PERFLUOROHEXANE SULFONATE (PFHxS)– SOCIO-ECONOMIC IMPACT, EXPOSURE, AND THE PRECAUTIONARY PRINCIPLE

IPEN Expert Panel
Rome

October 2019

IPEN
for a toxics-free future

PERFLUOROHEXANE SULFONATE (PFHxS)−SOCIO-ECONOMIC IMPACT, EXPOSURE, AND THE PRECAUTIONARY PRINCIPLE

September 2019

Bluteau, T. [a], **Cornelsen**, M. [b], **Holmes**, N.J.C. [c], **Klein**, R.A. [d], **McDowall**, J.G.[e], **Shaefer**, T.H. [f], **Tisbury**, M. [g], **Whitehead**, K. [h].

[a] Leia Laboratories, France
[b] Cornelsen Umwelttechnologie GmbH, Essen, Germany
[c] Department of of Science and Environment, Queensland Government, Australia
[d] Cambridge, United Kingdom, and Christian Regenhard Center for Emergency Response Studies, John Jay College of Criminal Justice, City University New York (CUNY), New York USA
[e] 3FFF Ltd, Corby, United Kingdom
[f] Sydney, Australia
[g] United Firefighters Union and Melbourne Metropolitan Fire Brigade (MFB), Australia
[h] Unity Fire & Safety, Oman

representing the IPEN Panel of Independent Experts

White Paper prepared for IPEN by members of the IPEN Expert Panel and associates for the meeting of the Stockholm Convention POPs Review Committee (POPRC-15), 1-4 October 2019, Rome, Italy

Corresponding authors: R. A. Klein <rogeraklein@yahoo.co.uk>, Nigel Holmes <Nigel.Holmes@des.qld.gov.au>

For your reference, the previously presented papers from the IPEN international expert panel include:

1) *Fluorine-Free Firefighting Foam*s—Viable Alternatives to Fluorinated Aqueous Film-Forming Foams (AFFF) available at: **https://ipen.org/documents/fluorine-free-firefighting-foams**

2) *The Global PFAS Problem: Fluorine-Free Alternatives as Solutions available* at: **https://ipen.org/documents/global-pfas-problem-fluorine-free-alternatives-solutions**

CONTENTS

FOREWORD

IPEN respectfully presents the third in a series of papers prepared by an international panel of experts on PFAS chemicals. This paper, Perfluorohexane Sulfonate (PFHxS)—Socio-Economic Impact, Exposure, and the Precautionary Principle, offers unique insights about threats to drinking water sources, public health and the occupational health of firefighters due to the particular physico-chemical properties of PFHxS, including its greater mobility, hydrogeological fractionation, and long elimination half-life in people.

The paper presents unequivocal evidence from recent studies that firefighters using aqueous film-forming foams (AFFF) have unacceptably elevated blood levels of both PFHxS and PFOS. It also highlights the inextricable link between PFHxS, PFOS and PFOA resulting from the inherently polluting electrochemical fluorination (ECF) manufacturing process. ECF manufacturing produces a high proportion of unintended PFAS by-products, with profound implications for environmental and human health. The authors examine significant sources of PFHxS/PFAS contamination, including manufacturing, textiles production, firefighting foams, sulfluramid production and use, wastewater and sewage sludge/biosolids. The costs and liabilities associated with continued use of PFHxS and other PFAS are extremely high and warrant a class-based approach to prevent further harm.

The POPs Review Committee concluded at the meeting in 2018 that PFHxS, its salts and related compounds are likely as a result of their long-range environmental transport to lead to significant adverse human health and environmental effects such that global action is warranted. PFHxS has been a regrettable substitute for PFOS and used in many consumer products and industrial applications. Technically feasible, cost-effective, alternatives are available for these uses.

We conclude that PFHxS its salts and PFHxS-related compounds should be recommended for listing in Annex A with no specific exemptions. In addition, the POPRC should recommend avoiding PFAS substitutes for PFHxS, as these will also have unacceptably negative environmental, human health and socio-economic impacts due to their persistency and mobility.

We hope that the evidence presented in this paper is useful in informing the decisions of the POPs Review Committee and in contributing toward the global elimination of PFHxS and other PFAS.

Pamela Miller
IPEN Co-Chair

September 17, 2019

IPEN

THE PFAS EXPERT PANEL MEMBERS

This White Paper represents a synthesis of IPEN PFAS Expert Panel member's contributions from various countries including Australia, France, Germany, and the United Kingdom. This White Paper follows on from the two papers presented at the 14th meeting of the Stockholm Convention POPs Review Committee (POPRC-14) in Rome 17-22 September 2018 and the 9th Conference of the Parties of the Stockholm Convention (SC-COP9) in Geneva 29 April-10 May 2019. It is mainly concerned with the Risk Management Evaluation for PFHxS which will be discussed and finalized in Rome 1-4 October 2019.

Dr. Thierry BLUTEAU

Leia Laboratories, Ormskirk UK and Essertines-en-Donzy (Lyon) France, PhD chemist; foam formulator and developer; formerly Croda-Kerr and Bio-Ex; developed Ecopol™ fluorine-free foam: also solvent-free and fluorine-free firefighting foams. free foam; he graduated in Paris University with a Masters in biochemistry, followed by a PhD in pharmaco-chemistry; he initiated work in firefighting technologies in 1992, as laboratory manager at Croda Fire Fighting in France; 6 years later, he created Bio-Ex, a company which specialized in firefighting foams, where he launched one of the first commercial Class B fluoro-free foams (Ecopol); in 2012 he started collaborating with 3FFF Ltd to design a new line of foams; later on, he joined Leia Ltd, where he has dedicated his time to creating innovative foams and as well as advising customers on specific firefighting projects; his latest achievement was presented by 3FFF Ltd in 2015 with the launch of Smart Foams™, a range of new foams totally free of fluorinated materials and solvents, with highly favourable ecological profile.

Dipl. Ing. Martin CORNELSEN

Cornelsen Umwelttechnologie GmbH, Essen, Germany, Qualified water treatment engineer; Dipl. Ing., MSc; development of a technically simple multi-tiered small filter system for the treatment of polluted water to drinking water in underdeveloped rural areas of advanced materials and processes for water and wastewater treatment using functional nanocomposites (BMBF - Federal Ministry of Education and Research, 2012-2013); development of a cost-effective adsorption process to purify water contaminated by PFAS (BMWi - Federal Ministry for Economic Affairs and Energy, 2010-2011); development of a liquid product (no adsorbent) for the cost-effective cleaning of water contaminated by PFAS (BMWi, 2013-2015); development and manufacture of textile adsorbant material for the remediation of water contaminated by chromates (BMWi, 2014-2016); recovery of precious metals from the waste streams of metal processing industries with the aid of fibre-fixed adsorbants (BMBF, 2016 until probably 2018); development of methodology for eliminating PFAS from water polluted by fire extinguishing agents (BMBF, 2016 -2018). Martin is bilingual in German and English.

Nigel HOLMES

Nigel Holmes is Principal Advisor Incident Management for the Queensland Department of Environment and Science (DES), the regulatory body for pollution management in Queensland; his role is as a state-wide resource advising on policy, standards, risk assessment, preparedness and response for incidents involving a diversity of hazardous materials. He also has over 30 years' multi-disciplinary experience in consulting and government roles across environmental, geotechnical and contamination assessment, regulation and policy development for land, marine, freshwater and groundwater pollution assessment, industry licensing, remediation, aquaculture and geotechnical assessment. Since 2012 he has been the project coordinator for the review, development and drafting of the Queensland Environmental Management of Firefighting Foam Operational Policy supported by extensive advice and input from a very wide range of Australian and international subject experts: provision of expert advice on risks of fluorinated organic compounds to foam end-users, suppliers and regulators across Australia on the practical assessment and management of risks posed by existing and proposed use of firefighting foams; liaison with interstate and overseas agencies on consistency of

regulatory measures; promoting consistency in the practical, achievable and economic regulation of PFAS. Facilitation of new analytical methods for PFAS risk assessment: Promoting the refinement of the total oxidisable precursor assay (TOP-A) and incorporation into Policy as a more comprehensive method than the limited standard PFAS suite; Queensland foam Policy implementation and compliance plan: Identification of industry sectors with PFAS firefighting foam and development of strategies and guidance on the practical transition to best-practice for foam use; expert witness to the 2015 Victorian Parliamentary Inquiry into CFA Fiskville PFAS contamination.

Dr. Roger A. KLEIN

Panel coordinator; currently independent consultant; trained as a medical doctor and PhD physical chemist (Cambridge); formerly Universities of Cambridge and Bonn; County Scientific Adviser, Cambridgeshire Fire and Rescue Service; adviser, UK Home Office, risk assessment for the fire service; co-organiser Reebok Foam Conferences 202, 2004, 2007, 2009, 2013, 1St National Foam Forum Adelaide Australia 2011; input to McKinsey Report on 9/11 disaster 2001; expert advice on firefighting foams and their environmental impact nationally and internationally especially in Australia; technical adviser to the Victorian Parliamentary Select Committee Inquiry into the CA Fiskville contamination; involved in an advisory role in the development of the Queensland foam management policy 2016; affiliated research faculty, John Jay College of Criminal Justice, City University New York (CUNY); chartered chemist CChem, chartered scientist CSci; Fellow Royal Society of Chemistry; Fellow International Union of Pure & Applied Chemistry (IUPAC).

JG (Gary) McDOWALL

3FFF Limited, Corby UK, Gary entered the industry in 1987 as the Works Engineer for the John Kerr Company based on Merseyside, which was then acquired by Croda at the end of the same year and became known as Croda Kerr. During his 12 years with Croda Kerr he was responsible for overseeing the capital investment of over £3M on this site including the transfer and development of the Monnex operation from ICI to Croda and redevelopment of the foam manufacturing facility. Working his way through management to become the Divisional Manager for Foams and Monnex dry powder and travelled extensively through the USA, Asia and Europe promoting new initiative firefighting products before forming a number of his own fire chemical related businesses including 3FFF Limited which was then formed in 2005.

During his 32 years in the industry he experienced the increased use and socio-economic impact of the fluorine chemistry used in firefighting foams and other fire protection related products and the subsequent need for change to more sustainable options. Since the turn of the century the science is has become much more understood and the legislation to inhibit the use of these materials around the world is on the increase. The company 3FFF Limited and its products under the brand known as '3F' was formed for this purpose, to innovate and develop new alternatives for the end user. These new and innovative products, some of which are both fluorine-free and solvent-free are now being approved to international standards and extensively used for many industry applications of foam. These applications also now include hand-held portable extinguishers as well as fixed fire systems, which are Gary's particular area of expertise and knowledge.

In addition to his company Directorships of four firefighting chemical businesses, he was one of the founding Directors of IAFPA (International Aviation Fire Protection Association) and currently the Chairman of the British Fire Consortium (BFC) which is one of the three main fire industry trade associations in the United Kingdom.
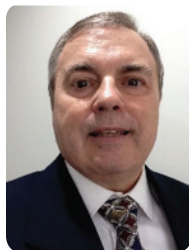
Ted SCHAEFER

Foam formulation chemist with more than 30 years of experience, formerly of the 3M Company and Solberg Asia-Pacific (General Manager) centred in St Marys Sydney Australia; developer of the first Class B fluorine-free firefighting foams (re-healing foams or RHF™) in the early 2000s whilst at 3M; also developed Class A FireBrake™ for wildland fires, considered to be one of the most important Australian inventions in the last hundred years; University of Waterloo 1980; 3M Canada Inc. as chemist AFFF firefighting foam; early 1980's worked AFFF technology; PFOS-based fluorosurfactants key additive for Class B foams; training foam with rapid and safe burn back allowing fire fighters more training opportunities; currently the Australian Defence Force (ADF), Royal Australian Navy, Royal Australian Air Force and the civilian Australian airports (Airservices Australia) use

training foam developed by THS; 1989 3M Australia to continue work on wildfire fighting foam technology; used during the largest wildfires in Australia since the early 1990s and on large bushfires in Queensland 2013; July 2001 the Australian Academy of Technological Sciences and Engineering and the Sydney Powerhouse Museum recognized FireBrake™ (a Class A foam) as one of the top 100 Australian inventions of the 20th Century; in 2000, THS investigated the feasibility of eliminating fluorochemicals from Class B firefighting foam culminating six years later in two World Patents for fluorine-free Class B foams (2003, 2006); currently seven fluorochemical-free flammable liquid firefighting foams have been based on these patents meeting global standards including ICAO, EN, UL, and LASTFIRE; he is also involved in collaborative research with the US NRL Department of the Navy; when still at Solberg October 2014 US EPA Presidential Green Chemistry Challenge Award for Re-Healing Foam for Effective Halogen-Free Firefighting; retiring in 2015, he is now consults for the Australian fire protection industry.

Michael TISBURY

Commander Mick Tisbury AFSM has been an MFB professional firefighter for almost 30 years; he is the spokesperson on PFAS for the United Firefighters' Union Australia which is a founding partner for the Global Alliance of Firefighting Unions, International Association of Fire Fighters; currently Project Coordinator MFB Firefighters PFAS Health study; Metropolitan Fire Brigade (MFB) Melbourne 1989; 29 years as an operational firefighter, training instructor and senior fire officer; development of training performance standards and a safety culture within the training environment; research into PFAS exposure for firefighters has led to the development of Operational PFAS Threshold Limits and best practice PFAS decontamination processes for firefighting appliances and equipment; commissioning a PFAS Blood Reduction Study of Firefighters; Vice President of the United Firefighters' Union; Commander Metropolitan Fire Brigade Melbourne;. Advanced Diploma of Public Safety (Firefighting Management); MFB Executive Officer Commendation; Australian National Service Medal; MFB Long Service and Good Conduct Medal; National Emergency Medal for 2009 Black Saturday bushfires in Victoria; Australian Fire Services Medal (AFSM) 2019.

Kevan WHITEHEAD

Kevan Whitehead has been directly involved in the Fire Industry for over 40 years as an operational Fire Officer and more recently as the Managing Director of a specialist Fire & Rescue company. He joined Greater Manchester County Fire Service in 1978 as a Firefighter. Greater Manchester was arguably the busiest Brigade in the UK at the time, each firefighter responding on a pro rata basis to more incidents than any other Brigade in the UK. He was exposed to a wide variety of incident types varying from city centre urban environments, large Industrial sites, high speed/heavy volume motorways, docklands, major international airport and rural/moorland scenarios. The Brigade boasted 41 Fire Stations and over 2700 personnel. He quickly rose through the ranks specialising as a Fire Safety Inspecting Officer, Incident Command Trainer, and Senior Technical Officer responsible for R&D, Specification and Procurement of firefighting PPE, equipment, foams and vehicles.

He has co-organised and managed multiple international conferences on the environmental impact of Firefighting Foams, these events becoming the centre of excellence for those personnel involved in firefighting foam, be they manufacturers, end users, regulators or academics. He has also focused on firefighting PPE and was a specialist advisor to a UK Government Department on the Integrated Clothing project.

Kevan studied at the University of Bolton in the UK, achieving an MBA with a dissertation relating to marketing. During his employment, he attended TEEX in the USA to study LNG Firefighting techniques. He has delivered training to international students in Libya and Sri Lanka, and has also operated in Iraq and Kurdistan.

In 2010, Kevan joined a Fire Training Academy in the Sultanate of Oman, before forming his own Company, Unity Fire and Safety Services LLC also in Oman in 2011. The company has developed four main work streams, these being Fire Service manpower, equipment, training and consultancy. Past and present clients include BP, Shell, Petrochina, Gazprom, Lukoil and Vale. The company currently employs over 60 personnel, the vast majority being professional firefighters and fire engineers.

ملخص تفصيلي

يعد حمض بيرفلوروهيكسا السلفونيك (PFHxS, CAS 355-46-4) ثابتاً بشدة من الناحية البيئية، ويُظهر قدرة على الانتقال بعيد المدى. كما إنه يتراكم بيولوجياً في الإنسان على نحوٍ أعلى ويشكل تهديداً أكبر بالمقارنة مع حمض بيرفلوروأوكتان السلفونيك (PFOS). كما إنه يمتلك خصائص ثابتة ومتراكمة بيولوجياً وسامة غير مقبولة على غرار PFOS وPFOA، وهما مادتان مدرجتان في اتفاقية ستوكهولم. فبمقارنته مع PFOS وPFOA، فإن PFHxS أكثر انحلالاً في الماء وأكثر انتقالاً في البيئة وأقل امتزازاً بالنسبة إلى التربة والرواسب والرواسب ولديه نصف عمر للإزالة لدى البشر أطول بكثير – بما يعادل ضعف نصف عمر PFOS.

وبسبب الخصائص الفيزيائية والكيميائية لـ PFHxS تكون قدرته على التنقل، وبالتالي عمود التلوث الخاص به، أكبر بشكل عام من قرينه الوثيق PFOS. كما تجعل خصائص PFHxS من الصعب للغاية أن تتم إزالته من مياه الشرب باستخدام الطرق القياسية حيث يتخلل وسائط التصفية بسهولة بسبب سوء امتصاص الكربون النشط له، وخاصة بوجود منافسة من ملوثات أخرى.

علاوة على ذلك، يمر PFHxS عبر عمليات معالجة مياه الصرف الصحي دون أي عائق يذكر، وينجم عن ذلك تلوث الحمأة الحيوية والنفايات السائلة بـ PFHxS (وغيره من مواد PFAS)، اللتان يمكن أن تدخلا إلى السلسلة الغذائية عند استخدامهما لأغراض زراعية. كما تعد النفايات السائلة الناجمة عن مياه الصرف الصحي والتي تحتوي على PFHxS مصدراً هاماً لتلوث المجاري المائية والمياه الجوفية حيث يتابع مسيرته ضمن البيئة المائية.

تؤدي المواقع الملوثة بنفايات PFAS التي تحتوي على أحماض بيرفلوروالألكي السلفونيك مثل PFOS وPFHxS وPFBS الخ.. من رغاوى إطفاء الحريق وعمليات التصنيع أو معالجة الأنسجة بـ PFAS إلى تلوث المياه الجوفية ومياه الشرب من خلال التسرب داخل التربة بشكل رئيسي. وهذا هو الحال خاصة بالنسبة إلى PFHxS وذلك من خلال قدرته العالية على التنقل وآليات التجزئة الهيدروجيولوجية، بالإضافة إلى تعزيز قدرته على التنقل والتي تحصل بسبب إزاحة PFHxS من مصفوفات التربة بواسطة PFAS ذات السلسلة الأطول والموجودة في الطبقات العليا. وتكون النتيجة عبارة عن مياه جوفية تحتوي على نسبة أعلى من PFHxS بالنسبة إلى غيره من PFAS وذلك بالمقارنة مع ما يحصل في مصدر التلوث الأصلي.

يعد تلوث إمدادات مياه الشرب بـ PFHxS قضية أساسية. فمع أن PFHxS يعد مركباً من مركبات الكربون ستة (C6)ولديه نفس سلوك PFAS قصيرة

السلسلة من الناحية الفيزيائية والكيميائية، إلا أنه وبالنظر إلى مخاطر الثبات والتراكم البيولوجي والسمية يتم تصنيفه مع PFAS طويلة السلسلة (أحماض بيرفلورالألكي السلفونيك C6 ≥). لو كان هناك حدود تنظيمية لمياه الشرب، لكانت مماثلة لتلك الخاصة بـ PFOS.

يمثل استمرار تصنيع بيرفلوروأوكتان السلفونيك فلوريد PFOSF باستخدام عملية سيمونز للفلورة الإلكتروكيميائية (ECF) في آسياً والاستخدام الزراعي لمبيد الحشرات sulfluramid في كل من آسيا وأمريكا اللاتينية مصدرين هامين جداً للتلوث البيئي المباشر بـ PFHxS بالإضافة إلى PFOS وطلائعه.

تعد عملية الفلورة الإلكتروكيميائية المتبعة لإنتاج المادة الطليعية PFOSF عملية تركيب اصطناعي 'قذرة' بشكل أساسي وينتج عنها مواد ثانوية غير مقصودة بما في ذلك كل من PFHxS وPFOA بمستوى 10%. ينتقل هذا التلوث إلى N-ethyl-perfluorooctane sulfonamide (N-ethyl-PFOSA) المستخدم في مبيد الحشرات sulfluramid.

