

# PERFOOD; PFAS levels in vegetables from Europe

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# Introduction

## Main aim of PERFOOD and WP3 (NILU)

### PERFOOD:

- Qualify and quantify PFAS in our diet
- Understand how PFAS are transferred from the environment into dietary items
- Quantify possible contribution of food/beverage contact materials and food/water processing to the overall PFAS levels in our diet
- Evaluate possible routes of human exposure to PFAS via diet

### WP3:

- Deliver standardized methods for the selection, sampling and handling of food items
- Deliver levels of PFCs in European food as well as the identification of major sources of PFC exposure via food.

# Objectives

1. Identification of EU relevant food baskets, covering common European nutrition habits as well as typical regional food items
2. Analyse the concentrations of PFAS in different food items, normally consumed by the European population
3. Identify the impact of food preparation
4. Input on prioritized pathways of PFAS exposure
5. Study geographical differences of PFAS levels
6. Assessment of PFAS in food produced near point sources.

# Sampling locations

represent WHO Food  
Consumption  
Clusters in Europe



# Sampling details

- Pooled samples of randomly selected individual items, eadible parts only
  - Two sampling campaigns
    - First campaign on raw, untreated food items according to EFSA's food categories (spring 2010)
- Results presented here



# Standardisation of sampling



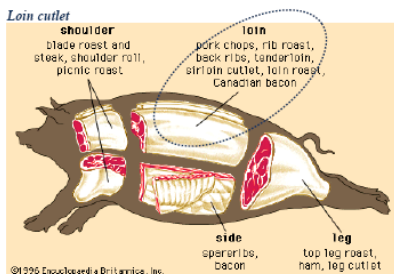
## Sampling meat - the PERFOOD project.

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based on Teleconference (22<sup>nd</sup> April 2010, 11.00 UTC)

### A. PORK MEAT

- Part to be taken from each animal: about 250 - 300 g (boneless, unpacked).
- In 2 - 3 supermarkets, buy fresh pork loin (centre part) from 4 - 5 animals.



- Put all samples individually in polyethylene (micotene) bags and transport them to the laboratory the same day. Temperature during transportation shall be kept at 2-4 °C but not exceeding 7 °C for more than 60 min
- Fill in Sampling records with information on individual samples.
- Remove the rest of bones (if any) and weight the meat. At least 250 g is necessary from each (individual) animal.
- Cut-off all fatty (lard) parts. Weight muscle tissue fraction and calculate the ratio of "pure" (muscle tissue) meat

## Sampling Protocol for food items for the PERFOOD project.

### 1. General

In this manual a detailed sampling protocol is presented for the sampling of food items in Europe for measurement of perfluor compounds, in order to generate data that allow to make a risk evaluation of PFCs present in food for human consumption.

Although the European Commission has published a recommendation on the monitoring of perfluoralkylated substances in food (COMMISSION RECOMMENDATION 2010/161/EU of 17 March 2010) this is not fully applicable for the present study. The recommendation refers to the sampling procedure as laid down in Annex I to Commission Regulation (EC) No 1883/2006 of 19 December 2006 laying down methods of sampling and analysis for the official control of levels of dioxins and dioxin-like PCBs in certain foodstuffs (2) in order to ensure that the samples are representative for the sampled lot. That procedure however, is developed for another purpose, i.e. to analyse pollutants in certain lots of food. Since the PERFOOD aims to get a preliminary global idea of the risks posed by consumption of food with respect of the PFC content, we prefer to follow a food basket study. However, some general sampling principles used in that document are withdrawn for our sampling strategy.

- Four countries, each representing a European region, are selected (N, Cz, B, I) where food items will be sampled.
- The two most important food distribution companies in a country have to be selected e.g.: for Belgium this are Colruyt, Delhaize or Carrefour. Food items are divided in 14 categories and sampling strategy and sample treatment will depend on the category.

During the first sampling period only raw samples and no composite samples neither couldrons are collected.

For all categories a sub-sample of each homogenized item (of a certain lot, which can be a single brassica or 100g homogenized peas) is preserved for later individual analysis if needed. Only edible parts of the food items will be selected for homogenization and analyses.

Food packaging consisting of cardboard or other paper-like material has to be stored for later analyses (10 x 10cm<sup>2</sup>) of each article. Storage: cool and dry.

In the selected supermarkets randomly 3-10 items are sampled, depending on the number of lots or marks present in both supermarkets together (see table 1).

In the list of items the category will be specified. All samples (pools) are extracted in duplicate.

The food samples will be analyzed by three different labs. Each lab will analyze certain matrices. In the sample list is indicated which lab is measuring what type of matrices.

