Migration of poly- and perfluorinated compounds from food contact materials into food – Part I

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Part I

Ludwig Gruber (Fraunhofer IVV):

Migration of poly- and perfluorinated compounds from food contact materials into food

* Screening for fluorinated compounds
* Migration at ambient temperature
* Migration at elevated temperature
* Formation of FTOH from precursors

Part II

Jutta Tentschert (BfR):

Actual situation: Poly- and perfluorinated compounds for food contact materials

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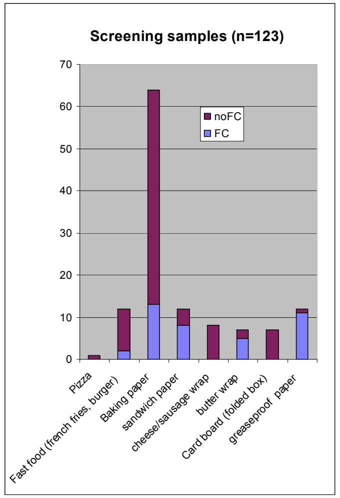
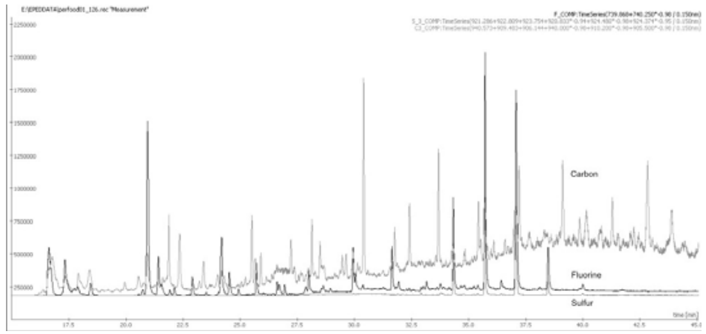
F-Screening methods for FCM

<u>Surface spectrometry</u>
- Sliding spark spectrometry
- WDXRF (new)
- neg: EDXRF and FTIR



<u>Volatile fluorinated Compounds</u>
- HS-GC-(EI)-MS
- P&T-GC-EPED



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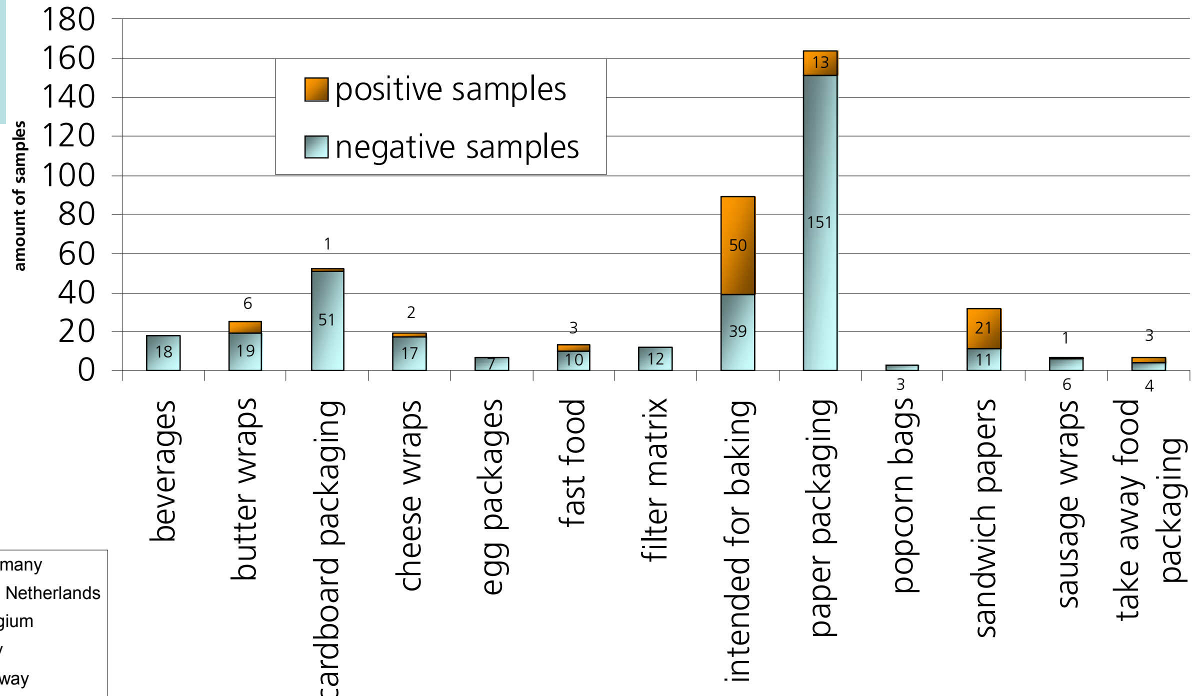
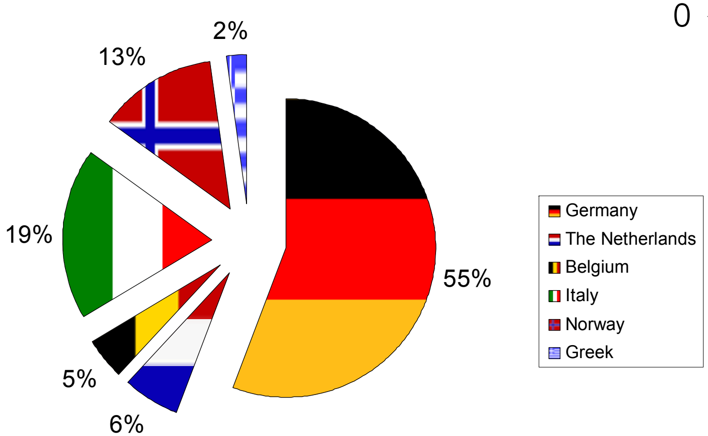
Results of F-Screening

