Session A: Perfluorinated compounds in our diet

A01 Retrospective analysis of food contamination with perfluorinated compounds and a tentative assessment of exposure via different food groups in Germany

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A02 Levels of PFCs in selected food commodities collected in various regions of EU

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A03 Presence and sources of anthropogenic perfluorinated alkyl substances (PFAS) in high consumption beverages

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A04 Retrospective analysis of food contamination with perfluorinated compounds and a tentative assessment of exposure via different food groups in Germany

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A05 Update on the occurrence of fluorinated compounds in European food packaging items

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A06 Perfluorinated alkylated substances in fruits collected in four European countries; PERFOOD

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Introduction

Resent studies suggest diet to be the primary route of exposure to perfluorinated alkyl substances (PFAS) in the general population. By now, no representative data on PFAS concentration in food are available in Germany. However, analysis of PFAS concentrations in various food items was part of the German food surveillance and monitoring programmes. These results can be used to derive a retrospective perspective on food contamination as well as to assess dietary exposure.

Methods

German surveillance and monitoring resulted in 4708 food samples that were collected between March 2006 and January 2011 and analysed for the occurrence of nine different PFAS (Table 1). Based on these data, a provisional assessment of dietary exposure using German food consumption data (National nutrition survey (NVS) II, diet history interviews, Max-Rubner-Institut, http://www.wasesse-ich.de) has been conducted.

	Perfluoroalkyl carboxylates				
1	PFBA	perfluorobutanoic acid	13		
r the	PFPeA	perfluoropentanoic acid	12		
sed	PFHxA	perfluorohexanoic acid	24		
ary	PFOA	perfluorooctanoic acid	98		
	PFNA	perfluorononanoic acid	23		
	PFDA	perfluorodecanoic acid	23		
-	PFDoDA	perfluorododecanoic acid	15		
	Perfluoroal	kyl sulfonates			
	DELLAS	norfluorobovonooulfonio opid			

Perfluorooctanesulfonic acid 98

 Table 1: PFAS analysed and % of analyzed samples in the
 German food surveillance and monitoring programmes

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n	62	u	11.5

Sample description

Most of the samples belong to the following food groups: meat (n=2683, including offal), fish (n=1143), drinking water (n=330), starchy roots (n=286), vegetables (n=88), milk (n=70) and eggs (n=57). Other food groups were not investigated or the number of samples was too low for evaluation. PFOS and PFOA were primarily assessed (in 98% of all samples). Other PFAS were less regularly included.

PFOS

Analytical power and resulting uncertainty

Except for water samples (LOQ: 0,001-0,011 ng/mL) most of the achievable LOQ were between 0.5 and 10 ng/g. Overall, 75% of all measurements resulted in values below the limit of detection (LOD), 8% were below the limit of quantification (LOQ) and 17% were above the LOQ. Lower bound (LB) approach were used to express the resulting uncertainty (Figure 1).



Contamination data

Highest concentrations were found in the food group meat followed by fish, eggs, root vegetables and milk (Table 2). The particularly high PFAS level in the food group meat results from edible offal from wild animals. Generally, meat from wild animals seems to be more contaminated than meat from farmed animals and the PFAS load in offal is higher than in meat.

Table 2: PFAS concentration (sum of mean of all measured PFAS in ng/g) in different food groups, a – food group "meat" without game offal, b – drinking water.

	Meat	Meat w/o ^a	Fish	Milk	Eggs	Potatoes	Root veg.	Water ^b
LB	91.17	7.00	13.15	0.77	1.20	0.03	0.57	0.01
UB	105.06	13.94	32.20	8.28	8.09	7.06	2.66	0.04

Due to their known toxicological relevance, PFOS and PFOA are of particular interest. These substances are not equally distributed in different food items (Figure 2). PFOS dominates in meat and fish whereas PFOA content outweigh PFOS in eggs. Highest contamination of single food items were detected in liver of wild animals (3480 ng/g PFOS, 174 ng/g PFOA).

