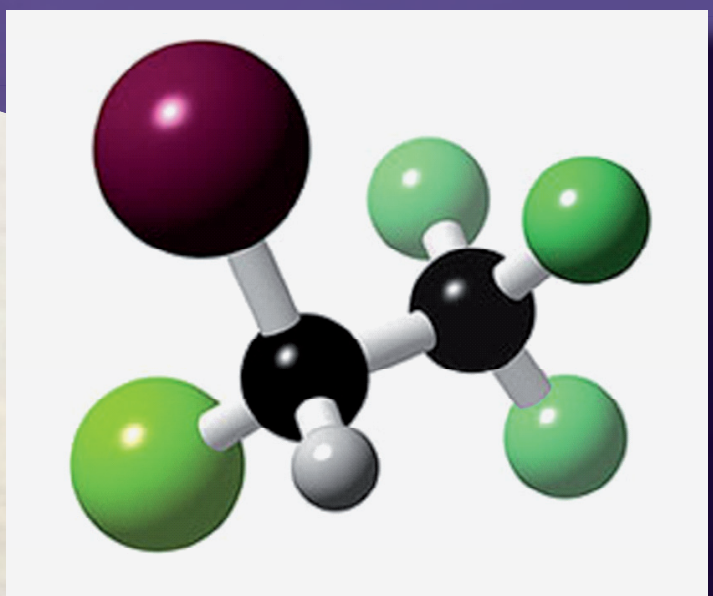
3rd INTERNATIONAL WORKSHOP ANTHROPOGENIC PERFLUORINATED COMPOUNDS



Abstract Book

June 15-17, 2011,
Amsterdam,
The Netherlands

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CHIRON CHIRON CHIRON

Word of welcome

Dear colleagues,

On behalf of the local organising committee and the scientific committee I would like to welcome you to the town and the University of Amsterdam. We are pleased and happy to see that again a group of international scientists is gathered to attend what is the third in a series of workshops on anthropogenic fluorinated compounds. The preceding, highly successful workshops were both held in Idstein, Germany in 2008 and 2010 and I am glad to see that the formula initiated by Professor Thomas Knepper and his colleagues from the University of Applied Sciences Fresenius in Idstein has come to another continuation, this time in Amsterdam.
The scientific program has been assembled by the scientific committee with international members from the perfluorinated substances research community and consists of four invited keynote lectures and 15 platform presentations, combined with poster sessions. The program will conclude with a forum discussion on the afternoon of the second day. You are invited to bring up discussion items for the forum discussion.
Special thanks are due to the sponsors of the workshop and the support provided to young Nordic researchers to travel to Amsterdam. The venue of the workshop is in the buildings that formerly housed the Chemistry division of the Science Faculty of the University of Amsterdam, located in the downtown area near the zoo. In order to enable you to also view and taste what the new buildings of the Science Faculty look like our Welcome reception will be held at the Science Park campus. But we will not renounce our origin: the workshop banquet will take you on a boat tour through the canals of Amsterdam, where you will enjoy the friendly atmosphere of our town and chatting and dining with your friends.
I wish you a very pleasant visit to Amsterdam and a scientifically rewarding experience.

Pim de Voogt
Chair Local Organizing Committee 3rd International Workshop Anthropogenic Perfluorinated Compounds

Scientific committee

Pim de Voogt, University of Amsterdam and KWR, Netherlands
Thomas Knepper, Europa University of Applied Sciences Fresenius, Idstein, Germany
Ian Cousins, Stockholm University, Sweden
Robert Buck, DuPont, Wilmington, USA
Stefan van Leeuwen, Vrije Universiteit, Amsterdam, Netherlands
Dorte Herzke, NILU, Tromsoe, Norway
John Parsons, University of Amsterdam, Netherlands

Local organising committee

Pim de Voogt, University of Amsterdam and KWR, Netherlands
Stefan van Leeuwen, Vrije Universiteit, Amsterdam, Netherlands
John Parsons, University of Amsterdam, Netherlands
Christian Eschauzier, KWR and University of Amsterdam, Netherlands
Sebastian Felizeter, University of Amsterdam, Netherlands
Helen Bergman, University of Amsterdam, Netherlands

Workshop organisation

Helen Bergman
Universiteit van Amsterdam
Institute for Biodiversity and Ecosystem Dynamics
P.O. Box 94248, 1090 GE Amsterdam
Visiting address: Science Park 904, 1098 XH Amsterdam
Email: H.Bergman@uva.nl
Phone: 0031-(0)20 525 7726

Workshop sponsors

Wellington Laboratories
DuPont
Campro Scientific
Chiron
Nordfluor – Nordforsk Network for Fluorinated Compounds

About the workshop

The main objective of the workshop is to bring together specialists from around the world in order to present and discuss scientific and regulatory developments related to human exposure to PFAS. The workshop will also present and discuss findings obtained by the EC funded project PERFOOD. The workshop focuses on the sources and pathways of human exposure to PFASs, the analytical techniques and quality control including reference materials for the determination of PFASs, the possible risks and hazards associated with exposure, and the remediation, regulation and alternatives of PFASs.

About the Institute for Biodiversity and Ecosystem Dynamics of the University of Amsterdam

A modern university with a rich history, the University of Amsterdam (UvA) traces its roots back to 1632, when the Golden Age school Athenaeum Illustre was established to train students in trade and philosophy. Today, with more than 30,000 students, 5,000 staff and 250 study programmes (Bachelor's and Master's), many of which are taught in English, it is one of the larger comprehensive universities in Europe. It is a member of the League of European Research Universities and also maintains intensive contact with leading research universities around the world.

At the broadest level, the mission of the Institute for Biodiversity and Ecosystem Dynamics (IBED) is to increase our understanding of the diversity and dynamics of ecosystems from the level of molecules and genes to entire ecosystems. Our aim is to unravel how ecosystems function in their full complexity, and how they change due to natural processes and human interference. The focus in IBED lies on the study of two interlinked aspects: (i) how do organisms interact with one another and with their abiotic environment, and (ii) what are the dynamics that emerge from these interactions, both in space and in time.

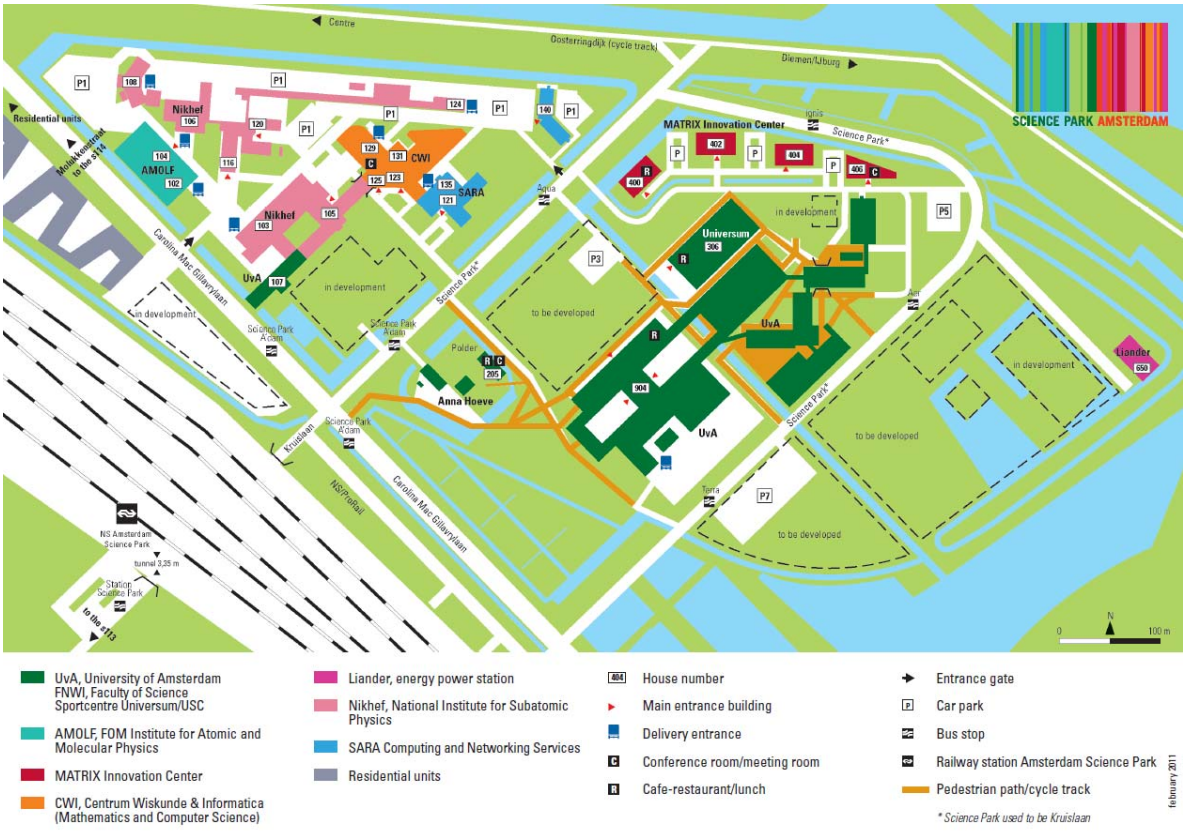
The research of IBED is organized in three themes:

Theme I: Biodiversity and Evolution
Theme II: Geo-ecology
Theme III: Community Dynamics

IBED is involved in the teaching of the BSc programmes of Earth Sciences, Biology, Chemistry and Future Planet Studies. In addition, IBED is involved in the MSc programmes of Earth Sciences, Biology, and Chemistry.

Workshop venues

Registration and the welcome reception take place on June 15 in the reception area in the building of the Faculty of Science at Science Park 904, 1098 XH Amsterdam.



The Faculty of Science can be reached by car and public transport.

By car

All motorways to Amsterdam come onto the Amsterdam circular road, the 'ring Amsterdam' (A10)

- Choose Ring *oost* (east ring)
- Take the exit *'Watergraafsmeer/S113'*('ring Oost'/east ring)
- Follow the signpost for '*Sciencepark'* onto Middenweg. You will see a cemetary (Oosterbegraafplaats) on the left-hand side.

Bus

Bus 40 from railway station Amsterdam Amstel to railway station Amsterdam Muiderpoort and back via Science Park.

Bus 240 between railway station Amsterdam Amstel and Science Park during rush hour.