## Annex I. Proposed Standard Sample Description for single (simple) food items

Reference: European Food Safety Authority; Standard sample description for food and feed. EFSA Journal 2010;8(1):1457 [54 pp.]. doi:10.2903/j.efsa.2010.1457. Available online: [www.efsa.europa.eu](http://www.efsa.europa.eu)

Code of the lab that performs the sampling	Perfood Acronimous i.e. ISS, NILU,
Language of the report	English
Country of sampling	International code (I) (B) (NL)
Area of Sampling	Region /subregion (Flandres, Wallonie, )
Country of origin of the product	International code
Area of origin of the product	For caught fish refer to FAO fisheries areas
Perfood category of the simple food item	i.e. for lettuce Lettuce_I_1b
Product description	Size of the batch/lot
Product code (if available)	batch, lot
Method of production	Conventional / organic
Packaging method (if relevant)	i.e. eggs packaged in board/plastic boxes
Product brand name (if relevant)	
Product manufacturer (if relevant)	
Date of Production	
Date of expiry	
Date of sampling	
Code of sampling	
Sampling method	
Sampling point	
STICK THE LABEL WITH THE INGREDIENTS IN THE CASE OF PACKAGED ITEMS	
STICK A PICTUTRE OF THE PRODUCT	

## Uniform sampling and sample treatment:

- COMMISSION RECOMMENDATION 2010/161/EU of 17 March 2010
- Annex I to Commission Regulation (EC) No 1883/2006 of 19 December 2006
- Grouping of food items according to EFSA → guarantee later use of results
- Documentation at each step of sample treatment assured

01. Cereals (6 types)

02. Sweets

03. Vegetables and pulses

04. Potatoes etc.

05. Fruit

06. Meat etc.

07. Fish, seafood etc

08. Eggs

09. Milk and dairy products

10. Fats

11. Miscellaneous

12. Water and non-alc. bev.

13. Coffee, tea (dry)

14. Alcoholic beverages

8 sub groups:  
Leafy veg., Stem veg., Root  
veg., Tomatoes, Brassica  
veg., Other veg., Pulses  
and legumes, Potatoes

