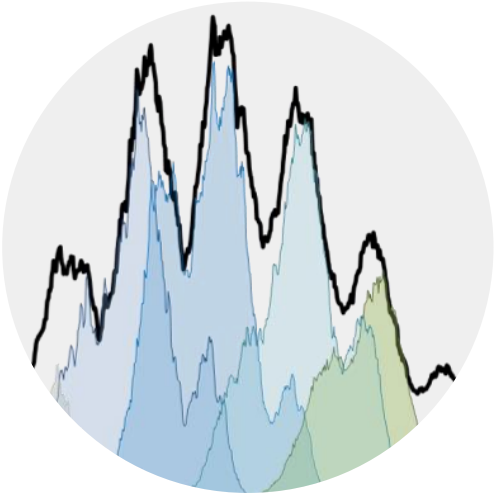
Polychlorinated alkanes (PCAs) – the next contaminant group of concern?

Occurrence, analysis and possible mitigation in oils and fats

Kerstin Krätschmer, Yang Shen, Wout Bergkamp, Stefan van Leeuwen



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FrieslandCampina · Unilever · Connect to Innovate · Noldus · NIOO · kikkoman seasoning your life · KeyGene · And many more...

WAGENINGEN UNIVERSITY & RESEARCH

Wageningen Food Safety Research

Official control laboratory for NL

National Reference Laboratory
All (bio)chemical compounds & viruses

EU Reference Laboratory
- Growth promotors
- Plant- & mycotoxins

Research Institute
2 Professors, 15 – 20 PhD students
Substantial EU, NWO funding

Training & Capacity Building
> 50 countries

24/7
Incident service for food/feed, environment, terrorist attacks

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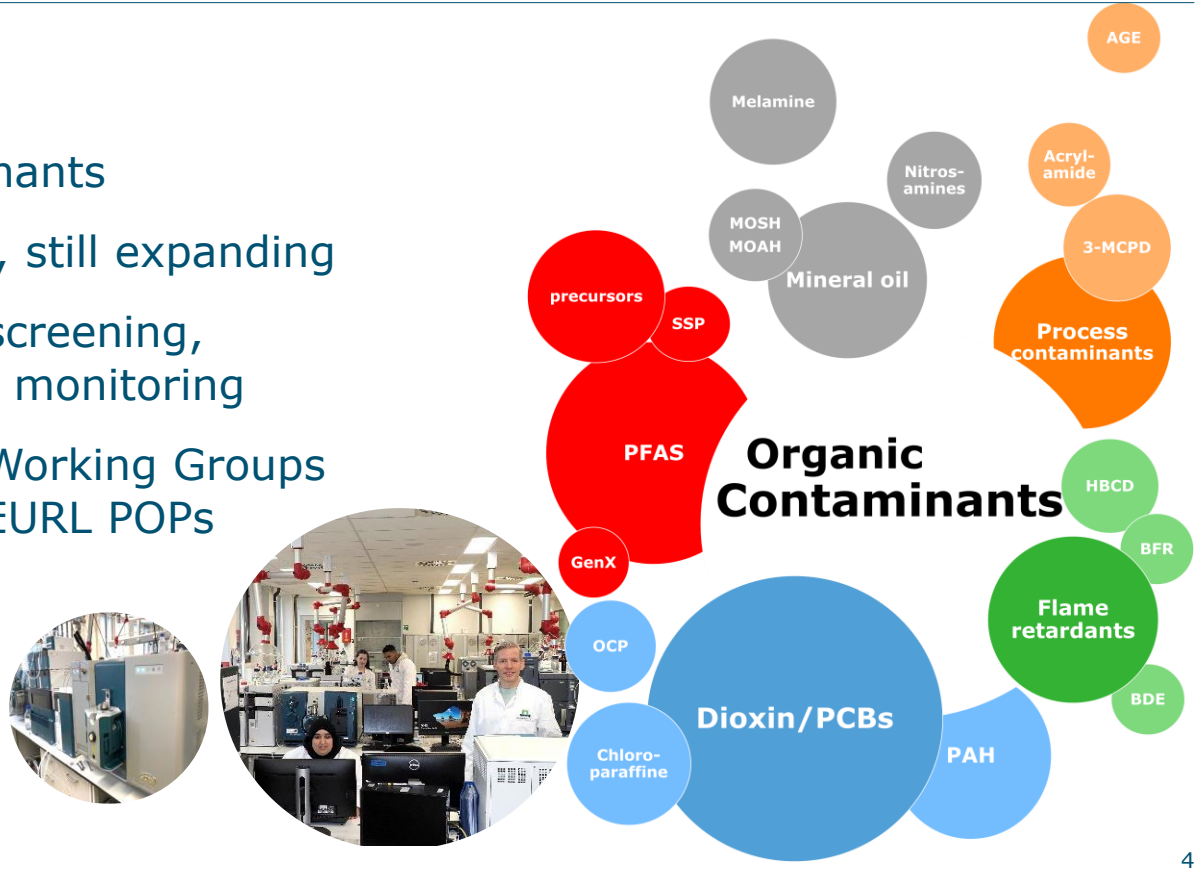
POPs analysis at WFSR

- Research unit Contaminants
- 26 dedicated members, still expanding
- Method development, screening, compliance testing and monitoring
- WFSR is chair of Core Working Groups PFAS and PCAs of the EURL POPs



Roadmap

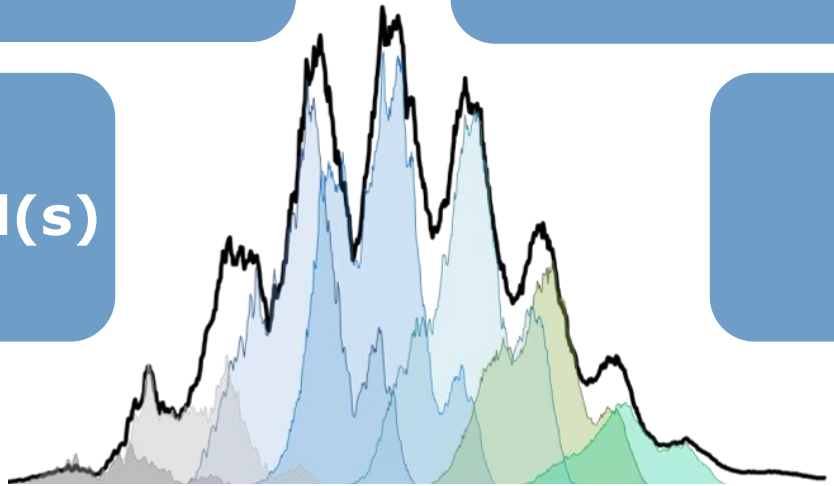
The basics

Our findings

PCA analysis

Occurrence in NL

The compound(s)



Mitigation?

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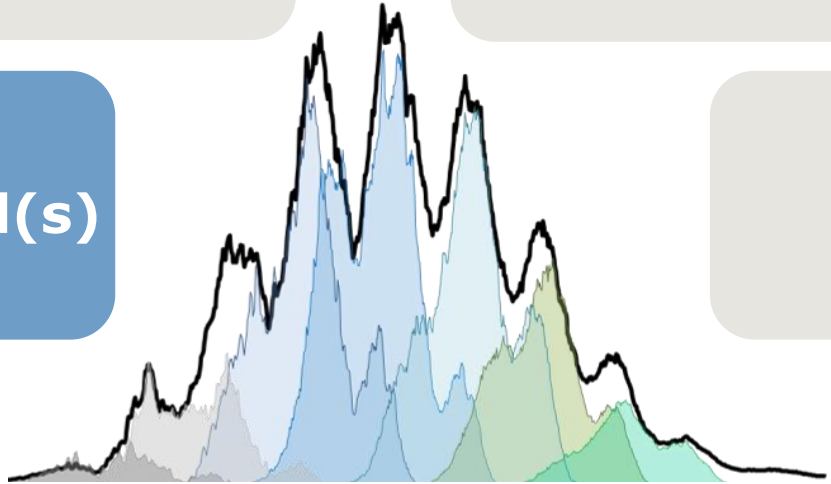


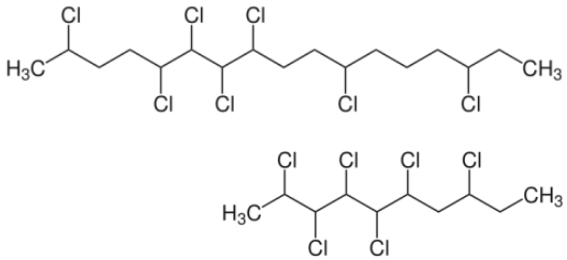
Mitigation?