Summary

- German food surveillance and monitoring programmes provides a huge pool of information on contamination of different food groups with PFAS, especially PFOS and PFOA
- These data are not representative: sampling was partly targeted and sampling did not cover either all regions in Germany nor all food items
- Analytical power varies by a several degrees and the sensitivity was comparatively low for most food items
- Particularly high degree of uncertainty in food groups meat, milk, potatoes, and root vegetables
- PFOS and PFOA are differently distributed in analyzed food items
- Fish, but also meat and milk seems to be the most relevant food groups regarding dietary exposure to PFAS, particularly PFOS
- Whereas freshwater fish might be more contaminated, marine fish is more relevant due to higher consumption



Figure 2 PEOS and PEOA contents

(ng/g) in different food groups. Meat w/o – food group "meat" without game offal Water – drinking water Root veg. – root vegetables

Exposure assessment

Based on the contamination data the contribution of different food groups to the dietary exposure was assessed. The highest estimated average adult dietary intake of PFOS is found to result from fish consumption (Figure 3). A particularly high degree of uncertainty is found for the food groups meat, milk, potatoes and root vegetables due to samples below LOD/LOQ.



The total estimated average adult dietary intake of PFOS from these food groups is 6.1 (LB) and 10.5 (UB) ng/kg b.w./d, respectively, and thereby 14-25 times below the tolerable dietary intake (TDI) established by EFSA in 2008. The total PFOA dietary intake by adults is estimated to be 0.9 (LB) and 5.4 (UB) ng/kg b.w./d, respectively. Hence, the margin of safety would be 280-1666 based on the TDI. This estimation should be seen with caution since not all food groups are analyzed and sampling was not reoresentative.

Since fish seems to be the most relevant source of PFOS the impact of the fish origin was of interest (Figure 4). Only samples which could be clearly attributed to either marine or freshwater fish were evaluated.



Figure 4

Comparison of marine fish and freshwater fish in terms of contamination with PFOS and PFOA (A) as well as in terms of their contribution to dietary intake of PFOS and PFOA (B).

Conclusion

- These results point out the probability of the relative importance of fish consumption to the overall dietary intake of PFC in the adult population in Germany.
- The degree of uncertainty is quite high due to a pretty low analytical power for most food groups as well as due to target orientated sampling.
- Both limitations will be overcome in PERFOOD.

Acknowledgement

The authors wish to thank the Federal Office of Consumer Protection and Food Safety (BVL) for providing contamination data sampled and analyzed by administrative bodies of the federal states in Germany. 3rd INTERNATIONAL WORKSHOP Anthropogenic Perfluorinated Compounds, Amsterdam, The Netherlands, June 15–17, 2011

