Analysis of C1-C4 Perfluoroalkyl Substances in House Dust from Japan, Colombia, and Belgium

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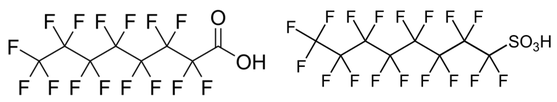
Introduction

What are perfluoroalkyl substances (PFAS)?

- Man-made chemicals which have fully fluorinated alkyl chain
- Classified as two large groups
  → Perfluorocarboxylic acids (PFCA)
  → Perfluorosulfonic acids (PFSA)
- Strong carbon-fluorine bond

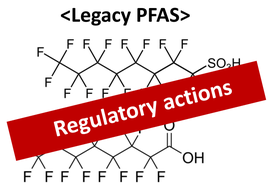


Harmful effects on environment and humans

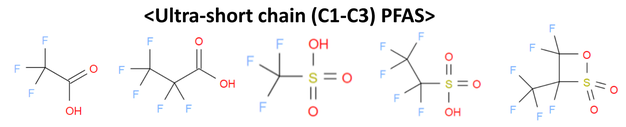
- Persistent
- Global environmental distribution
- Bioaccumulation and biomagnification
- Toxicity
  → hepatotoxicity
  → developmental toxicity
  → hormonal effects
  → carcinogenic potency
  → immunotoxicity

Shorter-chain PFAS

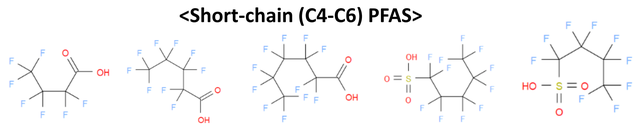
<Legacy PFAS>



<Ultra-short chain (C1-C3) PFAS>



<Short-chain (C4-C6) PFAS>



- Due to concerns about the adverse effects of PFAS exposure on human and wildlife health, various international organizations, individual countries, and local areas have implemented measures to **restrict PFAS manufacturing**
  → **manufacturers have turned to short-chain and ultra-short chain PFAS** and other fluorinated alternatives for commercial production (Chow et al., 2021)
- Short and ultra-short chain PFAS are equally as persistent as legacy PFAS, highly mobile, and have poor adsorption to organic matter, making them difficult to remove from the environment by natural barriers and treatment plants
  → **environmental accumulation can occur over time, leading to increased external exposure to humans and potential adverse effects** (Brendel et al., 2019)
- Most previous studies have primarily focused on long-chain PFAS, resulting in **limited available data regarding the occurrence of short and ultra-short chain PFAS in the environment and their exposure to the human body**

Occurrence of shorter-chain PFAS in house dust

- There is **one study** reporting concentrations of PFAS including ultra-short chain PFAS in indoor dust from **China** (Wang et al., 2021)
  → Their results provide evidence of the presence of shorter chain PFAS in indoors
  → However, they investigated **only 2 ultra-short chain PFAS in indoor dust**
- **Ingestion of dust** has been reported as an important exposure pathway for PFAS (Harrad et al., 2010; Shoeib et al., 2011; Egeghy and Lorber, 2010)
  → This highlights **the need for research on PFAS in house dust**

Research objectives

- To investigate **the occurrence of C1-C4 PFAS in house dust** collected from Belgium, Colombia, and Japan
- To compare of dust concentrations among three countries

Materials and method

Sample collection

	Belgium (2022)	Belgium (2019)	Japan	Colombia
N	**19**	**15**	**14**	**13**
Collection year	2022	2019	2017	2016

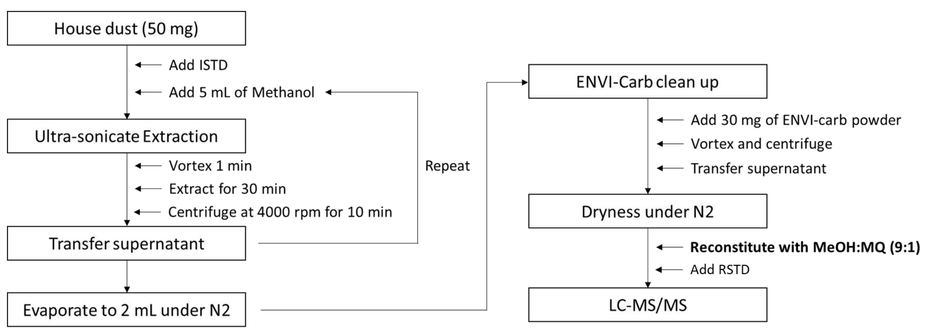
- House dust samples were collected using regular vacuum cleaners equipped with nylon socks

Target compounds

Compounds
TFMS (C1), TFAA (C2), PFEtS (C2), PFPrA (C3), PFPrS (C3), PFBA (C4), PFBS (C4)

- **4 PFSA and 3 PFCA** were investigated

Sample preparation



- Target C1-C4 PFAS in house dust samples were extracted by **ultrasonic extraction and ENVI-Carb clean-up method**
- ISTD: ^{13}C-TFAA, $^{13}C_3$-PFBA, and $^{13}C_3$-PFBS
- RSTD: $^{13}C_3$-PFPeA and $^{18}O_2$-PFHxS