See:
Fiedler et al.: Poster A05





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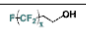
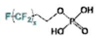
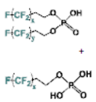
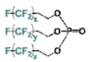
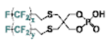
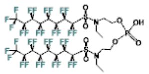
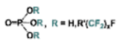
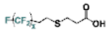
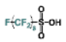
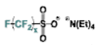
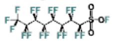
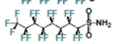
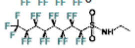
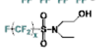
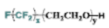
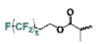
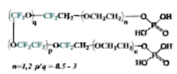
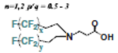
Per- and polyfluorinated compounds in food contact material

Common name	Tradename	Supplier	Used or present as	Structure	Composition	Measured structures
FTOH x:2 fluorotelomer alcohols	Zonyl BA-L	Sigma Aldrich	Starting chemical for syntheses of fluoromonomers and polymers		$F(CF_2)_xCH_2CH_2OH$ Solvent unknown	4:2, 6:2, 8:2, 10:2, 12:2, 14:2, 16:2
monoPAPS x:2 FTOH di-substituted phosphate surfactant	Synthesised std.: no tradename [1]	U. of Toronto / Chiron*	Food paper grease/water repellent; synthesis byproduct or degradation product of diPAPS		$F(CF_2)_xCH_2CH_2OP(O)(O)(O)H_2$	4:2, 6:2, 8:2, 10:2
diPAPS x:2/y:2 FTOH di-substituted phosphate surfactant *or* Disubstituted phosphate surfactants	Synthesised std.: no tradename	U. of Toronto/ Chiron*	Food paper grease/water repellent (incl. Zonyl NF)		$F(CF_2)_xCH_2CH_2OPO(O^-)(H$ or $NH_4^+)(O)CH_2CH_2(CF_2)_yF$ + $F(CF_2)_xCH_2CH_2OPO(OH)OH$	4:2/4:2, 6:2/6:2, 8:2/8:2, 10:2/10:2
	Zonyl NF Zonyl UR[2]	Sigma Aldrich /	Mold release spray and internal lubricant (polymers); semi release (adhesives); levelling and antisoling (caulks), (Zonyl UR)		NF: 19.5% solids; water UR: 100% solids	(x+y)=12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34
	Zonyl FSE	Mason/ Chiron*	Antisoiling (paints/coatings), levelling and gloss and semirelease agent (waxes, adhesives), external lubricant (polymers), hair conditioning and rinse		FSE: 14% solids 24% ethyleneglycol 62% water	(x+y)=12, 14, 16, 18, 20, 22, 24
triPAPS x:2/y:2/z:2 FTOH tri-substituted phosphate surfactant	Present in diPAPS, industrial blends and in microwave popcorn migrates	Chiron*	Synthesis byproduct of diPAPS		$[F(CF_2)_xCH_2CH_2O]_2P(O)$-$OCH_2CH_2(CF_2)_yF$	x:2/y:2/ z:2 triPAPS having diPAPS of (x+y)= 12, 14, 16, 18
S-diPAPS x:2/y:2 FTOH di-substituted thioether phosphate surfactant	Present in microw. popcorn migrates. (Lodyne P208E)	-	Food paper grease/water repellent		$[F(CF_2)_x(CH_2CH_2)_2SCH_2]_2$–$(CCH_2OP(O^-)(O)OCH_2)$	(x+y)=12, 14, 16, 18, 20, 22, 24, 26, 28
SN-diPAPS di (*N*-ethyl-2-perfluorooctane sulfonamido ethyl) phosphate	FC 807	Danish Vet. and Food Adm.	Food paper grease/water repellent		$[F(CF_2)_xS(O)(O)N$-$(CH_2CH_3)CH_2CH_2O]_2$-$P(O)OH$	(x+y) = 16
Alkyl-PAPS Perfluoro alkyl organic phosphate	FF-807	Wuhan	Food paper grease/water repellent		Mixture of mono-, di- and tri-PAPS (as FC807): 100%	(x+y) = (12),14, 16, 18, (20)
3-[2-(perfluoroalkyl)ethylthio] propionate	Zonyl FSA	Sigma Aldrich	Levelling and gloss (paints/coatings, waxes, adhesives), mold release spray and $CaSO_4$ scale removal (polymers),..		$F(CF_2)_xCH_2CH_2SCH_2CH_2COOH$ 50% solids, 37.5 % isopropylalcohol, 37.5% water	x = 4, 6, 8, 10, 12
PFOS Perfluorooctanesulfonate	T-PFOS (techn. mix)	Sigma Aldrich	Starting chemical for syntheses, degradation product of PFOS derivatives		$F(CF_2)_xS(O)(O)OH$ >98%	x=8
PFSA Perfluoroalkylsulfonate, tetraethylammonium salt	FT-248	Wuhan	Starting chemical for syntheses, degradation product of PFOS derivatives		$F(CF_2)_xS(O)(O)OH$	x= 4, 6, 8, 10
PFOSF Perfluorooctanesulfonate fluoride	FX-8	Wuhan	Starting chemical for syntheses		$F(CF_2)_xS(O)(O)OF$ >90%	x=8
PFOSA Perfluorooctane sulfonamide	FOSA	Wellington	Intermediate chemical		$F(CF_2)_xS(O)(O)NH_2$ 99%	x=8
Et-PFOSA Perfluorooctane 1-sulfonamide *N*-ethyl ester	FF-09	Wuhan	Intermediate chemical		$F(CF_2)_xS(O)(O)$-$NHCH_2CH_3$ >95%	x=8
Alkyl-PFOSA[6] Alkyl perfluorooctanesulfonamide[3]	FC-10	Wuhan	Intermediate chemical		$F(CF_2)_xS(O)(O)N(CH_2)_zCH_3)$-$CH_2CH_2OH$ >90%	x=8 z=1,2
Fluoroalkoxylate Perfluoroalkyl polyethoxylate alcohol	Zonyl FSN[4]	Sigma Aldrich	Teflon wetting aid (waxes/polishes /polymers), polystyrene coatings (coffee cups), defoamer, levelling, gloss and wetting agents		$F(CF_2)_x(CH_2CH_2O)_yH$ Zonyl FSN: 40% solids; 30% 2-Propanol, 30% water	x=6, 8, 10, 12, 14, y= 5,6,7,8, 9, 10,11,12,13, 14,15,16,17,18,19,20
	Zonyl FSO		Semi-release (adhesives), mold release and wetting agent (polymers), levelling, gloss and wetting agents (waxes/polishes/graphic)		Zonyl FSO: 50% solids, 25% ethylene glycol, 25% water	
Fluoroacrylate	Zonyl TM	Sigma Aldrich	For acrylate polymers; coatings of textiles, paper, leather; UV curable coatings, fire fighting agents and emulsifier for copolymers		$F(CF_2)_xCH_2CH_2OC(O)$-$C(CH_3)=CH_2$ Solvent unknown	x=5,6,7,8,9,10,11, 12,13,14,.. (cf. *m/z* 269, 319, 369, 419, ..919 are present)

