelomer alcohol (8:2FTOH), a precursor compound (top left) to multiple transformation [ ] and end-point compounds (blue boxes) including PFOA, PFNA, 7:3 FtCA, PFHxA and PFHpA. Bracketed compounds are proposed intermediate transformation compounds. (AfterWashington, Jenkins & Weber, 2015 [88] – 3D Molecule graphics generated by www.chemspider.com)

The TOPA C4-C14 analysis also allows us to test the general composition of existing foams and the C6-purity (FFFC in Washington cursorily told me that the transition to pure C6 as required by the USEPA is working well and I am awaiting a response from them how well is well) or fluorine-free claims of new generation foams without manufacturers having to divulge the trade secret compositions. We can also comprehensively test contaminated sites without missing dozens of transformation products. The standard suite of 20-28 PFCs is still needed for some specific compounds (PFOS, PFOA, PFHxS, PFBS) but is completely inadequate for revealing all the hidden PFCs which are 50% to 99% of compositions and contamination.

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From: Xenia Trier [mailto:Xenia.Trier@eea.europa.eu]
Sent: Wednesday, 4 May 2016 3:56 PM
To: Seow, Jimmy; Toke Winther; Anna & Arlene (Green Science Policy Institute)
Cc: Graham White; Arlene Blum ?; Balan, Simona@DTSC; Lau, Chris; Laurel Schaider; HOLMES Nigel (Nigel.Holmes@ehp.qld.gov.au); Vierke, Lena; pgrand@hsph.harvard.edu; Libelo, Laurence (Libelo.Laurence@epa.gov) (Libelo.Laurence@epa.gov); Field, Jennifer; Bert-Ove.Lund@kemi.se; Roland Weber POPs; 'Scheringer Martin'
Subject: RE: Total organic fluorine

Dear Jimmy

The way we have done it for TOrF in *food contact materials* in Denmark was to convert the TOrF value (*in the paper*) on a molar basis as if all the organic fluorine to PFOA units, using PFOA (and its TDI) as a lead compound for setting the limit. Knowing that all organofluorines might not be as toxic as PFOA (eg PFBA), and because not all migrated, we only used approximately 10% of that limit. Which fraction that is used (1, 10, 100%) is for risk managers to set. Another option is to use the 100% of the limit, and if the limit is exceeded, then make specific analysis by targeted methods. These must however include all known and relevant PFAS, incl. the precursors which otherwise might release PFAAs upon degradation over time, or due to remediation. An option is to put the responsibility onto the 'polluter' to demonstrate which organofluorines that contribute to the TOrF – they have more knowledge of what was used, and this would transfer the cost to the polluter as well.

I could/should translate the 28 pages to English really…

KR Xenia

From: Seow, Jimmy [mailto:Jimmy.Seow@DER.wa.gov.au]
Sent: 04 May 2016 08:46
To: Toke Winther <towin@mst.dk>; Xenia Trier <Xenia.Trier@eea.europa.eu>; Anna & Arlene (Green Science Policy Institute) <anna@greensciencepolicy.org>
Cc: Graham White <Graham.White@hc-sc.gc.ca>; Arlene Blum ? <arlene@arleneblum.com>; Balan, Simona@DTSC <Simona.Balan@dtsc.ca.gov>; Lau, Chris <Lau.Christopher@epa.gov>; Laurel Schaider <schaider@silentspring.org>; HOLMES Nigel (Nigel.Holmes@ehp.qld.gov.au) <Nigel.Holmes@ehp.qld.gov.au>; Vierke, Lena <Lena.Vierke@uba.de>;

pgrand@hsph.harvard.edu; Libelo, Laurence (Libelo.Laurence@epa.gov) (Libelo.Laurence@epa.gov) <Libelo.Laurence@epa.gov>; Field, Jennifer <jennifer.field@oregonstate.edu>; Bert-Ove.Lund@kemi.se; Roland Weber POPs <roland.weber10@web.de>; 'Scheringer Martin' <martin.scheringer@chem.ethz.ch>; Elina.KARHU@echa.europa.eu
Subject: Total organic fluorine

Dear Toke

How are you

You raise the notion of using total organic fluorine which is certainly very interesting as Nigel Holmes from the Queensland Dept of Environment and Heritage Protection and I talked about when we were drafting the foam policy 2 years ago.

