

Precautionary Stance

Understanding the F-GAS Forever Chemicals is unforgettable.

I have at last deemed myself to be semi-chemically minded after reading a 193 page report on PFAS (Poly- and perfluoroalkyl substances) chemicals in the UK and across the globe issued by the UK Health and Safety Executive.

The report goes into lots of varied details concerning all the differing types of PFAS chemicals and there spread across all parts of industry – food chain – human health and environmental areas.

Used in areas where moisture repellent is needed like Non Stick items , food wrappers, furniture polish and F-Gas.

It also highlights the many gaps we have in the UK as to the understanding of these chemicals and there type and quantity in the UK.

*Analysis of the most appropriate regulatory management options (hse.gov.uk)

(Link to the full report)

But as I sit here and try and digest the key takeaways I would say that, there is a very genuine concerns about these chemicals and a lot of talk of the ones used in the HFC – HFO refrigerant gases.

In the UK and with some of the links to the EU we have our REACH obligations and we have our F-GAS obligations and there is a multitude of other regulatory bodies that need to be reported on or data collected from within, and its seems that in some cases these differing areas of Health and Safety are missing that connective piece of the big Jigsaw puzzle that is called the PFAS Chemistry set.

"With a scarcity of information on the toxicology of most PFAS substances, there is potential concern regarding the risk to human health."

This highlights the Global issues with the PFAS Chemicals -

" There is no single globally adopted definition of PFAS for human health or environmental regulation. For the purposes of this RMOA, PFAS are defined as: Fluorinated substances that contain at least one fully fluorinated methyl carbon atom (without any hydrogen, chlorine, bromine or iodine atom attached to it), or two or more contiguous perfluorinated methylene groups (–CF2–)."

The report in terms of the refrigeration sector confirms that most the of the release of the PFAS chemicals in the sector are sent into the air. However, in the bigger scheme the UK Environment Agency have confirmed where they are finding the chemicals.

"Monitoring undertaken by the Environment Agency since 2014 suggests some PFAS are detectable in most groundwater, surface water bodies and biota in England"

The Environment Agency have also gone to the extend to say that due to lack of real evidence on the range of PFAS chemicals and there affect – that they should take the *"Precautionary Stance"* and they have worked through the types and applications and have identified alternative solutions to the use of refrigerants containing PFAS chemicals like HFC – HFO types. They also highlight that refrigerant gas types of PFAS chemicals are one of the largest in terms of tonnage in the UK and also the largest in terms of leakage into the Environment.

This is driving a thought that we need to include all F-GAS PFAS chemicals into the scope of REACH and then obviously COSHH etc.

This table highlights the estimated loss of F-GAS per annum in GB. They do say this is an estimate and a starting point.

Table 2.3.2: Summary of GB PFAS emissions estimates by industry sector

Sector	Tonnage in use (t/y)	Estimated emissions (t/y)	Environment al compartment
F-gases	52,000	4,050	air

"The PRTR value does not include emission estimates from wide ranging consumer or professional uses, such as leakage from refrigeration and air conditioning equipment, which has been estimated at 5% of the total refrigerant stock (UK call for evidence submission; Tomlein and Tomlein, 2019)"

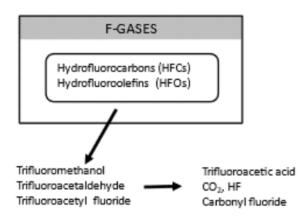
This table indicates the potential alternatives and also includes there *"Indication of potential hazards for alternatives"*

F-Gas	Refrigeration	Heat transfer	- Carbon Dioxide (CO _{2,})	CO ₂ is a greenhouse
		Working fluid	- Propane	Propane & isobutene
		Non flammable	- Isobutene	flammable.
	Mobile air conditioning	Heat transfer	- CO2	CO ₂ is a greenhouse
		Working fluids	- Propane	Propane is flammable

One comforting factor is that *"Human and environmental exposure to PFAS in GB can be reasoned to be prevalent and comparable to that seen on a global scale."*

So simple fact is that we are all in this together.

What puts PFAS Chemical and F-GAS apart is that when F-GAS breaks down they can turn into some unusual chemicals or TFA'S.



I was always told as an engineer that when CFC's where shown the naked flame of a gas torch they turned into World War 1 mustard gas. Urban legend or truth? I am sure that someone can help solve that mystery for me.