LEVELS OF PFCs IN SELECTED FOOD **COMMODITIES COLLECTED IN VARIOUS** ICT PRAGUE **REGIONS OF EU** Veronika Hlouskova, Petra Hradkova, Jan Poustka, Eva Tilgova, Ondrej Lacina, Jana Pulkrabova, Jana Hajslova Institute of Chemical Technology, Prague, Department of Food Chemistry and Analysis, Technicka 3, 166 28 Prague 6, Czech Republic E-mail: veronika.hlouskova@vscht.cz Introduction Aim of study The request for PFCs analysis March 2010 • To analyse of 25 PFCs in 20 different food commodities, February 2008 The European Commission recommended especially of animal origin, from 4 European regions The tolerable daily intakes (TDI) for PFOS of 150 to member states to monitor the presence of perfluoroalkylated substances in food of animal ng/kg b.w. and 1500 ng/kg b.w. for PFOA were **Characterisation of samples** established by EFSA (European Food Safety and plant origin and to use a method of analysis Authority), based on CONTAM (Scientific Panel on (with limits of quantitation below 1 µg/kg, recovery Country represented region of the EU:* Contaminants in the Food Chain) recommendation. in range 70-120 %). West EU East EU North EU South EU May 2009 Czech Republic Belgium Norway Italy PFOS and its salts were recorded on the list of the PERFOOD project - start August 2009 In each region, at least 3 different supermarkets were sampled Stockholm Convention. The EU project focused on: (i) the development of robust and reliable analytical methods (with limits <u>Milk and dairy products</u> Preserved whole cow milk Meat Hen eggs of quantitation below 5 ng/kg), (ii) distribution of Bovine **Analytical method** PFCs in foods and (iii) estimation of human exposure. Fats Poultry Preserved skimmed cow milk Vegetable/olive oil Pork Soft cheese Extraction Clean-up Identification and quantification Butter Bovine and Pig live Cheese QTRAP[®] 5500 Systems, Margarine Rabbit • Samples of meat, fish, milk, AB Sciex Alcoholic beverages Sheep/lamb Fish and seafood Recovery : 70–107 % Ionization: ESI-Detection: Scheduled MRM eggs and alcoholic beverages: Marine farmed fish Preserved pork meat Beer Relative standard deviation Water, acetonitrile Soya products Seafood Wine and formic acid 1–11 % UPLC-MS/MS addition, shaking Û Final pooled sample of foodstuff prepared from 3–15 subsamples 1-10 ng/kg with NaCl and Aliquot of Acquity UPLC, Waters supernatant treated anhydrous MgSO₄ Evaporation with C₁₈ silica + EnviCarb + MgSO₄ reconstitution in **Target analytes** Samples of fats: methanol eOH. 5mM CH.COONH. 98-117 % (oil, margarine, butter) (dispersive SPE) 25 representatives of PFCs: $\overline{1}$ Relative standard deviation Acetonitrile, formic Perfluorocarboxylic acids (PFCAs): C4-C14 1-17 % acid addition, UPLC-MS/MS Limit of quantification (IOO) Perfluorinated sulfonates (PFSAs): C4, C6, C8 and C10 sonication 2.5-250 ng/kg Xevo TOS, Waters for 10 min Perfluorooctanesulfoamides: FOSA, N-MeFOSA, N-EtFOSA ation: ESI tion: Scheduled MRM Perfluorooctanesulfoamidoethanols: N-MeFOSE. N-EtFOSE **Results & Discussion** Polyfluoroalkylphosphonic acids (PFPAs): C6, C8, C10 Czech Republic Seafood Seafood 2845 ampled 731 800 80% 612 150 a/ka sample 600 518 27 12 ⁰ 24 419 17 8 10 11 400 40% 228212 Belgium 20% 245 109 90 Fish Fish 33 Not 500 400 Italy ample 300 286 131 105 169 B¥200 ≤LOQ 61 LOQ 29 32 11 19 <10Q Norway Pig/bovine liver Pig/bovine liver 2612 418₃₈₀ 500 102 344 400 9duues 308 77 001 LOQ LOQ 37 26 60% 40% 41 38 0 2 Czeck Italy Σ PFSAs Σ PFCAs FOSA PFNA PFDA Italy PFOA PFUdA Czech Republic Belgium Norway Marine fish from Belgium, Italy, Norway and freshwater fish from the Czech Republic PFTrDA PFTeDA PFDoA Figure 1 Levels of ∑ PFCs (ng/kg) in individual food commodities from four countries Figure 2 Levels of 5 PFCs in the most contaminated Figure 3 PFCA profiles in the most contaminated commodities commodities Seafood L-PFOS **Pia/bovine liver** Fish Br-PFOS 21.2% 78.8% linear PFOS Br-PFOS Sample 21.2% branched PFOS of chee 60% ¹⁹F NMR analysis of standard PFOS supplied by Wellington Laboratorie 40% 78.8% L-PFOS L-PEOS 20% 8 1 Vot. 20% Br-PFOS Standard 0.05 ng/ml Italy Norway Italy Czech Belgium Czech Belgium Norway Czech Belgium Italy Republic Republic Conclusions Figure 5 Profile of Br- and L-PFOS - in the most contaminated commodities Figure 4 Chromatogram of Br- and L- PEOS The most abundant analyte was PFOS (present in approx. 50% of samples in range 2–1958 ng/kg) followed by PFOA, PFNA, PFDA, PFUdA , PFDOA (present in approx. 20% of samples) • The most contaminated foodstuff was seafood, followed by marine/freshwater fish, pig/bovine liver and hen eggs • Less contaminated were alcoholic beverages, rabbit, poultry and fats (vegetable oils, butter and margarines)