سيؤدي الاستخدام المستمر لـ PFHxS في طعوم sulfluramid للحشرات ورغاوى مكافحة الحريق والمواد المقاومة للماء ومعالجة الأنسجة، بعد أن حلّ محل PFOS، إلى تلوث مستمر للبيئة المائية، حيث سيدخل PFHxS إلى إمدادات مياه الشرب والسلسلة الغذائية.

يقتصر استخدام sulfluramid على استخدامه كمبيد حشرات/طعم للأغراض الزراعية وفقاً لاتفاقية ستوكهولم، ولكن استخدامه المنزلي لمكافحة الصراصير والنمل الأبيض منتشر على نطاق واسع في الصين والبرازيل وبعض بلدان أمريكا اللاتينية الأخرى. حظرت الصين إنتاج sulfluramid في آذار/مارس من عام 2019 وسيتم حظر كافة استخداماته بحلول 2020.

بالنسبة إلى الأشخاص الذين يتعرضون لهذه المادة بسبب طبيعة عملهم مثل رجال الإطفاء الذين يستخدمون رغوة PFAS فهناك أدلة قاطعة بأن العديد منهم لديهم مستويات عالية وغير مقبولة من PFHxS وPFOS في الدم، حيث يثير PFHxS القلق على نحو أكبر بالمقارنة مع PFOS وذلك بسبب نصف عمر الإزالة الأطول الذي يمتلكه البشر لدى يمتلكه.

تجعل علاقات الإنتاج المشترك والتلوث المشترك فيما بين مواد الـ PFAS التي يتم إنتاجها بواسطة الفلورة الإلكتروكيميائية والتي لا يمكن تفاديها من البديهي بشكل متزايد بأنه من غير المعقول أو المقبول النظر في مواد PFAS بشكل إفرادي ومنعزل كجزء من عملية تنظيمية. يجب أن يتم النظر في فئات

أو مجموعات المركبات المترابطة، كما هو موضّح في المثال الحالي للعلاقة الوثيقة بين PFHxS وPFOS وPFOA الناجمة عن عمليات التصنيع بواسطة الفلورة الإلكتروكيميائية التي لا تزال قيد الاستخدام، كما تتضح أيضاً من خلال التواجد وثيق الصلة في دم العمال الذين يتعرضون لهذه المواد. وقد تم الإقرار بالحاجة إلى مقاربة تستند إلى الفئة أو الصنف الكيميائي من قبل Patlewicz *et al* (2019).

حصل توسع سريع في المعرفة المرتبطة بتشابه سلوك ونطاق التأثير الضار لمواد PFAS، بما في ذلك PFHxS، فيما يخص القيم الاجتماعية-الاقتصادية والصحية والبيئية. وهذا مثال جليّ عن الحالات التي يجب فيها تطبيق المبدأ التحوطي، كما هو مطلوب بموجب القوانين البيئية الدولية والمحلية، فيما يخص القيود العالمية العاجلة على الإنتاج المباشر وغير المباشر لـ PFHxS واستخدامه وانبعاثه وغيره من مواد PFAS ذات الصلة.

حمض بيرفلوروهيكسا السلفونيك PFHxS

- **قابل للانتشار والتنقل على نحو كبير في التربة والمياه الجوفية على المستوى العالمي**

- **تعد عملية معالجته في التربة أو المياه صعبة للغاية**

- **يشكل خطراً على مياه الشرب وإزالته مكلفة وصعبة**

- **تؤدي التجزئة الهيدروجيولوجية إلى تخصيبه في المياه الجوفية**

- **يتواجد في/ينبعث باستمرار من العديد من المنتجات الاستهلاكية والصناعية**

- **يستخدم على نحو انتشاري في رغاوى مكافحة الحرائق وانبعاثات من النفايات**

- **ملوِّث رئيسي لـ PFOSF وPFOS وN-ethyl-FOSA وطعوم sulfluramid**

- **لا يمكن تفادي إنتاجه كجزء من عملية سيمونز للفلورة الإلكتروكيميائية**

- **يمتلك نصف عمر طويل لدى البشر بالمقارنة مع PFOS، خصائص الثبات والتراكم البيولوجي والسمية غير مقبولة**

- **يعتبر عضواً في فئة كيميائية سامة – أحماض بيرفلورالألكلي السلفونيك**

- **لا ينبغي أن يتم السماح بأغراض مقبولة أو إعفاءات محددة**

- **يحفّز المبدأ التحوطي ويفشل في جميع عوامل التقييم.**

摘要

全氟己烷磺酸（PFHxS，CAS 355-46-4）在环境中具有极强的持久性，能够远距离迁移，在人体中比全氟辛烷磺酸（PFOS）更具生物累积性和危害性，存在于一般人群和职业暴露群体中，并且和《斯德哥尔摩公约》已列出的全氟辛烷磺酸和全氟辛酸（PFOA）这两种物质一样，具有不可接受的持久性生物累积毒性（PBT）特征。与全氟辛烷磺酸或全氟辛酸相比，全氟己烷磺酸更具水溶性，在环境中的迁移能力更强，对土壤和沉积物的吸附性更低，并且在人体中的消除半衰期长得多，大约是全氟辛烷磺酸的两倍。

全氟己烷磺酸的物理化学性质导致其迁移性及相应的污染羽流程度通常高于其近亲全氟辛烷磺酸。全氟己烷磺酸的特性也使得难以用标准方法从饮用水中去除它，因为它很难被活性炭吸收，因而很容易穿透过滤介质，尤其是在与共污染物竞争的情况下。

此外，全氟己烷磺酸在很大程度上可不受阻碍地通过废水处理流程，导致该种物质（和其它全氟/多氟烷基化合物（PFAS））污染生物污泥和污水，然后当用于农业目的时可以进入食物链。含有全氟己烷磺酸的废水也是水道和地下水污染的重要来源，这是因为它通过水生环境进一步循环。

一些场地会被消防泡沫、制造工艺或全氟/多氟烷基化合物纺织品处理作业带来的含有全氟烷基磺酸（例如全氟辛烷磺酸、全氟己烷磺酸、全氟丁烷磺酸（PFBS）等）的全氟/多氟烷基化合物废弃物污染，进而引起地下水和饮用水污染，后一种污染主要是通过土壤渗透形成的。全氟己烷磺酸尤其如此，原因在于其更强的迁移性、水文地质分离机制，以及由上层的较长链全氟/多氟烷基化合物从土壤基质中将全氟己烷磺酸挤出所致的迁移性的进一步提高。结果是地下水中的全氟己烷磺酸相对于其它全氟/多氟烷基化合物的比例远高于原始污染源中的情形。

全氟己烷磺酸污染饮用水是一个大问题。尽管全氟己烷磺酸是一种C6化合物，其物理化学性质类似于短链全氟/多氟烷基化合物，但就其持久性生物累积毒性风险特征而言，它与长链全氟/多氟烷基化合物（全氟烷基磺酸≥C6）在同一组。如果存在饮用水监管限制，则它们与全氟辛烷磺酸相当。

亚洲使用Simons电化学氟化（ECF）法继续生产全氟辛基磺酰氟（PFOSF），并且亚洲和拉丁美洲将杀虫剂氟虫胺用于农业，二者是全氟己烷磺酸和全氟辛烷磺酸及后者的前体直接污染环境的重要起因。

用于生产全氟辛基磺酰氟这种前体的电化学氟化法基本是一种"肮脏"的工业合成，导致产生包括全氟己烷磺酸和全氟辛酸在内的非预期副产物，其含量约为10%。这种污染一直延续到杀虫剂氟虫胺中使用的N-乙基-全氟辛基磺酰胺（N-ethyl-PFOSA）。

全氟己烷磺酸今后对水环境的持续污染，以及对饮用水供应和食物链的影响，将是因为它被继续用于氟虫胺昆虫诱饵、消防泡沫、防水剂和纺织品处理作业，它在这些领域已经取代全氟辛烷磺酸。

根据《斯德哥尔摩公约》，氟虫胺仅限于用作农业杀虫剂/诱饵，但中国、巴西和拉丁美洲其它国家还广泛用它来杀灭家中的蟑螂和白蚁。中国于2019年3月禁止生产氟虫胺，并将从2020年1月起禁止其所有用途。

对于职业暴露群体，例如使用全氟/多氟烷基化合物泡沫的消防员，已经有明确的证据显示，许多人血液中的全氟己烷磺酸和全氟辛烷磺酸含量升高幅度达到了无法接受的地步，并与其职业相关，而且由于全氟己烷磺酸在人体内的消除半衰期要长得多，因此可能比全氟辛烷磺酸更令人担忧。

电化学氟化法生产的全氟/多氟烷基化合物之间不可避免的共生产和共污染关系引出了一个日益明显的结论：将个别全氟/多氟烷基化合物作为监管过程的一部分来单独考虑是不明智或不充分的。应考虑相关化合物的类别或组，这一点已通过仍在使用的电化学氟化制造工艺所生产的全氟己烷磺酸、全氟辛烷磺酸和全氟辛酸之间的密切关系这一当前实例得到凸显，并通过它们在职业暴露工人血液中的紧密共存得到进一步证明。Patlewicz等人（2019年）已经认识到需要基于类别或基于化学类别的方法。

关于全氟/多氟烷基化合物（包括全氟己烷磺酸）的行为及其对社会经济、健康和环境价值的不良影响方面的相似性，相关知识正迅速增长。这个极其重要的例子表明：国际和地方环境法所要求的预防原则必须被用于全氟己烷磺酸和其它相关全氟/多氟烷基化合物的直接和间接生产、使用和释放方面的全球紧急限制措施。

全氟己烷磺酸

- 在全球土壤和地下水中具有高度分散性和迁移性。

- 极难在土壤和水中补救。

- 对饮用水构成威胁，清除代价高昂且困难。

- 水文地质分离机制导致其在地下水中富集。

- 持续存在，并不断从各种消费品和工业产品中释放。

- 不断随消防泡沫的使用而扩散，并从废弃物中释放。

- 是全氟辛基磺酰氟、全氟辛烷磺酸、N-乙基-全氟辛基磺酰胺和氟虫胺诱饵的重要污染物。

- 作为Simons电化学氟化法的一部分，不可避免被生产出来。

- 与全氟辛烷磺酸相比，人体内的半衰期长，具有不可接受的持久性生物累积毒性特征。

- 被视为全氟烷基磺酸这一有毒化学物质类别的成员。

- 不应允许任何可接受用途或特定豁免。.

EXECUTIVE SUMMARY

Perfluorohexane sulfonic acid (PFHxS, CAS 355-46-4) is environmentally extremely persistent, exhibits long-range transport, it is more bio-accumulative and hazardous in humans than PFOS and is present in both the general population and in occupationally exposed groups, as well as having an unacceptable PBT profile like PFOS and PFOA two substances already listed in the Stockholm Convention. In comparison to PFOS or PFOA, PFHxS is more water-soluble, more environmentally mobile, less adsorbable to soils and sediments, and has a far longer elimination half-life in humans, about double that of PFOS.

Because of the physicochemical properties of PFHxS, its mobility and therefore the extent of its contamination plumes are generally greater than for its close relative, PFOS. PFHxS' properties also make it very difficult to remove from drinking water with standard methods as it breaks through filter media readily due to poor absorption on activated carbon, especially in the presence of competition from co-contaminants.

Moreover, PFHxS passes through wastewater treatment processes largely unhindered resulting in PFHxS (along with other PFAS substances) contamination of bio-sludge and effluent, which can then enter the food chain when used for agricultural purposes. Wastewater effluent containing PFHxS is also a significant source of contamination of waterways and groundwater as it further cycles through the aquatic environment.

Sites polluted by PFAS waste containing perfluoroalkyl sulfonic acids, e.g., PFOS, PFHxS, PFBS, etc., from firefighting foams, manufacturing processes, or PFAS textile treatment, give rise to contamination of groundwater and drinking water mainly by infiltration through the soils. This is especially the case for PFHxS through its greater mobility and the mechanisms of hydrogeological fractionation, plus promotion of its mobility that occurs because of displacement of PFHxS from soil matrixes by longer-chain PFAS in the upper layers. The result is groundwater that has a much higher proportion of PFHxS versus other PFAS than occurs in the original contaminant source.

PFHxS contamination of drinking water supplies is a major issue. Although PFHxS is a C6 compound and behaves physicochemically like a short-chain PFAS, in terms of its risk (PBT) profile it is grouped with long-chain PFAS (per-fluoroalkyl sulfonic acids rC6). If regulatory drinking water limits exist, they are comparable to those for PFOS.

Continued manufacture of perfluorooctane sulfonyl fluoride PFOSF using the Simons electrochemical fluorination (ECF) process in Asia and the agricultural application of the insecticide sulfluramid in both Asia and Latin America represent very significant sources of direct environmental contamination by PFHxS as well as PFOS and its precursors.

The ECF process used to produce the precursor, PFOSF, is a fundamentally 'dirty' industrial synthesis that results in the generation of unintended by-products including both PFHxS and PFOA at about the 10% level. This contamination is carried through to the N-ethyl-perfluorooctane sulfonamide (N-ethyl-PFOSA) used in sulfluramid insecticide.

Ongoing contamination of the aqueous environment, impacting drinking water supplies and the food chain by PFHxS will result from its continued use in sulfluramid insect baits, firefighting foam, waterproofing agents and textile treatments where it has replaced PFOS.

Sulfluramid is limited to use as an agricultural insecticide/bait under the Stockholm Convention, however its domestic use has also been widespread against cockroaches and termites in China, Brazil and other countries in Latin America. China banned sulfluramid production in March 2019 and all uses will be prohibited as of January 2020.

For occupationally exposed groups such as firefighters using PFAS foam there is already unequivocal evidence that many have unacceptably elevated and related blood levels of both PFHxS and PFOS with PFHxS potentially of greater concern than PFOS given its much longer elimination half-life in humans.

The unavoidable co-production and co-contamination relationships amongst PFAS produced by the ECF method makes it increasingly apparent that it is not sensible or adequate to consider individual PFAS chemicals in isolation as part of the regulatory process. Classes or groups of correlated compounds should be considered, as highlighted by the present example of the close relationship between PFHxS, PFOS and PFOA resulting from the ECF manufacturing process still in use and further demonstrated by the close co-occurrence in the blood of occupationally exposed workers. The need for a category-based or chemical class-based approach has been recognised by Patlewicz *et al* (2019).

There has been a rapid growth of knowledge about the similarities in behaviours and range of adverse effects of PFAS, including PFHxS, on socio-economic, health and environmental values. This is a prime example of where the Precautionary Principle, as required under international and local environmental law, must be applied in terms of urgent global restrictions on the direct and indirect production, use and release of PFHxS and other related PFAS.

PFHxS

- Highly dispersive and mobile in soils and groundwater globally.
- Extremely difficult to remediate in soils and water.
- A threat to drinking water and expensive and difficult to remove.
- Hydrogeological fractionation resulting in enrichment in groundwater.
- Ongoing presence/releases from a diversity of consumer and industrial products.
- Ongoing dispersive use in firefighting foam and releases from wastes.
- A significant contaminant of PFOSF, PFOS, N-ethyl-FOSA and Sulfluramid baits.
- Unavoidable production as part of Simons electrochemical fluorination (ECF).
- Long half-life in humans compared to PFOS, unacceptable PBT profile.
- Considered as a member of a toxic chemical class – perfluoroalkyl sulfonic acids.
- There should be no acceptable purposes or specific exemptions allowed.
- Triggers the Precautionary Principle and fails all the assessment factors.

SOMMAIRE

L'Acide Perfluorohexane sulfonique (PFHxS, CAS 355-46-4) est extrêmement persistant dans l'environnement, est transporté sur de longues distances, est présent à la fois dans la population générale et certains groupes professionnels exposés, ; de plus, il présente un profil PBT inacceptable, tout comme le PFOS et le PFOA déjà inscrits dans la Convention de Stockholm. En comparaison avec le PFOS ou le PFOA, le PFHxS est plus soluble dans l'eau, plus mobile dans l'environnement, moins adsorbable dans le sol ou les sédiments, et a un temps d'élimination de demi-vie plus long chez l'être humain, environ le double que pour le PFOS

En raison des propriétés physicochimiques du PFHxS, et de sa mobilité, l'étendue de sa contamination est bien supérieure à celle de son proche homologue le PFOS. Les propriétés du PFHxS le rendent très difficile à éliminer de l'eau potable par des méthodes traditionnelles car il passe à travers les filtres à cause de sa faible absorption sur le charbon actif, en particulier en présence d'autres contaminants associés.

De plus, PFHxS franchit les procédés de traitement d'eaux usées pratiquement sans être éliminé, ce qui entraine -avec d'autres substances PFAS- la contamination des effluents et des boues d'épuration, qui peuvent à leur tour contaminer la chaine alimentaire quand elles sont utilisées en fertilisants pour l'agriculture. Les eaux traitées contenant du PFHxS polluent de façon notable les rivières et les eaux souterraines car elles rentrent dans le cycle de l'environnement aquatique.

Les sites pollués par les effluents contenant des PFAS – Acides perfluoroalkyl sulfoniques, ex: PFOS, PFHxS, PFBS, etc...,- provenant des émulseurs anti-incendie, des procédés de fabrication, de traitements textiles, amènent la contamination des eaux souterraines et de l'eau potable par l'infiltration dans les sols. C'est plus spécifiquement le cas du PFHxS de par son extrême mobilité et les mécanismes de fractionnement hydrogéologique qui déplacent le PFHxS du sol, remplacé par les PFAS à longue chaine dans les couches supérieures du sol. Il en résulte que les eaux souterraines ont une proportion largement supérieure de PFHxS à celle d'autres PFAS présents dans le contaminant d'origine.

La contamination par le PFHxS des sources d'eau potable est un problème majeur. Bien que le PFHxS soit un composé en C6 et se comporte physiquement comme un PFAS à chaine courte, son comportement en termes de profil (PBT) est similaire au groupe des chaines longues PFAS (Acides perfluoroalkyl sulfoniques rC6). Quand il existe une réglementation avec des valeurs limite dans l'eau potable, ces valeurs sont comparables à celles du PFOS.

La production du perfluorooctane sulfonyl fluoride -PFOSF- par le procédé de fluoration électrochimique Simons -ECF- en Asie et l'utilisation en agriculture de l'insecticide Sulfluramide en Asie et en Amérique Latine représentent des sources importantes de contamination directe de PFHxS, de PFOS et de leurs précurseurs dans l'environnement.

Le procédé ECF produisant le précurseur PFOSF est une synthèse industrielle polluante par nature qui génère de façon non intentionnelle une quantité importante d'autres impuretés – PFHxS, PFOA etc... - à hauteur de 10%. Cette contamination est apportée par le N-ethyl-perfluorooctane sulfonamide (N-ethyl-PFOSA) utilisé dans l'insecticide Sulfluramide.

La contamination de l'environnement aquatique, impactant directement l'eau potable et la chaine alimentaire, par le PFHxS provient de son utilisation continue dans les appâts d'insectes au Sulfluramide, dans les émulseurs anti-incendie, dans les agents d'imperméabilisation et dans les traitements textiles là où il a remplacé le PFOS.

Le Sulfluramide est restreint à l'utilisation comme insecticide pour l'agriculture selon la Convention de Stockholm, cependant son emploi domestique est largement répandu contre les termites et les cancrelats, en Chine, au Brésil et d'autres pays d'Amérique Latine. La Chine a interdit la production du Sulfluramide en Mars 2019, et interdit son emploi à partir de Janvier 2020.

Pour certains groupes d'utilisateurs exposés, comme les pompiers utilisant des émulseurs contenant des PFAS, il existe déjà des preuves avérées que leur sang contient des niveaux élevés et inacceptables de PFOS et de PF-HxS, le PFHxS étant plus préoccupant que le PFOS de par son temps d'élimination bien plus long chez l'être humain.

L'inévitable relation entre la production et la contamination du PFAS par le procédé ECF montre clairement qu'il n'est pas possible de considérer individuellement chaque composé chimique PFAS dans un processus de contrôle réglementaire. Des classes ou groups de produits associés devraient être définis, ainsi qu'il est démontré dans l'exemple actuel de la relation entre PFHxS, PFOS et PFOA produits par le procédé ECF toujours utilisé aujourd'hui, et documenté dans les analyses de sang des travailleurs ayant été exposés. Le besoin d'une approche basée sur la définition d'une classe ou catégorie chimique est reconnue dans les travaux de Patlewicz *et al* (2019).