All this aside how concerned showed we be about these PFAS and there spinoff chemicals -

"The application of biosolids and waste materials is considered a significant route of entry of PFAS to the environment and the food chain."

We are eating them and in some areas drinking them in the water.

"Monitoring data from England (2014 – 2019) indicated PFAS are widely present in surface and groundwaters."

Also in terms of air quality, I know I go on about diesel fumes and eDonkeyfication but we can add the PFAS chemicals as well if you wish, and I would like the ULEZ to also cover this please Sadiq Khan and Transport For London.

PERFORCE project 2005-2006 "Concentrations in urban air were higher than semi-rural."

"Human exposure to PFAS arises from primary sources (consumer uses of PFAS containing products, occupational exposures) and secondary sources (via environmental contamination of, for example, drinking water and food)."

"In a GB context, the Food Standards Agency (FSA) has recently been made aware that the vast majority of paper packaging manufactured in the UK by Confederation of Paper Industry member companies does not use PFAS. PFAS are now predominantly used only in specialist packaging that has particular technical requirements such as moisture or grease resistance, for example for use in microwaveable popcorn bags (COT, 2022)"

The report goes on to state that inside and outside you are already breathing in PFAS type chemicals and indicates that one area of the UK that had tests completed showed high levels due to the location of a local factory and wind direction.

"United Kingdom. Maximum reported concentrations at Oyamazaki and Hazelrigg were 919 and 828 pg/m3 , respectively. ATSDR (2021) attributed the elevated concentrations at the Hazelrigg

location to emissions from a fluoropolymer production plant located 20 km upwind of this semirural community"

The average levels found in internationals testing was.

"Mean PFOA levels ranged from 1.54 to 15.2 pg/m3"

Now lets talk about the water we drink.

"Drinking water PFAS have been found in groundwater, and in the raw water of drinking water supplies on a global scale. However, the highest impacts are usually associated on, or near, industrial and other sites with a history of PFAS use e.g., fire-fighting or training facilities such as airport sites or military bases"

"Exposure to PFAS in the general population is thought to be at lower levels compared with those affected by occupational exposure or localised contamination (ATSDR, 2021)."

"Communities in the USA located near fluorochemical facilities, were reported to be at potential risk of higher PFAS exposures: PFOA, PFOS, PFBA, PFBS, PFNA and PFHxS have been detected in the municipal drinking water and private wells of some communities located near fluorochemical facilities (ATSDR, 2021)."

I would highly recommend people take the time to see a film called – "Dark Water" and also check out this article in WECT news from March 2nd 2023 in North Carolina *"Court denies motion by Chemours to dismiss NC PFAS lawsuit"*

"The state and Attorney General Josh Stein sued DuPont, Chemours and other related companies in Oct. 2020 to hold them accountable for the environmental impact of their use of PFAS."

Court denies motion by Chemours to dismiss NC PFAS lawsuit (wect.com)

Now back to the UK and the UK Governments stance on water quality.

"The Drinking Water Inspectorate (DWI) has issued guidance to the water industry on PFAS, using a risk based approach and a tiered system of actions based on sampling results. The Drinking Water Inspectorate is working with water companies to understand the risk to supplies from PFAS (DWI, 2021). "

"WHO have recently published a background document for the development of guideline standards PFOS and PFOA in drinking water, of 0.1 μ g/l and total PFAS of 0.5 μ g/l. These values are being reviewed by UK government stakeholders against environmental concentration data."

In addition, in terms of trying to find out the impact and concerns to human health in the EU.

"3.2.3 Human biomonitoring data

PFAS has been included in the list of chemicals of concern in the European Human Biomonitoring (HBM4EU) / Health Protection Unit (HPRU) study (HBM4EU, 2022)."

So ongoing test on the areas of concentration are on going in the EU and we are hoping to use there collected data to help the UK in their assessments etc.

But I did pick up a new industry sector that might raise concerns for the future.

"GB exposures can be reasoned to be comparable to those seen on a global scale. As summarised by De Silva et al. (2021), the use of PFAS are widespread, covering personal care products, cosmetics, firefighting foams, textile treatments for stain and water repellence, food contact materials, medical devices and membranes in fuel cells, and for varied uses across many industries (Glüge et al., 2020)"

We also have to take this into account that -

"Current monitoring evidence is therefore only a partial picture of the number of PFAS present in the GB environment given monitoring occurs only for a small number of the total PFAS in use."