See:
Trier X, Granby K and Christensen J: Polyfluorinated surfactants (PFS) in paper and board coatings for food packaging. Environmental Science and Pollution Research: 1-13, 2011.

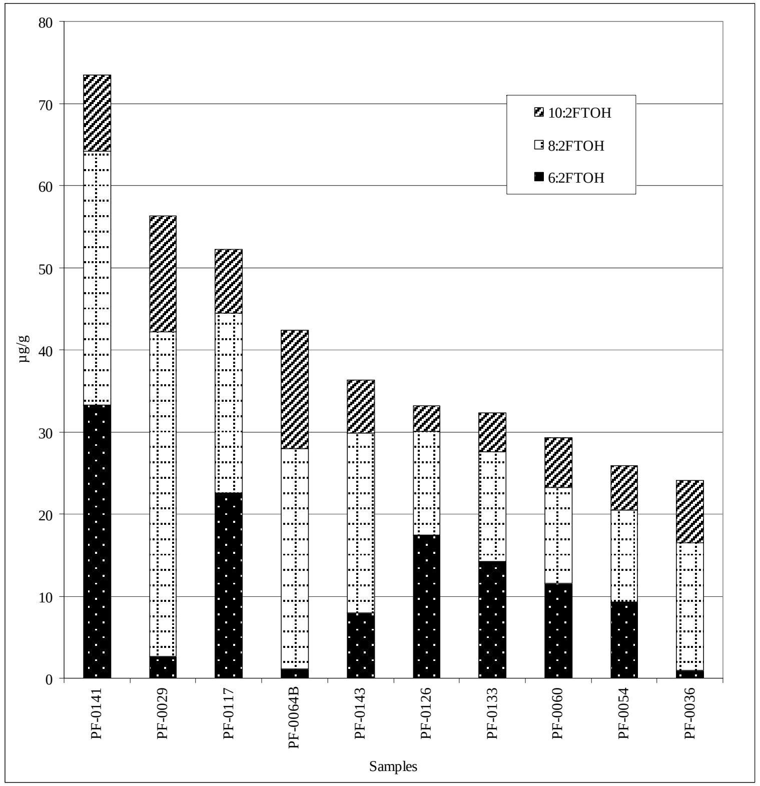
polyfluoropolyether (PFPE) di-(monophosphate)	Fomblin HC/P2 1000[5]	EU Joint Research Council (Solvay Solexis)	Food paper grease/water repellent, antistick and antiirritant in lipsticks, creams, hair conditioner Emulsifier/preservative-free systems, antimicrobial agent.		$HO(O)(OH)PO$-$(CH_2CH_2O)_n$-CH_2CF_2-$(OCF_2)_p$-$(OCF_2CF_2)_p$-OCF_2CH_2-$(OCH_2CH_2)_nOP(OH)$-$(O)OH$, 93% difuncitonal content	No chromatographic separation
di (*N*-ethyl perfluoroalkyl) *N*-propanoic acid	Lodyne 2000 (aqueous dispersion)	Danish Veterinary and Food Adm.	Food paper grease/water repellent etc.	 Additional structure: Tentschert et al. 2010	$[F(CF_2)_x(CH_2CH_2)]$ $([F(CF_2)_y(CH_2CH_2)])$-N-CH_2CH_2COOH $[F(CF_2)_x]([F(CF_2)_y])C_{14}H_{23}O_6N$ Solvent unknown	(x+y)=16, 18, 20, 22, 24 (x+y) = 16, 18 (*m/z* 1138, 1238) and *m/z* 1193, 1293