Comparing contamination levels and profiles of PFCs (especially PFCAs and PFOS) in various food commodities among sampling countries, no significant differences were found
 For two most contaminated food samples, livers from Belgium - 2600 ng/kg PFOS and seafood from Italy - PFOA 55 ng/kg, contributions to TDI were calculated for the common person with body weight: 60 kg and for food consumption: 150 g. Contribution to the TDI (150 ng / kg bw - PFOS and 1500 ng / kg bw - PFOA) is 4.3 % for PFOS through consumption if livers in Belgium and 0.009 % for PFOA from seafood in Italy.

* Sampling institutes: Institute of Chemical Technology, Prague, Czech Republic; Norwegian Institute for Air Research – NILU, Norway; University of Antwerp, Belgium; National Institute of Health, Rome, Italy

** Lacina O, Hradkova P, Pulkrabova J, Hajslova J (2011) Simple, high throughput ultra-high performance liquid chromatography/tandem mass spectrometry trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatography/tandem mass spectrometry trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatography/tandem mass spectrometry trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatography/tandem mass spectrometry trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatography/tandem mass spectrometry trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatography/tandem mass spectrometry trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatography/tandem mass spectrometry trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatography/tandem mass spectrometry trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatographylated distribution and the performance liquid chromatographylated origin and trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatographylated distribution and trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatographylated distribution and trace analysis of perfluorinated alkylated substances in food of animal origin: milk and fish, J Chromatographylated distribution and trace analysis of perfluorinated alkylated alk

Specific University Research (MSMT No. 21/2011).



PRESENCE AND SOURCES OF ANTHROPOGENIC PERFLUORINATED ALKYL ACIDS (PFAA) IN HIGH CONSUMPTION WATER-BASED BEVERAGES

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Introduction

• Perfluorinated alkyl acids (PFAA) have been found to be present in human blood serum in the ng/g range.

• Exposure pathways: house dust, air, food and drinking water (see fig. 1; Vesteraren 2009).

• Drinking water based beverages might have additional PFAA contamination sources: ingredients or food contact material.

• The purpose of the present study is to analyze cola mixed from tap water and syrup, coffee prepared from automatic coffee machines and draught beer for 17 different PFAA.

 Sources are tracked by performing leaching experiments with polytetrafluoroethylene (PTFE) and perfluoroalkoxy (MFA) FDA approved tubes.



Figure 1: PFAA exposur pathways to humans

Materials and methods

• Samples were collected in the city of Amsterdam, the Netherlands.

• Leaching experiments: liquid was pumped 24 h through tube at 5° C or 80° C, respectively (see fig. 2).

• Analysis of the samples:

250 mL beverage samples were spiked with the mass labelled internal standards. Samples were extracted with SPE. Extracts were analyzed with LC from Shimadzu using a ACE 3 C18-300 column connected to a tandem mass spectrometer (4000 Q Trap) operating in the negative ionization mode.

Figure 2: Set-up tube experiments

Results & Discussion

• Several PFAA were detected in post-mixed cola, coffee from automatic machines and tap water.

 \bullet In beer no analytes were detected above the LOQ which might be due to the low recoveries (1 – 11 %).

Cola

• Significantly decreased concentrations of PFBA, PFHpA, PFOA and PFHxS in cola compared to corresponding tap water (see fig. 3).

• Lower PFAA concentrations in the cola might be due to water purification step during the mixing process.