Nous avons désormais une bonne connaissance des similitudes, comportements et effets négatifs des PFAS, et du PFHxS, sur les valeurs socio-économiques, la santé et l'environnement. C'est un exemple parfait du principe de précaution, défini selon les lois environnementales nationales et internationales, ou il doit être appliqué en termes de restrictions urgentes et globales de la production directe et indirecte, de son emploi et des rejets de PFHxS et autres PFAS associés.

PFHxS

- Globalement très dispersif et mobile dans les sols et les eaux souterraines
- Extrêmement difficile à éliminer dans les sols et dans l'eau.
- Une menace pour l'eau potable, difficile et cher à éliminer.
- Le fractionnement hydrogéologique enrichit sa concentration dans les eaux souterraines.
- Rejets constants de par sa présence dans une diversité de produits industriels et ménagers.
- Emploi dispersif dans les émulseurs anti incendie et les effluents.
- Contaminant significatif des PFOSF, PFOS et N-ethyl-FOSA dans les appâts au Sulfluramide.
- Produit inévitable du procédé d'électro fluoration Simons (ECF).
- Temps de demi-vie chez l'homme très long comparé au PFOS, profil PBT inacceptable.
- Considéré comme membre de la classe de produits chimiques toxiques, les acides PerfluoroSulfoniques.
- Il ne devrait pas être permis d'exemption spécifique ou d'utilisation acceptable.
- Justifie le Principe de Précaution et ne répond pas aux facteurs d'évaluation.

ИСПОЛНИТЕЛЬНОЕ РЕЗЮМЕ

Перфторгексансульфоновая кислота (ПФГС, CAS 355-46-4) является исключительно стойкой в окружающей среде, демонстрирует перенос на большие расстояния, является более склонной к биоаккумуляции и более опасной для человека, чем ПФОС, присутствует как в населении, так и в группах, подвергающихся профессиональной экспозиции, а также имеет неприемлемый профиль СБТ, подобно ПФОС и ПФОК, двух веществ, уже включенных в перечень Стокгольмской конвенции. По сравнению с ПФОС или ПФОК, ПФГС лучше растворима в воде, более мобильна в окружающей среде, хуже адсорбируется в почвах и в отложениях и имеет гораздо более длительный период полувыведения для человека, примерно в два раза больше, чем у ПФОС.

Соответственно, в силу физико-химических свойств ПФГС и ее мобильности, степень распространения пятен загрязнения этим веществом, как правило, больше, чем у его близкого родственника - ПФОС. Свойства ПФГС также очень затрудняют ее удаление из питьевой воды стандартными методами, так как она легко проходит через фильтрующие материалы из-за плохой абсорбции на активированном угле, особенно в присутствии конкурирующих с ней одновременно присутствующих загрязнителей.

Кроме того, ПФГС в основном беспрепятственно проходит через процессы очистки сточных вод, что приводит к загрязнению ПФГС (наряду с другими веществами класса ПФАС) активного ила и стоков, которые затем могут попадать в пищевые цепи при использовании в сельскохозяйственных целях. Сточные воды, содержащие ПФГС, также являются значительным источником загрязнения водотоков и грунтовых вод, поскольку она продолжает циркулировать в водной среде.

Участки, загрязненные отходами ПФАС, содержащими перфторалкилсульфоновые кислоты, например, ПФОС, ПФГС, ПФБС и т. д. от используемых для пожаротушения пен, от производственных процессов или от обработки текстиля ПФАС, вызывают загрязнение грунтовых вод и питьевой воды, главным образом, из-за инфильтрации через почвы. Это особенно актуально для ПФГС благодаря ее большей подвижности и механизмам гидрогеологического фракционирования, а также из-за повышения ее мобильности, в результате вытеснения ПФГС из почвенных матриц ПФАС с более длинной цепью в верхних слоях грунта. В результате, в грунтовых водах имеется гораздо большая доля ПФГС по сравнению с другими ПФАС, чем в первоначальном источнике загрязнения.

Загрязнение питьевой воды ПФГС является серьезной проблемой. Хотя ПФГС - это соединение с углеродной цепочкой С6 и ведет себя с физико-химической точки зрения как короткоцепочечная ПФАС, с точки зрения профиля риска (СБТ) ее относят к группе длинноцепочечных ПФАС (перфторалкилсульфокислоты ≥С6). Если существуют нормативно установленные пределы для питьевой воды, то они сопоставимы с таковыми для ПФОС.

Продолжение производства перфтороктансульфонилфторида ПФОСФ с применением процесса электрохимического фторирования Симонса (ЭХФ) в Азии и сельскохозяйственное применение инсектицида сульфурамида как в Азии, так и в Латинской Америке, представляют собой весьма существенные источники прямого загрязнения окружающей среды ПФГС, а также ПФОС и ее прекурсорами.

Процесс ЭХФ, используемый для получения прекурсора (ПФОСФ), является принципиально «грязным» промышленным синтезом, который приводит к непреднамеренному образованию побочных продуктов, включая как ПФГС, так и ПФАС на уровне около 10%. Эти загрязнители переносятся и в N-этил-перфтороктансульфонамид (N-этил-ПФОСА), используемый в инсектициде сульфурамиде.

Продолжающееся загрязнение водной среды, воздействие ПФГС на питьевую воду и на пищевые цепи будет результатом его постоянного использования в сульфурамидных приманках для насекомых, в используемых для пожаротушения пенах, в гидроизолирующих веществах и при обработке текстиля, где ПФГС заменила ПФОС.

В соответствии со Стокгольмской конвенцией установлены ограничения для применения сульфурамида в качестве сельскохозяйственного инсектицида/в приманках, однако он широко применяется в бытовых целях для борьбы с тараканами и термитами в Китае, Бразилии и в других странах Латинской Америки. Китай запретил производство сульфурамида в марте 2019 года, а все виды его применения будут запрещены с января 2020 года.

Для групп с профессиональной экспозицией, таких как пожарные, использующие пену на основе ПФОС, уже есть однозначные доказательства того, что у многих имеются недопустимо повышенные и связанные между собой уровни как ПФГС, так и ПФОС в крови, причем ПФГС, потенциально опаснее ПФОС, учитывая более длительный период ее полувыведения для человека.

Неизбежные взаимоотношения совместного образования и совместного загрязнения между ПФАС, произведенных методом ЭХФ, делают все более очевидным, что нецелесообразно или недостаточно рассматривать отдельные химические вещества класса ПФАС изолированно в процессе регулирования. Следует рассмотреть классы или группы

связанных между собой соединений, как это и отмечается в данном примере тесной взаимосвязи между ПФГС, ПФОС и ПФАС вследствие производственного процесса ЭХФ, который все еще используется, и как на это дополнительно указывает их неразрывное совместное присутствие в крови подвергшихся профессиональной экспозиции работников. Патлевич и др. (2019) признали необходимость подхода, основанного на категориях или на классах химических веществ.

Наблюдается быстрый рост знаний о сходстве в поведении и в диапазоне негативных воздействий ПФАС, включая ПФГС, на социально-экономические, медицинские и экологические показатели. Это яркий пример того, где Принцип предосторожности, как того требует международное и национальное экологическое право, должен применяться с точки зрения срочного введения глобальных ограничений на прямое и косвенное производство, использование и выпуск ПФГС и других связанных с ней ПФАС.

ПФГС

- **Высокая склонность к рассеиванию и мобильность в почвах и грунтовых водах в глобальном масштабе.**

- **Чрезвычайно трудно удалить из почв и воды.**

- **Угроза для питьевой воды, удаление дорогое и сложное.**

- **Гидрогеологическое фракционирование приводит к обогащению подземных вод.**

- **Постоянное присутствие/выделение из разнообразных потребительских и промышленных товаров.**

- **Постоянное рассеянное использование в пенах для пожаротушения и выделение из отходов.**

- **Значительный загрязнитель ПФОСФ, ПФОС, N-этил-ФОСА и сульфурамидных приманок.**

- **Неизбежное образование в процессе электрохимического фторирования Симонса (ЭХФ).**

- **Длительный период полувыведения у человека по сравнению с ПФОС, неприемлемый профиль СБТ.**

- **Рассматривается как представитель класса токсичных химических веществ - перфторалкилсульфоновых кислот.**

- **Не должно быть никаких приемлемых целей или конкретных исключений.**

- **Требует применения принципа предосторожности и не отвечает всем факторам оценки.**

RESUMEN EJECUTIVO

El Ácido Perfluorohexano sulfónico (PFHxS, CAS 355-46-4) es sumamente persistente en el medio ambiente, transportado a largas distancias, esta presente en la población y en los grupos profesionales expuestos, y tiene un perfil PBT inaceptable similar al PFOS y el PFOA, ya inscritos en el Convenio de Estocolmo. En comparación con el PFOS o el PFOA, el PFHxS es mas soluble en el agua, mas móvil en el medio ambiente, menos absorbente en el suelo y los sedimentos, y tiene un tiempo de eliminación de media vida mas largo en el ser humano, aproximadamente del doble que para el PFOS.

Debido a las propiedades fisicoquímicas del PFHxS, y a su movilidad, el nivel de contaminación es muy superior a la de su homologo parecido el PFOS. Las propiedades del PFHxS le resultan muy difícil de eliminar del agua potable por los métodos tradicionales porque pasa a través de los filtros debido a su baja absorción sobre el carbón activo, en particular con la presencia de otros contaminantes asociados.

Además, el PFHxS pasa los procesos de tratamiento de las aguas negras prácticamente sin estar eliminado, lo que provoca la contaminación – con otras sustancias PFAS- de los efluentes y del lodo de depuración, quien puede a su vez contaminar la cadena alimentaria cuando es utilizado como fertilizante para la agricultura. Las aguas tratadas conteniendo PFHxS contaminan de forma importante los ríos y las aguas subterráneas ya que entran en el ciclo del medio ambiente acuático.

Los sitios contaminados por los efluentes conteniendo PFAS – Ácidos perfluoroalkil sulfónicos, ej: PFOS, PFHxS, PFBS, etc…,- provenientes de las espumas contra incendios, de los procesos de fabricación, de los tratamientos de textiles, generan la contaminación de las aguas subterráneas y del agua potable por la infiltración en los suelos. Es mas especifico para el PFHxS por su movilidad muy elevada y por los mecanismos de fraccionamiento hidrogeológico existentes, desplazando el PFHxS del suelo por los PFAS con cadenas largas en los niveles superiores del suelo. Resultando que las aguas subterráneas tienen un porcentaje de PFHxS mucho mas alto que los demás PFAS en comparación con el porcentaje del contaminante de origen.

La contaminación por el PFHxS de las fuentes de agua potable es un problema mayor. Aunque el PFHxS sea un compuesto con C6 y de comportamiento físico idéntico a los PFAS de cadena corta, su funcionamiento en tema de perfil PBT es similar a los del grupo PFAS con cadenas largas (Ácidos perfluoroalkil sulfónicos rC6). Cuando existe una regulación con limites para el agua potable, son comparables con los valores para el PFOS.

La fabricación del Perfluorooctano sulfonil fluoride -PFOSF- por el proceso de fluoración electroquímico Simons -ECF- en Asia y el uso en agricultura del insecticida Sulfluramide en Asia y en América Latina representa una fuente importante de contaminación directa del PFHxS y demás precursores del PFOS en el medio ambiente.

El proceso ECF produciendo el precursor PFOSF es una síntesis industrial muy contaminada por esencia, generando una cantidad no deseada importante de impurezas– PFHxS, PFOA etc… - a un nivel del 10%. Esta contaminación se genera por el N-etil-perfluorooctano sulfonamide (N-etil-PFOSA) utilizado en el insecticida Sulfluramide

La contaminación del medio ambiente acuático impacta directamente el agua potable y la cadena alimentaria, por el PHxS proveniente del uso continuo en los cebos para insectos con Sulfluramide, en las espumas contra incendios, en los agentes impermeabilizantes y en los tratamientos para textiles, donde ha remplazado el PFOS.

El Sulfluramide tiene un limite de uso como un insecticida para la agricultura por debajo del Convenio de Estocolmo, pero su uso doméstico es muy importante contra las termitas y las cucarachas, en China, Brasil y otros países de Latino América. China prohibió la fabricación del Sulfluramide en marzo 2019 y el uso estará prohibido en enero 2020.

Para unos grupos de personas expuestas, como los bomberos utilizando espuma con PFAS, ya existe la evidencia que la sangre contiene niveles elevados e inaceptables de PFHxS y PFOS; el PFHxS siendo mas preocupante que el PFOS por su tiempo de eliminación mucho mas largo en el ser humano.

La relación entre la fabricación y la contaminación de los PFAS por el proceso ECF demuestra claramente que no se puede considerar de modo individual cada compuesto químico en un proceso de regulación. Clases o grupos de productos deberían de ser definidos, como se nota en el ejemplo actual de la relación entre PFHxS, PFOS y PFOA producidos por el proceso ECF todavía utilizado hoy en día, y documentado en los estudios científicos del análisis de sangre de los trabajadores expuestos. La necesidad de contemplar una definición de clase o categoría de químicos se comenta en los estudios de Patlewicz *et al* (2019).

Ya se tiene un buen conocimiento de las similitudes, comportamientos y efectos negativos de los PFAS, y del PFHxS, en los valores socioeconómicos, la salud y el medio ambiente. Es un ejemplo perfecto del principio de precaución, definido según las leyes nacionales e internacionales para

el medio ambiente, donde se debe de aplicar restricciones urgentes y globales para la producción directa e indirecta, el uso y los desechos del PFHxS y de los demás PFAS asociados.

PFHxS

- Globalmente muy disperso y móvil en los suelos y las aguas subterráneas.

- Excesivamente difícil de eliminar en los suelos y las aguas.

- Una amenaza para el agua potable, difícil y económicamente costoso de eliminar.

- El fraccionamiento hidrogeológico enriquece su concentración en las aguas subterráneas.

- Presencia constante debido a su uso en una gran diversidad de productos industriales y domésticos.

- Uso disperso en las espumas contra incendios y los efluentes.

- Contaminante significativo de los PFOSF, PFOS et N-ethyl-FOSA en los cebos con Sulfluramide.

- Producto ineludible en el proceso de electro fluoración Simons (ECF).

- Tiempo de media vida en el ser humano, muy largo en comparación con el PFOS, perfil PBT, lo cual es inaceptable.

- Considerado como miembro de la clase de químicos tóxicos, los ácidos PerfluoroSulfónicos.

- No se debe aceptar una exención especifica o un uso aceptable.

- Se justifica el Principio de precaución y no cumple con los factores de evaluación.

PRELIMINARY REMARKS

PFHxS, PFOS and PFOA have been subject to evaluation by the Stockholm Convention Persistent Organic Pollutants Review Committee (POPRC). Both PFOS and PFOA are now subject to restrictions under the treaty after decisions in 2009 (PFOS) and 2019 (PFOA). Tied to the POPRC and COP discussions is the realisation that all fluorinated organic compounds (PFAS) have the potential for adverse socio-economic, health and environmental effects from their production, use, release and degradation.

Most, if not all, of the considerations of the POPRC for PFOS and PFOA apply equally and even more so to PF-HxS and will ultimately translate to other PFAS as further research is carried out. PFHxS, PFOS, PFOA and thousands of other highly persistent PFAS compounds are inextricably linked in their production, occurrence, behaviour and effects, and so need to be considered holistically in terms of their use and the resultant threats to socio-economic, human health and environmental values.

The overarching arguments applying more generally to PFAS have been, with the exception of those relating specifically to PFHxS and recent findings, reported on in the two previous IPEN White Papers presented at the 14th meeting of the Stockholm Convention POPs Review Committee (POPRC-14) in Rome 17-22 September 2018 and the 9th Conference of the Parties of the Stockholm Convention (SC-COP9) in Geneva 29 April-10 May 2019.

The present White Paper is intended to support and assist the POPRC in their consideration of the draft Risk Management Evaluation (RME) (POPRC, 2019) for PFHxS and PFHxS-related substances (Norway, 2019).

1. INTRODUCTION

Perfluorohexane sulfonate (PFHxS) is prominent amongst long-chain perfluoroalkyl sulfonates (PFSAs) including C7 PFHpS, C8 PFOS, C9 PFNS and C10 PFDS that are of established and growing concern as persistent organic pollutants through their:

- **Wide spread distribution** in the environment, humans and other biota.
- **Potential for long range-transport** in various media.
- **Bioaccumulation potential** at all trophic levels.
- **Long biological/bio-elimination half-lives** in humans.
- **Extreme environmental persistence** in common with all PFAS.
- **Established links to specific diseases** or pathological conditions.

In spite of efforts to stop production of PFOS-based chemicals, including the decision by the 3M Company in May 2000 to phase out manufacture – as well as measures such as the PFOS ban by the EU from June 2011 – some countries are still producing and releasing PFSA chemicals, as evidenced by studies of continuing contamination of local, regional and remote areas including the Arctic

> - **Global contamination of the environment and biota with PFAS including PFHxS is totally anthropogenic with no known natural sources and no degradation pathways.**
> - **Management of PFHxS needs to be considered in conjunction with PFOS and PFHpS as ECF production results in mixtures which are not sufficiently purified before use.**

Long-chain PFAS are classified under two sub-categories by the United States Environmental Protection Agency (USEPA), a definition that is now widely accepted:

- **Long-chain perfluoroalkyl carboxylic acids** (PFCAs) with eight or more carbons (rC8), including perfluorooctane carboxylic acid (C8 PFOA).
- **Long-chain perfluoroalkane sulfonates** (PFSAs) with six or more carbons (rC6), including perfluorohexane sulfonic acid (C6 PFHxS), perfluoroheptane sulfonic acid (C7 PFHpS) and perfluorooctane sulfonic acid (C8 PFOS).
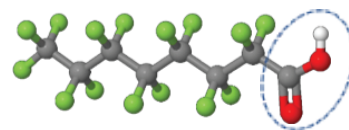
C8 carboxylate PFOA (COOH functional group)
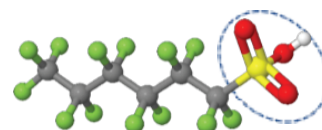
C6 sulfonate PFHxS (SO3H functional group)

Figure 1A illustrates the perfluorinated carbon chains and functional groups (circled) of the primary PFAS endpoint compounds for the *carboxylates* (e.g., PFOA) and the *sulfonates* (e.g., PFHxS). Atoms: grey-carbon, green-fluorine, yellow-sulfur, red-oxygen, white-hydrogen.
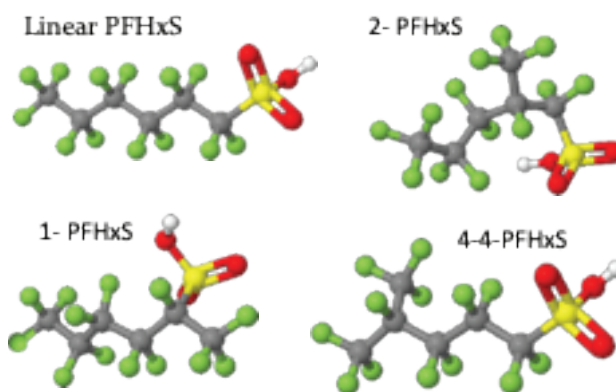

Figure 1B. Isomers of PFHxS.

PFAS substances can cause long-term adverse effects at low concentrations. PFCA chemicals with fewer than eight carbons, such as perfluorohexanoic acid (C6 PFHxA), and PFSA chemicals with fewer than six carbons, such as perfluorobutane sulfonic acid (C4 PFBS) are also very persistent (vP) in the environment. The POPRC Risk Profile on PFHxS notes that PFAS substances are subject to long-range transport but the pathway is dependent on the physiochemical properties and geographical locations of the substance.

The behaviour and effects of the perfluoroalkyl sulfonates PFHxS, PFHpS and PFOS (C6, C7 & C8) need to be con-

sidered as a group, not separately, as the synthetic methods used in their manufacture do not produce clean batches of pure, chemically distinct compounds. The Simons ECF process produces not only PFSA homologues of different odd and even carbon-chain lengths (unlike the fluorotelomer process which produces only even chain-length PFAS) but also an interrelated mixture of straight and branched-chain structural isomers of the same compound (Figure 1B). This is discussed more fully below in Section 4.