PFAS levels in food contact material

<u>Fluorine containing coatings</u>
- e.g. PAPS
- 0,2 % F (surface)
- ~100 µg/dm²

<u>Precursors</u>
- FTOH dominate
- up to 10 µg/dm²
- 8:2 dominating congener

<u>PFCA</u>
- nn - 900ng/g
- broad spectrum
- No fixed ratio of ΣFTOH/ΣPFCA



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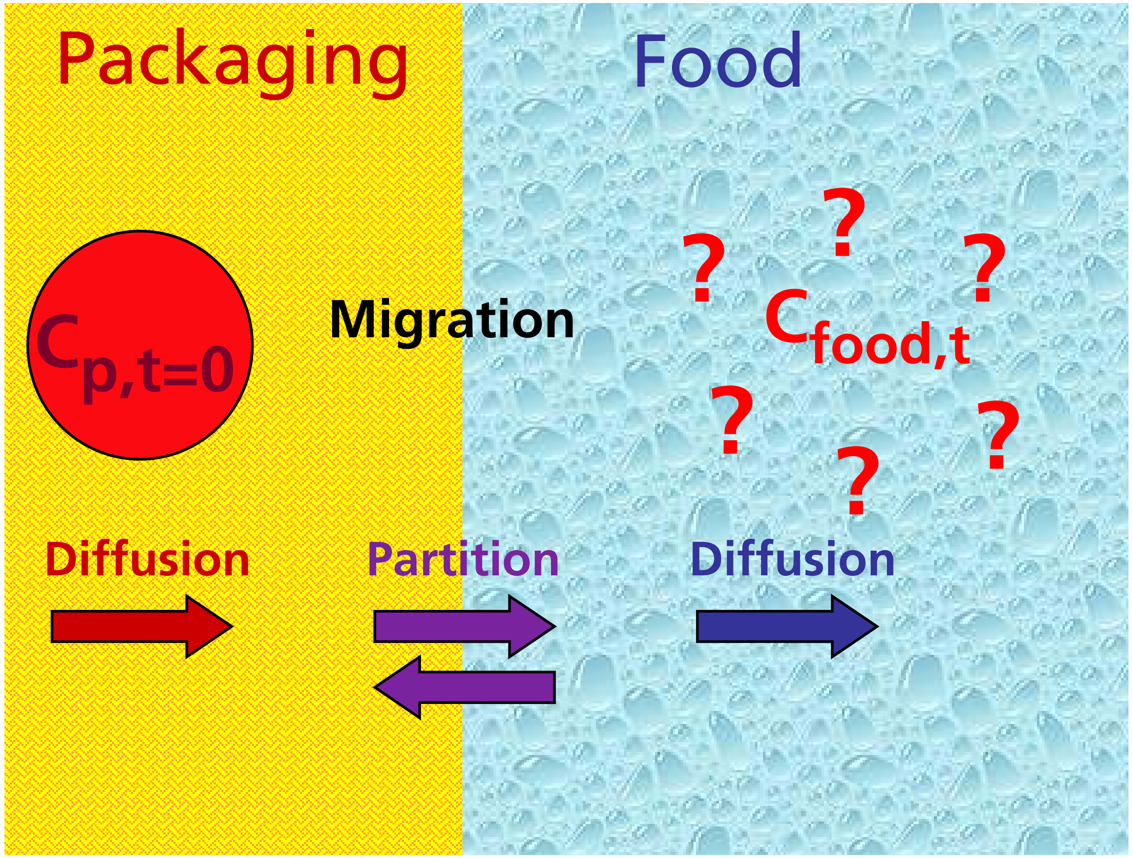
What is migration ?



