Development of a novel non-targeted approach in mass spectrometry for PFASs imaging

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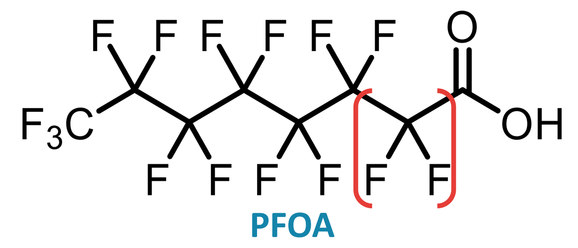
Introduction

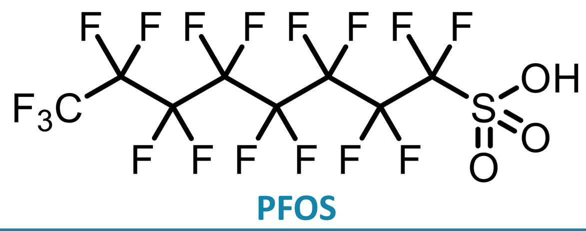
Per- and polyfluoroalkyl substances (**PFASs**) are synthetic chemicals widely used in industrial applications due to their resistance to water, oil, and heat. However, their **persistence in the environment** and **potential to bioaccumulate** pose significant risks to both ecosystems and human health. Despite numerous studies highlighting their toxic effects, challenges remain in fully understanding PFAS behavior in complex environmental samples. This project seeks to address these gaps by developing an **advanced analytical approach** using mass spectrometry imaging (**MSI**) combined with ion mobility spectrometry (**IMS**) to **map and identify PFASs** in biological tissues and soils.

Objectives

- Develop an analytical workflow to **image** and **characterize** all the PFASs present in biological tissues
  - → Assist other fields in **understanding the fate of PFASs** in environmental and biological matrices

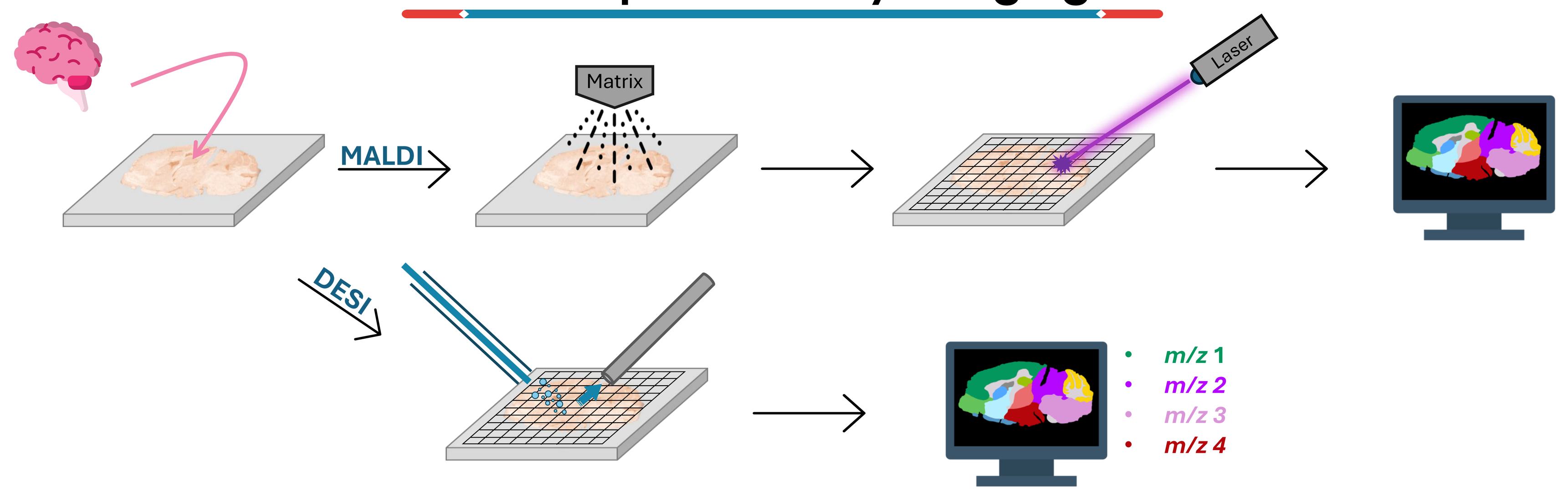

PFOA

- Discriminate PFASs from all the other compounds contained in the tissues through the use of IMS and advanced data treatment