It is misleading to assess the properties and risks of single chemicals in such circumstances while ignoring the commercially available technical products. It is especially important for those that are highly mobile and used in dispersive applications. Mixtures of different chain lengths plus various isomers should also be taken into account as part of any risk management evaluation.

Considerable data exist in the literature evidencing widespread environmental contamination as the result of legacy use of perfluoroalkyl substances such as PFOS and PFOA in many industrial and domestic applications, and especially as the result of dispersive use such as firefighting and firefighter training (IPEN, 2018, 2019).

Public awareness of the long-chain PFAS contamination problem dates from the seminal decision, announced on the 16th May 2000, by the 3M Company to phase-out electrochemical fluorination (ECF) manufacture of PFOS-based products used in many applications. This phase-out included 3M Light Water™ and ATC™ AFFF foam concentrates and ScotchGard™ fabric and leather treatments. 3M also withdrew completely from the firefighting foam market (3M Company, 2000). However, the phase out did not include shorter-chain PFSA use.

Early papers in the scientific literature soon established that perfluorinated chemicals, in particular PFOS and PFOA, were found widely distributed on a global scale appearing in the blood, liver and eggs of many species in locations that were far removed from any obvious sources of contamination, such as in the remote polar regions (for example, Kannan *et al*, 2002, Busch *et al*, 2010).

Human blood samples were also found to be widely and generally positive for PFAS substances. In contrast stored human blood bank samples from prior to the industrial manufacture of fluorochemicals post World War II were uniformly free of organofluorine compounds (Taves, 1968a, 1968b).

Perfluoroalkyl substances (PFAS) are extraordinarily persistent in the environment to the extent of being permanent pollutants, exhibiting long-range oceanic and atmospheric transport over thousands of kilometres, contaminating a wide range of biota and bodies of water, with no known environmental degradation pathways for their perfluorinated end-point products.

At least 90 sites across Australia are under investigation for elevated levels of p fluoroalkyl [PFAS] chemicals.
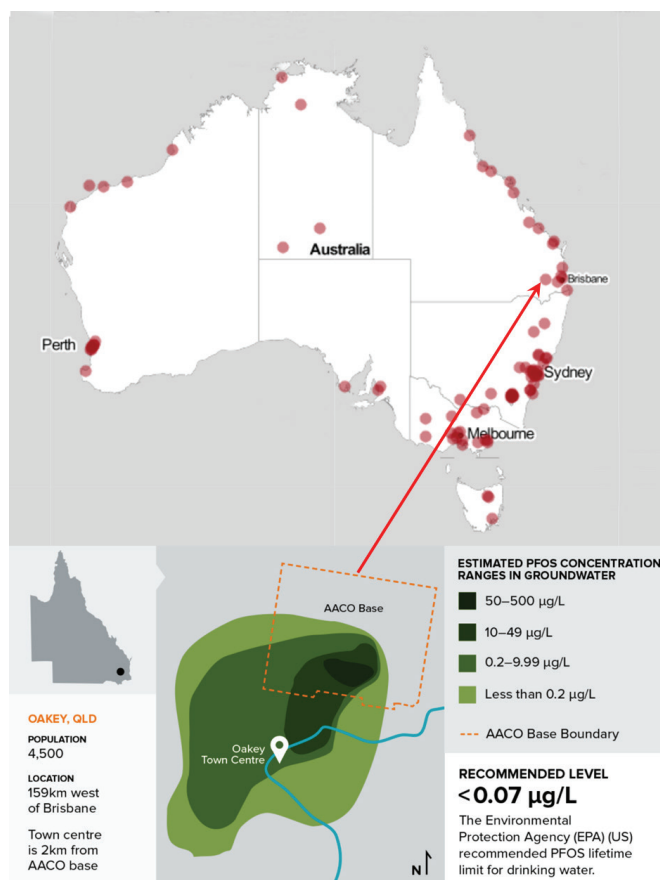

Figure 1C. Australia, Oakey Army Aviation Centre PFOS contamination plume.

It was soon established that the uncontained use of AFFF firefighting foams, especially when used unconfined for training, resulted in very high levels of groundwater contamination. Historically, the use of foams containing PFOS and PFOA has led to substantial groundwater contamination. However, more modern fluorotelomer firefighting foams have also resulted in elevated PFAS levels in the water table, for example, with the 8:2 and 6:2 fluorotelomer sulfonate (8:2 and 6:2FtS) and their precursors.

Former and current military fire training areas were shown to constitute a major source of environmental pollution giving rise to very large contaminant plumes downstream hydrologically. Civilian aviation firefighting (ARFF) training areas, although often smaller, were also sources of substantial PFAS releases into the environment. Both these military and civilian fire-training areas are characterised by intensive regular use over long periods.

Of the 90 PFAS-contaminated sites so far identified in Australia (Figure 1C) the Australian Defence Force (ADF) Army Aviation Centre at Oakey in Queensland is an example of widespread pollution with a substantial hydrologi-

cal down-gradient PFAS contaminant plume. As for many other sites this has affected water supplies for both the township as well as surrounding farming areas (Australian Government Foreign Affairs, Defence and Trade References Committee, 2016).

At Oakey in Queensland, it was estimated that approximately 1.43 million litres of mostly PFOS-based AFFF concentrate was used over a 25-year period. Effectively 1000 litres of AFFF concentrate per week had been discharged to soils and groundwater for a quarter of a century!

This rate of use equates to the release of 10-20 kilograms of PFAS every week for 25 years directly to the soils, ultimately infiltrating down to the underlying water table.

The extent of the PFAS pollution at Oakey Army Aviation Centre has led to a large kilometre-scale contaminant plume downstream resulting in:

• Degradation of the township of Oakey's drinking and irrigation water supply.

• Contamination of watercourses and biota.

• Loss of livelihoods and agricultural output.

• Depression of property prices and the inability to sell properties.

• Widespread public concern over the health effects of the contamination on those living in the area, with elevated blood levels for residents detected in many cases.

The PFHxS content of a sample of PFOS foam from Oakey was about 16% or one-sixth (Figure 1D); the PFHxS contamination plume can be expected to be significant and well beyond the extent of the PFOS plume in Figure 1C.

The scenario in Oakey has become an example of what can typically happen with the uncontrolled release of PFAS to the environment. This has been mirrored many times over at US and Australian military bases and airports as well as at civilian airports elsewhere including in Europe.

In addition to poorly managed releases from training and spills, major incidents can result in large volumes of PFAS contaminated firewater running to tens of millions of litres being released to the environment, as occurred at incidents including:

• Sandoz Schweizerhalle Basel chemical and pesticide fire in 1986 contaminating the Rhine (Switzerland).

• Coode Island acrylonitrile and benzene tank fire (Victoria, Australia) in 1991.

• Buncefield petrochemical explosion and fire (UK) in 2005.

Incidents like these are relatively infrequent but nonetheless have long-term, large-scale effects on environmental values, wildlife, groundwater quality, drinking water supplies, and public health, and hence class as being of very high risk.

At the Buncefield incident the loss of containment of the large volume of PFOS and PFHxS-containing firewater was caused by bund wall failures and subsoil clay layer penetration resulting in PFAS contamination of an aquifer supplying north London with drinking water that will remain unusable for many years to come (UK HSE COMAH, 2011; Gable, 2017).
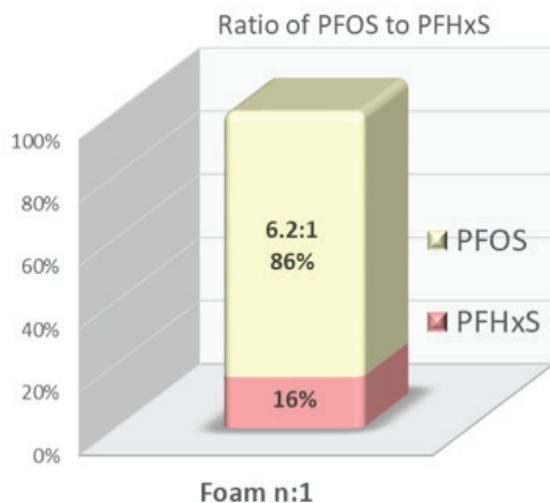

Figure 1D. PFHxS content of Oakey PFOS foam (after Defence/AECOM, 2015).

2. PFHxS IS A SUBSTANCE OF VERY HIGH CONCERN (SVHC)

The scientific literature to date has been focussed mainly on PFOS and PFOA, while PFHxS has been largely over-shadowed. However, striking similarities to PFOS and other PFSAs in persistence, toxicity and behaviour are evident in what has been published and research that is now emerging.

In 2017, PFHxS and its salts were identified as Substances of Very High Concern (SVHC) and added to the EU REACH Candidate List due to their persistent and bio-accumulative properties (ECHA, 2017). Toxicity and ecotoxicity were not subject to evaluation as PFHxS fulfilled the criteria for a very persistent and very bio-accumulative (vPvB) substance. The criteria for classification of a substance as vPvB are almost identical in the EU and USA; vPvB substances must be declared in the Safety Data Sheet when present at >=0.1%.

Regrettable substitution, as has occurred for PFOS by the use of PFHxS for some products, has been defined as occurring:

> *"when a toxic chemical is replaced by another chemical that later proved unsuitable because it, too, turned out to be a persistent, bio-accumulative and toxic (PBT) substance, or because of other concern"* (US National Research Council, p.10 para 3, 2014)

This has also been termed a *"regret spend"* or *"regrettable investment"* by industry in reference to poorly-considered short-term choices and expenditures that do not result in the best outcome in terms of long-term sustainability and management of liability. The financial implications include the potential need for significant expenditures on reversal or rectification of any originally poor, short-term choices.

The *regret spend* principle is now considered as part of holistic cost-benefit analysis in assessing whether the procurement and use of a product can be demonstrated to be sustainable, or if it may later turn out to have been an undesirable substitution requiring replacement once whole-of-life costs and liability are considered.

Figure 2A. PFHxS waterproofing agent (Huang *et al* 2013).

For example, since the 3M phase-out of PFOS, C4 PFBS and C6 PFHxS have been used variously as PFOS replacements in stain repellents, surfactants, firefighting foams (IPEN, 2019, Renner, 2006) and surfactants for oil production ((Huang *et al*, 2013). The use of shorter-chain PFAS has been justified largely on the tenuous basis of a shorter half-life in humans (not the case for PFHxS) but without specific studies conducted to determine long-term safety in humans or the environment.

3. FIREFIGHTER OCCUPATIONAL EXPOSURE

Firefighters can be significantly exposed to PFHxS and other PFAS from firefighting foam via various occupational mechanisms including direct exposure during use as well as exposure from contaminated personal protective equipment (PPE), handling of contaminated equipment, managing PFAS foam wastes, occupation of contaminated fire stations and consumption of contaminated local water and produce. Cross-contamination and legacy PFAS residues from inadequately decontaminated appliances after transitioning to fluorine-free foam can remain a long-term problem.

> **Ongoing exposure to PFHxS, PFOS and other PFAS amongst firefighters remains a major occupational health issue with both political and trust implications for employers.**

Bio-accumulation and very slow bio-elimination may be very significant influencing factors in PFHxS exposure. For example, a study of firefighters exposed to a commercial AFFF on three occasions during training showed an increase in serum PFHxS, in spite of low concentrations in the AFFF sample (Figure 3A, Laitenen *et al*, 2014).

Although the study had a small sample size and large standard deviations in the data that make conclusive interpretation difficult, the results provide sufficient reason for application of the precautionary principle for the avoidance of PFHxS use and exposure.

A recent unpublished Australian fire service occupational health study of firefighter exposure to firefighting foams amply confirms earlier findings by Rotander *et al* 2015 that elevated blood levels are found concurrently for both PFOS and PFHxS. Moreover, there appears to be a direct correlation between blood levels of PFOS and those for PFHxS. The ratio of PFOS to PFHxS is approximately 3:1 to 4:1 in blood and highly correlated as shown in Figure 3A. This ratio corresponds quite closely to that observed for all PFOS and PFHxS-related derivatives in legacy AFFF – Backe *et al* (2013) recalculated, see below.

However, of greater concern is that firefighter blood levels for PFOS and PFHxS are many times higher than the median values for the general Australian population of PFHxS-3.2 ng/ml and PFOS-12 ng/ml (Rotander *et al*, 2015).

Results from another Australian fire service monitoring programme based on a very large cohort of >700 participants and reported in the IPEN F3 Panel's 2019 White Paper presented at COP-9 in Geneva, showed that approximately 23% of the firefighters tested had blood levels of PFOS above the population average (Figure 3B); this study also shows that PFHxS levels were elevated, confirming the established linkage between PFHxS and PFOS.
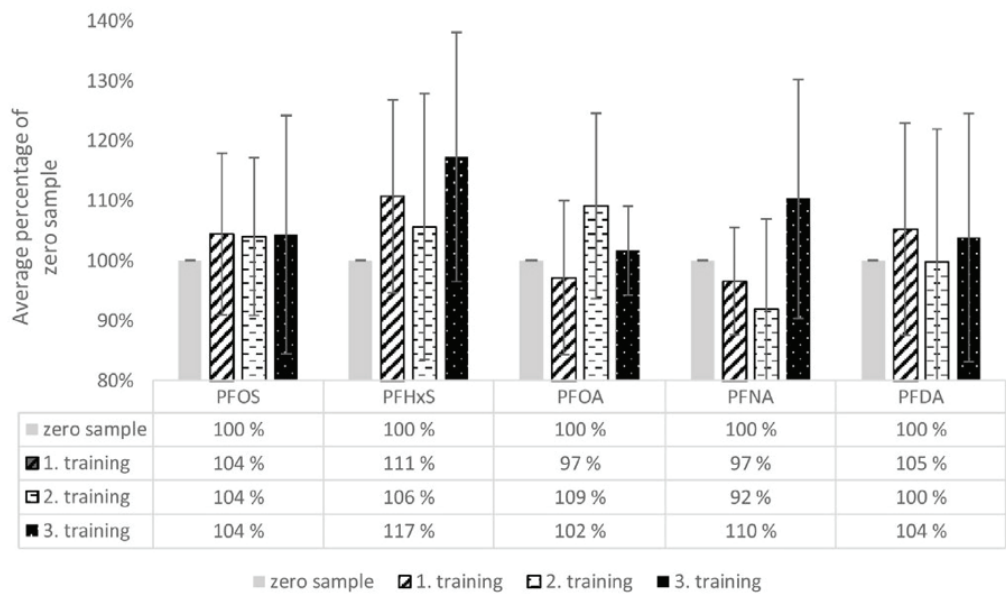

	PFOS	PFHxS	PFOA	PFNA	PFDA
zero sample	100 %	100 %	100 %	100 %	100 %
1. training	104 %	111 %	97 %	97 %	105 %
2. training	104 %	106 %	109 %	92 %	100 %
3. training	104 %	117 %	102 %	110 %	104 %

Figure 3A. Average and standard deviation of PFAA compounds in firefighters' serum during the three month training period. (Laitenen *et al* 2014)
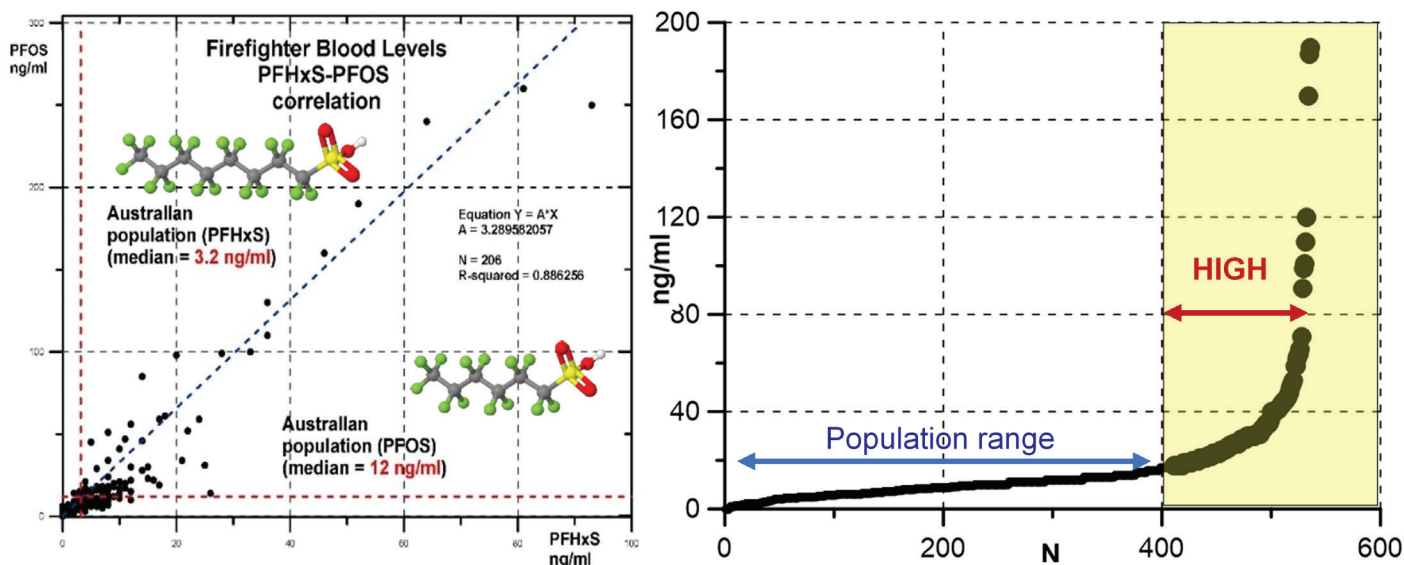
Figure 3B. PFHxS in firefighters' blood (left). Range of PFOS in firefighters' blood (right).

Occupational exposure of fire fighters to PFAS and especially to PFOS and PFHxS, is of particular significance and concern. Elevated blood levels are found not just in long-serving personnel who may have been exposed to legacy PFOS-containing AFFFs, but also in much younger fire-fighters and recruits who have never used or been trained with these foams.

Recent examples have emerged of firefighters who have not used PFOS foams at incidents such as fires, but nonetheless have been significantly exposed as evidenced by high PFOS and PFHxS levels in their blood. In other words, they have not been subject to exposure pathways such as inhalation and ingestion of aerosols from bursting foam bubbles or foam solution at incidents or during training. Lack of attention to personal decontamination on site or at the station remains a possibility for further exposure. It would appear that a significant exposure pathway can occur during routine activities such as equipment maintenance and clean-out as well as during foam concentrate transfer from bulk containers to appliances. This implies that there may have been significant exposure to concentrate through inhalation, ingestion or skin absorption of aerosols and splashes; there is also the possibility of skin absorption when handling contaminated equipment, with the penetration of PFAS, such as PFOS and PFHxS, through the skin aided by the aggressive detergent-like properties of the surfactants present in foam concentrate as well as penetrative effects of the glycol ether solvents. Glycols and glycol derivatives are capable of both moisturising and penetrating human skin, as used in cosmetics or the preparation of museum specimens. It is likely that adequate personal protective equipment (PPE) was not used during such routine maintenance activities as there is the assumption, with the lack of appropriate handling cautions in safety data sheets,

that concentrates are relatively benign and need no special precautions.

It also seems likely that more recent PFHxS and PFOS exposure may have resulted from contaminated training areas where the use of modern foam surfactants may have brought about the liberation of PFAS residues from contaminated concrete aprons or soils previously used with legacy PFOS foams.

For firefighters and the general population, the significance of PFHxS and PFOS levels in humans is beyond dispute in terms of the potential for adverse effects across a wide range of health values, especially for sensitive groups.

There continues to be debate about what constitute "safe" thresholds and exposure levels in diets, drinking water and through occupational exposure which is influenced by rapidly changing scientific information. However, conservative values, in particular for drinking water, are now being widely adopted with the recognition that direct effects and promotion of other adverse health conditions by individual or combined PFAS substances may well occur at very low exposure levels.

PFHxS and PFOS levels in the blood of firefighters and the general population are clear evidence that exposure from direct and diffuse sources is ongoing and significant especially in respect of there being many instances of no clear sources or pathways such as where workers are involved in PFAS manufacture or intensive industries. Application of established assessment standards have direct implications for triggering the Precautionary Principle.