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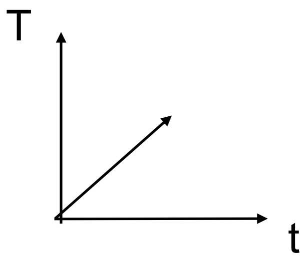
Development of migration methods

Refrigerator (16 tests)

- Long-term storage 1 – 30 days
- Low temperature (5°C)
- 3 food items, 4 simulants



Fast-Food Restaurant (8 tests)

- Short-term storage up to 30 min
- Elevated temperature (60-80°C)
- 1 food items, 1 simulant

Ambient conditions (8 tests)

- Medium-term storage 1 – 10 d
- Ambient temperature (20-40°C)
- 3 food items, 1 simulant

Food / simulant

real / worst case conditions

Oven (11 tests)

- Short-term heating 10 – 120 min
- High temperatures (180-250°C)
- 3 food items, 1 simulant

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FTOH-Analysis of migration samples

Muffins were homogenized and sub samples of about 3g were fortified with isotope-labelled standards and extracted with n-hexane by pressurized liquid extraction (ASE 200, Dionex, Germany), applying Teflon®-free equipment.

Butter and **Tenax** samples were extracted with n-hexane by vortexing and ultrasonic bath after fortification with labeled standards. Afterwards, the extracts were cleaned by solid phase extraction using silica as adsorbent (Phenomenex Strata Si 1). Reduced extracts were subjected to GC/CI-MS analysis (TSQ 7000, Thermo) using methane for chemical ionisation.

Quantification was carried out by an isotope dilution method. Using the same analytical approach Tenax, both types of muffin dough and butter were analysed for FTOH blanks.

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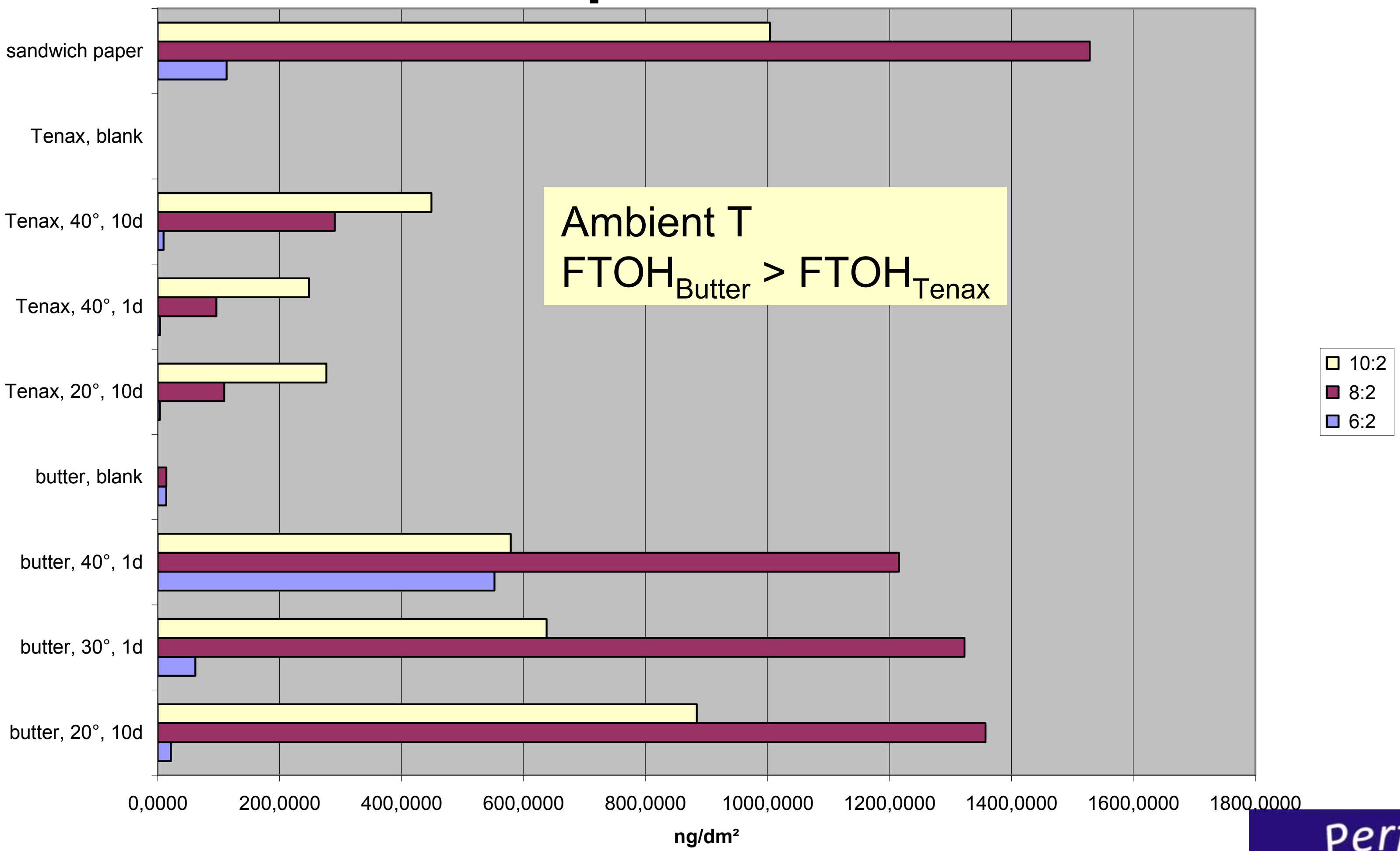
FTOH-Migration at ambient temperature



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PFCA-Analysis of migration samples

Muffins, Butter and **Tenax** samples were extracted with methanol by using an ultrasonic bath after fortification with labeled standards.