→ 20 species

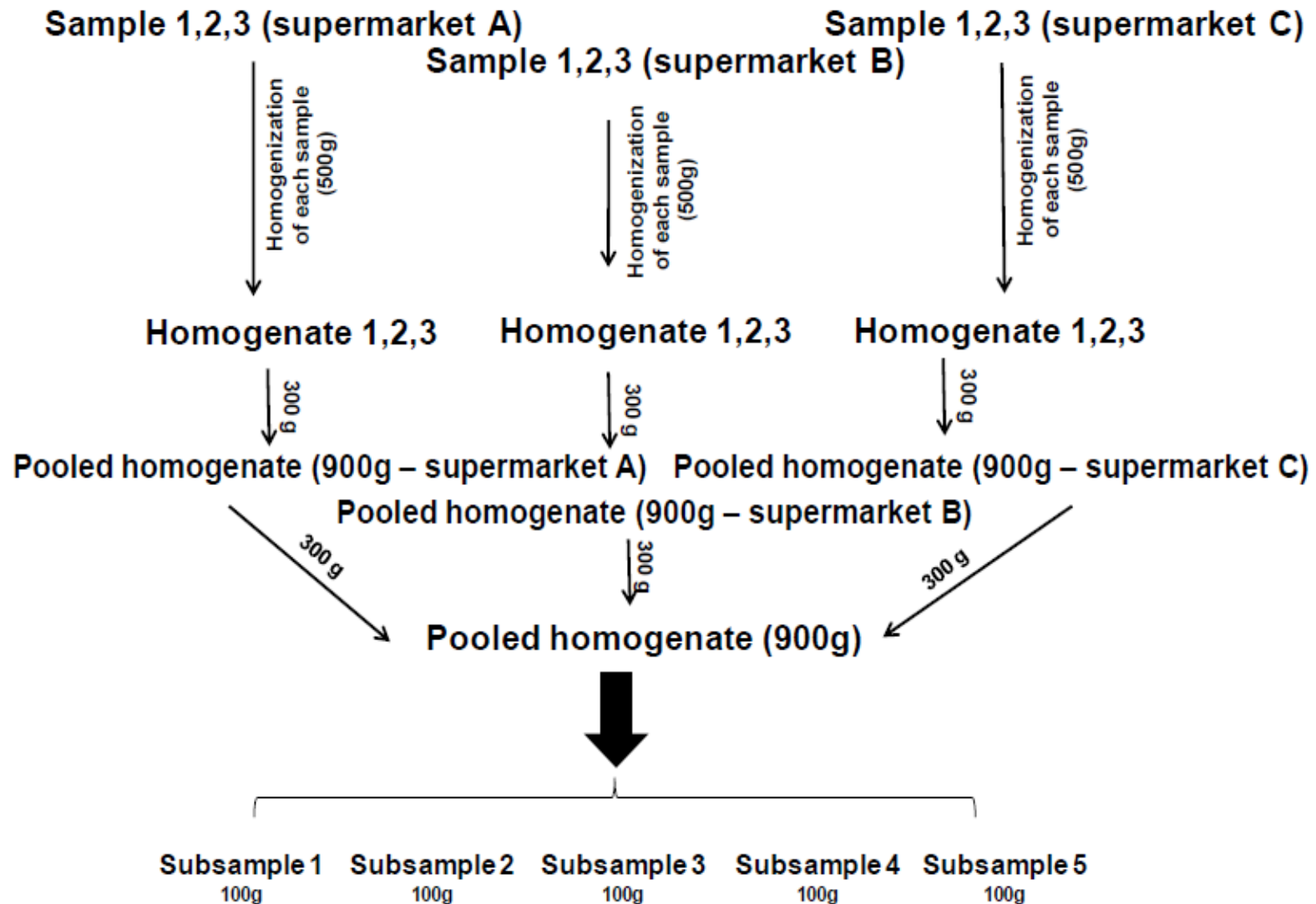


03. Vegetables and pulses	EAST EU	WEST EU	NORTH EU	SOUTH EU
	CR	BE	NW	IT
<b>Leafy vegetables</b>				
<i>lettuce and other salads</i>	x	X	x	X
<i>spinaches</i>	x	X		
<i>chicory</i>		x		X
<b>Stem vegetables</b>				
<i>asparagus</i>	X	x	x	X
<i>celery</i>	X	X		
<i>fennel</i>		X	X	
<b>Root vegetables</b>				
<i>onion</i>	X			X
<i>carrots</i>	x	X	X	x
<b>Tomatoes</b>	X	X	X	X
<b>Brassica vegetables</b>				
<i>cauliflower</i>	X	X	x	x
<i>cabbage</i>	x	x	X	X
<i>broccoli</i>	X	X		
<b>Other vegetables</b>				
<i>courgettes</i>		X		x
<i>cucumbers</i>	x	x	x	x
<i>cultivated mushrooms</i>	X		X	
<i>aubergine</i>		X		X
<i>peppers</i>	X	x	x	X
<b>Pulses and legumes</b>				
<i>peas</i>	x	X	X	x
<i>beans</i>	X	x	x	X



# Homogenization and food samples processing

Sampling strategies and processing depend on number of samples:  
(3 different samples representing particular kind of food)



# Harmonised method requirements:

- Minimum required performance limit: 5 ng/kg on the basis of consumption data (required LOD)
- Preparation of internal reference materials for vegetables
- Document : “Validation protocol for methods used in WP3”
- Guideline for quantification of linear and branched PFOS