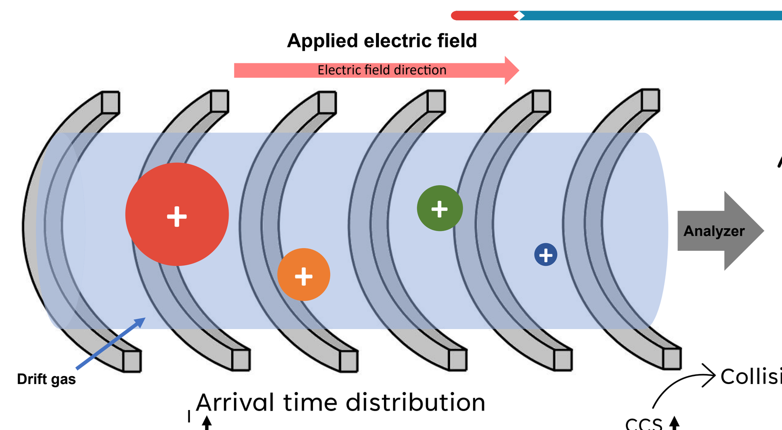

PFOS

Methods

Mass spectrometry imaging

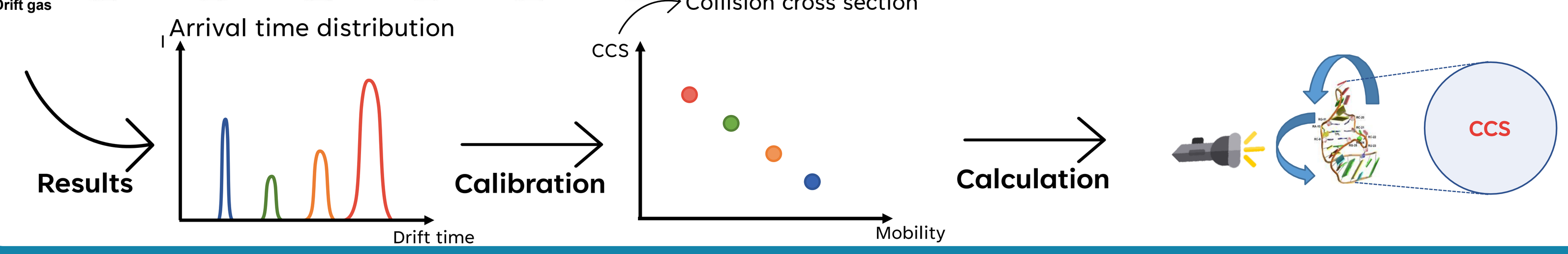


Ion mobility spectrometry



Separate ions based on shape and charge

- Enables the separation of isomers
- Possibility to establish **trends in apparent density**