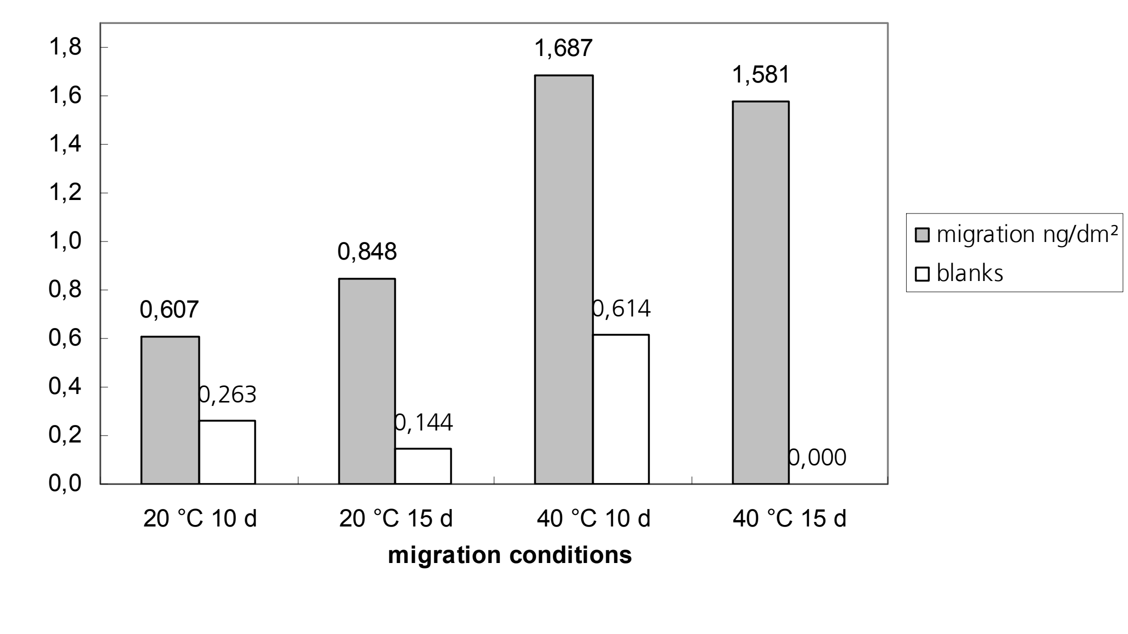
Extracts were cleaned by solid phase extraction using a weak ion exchanger as adsorbent (Phenomenex Strata XAW) and analyzed with HPLC-ESI-MS (Waters Quattro LC).

Quantification was carried out by an isotope dilution method. Using the same analytical approach Tenax, both types of muffin dough and butter were analysed for blanks.

PFOA-Migration at ambient temperature

- PFOA migrates into Tenax
- Migration depends on time and temperature
- Blank levels are an issue to be solved

Migration of PFOA from butter wrap into food simulant Tenax



Migration conditions at elevated T

T [°C]	time [min]	food item/ simulant	T [°C]	time [min]	food item/ simulant
120	15	butter	200	10	muffin dough 2
150	5	butter	200	20	muffin dough 1
150	10	butter	200	20	muffin dough 2
150	15	butter	200	30	muffin dough 2
180	30	muffin dough 2	220	20	muffin dough 2
180	40	muffin dough 1	220	60	TENAX®
180	40	muffin dough 2			