What are polychlorinated alkanes?

- **Product: Chlorinated paraffins (CPs)**
- Flame retardant, plasticizer, lubricant
- Used in a wide variety of consumer and industrial products, pure or as ingredient:

What are chlorinated paraffins?

- Chlorinated paraffins (CPs): chlorinated alkane stock, 30-70% Cl
  - short-chain CPs (**SCCPs**): C_{10}-C_{13}
  - medium-chain CPs (**MCCPs**): C_{14}-C_{17}
  - long-chain CPs (**LCCPs**): C_{18+}



BUT:

- Definitions vary in literature and legislation
- Recommended harmonised terms published

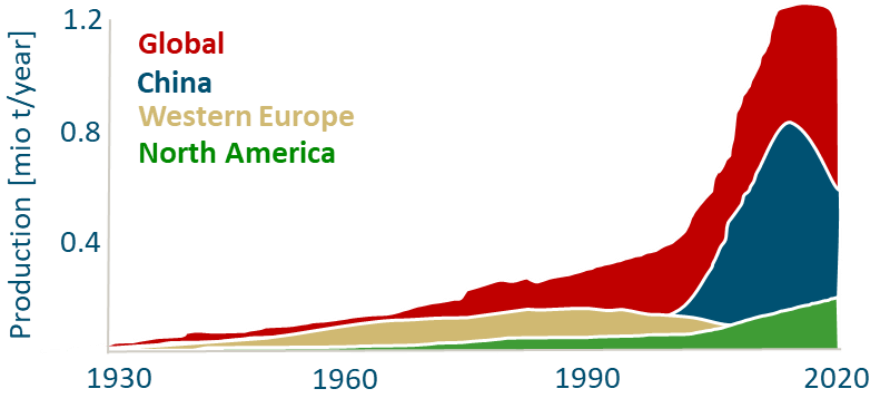
HELCOM

LRTAP
Long-range Transboundary Air Pollution

Stockholm Convention

Production trends of CPs

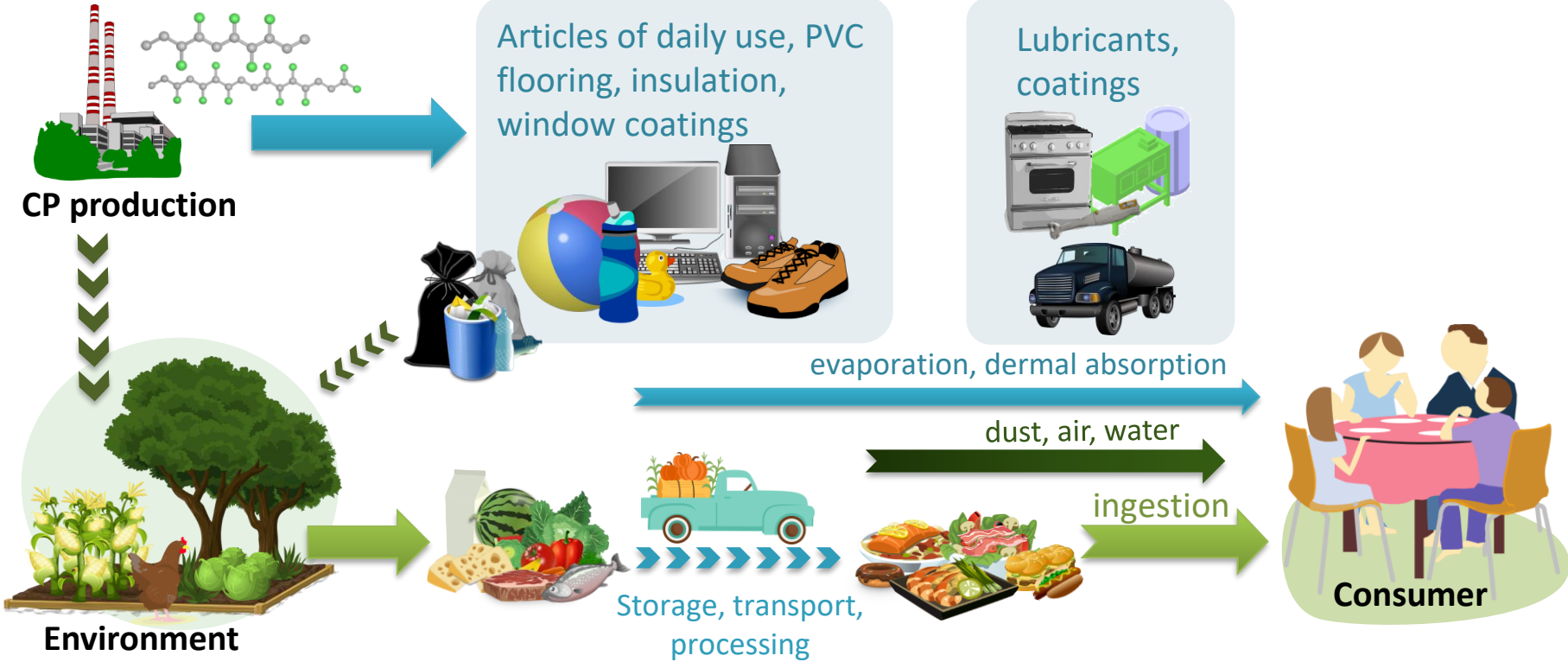
- Main producing countries China, India and other SEA countries
- **Total volume of CPs produced until today: ~20-30 mio t**
- 30x the total amount of PCBs ever produced



Distribution of CP production 1930-2020

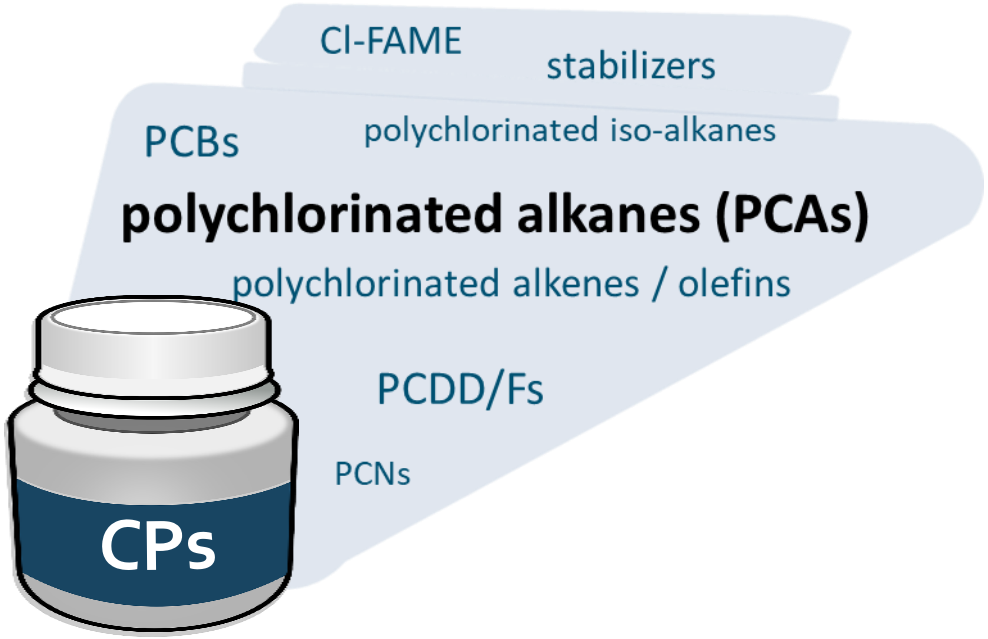
Glüge et al. (2016), *Sci. Total Environ*. 573, 1132-1146
Chen et al. (2022), *Environ. Sci. Technol.* 56, 7895-7904
Vetter, Sprengel and Krätschmer (2022), *Chemosphere* 287 (1), 132032
Transparency Market Research (2018), Chlorinated Paraffin Wax Market Analysis

The many pathways of CP/PCA exposure



CPs or polychlorinated alkanes?