4. PFOS-PFHxS MANUFACTURE BY SIMONS ELECTROCHEMICAL FLUORINATION (ECF)

The 3M Company announced in May 2000 that it was phasing out fluorosurfactant production based on PFOS chemistry, and withdrawing entirely from the fluorinated AFFF firefighting foam market marking an end to the availability of Light Water™ and Light Water™ ATC™ formulations (3M Company (2000)). Other products using PFOS included ScotchGuard™ stain and water repellent treatments. Production is thought to have ceased entirely around 2002.

Until that time PFOS had been manufactured using the Simons electrochemical fluorination (ECF) process (3M Company, 1999; Ignat'ev et al, 2009; Sartori and Ignat'ev, 1998). This process involves replacing the hydrogen atoms of octyl sulfonate using hydrogen fluoride electrolytically in order to generate perfluorooctane sulfonyl fluoride, PFOSF.

PFOS production using electrochemical fluorination (ECF) was, and remains, an inherently 'dirty' process resulting in a wide range of structural isomers, both straight chain and branched with CF-CF3 and C-(CF3)2 side chains, as well as odd and even chain length homologues such as C4 PFBS, C6 PFHxS and C7 PFHpS. As a result, technical grade PFOS was always and continues to be contaminated with a significant percentage of PFHxS.

In addition, the perfluoroalkyl chains of both PFOS and PFHxS can form left- or right-handed helices resulting in pseudo-racemates that have been detected in human sera (Wang et al, 2011; Naile et al, 2016; Sasaki et al, 2018).

Quoting from the ECHA (13 June 2019) PFHxS restriction proposal:

> *"...Sources indicate that when manufacturing per-fluorinated compounds, a mixture of compounds of varying chain- length is usually formed, with typical amounts of PFHxS formed when manu-facturing PFOS being between 4 and 14% (from (BiPRO, 2018) citing (Ren, 2016). These numbers are supported by measurements of PFHxS in com-mercial PFOS-products, namely 3.5%–9¬.8% in 3M's FC-95 (from (BiPRO, 2018) citing 3M (2015) and 11.2 % – 14.2% in three products from China (Jiang et al, 2015). BiPRO also note, however, that the amount of the C6-component may be reduced by purification at different stages of the production line...."*

4.1. PFOS PRODUCTION AND USE A SIGNIFICANT SOURCE OF PFHxS

The deliberate production, use and release of PFHxS is supplemented by the unintended production of PFHxS and its precursors as co-contaminants of PFOSF from the ECF method and the subsequent use of impurity-containing technical PFOS in products such as sulfluramid.

- **PFHxS is a significant contaminant of PFOS, N-Et-FOSA and related PFAS produced by ECF.**

- **Restriction on the use and release of PFHxS must also consider its occurrence as a contaminant in PFOS-based products such as Sulfluramid.**

- **As well as being more mobile, short-chain PFAS are displaced by longer-chain PFAS in soil columns promoting infiltration to groundwater.**

Contamination of technical-grade purity PFOS with significant PFHxS ~9% (and PFOA ~12%) is not an impediment to its effectiveness in insecticides (e.g., Sulfluramid) or firefighting foam surfactants so manufacturers typically do not go to the expense of purification. Therefore, the use of PFOS and related products will likely also represent a significant release of PFHxS and PFOA. This has implications for full compliance with the Stockholm Convention listings of PFOS and PFOA and provides further rationale for ending all uses, including the use of sulfluramid.
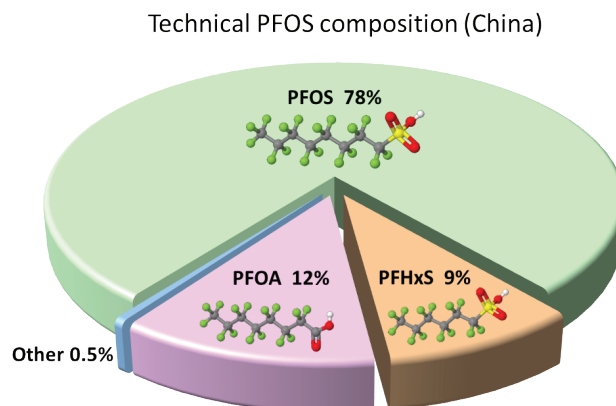
Technical PFOS composition (China)

PFOS 78%

PFOA 12%

PFHxS 9%

Other 0.5%

Figure 4.1A. After Jiang *et al*, 2015.

ECF method product composition

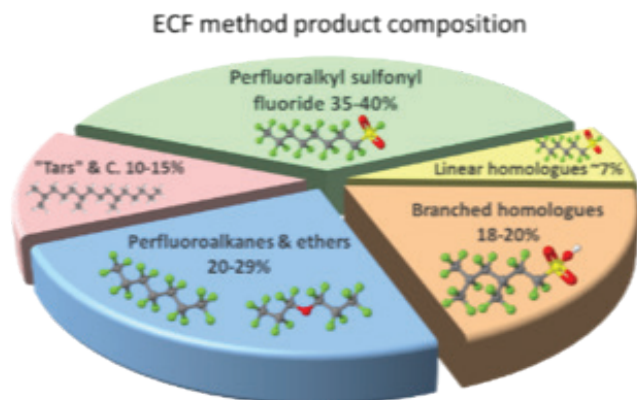FC-95 technical grade PFOS homologue distribution

Figure 4.1B. 3M production data, 1998.

A comparison of the composition of a recent sample of technical grade PFOS ECF product from China (Figure 4.1A, Jiang *et al*, 2015) with the 3M composition for ECF by-products technical grade PFOS (FC95) (Figure 4.1B, 3M, 1998) shows that, while there is variability in composition between different manufacturing sites and year of manufacture, the inclusion of PFHxS and other PFAS contamination is inevitable.

The composition of sulfluramid is usually cited as N-Ethyl-FOSA (Figure 4.1C): however, although this may be the main component, it is very likely to have significant levels of other contaminants including PFHxS, PFOS and PFOA.

The total ion chromatogram from a Waters Technical Note (Figure 4.1D) clearly indicates the complexity of the PFSA isomers produced by the ECF process.

Detailed mass-spectrometric analysis published by the Kärrman group from Orebro University in Sweden (see bibliography Section §10) has identified definitively many of the branched chain structural isomers for both C8 PFOS and PFOA. Biological uptake and activity appear to be isomer specific.
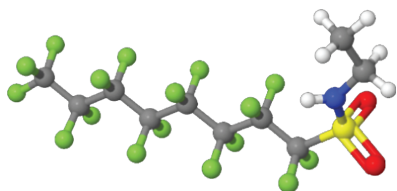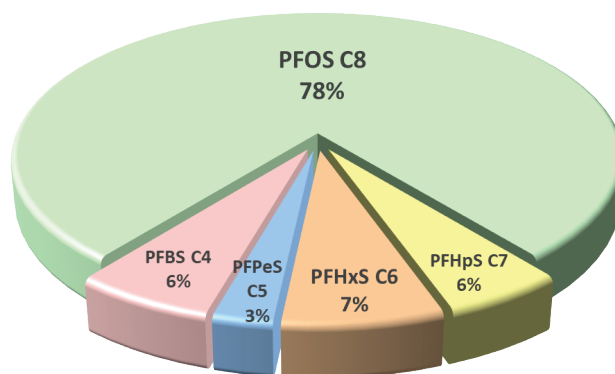
Similar variability in activity as well as biological uptake is expected for C6 PFHxS although with fewer branched isomers possible.

This raises the important issue that groups of isomers and related homologues need to be evaluated together in combination and not as single chemicals.
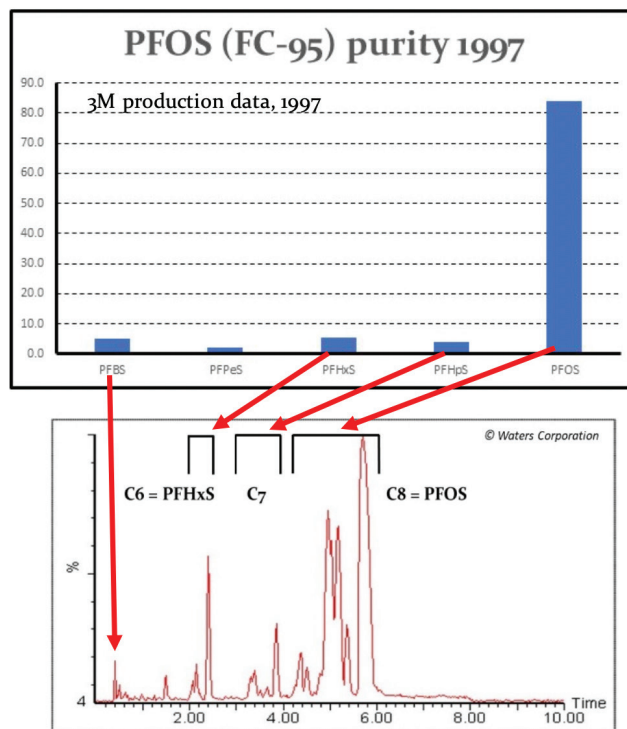

Figure 1. Total Ion Chromatogram of Technical Grade PFOS Sample.

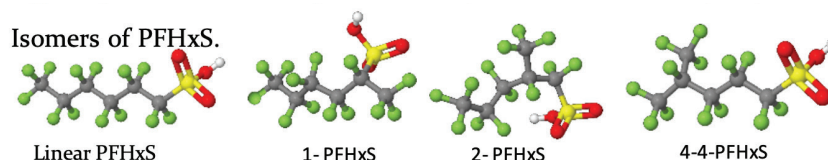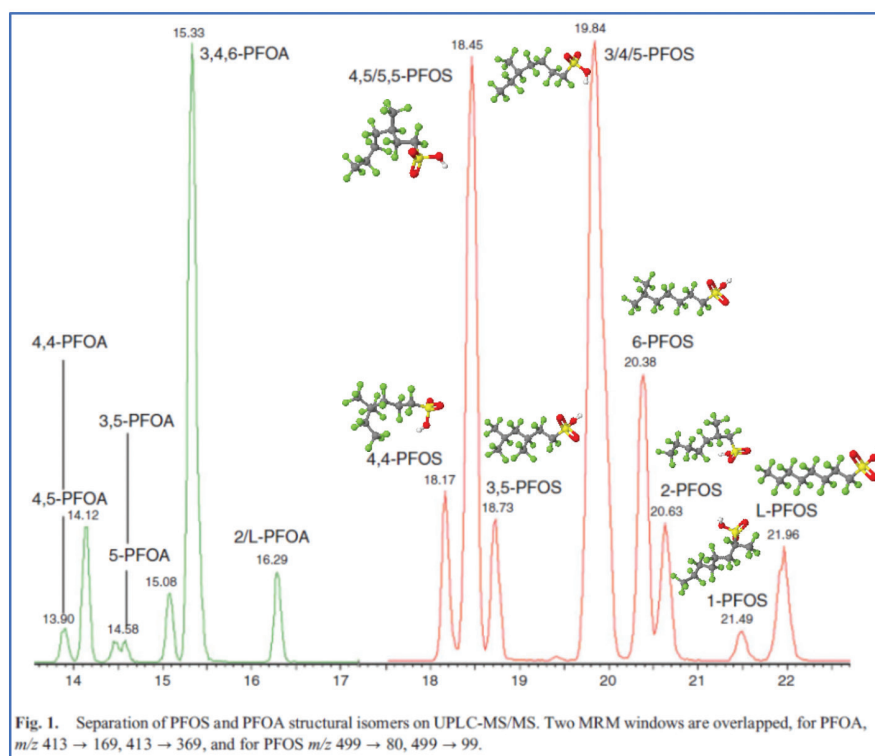Figure 4.1B(a). Technical grade PFOS contamination.

Figure 4.1C. N-Ethyl FOSA (PFOS precursor).

Fig. 1. Separation of PFOS and PFOA structural isomers on UPLC-MS/MS. Two MRM windows are overlapped, for PFOA, *m/z* 413 → 169, 413 → 369, and for PFOS *m/z* 499 → 80, 499 → 99.

Isomers of PFHxS.

Linear PFHxS   1- PFHxS   2- PFHxS   4-4-PFHxS

Figure 4.1D. PFOS diversity of isomers (After Kärrman *et al*, 2011).

4.2. FIREFIGHTING FOAMS AND OTHER SOURCES OF PFHxS

In the past, legacy PFOS-based fluorosurfactants have been used in many commercial applications as shown in the table from the ECHA PFHxS Annex XV *Restriction Report: Proposal for a Restriction, April 2019*, Table 8, summarised in Figure 4.2A to highlight the common uses and proportions across the main uses.

More recent data on PFHxS uses is limited but applications across legacy uses are likely to be similar. The implication is that while firefighting foam is a dispersive use and a very significant cause of contamination, the in-use washing and end-of-life disposal to landfill of the carpets, leather, textiles and fabrics ultimately represent a substantial source of PFHxS releases via waste water treatment plant (WWTP) effluent, biosolids and landfill leachate.

Early and seminal results for contaminated groundwater at military fire training areas in the United States published by Schultz, Barofsky and Field (2004) clearly indicated substantial proportions of PFHxS in the groundwater compared to PFOS which was also present. This has been amply confirmed by later results from the same group (Backe *et al* 2013).

The groundwater data are shown in part and illustrated below (Figure 4.2B) with the most contaminated sites highlighted in yellow. The elevated proportions of PFHxS (26% to 56%) compared to PFOS relative to the original PFOS foam composition of about 10% free PFHxS content exemplifies the greater mobility of PFHxS down to groundwater via poor adsorption to soils and displacement through
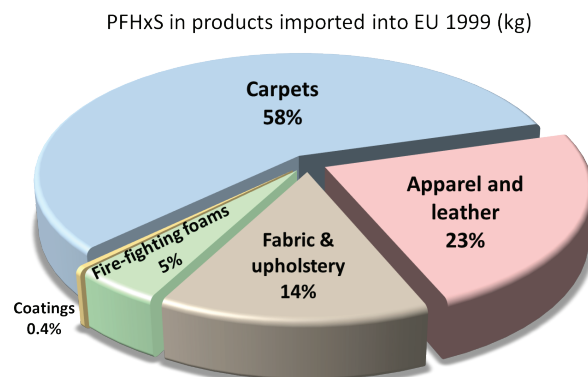

PFHxS in products imported into EU 1999 (kg)

Carpets 58%
Apparel and leather 23%
Fabric & upholstery 14%
Fire-fighting foams 5%
Coatings 0.4%

Figure 4.2A. PFHxS uses and proportions 1999 (From ECHA, 2019).

TABLE 2. Concentrations of Fluorotelomer Sulfonates, Perfluoroalkyl Sulfonates, and Perfluoroalkyl Carboxylates in Groundwater Samples from NAS Fallon (NASF), Tyndall AFB (TAFB), and Wurtsmith AFB (WAFB) (μg/L)[a]

sample	4:2 FtS	6:2 FtS	8:2 FtS	PFBS	PFPS	PFHxS	PFHpS	PFOS	PFHxA	PFHpA[b]	PFOA
NASF MW 51U	nd	nd	nd	210	216	876	nd	380	$372 \pm (1)^c$	$149 \pm (2)^c$	$6570 \pm (1)^c$
NASF MW 16	nd	nd	nd	54	38	115	nd	≤LOQ	$57 \pm (6)^c$	$18 \pm (5)^c$	$460 \pm (2)^c$
NASF MW 50U	nd	nd	nd	nd	nd	≤LOQ	nd	≤LOQ	nd^c	nd^c	nd^c
NASF MW 17	nd	nd	nd	≤LOQ	≤LOQ	≤LOQ	nd	≤LOQ	nd^c	nd^c	nd^c
TAFB PW-10	7.3	14 600	3.3	144	134	920	nd	2300	144^c	38^c	116^c
TAFB PW-07	5.7	7100	0.70	82	73	540	nd	270	73^c	22^c	64^c
TAFB T11−2	4.2	$4630 \pm (8)$	≤LOQ	58	70	360	nd	210	$64 \pm (3)^c$	$19 \pm (2)^c$	$42 \pm (2)^c$
TAFB TY22FTA	1.1	1080	17	10	8.3	107	nd	147	nd^c	nd^c	nd^c

Note
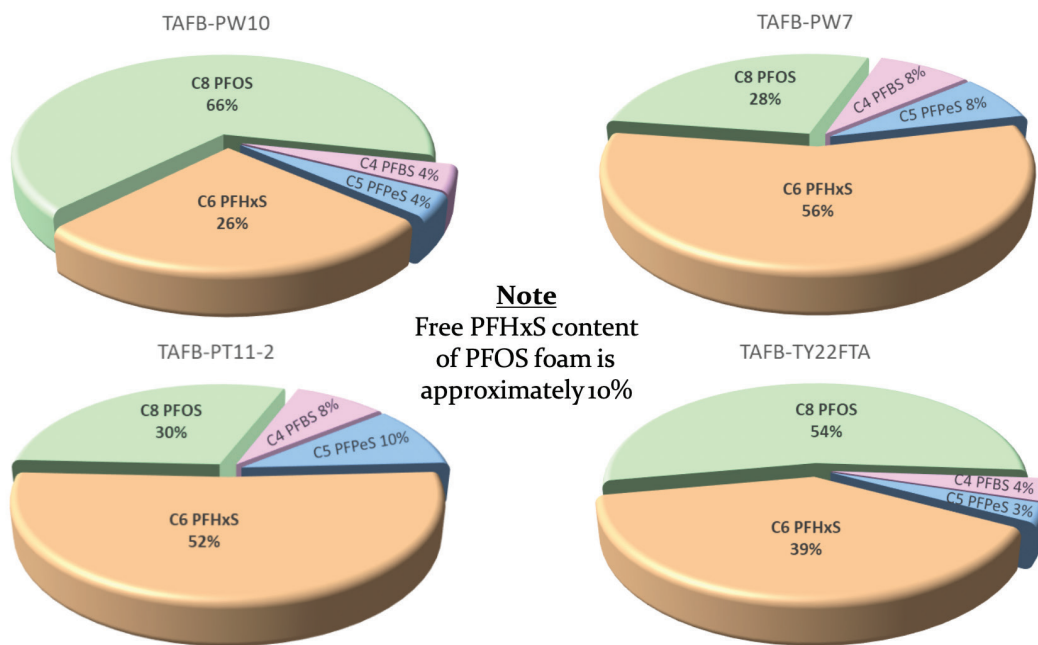Free PFHxS content of PFOS foam is approximately 10%

Figure 4.2B. Amplification of PFHxS versus PFOS in groundwater (After Schultz *et al*, 2004)

competition for binding sites resulting in hydrogeological fractionation.

A remarkable feature of these data is the proportionally high levels of PFHxS (26% to 56%) of the sulfonates found in groundwater samples 10-15 years after the sites were last used for AFFF firefighting foam training relative to the ~10% free PFHxS for the original PFOS foam.

The PFHxS co-occurrence and contamination is to be expected but the PFHxS levels being comparable to and exceeding the PFOS levels raises the PFHxS risk profile significantly. Additionally, there may also be some contribution from PFOA.

In a subsequent section (§4.3), we address the issue of why there appears to be an increased proportion of PFHxS in groundwater compared to PFOS and that part of this may be unrecognised PFHxS derivatives. This has considerable significance when contaminated ground water is used as a drinking water source, as PFHxS is difficult to remove using standard granulated activated carbon (GAC) water treatment.

Hydrogeological fractionation of PFHxS amplifies its occurrence in groundwater because of its higher water solubility, displacement from overlying soils by longer-chain PFAS and lower log(Koc) values, the latter leading to less adsorption to sediments and organics, and greater environmental mobility than for PFOS, as discussed in §5 on remediation.