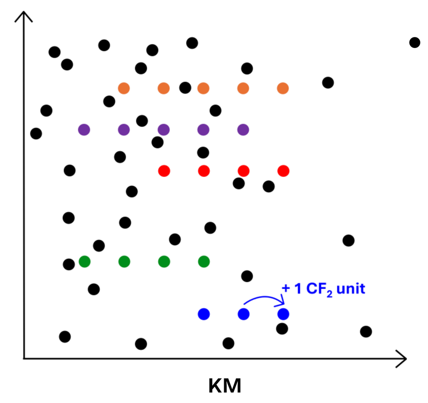
Data handling

Kendrick mass defect

$M_{Theoretical} = 49{,}9968$ For CF_2

$$KM = M_{Theoretical} \times \frac{50.0000}{49{,}9968}$$

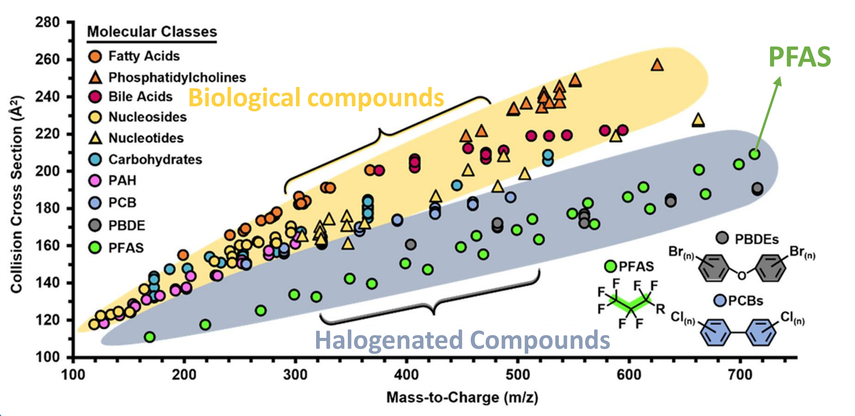
$$KMD = M_{Theoretical} - KM$$



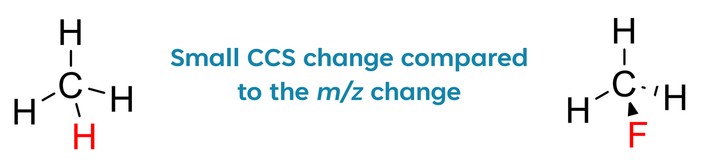
- Used to identify repeating molecular units by adjusting mass to a reference (here CF_2)
  - → Help revealing homologous PFAS series and distinguish similar compounds

Mobility/CCS trends

1



- **Halogenated** compounds can be **distinguished** from other compounds based on **CCS *vs.* m/z trends + isomers separation**



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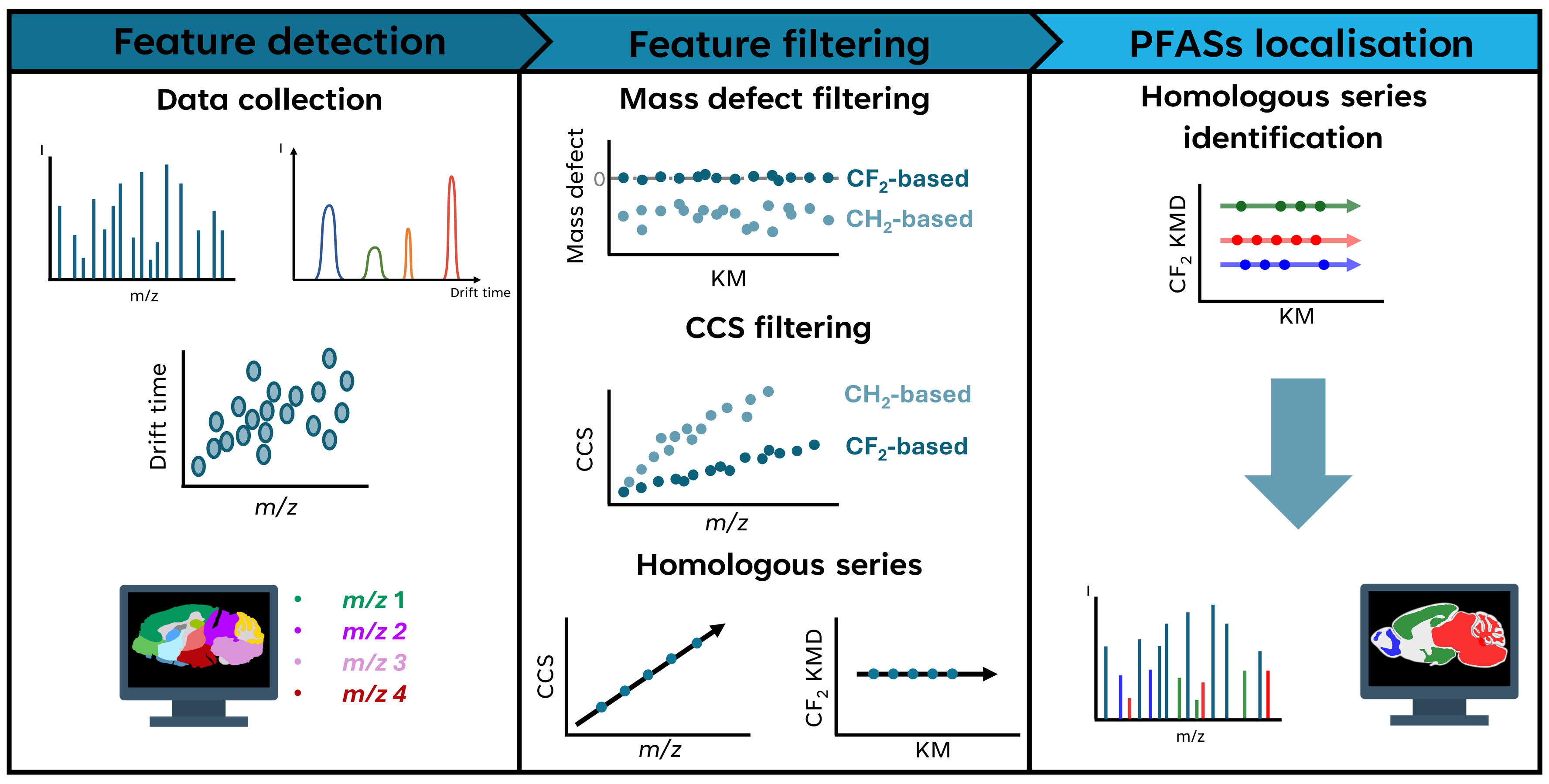
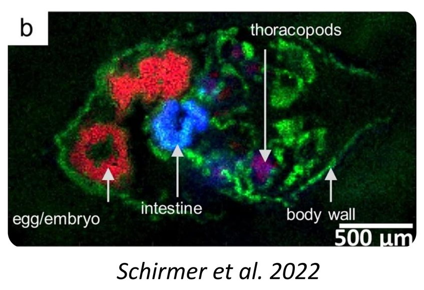