- CPs are the industrial product
- Main component are polychlorinated alkanes (PCAs)
- Main focus on PCAs, though often reported as CPs



https://doi.org/10.1016/j.trac.2023.117363

Regulatory status –substance production / use

- ΣPCAs-$C_{10\text{-}13}$ (short-chain PCAs) are
  - POPs under UN Stockholm Convention
  - Use is also **forbidden** under EU POPs Regulation
  - **Restricted** by USEPA and under the CEPA
- ΣPCAs-$C_{14\text{-}17}$ (medium-chain PCAs) are
  - POPs candidates, restricted under the CEPA
  - **Under scrutiny** by ECHA, USEPA

Stockholm Convention

European Commission

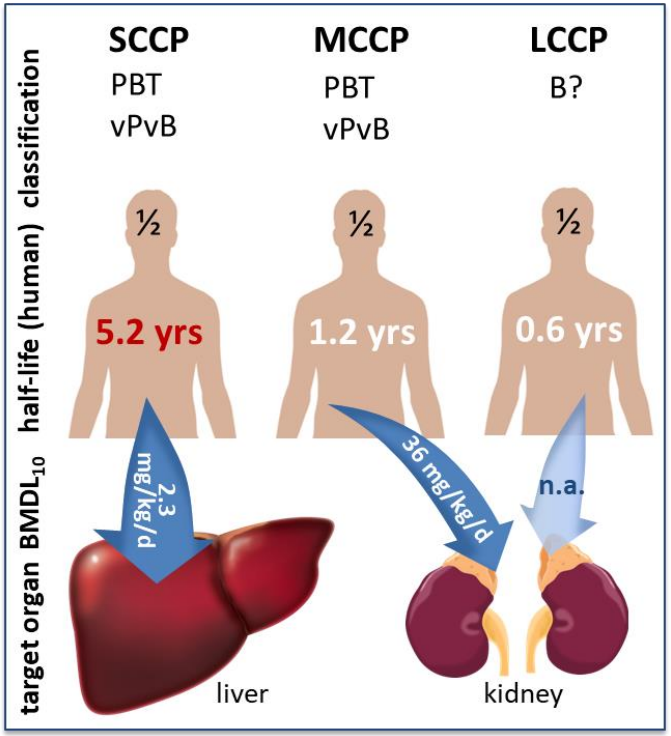
EPA

Environment and Climate Change Canada
Environnement et Changement climatique Canada

ECHA
EUROPEAN CHEMICALS AGENCY

Why the interest?

- **Ubiquitous**:
  Found even in the Antarctic and on remote Pacific islands
- **Persistent**:
  Does not or very slowly break down
- **Bioaccumulative**:
  Moves up through the food web
- **Toxic**:
  Tumours found in liver and kidneys



Krätschmer KS (2022), *Dissertation, ISBN 978-3-8439-4998-9*

....and what about food?

- 2020: EFSA Scientific Opinion did not conclude about definitive risk to consumers due to **lack of data**
- Call for more data and tox studies
- 2024: Discussion of a **potential monitoring recommendation** in food to increase dataset

No regulation or limitation in food or feed (yet)!

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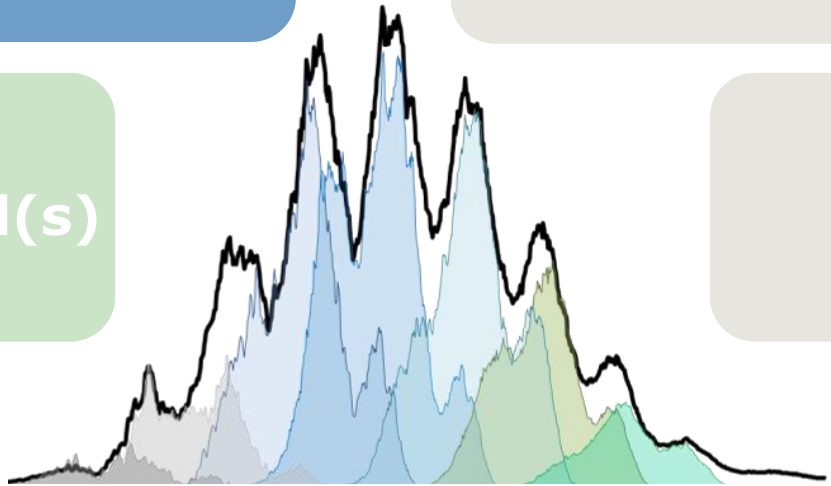
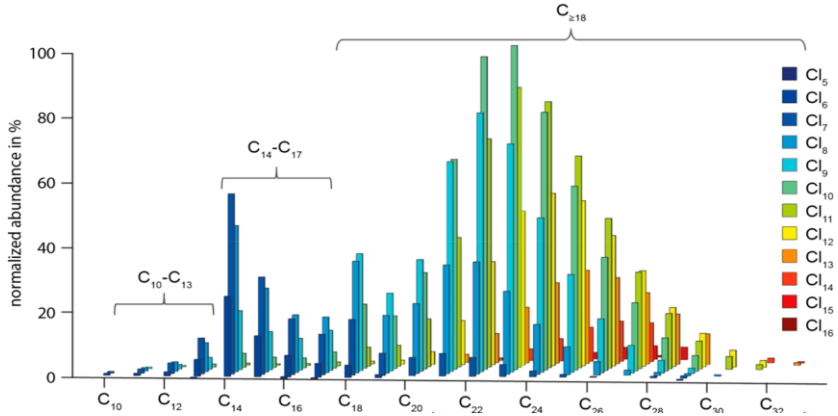


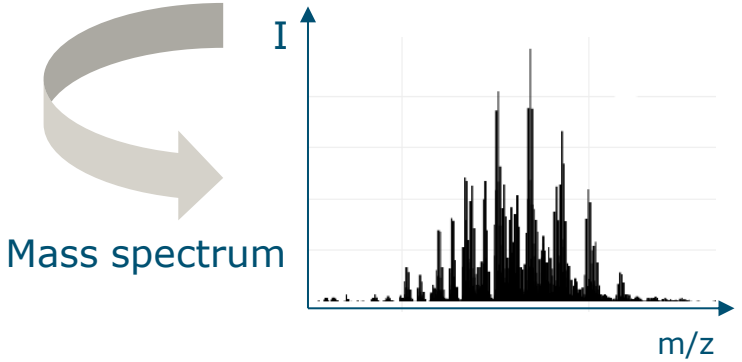
Mitigation?

Analytical challenges

- High complexity: even standards are mixtures of thousands of compounds
- Response depending on chlorination degree
- Too many compounds for individual standards



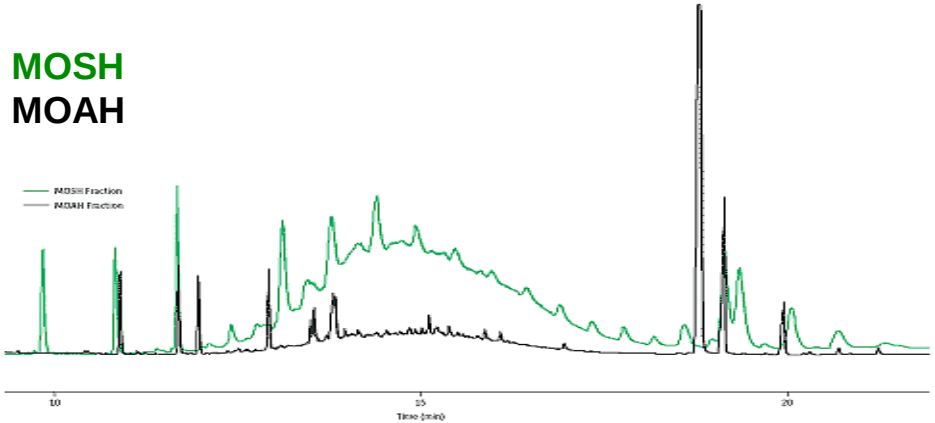
Schinkel et al (2018), *Environ. Sci. Technol. Lett*. 5 (12), 708-717



Mass spectrum

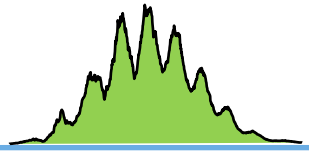
Why not analyse like MOSH/MOAH?