As you would know firefighting foams with PFC has a variety of composition of which the manufacturers are very reluctant to divulge on the argument it is proprietary formula and not to be shared which makes it difficult for regulators and also research people to know what is exactly in the foam make up to properly do an environmental and health impact assessment. To compound the problems the PFC ingredients also have precursors which can transform to PFOA and PFCA and PFSA. Therefore we are dealing with a cocktail of PFC and the impact is no longer just PFOS and PFOA but also PFC species of concern.

A good paper on PFC composition is a paper by:
Place, B., Field, J., 2012. Identification of novel fluorochemicals in aqueous film forming foams used by the US military. Environ. Sci. Technol. 46, 7120–7127.

I told Dr Field that her paper is a milestone paper as to my knowledge was the first to show what those commercial foam used by the US military contained, and that now with advanced techniques of FAB and QTOF techniques one can reverse engineer to figure out what they contained. I even suggested to the foam manufacturers informally that it would be a good idea to start telling what their foam really contain.

Arlene as a key player for the Madrid Statement would agree with me that one of the recommendations made in both the Madrid and Helsingor Statements in 2015 was that the foam manufacturers should say fully what are for the foam ingredients.

Nigel and I discussed at length whether we could use the notion of total organic fluorine as guidelines rather and individual values for PFOS and PFOA and then PFBS, PFBA, PFHxS and the other PFCs as denoted in the Danish and Swedish groups of which you explained below in your email, and we even explored with various labs in Australia how feasible commercially to analyse for total organic fluorine as it is not that straight forward.

Combustion ion chromatography can be used to measure total and adsorbable organic fluorine but cannot be used to identify individual PFASs however oxidizable precursor assay, which is based on the oxidation of polyfluoroalkyl "precursor" substances to perfluoroalkyl carboxylic acids (PFCAs) can be used to quantify precursors in urban runoff and groundwater.

Attached are two papers for the above methods. I will be discussing this further with Dr Field when she comes to Perth in October.

Nigel just told me that ALS (a multination lab) in Sydney are developing the total oxidisable precursors assay method (TOPA C4-C14) for commercialisation and look to be close to finalising it. Nigel and I have also been talking to Eurofin which is a French multinational lab now operating in Australia also on TOF.

To me the big issue is that even though we can commercially analyse for TOF how can it be used as guideline values as so far all research on environmental and health impact is for PFOS and PFOA which means there needs to be

transference methodology or model for transference of TOF values to those impacts. Not an easy tasks and can be challenging.

Thoughts ?

Regards

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From: Toke Winther [mailto:towin@mst.dk]
Sent: Friday, 29 April 2016 5:18 PM
To: Xenia Trier; Seow, Jimmy; Anna & Arlene (Green Science Policy Institute)
Subject: SV: {Revised} PFAS call notes (Feb. 23, 2016)

Dear all

The Danish drinking water (ground water) limit value is a sum criteria of 12 PFASs. These 12 PFASs were partly chosen because of analysis available at a reasonable price from a commercial lab. So we (Danish EPA and Danish Nature Agency) have been wondering – is this "good enough", are these 12 PFASs the right choice. A way to test this is by measuring Total Organic Fluorine. We did a pilot test by using the AOF method but unfortunately the LOQ (1µg/l) of this method are too high compared to our drinking water limit value (0.1 µg/l). We will still consider using the AOF method when testing for point source contamination. With the sum criteria of 12 PFASs I think that we have opened the door for (over time) setting our drinking water limit value as Total Organic Fluorine, if we should find that the 12 PFASs are not "good enough".
So my questions are simply:

1. Are other countries or regions having the same thoughts/considerations?
2. Do other methods for testing Total Organic Fluorine than the AOF method? For such a method to be relevant for us it should have a LOQ in the ng/l region.