# Extraction procedure for vegetables<sup>ITM</sup>

**Sample homogenisation**

**NaOH in water addition**

**MTBE** addition, shaking for 1 min, sonication for 10 min, then centrifugation and evaporation

Aliquot of supernatant treated with  
**Florisil**

Evaporation+ **EnviCarb**

**LC-MS/MS**

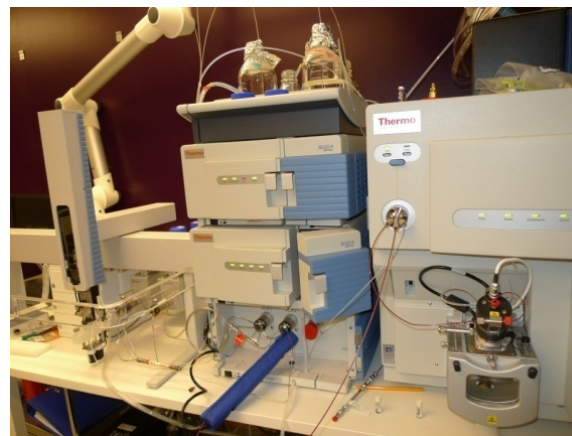
**Quality control:**



**Duplicate analysis  
of each sample**

**Extraction batch (10 samples) of particular commodity:**

- Spike at level 25 ng/kg sample
- Procedural blank
- Triplicate measurements



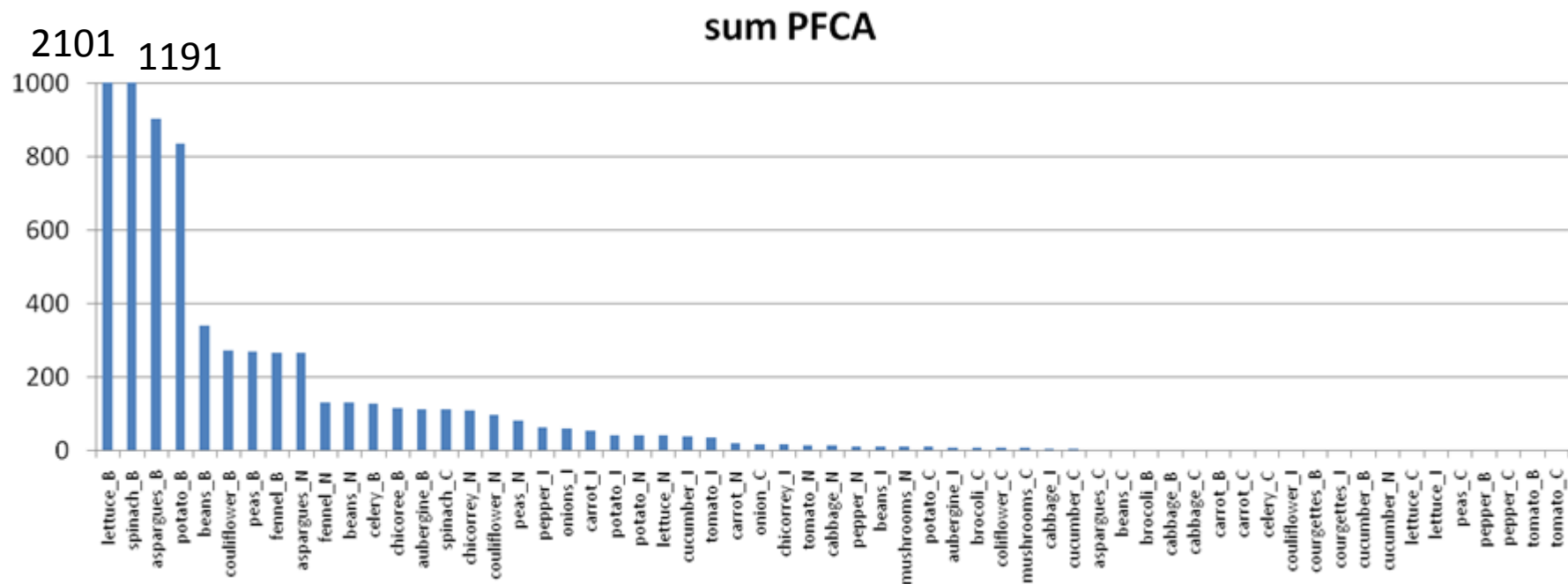