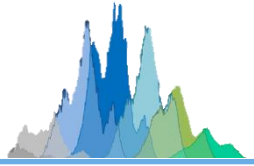
- Online LC/GC-FID makes no sense, as all compounds are in the MOSH fraction
- Regulations not applicable to all compounds in this fraction
- GCxGC-MS possible, but still insufficient peak separation

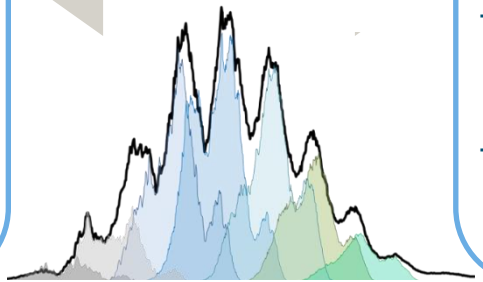


MOSH (green) and MOAH (black) compounds on Online LC/GC Coupling.
Source: https://www.restek.com/chromatogram/view/GC_FS0500

Proposed monitoring approach: two pathways







ΣPCA-C_{10-17} methods

- Infrastructure likely available at labs
- GC-MS/MS, GC-LRMS
- PTs show sum parameters are comparable
- General overview of occurrence possible

Characterisation methods

- Need (LC/GC) HRMS
- Give more information regarding chain length specific distribution
- Good for source identification

PCA analysis at WFSR

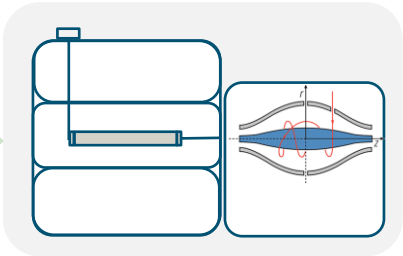
- If necessary, cold liquid-solid lipid extraction
- Acid digestion with concentrated sulphuric acid
- Removal of interferants (fractionation) on a silica column

1. fat extraction, 2. acid digestion, 3. silica clean-up

PCA analysis at WFSR

- Accela UHPLC system, Acquity UPLC BEH C18 column, 2.1 x 5 cm, 1.7 µm
- 5 µL injection, gradient with H_2O and MeOH:NH_4Cl 50 µM
- Exploris Orbitrap-HRMS, R=140k, full scan m/z 120-1500, ESI(neg)

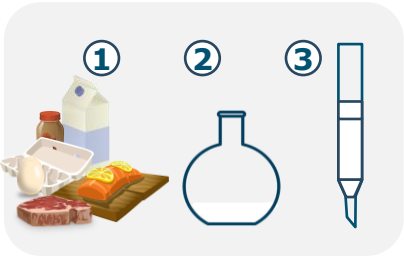
1. fat extraction, 2. acid digestion, 3. silica clean-up



LC-ESI(-)-Orbitrap-HRMS (NH_4Cl-enhanced)

PCA analysis at WFSR

- Chain-length specific standards with different average chlorination degrees, C_{10}-C_{24}, 39-70%Cl, in 6 mixtures with 4-point calibration
- linear regression based on %Cl, quantification on carbon chain level
- Use of R script for data handling after peak integration



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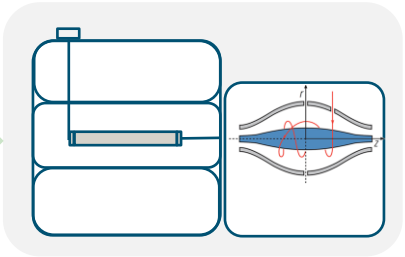

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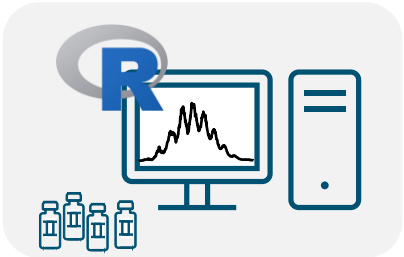

%Cl-calibration using R

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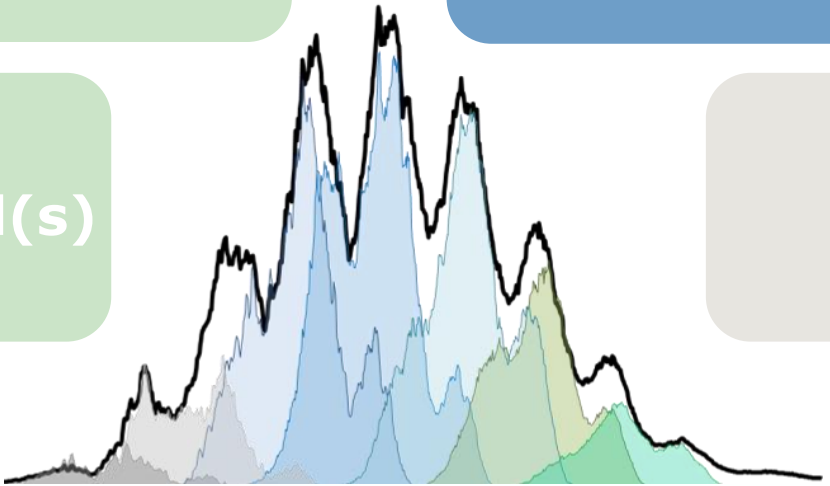


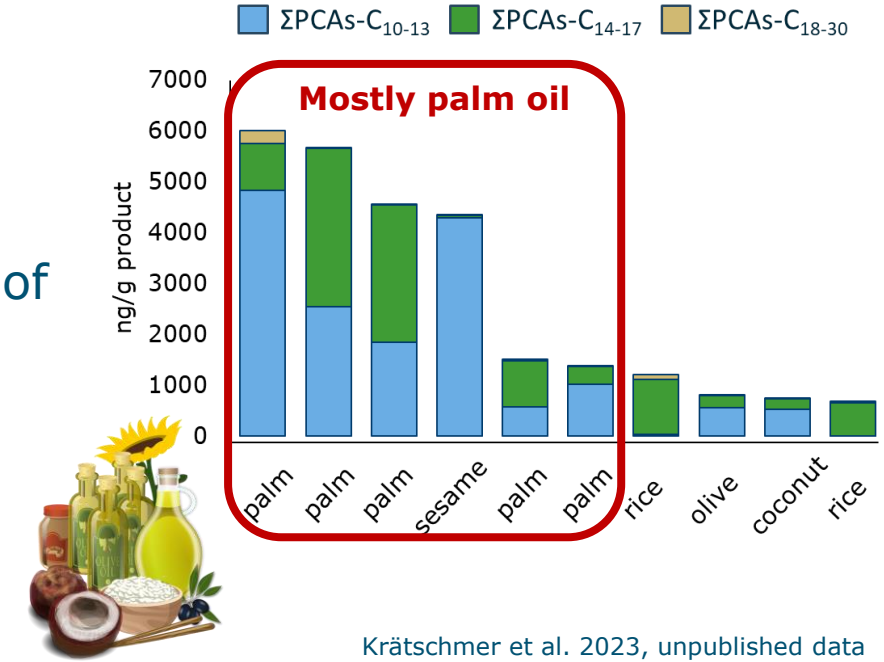
Why monitor edible oils and fats?

- Used in dressings, cooking and baking recipes (ingredient)
- Used for most types of deep frying (medium)
- Netherlands: 3rd highest fat consumption in comparison of 12 European countries [1]

[1] RIVM Report 2016-0195 (2017), https://www.rivm.nl/bibliotheek/rapporten/2016-0195.pdf

Oils from the Dutch market (2023)

- ΣPCAs 4.0-6000 ng/g (average ~610 ng/g, n=55)
- Top 10: dominated by palm oils
- Refined oils mostly at lower end of concentration range
- No data for comparison (palm), comparable to other European results (sesame, rice, olive...)