Bus stop: Science Park Terra

Train

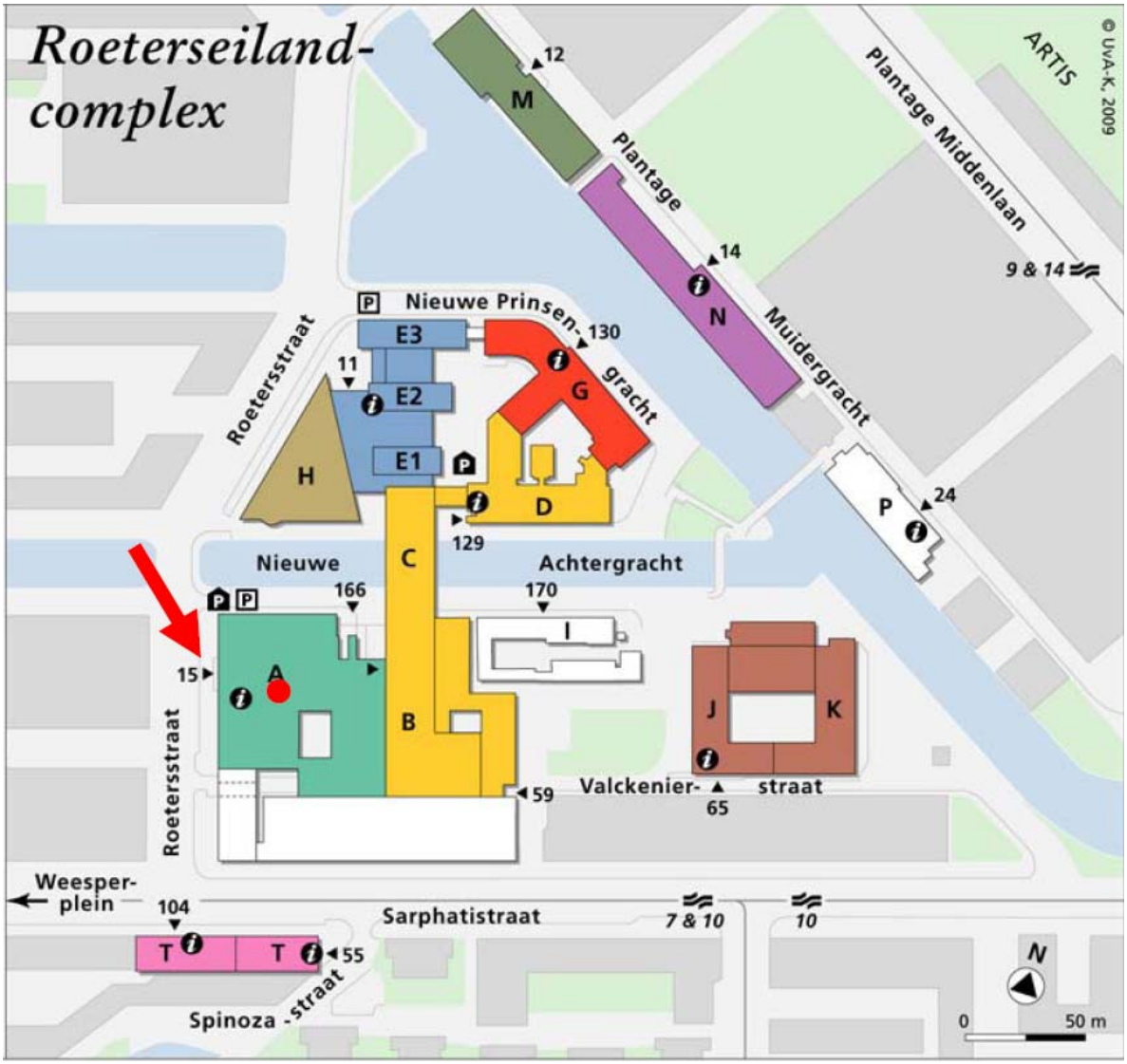
Railway station Amsterdam Science Park is within walking distance from the faculty building.

Oral session, posters and the exhibition take place in Building A of the Roeterseiland complex (REC) at Roeterstraat 15, 1018 WB Amsterdam.

Oral sessions are in lecture room A.

Poster sessions and the exhibition are in the foyer.

Coffee and refreshments will be offered during the coffee breaks in the foyer.



How to get to the Roeterseiland complex:
Metro
From the NS station Amsterdam Centraal: Take any Metro line (51, 53, 54) to station Weesperplein
From the NS station Amstel: Take any Metro line (51, 53, 54) in direction of Centraal station to station Weesperplein
From the NS station Duivendrecht: Take Metro line 54 in direction of Centraal station to station Weesperplein
At station Weesperplein take the exit Valckenierstraat.
Tram
Tram lines 7 or 10 to Weesperplein or tram lines 9 or 14 to Plantage Badlaan

Poster presentations
Posters must be in place by 9:00 on June 16 and must be removed at 16:00 on June 17. Refer to the poster number in this final program for board assignments. Please use **only** the supplied materials for mounting the posters (available at the registration desk).

Poster attendance
Authors must be present during the scheduled poster sessions indicated in the program.

Exhibitors
The following companies will be exhiting adjacent to the poster area:

Campro Scientific
Chiron
Thermo Scientific
Wellington Laboratories

Special events for registrants

Wednesday, June 15, 17:00
Welcome get-together - foyer, ground floor, Faculty of Science, Science Park 904.

Thursday, June 16, 18:30
Boat tour and dinner – departs from Roeterseiland complex (Corner Roetersstraat and Nieuwe Prinsengracht).

Workshop regulations
Name badges are required for all sessions and events.

Workshop Programme

Wednesday, June 15 (Faculty of Science, Science Park 904)

17:00-20:00 Registration & Get-together

Thursday, June 16 (Building A, Roetersstraat 15)

8:00 Registration and poster mounting

9:00– 9:15 Welcome:
Pim de Voogt (University of Amsterdam & KWR, The Netherlands)

Session A: Perfluorinated compounds in our diet

Chair: Pim de Voogt

9:15-10:00 *Keynote:* Farm cattle exposure to PFAAs
Kerry Dearfield (U.S. Department of Agriculture, USA)

10:00-10:20 EFSA Activities on Perfluorinated Alkyl Substances (PFASs)
Valeriu Curtui (European Food Safety Authority, Italy)

10:20-10:40 Perfluorinated alkylated substances in vegetables collected in four European countries; PERFOOD
Dorte Herzke (NILU, Norway)

10:40-11:10 Coffee / tea break and poster session

Chair: Dorte Herzke

11:10-11:30 Uptake of perfluorinated alkyl substances by hydroponically grown lettuce
Sebastian Felizeter (University of Amsterdam, The Netherlands)

11:30-11:50 Impact of treatment processes on the occurrence of perfluoroalkyl acids in the drinking water production chain Christian Eschauzier (KWR & University of Amsterdam, The Netherlands)

11:50-12:10 Influence of Food Processing on the Distribution of Perfluorinated Compounds in Carbohydrate Rich Food and Milk Products
Martina Sauer (Hochschule Fresenius, Idstein, Germany)

12:30-14:00 Lunch and poster session

Session B: Sources, pathways, analysis

Chair: Ian Cousins

14:00-14:45 *Keynote:* Isomer and enantiomer signatures of perfluorinated acids in humans and the environment
Jonathan W Martin (University of Alberta, Canada)

14:45-15:05 Migration of poly- and perfluorinated compounds from food contact materials into food
Ludwig Gruber (Fraunhofer Institute for Process Engineering and Packaging IVV, Germany)

15:05-15:25 Perfluorinated compounds in food contact materials
Jana Hajslova (Institute of Chemical Technology, Czech Republic)

15:25-16:00 Coffee / tea break and poster session

Chair: Stefan van Leeuwen

16:00-16:20 Analysis of PFCA and PFAS with different chain length in several kinds of matrices of animal origin
Susan Ehlers (Chemical and Veterinary Analytical Institute (CVUA-MEL) and University of Münster, Germany)

16:20-16:40 Validation of perfluorinated substances in fish using the saponification/ WAX SPE clean up method
Kit Granby (Technical University of Denmark, Denmark)

16:40-17:00 Simple, high throughput UHPLC-MS/MS ultra trace analysis of perfluorinated compounds in foods of animal origin: milk and fish
Ondrej Lacina (Institute of Chemical Technology, Czech Republic)

17:00-18:00 Poster session

18:30-21:00 Boat tour and dinner

Friday, June 17

Session C: Exposure, toxicity and regulation

Chair: John Parsons

9:15-10:00 *Keynote:* Epidemiology of PFOA and PFOS - new findings
Tony Fletcher (London School of Hygiene & Tropical Medicine, United Kingdom)

10:00-10:20 Developmental toxicity of PFOS, PFBS, PFOA and PFUnDA to chicken (*Gallus gallus domesticus*), great cormorant (*Phalacrocorax carbo sinensis*) and herring gull (*Larus argentatus*)
Marcus Nordén (Örebro University, Sweden)

10:20-10:40 Evidence of biotransformation of fluorotelomer alcohols to perfluorocarboxylates in humans
Helena Nilsson (Örebro University, Sweden)

10:40-11:30 Coffee / tea break and poster session

Chair: Thomas Knepper

11:30-11:50 Exposure of the Flemish population to PFOS and PFOA
Christa Cornelis (VITO, Belgium)

11:50-12:10 Analysis of various PFC groups in Czech household dust
Jana Pulkrabova (Institute of Chemical Technology, Czech Republic)

12:10-12:30 Fish consumption and perfluorinated compounds – risk or over-estimated threat
Jani Koponen (National Institute for Health and Welfare (THL), Finland)

12:30-14:00 Lunch and poster session

Closing session

Chair: Pim de Voogt

14:00-14:40 *Keynote:* Perfluoroalkyl and polyfluoralkyl substances (PFASs) in the environment: terminology, classification, and origins
Robert C. Buck (E.I. du Pont de Nemours & Co. Inc., USA)

14:40-14:50 Short break

Chair: Bob Buck

14:50-16:00 Round table discussion

16:00 Closing remarks

Posters

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
Stefanie Klenow, Gerhard Heinemeyer
Federal Institute for Risk Assessment (BfR), Berlin, Germany

A02
Levels of PFCs in selected food commodities collected in various regions of EU
Veronika Hlouskova, Petra Hradkova, Jan Poustka, Eva Tilgova, Ondrej Lacina, Jana Pulkrabova, Jana Hajslova
Institute of Chemical Technology, Department of Food Chemistry and Analysis, Prague, Technicka 3, 166 28 Prague 6, Czech Republic

A03
Presence and sources of anthropogenic perfluorinated alkyl substances (PFAS) in high consumption beverages
Maria Hoppe[1], Christian Eschauzier[2,1] and Pim De Voogt[a1,2]
[1]Earth Surface Sciences, Institute for Biodiversity and Ecosystem Dynamics, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands
[2]KWR Watercycle Research Institute, P.O.Box 1072, 3430 BB Nieuwegein, Netherlands

A04
Preliminary results of estimation of dietary intake of some perfluorinated hydrocarbons from consumption of drinking water
G. Heinemeyer[1], S. Klenow[1], G. Brambilla[2], E. Dellatte[2], J. Poustka[3], D. Herzke[4], W. D'Hollander[5], S. van Leeuwen[6], C. Eschauzier[7], and P. de Voogt[7]
[1] BfR, Berlin, Germany
[2] ISS, Rome, Italy
[3] ICT, Prague, Czech Republic
[4] NILU, Tromsoe, Norway
[5] University Antwerp, Belgium
[6] VU Amsterdam, The Netherlands
[7] University Amsterdam and KWR, The Netherlands

A05
Update on the occurrence of fluorinated compounds in European food packaging items
Dominik Fiedler, Martin Schlummer, Markus Kizlauskas, Ludwig Gruber
Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany

Session B: Sources, pathways, analysis

B01
Simultaneous determination of perfluoroalkyl carboxylates (PFCAs), sulfonates (PFSAs) and phosphonates (PFPAs) in food cauldrons
Shahid Ullah, Robin Vestergren, Tomas Alsberg, Urs Berger
Department of Applied Environmental Science (ITM), Stockholm University, Stockholm, Sweden

B02
A matrix effect-free method for ultra trace analysis of perfluoroalkyl acids in dietary samples
Robin Vestergren, Shahid Ullah, Ian T. Cousins and Urs Berger
[1] Department of Applied Environmental Science (ITM), Stockholm University,
Svante Arrhenius väg 8, SE-10691 Stockholm, Sweden

B03
Comparison of quantitative LC-MS based analytical methods for the determination of low level PFAS concentrations in selected food samples
Sandra Huber[1], Ondrej Lacina[2], Petra Hradkova[2], Jana Pulkrabova[2], Dorte Herzke[1], Roland Kallenborn[3] and Jana Hajslova[2]
[1]Norwegian Institute for Air Research (NILU), FRAM Centre, Hjalmar Johansens gate 14, NO-9296 Tromsø, Norway
[2]Institute of Chemical Technology, Prague, Department of Food Chemistry and Analysis, Technicka 3, 166 28
Prague 6, Czech Republic
[3]Norwegian Institute for Air Research (NILU), Instituttveien 18, NO-2007 Kjeller, Norway

B04
A validation program for analytical methods for PFASs in food
Stefan P.J. van Leeuwen, Kees Swart
Institute for Environmental Studies (IVM), VU University, De Boelelaan 1087, 1081 HV Amsterdam

B05
Isotope dilution technique in the analysis of PFOS and PFOA in water samples.
Sami Huhtala[1], Noora Perkola[1], Petra Kosubova[2],
[1]Finnish Environment Institute, Laboratories, Research and Innovation Laboratory, Helsinki, Finland
[2]Central Institute for Supervising and Testing in Agriculture, Brno, Czech Republic

B06
Simple and high throughput method for quantitation of perfluoroalkyl substances using LC-MS/MS
Jani M. Koponen, Päivi Ruokojärvi, Hannu Kiviranta
National Institute for Health and Welfare (THL), Department of Environmental Health, Kuopio, Finland