In the terms of potential Human Exposure – I.e a Transport Refrigeration engineer working with the gases and working with the oil etc.

"ATSDR established that workers involved in making or processing PFAS and PFAS containing materials are more likely to be exposed than the general population. It is clear that a worker's occupation and work activities can impact the specific PFAS they are exposed to, how much they are exposed to, and how they are exposed (as detailed by ATSDR, 2021)."

The report has admitted that in the top tier of groups identified -

"There are no GB human biomonitoring data for the PFAS groups identified in the bullet points."

"Ultimately, the limited exposure data for the majority of PFAS poses a significant challenge and a potential barrier to effective risk management"

Group	Reason for assessment		
	High tonnage/use	Manufactured in GB	Detected in the GB environment
Perfluoroalkenes	Y	Y	
Polyfluoroalkyl substances: HFCs, HFEs and HFOs	Y	Y	
PFECAs and precursors		Y	Y
PFEs, epoxides and vinyl ethers		Y	
Perfluoroalkanes and perfluorocycloalkanes		Y	

 Table 4.1.1: Groups identified for hazard assessment

In simple terms we have not enough data and or agreements on the scale of the potential issue and or the areas or people that are excessively affected or detected with high levels of PFAS chemicals.

But with phases like we have seen evidence of some carcinogen issues in rats -

"but that the information is insufficient to reach a firm conclusion on whether they are human carcinogens."

Or the lack of evidence in reproductively.

"There was insufficient information to indicate that PFAS were associated with other adverse development or reproduction outcomes in humans."

"There are indications from a developmental toxicity study that trifluoroacetic acid (TFA) (shortchain PFCAs) might cause rare abnormalities in rabbit offspring. This is important because TFA is an arrowhead substance to which many PFAS can transform, such as those with isolated CF3– moieties (which includes some substances used in pharmaceutical or biocide/pesticide applications)."

"PFCAs and precursors – short-chain The main potential concern identified for registered substances in this sub-group is developmental toxicity following exposure to trifluoroacetic acid (TFA)"

"In addition, the volatility of those substances identified as F-gases, e.g. polyfluoroalkyl substances: HFCs, HFEs and HFOs, fall into the category of difficult to test substances. This is due to their increased potential to partition to air within standard study designs. There is therefore uncertainty in interpreting data for a substance does not fall within the applicability domain of the study design, resulting in a reduction in reliability of data. Data should therefore be treated cautiously as inherent volatility would be observed in the natural environment."

"a reliable understanding of hazard for many PFAS is not yet possible (individually or at group level), beyond the accepted view that they are in general very persistent."

TFA – A new additional to F-GAS knowledge...

"Considering the short-chain PFCAs, many of these substances may have a hazard associated with PMT/vPvM type concerns. This hazard assessment notes that TFA is a substance of concern, since there are indications that it might cause developmental toxicity. In addition, in the EU proposal to restrict PFHxA, one of the lines of evidence presented was enrichment in plants (Brendel et al., 2018), which may be a potential route for entering the human food chain (see Section 3) and a potential for developmental toxicity was also highlighted. Thus, in line with the short chain PFSAs, it could be inferred that all chain lengths in between TFA and PFHxA, which encompass the short-chain PFCAs, might be problematic. In relation to TFA, it is noted that some of the substances in the HFCs, HFEs and HFOs group (i.e., a commercially significant, high tonnage group in the UK) are F-gases that could potentially transform to TFA under the correct conditions.

F-gases REACH registration information, a non-UK assessment and informal environmental assessments for several substances in the group 'polyfluoroalkyl substances: HFCs, HFEs and HFOs' did not highlight a hazard concern of relevance to this RMOA for human health. However, substances in this group can transform to TFA (itself a member of the short-chain PFCAs group), for which a potential concern for developmental toxicity has been identified. Some of the substances screened as P/vP or vM."

Does COSHH -- Come to help?

"COSHH can also impose a Workplace Exposure Limit (WEL). There are no current WELs for any PFAS due to the uncertainty with regard to human health hazard profiles of the various groups as well as the use in the workplace. Those that are classified as carcinogenic are subject to ALARP."

Does F-GAS Come to help?