• In bottled cola only PFHpA was detected.



cola and corresponding tap water (n = 4)

Coffee

• Significantly increased concentrations of PFPeA, PFHpA, PFOA, PFDA and L-PFOS in coffee from automatic coffee machines in comparison to corresponding tap water (see fig. 4)

Tap water and hot water do not show different PFAA concentrations (see fig. 4)
For coffee no PFBA, PFHxA, PFNA and PFHxS analyte peaks could be quantified → probably due to matrix effects.



Figure 4: Comparison PFAA concentrations in hot water and coffee from automatic machine and corresponding tap water (n = 1)

No leaching of PFAA into an EtOH:H₂O 2:8 mixture from the PTFE and MFA tube at 5°C.

Leaching experiments

Increased concentration compared to the methode blank in water pumped
 Increased concentration compared to the methode blank in water pumped

through PTFE tube at 80°C for PFHxA, PFHpA and PFOA (see fig. 5). • Increased concentration compared to the method blank in water pumped through MFA tube at 80°C for PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDoA, L-PFOS and Br-PFOS (see fig. 5).



Figure 5: PFAA pattern for leaching experiments with water at 80°C for different tubes (n = 2)

Conclusions

- PFAA are present in coffee and cola from automatic machines.
- Concentrations in cola decreased in comparison to tap water.
 → Purification of tap water?

• Coffee was found to have significantly higher analyte concentrations than tap water for PFPeA, PFHpA, PFOA, PFDA and L-PFOS.

Additional PFAA sources to the coffee could be the coffee beans and the contact with PTFE tubing.

• PTFE tubes are found to leach out PFHxA, PFHpA and PFOA at 80°C.

• PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDoA, L-PFOS and Br-PFOS leached out of MFA tubes at 80°C.

• Tubes which are composed of fluoro-polymers are a potential exposure source to beverages.

 \rightarrow 24 h experiment is not realistic, running time of beverages through automatic machine tubes is shorter.

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Preliminary results of estimation of dietary intake of some perfluorinated hydrocarbons from consumption of drinking water

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Introduction

The aim of the ongoing PERFOOD project is the quantification of perfluorinated alkyl substances (PFAS) in food and to calculate the resulting intake of PFAS via food based on national food consumption databases.

The growing occurrence of PFAS in the environment is an increasing matter of health risk assessment. Water is one of the most important environmental compartments in which PFAS are distributed. Consequently, it appears also in drinking water. Drinking water is not only consumed as such but also used to prepare other beverages like coffee and tea (household production) as well as by industrial production of soft drinks and for cooking (Figure 1). Thus, even though drinking water is contaminated at low levels the amount consumed via different food items could make water a major source of PFAS.



Figure 1 Use of drinking water: tap water for coffee, tea and preparation of foods like soups and sauces, bottled mineral and spring water

Methods

Tap water (n=37) and bottled water (n=12) samples from Belgium (BE), Italy (IT), Norway (NO) and Czech Republic (CZ) were analyzed for seven different PFAS (Figure 2 and Table 1). The total amount of all PFAS have been evaluated to get a first impression on the contamination level. For exposure estimation, the pathways of water directly and indirectly consumed have been characterised by the information given by the recently published comprehensive database of food consumption data by the EFSA#. This database comprises national food consumption data in a harmonised manner to be used for exposure assessments. Data were available for CZ, BE and IT only. As for NO, food consumption data were taken from the Norwegian internet site*.



Perfluoroalkyl carboxylates

perfluorobutanoic acid

perfluorohexanoic acid

perfluoroheptanoic acid

perfluorooctanoic acid

perfluorononanoic acid

 Perfluoroalkyl sulfonates

 PFHxS
 perfluorohexanesulfonic acid
 C₆HF₁₃O₃S

Perfluorooctanesulfonic acid C₈HF₁₇O₃S

approach (LB and UB) were used to express the resulting uncertainty.

derived from Po river close to its delta (surface water).