Models

Aquatic organisms

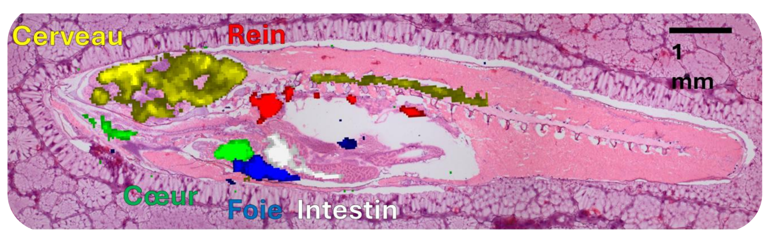
Invertebrate model *Daphnia Magna*:

- Controlled contamination of the media



Schirmer et al. 2022

Vertebrate: Zebrafish



Courtesy of Mathieu Tiquet (MSLab)

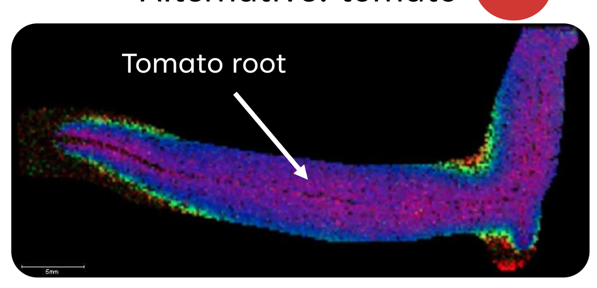
→ Comparison with LC-ESI-IM-MS

Vegetal organisms

Study of the migration and soils-plants transfers:

Cabbage and potato selected as models

Alternative: tomato



Debois et al. 2014

Growth in a controlled and contaminated media **(Agar gel)**

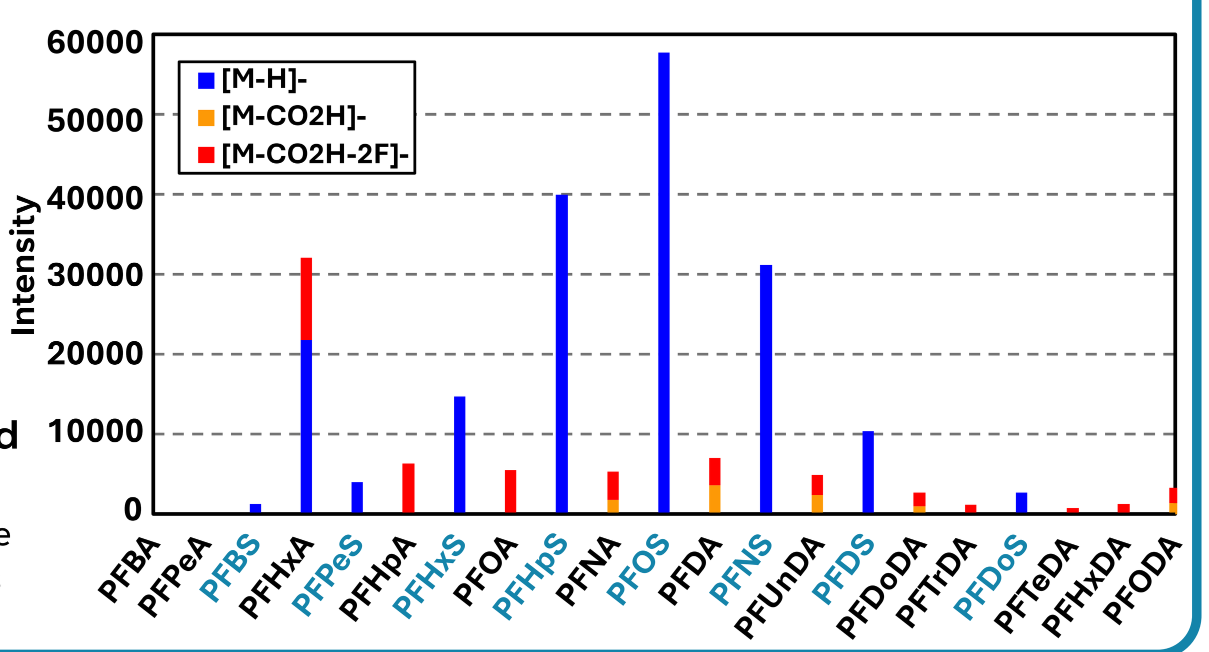
→ Comparison with LC-ESI-IM-MS

→ Real samples **(PFASFORWARD)**

MALDI optimization

Optimizations were performed on dried droplets

- Instrumental parameters and matrix optimization on a **PFAS mix** (In 50:50 $MeOH:H_2O$)
  - → Containing both sulfonic acids (**PFSAs**) & carboxylic acids (**PFCAs**)
- **CHCA** (better for **PFSAs**) & **DAN** (better for **PFCAs**) saturated solutions mixed (50/50)
  - → Improve matrix **crystallization**
- All the **PFSAs** were detected using this matrix mix with no fragmentation
- Most **PFCAs were detected**
  - → **$[M-CO_2H-2F]^-$** as the most intense species



Contact and further information

Conclusion & perspectives

✓ **Laser parameters and ionization mode were optimized**

→ PFASs detected using **negative** ionization **mode** and the **reflectron** geometry

✓ **CHCA delivered better performances for PFSAs detection while DAN showed better performances for PFCAs detection**

→ **Mixing** these two matrices allowed the **detection of both PFSAs** and **PFCAs**

→ Extensive **fragmentation** of **PFCAs** was observed (**$[M-CO_2H-2F]^-$** most intense species)

→ **No fragmentation** and more **efficient detection** of **PFSAs**

What's next?

- Test **other substrates** to assist the desorption/ionization
  - → For instance, **nanostructures**
- Implement and optimize **ion mobility** for PFASs analysis
  - → Develop and optimize the **data treatment workflow**
- First **imaging experiments**

MS LABORATORY SPECTROMETRY

References:
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4. Debois, D.; Jourdan, E.; Smargiasso, N.; Thonart, P.; De Pauw, E.; Ongena, M. *Anal Chem* 2014, *86* (9), 4431–4438.