4.3. THE HIDDEN SOURCES OF PFHXS IN FIREFIGHTING FOAM FORMULATIONS

Data published by Jennifer Field's group on PFOS foam composition further underlines the significance of PFHxS (Table 4.3, Backe *et al*, 2013) and exposes the additional sources of PFHxS in legacy products and the contamination resulting from them. On face value, of the free PFSA (sulfonates) content, the proportion of PFHxS in 3M Light Water™ firefighting foams over the period of 1989 to 2001 indicated a steady 9-11% for PFHxS content (3M Company, 1998) (Figure 4.3A). For FC-95 (potassium perfluorooctanoate), the main source of PFOS in AFFF foams, the 3M safety data sheet information suggests lower levels of PFHxS contamination.
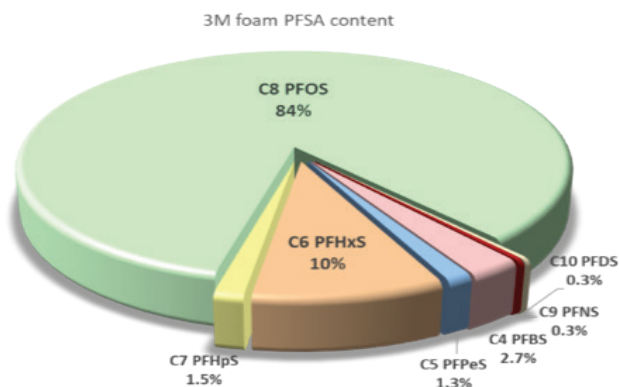
Figure 4.3A. Free PFOS, PFHxS and other PFSAs in 3M foam 1989 to 2001. (After Backe et al, 2013).

The reality is that when PFHxS and all PFHxS derivatives are taken into account, as shown by Backe et al (2013), the relative proportion of PFHxS to PFOS related substances increased significantly from the 1989 sample of 3M Light Water™ AFFF up to when PFOS-based production was being phased out.

The total of PFHxS and its derivatives increased from a ratio of ~1:8 to around ~1:3 relative to PFOS or from 11% to ~26% of total PFSA content (Figure 4.3B).

The two most significant PFSA derivatives detected by Backe et al (2013) in firefighting foam were the PFHxS and PFOS derivatives:

- "PFHxSaAm" C6 Perfluorhexyl sulfonamido propyl amine CAS 50598-28-2 $[C_6F_{13}SO_2N(CH_3)_2-CH_2CH_2CH_2-NH_4(+)]$
- "PFOSaAmA" C8 Perfluorooctyl sulfonamide propyl amino carboxylate $[C_8F_{17}SO_2NH(CH_2CH_2COO^-)-CH_2CH_2NH_2(CH_3)_2(+)]$

The C6 derivatives (PFHxSaAm and PFHxSAmA) were the predominant species occurring from 660 mg/L to 930 mg/L in 3M Light Water™ foams. Individually these PFHxS derivatives were at similar concentrations to the free PFHxS content (Figure 4.2C & 4.2D). They appear to have been added to later formulations (1993 onwards) possibly as foaming or foam stabilising agents.

These data also make it clear that the PFHxS derivatives (PFHxSaAm and PFHxSaAmA) were added intentionally to AFFF formulations, and that they and PFHxS were not present just as an unintentional contaminant of ECF produced PFOS.

These results highlight the unreliability of only considering free PFOS and free PFHxS values and that it is essential to consider the presence of related PFAS that are likely to be toxic in their own right and will transform to PFSAs.

All of the measured values detailed above for the relative proportion of PFHxS compared to PFOS in AFFF firefighting foams above are in conflict with 3M data for the fluorosurfactants used in the formulations quoted in the ECHA (2019) Annex XV PFHxS Restriction Proposal Table 8 which indicates much lower values for PFHxS-related substances in the product of closer to ~2%.

The reality of the high levels of PFHxS-related substances in legacy AFFF plus contamination of currently produced
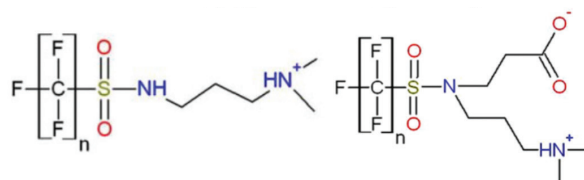

Figure 4.3C. PFHxSaAm (n=6) and PFHxSaAmA (n=6) (Field, SERDP, 2018) PFHxS precursors.
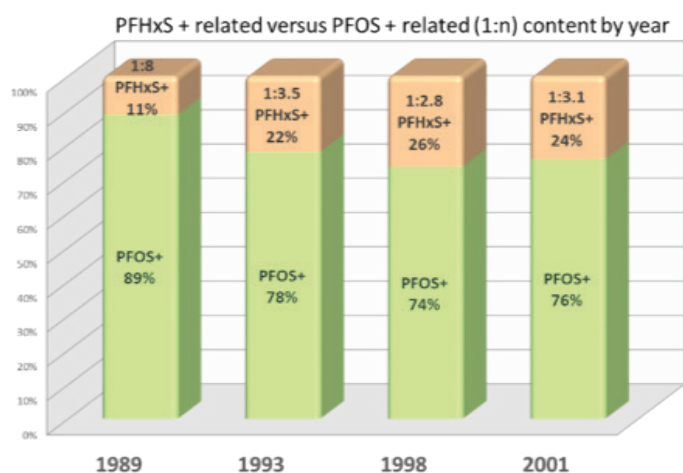

Figure 4.3B. FPFOS versus PFHxS derivatives and free PFSA composition in 3M foam 1989 to 2001. (After Backe et al, 2013)
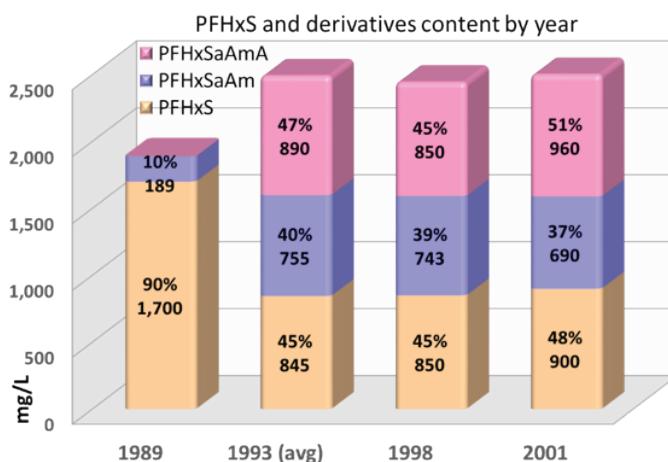

Figure 4.3D. Increase in PFHxS derivatives in 3M foam from 1989 to 2001. (After Backe et al, 2013)

Table 4.3. 3M foam composition 1989 to 2001 (Backe *et al*, 2013)

12 Table S6. Concentrations (mg/L) of newly-identified and legacy perfluorinated chemicals in 3M
13 aqueous film forming foam formulations manufactured from 1989-2001.

	1989 mg/L	1993a mg/L	1993b mg/L	1998 mg/L	2001 mg/L
PFBSaAm [a]	9	120 ± 2.0	180	140	110
PFPeSaAm [a]	8	140 ± 1.8	180	140	110
PFHxSaAm [a]	189	660 ± 8.1	850	743	690
PFHpSaAm	ND	12 ± 0.40	15	30	24
PFOSaAm	9.9	62 ± 1.1	75	67	37
PFBSaAmA [a]	ND	140 ± 3.1	120	110	150
PFPeSaAmA [a]	4	200 ± 6.3	170	140	130
PFHxSaAmA [a]	ND	930 ± 13	850	850	960
PFHpSaAmA	ND	17 ± 0.16	17	34	44
PFOSaAmA [a]	ND	72 ± 0.81	58	53	65
PFBS	380	220 ± 2.0	160	210	250
PFPeS	210	120 ± 1.5	80	90	120
PFHxS	1700	910 ± 14	760	850	900
PFHpS	410	120 ± 2.0	120	93	140
PFOS	15000	8000	9300	6700	7900
PFNS	160	53 ± 0.97	56	9	27
PFDS	102	51 ± 0.34	52	11	27
PFBA	37	24 ± 0.48	35	31	38
PFPeA	47	36 ± 0.14	52	43	48
PFHxA	170	99 ± 1.1	110	99	170
PFHpA	54	25 ± 0.28	22	26	37
PFOA	150	83 ± 1.3	93	86	170
PFNA	ND	ND	ND	ND	ND
PFDA	ND	ND	ND	ND	ND
PFUdA	ND	ND	ND	ND	ND
PFDoA	ND	ND	ND	ND	ND
PFTrA	ND	ND	ND	ND	ND
PFTeA	ND	ND	ND	ND	ND
PFS/PFA [b]	39	35	34	28	20
Legacy/Newly-Identified	84	4.1	4.3	3.6	4.2
PFOS/PFHxS	8.8	8.8	12	7.9	8.8

PFOSF by the Simons ECF process, together with the phenomenon of hydro-geological fractionation observed in groundwater impacted by AFFF highlights the need to prevent further release of material containing PFHxS to the environment.

4.4. CURRENT PRODUCTION OF PFOSF, PFHXSF AND DERIVATIVES

Continued manufacture of PFOSF using the Simons electrochemical fluorination (ECF) process in Asia and agricultural application of the PFOS derivative sulfluramid in China, Brazil and other Latin American countries represent highly significant sources of environmental contamination with PFHxS.

The ECF process used to produce the precursor PFOSF is a fundamentally 'dirty' industrial synthesis that results in the generation of by-products including both PFHxS and PFOA at about the 10% level for each compound (Jiang *et al*, 2015). Subsequent treatment of PFOSF with ethylamine to produce sulfluramid (N-ethyl-perfluorooctane sulfonamide, N-ethyl-PFOSA) will result in this insecticide being contaminated with a significant level of PFHxS.

A submission to the Basel Convention by Huang and co-authors (Huang *et al*, 2013) from the School of Environment, Tsinghua University and the China Association of Fluorine and Silicone Industry (CAFSI), highlights the state of PFOSF production facilities in China, located particu-

Figure 4.4A. ECF production facilities in China. (Huang *et al*, 2013)

larly in the Hubei and Fujian Provinces, using the Simons ECF process.

Annual PFOSF production in China reported by these authors was **139 tons** with:

- **89.5 tons** (64%) for domestic use.
- **49.5 tons** (36%) for export, mainly to Brazil for sulfluramid synthesis.
- **10.4 tons** (7.5%) destined for home use in the manufacture of perfluoroalkyl sulfonyl quaternary ammonium iodides as fluorosurfactant FC-134 destined for AFFF firefighting foam.
- **3.1 tons** (2.2%) were used for manufacturing FC-09 N-ethyl-perfluorooctane-sulphonamide, better known on the market as the insect bait Sulfluramid.

Average PFOSF production in the period 2009-2012 had been 100-160 tons per annum. Primary applications for PFOSF were for mist suppressants used in hard chromium (Cr^VI) plating, fluorosurfactants for AFFF firefighting foams and for sulfluramid baits, with widespread manufacturing facilities, primarily throughout eastern China (Zhang *et al*, 2012). Other uses included textile and leather finishing as well as surfactants for the oil industry.

Production and use of sulfluramid in Brazil and for domestic use in China (Huang *et al* 2013) represents a globally significant emission source not only of N-Et-PFOSA but also of PFOS. Löfstedt Gilljam *et al* (2016) have reported that some thirty companies in Brazil manufacture 70-80 sulfluramid products for both agricultural and domestic use, for controlling leaf-cutting ants (currently permitted under the Stockholm Convention) or for cockroaches, household ants and termites (non-compliant with the Convention), giving rise to annual emissions of around 50 tons of PFOS equivalent. China banned sulfluramid production

in March 2019 and all uses will be prohibited as from 1 January 2020.

Brazil's annual use of sulfluramid would be sufficient to contaminate a billion (109) cubic metres (tons) of water to a level of 50 ppt PFOS (compared to the US EPA health advisory level of 70 ppt for PFOS and PFOA in drinking water, a non-regulatory standard that is at least an order of magnitude too high and not health protective, with significantly more stringent regulatory limits enacted by individual US States. These PFOS emissions would be sufficient to add ~5 tons of PFHxS annually to the globally release inventory of this contaminant.

Apart from polluting drinking water, sulfluramid (N-Et-PFOSA) as well as the related compound N-Ethyl-perfluorooctanesulfamido-acetic acid (N-Et-PFOSAA) are also known to be taken up and transformed to PFOS in hydroponically grown plants, root vegetables such as carrots, alfalfa, lettuce, maize, mung bean, radish, rye-grass and soybean, thus potentially contaminating the food chain (Wen *et al*, 2018; Zabaleta *et al*, 2018; Zhao *et al*, 2018a, 2018b).

A misconception currently appearing in the literature is that sulfluramid can be bio-transformed to PFHxS and PFBS. This is highly improbable as perfluoroalkyl chains are notoriously resistant to chemical attack. This misconception probably arises from a lack of understanding that both PFHxS and PFBS are ECF process impurities present in the PFOSF feedstock used in the synthesis of sulfluramid.

Alternatives to PFOS-based baits for leaf-cutting ants have been discussed in a recent IPEN technical note (IPEN, March 2019).

An example of the use of PFHxS as a replacement for PFOS in AFFF firefighting foam was also reported for the feed-
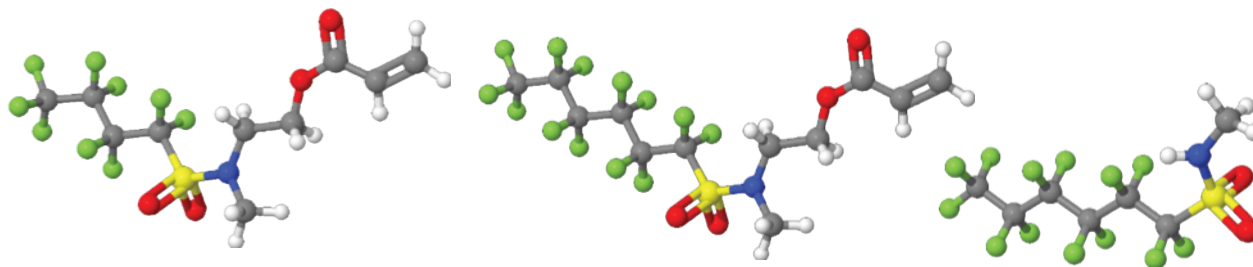
Figure 4.4B. Perfluoroalkyl sulfonyl amino ethyl acrylates (C6 & C8) and N-Meth-FHxSA structures.

CAS 67584-55-8,   CAS 67584-57-0   CAS 68259-15-4.

stock VF-9126 (Vattern): which is PFHxS-based. Various PFHxS derivatives (Figure 4.4B) are available commercially from companies in Hubei Province including:

- 2-[methyl[(nonafluorobutyl)sulphonyl]amino]ethyl acrylate (*CAS 67584-55-8*)
- 2-[methyl[(tridecafluorohexyl)sulphonyl]amino]ethyl acrylate (CAS 67584-57-0)
- N-methyl-perfluorohexane-1-sulfonamide (CAS 68259-15-4).

As of November 2016, it is clearly the intention of the Chinese authorities to phase out PFOS and PFOS-related compounds in the near future, (Foreign Economic Cooperation Office, Ministry of Environmental Protection (FECO) and *Hubei Academy of Environmental Sciences* (HAES), 2017). However, PFHxS and PFHxSF are still being produced for use across a diversity of applications that inevitably result in releases to the environment. The Norwegian Environment Agency (2018) estimated from market research reports that global PFHxS(F) consumption was between 80 and 400 tonnes per annum.

The reported proportions for various PFHxSF uses are shown in Figure 4.4C. The quantities labels are based on a median total value of US$662.5M, equating to about 110.4 tonnes at ~$6K per kilogram. This does not include PFHxSF occurring as a co-contaminant of PFOSF production resulting, for example, in around 9% PFHxS in technical PFOS along with about 12% PFOA (Jiang *et al*, 2015). Notably around 4% of PFHxSF is estimated to be used for surfactants and firefighting foams despite the majority of PFAS use for firefighting foam globally having transitioned to fluorotelomer PFAS.
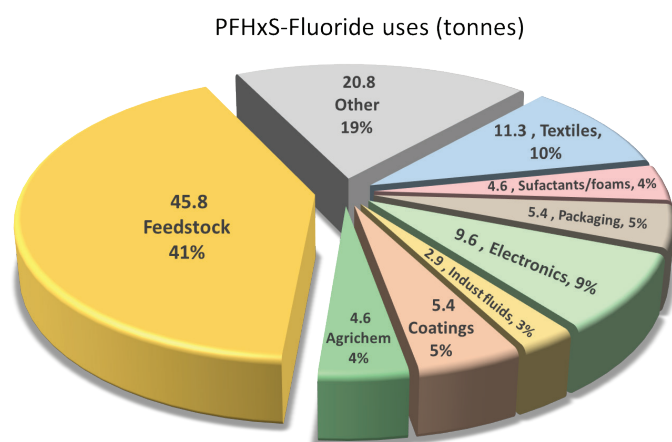
PFHxS-Fluoride uses (tonnes)

Figure 4.4C. After Norwegian Environment Agency, 2018
Investigation of sources to PFHxS in the environment - Report.

5. REMEDIATION OF SOILS AND DRINKING WATER SUPPLIES

The remediation of soils and drinking water supplies that are contaminated with PFAS is a very widespread and expensive problem. Communities, industry and end-users now face considerable costs from legacy and ongoing contamination. Whilst PFOS and PFOA have been the focus of attention, PFHxS has become recognised as being just as problematic along with other shorter-chain PFAS, which are increasingly coming under scrutiny.

5.1. PFHXS - SOIL AND GROUNDWATER REMEDIATION CHALLENGES

The significant additional challenges with treating more mobile, water-soluble PFAS, such as PFHxS, have been reviewed by several authors (Merino *et al*, 2016; Dickenson and Higgins, 2016; Ross *et al*, 2018), as well as currently being experienced in the real world by drinking water and wastewater infrastructure providers and by those responsible for site remediation.

Conventional water treatment technologies are not effective in treating PFHxS contamination without considerable modification and additional expense to meet the particular challenges posed by this C6-chain PFAS.

- **PFHxS and other short-chain PFAS are very difficult and expensive to remediate.**
- **PFHxS is highly mobile and will circulate readily through the environment and biota.**
- **Drinking water supplies are under increasing threat of contamination from PFHxS migrating into water supplies from contaminated sites, industry, WWTP effluent and landfill leachate.**

Once released to the environment, highly mobile, water-soluble PFHxS and related PFAS recirculate in the aquatic environment contaminating drinking water, crops, livestock, seafood, wildlife and humans not only through direct exposure but also via the food chain.

For these reasons, short-chain perfluoroalkyl acids (PFAA) are becoming of increasing regulatory concern especially under REACH (Brendel *et al*, 2018).

PFHxS is classed as a "*long-chain*" PFAS by the US EPA based on its retention, effects and bioaccumulation in organisms, which are similar to those for C8 PFOS. However, it is nonetheless a short-chain C6 PFAS in terms of its physical and chemical characteristics, particularly in terms of its mobility in soils, dispersion and solubility in water and lack of affinity for adsorbents, this being reflected in the difficulties associated with its remediation and removal from soils and water.

The main concerns over the fate, transport and remediation of PFHxS are that it is highly mobile in the environment and much more difficult to remove from water using conventional water treatment technologies such as granular activated carbon (GAC).

Higher mobility and greater difficulties in its removal compared to both PFOS and PFOA result from PFHxS's greater aqueous solubility (2.3 g/L) and diminished sorption potential to soil organics and sediments (Log K_{oc} 1.78 L/kg; Pancras *et al*, 2016). By comparison, PFOS water solubility is 0.68 g/L and log K_{oc} 2.68 L/kg.

The behaviour of multi-component PFAS mixtures, for example in AFFF firefighting foams, in interacting with soil and sediments followed by percolation into groundwater is complex, with hydrogeological fractionation taking place. This is determined both by the structure of individual PFAS molecules, i.e., chain-length and functional group, as well as by the absorptive properties of the particular soils or sediments (Hatton *et al*, 2018; Hunter Anderson *et al*, 2019; Li *et al*, 2018).

Solubility and therefore mobility of PFAS generally follow carbon chain length as illustrated in Figure 5.1A (after Ding and Peijnenburg (2013)) with some influence by the functional group. This increased mobility of short-chain PFAS promotes more extensive contamination plumes for PFHxS than for longer-chain PFAS such as PFOS.