# Target analytes

Analytes			Internal standards
PFCAs	C4	PFBA	13C4 PFBA
	C5	PFPeA	13C4 PFBA
	C6	PFHxA	13C2 PFHxA
	C7	PFHpA	13C2 PFHxA
	C8	PFOA	13C4 PFOA
	C9	PFNA	13C4 PFOA
	C10	PFDA	13C2 PFDA
	C11	PFUdA	13C2 PFDA
	C12	PFDoA	13C2 PFDoA
	C13	PFTTrDA	13C2 PFDoA
	C14	PFTeDA	13C2 PFDoA
PFSA's	C4	PFBS	13C4 PFHxS
	C6	PFHxS	13C4 PFHxS
	C8	PFOS	13C4 PFOS
	C10	PFDS	13C4 PFOS
	C8	FOSA	13C8 FOSA

**11 perfluorocarboxylic acids  
(PFCAs)**

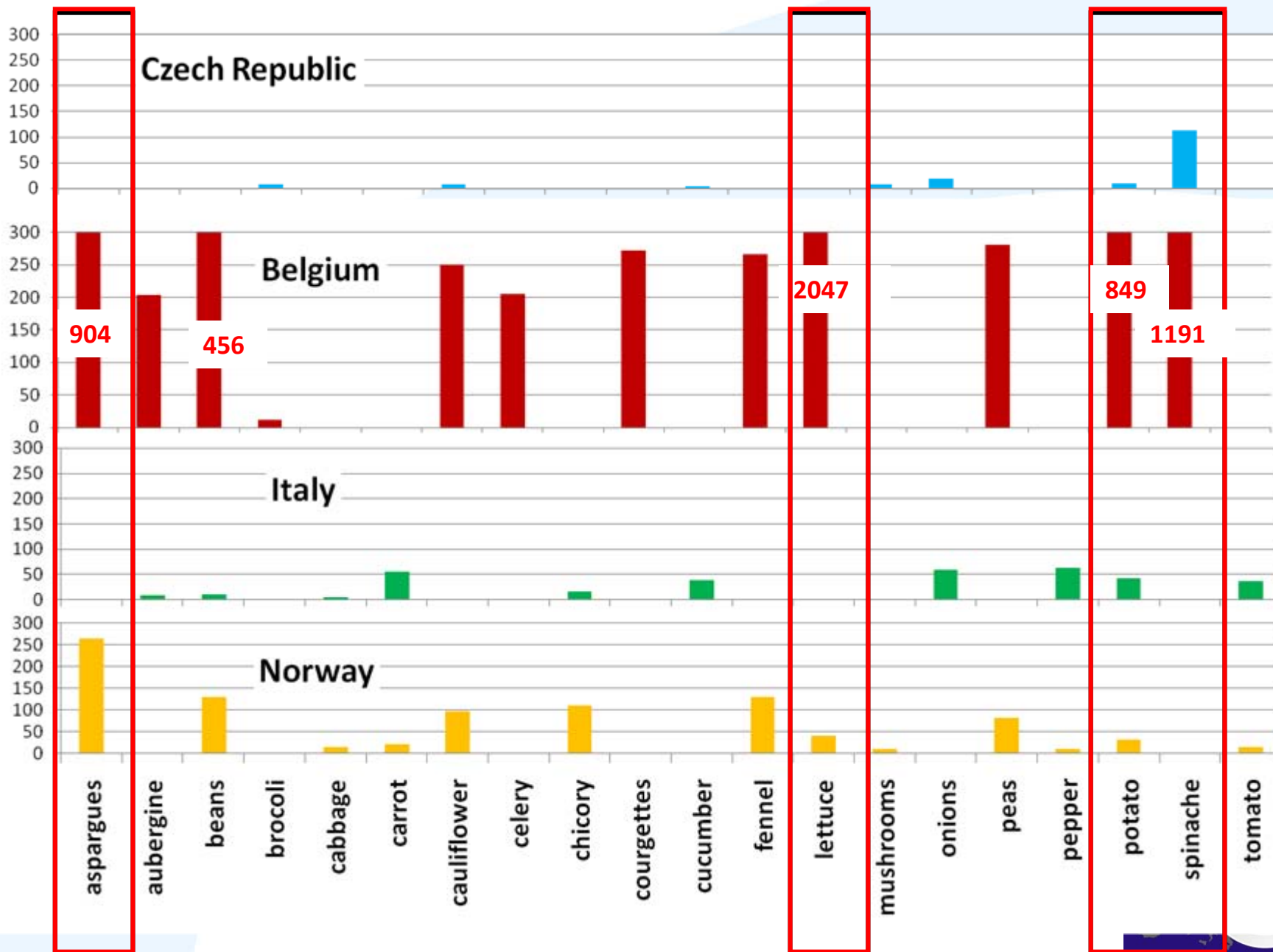
**4 perfluorosulfonic acids  
(PFSAs)**

# Results in ng/kg



- 16% of the samples with sumPFAS > 200 ng/kg
- Majority of samples close to or < LOQ