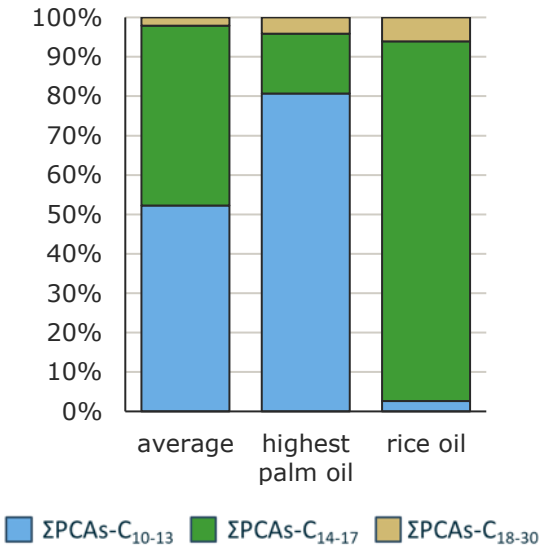


Krätschmer et al. 2023, unpublished data

Characterization of PCAs

- Rice oils and one palm oil were dominated by ΣPCA-C_{14-17}, the rest by ΣPCA-C_{10-13}
- Patterns match technical CP products closely: likely process contamination, not taken up by fruits/seeds
- 18 samples of EU origin:
  - All dominated by ΣPCA-C_{14-17}
  - Only 5 above 100 ng/g content (EVOO)
  - none of them had ΣPCAs >500 ng/g

Distribution of PCA groups

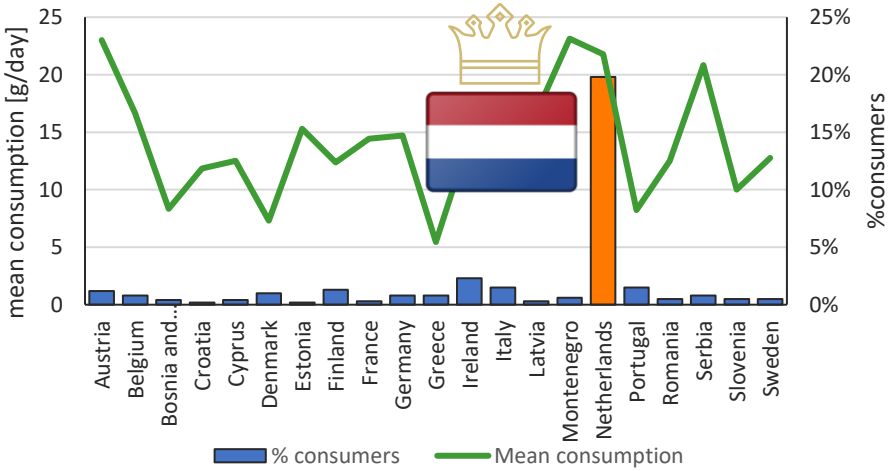


Krätschmer et al. 2023, unpublished data

Spreads – an important food group in NL

- Chocolate and hazelnut spreads popular throughout Europe
- 1/5th of Dutch adults eat daily ~20 g peanut butter
- Spreads are often made with palm oil, only recently more PO free products

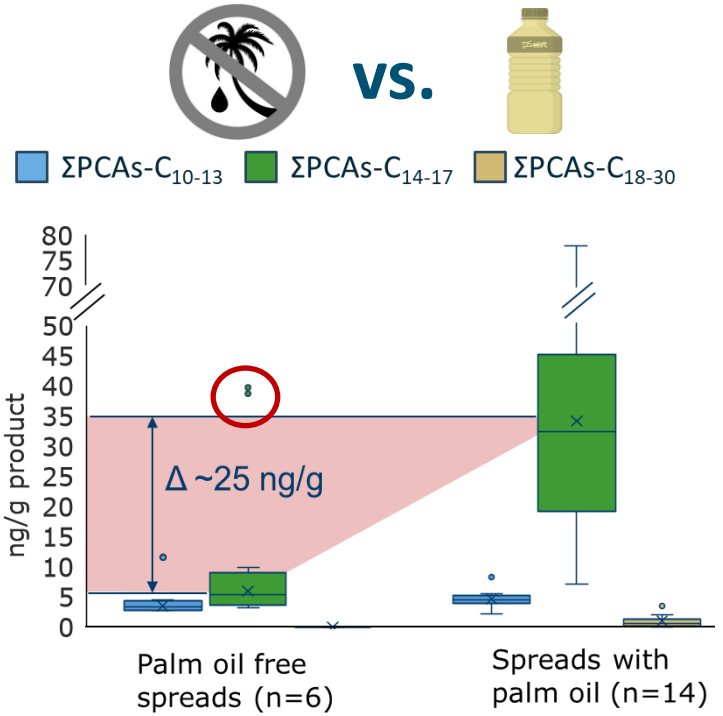
Peanut butter consumption EU



Source: EFSA consumption database

Spreads with and without palm oil

- More spreads with than without declared palm oil or fat
- Difference in ΣPCAs-C_{14-17} on average 25 ng/g product
- Other PCAs around LOQ
- 2 PO free spreads would fit better with PO spreads – ongoing...



Krätschmer et al. 2023, unpublished data

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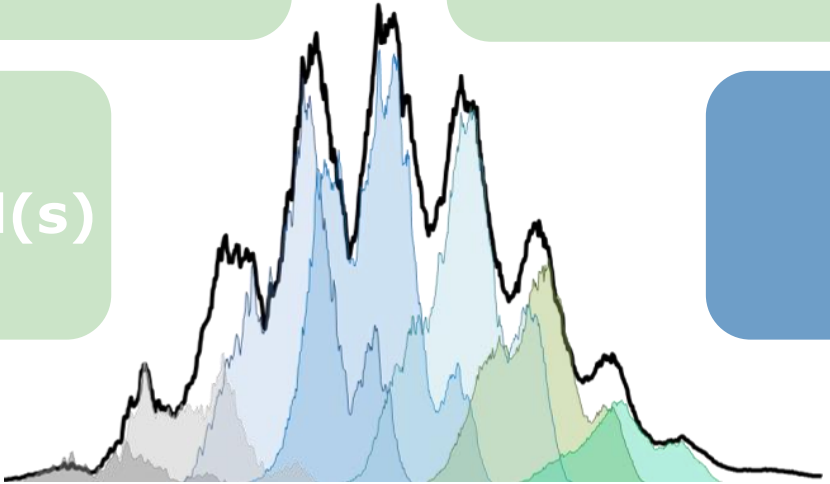
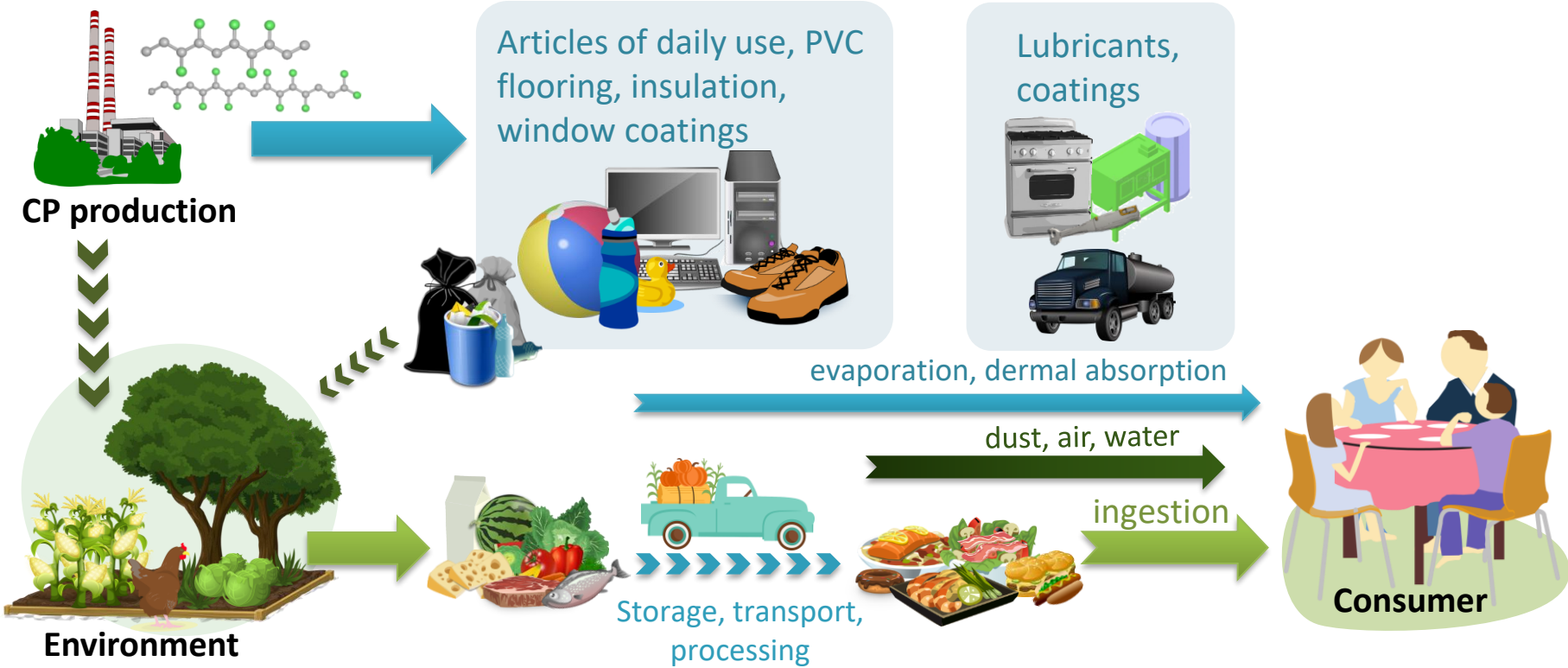
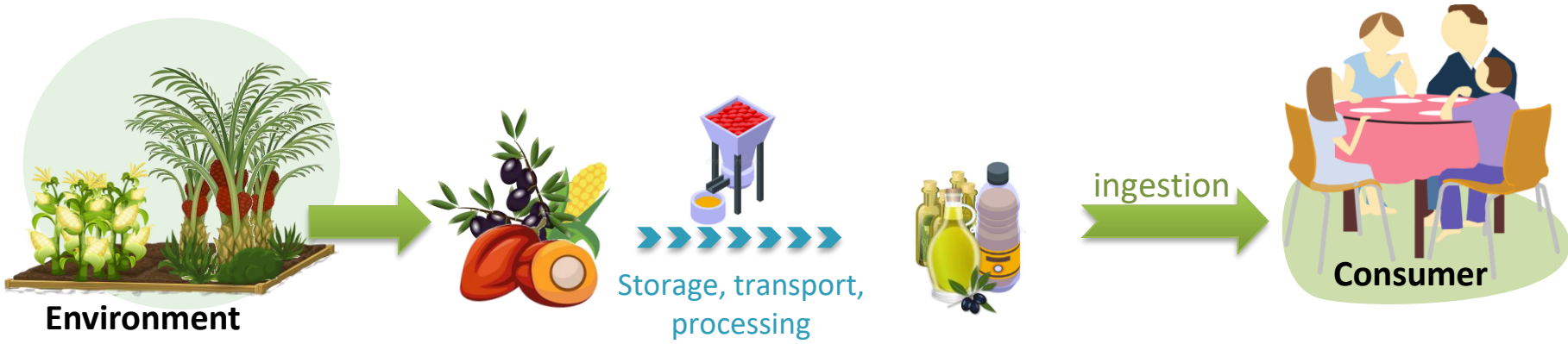