PFBA

PFHxA

PFHpA

PFOA

PFNA

PFOS

Results

Contamination data

concentrations.

Figure 2 Tap water sampling points in

- Europe:
- 1 Nijlen, Belgium
- 2 Zwijndrecht, Belgium
- 3 Malmédy, Belgium
- 4 Alessandria, Itlay
- 5 Rome, Italy 6 - Firenze, Italy
- rirenze, Italy
 7 Ferrara, Italy
- 8 Trissino, Itlav
- 9 Brescia, Italy
- 10 Tromsoe, Norway
- 11 Kjeller, Norway 12 – Trondheim, Norway

Table 1

C₄HF₇O₂

C₆HF₁₁O₂

C7HF13O2

C₈HF₁₅O₂

C_oHF₁₇O₂

Half of the results were below the limit of quantification. Thus, the lower and the upper bound

PFBA was most frequently quantifiable in water samples and was generally present in the highest

Overall, the average contamination (sum of all analyzed PFAS) was higher in tap water samples (18/19 ng/L, LB/UB, respectively) than in bottled water samples (3/5 ng/L) with distinct regional

differences (Figure 3 and 4). In addition, not only the total amount differed in samples but also the

relative composition of PFAS. The highest total contamination was detected in tap water from Ferrara (IT, 103 ng/L) which also contained the highest PFOA contamination. Ferrara tap water is

PFAS analyzed in present study

13 – Czech Republic





Figure 3

Contamination of **bottled water** with PFAS in Belgium (BE), Italy (IT), Norway (NO) and Czech Republic (CZ). Estimation is based on the lower bound approach (LB) and the upper bound approach (UB).

Figure 4 Contamination of tap water with PFAS in Belgium (1-3), Italy (4-9), Norway (10-12) and Czech Republic (13). For details see Figure 2. Estimation is based on the lower bound approach (LB) and the upper bound approach (UB).

Consumption data

/ Bu

Some differences in water consumption (Figure 5) are probably due to different survey methods (particularly Norway) and this will have an impact on the exposure estimation. Consumption of tap water, coffee and tea were used to calculate exposure to PFAS via tap water. Similarly, consumption of bottled water and soft drinks were used to estimate dietary intake of PFAS via bottled water.



Figure 5

Consumption of water in Belgium (BE), Italy (IT), Norway (NO) and Czech Republic (CZ).

Exposure data

The average PFAS intake by water consumption is estimated to be 8.3/9.3 (LB/UB) ng/d, 13.3/18.2 ng/d, 8.4/9.9 ng/d, 1.2/1.4 ng/d, in BE, CZ, IT and NO, respectively. Thus, people in CZ seem to have the highest PFAS intake via drinking water. Water from hot spots resulted in higher exposure, e.g. 33.2 ng/d in Ferrara (IT). The exposure in Ferrara is 2-70-fold (LB) / 2-37-fold (UB) higher than in other investigated regions in Europe.

Overall exposure to PFAS is not equal to intake of PFOS and PFOA, the two substances which are toxicologically relevant according to present knowledge. Total dietary intake of PFOS via drinking water ranges from 0/0.03 (LB/UB) to 1.4 ng/d. Highest exposure is found in Zwijndrecht (BE). PFOA intake vary to a greater degree: 0/0.09 (LB/UB) to 10.6 ng/d with highest intake in Ferrara.



Figure 6

Estimated dietary intake of PFAS from consumption of drinking water (via tap water, coffee, tea, bottled water, soft drinks) in different regions of Europe: Belgium (1-3), Italy (4-9), Norway (10-12) and Czech Republic (13). For details see Figure 2. Estimation is based on the lower bound approach (LB) and the upper bound approach (UB).

Conclusion

It is concluded that water consumption may serve as an important source of PFAS. In addition, geo-referenced source should be paid a special attention. Uncertainties are related to inconsistent food (water) descriptions and missing information (NO) due to particularities in the food consumption study methodology. This evaluation does not take into account other liquid intakes e.g. beer, which will be assessed separately, and only in part additional water intake from cooking.