Regarding the firefighting foams. The idea is to make a "voluntarily" phase out by introducing a centralised purchasing agreement/contract through the Danish Emergency Management Agency (Beredskabsstyrelsen) so that they are in charge of all purchase of firefighting foam. As this project is in its very beginning we lean on the experiences from Sweden. Please see these 3 reports:
http://www.kemi.se/global/rapporter/2016/rapport-1-16-forslag-till-nationella-regler-for-hogfluorerade-amnen-i-brandslackningsskum.pdf
http://www.kemi.se/global/pm/2015/pm-5-15-survey-of-fire-fighting-foam.pdf

http://www.kemi.se/global/pm/2015/pm-6-15.pdf

Kind Regards
Toke

Fra: Xenia Trier [mailto:Xenia.Trier@eea.europa.eu]
Sendt: 27. april 2016 20:40
Til: Toke Winther
Cc: Seow, Jimmy; Anna & Arlene (Green Science Policy Institute)
Emne: RE: {Revised} PFAS call notes (Feb. 23, 2016)

Dear Toke

Could you please send a few lines to Anna on which types of analysis that you would like to see (total organic fluorine) and your point whether other countries were interested in pursuing a limit based on the total organic fluorine in ground/drinking water.

Another question that was raised, was whether the phase-out of PFAS in fire fighting foams (cf beredskabsstyrelsen in relation to the recent big fire in the harbour of Fredericia) in Denmark are done voluntarily or if they are legally binding? Is there some evaluation available on the functionality of the non-fluorinated alternatives Toke? The group would be very interested if DK or other countries have made functionality assessments of the alternatives – do they have sufficient functionality?

Thanks!
KR Xenia

From: Seow, Jimmy [mailto:Jimmy.Seow@DER.wa.gov.au]
Sent: 27 April 2016 18:24
To: Anna & Arlene (Green Science Policy Institute) <anna@greensciencepolicy.org>; Xenia Trier <Xenia.Trier@eea.europa.eu>
Subject: Re: {Revised} PFAS call notes (Feb. 23, 2016)

Thanks Anna, Arlene and Xenia

Thanks alot. Such a worthwhile discussion to stay up late for.

I very much like to follow up with some of the EU and Health Canada participants on their comments.

Could you kindly share the emails of the participants.

Much appreciated.

From: Anna & Arlene (Green Science Policy Institute) <anna@greensciencepolicy.org>
Sent: Wednesday, 27 April 2016 10:00:12 PM
To: Seow, Jimmy
Subject: {Revised} PFAS call notes (Feb. 23, 2016)

Dear Jimmy,

In case you might find it of interested below you will find revised key points from our February PFAS call.

Also, here are some additional publications that we shared with the group with the revised notes:
- A paper by Zhanyun Wang et al. accepted for publication in Environment International (attached)
- "A chemical shell game - How DuPont Concealed the Dangers of the New Teflon Toxin" by Sharon Lerner (link)
- "New Teflon toxin causes cancer in lab animals" by Sharon Lerner (link)

Best wishes,
Anna

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Staff Changes
Due to a possible conflict of interests at her new job at the European Environmental Agency (EEA) beginning March 1st 2016, Xenia Trier has step down from leading the PFAS analysis calls. It has been decided that it might be best for now to merge the PFAS policy and analysis calls. Having regular calls is informative and useful way to explore collaborative opportunities. If a breakout group is needed, it will form.

Simona Balan has also accepted a new position with the California Department of Toxic Substances Control. In the interim, Anna Soehl (Green Science Policy Institute) will help with coordinating calls and communication for the combined monthly calls.

Study topics currently investigated by participants
Germany:
Interested in the transfer of PFAS in the food chain.
Questions to the EFSA (EU Food Safety Authority) investigating the need for new safe limits for PFOA and PFOS; looking at exposure.
Bundesinsititut for Risk assessment (BfR) is waiting to see what EFSA will decide before going forward with their own investigations.