Spurious assertions about shorter-chain PFAS being tolerable are strongly countered by new scientific evidence of increased risk of exposure due to greater mobility, higher solubility and greater uptake into the food chain, there being no difference in extreme environmental persistence leading to increasing and irreversible exposure if releases continue.
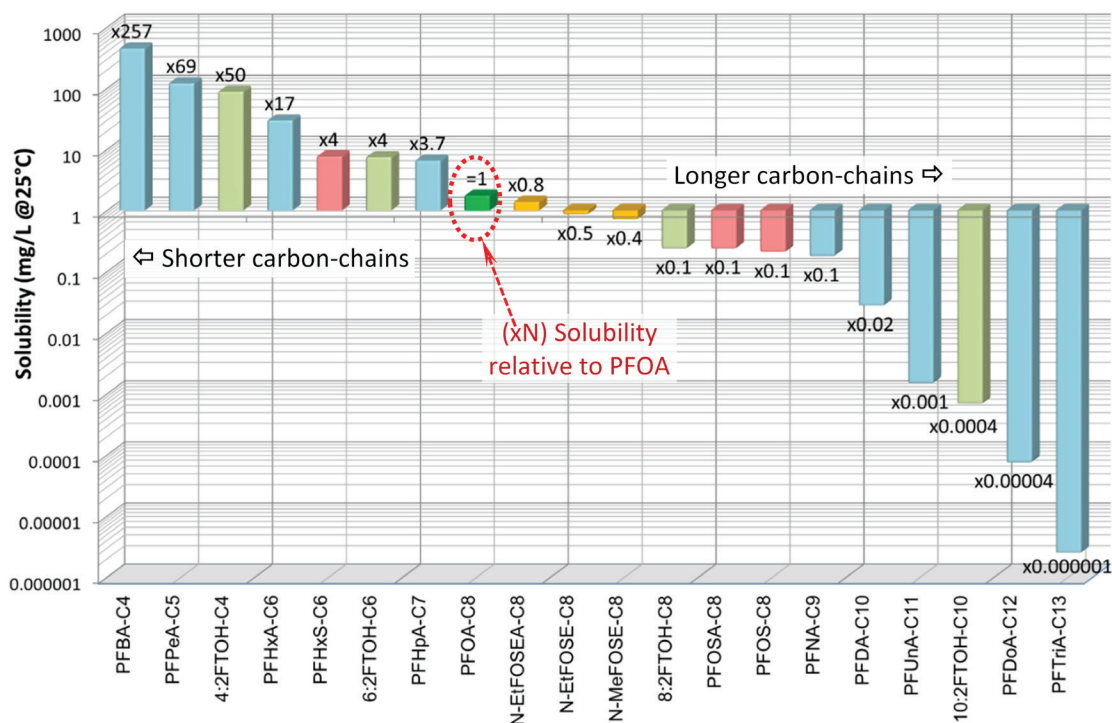
Figure 5.1A. Relative solubility of PFAS plotted by ~carbon-chain length (data from Ding *et al*, 2013)

When activated carbon is used for the treatment of contaminated water containing long-chain PFAS the PFHxS and other short chain PFAS can break through the carbon filter bed far more rapidly than PFOS and PFOA.

This is a particular issue for PFHxS treatment as PFHxS is classed as a long-chain PFAS and thus subject to inadequately protective drinking water standards (where they exist). Thus, early breakthrough of PFHxS using GAC filter beds requires monitoring much more frequently as well as more frequent GAC filter bed replacement resulting in greatly increased maintenance costs.

Treatment of PFAS can be achieved using extractive processes, including pre-treatment with specialised PFAS precipitants that are based upon separation by charge such as ion-exchange resins, for example, PerfluorAd™, as opposed to hydrophobic interactions. Using such resins, it is possible to achieve removal of both long- and short-chain PFAS. However, this may not be appropriate in the presence of organic co-contaminants such as petroleum hydrocarbons, e.g., in firewater runoff containing AFFF foam plus fuel residues, as the resins become fouled and lose their effectiveness.

Similarly, the use of ion-exchange resins to treat PFAS in water containing high concentrations of naturally occurring ions such as sulphates, nitrates and carbonates may also not be possible because these ions compete for binding capacity.

As PFHxS is a perfluoroalkyl sulfonic acid, its capacity to be chemically oxidised is negligible and so simple destructive treatment options are limited. For destructive treatment options to be cost effective, PFHxS must first be concentrated from the high-volume/low concentration wastes as usually encountered in contaminated firewater and groundwater, for example, by reverse osmosis. Although feasible, this is costly.

Destructive options to mineralise PFAS are generally expensive as they rely on high temperatures to break the carbon-fluorine bonds, conditions that cannot be maintained reliably in even the most sophisticated waste disposal incinerators. Lower energy destructive options, such as sonolysis and electrochemical oxidation are evolving but are not currently commercially available.

When considering options for treating PFHxS in soils, the stabilisation or fixation of PFHxS will be hindered by its high aqueous solubility. The presence of cationic (+ve) and zwitterionic (dual charge) PFHxS precursors in soils impacted by aqueous film-forming foams (AFFF) will cause diminished performance by technologies such as soil washing. The current challenge is that that analytical quantification of the PFHxS precursors is not currently commercially possible or practicable as these cannot be extracted from soils in order to be measured using conventional extraction techniques commercially now available, all of which target the anionic (-ve) PFAS (Kempisty *et al*, 2018).

Moreover, Dauchy *et al* (2019) have shown that PFAS from AFFF firefighting foams, both from legacy and those in current use, can penetrate extremely deeply into soils at former foam training sites reaching depths of 15-20 metres despite the presence of clay layers, thus contaminating underlying groundwater.

Li *et al* (2019) have very recently published a succinct summary of the main issues and concerns over environmental contamination with short-chain perfluoroalkyl substances (PFAS). Based on their comments these are:

- **Aquatic presence**–Short-chain PFAS are more widely detected, more resident [i.e., remain longer] and are more mobile than longer chain PFAS in aquatic systems; thus they may pose greater risks to human health and wider ecosystems.

- **Treatment challenges**–Conventional adsorption, ion-exchange, and membrane filtration are able to remove short-chain PFAS but are considerably less effective than for long-chain homologues (see below) resulting in potential releases in effluent streams from waste water treatment plants (WWTP); moreover, poor absorbent regeneration efficiency and disposal of process waste residues pose further challenges.

- **Destruction difficulties**–Advanced oxidation methods such as sonolysis can achieve complete mineralization to carbon dioxide CO_2 and fluoride anion F^- but are expensive and are not readily available commercially.

- **Emerging treatments**–Direct photolysis, oxidation/reduction, photocatalysis or electrochemical reactions all result in degradation of short-chain PFAS following similar pathways as for long-chain PFAS but at slower rates: photocatalytic processes using high intensity UV-light appear to be amongst the most promising.

5.2. PRACTICAL DIFFICULTIES IN REMOVING PFHXS FROM DRINKING WATER SUPPLIES

It is well known that, depending upon the group of specific substances (e.g., PFCA, PFSA, fluorotelomers), both the functional group and the perfluoroalkyl chain-length together determine the particular physicochemical properties. These properties influence the effectiveness of removal via common water treatment processes in the same way they affect the mobility of PFAS in contaminated groundwater after release to the environment.

Figure 5.2A shows the adsorption behaviour of PFOS and PFHxS on granulated activated carbon (GAC), using a suitable grade of activated carbon, with different GAC concentrations (mg/L). The percentages of PFOS and PFHxS that were removed as a function of GAC concentration are shown. The data shown in Figures 5.2A and 5.2B are experimental data courtesy of Martin Cornelsen.
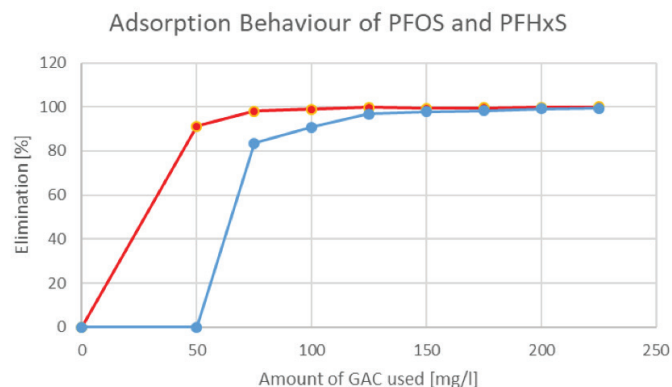

Figure 5.2A. Adsorption Behaviour of PFOS and PFHxS versus GAC.

It clear that the adsorption of PFHxS by the GAC is much less effective at small concentrations of GAC than it is for PFOS. The curves for the elimination of the two substances do not approach one another or 100% until very high levels of activated carbon are present. For low amounts of activated carbon, the difference is more than 90%. This discrepancy decreases to approximately 15% for intermediate GAC concentrations (>75 mg/L) until elimination of both PFHxS and PFOS reaches close to 100% at extremely high concentrations of adsorbent.

Processing technologies must therefore ignore previously held simplistic views about PFOS and PFOA and take into account the different adsorption behaviours of individual PFAS compounds of differing carbon-chain lengths and the diversity of functional groups. Thus, adsorption systems need to be designed encompassing the adsorption properties of the substances to be removed, as well as allowing for a considerable operational safety margin.

In addition, the demand for activated carbon increases for compounds with lower adsorption coefficients. Moreover, the question of operational safety, i.e., the avoidance of early and undetected breakthrough, must also be taken into account. In practice, this often means that several filter stages have to be connected in series, adding to the overall cost.

These caveats become even more important if the input stream is contaminated not just with PFAS but also with other organic substances, such as fuel residues, glycols, carbohydrates or other high organic-content waste streams. This is usually the case with firewater runoff as, apart from anything else, the background matrix of firefighting foams consists of different organic substances such as high levels of glycols. Furthermore, additional organic substances are likely to be released as combustion products of the fire itself.

The resulting competition between readily adsorbed substances (Dissolved Organic Carbon (DOC); and polycyclic
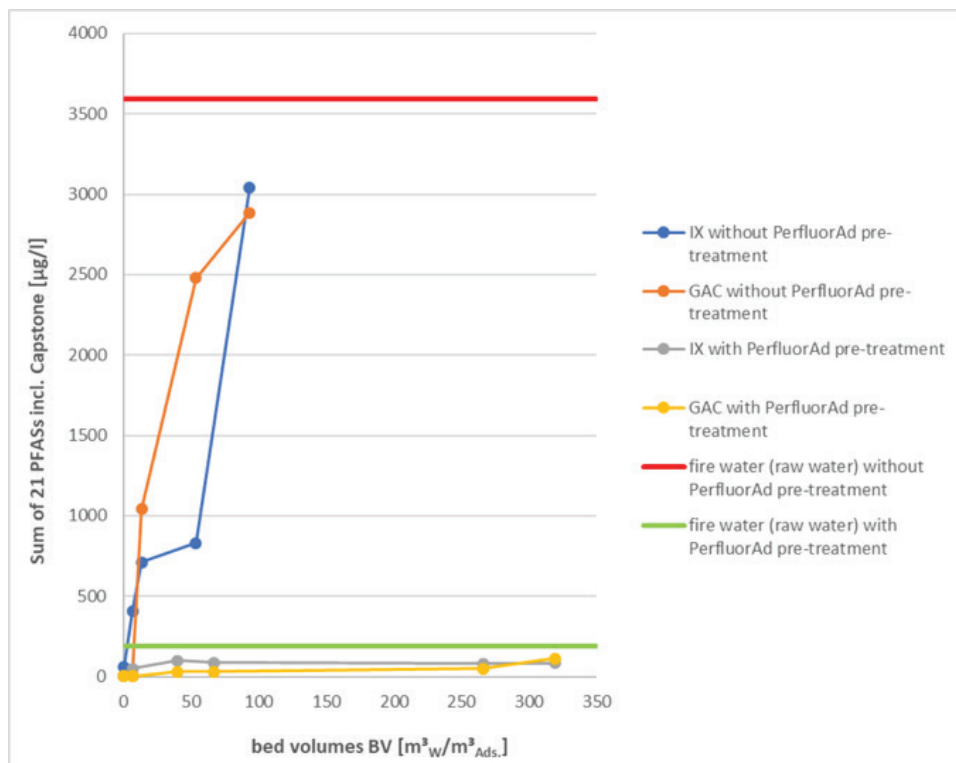
Figure 5.2B. Breakthrough behaviour of PFAS on GAC and IX with and without PerfluorAdÐ pre-treatment.

aromatic hydrocarbons (PAHs); and others) and PFAS during the adsorption process on GAC means that filter systems have to be larger and the demand for activated carbon is greater. With extreme organic background loads in the wastewater, early breakthrough may occur leading to uncontrolled release of PFAS.

Figure 5.2B shows a comparison of the breakthrough behaviour of PFAS on both activated carbon filters and ion exchange beds for artificial firewater runoff (1% AFFF premix), with and without pre-treatment using PerfluorAd™. The organic content of this firewater runoff was approximately 2 g/l DOC (Dissolved Organic Carbon) and underlines the important point that neither activated carbon nor ion exchangers are suitable for removing PFAS in competition with high levels of organic material (i.e., with a high DOC content). Only when highly contaminated fire extinguishing water is pre-treated with PerfluorAd™ can removal of the PFAS using either GAC or the ion-exchange resin IX be achieved satisfactorily.

Moreover, shorter chain PFAS molecules such as PFHxS give rise to a higher proportion in groundwater than in soil samples compared to longer chain molecules such as PFOS, due to differences in their properties. Hydrogeological fractionation can clearly be observed in groundwater samples impacted by legacy PFOS-containing AFFF-type firefighting foams with relative PFHxS levels far higher than would be expected, even sometimes exceeding measured PFOS levels (Schutz *et al*, 2004).

6. THE FEASIBILITY OF OPERATIONAL CONTAINMENT OF FIREFIGHTING FOAMS

The recommendation that all fluorinated foam firewater runoff should be contained and appropriately disposed of, also reflected in a similar recommendation from the POPRC, made by industry trade associations, manufacturers and others, whilst protecting them against potential legal action, is operationally impractical at most major fire incidents.

In general, reasonable containment is only possible at fixed petrochemical installations such as refineries, chemical, process plants or fuel storage-tank farms where there are containment bunds surrounding the storage-tanks and where production equipment may be at risk. Even so, at any large incident firewater runoff will usually exceed the capacity of the bunding as standard regulations only allow for the storage tank contents plus 10%. In many cases, moreover, the bunding also is not completely impervious or intact due to poor maintenance or design with infiltration to groundwater likely.

Fires and spills at airports, on railways, waterways or roads are virtually impossible to contain at the site of the incident as it is likely to be in an unmanaged and un-bunded area. Moreover, incidents at well-bunded sites represent the minority of incidents due to the strict control of activities and high safety standards at such sites.

Very large incidents like the Sandoz Basel fire in 1986, Coode Island Melbourne in 1991 or the explosion at the Buncefield fuel storage depot UK in 2005, resulted in tens of millions of litres of contaminated firewater runoff with substantial volumes of foam concentrate being used – 786 tons of AFFF concentrate (equivalent to ~13 million litres of finished foam for a 6% concentrate or double that for a 3% concentrate) were used at Buncefield in 2005. Such sites are often close to rivers or other bodies of water such as estuaries. Moreover, bunding systems may fail catastrophically as happened at the Buncefield incident where hot hydrocarbon fuel dissolved the mastic seals between bund walls as well as any sealing (if present at all) of pipework passing through the bund walls causing loss of containment as illustrated in the two photographs of bund walls (Crown © UK Health and Safety Executive)

These findings have prompted further studies of PFAS in occupationally exposed firefighters to further monitor levels, explore the extent of exposure and determine possible factors affecting elimination and reduction in blood levels.

In the United States in July 2018, President Trump signed into US law H.R. 931, the "*Firefighter Cancer Registry Act of 2018*", this establishes and maintains a voluntary registry of firefighters to collect data on cancer incidence. Culminating after more than two years of intense lobbying and hard work by the IAFF and its leadership, the Firefighter Cancer Registry Act of 2018 (H.R. 931) means that the US Federal Government has taken the first steps towards establishing a one-of-a-kind national cancer registry specifically for fire fighters.

7. THE OPERATIONAL USE OF FIREFIGHTING FOAM

This definition taken from the PFOA COP9 decision, but equally applicable to PFOS and PFHxS, would allow any use including in fire appliances.

> *Fire-fighting foam for liquid fuel vapour suppression and liquid fuel fires (Class B fires) in installed systems, including both mobile and fixed systems, in accordance with paragraph 2 of part X of this Annex*

"Mobile systems" could be read to cover all fire appliances that carry foam ready for use in containers or in their tanks, for example ARFF crash tenders or some municipal fire brigade vehicles. This is not necessary as it is quite simple and relatively inexpensive to change the comparatively low-volume tank contents and, if necessary, deep-clean the tanks before switching to the use of a non-persistent, fluorine-free foam; this has been successfully achieved using a multi-stage decontamination process by Melbourne MFB (Victoria).

 "Mobile systems" could and would be read to also include all hand-held and trolley type fire extinguishers, including those sold for commercial or domestic use. It is not clear

that the exemption is probably only meant to apply just to finished foam already in large and complex fixed commercial systems which would be difficult and expensive to refill.

There are two types of fixed installations that must be considered:

- **Units not normally filled with foam** associated with standing pipework or mobile foam solution sources, for example, at refineries or large chemical process facilities.
- **Foam-filled permanently connected storage tanks** or bladder tanks, for example, for use with automatic fixed monitor or sub-surface injection systems and deluge systems at chemical and petrochemical process plant or airport fuel storage tank farms.

In the first case, foam concentrate stocks are held and then supplied from 1000 litre intermediate bulk containers (IBCs) or from 24,000 litre ro-ro (roll-on/roll-off) shipping container storage tanks that are only connected to the pipework via a large hose connector or manifold when required. This is essentially a mobile application since stocks of foam concentrate can be moved to where it is required.

8. EXEMPTIONS

As pointed out very recently by Richter, Cordner and Brown Exemptions under the Stockholm Convention for manufacture or use in dispersive applications that ultimately release PFHxS, including the growing use of PFHxS in textile treatments, packaging and firefighting foams, will continue to contribute to widespread environmental contamination with PFHxS and other perfluoroalkyl substances. Exemptions for PFAS production and use are not just the concern of countries that register for them. Exemptions permit ongoing, wider global and irreversible PFAS pollution.

PFAS give rise by transformation to perfluoroalkyl end-products such as perfluorocarboxylic acids (PFCA) or perfluoroalkyl sulphonic acids (PFSA) including PFHxS. These perfluorinated end-products involve:

(i)   **Extreme persistence** in the environment, i.e., effectively permanent pollutants.

(ii)   **Biological half-lives** for humans of the order of years.

(iii)   **Mobility in both soil and groundwater** resulting in contamination of the water table effecting both agricultural and drinking water supplies.

(iv)   **Bio-accumulative potential** and/or toxicity to varying degrees.

(v)   **Pollution far from the source of contamination** impacting snow, sediments, streams, rivers, lakes, estuaries and the marine environment due to persistence and mobility.

(vi)   **Long-range transport** (LRT) via atmospheric and oceanic transport on a global scale.

(vii)   **Elevated PFAS levels in biota** including humans and top predators such as polar bears or high trophic level marine species being particularly effected.

(viii) **Increasing PFAS levels in blood** for the general population and those who are occupationally exposed, such as firefighters, with probable links to a range of disorders and diseases.

(ix)   **Major socio-economic impacts** are being felt and increasing with rising levels of public concern.

(x)   **Intergenerational impacts** are likely because of their dispersion and extreme persistence.

> **The Precautionary Principle obligations (Preston, 2017) under international environmental law are triggered for assessment factors involving long-term and widespread harm but are generally ignored or poorly applied by manufacturers, industry and end-users.**

8.1. LAST-MINUTE PROPOSALS FOR EXEMPTIONS

Unfortunately, the multi-year evaluations conducted by the POPRC and their subsequent recommendations have often been undermined at Conferences of the Parties (COP) by last-minute proposals for exemptions that the Committee did not recommend for scientific reasons. This is damaging to the Committee and the evaluation process and fails to account for significant factors that are pertinent to long-term sustainability.