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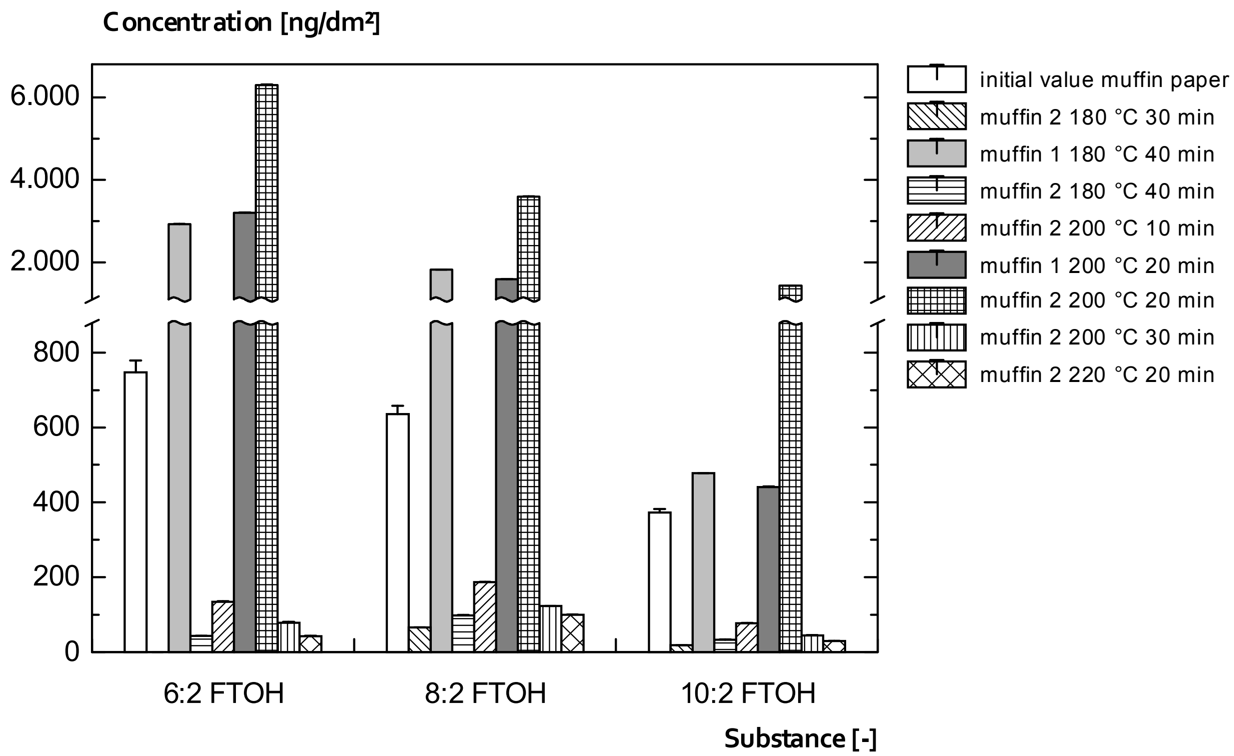
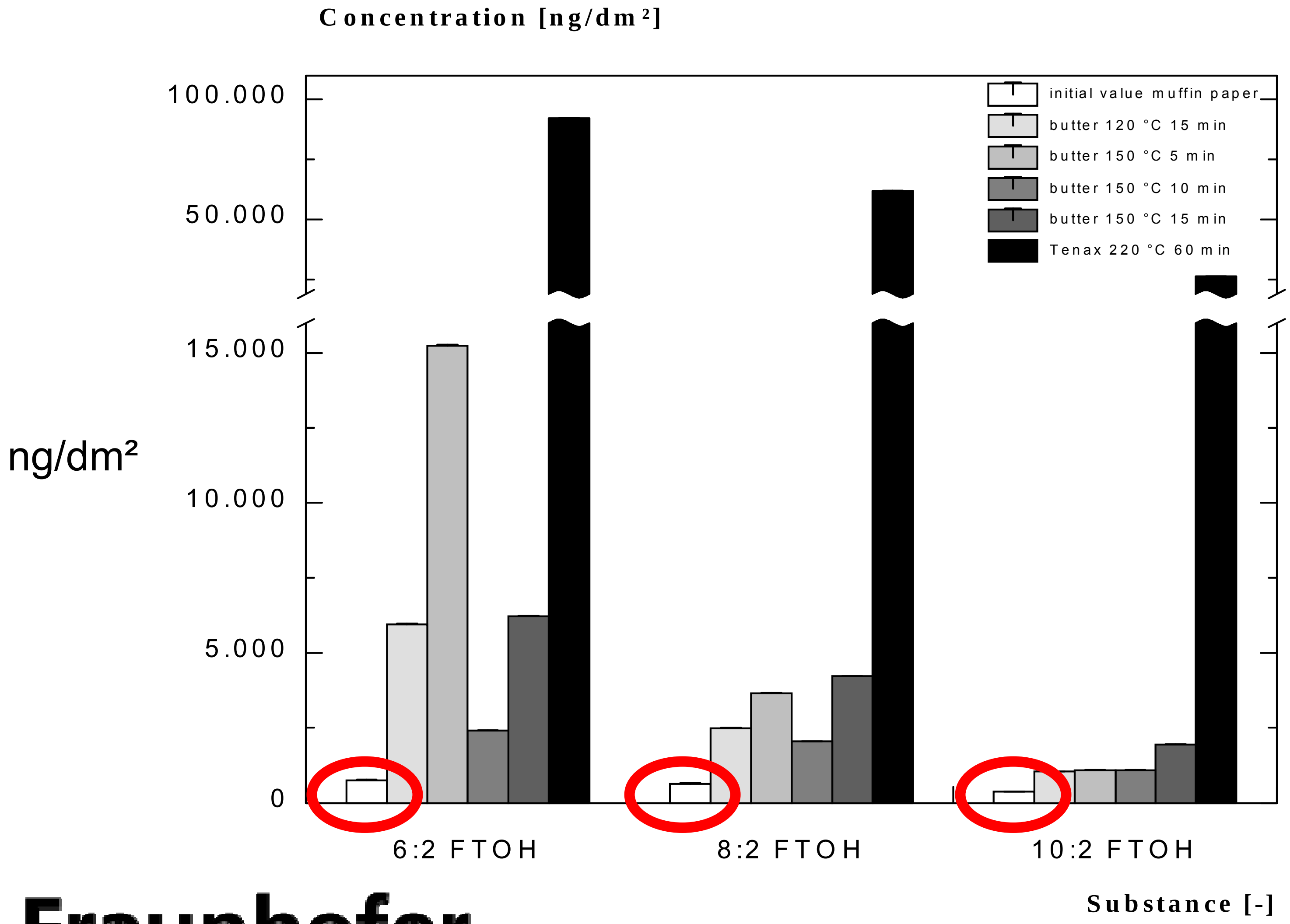
FTOH-Migration at elevated T