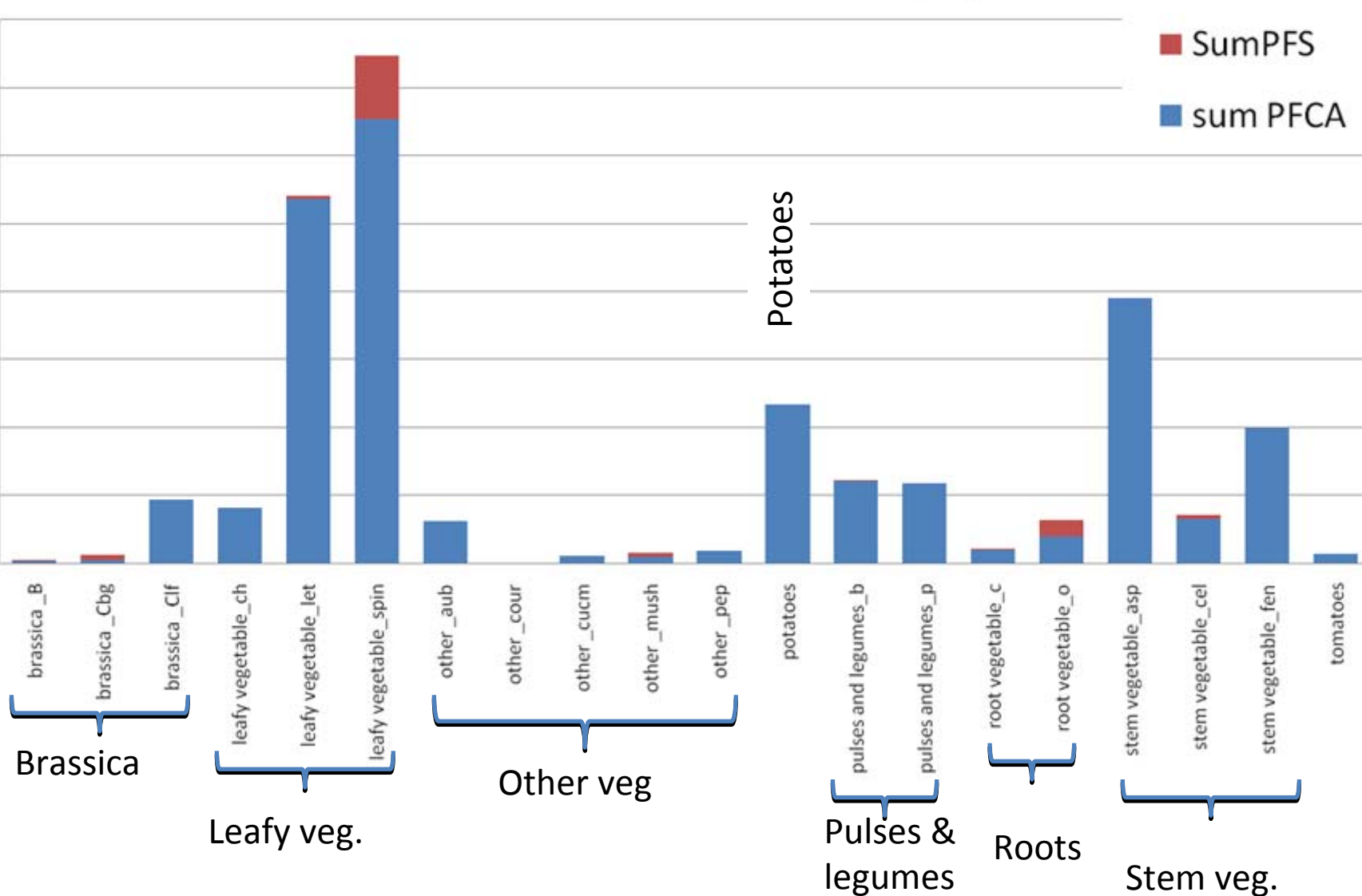
# SumPFAS in vegetables (ng/kg)