B07
Inputs of perfluorinated chemicals from skiing activities to the Norwegian environment
Katherine Langford, Lucy Brooks and Alfhild Kringstad
Norwegian Institute for Water Research, Gaustadaleen 21, 0349, Oslo, Norway
Email: kla@niva.no

B08

Withdrawn

B09
Recent time trends of PFOS in cod and hake liver
C.J.A.F. Kwadijk[1], M. Hoek-van Niewehuizen[1], A.A. Koelmans[1,2]
[1]IMARES, WAGENINGEN UR – Institute for Marine Resources & Ecosystem Studies, P.O. Box 68, 1970 AB IJmuiden, The Netherlands
[2]Wageningen University, Aquatic Ecology and Water Quality Management Group, PO Box 47, 6700 AA Wageningen

B10
Polyfluoroalkyl compounds in the atmosphere at a wastewater Treatment Plant
Lena Vierke[1], Lutz Ahrens[2], Mahiba Shoeib[2], Eric J. Reiner[3], Guo Rui[3], Wolf-Ulrich Palm[4], Tom Harner[2], Ralf Ebinghaus[5]
[1]Federal Environment Agency, Germany
[2]Environment Canada, Canada
[3]Ontario Ministry of the Environment, Canada
[4]Leuphana University of Lüneburg, Germany
[5]Helmholtz-Zentrum Geesthacht, Germany)

B11
Estimating physicochemical properties of poly- and perfluorinated alkyl substances (PFAS) with a quantum chemistry-based model
Zhanyun Wang[1], Matthew MacLeod[2], Ian Cousins[2], Martin Scheringer[1], Konrad Hungerbühler[1]
[1]Institute for Chemical and Bioengineering, Swiss Federal Institute of Technology, ETH Zurich, CH-8093 Zurich, Switzerland
[2] Department of Applied Environmental Science (ITM), Stockholm University, SE-10691 Stockholm, Sweden

B12
Inhalation anaesthetics and climate change
Ole J. Nielsen[1], Mads P. Sulbaek Andersen[2]*, Stanley P. Sander[2], Deborah S. Wagner[3], Theodore J. Sanford Jr. [4]
[1]Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen, Denmark
[2]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Mail Stop 183-901, Pasadena, CA 91109, USA
[3]Department of Clinical Sciences, College of Pharmacy, University of Michigan, 428 Church Street, Ann Arbor, Michigan 48109-1065, USA
[4]Department of Anesthesiology, University of Michigan Medical School, 1500 East Medical Center Drive, Ann Arbor, Michigan 48109-5048, USA

B13
Degradation of 8:2 FTOH and formation of PFOA in laboratory experiments with brackish sea water
Juha Keränen[1], Juha Knuutinen[1], Sirpa Herve[2], Heidi Ahkola[2], Marko Reinikainen[3], Jaana Koistinen[3]
[1]University of Jyväskylä, Laboratory of Applied Chemistry, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyväskylä, Finland
[2]Finnish Environment Institute (SYKE), Jyväskylä unit P.O.Box 35, FI-40014 University of Jyväskylä, Finland
[3]University of Helsinki, Tvärminne Zoological Station, J.A. Palménin tie 260, FI-10900 Hanko, Finland

B14

Fluorotelomer alcohol biodegradation pathways
Robert C. Buck, Ning Wang, Patrick Folsom, Barry Wolstenholme
E. I. DuPont de Nemours and Company, Inc., Wilmington, Delaware, USA

B15
Atmospheric Chemistry of $CF_3CH_2OCH_3$
Freja From Østerstrøm[1], Ole John Nielsen[1], Mads P.S. Andersen[2]
[1]CCAR, University of Copenhagen,5 Universitetsparken 5, 2100 Copenhagen Ø, Denmark, [2]Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Mail Stop 183-901, Pasadena, CA 91109, USA

B16
Development of a method to combine the extraction of both PFCs and legacy-POPs from human serum.
Christian Bjerregaard Olesen, Eva Cecilie Bonefeld-Jørgensen
Centre for Arctic Environmental Medicine & Unit of Cellular and Molecular Toxicology, School of Public Health, Aarhus University, Denmark
Bartholins Allé 2, 8000 Aarhus C, Denmark.

Session C: Exposure, toxicity and regulation

C01
Perfluoro acrylates as surface refining agents for paper and board: investigations on their resistance at higher temperature
Jutta Tentschert[1], Jochen Heidler[1], Ulrike Braun[2], Stephan Richter[1], Oliver Kappenstein[1], Andreas Luch[1], and Karla Pfaff[1]
[1]BfR—German Federal Institute for Risk Assessment, Thielallee 88 – 92, 14195 Berlin
[2]BAM—German Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin

C02
Detection of FTOHs in indoor air of work places
Martin Schlummer[1], Markus Kizlauskas[1], Ludwig Gruber[1], Dominik Fiedler[1], Josef Müller[2], Annegret Biegel-Engler[3]
[1]Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany
[2]Fraunhofer Institute for Molecular Biology and Applied Ecology IME, Schmallenberg, Germany
[3]Federal Environment Agency, Dessau, Germany

C03
Perfluorinated compounds in human breast milk from the Czech Republic: results of a pilot
Darina Lankova, Ondrej Lacina, Jana Pulkrabova, Beata Fischerova, Jana Hajslova
Department of Food Chemistry and Analysis, Institute of Chemical Technology Prague, Technicka 3, 166 28 Prague 6, Czech Republic;
e-mail: darina.lankova@vscht.cz

C04
Perfluorinated alkyl substances in whole blood and plasma; an assessment in maternal and umbilical cord samples from two communities in Russia and Uzbekistan.
Linda Hanssen[1,3], Alexey Dudarev[2], Jon Øyvind Odland[1], Torkjel M. Sandanger[3]
[1.] Department of Community Medicine, University of Tromso, NO-9037 Tromso, Norway
[2.] The Northwest Public Health Research Center, St. Petersburg, Russian Federation
[3.] Norwegian Institute for Air Research (NILU), FRAM Centre, Hjalmar Johansens gate 14, NO-9296 Tromsø, Norway

C05
Temporal trends in perfluoronate exposure in a US population exposed to raised levels of PFOA through drinking water
Debapriya Mondal, Tony Fletcher, Maria-Jose Lopez-Espinosa
London School of Hygiene & Tropical Medicine, United Kingdom

C06
Per- and polyfluorinated compounds in consumer products
Heinrich Jürling[1], Martin Schlummer[2], Annegret Biegel-Engler[3], Josef Müller[1]
[1]Fraunhofer Institute for Molecular Biology and Applied Ecology IME, Schmallenberg, Germany
[2]Fraunhofer Institute for Process Engineering and Packaging IVV, Freising, Germany
[3]Federal Environment Agency, Berlin, Germany

C07
The Toxicology of 6:2 fluorotelomer sulfonate (C6F13CH2CH2SO3-, 6:2 FTSA)
Robert C. Buck, Robert A. Hoke, and Tessa L. Serex
E. I. DuPont de Nemours and Company, Inc., Wilmington, Delaware, USA

C08
Level and temporal trend of perfluoroalkyl acids in Greenlandic Inuit
Manhai Long[1], Rossana Bossi[2] and Eva C. Bonefeld-Jørgensen[1]
[1] Aarhus University, School of Public Health, Centre of Arctic Environmental Medicine, Bartholins Allé 2, 8000 Århus, Denmark
[2]Aarhus University, National Environmental Research Institute, Frederiksborgvej 399, 4000-Roskilde, Denmark

C09
PFOS, PFOA and PFBS induce chicken hepatic fatty acid oxidation in chicken eggs
Marcus Nordén[1], Ola Westman[1], Nikolaos Venizelos[2], Magnus Engwall[1]
[1]MTM Research Center, School of Science and Technology, Örebro University, SE-70182 Örebro, Sweden
[2]School of Health and Medical Science, Örebro University, SE-70182 Örebro, Sweden

Abstracts of oral presentations

Session A: Perfluorinated compounds in our diet

Keynote

Farm cattle exposure to PFAAs

Kerry Dearfield
U.S. Department of Agriculture, Food Safety and Inspection Service, Washington, DC USA

The U.S. Department of Agriculture examined farm cattle that were exposed to biosludge containing perfluorinated compounds (PFCs) that was applied to agricultural lands in southeast United States. A model was developed to predict beef concentration of PFCs, specifically perfluorooctane sulfonate (PFOS) and perfluoroctanoic acid (PFOA), that would result from cattle grazing on these lands. Samples of beef were subsequently obtained and measured for PFOS and PFOA, and the measurements of PFOS and PFOA were consistent with modeled values. Consumption of beef at these modeled concentrations would likely result in low acute and chronic levels of concern for PFOA and a low acute level of concern for PFOS. Likely PFOS chronic exposure scenarios would also likely result in exposures less than chronic levels of concern.

EFSA Activities on Perfluorinated Alkyl Substances (PFASs)

Valeriu Curtui
European Food Safety Authority (EFSA), Largo N. Palli 5/A, 43123-Parma, Italy

In 2008, in its Scientific Opinion on perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA)[8], the EFSA Panel on Contaminants in the food chain recommended that the presence and levels of PFASs in different foods and in the human body should be further investigated to better estimate human exposure. In consequence, the European Commission issued the Recommendation 2010/161/EU on the monitoring of PFAS in food[9]. Member States were recommended to monitor during 2010 and 2011 the presence of PFASs in food and submit to EFSA the data obtained from the monitoring as well as possible data from previous years. In 2010, EFSA launched a public call for data on PFAS in food[10] with the aim to collect the PFAS occurrence data available in the European countries. A first report on the PFAS occurrence in food was published in February 2011[11]. The report summarises the results obtained on 4,881 food samples collected in the period 2000 – 2009 in seven Member States. Data comprised different sets of 17 PFASs resulting in 24,204 single observations. The most frequently found PFASs were PFOS (31 %), PFOSA (17 %), PFTriDA (17 %), PFOA (12 %), PFDA (11 %), PFDoDA (9.8 %), PFNA (9.3 %) and PFUnDA (7 %). PFBA, PFPA and PFHpS were not detected in any of the samples analysed. The highest contamination both in terms of frequency and mean level was found in meat and edible offal of game animals, and in fish and seafood, whereas meat and edible offal of farmed animals were less contaminated. To ensure an accurate assessment of the presence of PFASs in food and beverages, further improvement of the analytical methods, sampling and data reporting are recommended. The EFSA call for data on PFASs in food is still on-going. The collected data will be summarised in a final report in 2012 as support to the European Commission in deciding on possible risk management measures.

[8] http://www.efsa.europa.eu/en/efsajournal/pub/653.htm
[9] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2010:068:0022:0023:EN:PDF

[10] http://www.efsa.europa.eu/en/data/call/datex100429.htm

[11] http://www.efsa.europa.eu/en/efsajournal/pub/2016.htm

Perfluorinated alkylated substances in vegetables collected in four European countries; PERFOOD

Dorte Herzke[1], Sandra Huber[1], Lieven Bervoets[2], Wendy D'Hollander[2], Jana Hasjlova[3], Gianfranco Brambilla[4], Stefania Paola De Filippis[4], Pim de Voogt[5]
[1]NILU (Norwegian Institute for Air Research), Tromsoe, Norway
[2]UA, University of Antwerp, Laboratory for Ecophysiology, Biochemistry and Toxicology, Antwerp, Belgium
3ICT, Institute of Chemical Technology. Prague, Czech Republic
[4]Istituto Superiore di Sanità, Toxicological chemistry unit, Rome, Italy
[5]IBED, University of Amsterdam, Amsterdam, The Netherlands

Introduction

The diet is considered a general source contributing to the overall PFAS burden of the human population. Possible exposure pathways include beverages, food in general and migration from food packing or cookware (Fromme et al., 2007, Lau et al., 2007).
Most European countries carry out national monitoring programs (food basket studies) in order to assess the daily intake of persistent organic pollutants. PFASs have not yet been included in these studies in most countries. In addition, since food basket studies mainly are carried out by national authorities, no coordinated approach is used, making comparison between different countries difficult.
In the EU project PERFOOD, standardized selection of food items, sampling procedures and analytical methods as well as evaluation strategies were applied, enabling a unique assessment of the occurrence of PFASs in European food as well as the identification of major sources of PFAS exposure via food. During PERFOOD, in a 1st campaign, food items covering all types of food stuff 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 cover the analytical results for vegetables acquired in Norway, Belgium, Czech Republic and Italy.