The many pathways of CP/PCA exposure



Points of Attention – oil production

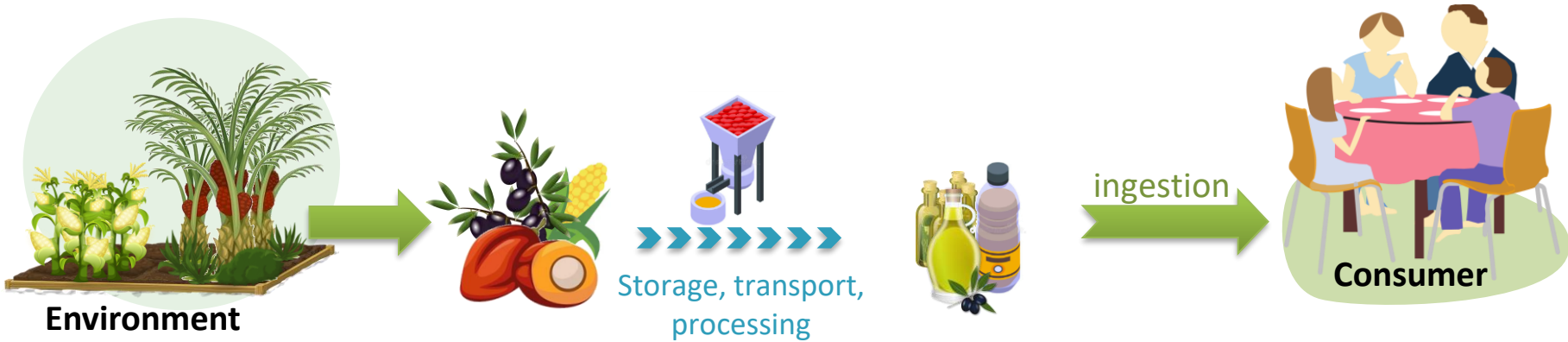
- Similar measures to MOSH/MOAH prevention?
- Look at open sources of lubricants, storage conditions, packaging material during shipment, harvesting tools and methods in use



Points of Attention – oil production

- Data indicates that point sources are likely – different contamination levels possible in different oil mills, different batches
- Virgin oils: screen oilseeds/ fruits!

However…



What happens during oil refinement?

Shen et al. 2023, 10.1016/j.foodcont.2023.109889

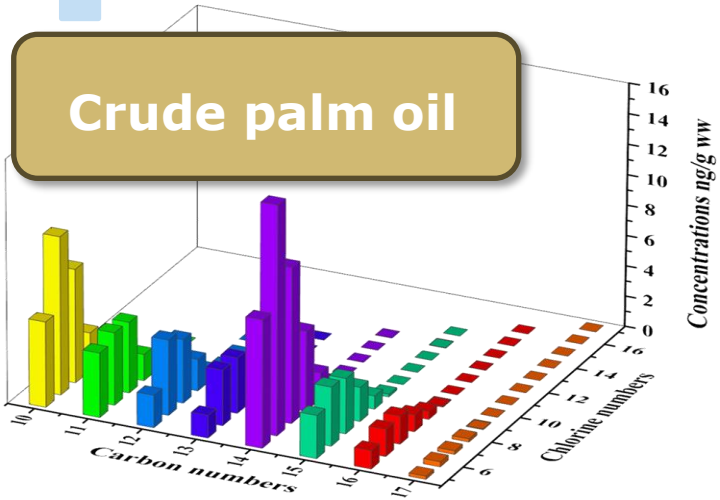
Degumming → Bleaching → Deodorization

Acid

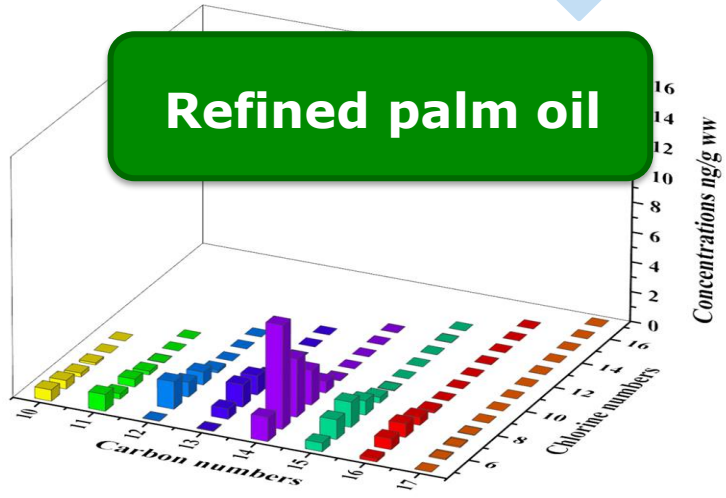
Bleaching earth, active carbon and filtration aid