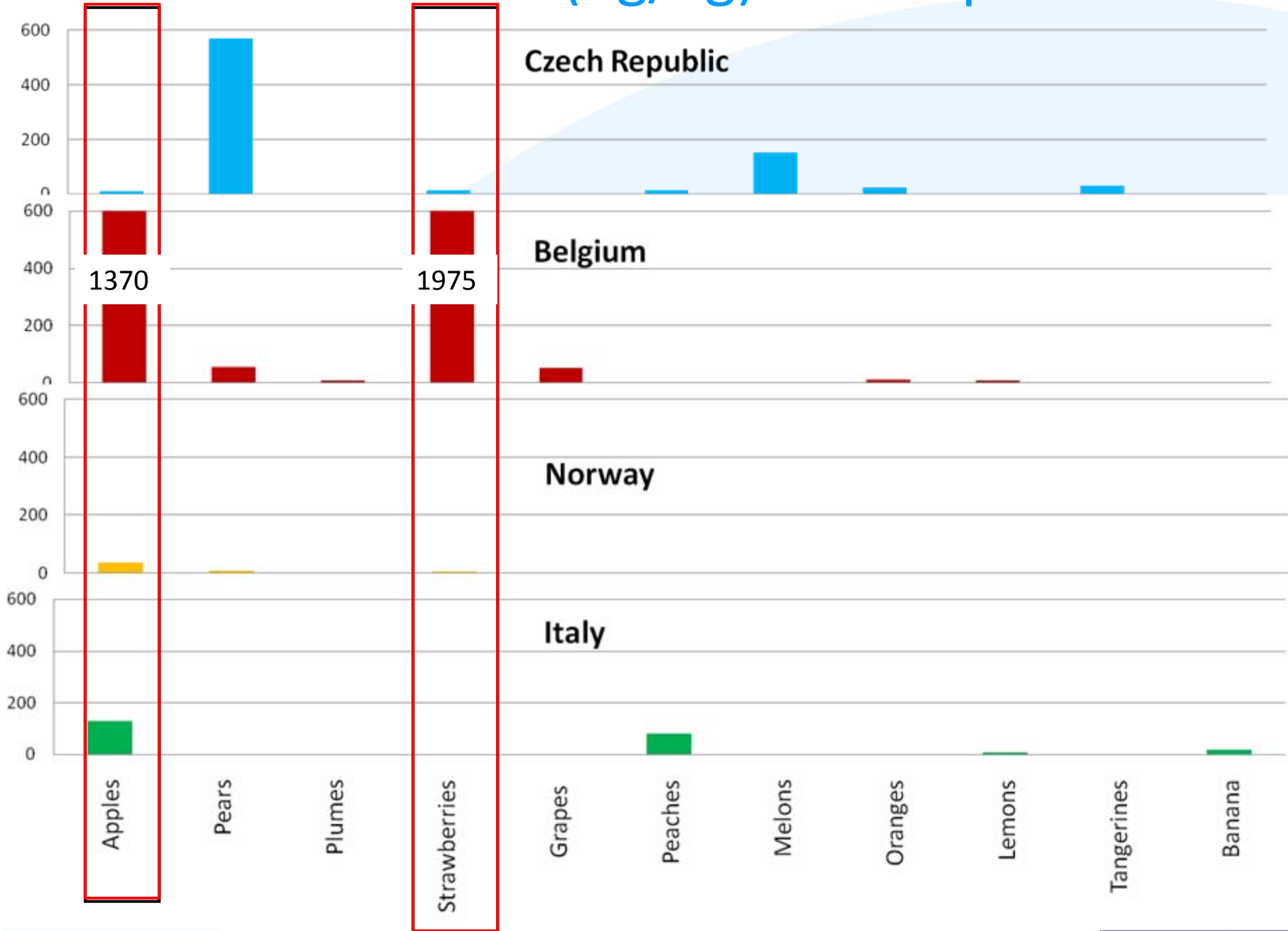


# Results – Vegetable sub-groups

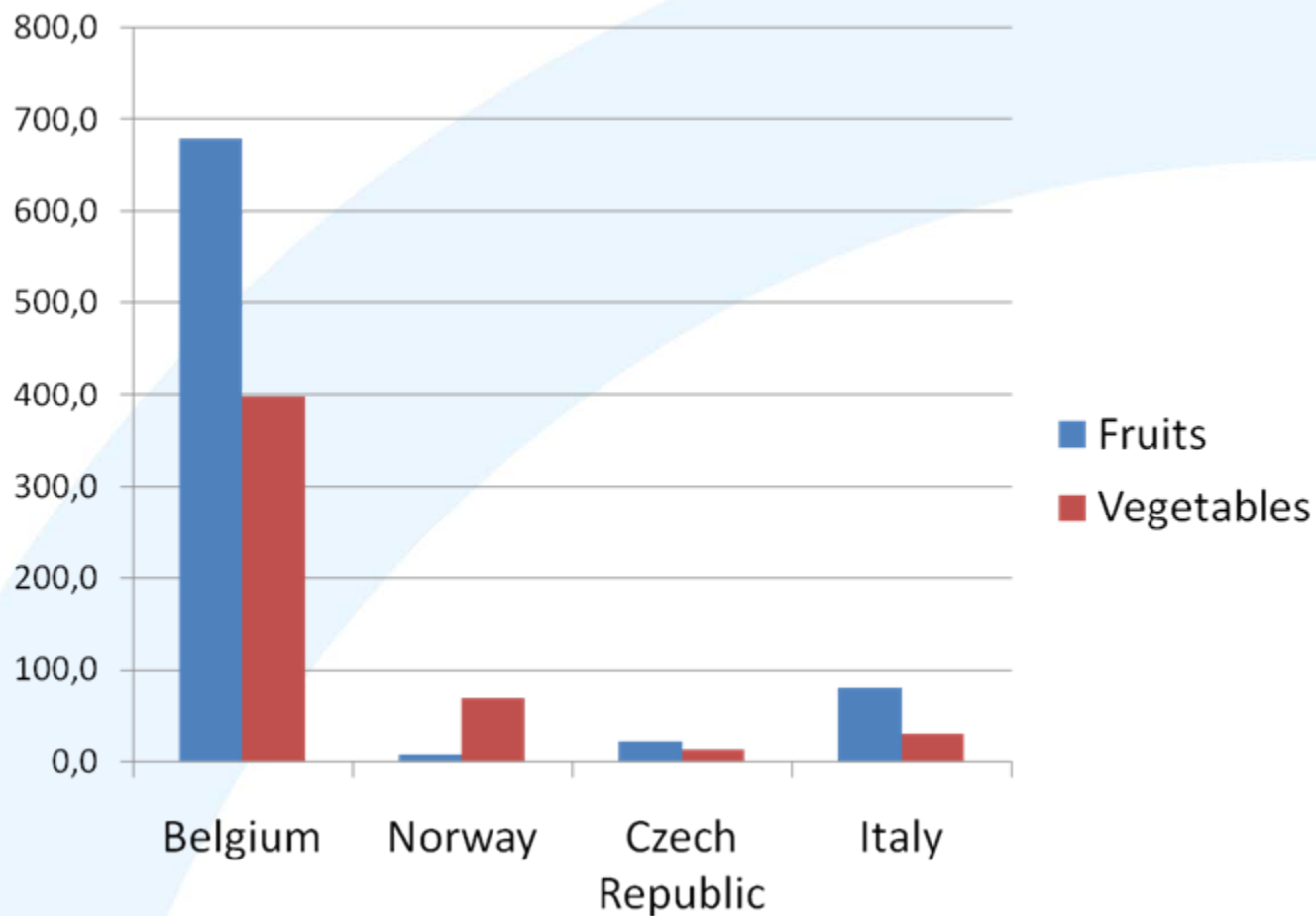
AVERAGE OF ALL 4 COUNTRIES (ng/kg)