Results

In spring 2010 between 13 and 18 different types of vegetables were sampled in all four countries. Species representing the subgroups of leafy vegetables, stem vegetables, root vegetables, brassica vegetables, pulses and legumes as well as potatoes were collected. Randomly selected individual samples per species were pooled together in each country. Only the edible parts were processed for analyses.
In general the PFAS levels found were very low, and mostly short chained PFASs up to C_8-chains were detected. However, the most PFASs were detected in samples from Belgium and Norway, followed by samples from Italy and Czech Republic. Mainly PFCAs were detected and occasionally some PFSs, in few samples. Figure 1 shows the average value of the sumPFCAs of all vegetables combined.

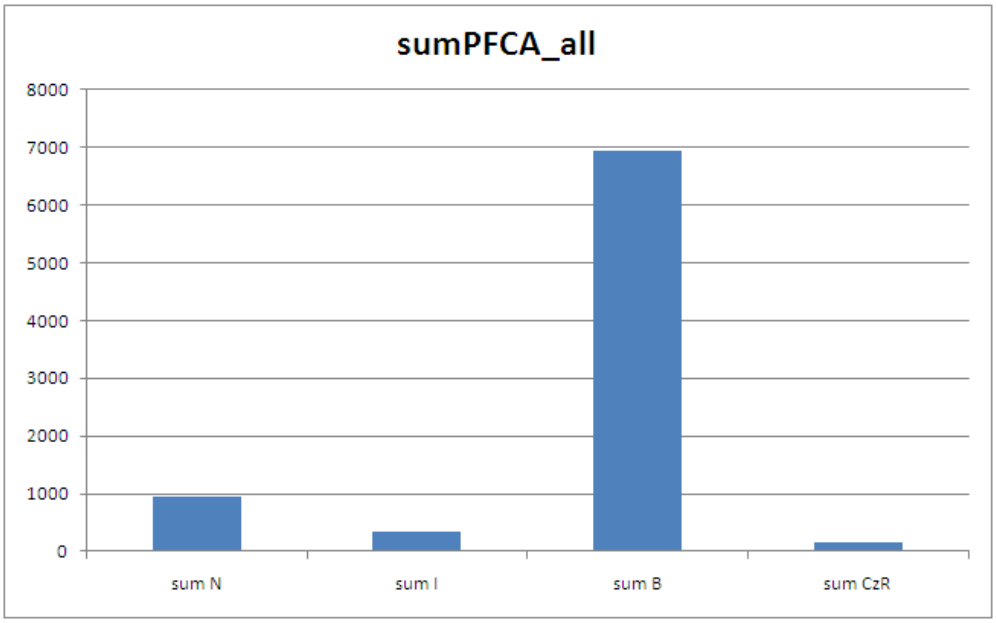


Figure 1: Average sum of PFCAs in all analysed vegetables (pg/g ww); N: Norway, I: Italy, B: Belgium, CzR: Czech Republic

Maybe due to the close vicinity to a former PFOS manufacturing production plant, Belgian samples were in general more highly contaminated with PFCs than the others. Samples from Italy and Czech Republic showed very low levels. In comparison, Norwegian samples seem to be exposed to higher levels of PFASs, maybe due to the fact that the majority of vegetables available in Norway are imported from Belgium, Israel or South America. In general, vegetables seem not to be a main contributor to the human exposure of PFASs via the food if not harvested close to point sources. However, the data from Belgium show that plants used as vegetables in human diet are able to take up a number of PFCs in the edible parts when exposed to them.

Uptake of perfluorinated alkyl substances by hydroponically grown lettuce

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Perfluorinated alkyl substances (PFAS) are bioaccumulative persistent, organic pollutants (POPs), which can be detected ubiquitously in the environment. PFAS pose a risk to human health due to accumulation in the food chain. The occurrence of PFAS in animals, such as fish, birds and mammals including humans is fairly well documented, but little can be found in the literature about crops or plants in general. Also, most studies focus just on the two main compounds perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA).
Plants appear to accumulate PFAS differently, as has become apparent from published data on PFAS concentrations in crops, e.g. potatoes or cereals. Humans are possibly exposed to PFAS through consumption of vegetables and other plant-related food items. The objective of this study is to understand the accumulation process of PFAS in crops.
In a first experiment lettuce was grown hydroponically in a greenhouse with a contaminated nutrient solution to avoid sorption to soil and to make sure the offered PFAS are completely bioavailable. The lettuces were exposed to a set of 10 perfluorinated carboxylic acids and 3 perfluorinated sulphonates in four different concentrations to assess the difference in behavior between PFAS and concentration dependencies. In another experiment lettuces were sampled in a 4-5 days interval to investigate changes of the uptake during the growth period.
The experiment was set up under the assumption that because of the high water solubility of the compounds the PFAS will be taken up by the root system of the plants and will be distributed through the plants water system. Hence it was assumed that evaporation plays an important role in the uptake, therefore bioaccumulation hypothetically takes place especially in the leaves of the plants. To confirm this hypothesis correlations of the PFAS uptake with the water uptake were examined.
The results however show that except for the short chained PFCAs PFBA and PFPeA the concentrations in the roots were higher than in the leaves. Furthermore the results show that the uptake for the PFAS with a chain length of more than 6 Carbon atoms is not linear with increasing concentration, but follows a Langmuir isotherm instead. This indicates that adsorption plays a more important role in the uptake than the water uptake.

Keywords: PFAS, crop, accumulation, exposure

Impact of treatment processes on the occurrence of perfluoroalkyl acids in the drinking water production chain

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Perfluoroalkyl substances (PFASs) have been detected in drinking water at concentrations typically in the low ng/L range. These findings suggest that PFASs are not or poorly removed during drinking water treatment. Since the exposure of humans to PFASs occurs partly via drinking water, information is needed about their presence in drinking water and their removal during treatment processes.
A total of 54 samples were collected in January and September 2010. Samples were taken at influent, coagulation effluent and rapid sand filtration effluent of the pre-treament and influent, rapid sand filtration effluent, GAC filtration influent, effluent of a first GAC filters set and effluent of a second GAC filters set and in the finished water of the post-treatment.
The source water used for the production of drinking water is river Rhine water. The analysis of water samples after the different drinking water production steps showed the presence of PFASs in all samples analyzed. Of all PFAS measured PFBA and PFBS showed the largest variability in concentrations, especially in the pre-treatment steps. Concentrations of PFBA and PFBS after pre-treatment ranged from 7.8 to 52 ng/L and from 11 to 42 ng/L respectively. The other analytes measured: PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFHxS and PFOS were on average between 0.69 and 8.3 ng/L over the two sampling campaigns. A significant decrease was observed for PFOS after the first GAC effluent treatment steps. In the second GAC filtration step a significant decrease was found for PFOA, PFNA, PFHxS and PFOS. The concentrations of PFOS and PFHxS drop to below their detection limits while PFOA decreases to 5.3 ng/L (about 50%) after the GAC filtration. A significant higher decrease in linear PFOS and PFOA concentration was observed compared to the branched isomers.
PFAS concentrations in the finished drinking water were highest for PFBA and PFBS, 33 and 24 ng/L max, respectively. PFPA, PFHpA, PFOA and PFHxS were present at concentrations varying between 0.43 and 4.4 ng/L. The present study shows that the removal of short chained PFAS such as PFBA, PFHxA and PFBS from drinking water is problematic. It is expected that PFBS and PFHxA will become more abundant in the future as they are slowly replacing PFOS and PFOA as a result of reductions in emissions and production volumes of the latter two PFASs due to implemented guidelines. Concentrations observed are no reason for concern for human health as the margins to the existing provisional health-guideline values for the different PFAS remain sufficiently high and the Risk Quotients remain low.

Acknowledgement
Wellington-Labs is gratefully acknowledged for the gift of several standards. The study is part of the EU project PERFOOD (KBBE-227525), and the financial support of the European Union is gratefully acknowledged.

Influence of Food Processing on the Distribution of Perfluorinated Compounds in Carbohydrate Rich Food and Milk Products

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Perfluorinated Compounds (PFCs) have been found in water and different types of food like in fish, crustacean and in low levels in eggs, potato- and milk products (EFSA 2011). What is happening to PFCs during home cooking and industrial processes is hardly known and should be analyzed as a part of the PERFOOD project.
In this study two different types of food processes were examined: The cooking of carbohydrate rich food in water and the processing of milk products. Potato dumplings and pasta were chosen and either water or food was spiked with different perfluorinated carboxylic and sulfonic acids (PFCAs and PFSAs). For the processing of milk products both, spiked milk and cream were used. The concentrations of PFCs in all phases before and after food processing were determined and mass distributions were calculated. Sample preparation involved different methods: Extraction with ion-pairing reagent/methyl tert-butyl ether (potatoes), tetrahydrofuran/water (pasta) and methanol (milk products), following SPE (Strata X-AW) for pasta and milk products. Water samples were analyzed directly or concentrated by solid phase extraction if necessary. Measurements were done by LC-MS/MS (ESI, negative).
The results for carbohydrate rich food show, that a transfer of PFCs in both directions (from food to water and water to food) is possible, but cooking times were too short to reach equilibrium between both phases. The transfer is influenced by surface area and water content of the raw food and is dependent on the chain length of PFCs. Short-chain PFCs leached easier from food into water and showed less transfer from contaminated water to food than PFCs with longer chains. After phase separation of different milk products especially the long-chain PFCs preferred to stay in the fatty phase, even if this is the phase with lower protein content. Compared to the results of carbohydrates the distribution of PFCs in milk products is also influenced by the hydrophilic group. In the processing of cream and butter PFSAs accumulated stronger in the fatty phase than PFCAs.

Reference:
European Food Safety Authority: Results of the monitoring of perfluoroalkylated substances in food in the period 2000 – 2009. EFSA Journal 2011; 9 (2):2016

Session B: Sources, pathways, analysis

Keynote

Isomer and enantiomer signatures of perfluorinated acids in humans and the environment

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Perfluorinated acids rank among the most prominent and persistent organic contaminants of wildlife and humans today, yet their exposure sources, environmental behaviour, and disposition are poorly understood. Perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) are the most notorious chemicals in this group, and both continue to be manufactured today. From a risk and chemical regulatory perspective, there is a need to understand the sources of PFOS and PFOA to humans and wildlife. To address such questions, sensitive and specific analytical methods have developed to read the isomer and enantiomer signatures of PFOS or PFOA in various human and environmental samples. Such signatures from remote ocean waters, high alpine lakes, the Great Lakes, maternal blood, umbilical cord blood, and house dust will be discussed with respect to exposure sources today, and in the future.

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

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Grease proof packaging and other food contact materials (FCM) have been reported to contain fluorine-based organic coatings. As proofed by Begley et al. these fluorinated substances or their degradation products may migrate from such materials into food items and may become a source of per- and polyfluorinated compounds (PFAS) in humans.

In previous studies we investigated FCM with analytical screening methods for the presence of fluorine coatings. Furthermore, fluorine positive samples were analyzed for FTOH, perfluoroalkyl carboxylates (PFCA) and sulfonates (PFSA). The results showed significantly higher levels of FTOH compared to PFCA. PFSA were not found in any sample at levels above 1 ng/g.

In this study we explored the migration of PFCA and FTOH from FCM. The selection of FCM was performed with respect to the use pattern of typically fluorine-containing FCM. Four application profiles were distinguished:
a) long-term packaging at fridge temperatures
b) long-term packaging at ambient temperatures
c) short-term packaging at elevated temperatures (~80°C)
d) baking applications (short-term contact at high temperatures).

Real food items and food simulants were applied, including polar and non-polar solvents as well as Tenax®.