230 – 260°C

Crude palm oil



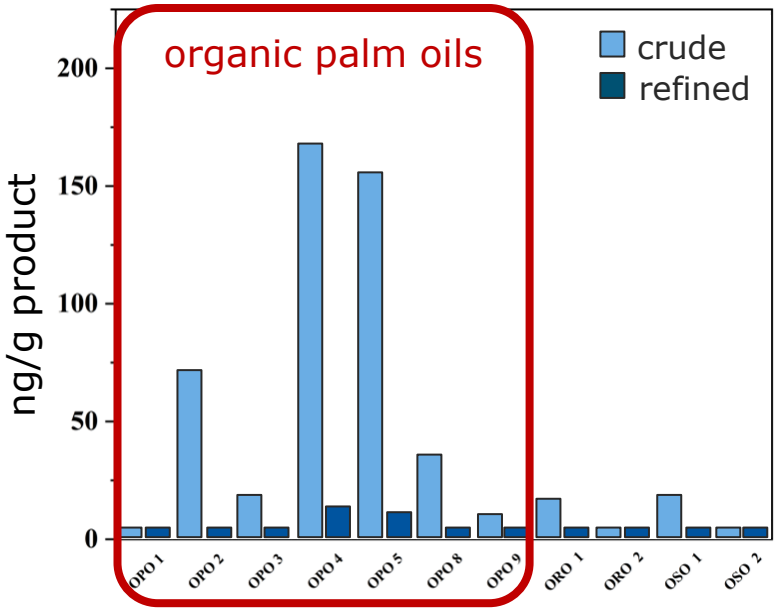
Refined palm oil



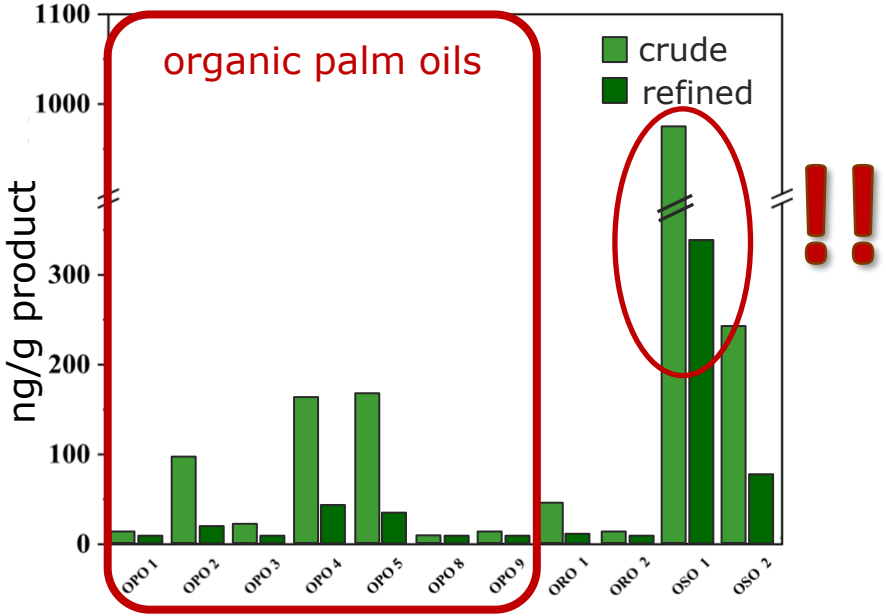
Study: PCA reduction in organic oils

Shen et al. 2023, 10.1016/j.foodcont.2023.109889

ΣPCA-C_{10-13} **-83%**



ΣPCA-C_{14-17} **-71%**

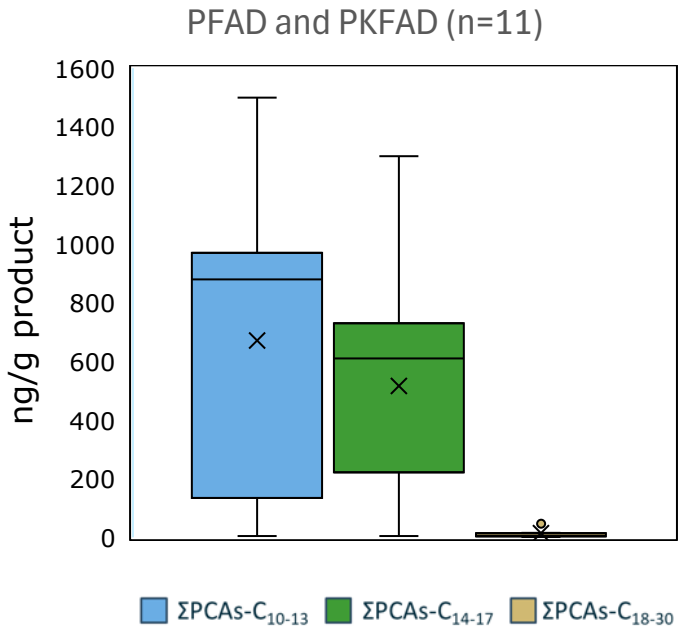


(OPO = organic palm oils; ORO = organic rapeseed oils; OSO = organic sunflower oils)

Where do the PCAs go?

- Survey of 8 PKFADs and 3 PFADs (2024)
- PCA findings 15-2800 ng/g product
- No paired raw/ refined material available: mass balance unclear

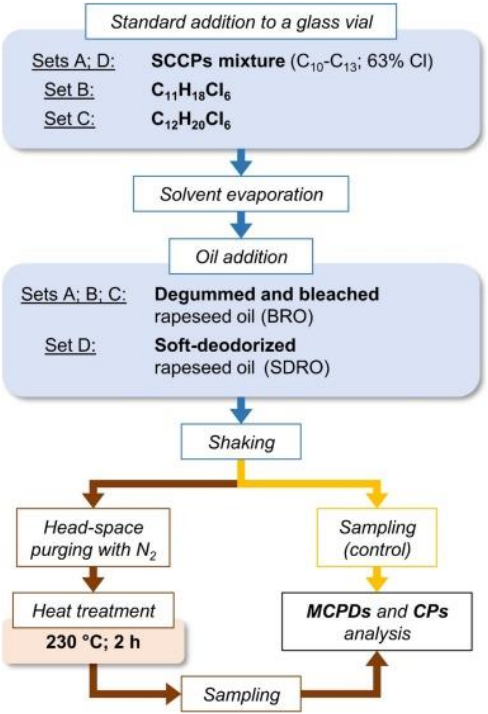
- Source of PCAs in feed -> food of animal origin



Krätschmer et al. 2024, unpublished data

Where do the PCAs go?

- Lab experiment: addition of 1-20 mg/kg SCCP, $C_{11}Cl_6$ or $C_{12}Cl_6$-standards
  - Degummed and bleached RO
  - Soft-deodorised RO
- Heat treatment at 230°C resulted in significant increase of 3-MCPD and 2-MCPD compared to control even at lowest fortification level



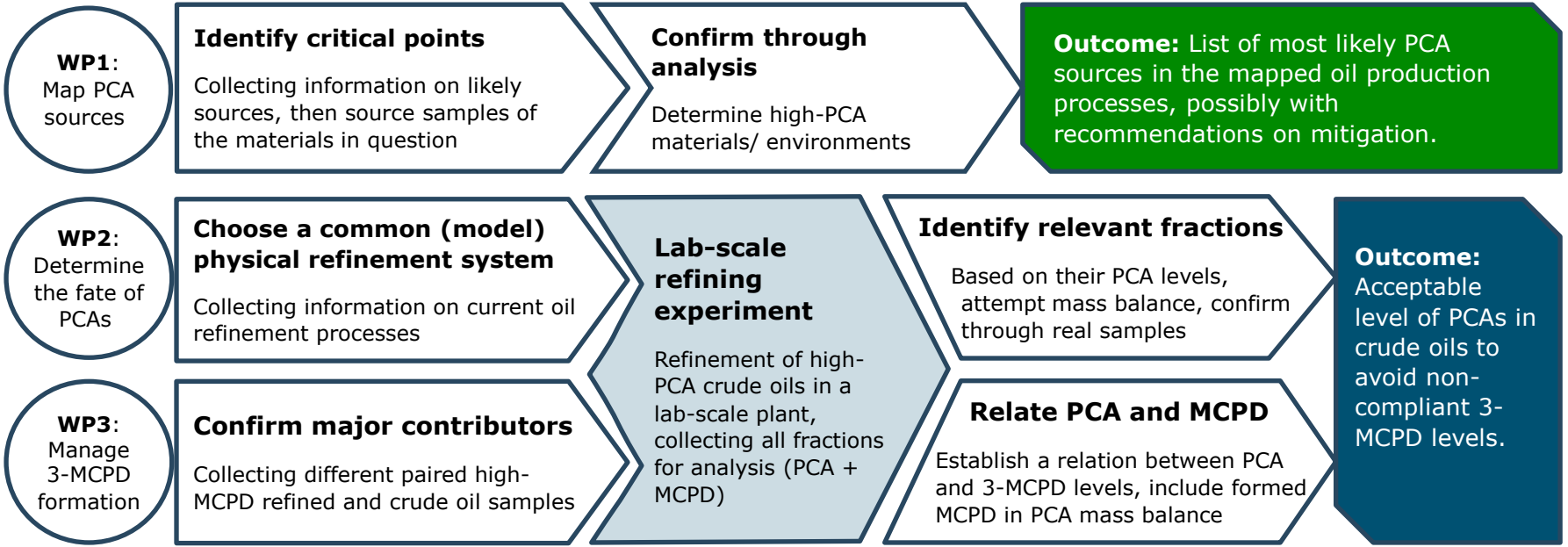
Kourimsky et al. 2025, 10.1016/j.foodchem.2024.141919

Further investigation needed!