UK & Sweden collaboration: looking at firefighting foams

US:
PFOS in monitored drinking water: looking at the correlation between the elevated observed concentrations and proximity to airports, firefighting testing grounds, and industrial sites. So far the elevated concentrations seem to only correlate with the proximity to the industrial site.
In Germany there is an existing recommendation to use non-fluorinated chemicals in firefighting tests; it would be good to know what is happening in practice at German airports and military bases.

New Jersey: working on recommendation for PFOA in drinking water; worked on it in 2010, but it never was finalized; in 2012 a paper was published reviewing the information gathered in 2010; working on PFOS now. Information search resulted in about 2000 citations.
Advisory document should be coming out soon.

Washington State:

Dept. of Ecology might start looking at firefighting foam – oil will be shipped by train through the state, locations along the roots with firefighting foams (non-fluorinated foam).
Product testing for fluorinated chemicals in consumer products -- any suggestions are welcome.
Alex Stone is retiring at the end of the year.

Policy statement for American Public Health Association (APHA) on PFASs has been accepted for review – can be pointed to for policy decisions.
Get in touch with Anna or Arlene if you might want to contribute and help author this document.

News & other updates:
Hoosick Falls, NY Incident:
- Small town in upstate NY
- Location of a number of chemical companies
- For a long time there was a perception that there were a lot of incidents of cancer.
- Drinking water tests for PFOA: 600 ppt
- Nothing was done for a while, Health Dept initially indicated that no special precautionary measures were necessary
- Eventually USEPA Region 2 issued a do not drink or cook with the water advisory
- USEPA is being petitioned to declare it a superfund site and quickly develop a chronic number
- Current advice being given: do not drink or brush teeth, crack window when taking a shower
- Private wells will need to be tested individually
- Temporary limit applied by USEPA Region 2: 100 ppt
- Another recent discovery of elevated drinking water levels: Petersburgh, NY water tests for PFOA came back with 95.9 ppt. Company that is suspected to have contaminated the water is providing drinking water.
- New York Governor's press release (link) and PowerPoint (link) about statewide water quality initiatives mentioning the Hoosick Falls incident.
- Some biomonitoring is being done (blood samples) and a cancer study
- Related anecdote: DecaBDE manufacturers warned in the past that the use of alternatives would increase the use perfluorinated compounds
- Village of Hoosick Falls (NY) Water Website (link)
- Article from Inside EPA's Risk Policy Report for February 16, 2016 (attached)
- BNA Snapshot:" EPA Recommends Bottled Water in PFOA Contaminated Areas" (attached)
- Article by Sharon Lerner "Flint residents may have been drinking PFCs in addition to lead" (link)

Arlene's Editorial for Science: March 11 -- four organizations that phased out highly fluorinated chemicals will be disclosed; hope for a snowball effect.

Recent publications:
Septic systems as sources of organic wastewater compounds in domestic drinking water wells in a shallow sand and gravel aquifer
Laurel A. Schaider, Janet M. Ackerman, Ruthann A. Rudel
Science of The Total Environment Volume 547, 15 March 2016, Pages 470–481. Available online 27 January 2016 (link)
•Tested 20 domestic drinking water wells for 117 organic wastewater compounds.
•PFASs, pharmaceuticals, and an artificial sweetener were most frequently detected.
•Nitrate, boron, and well depth were all correlated with PFASs and pharmaceuticals.
•Acesulfame (artificial sweetener) is a sensitive marker of OWCs in groundwater.
•Septic systems are likely the main source; landfills may also affect some wells.

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If you no longer wish to receive our periodic updates, please respond to me and write UNSUBSCRIBE in the subject line.

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The Green Science Policy Institute provides unbiased scientific information to government, industry, and non-governmental organizations to facilitate more informed decision-making about chemicals used in consumer products in order to protect health and environment world-wide.

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