For each group of FCM a set of migration test conditions was investigated, whereat contact time, contact temperature and food items varied in a reasonable range. Before and after the migration contact, FCM, food items and food simulants were extracted and analyzed for PFSA, PFCA and FTOH by LC-ESI-MS/MS or GC-CI-MS. High-molecular fluorinated compounds originally used for coating were not analyzed due to the absence of certified standards.

Results of FCM were expressed in ng/dm² FCM. Levels identified in food (simulants) were reported in terms of ng/dm² of FCM, these food items were exposed to. This approach bases on the assumption that all PFAS found in food origin the investigated FCM.

Levels of PFOA in investigated food items increased only slightly after the migration contact. This indicates at rather low migration rates. In contrast, FTOH levels increased significantly after the migration contact. Migration values from butter wraps into butter accounted for 10 to 200 ng/dm². This is significantly lower than the migration potential of the butter wrap (> 1000 ng/dm²) and indicates at rather low migration rates.

However, migration of FTOH increased with increasing temperatures and durations of the migration experiments. At baking temperatures, migration values exceeded the migration potential, i.e. the total amount present in the original packaging, by far. This clearly indicates at a release of FTOH from high molecular mother compounds.

Such an effect was not detected when the same baking paper was heated to 150°C for 1h in absence of any food items, suggesting degradation in the food matrix after a migration of mother compounds from FCM into the food.

Acknowledgements
The study was financed by the EU project PERFOOD (KBBE-227525), and the financial support of the European Union is gratefully acknowledged.

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Perfluorinated compounds in food contact materials

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A wide range of perfluorinated compounds (PFCs) has been detected in human blood worldwide, with increased levels observed in industrialized areas. Many studies have been initiated to understand the origin of this contamination. Polyfluoroalkyl phosphate esters (PAPs) are a source of fluorinated telomer alcohols (FTOHs), which could be (bio)transformed to perfluorocarboxylic acids (PFCAs). PAPs are nonpolymeric surfactants used in various applications to make non-stick products such as kitchen pans or food contact paper packaging from which they may penetrate into foodstuffs.
Within this study, ultra-high-performance liquid chromatography hyphenated with tandem mass spectrometry (UPLC-MS/MS) was used for the analysis of PAPs in food contact materials. In the first phase, the mono- and di- PAPs were analyzed in ESI- mode, in which also in-source fragments of tri-PAPs could be detected, however, the structure information was lost. Significantly better results were obtained in ESI+ mode, tri-PAPs provided very intensive $[M+H]^+$ ions, moreover, the fragmentation pattern obtained under this condition allowed to determine structure of the tri-PAPs (loss of one, two or three bonded FTOHs occurred).
It should be mentioned that due to fairly significant differences in physico-chemical properties, such as polarity, careful optimization of extraction conditions had to be carried out (two solvent, methanol and ethyl acetate, were used). In this presentation, the data obtained by analysis of food wrappers, popcorn bags, baking papers etc. will be shown.

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Analysis of PFCA and PFAS with different chain length in several kinds of matrices of animal origin

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The background exposure of the general population to perfluorocarboxylic acids (PFCA) and perfluoroalkylsulfonates (PFAS) is well established. Food of animal origin appears to be an important source for human PFC exposure. At the Federal Institute for Risk Assessment (BfR) in Berlin feeding experiments with lactating sheep and cows were performed to investigate the carry-over of PFCA and PFAS from naturally contaminated feed into food producing animals. The samples of these feeding experiments were analyzed at the Chemical and Veterinary Analytical Institute (CVUA-MEL) in Münster. The toxicity and the accumulation potential of PFCA and PFAS with other chain lengths than eight carbons are not well known. Therefore the European Commission (Rec. 2010/161/EU) recommends to analyse PFCA and PFAS with different chain length in various food samples. Following this recommendation, not only the marker substances PFOS and PFOA, but also PFCA and PFAS with other chain lengths were analyzed in this study.

Materials and Methods
Within the project PFC-concentrations in different kinds of matrices, such as blood, urine, faeces, meat, liver, kidney, milk and feed were analysed. Considering the interactions between PFC and proteins, matrix specific preparation methods were developed. For some kinds of samples a hydrolysis using enzymes were performed and from other matrices the PFC were extracted without enzymatic digestion. The objective was to achieve good recoveries for PFCA with six to twelve carbon atoms and PFAS with four, six, seven, eight and ten carbon atoms. Because of the high number of samples there was a need for simple preparation methods. The final extracts were measured using LC/MS-MS. Quantification was performed using isotope labeled internal standards. Because of the surface activity of the PFCA and PFAS, it was important to minimize a potential carry-over from Teflon containing parts of the analytical instrument and/or from highly contaminated samples as far as possible. The ratio of the first and the second transition was used to identify the PFC unequivocally. The limits of detection were very low despite the requirement of a signal to noise ratio of the second transition of 3:1 at this point.

Results
In spiking experiments recoveries between 65 and 110 % were observed. The described methods were also tested successfully in inter laboratory comparisons. Until now more than 700 samples were analysed within the project.

Validation of perfluorinated substances in fish using the saponification / WAX SPE clean up method

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Perfluorinated substances may be present in the food as an accumulated environmental contaminant or as a migrant from the usage of perfluorinated substances in food contact materials like popcorn bags or other food packaging. In March 2010 the European Commission issued a recommendation for member states to monitor the per- and polyfluorinated substances in food.
We have validated an analytical method modified from Taniyasu et al. 2005. The principle of the method is extraction with methanol, evaporation of the methanol and saponification overnight of the extracted material. After pH adjustment clean-up is performed automatically on Oasis WAX SPE columns. The eluate is concentrated and the perfluorinated substances detected by LC-MS/MS using external standards and labelled internal standards for PFOS and PFOA.
The method is validated on fish at three spiking levels 0.6 µg/kg, 1.7µg/kg and 5.6 µg/kg. Standard curves at 6 point calibration are linear in the range from 0.25 to 20 ng/ml ~ 0.14 to 11 µg/kg fish, usually with correlation coefficient $r^2 > 0.95$. The limit of detection (LOD) given as 3 * sB is for PFOS and PFOA 0.5 µg/kg and for the other analytes 0.3-0.8 µg/kg. The accuracy, repeatability and internal reproducibility may be acceptable for the PFOS and PFOA for which labelled standards were used, but might need improvement for other PFCs. DiPAPS were attempted analysed but are not yet validated.

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Simple, high throughput UHPLC-MS/MS ultra trace analysis of perfluorinated compounds in foods of animal origin: milk and fish

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In order to enable a risk assessment associated with dietary exposure to PFC (perfluorinated compounds), EFSA (the European Food Safety Authority) recommended that further data on PFCs levels in foods and in humans would be desirable, particularly with a respect to the human exposure assessment. For this purpose, it is required to use a method of analysis that has been proven to generate reliable results with ultra trace limits of quantification (LOQs), since PFCs levels in food are expected very low.
The presented study documents the development and validation of a novel, highly sensitive approach for determination of 23 PFCs in foods of animal origin represented by milk and fish. The list of target analytes comprises four classes of PFCs, both ionic and non-ionic: 11 perfluorocarboxylic acids (PFCAs), 4 perfluorosulphonic acids (PFSAs), 5 perfluorosulphonamides (FOSAs) and 3 perfluorophosphonic acids (PFPAs). The fast sample preparation procedure is based on extraction of analytes with acetonitrile and their transfer (supported by salts and acidification) into the organic phase. Removing of matrix co-extracts by a simple dispersive solid phase extraction (SPE) employing ENVI-Carb and C18 sorbents enables an efficient sample pre-concentration. This is performed by acetonitrile evaporation followed by dilution of residue in a small volume of methanol (matrix equivalent in the final extracts was 16 and 8 g mL^{-1}, for milk and fish respectively). Target PFCs were detected by ultra-high performance liquid chromatograph (UHPLC) hyphenated with a tandem mass spectrometer (MS/MS). The method was validated for fish and milk matrices with LOQs in the range 1–12 ng/kg and recovery between 70–120% and repeatability below 20% for all 23 target PFCs.

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Session C: Exposure, toxicity and regulation

Keynote

Epidemiology of PFOA and PFOS - new findings

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Interest in potential human health effects of perfluorinated compounds in general and perfluorooctanoic acid (PFOA also called C8), and perfluoroctane sulfonic acid (PFOS) in particular has expanded in recent years. Published epidemiological findings on these compounds derive from environmental and occupational exposures, with the occupational studies generally involving smaller populations and much higher exposures. There is some evidence of biological activity in terms of associations with some clinical markers measured in blood including cholesterol, uric acid and liver enzymes, and evidence of associations with age of reaching puberty. There are some sporadic findings on some disease and cause of death categories including cardiovascular disease and some cancers, but no consistent convincing evidence of direct effects of PFOA or PFOS as yet. The largest community exposure to PFOA is currently subject to a comprehensive study by the C8 Science Panel and new findings emerging from this study will be summarized.

A large Teflon manufacturing facility in the Mid-Ohio Valley, USA released PFOA into the air and Ohio River from the 1950s until recently. PFOA reached drinking water supplies by entering the groundwater and was detected in six water districts near the plant in 2002. A class action lawsuit brought by the communities against the company resulted in a Settlement Agreement which among other provisions, established the C8 Science Panel, members of which are leading a programme of epidemiology on potential health effects of PFOA. This includes analyses of data gathered through questionnaires and blood samples from about 69,000 people living near the plant in West Virginia and Ohio. Results of associations studied from this large scale survey will be presented, including positive associations between PFOA and cholesterol, uric acid and delayed menarche, and absences of an association with miscarriage, diabetes or childhood attention deficit disorder.

Developmental toxicity of PFOS, PFBS, PFOA and PFUnDA to chicken (*Gallus gallus domesticus*), great cormorant (*Phalacrocorax carbo sinensis*) and herring gull (*Larus argentatus*)

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Perfluoroalkyl acids (PFAA) have been used in wide range of applications such as stain and oil resistant coatings, fabric treatments, fire-fighting foams. PFAAs are commonly found in various environmental samples and high concentrations have been found in bird eggs (Holmström et al. 2005). The aim of this study is to investigate the sensitivity of different species of birds to a number of PFAAs and to determine the toxic potential of these chemicals to the developing birds. In this study the two wild species great cormorant (*Phalacrocorax carbo sinensis*) and herring gull (*Larus argentatus*) and the domestic white leghorn chicken (*Gallus gallus domesticus*) were used to study the toxicity of perfluorooctane sulfonate (PFOS), perfluorobutane sulfonate (PFBS), perfluorooctanoate (PFOA) and perfluoroundecanoate (PFUnDA). Eggs were collected from bird colonies in Lake Vänern, Sweden, or purchased and incubated at 37.5°C. When the developmental stage equivalent to four days of incubation for chicken was reached the eggs were injected with a solution of one of the PFAAs. Survival was monitored until day 19 of incubation (chicken) or at the beginning of hatching process (cormorant and herring gull). Embryos were dissected and some control and exposed livers were analyzed for PFAAs. High levels of PFAAs were found in control livers of cormorant and herring gull indicating that these populations have a high environmental exposure to PFAAs. Chicken was found to be more sensitive than the wild species with effects on survival seen on PFOS doses close to environmental levels found in bird eggs and livers. PFOA followed by PFOS were found to be the most toxic of the tested chemicals but the high environmental levels of PFOS leaves a small margin of safety. Populations of birds that have a high exposure to PFAAs could reach levels where embryo survival is affected.

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Evidence of biotransformation of fluorotelomer alcohols to perfluorocarboxylates in humans

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Introduction

In recent years the debate of human exposure to perfluorinated compounds (PFCs) is increasingly focusing on precursor compounds known to degrade to perfluorooctanoic acid (PFOA). Known metabolic products from fluorotelomer alcohol (FTOH) exposure in animal studies are fluorotelomer unsaturated acids (FTUAs) and fluorotelomer saturated acids (FTSAs). Dinglasan et al show that biotransformation of 8:2 fluorotelomer alcohol yields PFOA through the intermediate compound fluorotelomer unsaturated acid (FTUCA) in a microbial system. The same metabolisation was later proved to occur in rats where perfluorinated nonanoic acid (PFNA) was also determined as a minor metabolite. By far the most dominating compound in the air samples of our study was the 8:2 FTOH (range =830-250 000 ng/m^3) with individual concentrations 8 to 32 times higher than PFHxA (range=57-14 000 ng/m^3) and 10 to 800 times higher than PFOA (range=80-4 900 ng/m^3)[5] and in blood the dominating compound is PFOA (range 5-535 ng/mL whole blood) with PFNA showing the second higest levels.
The objective of this study was to determine blood concentrations of PFCAs and PFSAs as well as the metabolic products from fluorotelomer alcohols to PFCAs previously seen in animal studies.