ng/dm²



FTOH-Migration at elevated T



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Daily Intake ?

Simplified calculation example:

A migration/formation of
10.000 ng/dm² ΣFTOH
equates to a daily Intake of
1.000 ng ΣFTOH / kg b.w.

Assumptions (Conventional approach):
- *EU cube (6 dm², 1 kg food)*
- *Consumption of 1 kg food*
- *60 kg bodyweight*

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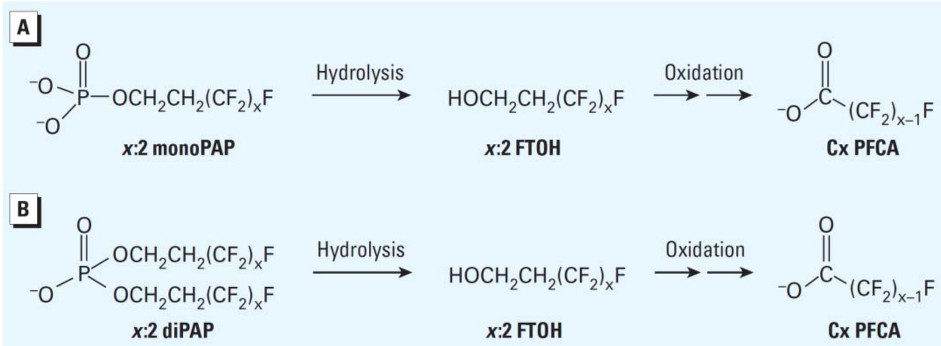
Formation of FTOH from precursors

Migration at elevated T

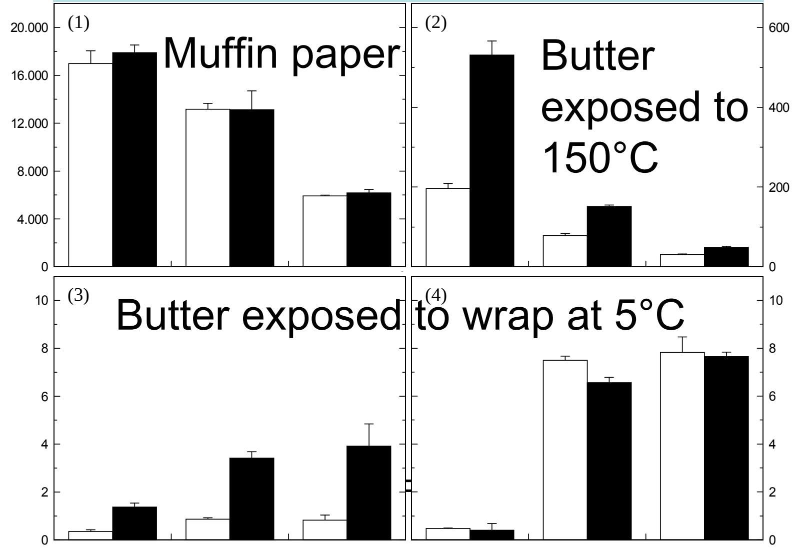
- Precursor transfer upon baking
- FTOH-Formation from precursors in the food
  - ppm levels
  - most likely hydrolysis
- Found Precursors now identified as diPAPs. Work is ongoing.



See: D'eon JC and Mabury SA: Environmental Health Perspectives 119: 344-350, 2011.

Results after another heating

White before, black after another 15 min@150°C



- Pure muffin paper (1)
- Butter previously in contact with muffin paper at 120 °C for 15 min (2)
- Pure butter 1, contaminated from butter wrapper (3)
- Pure butter 2, from diPAP-free butter wrapper (4)

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Precursor migration into food

- No change in FTOH levels for butter and paper, treated separately with temperatures of 150°C
- Butter previously exposed to muffin papers exhibits significantly higher levels following a second heat exposure.

→**Precursor compounds have migrated into the butter during the first heating process and delivers further FTOH by degradation during the second heating phase.**

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Summary

- Butter and Tenax are appropriate food simulants at ambient temperatures.
- Butter, Tenax and also some doughs are appropriate food simulants for elevated temperature.
- Migration experiments at elevated temperatures show formation of FTOH from precursors (diPAPs) orders of magnitude higher then initial FTOH values.

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Thank You for your attention !

Acknowledgements:

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