GB regulation of F-gases

"F-gases are highly volatile hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulphur hexafluoride and other greenhouse gases that contain fluorine. They exert a Global Warming Potential (GWP) higher than carbon dioxide (CO2), sometimes many thousands of times higher (on a weight for weight basis). Introduced as replacements for the ozone-depleting chlorofluorocarbons (CFCs), the high GWP F gases are being phased downwards to meet climate change mitigation targets. EU Regulation No. 517/2014 25 on fluorinated greenhouse gases has been retained in UK law, and is enforced through The Fluorinated Greenhouse Gases Regulations 201526. It:

• establishes rules on containment, use, recovery and destruction of F-gases, and on related ancillary measures;

• imposes conditions on the placing on the market of specific products and equipment that contain, or whose functioning relies upon, F-gases;

• imposes conditions on specific uses of F-gases; and

• establishes quantitative limits for the placing on the market of HFCs. Annex I of the Regulation is a non-exhaustive list of specific HFCs, PFCs and sulphur hexafluoride."

EU Approach to PFAS and one that we have seen recently entering the EU Parliament -

"EU regulation of F-gases A proposed new F-gas Regulation was published on 5 April 2022. It proposes, amongst other things, going even further on the HFC phasedown and new bans. This is in line with a climate law proposal, which requires the European Commission to review, and where necessary revise, all relevant policy instruments to achieve the additional 2030 emission reductions."

In the USA there approach to PFAS Chemicals.

"5.2.2 United States of America – Federal risk management of PFAS

The US approach to PFAS sets out an important range of management approaches alongside EU activities. The following sections provide a summary of US activity for reference purposes. PFAS action plan

There are three central goals of the roadmap, with associated objectives:

• Research: Invest in research, development, and innovation to increase understanding of PFAS exposures and toxicities, human health and ecological effects, and effective interventions that incorporate the best available science.

• Restrict: Pursue a comprehensive approach to proactively prevent PFAS from entering air, land, and water at levels that can adversely impact human health and the environment.

• Remediate: Broaden and accelerate the clean-up of PFAS contamination to protect human health and ecological systems."

Interestingly the USA has product a PFAS Roadmap which includes-

"1. Consider the full lifecycle of PFAS; their properties, uses and exposure pathways.

2. Prevent PFAS from entering the environment in the first place.

3. Hold polluters and other responsible parties accountable"

Refer back to my previous note on the North Carolina State-

"The state and Attorney General Josh Stein sued DuPont, Chemours and other related companies in Oct. 2020 to hold them accountable for the environmental impact of their use of PFAS"

Whilst in the EU -

"Under the auspices of a European Human Biomonitoring (HBM4EU) / Health Protection Unit (HPRU) study (HBM4EU, 2022), general population samples of blood and urine are being collected, with publication of results expected in 2024"

Watch out for the TFA's

"Whilst there is no evidence that any PFAS causes adverse development or reproduction outcomes in humans, EFSA concluded that 'there may well be a causal association' between maternal serum PFOA and PFOS levels and low birth weight. The current assessment highlighted a potential concern for developmental toxicity in laboratory animals for two substances, the arrowhead substance trifluoroacetic acid (TFA) and EEA-NH4."

"A potential concern for developmental toxicity in experimental animals has been identified for the arrowhead substance TFA. Some of the substances in the HFCs, HFEs and HFOs group (i.e. a commercially significant, high tonnage group in GB) are F-gases that may transform to TFA."

Now we have some control with the F-GAS Regulations-

"Some PFAS are covered by the fluorinated gas (F-gas) regulation and will be subject to the internationally agreed phasedown of hydroflurocarbons. This includes five substances belonging to two PFAS groups (Polyfluoroalkyl substances: hydrofluorocarbons (HFCs), -ethers (HFEs), -olefins (HFOs) and Perfluoroalkanes and perfluorocycloalkanes) with another in the first category subject to monitoring and reporting."

Now a question about food contact or exposure should also be if there are F-GAS leaks within the refrigerated box, where food is being stored or transited. Common sense will say that in some cases like fruit or vegetables or hanging meats that the load will be contaminated with PFAS chemicals, that's if not already contaminated.

"It can be concluded that although there are measures in place within the GB framework, there are certain gaps in regulation for both consumer exposure (products and coatings, drinking water and food contact) and environmental control with emissions only controlled at source for certain installations and an EQS only in place for one individual PFAS in scope of this RMOA."