Materials and Methods

The population used for the study are a group of professional ski wax technicians. The technicians (*n=8*) are employed by the Swedish and US national cross-country ski teams. During the exposed skiing season from December through to March the technicians apply fluorinated ski wax for approximately 30 hours a week.
Blood samples were collected during World Cup events in 2007-2010. The extraction was performed using Waters Oasis Wax SPE-cartridges. Levels of PFCAs C5-C11, PFSAs C4, C6, C8, C10 and 3:3, 5:3, 7:3 FTSAs and C6, C8, C10-FTUAs were analyzed using an UPLC- MS/MS.

Results and discussion

The most abundant of the metabolic products is 5:3 FTUA which was found in most samples up to 5 ng/mL whole blood. 7:3 FTUA was the second most abundant compound and 8:2 FTOUA was present in a few samples at very low levels.
A key question that arises when considering air concentrations in relation to the elevated blood levels of PFCAs from our previous study, is whether the exposure to PFOA is indirect through precursor 8:2 FTOHs or if the levels of PFOA detected in the air are responsible for the increased PFOA blood levels. PFNA was the second most abundant perfluorocarboxylate in blood from wax technicians. In our previous report we suggest a metabolic lag time for PFOA in human blood. The World Cup ends in March, still the levels of PFOA in blood continued to rise until April or even May in 3 technicians even though they were unexposed to ski waxes. This information suggests that the PFOA exposure is in fact indirect and that metabolic biological systems are active for some time after the exposure. However, there is also a direct exposure to PFOA through air which will also contribute to the internal PFOA exposure.

Acknowledgements
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Exposure of the Flemish population to PFOS and PFOA

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We evaluated exposure of the Flemish population to PFOS and PFOA, two of the more well-studied representatives of the large group of perfluorinated compounds. We calculated intake through food, settled dust (home, offices), soil and air (outdoor, indoor). Concentrations in food were estimated from measurements in food products at production level in Flanders complemented with literature values. Concentrations in settled dust were measured in homes and offices. Concentrations in air and soil were taken from the literature. We used Flemish food consumption data and time-activity information.
We used a one-compartmental pharmacokinetic model to backcalculate the measured levels of PFOS and PFOA in serum of Flemish adults from the 2002 – 2006 and the 2007-2011 biomonitoring campaigns. In the first campagin, PFOS and PFOA were measured on pooled samples. In the second campaign, PFOS and PFOA were measured on individual samples. The parameters of the pharmacokinetic model were taken from three authors (Trudel et al., 2008, Fromme et al., 2007 and Thompson et al., 2010).
Modelled intake was dominated by dietary exposure and amounted to an average of 24 ng/kg.d for PFOS and 6 ng/kg.d for PFOA. Intakes based on average measured serum levels from the 2010-2011 biomonitoring campaign were 11.5, 1.4 and 1.0 ng/kg.d for PFOS, respectively using the Trudel, Fromme and Thompson model parameters. For PFOA, the estimates were 5.6, 0.28 and 0.49 ng/kg.d, respectively. If we take the biomonitoring results from the 2002-2006 biomonitoring campaign, we get quite different results for PFOS: 57, 6.7 and 5 ng/kg.d. For PFOA, the results are more convergent: 3.6, 0.18 and 0.32 ng/kg.d.
Taking into account the variability on the concentrations and the high number of results below the limit of quantification in food samples, we estimated the exposure modelling to be at the high side. This seems to be confirmed by the results of the biomonitoring. However, we see that two biomonitoring campaigns with different set-ups, two labs and two analytical methods used, results in quite different levels – at least for PFOS. Moreover, the accuracy of the pharmacokinetic model and its parameters is essential to enable interpretation of biomonitoring results with regard to intake levels and sources of exposure.

Acknowledgment
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Analysis of various PFC groups in Czech household dust

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Perfluorinated compounds (PFCs), such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been shown to be globally distributed, environmentally persistent and bioaccumulative chemicals occurring in various, both biotic and abiotic matrices. Human exposure pathways to these chemicals include mainly ingestion of contaminated food (fish, meat, eggs, vegetable, etc.), incidental inhalation, ingestion and dermal absorption of indoor and outdoor air and dust, respectively.
The main aim of this study was *(i)* to develop an analytical procedure for analysis of selected PFCs [11 perfluorocarboxylic acids (PFCAs), 4 perfluorosulphonates (PFSAs), 5 perfluorosulphonamides (FOSAs) and 3 perfluorophosphonic acids (PFPAs)] in dust, *(ii)* to evaluate the levels and profiles of PFCs in dust from the Czech households and *(iii)* to compare generated data with those already published in other studies worldwide and estimate human daily exposure to these PFCs.
In the presented study a high throughput dust extraction by a mixture of water and acetonitrile with subsequent phase partition induced by added salts. In the final step, determination by ultra high-performance liquid chromatography–tandem mass spectrometry (UHPLC–MS/MS) was employed for simultaneous determination of 23 PFCs in dust. The performance characteristics obtained by method validation were as follows: recoveries 83 and 97% and repeatibilities 4–16%, respectively, for the different analytes at the spike level 40 ng/g dust. Altogether 30 household dust samples were examined by this method. Almost all target PFCs were determined in at least several samples, the most abundant were PFSAs, PFOA, PFHxA and FOSEs with mean levels around 20 ng/g dust.

This study was supported from (i) the FP7 within the project PERFOOD (PERFluorinated Organics in Our Diet), grant agreement no. 227525, (ii) project MSM 6046137305 and (iii) Specific University Research (MSMT No. 21/2011).

Fish consumption and perfluorinated compounds – risk or over-estimated threat

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Concentration of perfluorinated compounds (PFAS) in the serum samples of a study population with high fish consumption (139 men and 162 women) were analysed to study dietary exposure through Baltic fish in Finland. All the instrumental analyses were performed with LC-MS/MS. Fish consumption (g/day) was measured by a validated 128-item food-frequency questionnaire (FFQ) designed to cover the diet over the preceding 12 months. Within the study population the average fish consumption for the men and women was 80 and 59 g/day, respectively. The PFAS concentration in serum samples ranged from 3.7 to 280 ng/ml among the men and from 3.2 to 100 ng/ml among the women. The main compounds found in serum were perfluorooctanesulfonate (PFOS), perfluorooctanoate (PFOA), perfluorohexanesulfonate (PFHxS) and perfluorononanoate (PFNA). The Spearman correlation coefficient between fish consumption and serum concentration of PFAS was 0.40 among the men and 0.32 among the women. The Spearman correlation coefficient between an age of the consumer and the PFAS concentration in serum was 0.33 among the men and 0.57 among the women. All the correlations were significant at the level $p<0.01$. Fish consumption is an important source of PFAS, and it correlates positively with the PFAS concentration found in the study population. Regardless of the fish consumption and age of the consumer the PFAS concentration found in women are clearly lower than those found in men.

Closing Session

Keynote

Perfluoroalkyl and polyfluoralkyl substances (PFASs) in the environment: terminology, classification, and origins

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The primary aim of this paper is to provide an overview of "perfluoroalkyl and polyfluoroalkyl substances" (PFASs) detected in the environment, wildlife and humans and recommend clear, specific and descriptive terminology, names and acronyms for PFASs. A particular emphasis is placed on long-chain perfluoroalkyl acids, substances related to the long-chain perfluoroalkyl acids, and substances intended as alternatives to the use of the long-chain perfluoroalkyl acids or their precursors. First, we define PFASs, classify them into various families and recommend a pragmatic set of common names and acronyms for both the families and their individual members, in order to harmonize usage within the community of PFAS producers, users, researchers and regulators. Terminology related to fluorinated polymers is an important aspect of our classification. Second, we provide a brief description of the two main production processes, electrochemical fluorination and telomerization, used for introducing perfluoroalkyl moieties into organic compounds and we specify the by-products (isomers and homologues) likely to arise in these processes. Third, we show how the principal families of PFASs are inter-related as industrial, environmental or metabolic precursors or transformation products of one another. We pay particular attention to those PFASs having the potential to be converted, by abiotic or biotic environmental processes or by human metabolism, into long-chain perfluoroalkyl carboxylic or sulfonic acids, which are currently the focus of regulatory action. The Supplemental Data lists 42 families and sub-families of PFASs, and 268 selected individual compounds, providing recommended names and acronyms, and structural formulas, as well as CAS registry numbers.

Abstracts of posters

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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Introduction
Resent studies suggest diet to be the primary route of exposure to perfluorinated compounds (PFC) in the general population. By now, no representative data on PFC concentration in food are available in Germany. However, analysis of PFC 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 PFC (perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), perfluoropentanoic acid, perfluorohexanoic acid, perfluorononanoic acid, perfluorodecanoic acid, perfluorododecanoic acid, perfluorobutanoic acid, perfluorohexane sulfonate). Based on these data, a provisional assessment of dietary exposure using German food consumption data (National nutrition survey (NVS) II, diet history interviews) has been conducted.

Results
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). PFOS and PFOA were primarily assessed (in 98% of all samples). Other PFC were less regularly included.
Except for water samples (LOQ: 1-11 ng/kg) 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) and upper bound (UB) approach were used to express the resulting uncertainty.
Highest concentrations (sum of mean of all measured PFC in ng/g) were found in the food group meat (94.0/108.4, LB and UB, respectively) followed by fish (13.3/34.9), eggs (1.2/8.1), root vegetables (0.6/2.7) and milk (0.8/8.3). The particularly high PFC 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 PFC load in offal is higher than in meat.
Based on these contamination data the contribution of different food groups to the dietary exposure was assessed. The highest estimated average adult dietary intake of PFC was found to result from fish consumption (4.1/10.8 ng/kg b.w./d). The consumption of marine fish contributes more to the dietary exposure to PFC than freshwater fish. The estimated average adult dietary intake from milk, meat, root vegetables, eggs, drinking water and starchy roots were 1.3/14.3, 1.3/4.0, 0.5/2.1, 0.4/2.8, 0.4/1.0, and 0.03/7.4 ng/kg b.w./d (LB/UB), respectively.

Conclusion

Altogether, 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. Nevertheless, 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.

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

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In this contribution, the study within the 7FP EU project PERFOOD focused on the distribution of PFCs in foods is presented. PFCs have been analysed in 67 samples of selected foods such as variety of meat, seafood, fish, milk and dairy products, fats, hen eggs and alcoholic beverages (wine, beer) from 4 EU regions represented by the Czech, Norwegian, Italian and Belgian markets.
For these purposes, a new sample preparation method, including extraction based on the alternative QuEChERS procedure, for the determination of 25 representives of PFCs group in matrices tested above was developed and validated. For separation and detection,
ultra-performance liquid chromatography (UPLC) coupled to tandem mass spectrometry (MS/MS) employing electrospray ionisation (ESI) was applied; this method will be presented in detail by Lacina et al[1].
The target PFCs monitored in sample extracts were:
13 perfluorocarboxylic acids (PFCAs), 4 perfluorosulfonic acids (PFSAs), 3 perfluorophosphonic acids (PFPAs), 3 perfluorooctanesulfonamides (FOSAs) and 2 perfluorooctanesulfonamidoethanols (FOSEs) were monitored. Altogether 17 of them were detected in various food samples. The most often detected analyte was perfuorooctane sulfonate (PFOS) that was presented in approx. 50% of samples (in range 1–1958 ng/kg); others detected analytes, PFCAs with C_8-C_{14} carbon chain, were presented in approx. 20% of samples. The concentration ranges of individual compounds in the respective group of PFCs were as follows:
2–76 ng/kg for PFSAs (without PFOS), 5–961 ng/kg for PFCAs, 11–95 ng/kg for PFPAs and 2–519 ng/kg for FOSA. Seafood, followed by farmed fish, pig/bovine liver and hen eggs were the most contaminated foodstuffs. On the other hand, alcoholic beverages, rabbit, poultry and fats (vegetable oils, butter and margarines) were not contaminated or at very low levels. Comparing contamination levels and profiles of PFCs (especially PFCAs and PFOS) in various food commodities among sampling countries, no significant differences were found.