Instrumental Analysis

- **Instruments (UPLC-MS/MS)**
  Agilent 1290 Infinity ultra-performance liquid chromatography & Agilent 6495 electrospray triple-quadrupole mass spectrometry
- **Column**
  Raptor Polar X (100 mm x 2.1 mm, 2.7 µm)
- **Mobile phase**
  A : 5 mM aqueous ammonium acetate + 0.05% formic acid
  B : Mixture of acetonitrile and methanol (60:40, v/v) + 0.05% formic acid

Quality Assurance/Quality Control

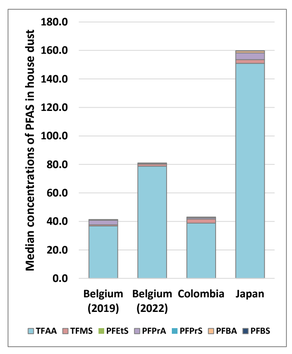
- Method detection limits (EPA method): 0.276 – 0.639 ng/g
- Accuracy: 69 – 139 %
- Precision: 3.39 – 6.18 %

Results and discussion

C1-C4 PFAS concentrations in house dust

<Concentrations and distribution pattern>

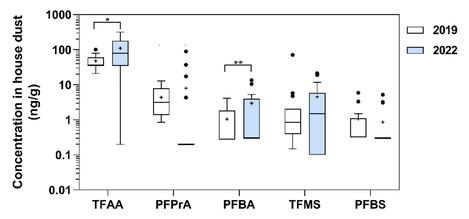
	Belgium (2019)			Belgium (2022)			Colombia			Japan		
	Range (DF)	Median	Mean	Range (DF)	Median	Mean	Range (DF)	Median	Mean	Range (DF)	Median	Mean
TFAA	20.9-100 (100)	36.8	47.7	ND-317 (95)	78.7	109	13.1-366 (100)	38.8	74.8	85.0-371 (100)	151	175
PFPrA	0.851-12.9 (100)	3.16	4.35	ND-88.9 (21)	ND	7.93	ND-66.2 (77)	0.874	8.23	ND-182 (86)	4.73	22.0
PFBA	ND-4.14 (40)	ND	1.05	ND-13.6 (47)	ND	2.95	ND-871 (46)	ND	67.7	ND-6.06 (57)	1.25	1.50
TFMS	ND-71.1 (80)	0.852	5.99	ND-21.2 (53)	1.46	4.52	ND-109 (85)	2.83	22.2	0.476-277 (100)	2.62	24.1
PFEtS		ND			ND			ND			ND	
PFPrS		ND			ND			ND			ND	
PFBS	ND-5.90 (33)	ND	1.07	ND-5.17 (16)	ND	0.874	ND-602 (38)	ND	47.3	ND-33.3 (29)	ND	2.86



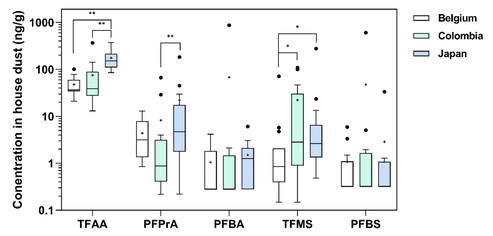
- In general, **TFAA showed the highest concentration** (median: 36.8–151 ng/g) and high detection frequencies (DF; 95–100%) in house dust collected from three countries
- PFEtS and PFPrS were not detected
- **TFAA, PFPrA, and TFMS were frequently detected in house dust from the three different countries**
  → TFMS is likely to be released into the environment through indoor use such as machine wash liquids/detergents, automotive care products, paints, and coating. This could explain the frequent detection of TFMS in house dust
  → TFAA and PFPrA can be present in outdoor air due to their formation through the atmospheric transformation of HFCs and HCFCs. This might contribute to their presence in house dust because outdoor air/dust can be a source of house dust

Comparison of dust concentrations

<Comparison between 2019 and 2022 results>



<Comparison among 3 countries>



- When comparing the concentrations in dust collected between 2019 and 2022, **significantly higher concentration of TFAA ($p < 0.05$) and PFBA ($p < 0.01$) were observed in 2022**
  → This suggested that **production/emissions of shorter-chain PFAS increase** due to regulations of longer-chain PFAS production and usage
- When comparing the concentrations of C1-C4 PFAS in house dust among the three countries, **TFAA and PFPrA showed statistically high concentrations** in house dust from Japan compared to Belgium and Colombia ($p < 0.01$)
- Concentrations of TFMS in Belgian dust were **statistically lower** than those from Colombia and Japan ($p < 0.05$)

Conclusion

- **This study is the first to investigate C1-C4 PFAS occurrence in house dust from Japan, Colombia, and Belgium**.
- Among target C1-C4 PFAS, **TFAA was the dominant compound in house dust**. TFAA is reported to form through the photodegradation or thermolysis of fluoropolymers, which are commonly employed in various consumer products such as electronic, cookware, and textiles. This could explain the higher concentration of TFAA in house dust compared to other compounds.
- **The increased TFAA and PFBA concentrations in Belgian dust from 2019 to 2022 suggest a shift in PFAS production towards shorter chain PFAS.**
- **Significant differences in TFAA, PFPrA, and TFMS concentrations among three countries were observed.** To explain this, further investigation into PFAS production, emission volumes, and usage patterns between countries is necessary.
- **Our findings underscore the widespread presence of C1-C4 PFAS in indoor environments, highlighting potential exposure for the general population.**

References

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