# SumPFAS in fruits (ng/kg) → see poster



# Comparison vegetables and fruits (ng/kg)

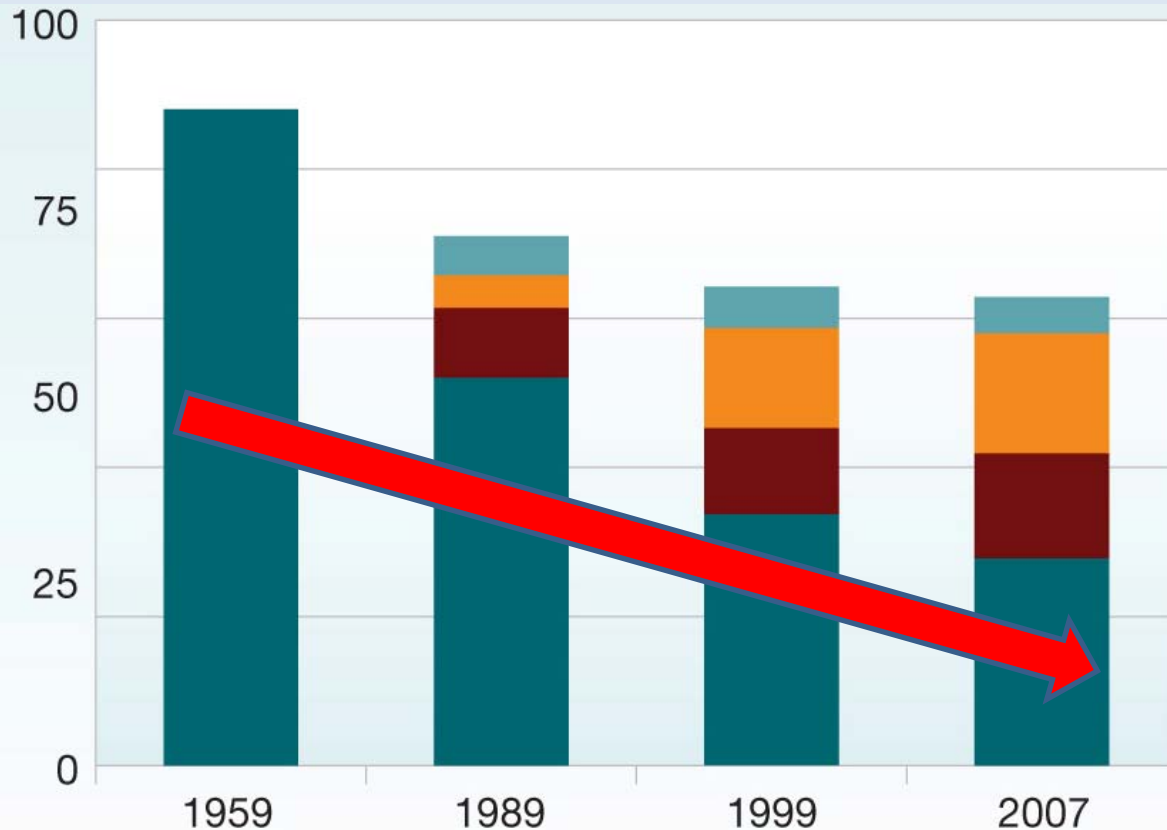


sumPFAS in fish: 500 ng/kg; seafood: 1500 ng/kg

# What does that mean?

# Food habits change over time → increased processing

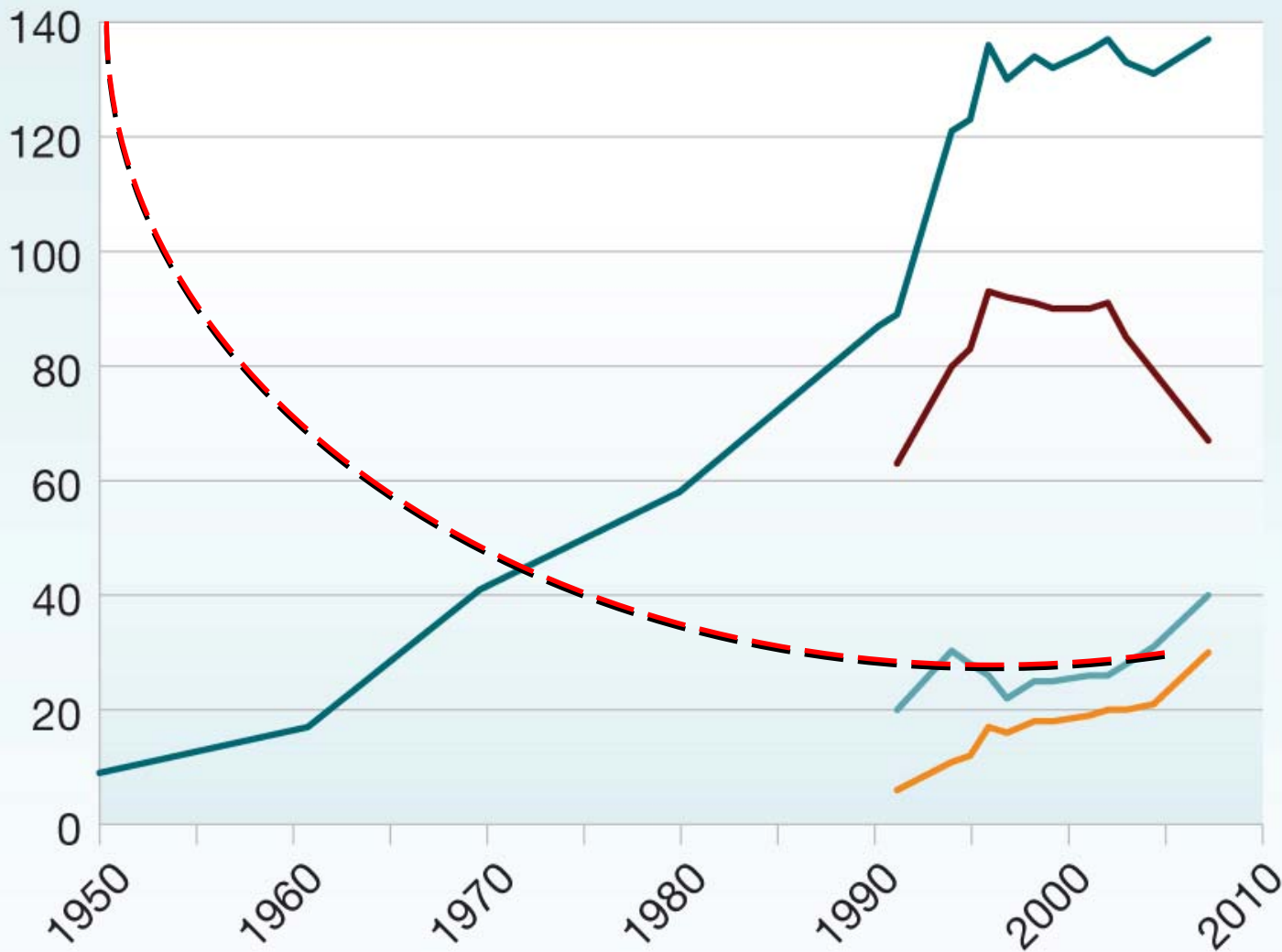
Potato product consumption (kg/person/year) in Norway



■ Cooked potatoes ■ Chips  
■ Pommies frites ■ Mashed potatoes

From: Norgemat

# Mineral water production in Norway (L/person/year)



MILK

Total

sugar

sweetener

Non-sweet

From: Norgemat





# Outlook

- Follow up elevated samples
- Investigate ready-to-cook/eat products with vegetable as main content (f.ex. spinach, potatoes, strawberryjam)
- Sample vegetables from hot spots for worst-case risk assessment
- Give input into other WPs dealing with plant uptake and animal uptake



# Summary

- Harmonised sampling and sample treatment
- PFAS amounts in vegetables from Europe are low
- Indications for geographical differences
- Detection of mostly short chained PFCAs
- Little PFOS/PFOA (close to hot spots?)
- High standards of QA/QC are necessary to be able to analyse a broad range of PFAS at trace levels

# Acknowledgements

We like to thank EU FP7/ KBBE, Wellington and all collaborators in PERFOOD consortium