- Identify PCA sources in raw oil production
- Confirm findings of Kourimsky et al in a (lab-scale) refinery
- What is the lowest PCA concentration leading to significant effects?
- Mass balance between main- and side-streams

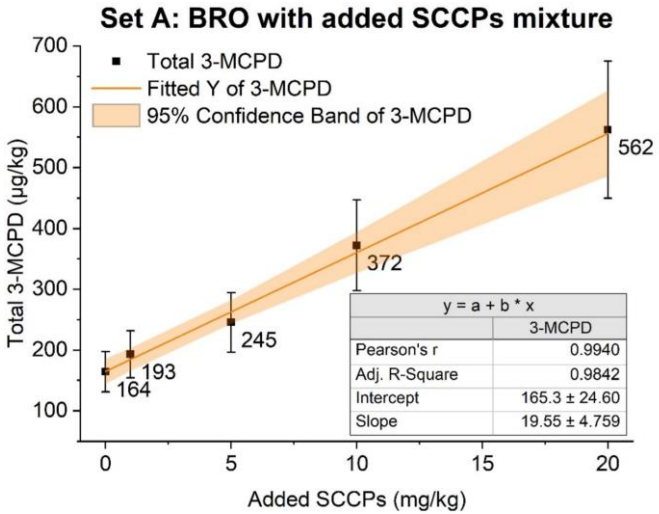
Project proposal: Managing 3-MCPD formation during Oil Refinement by PCA Source Detection [CP-forecast]

CP-forecast: Design



CP-forecast: Refining experiment

	Palm oil		Rapeseed oil (tbd)	
spiking levels	5		5	
#repetitions	3		3	
samples taken	PCA	MCPD	PCA	MCPD
crude oil	x	x	x	x
neutralised	x		x	
bleached	x	x	x	x
FAD	x		x	
refined oil	x	x	x	x
#analyses per sample	2	2	2	2
total analyses	**150**	**90**	**150**	**90**



Kourimsky et al. 2025, https://doi.org/10.1016/j.foodchem.2024.141919

- Statistically robust experiment
- Able to extrapolate critical PCA concentrations

CP-forecast: Gains and needs

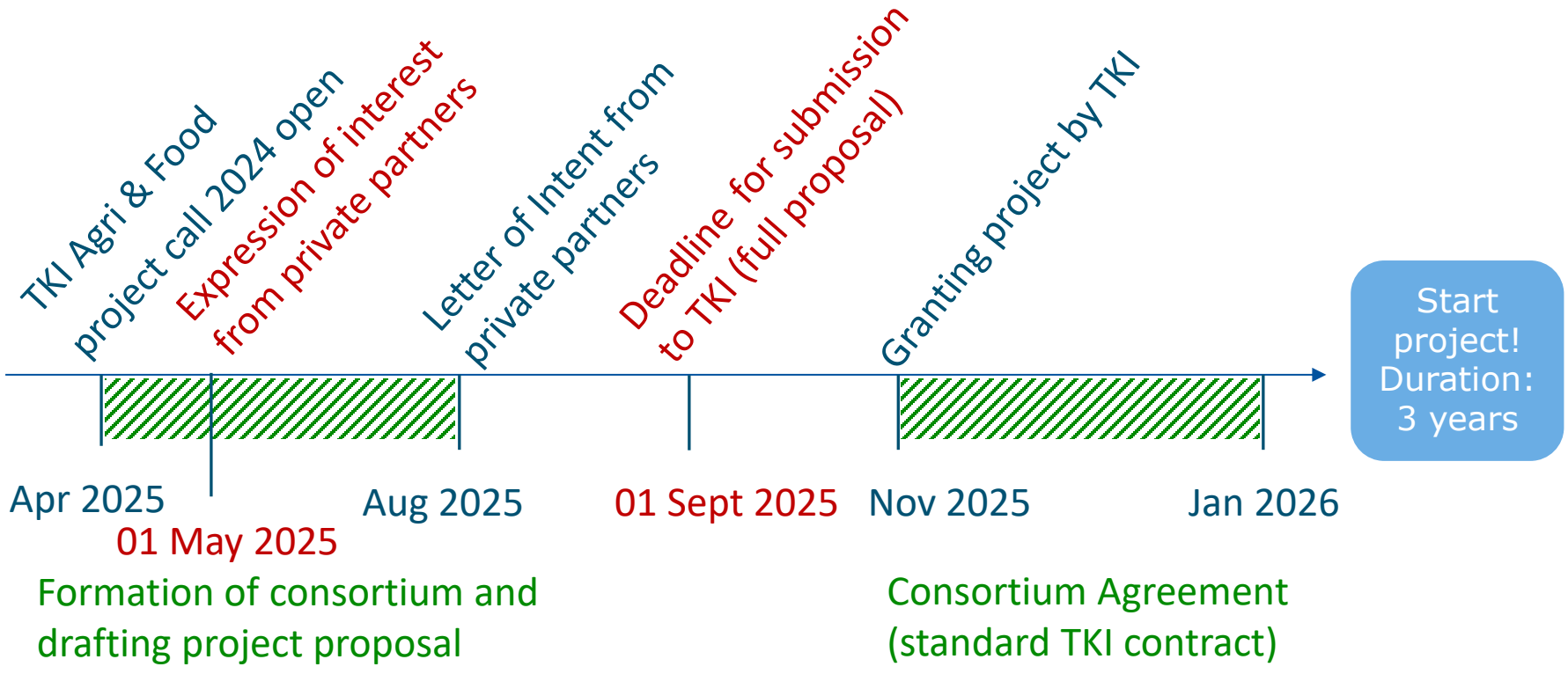
- **Expected gain:**
  - Identified PCA contamination sources of crude oils
  - Mapping the presence of PCA in oil refinement
  - **Model for acceptable PCA levels in crude oils (avoiding non-compliant 3-MCPD levels)**
- **Needed contribution:**
  - In cash: Co-funding needed!
  - In kind, e.g.:
    - Information on production and refinement process, side stream valoration
    - Supply of samples
    - Access to lab-scale model plant

Possible consortium and financing

	2 partners				3 partners				4 partners			
[example budget in k€]	**2026**	**2027**	**2028**	**Total**	**2026**	**2027**	**2028**	**Total**	**2026**	**2027**	**2028**	**Total**
Private contribution (in cash)												
Company 1	17	17	17	51	12	12	12	36	8.5	8.5	8.5	25.5
Company 2	17	17	17	51	11	11	11	33	8.5	8.5	8.5	25.5
					11	11	11	33	8.5	8.5	8.5	25.5
									8.5	8.5	8.5	25.5
Total cash	34	34	34	102	34	34	34	102	34	34	34	102
Private contribution (in kind)												
Company 1	17	17	17	51	12	12	12	36	8.5	8.5	8.5	25.5
Company 2	17	17	17	51	11	11	11	33	8.5	8.5	8.5	25.5
					11	11	11	33	8.5	8.5	8.5	25.5
									8.5	8.5	8.5	25.5
Total in kind	34	34	34	102	34	34	34	102	34	34	34	102
Public contribution requested (50% in cash)	68	68	68	204	68	68	68	204	68	68	68	204
Total	**136**	**136**	**136**	**408**	**136**	**136**	**136**	**408**	**136**	**136**	**136**	**408**

- 50% government funding (TKI)
- 50% co-financing from industry (of which max. half can be in-kind contribution)
- The knowledge institute (WFSR) holds the budget

Procedure and Timeline



Summary and conclusions

- High PCA levels found in **palm oils**, lower in refined / European oils
- Visible difference between ΣPCAs-C_{14-17} levels in **spreads** with and without palm oil
- Standard **oil refinement** can reduce PCA levels, but struggles with high amounts of ΣPCAs-C_{14-17}
- Research indicates that PCAs in crude oils can be **major contributors to 2-/3-MCPD levels** in refined oils

PCAs are a present concern in oils and oils products, on their own and in connection with regulated chlorinated contaminants

Thank you for your attention!

Interested in joining the PPP?

Contact us before 1st May!

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