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UPDATE ON THE OCCURRENCE OF FLUORINATED COMPOUNDS IN EUROPEAN FOOD PACKAGING ITEMS

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Introduction

In a previous study screening methods aiming at the detection of fluorine in paper-based packaging and other food contact materials (FCM) are developed [1]. Besides a more sophisticated screening approach by headspace-GC-MS, sliding spark spectrometry (SSS) turned out to be a quick and reasonable precise screening tool.

Target of this investigation was an identification of fluorine containing FCM on a European basis. Therefore, the screening study was extended to a total number of 430 samples from 6 European countries. FCM were sorted with respect to their function, in order to find out which groups of FCM items exhibit the highest share of F positive samples.

Screening Methods

- **SSS:** Sliding spark spectroscopy is normally used for plastic characterization and sorting. The basic principle of the method is the thermal vaporization of a small amount of the sample surface using a train of defined high-current sliding sparks. The material components in the spark plasma are vaporized, atomized and activated to emit radiation [2]. Software analysis of the delivered spectra gives information on the content of elementary fluorine on top of the surface.
- **HS-GC-EI-MS:** Headspace GC-EI-MS (PerkinElmer Clarus 600GC, PerkinElmer Clarus 600C MS combined with PerkinElmer TurboMatrix 40 Trap HeadspaceSampler) is used for development and testing of an alternative screening method. About 1dm² of the FCM like packaging paper was placed into a 10ml headspace vial. At a temperature of 150°C volatile fluorinated compounds are released from packaging material into the headspace. An aliquot of the headspace volume is transferred onto a GC column and detected by EI-MS after chromatographic separation.

Results and discussion

A total of 430 European packaging and other food contact materials were analyzed. The samples were collected mainly in Germany (n=238), Italy (n=83) and Norway (n=56), a limited number of samples came from the Netherlands (n=13), Belgium (n=16), and Greece (n=10) (see Fig. 1). Samples were assigned to 13 FCM categories, whereas about 5 non-paper food packaging items were allocated to paper packaging. TEFLON® coated multiuse baking papers are allotted to FCM intended for baking.

Figure 2 shows the relative contribution of different FCM categories. Miscellaneous paper-packaging shows the highest share of all samples (32,9%), followed by FCM intended for baking (21,7%). The amount of fluorine positive and negative samples in the different FCM categories is presented in Fig. 3.

It seems, the share in fluorine containing FCM in Germany, Norway, the Netherlands, Belgium, Italy, and Greece accounted for 27%, 0%, 23%, 19%, 12% and 0% of the samples delivered from these countries. However, due to differing sampling strategies and the number of delivered samples, data sets of the different countries are not well comparable. Therefore, further investigations are focused on the whole data set.

The studied food contact materials were grouped with respect to their function, i.e. the typical use as packaging material or baking aid for a special type of food. The share of fluorine positive samples in these groups differed significantly. No positive samples were found in packaging of beverages and eggs, filters and popcorn bags. The share of positive samples is below 10 % in cheese/sausage packaging and miscellaneous packaging. In contrast, the occurrence of fluorine positive samples in butter wraps, fast food packaging, papers intended for baking, sandwich papers and take away food packaging accounted for 24 %, 23%, 56 %, 66 % and 43 %.

Acknowledgments

References

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13% 19% 55% 6%

2%

Fig. 1: Origin of the investigated packaging samples



Fig. 2: Application related categories of the investigated food contact materials



[1] Fiedler, Dominik; Schlummer, Martin; Gruber, Ludwig; Wolz, Gerd. Screening of packaging materials from the German market for fluorine containing coatings by Sliding Spark Spectroscopy (SSS) and Headspace-GC/MS. 2rd International Workshop on Fluorinated Surfactants: New Developments, 2010, Abstract C-08. <u>http://pfl.hs-fresenius.de/images/PDF/abstract%20book.pdf</u> [2] Seidel, T., Golloch, A., Beerwald, H., Böhm, G., 1993. Fresenius' Journal of Analytical Chemistry 347, 92-102.