Now following on the TFA outcomes from the breakdowns of some of the F-GAS, they have stated that -

"The main concern based on the conclusion of this RMOA would be with respect to degradation to the arrowhead substance."

In the EU -

"Additionally, the European Commission has reviewed and revised the F-Gas regulations and is proposing to go beyond the current HFC phasedowns and introduce new bans. This could be considered in GB, however this is only applicable to certain groups of substances in scope of this RMOA"

In the USA – (Looks like they are acting decisively)

"Additionally, the USA has ended low volume exemptions and will review risk assessments for new chemicals before they enter the marketplace, with unreasonable risks required to be mitigated before manufacture can commence. At a federal level there are also controls of FFFs in the USA with a phase-out of all PFAS FFF by October 2024."

In the UK -

"The Agency considers that based on the current information, UK REACH authorisation is unlikely to be an effective regulatory tool to minimise PFAS emissions, primarily because of the time required to take substances (or groups) through the SEv process to enable SVHC identification, and the limited number of PFAS that might end up being SVHCs under the current criteria due to the uncertainty on the hazard profile of many of the PFAS groups"

But what we have concluded is that we need to increase the amount of PFAS within the scope of the UK REACH regulations.

Table 6.2.1: UK REACH registered volatile PFAS not included in Annex I or II of
the F-gas Regulations

PFAS	CAS No.	PFAS Group
Ethene, 1,1,2-trifluoro- 2-(trifluoromethoxy)-	1187-93-5	Perfluoroalkyl ethers (PFE), epoxides & vinyl ethers
Hexafluoropropene (1- Propene, 1,1,2,3,3,3- hexafluoro-)	116-15-4	Perfluoroalkenes
3,3,4,4,4- Pentafluorobut-1-ene	374-27-6	Polyfluoroalkyl substances: hydrofluorocarbons (HFCs), - ethers (HFEs), -olefins (HFOs)
(Z)-1-Chloro-2,3,3,3- tetrafluoropropene	111512-60-8	Polyfluoroalkyl substances: halides (i.e. iodide, chloride and bromide)

It is concluded that these PFAS could be considered for inclusion in the F-gas regulations.

The report starts to conclude -

"Further evaluation and investigation of substances that have been highlighted to be of concern"

"• The arrowhead substance TFA has been identified as a concern for developmental toxicity, it is noted that some of the substances in the HFCs, HFEs and HFOs group (i.e. a commercially significant, high tonnage group in the UK) are F-gases that may transform to TFA. Further assessment (e.g. substance evaluation within UK REACH or informal evaluation) could be carried out on the arrowhead substance TFA and its precursors due to the concern highlighted for developmental toxicity.

Such an exercise could be extended to other registered PFAS to assess whether additional data could be sought to clarify the risks they pose to the environment and human health. For formal evaluation of a substance under UK REACH the substance would have to be registered. TFA is not currently registered. For TFA, and also EEA-NH4 which also has concerns on reproductive toxicity, an MCL report could be considered to look into ensuring the substances have the correct classification and can be managed accordingly."

"A review of the F-gas regulations to determine whether additional PFAS registered under UK REACH should be brought within scope."

As I said at the start I am not a chemist but have a good understanding when reading articles of the good points and the potential bad points.

In this very through report, I consider that there are many bad points.

I have tried to keep my comments focused on the F-GAS elements to avoid being drawn into the overall discussion of these PFAS chemicals.

But I hope that the UK will team up further with the EU and USA to provide a total report and future control on these chemicals and I hope that we also adopt the new USA approach where no new chemical can reach the market without full evaluation.

I hope that these reports and the works done around the world will start to bring constructive controls on new chemicals and ask the question is there a natural version that will do the job.

I have also picked up in the report that there is a potential call to allow some areas that use the F-Gas to may be having exemptions.

My view is that we need a comprehensive approach with no niches – heat pumps and refrigeration were noted as possible exemptions even though in the report they state the possible alternatives that are, actually already being used today.

One phase to take away, would you be happy to live with this -

"Precautionary Stance"

About Norman Highnam MinstR

A leadership awarding winning and published transport refrigeration consultant having spent over 35 years in the industry at all levels from engineering to senior board level appointments.

I look to help people understand the industry and I actively lobby for engineer safety including the removal and control of all emissions in the transport refrigeration sector. <u>About (highnamassist.co.uk)</u>