Concerns over last-minute proposals for exemptions have resulted in consensus decisions at COP8 when significant numbers of new exemptions were proposed for both DecaBDE and SCCPs. Parties were sufficiently concerned about this practice to mandate a review process examining exemptions for these substances. Decisions SC-8/13 and SC-8/14 outline a process for Parties requesting specific exemptions for these substances to provide information on transitioning to alternatives for DecaBDE and SCCPs along with information on production, uses, efficacy and efficiency of possible control measures, control and monitoring capacity and any national or regional control actions. This will be part of the Committee's work in 2019 - 2020.

9. CONCLUDING REMARKS

A rigorous listing proposal for PFHxS in Annex A is justified by the following:

- **PFHxS co-occurs with PFOS** due to ongoing production by ECF.

- **Co-exposure occurs with PFOS** especially in occupational exposure.

- **Toxicity is similar to PFOS**, or worse due to bioaccumulation.

- **PFHxS has a long elimination half-life** in humans, about twice that of PFOS.

- **It is more mobile in soils and waters** and recirculates in the environment.

- **It is in ongoing use in dispersive applications** such as firefighting foams.

- **It is a contaminant in sulfluramid** with widespread direct releases.

- **It is taken up into edible crops** from effluent and biosolids application.

- **It is expensive and difficult** to remediate in soils.

- **Removal from drinking water** is difficult and expensive.

Based on what is now known about the environmental profile and PBT properties of PFHxS and PFHxS-related compounds and the existence of alternatives, there should be no specific exemptions allowed under the Stockholm Convention. This is especially true considering directly dispersive applications as well as diffuse releases from products in use or at end-of-life disposal. For human health values the long elimination half-life for PFHxS presents a very significant risk factor if releases are allowed to continue (Figure 9).

In addition to the ongoing use of PFHxS in various direct applications, it must also be recognised that continued use of PFOS products such as sulfluramid will act as a source of environmental and human contamination with PFHxS because of unavoidable co-contamination in the ECF production of PFOS.

It is far too expensive and not commercially viable for manufacturers to remove these by-products from PFOS for its subsequent use in a technical grade material. This reinforces the urgency of globally eliminating PFOS use.

Rather than dealing with individual PFAS chemicals on an individual one-by-one basis, it is more prudent from a regulatory point of view to deal with classes of like compounds

as has been long accepted for a range of toxic chemicals such as PAHs, benzo-dioxins, and PCBs. This should also be the approach for all PFAS substances and their related precursors. Such an approach would be totally in keeping with the Precautionary Principle established by the Rio Convention in the 1992

In the US the Center for Disease Control (CDC) are now directed to undertake the collection of detailed data on the occurrence of cancer in fire fighters. The data will provide scientists with specialized information needed to research the relationship between these diseases and the job, strengthening understanding of probable links between firefighting and cancer and thus potentially leading to better prevention and safety protocols.
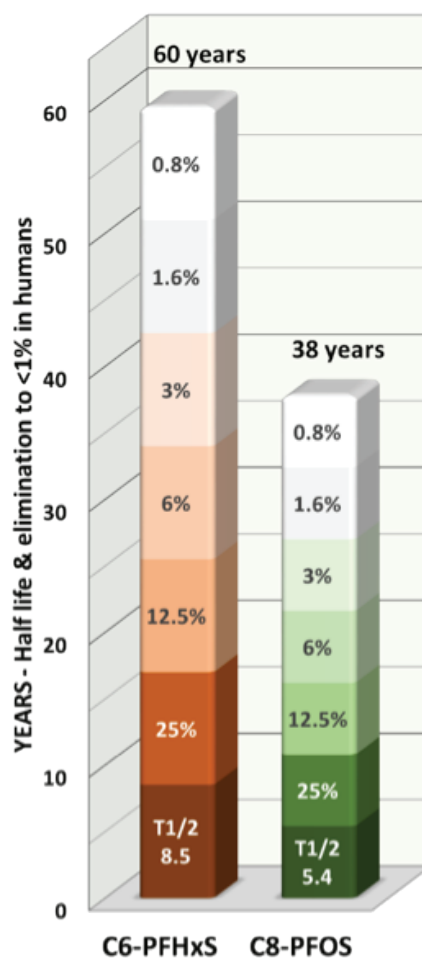

Figure 9. Human bio-elimination of PFHxS and PFOS.

10. REFERENCES

3M Company Minnesota, "3M Fluorad FC-95 Fluorosurfactant SDS," 1998.

3M Company Minnesota. "3M Phasing Out Some of Its Speciality Materials." MInnesota, 2000.

3M Company Minnesota. "THE SCIENCE OF ORGANIC FLUOROCHEMISTRY 3M The Science of Organic Fluorochemistry." Vol. OPPT-2002-, 1999.

Backe, Will J, Thomas C Day, Jennifer A Field, and Life Science Building. "Zwiterionic, Cationic, and Anionic Fluorinated Chemicals in Aqueous Film Forming Foams Formulations and Groundwater from U.S. Military Bases by Non-Aqueous Large-Volume Injection HPLC-MS/MS." *Environmental Science and Technology* 47 (2013): 5326–5234.

BiPRO M-961|2018. "Investigation of Sources to PFHxS in the Environment Investigation of Sources to PFHxS in the Environment Final Report," 2018. http://www.bipro.de.

Brendel, Stephan, Éva Fetter, Claudia Staude, Lena Vierke, and Annegret Biegel-Engler. "Short-Chain Perfluoroalkyl Acids: Environmental Concerns and a Regulatory Strategy under REACH." *Environmental Sciences Europe* 30, no. 1 (2018). https://doi.org/10.1186/s12302-018-0134-4.

Busch, J, L Ahrens, Z Xie, R Sturm, and R Ebinghaus. "Polyfluoroalkyl Compounds in the East Greenland Arctic Ocean." *Journal of Environmental Monitoring* 12, no. 6 (2010): 1242–46. https://doi.org/10.1039/c002242j.

Dauchy, Xavier, Virginie Boiteux, Adeline Colin, Jessica Hémard, Cristina Bach, Christophe Rosin, and Jean François Munoz. "Deep Seepage of Per- and Polyfluoroalkyl Substances through the Soil of a Firefighter Training Site and Subsequent Groundwater Contamination." *Chemosphere* 214 (January 1, 2019): 729–37. https://doi.org/10.1016/j.chemosphere.2018.10.003.

Dickenson, Eric RV, and Christopher Higgins. "Treatment Mitigation Strategies for Poly- and Perfluoroalkyl Substances," 2016.

Ding, Guanghui, and Willie J.G.M. Peijnenburg. "Physicochemical Properties and Aquatic Toxicity of Poly- and Perfluorinated Compounds." *Critical Reviews in Environmental Science and Technology* 43, no. 6 (2013): 598–678. https://doi.org/10.1080/10643389.2011.627016.

European Chemicals Agency (ECHA). "Agreement Of The Member State Committee On The Identification Of Perfluorohexane-1-Sulphonic Acid And Its Salts As Substances Of Very High Concern," 2017.

European Chemicals Agency (ECHA). "Annex XV Restriction Report Proposal For A Restriction. Proposal for a Restriction. SUBSTANCE NAME(S): Perfluorohexane Sulfonic Acid (PFHxS), Its Salts and PFHxS-Related Substances.," 2019.

Foreign Affairs Defence and Trade References Committee. *Inquiry into Firefighting Foam Contamination: Part B - Army Aviation Centre Oakey and Other Commonwealth, State and Territory Sites*, 2016.

Foreign Economic Cooperation Office, Ministry of Environmental Protection (FECO), and Hubei Academy of Environmental Sciences (HAES). "GEF - Reduction and Phase-out of PFOS in Priority Sectors in China: Part I Environmental Management Framework." January, 2017.

Gable. M. "The Environmental Impact of Fire Service Activities." *International Fire Fighter* Setember (2017): 36–38.

Hatton, Jim, Chase Holton, and Bill DiGuiseppi. "Occurrence and Behavior of Per- and Polyfluoroalkyl Substances from Aqueous Film-Forming Foam in Groundwater Systems." *Remediation* 28, no. 2 (March 1, 2018): 89–99. https://doi.org/10.1002/rem.21552.

Huang, Jun, Gang Yu, and Shengfang Mein. "PFOS in China: Production, Application & Alternatives (Presentation)." *UNEP Basel Convention Submission*, 2013, 1–51. http://www.basel.int/Implementation/POPsWastes/TechnicalGuidelinesarchives/tabid/2381/ctl/Download/mid/13358/Default.aspx?id=13&ObjID=11613.

Hunter Anderson, R., Dave T. Adamson, and Hans F. Stroo. "Partitioning of Poly- and Perfluoroalkyl Substances from Soil to Groundwater within Aqueous Film-Forming Foam Source Zones." *Journal of Contaminant Hydrology* 220 (January 1, 2019): 59–65. https://doi.org/10.1016/j.jconhyd.2018.11.011

Ignat'ev, N V, H Willner, and P Sartori. "Electrochemical Fluorination (Simons Process) – A Powerful Tool for the Preparation of New Conducting Salts, Ionic Liquids and Strong Brønsted Acids." *Journal of Fluorine Chemistry* 130, no. 12 (2009): 1183–91. https://doi.org/https://doi.org/10.1016/j.jfluchem.2009.09.016.

International POPs Elimination Network (IPEN). "Say No To Sulfluramid: Reasons For A Worldwide Ban On This Agritoxic Chemical ," 2019.

IPEN. "Fluorine-Free Firefighting Foams (3F) Viable Alternatives to Fluorinated Aqueous Film-Forming Foams (AFFF)," September (2018) <www.ipen.org>.

IPEN. "The Global Pfas Problem : Fluorine-Free Alternatives As Solutions Firefighting Foams And Other Sources" May (2019). <www.ipen.org>

Jiang, W, Y Zhang, L Yang, X Chu, and L Zhu. "Perfluoroalkyl Acids (PFAAs) with Isomer Analysis in the Commercial PFOS and PFOA Products in China." *Chemosphere* 127 (2015): 180–87. https://doi.org/10.1016/j.chemosphere.2015.01.049.

Kannan, K, S Corsolini, J Falandysz, G Oehme, S Focardi, and J P Giesy. "Perfluorooctanesulfonate and Related Fluorinated Hydrocarbons in Marine Mammals, Fishes, and Birds from Coasts of the Baltic and the Mediterranean Seas." *Environmental Science and Technology* 36, no. 15 (2002): 3210–16. https://doi.org/10.1021/es020519q.

Kärrman, A., K. Elgh-Dalgren, C. Lafossas, and T. Mskeland. "Environmental Levels and Distribution of Structural Isomers of Perfluoroalkyl Acids after Aqueous Fire-Fighting Foam (AFFF) Contamination." *Environmental Chemistry* 8, no. 4 (2011): 372–80. https://doi.org/10.1071/EN10145.

Kärrman, Anna, Ingrid Langlois, Bert van Bavel, Gunilla Lindström, and Michael Oehme. "Identification and Pattern of Perfluorooctane Sulfonate (PFOS) Isomers in Human Serum and Plasma." *Environment International* 33, no. 6 (August 1, 2007): 782–88. https://doi.org/10.1016/J.ENVINT.2007.02.015.

Kempisty, David M., Yun Xing, and Lee Ann Racz. *Perfluoroalkyl Substances in the Environment : Theory, Practice, and Innovation. CRC Press*, 2018.

Laitinen, J A, J Koponen, J Koikkalainen, and H Kiviranta. "Firefighters' Exposure to Perfluoroalkyl Acids and 2-Butoxyethanol Present in Firefighting Foams." *Toxicology Letters* 231, no. 2 (2014): 227–32. https://doi.org/10.1016/j.toxlet.2014.09.007.

Li, Fan, Jun Duan, Shuting Tian, Haodong Ji, Yangmo Zhu, Zongsu Wei, and Dongye Zhao. "Short-Chain Per- and Polyfluoroalkyl Substances in Aquatic Systems: Occurrence, Impacts and Treatment." *Chemical Engineering Journal* In press, no. 16 August online 122506 (August 16, 2019). https://doi.org/10.1016/J.CEJ.2019.122506.

Li, Yasong, Danielle P. Oliver, and Rai S. Kookana. "A Critical Analysis of Published Data to Discern the Role of Soil and Sediment Properties in Determining Sorption of per and Polyfluoroalkyl Substances (PFAS)." *Science of the Total Environment*. Elsevier B.V., July 1, 2018. https://doi.org/10.1016/j.scitotenv.2018.01.167.

Löfstedt Gilljam, John, Juliana Leonel, Ian T. Cousins, and Jonathan P. Benskin. "Is Ongoing Sulfluramid Use in South America a Significant Source of Perfluorooctanesulfonate (PFOS)? Production Inventories, Environmental Fate, and Local Occurrence." *Environmental Science and Technology* 2016: 50 (2), 653–59. https://doi.org/10.1021/acs.est.5b04544.

Merino, Nancy, Yan Qu, Rula A. Deeb, Elisabeth L. Hawley, Michael R. Hoffmann, and Shaily Mahendra. "Degradation and Removal Methods for Perfluoroalkyl and Polyfluoroalkyl Substances in Water." *Environmental Engineering Science* 33, no. 9 (September 1, 2016): 615–49. https://doi.org/10.1089/ees.2016.0233.

Naile, Jonathan E., A. Wayne Garrison, Jimmy K. Avants, and John W. Washington. "Isomers/Enantiomers of Perfluorocarboxylic Acids: Method Development and Detection in Environmental Samples." *Chemosphere* 144 (February 1, 2016): 1722–28. https://doi.org/10.1016/J.CHEMOSPHERE.2015.10.075.

National Research Council (U.S.). Committee on the Design and Evaluation of Safer Chemical Substitutions., National Research Council (U.S.). Board on Chemical Sciences and Technology., National Research Council (U.S.). Board on Environmental Studies and Toxicology., and National Research Council (U.S.). Division on Earth and Life Studies. *A Framework to Guide Selection of Chemical Alternatives*, 2014.

Norway. "Perfluorohexane Sulfonic Acid (PFHxS), Its Salts and PFHxS- Related Compounds Draft Risk Management Evaluation (RME) for the Stockhom Convention POPRC15," no. May (2019): 1–86.

Pancras, T, G Schrauwen, T Held, K Baker, I Ross, and H Stenders. "Environmental Fate and Effects of Poly-and Perfluoroalkyl Substances (PFAS) ." *CONCAWE Brussels (Arcadis)*, 2016.

Patlewicz, Grace, Ann M. Richard, Antony J. Williams, Christopher M. Grulke, Reeder Sams, Jason Lambert, Pamela D. Noyes, *et al.* "A Chemical Category-Based Prioritization Approach for Selecting 75 Per- and Polyfluoroalkyl Substances (PFAS) for Tiered Toxicity and Toxicokinetic Testing." *Environmental Health Perspectives* 127, no. 1 (January 1, 2019): 14501. https://doi.org/10.1289/EHP4555.

Preston, B.J. "The Judicial Development of the Precautionary Principle" Queensland Government Firefighting Foam Management Seminar, Brisbane (2017).

Renner, R. "The Long and Short of Perfluorinated Replacements." *Environmental Science and Technology* . Vol. 40, 2006. https://pubs.acs.org/sharingguidelines.

Ross, Ian, Jeffrey McDonough, Jonathan Miles, Peter Storch, Parvathy Thelakkat Kochunarayanan, Erica Kalve, Jake Hurst, Soumitri S. Dasgupta, and Jeff Burdick. "A Review of Emerging Technologies for Remediation of PFAS." *Remediation Journal* 28, no. 2 (2018): 101–26. https://doi.org/10.1002/rem.21553.

Rotander, A, A Kärrman, L M Toms, M Kay, J F Mueller, and M J Gómez Ramos. "Novel Fluorinated Surfactants Tentatively Identified in Firefighters Using Liquid Chromatography Quadrupole Time-of-Flight Tandem Mass Spectrometry and a Case-Control Approach." *Environmental Science and Technology* 49, no. 4 (2015): 2434–42. https://doi.org/10.1021/es503653n.

Sartori, P., and N. Ignat'ev. "The Actual State of Our Knowledge about Mechanism of Electrochemical Fluorination in Anhydrous Hydrogen Fluoride (Simons Process)." *Journal of Fluorine Chemistry* 87, no. 2 (1998): 157–62. https://doi.org/10.1016/S0022-1139(97)00139-5.

Sasaki, Toshiyuki, Akiko Egami, Tomoko Yajima, Hidehiro Uekusa, and Hisako Sato. "Unusual Molecular and Supramolecular Structures of Chiral Low Molecular Weight Organogelators with Long Perfluoroalkyl Chains." *Crystal Growth and Design* 18, no. 7 (July 5, 2018): 4200–4205. https://doi.org/10.1021/acs.cgd.8b00779.

Schultz, Melissa M., Douglas F. Barofsky, and Jennifer A. Field. "Quantitative Determination of Fluorotelomer Sulfonates in Groundwater by LC MS/MS." *Environmental Science and Technology* 38, no. 6 (2004): 1828–35. https://doi.org/10.1021/es035031j.

Stockholm Convention (POPRC). "POPRC-15 Stockholm Convention on Persistent Organic Pollutants Draft PFHxS Risk Management Evaluation (RME)," no. May (2019): 1–38.

Taves, D.R, "Electrophoretic Mobility of Serum Fluoride." *Nature* 220, (1968a): 582–83.

Taves, D.R. "Evidence That There Are Two Forms of Fluoride in Human Serum." *Nature* 217, (1968b): 1050–51.

Twohig, Marian, Nicholas Ellor, Keith Worrall, Tim Jenkins, and Gordon Kearney. "Separation of Branched PFOS by UPLC with MS MS Detection." *Wellington Laboratories: Waters Application Note* Waters_App, no. Waters Corporation (2006): 1–7.

UK Health and Safety Executive (HSE). "Control of Major Accident Hazards Buncefield: Why Did It Happen?," 2011. www.hse.gov.uk/comah/remodelling/index.htm

Wang, Yuan, Sanjay Beesoon, Jonathan P. Benskin, Amila O. De Silva, Stephen J. Genuis, and Jonathan W. Martin. "Enantiomer Fractions of Chiral Perfluorooctanesulfonate (PFOS) in Human Sera." *Environmental Science and Technology* 45, no. 20 (October 15, 2011): 8907–14. https://doi.org/10.1021/es2023434.

Wen, Bei, Ying Pan, Xiaoli Shi, Hongna Zhang, Xiaoyu Hu, Honglin Huang, Jitao Lv, and Shuzhen Zhang. "Behavior of N-Ethyl Perfluorooctane Sulfonamido Acetic Acid (N-EtFOSAA) in Biosolids Amended Soil-Plant Microcosms of Seven Plant Species: Accumulation and Degradation." *Science of the Total Environment* 642 (November 15, 2018): 366–73. https://doi.org/10.1016/j.scitotenv.2018.06.073.

Zabaleta, Itsaso, Ekhine Bizkarguenaga, Deborah B.O. Nunoo, Lara Schultes, Juliana Leonel, Ailette Prieto, Olatz Zuloaga, and Jonathan P. Benskin. "Biodegradation and Uptake of the Pesticide Sulfluramid in a Soil-Carrot Mesocosm SUPPLEMENTAl INFORMATION ." *Environmental Science and Technology* 52, no. 5 (March 6, 2018): s1–38. https://doi.org/10.1021/acs.est.7b03876.

Zhang, Lai, Jianguo Liu, Jianxin Hu, Chao Liu, Weiguang Guo, and Qiang Wang. "The Inventory of Sources, Environmental Releases and Risk Assessment for Perfluorooctane Sulfonate in China." *Environmental Pollution* 165 (June 1, 2012): 193–98. https://doi.org/10.1016/J.ENVPOL.2011.09.001.

Zhao, S, T Zhou, L Zhu, B Wang, Z Li, L Yang, and L Liu. "Uptake, Translocation and Biotransformation of N-Ethyl Perfluorooctanesulfonamide (N-EtFOSA) by Hydroponically Grown Plants." *Environmental Pollution* 235 (2018a): 404–10. https://doi.org/10.1016/j.envpol.2017.12.053.

Zhao, S, T Zhou, B Wang, L Zhu, M Chen, D Li, and L Yang. "Different Biotransformation Behaviors of Perfluorooctane Sulfonamide in Wheat (Triticum Aestivum L.) from Earthworms (Eisenia Fetida)." *Journal of Hazardous Materials* 346 (2018b): 191–98. https://doi.org/10.1016/j.jhazmat.2017.12.018.

IPEN

IPEN

for a toxics-free future