PERFLUORINATED ALKYLATED SUBSTANCES IN FRUITS COLLECTED IN FOUR EUROPEAN COUNTRIES; PERFOOD Wendy D'Hollander ⁽¹⁾, Dorte Herzke ⁽²⁾, Lieven Bervoets ⁽¹⁾, Jana Hasjolva ⁽³⁾, Gianfranco Bramibilla ⁽⁴⁾, & Pim de Voogt

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Introduction

Human exposure assessments have indicated that non-occupational exposure to perfluorinated alkylated substances (PFAS) can occur through a variety of exposure routes. Although, dietary intake appears to be the major exposure pathway (Fromme et al., 2009), data on levels of PFAS in the human diet and drinking water remain scarce (D'Hollander et al., 2010).

In the EU project PERFOOD, standardized selection of food items, sampling procedures and analytical methods as well as evaluation strategies enabled a unique assessment of the occurrence of PFAS in European food as well as the identification of major sources of PFAS exposure via food. In the first campaign food items, covering all types of food, were selected in respect to their average consumption amounts typical in four European main regions (East, West, North and South). During the sampling campaign more than 800 raw food items were purchased, homogenized and after pooling analysed in selected laboratories. This presentation will show the PFAS levels in fruit sampled in four different countries.

Materials & Methods

Sample collection

- Spring- summer 2011 in Czech Republic, Italy, Norway & Belgium
- 12 different kinds of fruit representing 4 fruit categories:
 - ✓ Berries
 - \checkmark Citrus fruit
 - \checkmark Pip and stone fruit
 - \checkmark Exotic fruit
- Individual (3-10) samples of each country were pooled

Analysis

- Methanolic KOH extraction + Oasis Wax ® clean up
- Extraction in duplicate
- Target analytes:
 - ✓ Sulfonates: PFBS, PFHxS, PFOS and PFDS
 - ✓ Carboxylates: PFBA, PFPeA, PFHxA, PFOA, PFNA, PFDA, PFUdA, PFDoA, PFTrDA and PFTeDA
- UPLC MS/MS

Results

 ΣPFAS levels in fruit in pg/g range except two samples from Belgium (apples 1.4 ng/g & strawberries 1.9 ng/g) PFCAs more abundant compared to PFSAs (fig.1+2)



Fig.1. ΣPFCAs (pg/g) in fruits sampled in 4 countries

• In general, both PFCAs and PFSAs in Belgian samples were higher, except pears originating from Czech Republic.

 Highest levels of individual PFAS were found for PFBA (1.2 ng/g in Belgian strawberries) and PFOS (0.5 ng/g in Italian pears and 0.3 ng/g in Belgian apples)

• Detection frequency:

- ✓ PFPeA (68%) > PFOA (60%) > PFOS (44%) > PFNA (32%) > PFHxA (24%) > PFBS (16%)
- ✓ PFDoA & PFTeA only detected in Belgium pears
- ✓ PFHpA, PFDA, PFUdA, PFDS, PFTrA < LOD





• Patterns between different countries in same fruit species as well as patterns of different fruits originating from one country are totally different (fig. 3).



Fig. 3. Different patterns of all analyzed fruits of Belgium, Czech Republic, Italy and Norway

Conclusions

• Higher levels found in fruits orginating from Belgium could be possibly explained by the presence of a perfluorochemical manufacturing plant. • No clear trend was observed in the patterns of the different PFAS. • In general, fruit will not be the main contributor to the intake of PFAS through our diet but these data show that fruit can be a potential source of

PFHxA

PFPeA

PFBA

exposure, especially if the fruit origins from locations in the vicinity of point sources.

Fromme H, Tittlemier SA, Völkel W, Wilhelm M, Twardell D (2009). Perfluorinated compounds - exposure assessment for the general population in Western countries. Int J Hyg Environ Health 212: 239-270.

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