Acknowledgments
This study was supported from (i) the FP7 within the project PERFOOD (PERFluorinated Organics in Our Diet), grant agreement no. 227525, (ii) project MSM 6046137305 and (iii) Specific University Research (MSMT No. 21/2011).

[1] O. Lacina, J. Pulkrabova, P. Hradkova, V. Hlouskova, D. Lankova, J. Hajslova: SIMPLE, HIGH THROUGHPUT UHPLC-MS/MS ULTRA TRACE ANALYSIS OF PERFLUORINATED COMPOUNDS IN FOODS OF ANIMAL ORIGIN: MILK AND FISH

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

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Perfluorinated alkylated substances (PFAS) were used in recent years for a variety of industrial applications and products. They appear to be persistent in the environment, and in some cases bioaccumulative and toxic. PFAS have been found to be present in human serum. One of the identified exposure pathways of PFAS to humans is food consumption. Few studies investigated the part beverages take in the total human exposure to PFAS.
The aim of this study was to gain a general idea of the concentration range of different PFAS in coffee, hot water, beer and cola. Furthermore, possible sources to the beverages of interest were tracked by investigating the different food contact materials and the food preparation processes involved. Examples are cola prepared from syrup and tap water (postmixed); paper cups and tubing. Samples were collected in the city of Amsterdam, The Netherlands, and analyzed for a series of 18 different PFAS.
Hot water from coffee machines contains similar concentrations as corresponding tap water. However, the corresponding coffee from these machines contained slightly higher concentrations. Bottled cola contained little or no PFAS while postmixed cola concentrations were in the same range of the respective tap water from which it was prepared. The beer sampled did not contain measurable amounts of PFAS. Recoveries of the several PFAS in cola, tap water and hot water ranged between 17 – 88 % and beer from 1 to 12 %. Recovery of the coffee was 20 % on average.
Apparently coffee is the beverage with the highest PFAS concentrations. Sources of PFAS to the coffee are currently being investigated in leaching experiments from Teflon-containing tubes and paper cups.

This study is part of the EU-sponsored PERFOOD, FP7-227525.

Keywords: PFAS; PFOA; beverages; sources; coffee; cola; beer; water; PERFOOD

A04
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 (PFASs) in food and to calculate the resulting intake of PFASs via food based on national food consumption databases.
The growing occurrence of PFASs in the environment is an increasing matter of health risk assessment. Water is one of the most important environmental compartments in which PFASs 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. Thus, even though drinking water is contaminated at low levels the amount consumed via different food items could make water a major source of PFASs.

Methods
Tap water and bottled water samples from Norway (NO), Czech Republic (CZ), Belgium (BE) and Italy (IT) were analyzed for seven different PFASs. The total amount of all PFASs 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*.

Results
Some of the results were below the limit of quantification. Thus, the lower and the upper bound approach (LB and UB) were used to express the resulting uncertainty. Perfluorobutanoic acid was most frequently quantifiable in water samples and was present in the highest concentrations. Overall, the average contamination (sum of all analyzed PFASs) was 18/19 ng/L (LB/UB) and 3/5 ng/L for tap and bottled water, respectively. The highest total contamination was detected in tap water from Ferrara (IT, 103 ng/L).
A preliminary estimate of PFASs intake by water consumption revealed 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, for BE, CZ, IT and NO, respectively. Water from hot spots resulted in higher intake rates, e.g. 33.2 ng/d for Ferrara (IT). Based on consumption data, people in CZ have the highest PFC intake via drinking water.

Conclusion
It is concluded that water consumption may serve as an important source of PFASs. 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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*http://www.ssb.no/fbu/arkiv/tab-2009-06-10-07.html

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

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Grease proof packaging materials have been reported to contain fluorinated organic coatings. These fluorinated coatings may contain fluorotelomer-based side groups, which might be emitted from such surfaces and be degraded into perfluorinated carboxylates. Thus, packaging is discussed as a source of per- and polyfluorinated compounds (PFAS) in food.

In a previous study[1] we developed screening methods aiming at the detection of fluorine in paper-based packaging and other food contact materials. Besides more sophisticated methods as headspace-GC-MS, P&T-GC-EPED and MS-DART sliding spark spectrometry (SSS) turned out to be a quick and reasonable precise screening tool. With SSS material components are vaporized in the spark plasma, atomized and activated to emit radiation. Software analysis of the delivered spectra gives information on the content of elementary fluorine on top of the surface. Basing on screening results for 146 samples from the south of Germany obtained by SSS and HS-GC-MS, we could proof the equivalence of both screening methods and the reliability of SSS.

Here we present screening data from 456 SSS measurements of European packaging and other food contact materials. Samples were collected in Germany (n=238), the Netherlands (n=13), Belgium (n=16), Italy (n=83), Norway (n=56) and Greek (n=10), whereas a focus was set on food contact materials, which were positively tested during the method development study. These were baking (muffin) papers, sandwich wraps, butter wraps, and cheese packaging. In addition, cardboard-based packaging items with a potential share of recycled paper were tested.

Results indicate that the share of fluorine containing FCM in Germany, Norway, the Netherlands, Belgium, Italy, and Greek 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 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 coffee/tea filters, cardboard packaging and packaging of beverages and take away food. The share is of positive samples is below 10 % in cheese/sausage packaging, sweet packaging and miscellaneous. However, the occurrence of fluorine positive samples in butter wraps, fast food packaging, baking papers and sandwich wraps accounted for 13 %, 19%, 19% and 56%.

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

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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. However, dietary intake appears to be the major exposure pathway (Fromme et al., 2009). Nevertheless, data on levels of PFCs in the human diet and drinking water are still rather 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 were applied, enabling a unique assessment of the occurrence of PFAS in European food as well as the identification of major sources of PFAS exposure via food. During PERFOOD, in a 1st campaign, food items covering all types of food stuff 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.

During spring-summer 2010 fruit was sampled in four different countries; Czech Republic, Italy, Norway and Belgium. The selected fruit samples covered 4 groups of fruit categories i.e. berries, citrus fruit, pip and stone fruit and others and exotic fruit. Target analytes were 4 perfluorosulfonates (C4, C6, C8 and C10) and 11 perfluorocarboxylates (C3 – C14). Extractions were performed with methanolic potassium hydroxide followed by a clean-up with Oasis Wax cartridges. Analysis was performed using an ACQUITY UPLC coupled to a tandem quadrupole mass spectrometer (ACQUITY, TQD, Waters, USA).

Overall, the PFAS levels in the fruit samples were low (pg/g range) with the exception of two samples from Belgium which reached levels up to 1-2 ng/g for the sum of the target analytes. Short chain PFAS were more abundant compared to the longer chains that were only present in one sample. The detection frequency of the perfluorocarboxylates was higher compared to the perfluorosulfonates. PFBA and PFOS showed the highest levels among the target analytes. In general concentrations in samples originating from Belgium were highest, followed by Czech Republic, Italy and Norway. The higher levels found in Belgian could be possibly explained by the presence of a perfluorochemical manufacturing plant. Overall, fruit will not be the main contributor to the intake of PFCs through our diet but these data showed that fruit can be a potential source of exposure, especially if the fruit origins from locations in the vicinity of point sources.

Session B: Sources, pathways, analysis

B01
Simultaneous determination of perfluoroalkyl carboxylates (PFCAs), sulfonates (PFSAs) and phosphonates (PFPAs) in food cauldrons

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A multi-chemical method based on ultra performance liquid chromatography coupled to quadrupole time-of-flight high resolution mass spectrometry (UPLC-qToF-HRMS) was developed and validated for the determination of PFCAs (C4-12), PFSAs (C4,6,8,10) and PFPAs (C6,8,10), together referred to as perfluoroalkyl acids (PFAAs), in food cauldrons. Initially, a food cauldron consisting of 14 different food groups without beverages was used for method development and validation. This was later replaced by a composite baby food matrix, which was found to be free from detectable levels of PFAAs. Homogenized samples were extracted with acetonitrile:water (90:10) followed by enrichment of the analytes on a mixed mode co-polymeric sorbent (C8 + quaternary amine) using solid phase extraction. Chromatographic separation was achieved on a Acquity UPLC BEH C18 reversed phase column (50×2.1 mm, 1.7 µm particles) at 40 ºC using a mobile phase gradient consisting of water, methanol, and acetonitrile containing 2 mM ammonium acetate and 5 mM 1-methyl piperidine. The mass spectrometer was operated in electrospray negative ionization mode. Use of 1-methyl piperidine in the mobile phase resulted in a significant increase of detector response and improved chromatographic resolution for PFAAs. Typical method detection limits for all analytes on a food wet weight basis were in the low pg/g range. Average method recoveries (n=3 at three different days) at a spiking level of 0.1 ng/g were 73-109%, 86-130% and 117-260% for PFCAs, PFSAs and PFPAs, respectively, and at a spiking level of 0.8 ng/g the corresponding recoveries were 78-97%, 88-123% and 90-208%. Whole method linearity was evaluated with spiked baby food samples at five different concentrations (spike range 0.06 - 1.2 ng/g) and a blank (unspiked sample). Excellent r^2 values >0.996 were obtained for all analytes. A matrix effect (signal enhancement) was observed for PFPAs in food extracts (see recoveries), however, the matrix effect was not concentration dependent, given the good method linearity. Thus PFPAs can still be quantified using matrix-matched calibration standards. This is the first multi-chemical analytical method for PFAAs including PFPAs described for food samples. The method will be applied to a food cauldron, baby food and diet composite samples and results will be presented on the poster.

B02
A matrix effect-free method for ultra trace analysis of perfluoroalkyl acids in dietary samples

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Perfluoroalkyl acids (PFAAs) are a class of highly persistent compounds. Longer chain PFAA homologues are also bioaccumulative as well as toxic in laboratory studies and thus could pose a risk to human health. Long-chain PFAAs have been found at relatively constant concentrations (low μg L^{-1}) in human sera from background exposed populations throughout the industrialized world. Recent modeling studies indicated that human exposure of the background population occurs primarily via dietary intake. In order to better constrain exposure estimates there is a need for lower detection limits and improved accuracy in quantification of PFAAs in dietary samples. In this work, we present an ultra sensitive, matrix effect-free analytical methodology for accurate quantification of C_6-C_{12} perfluorinated carboxylates (PFCAs) as well as C_6 and C_8 perfluorinated sulfonates (PFSAs) in complex food mixtures including duplicate diet samples, baby food and vegetable composites.
The presented analytical method employed a modified ion-pair extraction procedure (Hansen et al., 2001) followed by solid phase extraction on Florisil/ENVI-Carb columns and UPLC/MS/MS analysis. The analytical methodology was developed and optimized for water rich duplicate diet samples. A sample matrix was generated for method development by collecting duplicate diet samples (including drinks) over several days from a volunteer. Mean recoveries for ^{13}C isotope labeled PFAAs spiked to this food matrix ranged from 71 to 88% for C_6-C_{12} PFCAs and 93 and 98% for C_6 and C_8 PFSAs, respectively. Effects from co-eluting matrix components on the PFAA ionization efficiency were found to be negligible by comparing the response of PFAAs in spiked food extracts (corresponding to 100 pg/g food) with a PFAA standard solution. Fortification with ^{13}C isotope labeled standards demonstrated method detection limits <10 pg/g and excellent whole method linearity (R^2>0.99) for all investigated analytes in the range 10−10,000 pg/g. Thorough testing identified solvents used in the extraction and clean up to account for a majority of the procedural background contamination. A procedure for minimizing solvent volumes and purifying solvents was developed to reduce background contamination.
The method was further applied to measure levels of PFAAs in a baby food composite sample, a vegetable composite sample and twelve duplicate diet samples. The duplicate diet samples had been previously analyzed by a different laboratory (Fromme et al., 2007), which allowed method intercomparison. Results from these analyses will be presented on the poster.

References
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B03
Comparison of quantitative LC-MS based analytical methods for the determination of low level PFAS concentrations in selected food samples

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Expanding monitoring activities as well as advances in available instrumentation have resulted in the detection of various xenobiotics in the human environment which have been escaping attention for decades. Perfluoroalkylated substances (PFAS) represent one group of emerging contaminants which are of high concern. They are generally persistent in the environment, they can be found over a broad concentration range and within the most parts of the food web in both aquatic and terrestrial organisms. Human food items, produced from natural ingredients (wild or farmed), is likely to be contaminated with PFAS as well, giving rise to human exposure. In terms of monitoring the food contamination, most European countries, as well as Czech Rep. and Norway, carry out national monitoring programs in order to access the daily intake of persistent organic pollutants. To date, only very few international studies focused on PFAS in food and the assessment of dietary intake has been published in Europe.
In this study 18 different PFAS substances, including carboxylates (C_4 – C_{14}), sulfonates (C_4, C_6, C_8, C_{10}), perfluorooctane sulfonamid and N-alkylsulfonamides, were investigated. Lean and fatty fish samples (trout and salmon respectively) were prepared with the in-house methods of ICT and NILU. In order to compare the efficiency, accuracy and reproducibility of the methods spiking experiments were performed. Analysis was done on two different MS instruments, which were a hybrid quadrupole–linear ion trap (AB Sciex QTrap 5500) and a high resolution time–of–flight (Waters LCT Premiere XE). The instruments were coupled to a Waters Acquity UPLC system for analyte separation. With this set-up, linearity performance, detection limits and accuracy of the different instruments were investigated by analysing solvent standards and matrix matched standards from the lean as well as the fatty fish. Moreover some fish samples of different fish species were run on each instrument for testing the applicability in "real-life".

Acknowledgement
This study was funded by the Research Support Fund of the National Training Fund within the project EMERCON (Identification and quantification of emerging organic contaminants in the Czech aquatic ecosystem and food market supply) with focus on perfluorinated alkylated compounds (PFC) and with NILU internal funding.

B04
A validation program for analytical methods for PFASs in food

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Introduction
Limited data on PFASs in food is available. More data is needed to carry out exposure assessments and ultimately, risk assessments. Analytical methods need to be developed for that purpose. This is challenging because of (i) low PFASs levels in food (often at the fg/g to sub-ng/g level), and (ii) the diversity of matrices (e.g. dairy, vegetables, cereals, meat, fruits and drinking water). Within the EU project PERFOOD, methods have been developed that meet these challenges (i.e. diversity of matrices, low levels). In addition, methods should be simple and easy transferable to interested food analysis laboratories. The compounds of interest are perfluorocarboxylates (PFCAs), perfluorosulfonates (PFSAs) and perfluorophosphonates (PFPAs).

Approach
The methods have first been validated in the laboratory where they were developed or implemented. Laboratories evaluated these methods in terms of accuracy, precision, robustness and sensitivity). The next step is a rigorous 2-round validation scheme (see Table 1) to which methods are subjected.

Table 1. Step-by-step validation scheme for methods for PFASs in food

Sample type	Levels, replicates	Information obtained
Round 1		
Standard solutions	5 levels, n=4	Precision, detection capability, calibration, accuracy, robustness
Standard solution + interferences	1 level, n=2	
Vegetables (spinach) extract 1	spiked, n=4	
Fish (herring) extract 2	n.c., n=4	
Round 2		
Fish fillet**	n.c., n=3	Accuracy, precision, robustness (e.g. matrix effects), reproducibility
Pork liver**	spiked, n=3	
Vegetables	n.c., n=3	
Drinking water**	spiked, n=3	
Standard solution	spiked, n=2	

* n.c.: naturally contaminated
** Samples for the 'open' world-wide interlaboratory study

In round 1, the laboratories received standard solutions of PFPAs, PFCAs and PFSAs with undisclosed concentrations. One PFSA solution included an undisclosed interference for PFOS, being taurodeoxycholic acid (TDCA). Furthermore, participants received a herring and vegetables extract. Participants use their in-house methods. The samples of round 2 are currently being analysed.

Results
The samples of round 1 were analysed by the participants and data was evaluated. The results show that the precision of the data is concentration dependent. At lower concentrations, the uncertainty increases.
For the standard solutions, the laboratories were generally close to the theoretical value of the standard, although some results substantially deviated. This is most likely due to dilution errors, calculation errors or data transmission errors. In addition, technicians do not routinely analyse standard solutions, which may be an error source as routine analytical, calculation and reporting procedures do not apply.

TDCA can interfere with the PFOS quantification (co-elution and the same transition m/z 499>80). TDCA was spiked to 1 standard solution to determine if results would suffer from this interference. However, the participants generally successfully resolved this interference from PFOS and circumvented potential inaccuracies rising from TDCA.

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B05
Isotope dilution technique in the analysis of PFOS and PFOA in water samples.

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Background
The use of isotope dilution mass spectrometry (IDMS) has become more common with the increase of mass spectrometric instrumentation and applications. IDMS technique enhances the accuracy of measurements, especially in difficult sample matrix. The availability of isotopic labeled standards (^{13}C- or deuterium) has improved in recent years. Nonetheless, the nomenclature of analytical standard solutions (e.g. surrogate, recovery standard, performance standard or instrument standard) is inconsistent and the purpose of the standard not readily apparent. In this study, we present the IDMS procedure to the determination of two most common perfluorinated substances (PFCs) perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in water samples. The effects of different applications of internal standards to the results are demonstrated.

Analytical method
Analytes were extracted by Oasis HLB SPE cartridges. Prior to SPE, 20 µL of surrogate standard ($^{13}C_4$ PFOS and $^{13}C_4$ PFOA, 50 ng mL^{-1}) and 0.1 mL NH_4OAc were added to the samples. The analytes were eluted with methanol. The extracts were evaporated to dryness and redissolved in 0.6 mL of methanol. For LC-MS analysis, 0.3 mL of extract was transferred to a polypropylene vial, and 0.7 mL of Milli-Q water and 20 µL of instrument standard ($^{13}C_8$-PFOS and $^{13}C_8$-PFOA, 25 ng mL^{-1}) were added.
The diluted extracts were analyzed using ultra performance liquid chromatography (UPLC®) coupled with tandem mass spectrometry (MS/MS). An isolator column was placed before the injector to delay signals originating from the instrument. The analytes were determined using triple quadrupole mass spectrometer (Xevo TQ MS, Waters) using electrospray ionization (ESI) and multiple reaction monitoring mode.

Test procedure
Three different water samples (Milli-Q water, natural water and waste water) are analyzed as four replicate measurements repeated three times on different days. The *within-day* repeatability and *day-to-day* reproducibility are evaluated. The calculations of PFOA and PFOS concentrations are done varying the functions of applied internal standards.

Conclutions
The use of isotopically labeled internal standards improves the quality of analytical results in water samples at trace level concentrations. It is recommended to use the isotopically labeled internal standard (analog to the analyte) as surrogate when possible. The means that internal standards are used should be reported when publishing quantitative data to make the data more comparable. The benefits achieved with the correct application of mass labeled internal standards are clear: data handling is simplified, the accuracy and the quality of reported results are increased.

B06
Simple and high throughput method for quantitation of perfluoroalkyl substances using LC-MS/MS

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Abstract:
A simple and high throughput method for analysis of perfluoroalkyl substanes (PFAS) in serum was developed and validated. Sample pre-treatment consisted only of two precipitation steps performed in neutral and acidic conditions. Separation and detection of 9 perfluorocarboxylates and 4 perfluorosulfonates was performed with liquid chromatography (LC) coupled to triple quadrupole mass spectrometer (MS/MS). A fast, sensitive and selective LC-MS/MS method was achieved using small particle ultra-high pressure columns and single reaction monitoring (SRM) and pseudo-SRM techniques. All the studied analytes were sepated and eluted within 11 minutes. All the validation parameters were considered to be acceptable for human serum analysis..Limit of quantification (LOQ) for 0.5 ml serum sample was 0.3 ng/ml for each analyte. Variations between the analytes were observed in the accuracy and inner- and inter-batch precisions, and these parameters were dependent on the studied concentration levels. Inter-laboratory reproducibility for the available analytes was highly acceptable.
To study the high throughput performance of the validated method, 120 human serum samples were analyzed. The main PFASs found in samples were perfluorooctanesulfonate (PFOS) and perfluorooctanoate (PFOA), perfluorohexanesulfonate (PFHxS) and perfluorononanoate (PFNA). The analysis of all the 120 samples was performed from the sample pre-treatment to the quantitated results in one working week demonstrating the high throughput performance of the method. Besides the high throughput performance, the developed method is suitable for studies where the sample volume is limited since a low sample volume only from 0.2 to 0.5 ml serum is needed.

B07
Inputs of perfluorinated chemicals from skiing activities to the Norwegian environment

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During the winter season, cross-country skiing is Norway's most popular outdoor activity. Advances in wax technology have lead to the use of perfluorinated compounds (PFCs) in waxes, in particular race waxes. PFCs have been used in non-stick cooking surfaces for many years, and they are now used for the same reasons in ski waxes, to improve the ski glide. PFCs have previously been measured in the blood of ski wax technicians and now they have also been measured in snow in the Oslo area.

During a ski trip the wax is eroded by the snow and remains in the snow until the spring snow melt, at which point the PFCs are mobilised and enter the aquatic environment through melt water. Snow samples were collected from the course of the 2011 FIS Nordic World Ski Championships in Oslo and the concentrations of PFCs in the snow and particulates from the ski area were measured. Spring snow melt samples were also analysed from a pond below the ski tracks. The pond collects melt water which is recycled and used to produce artificial snow. The artificial snow produced from this source also showed elevated PFC concentrations.

The highest concentrations were measured in the snow from the competition test tracks, but elevated concentrations were also measured in the spring melt water from the same area. PFOA was the dominant compound with PFHxA, PFHpA and PFNA also detected at high concentrations.

B09
Recent time trends of PFOS in cod and hake liver

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Since the announced phase out of Perfluorooctane sulfonate (PFOS) in 2000 by 3M and after a restriction was put on the use of PFOS in the European Union in 2006, it was generally assumed that PFOS levels in the environment would decrease. To confirm this hypothesis, cod and hake were sampled annually at three locations in the North Sea, between 2003 and 2010 and analyzed for PFOS. PFOS was detected in livers from cod and hake using LCMS. While no upward or downward trend was observed for hake from the South-Western North Sea, an increasing trend was found for cod from the Central and the Southern North Sea. For these locations, PFOS levels increased by almost a factor of 6 (about 250 - 300 µg/kg ww increase per year) in the period between 2005 and 2009. Current levels in cod liver are 1300 - 1600 µg/kg ww, which is high compared to the 210 µg/kg ww in hake liver from the south-western North Sea. The increase is unexpected as levels in freshwater fish have been in decline during this period (Kwadijk et al 2010).

B10
Polyfluoroalkyl compounds in the atmosphere at a wastewater Treatment Plant

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Introduction
Sources, transport mechanisms and fate of polyfluoroalkyl compounds (PFCs) in the environment are not yet fully understood. Perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs), which are persistent in the environment, have been shown to be transported mainly via ocean currents, whereas their volatile precursors (i.e. fluorotelomeralcohols (FTOHs), perfluoroalkyl sulfonamides (FOSAs) and sulfonamidoethanols (FOSEs)) can be transported in the atmosphere. However, the amounts transported by these two pathways are not sufficient to fully explain the levels detected in remote regions. Thus the direct transport of PFCAs and PFSAs in the atmosphere, bound on particles or in the gas phase, is discussed. In the present study a wastewater treatment plant (WWTP) was investigated as a possible source for PFCs in the atmosphere and partitioning behaviour of PFCs between the gas and particle phase has been explored.

Materials & Methods
High volume air samples using PUF/XAD/PUF cartridges and glass fiber filters and passive air samples using sorbent impregnated polyurethane foam (SIP) disks were collected at an aeration tank and a secondary clarifier at a WWTP. The target analytes included precursors (6:2, 8:2, 10:2 FTOHs, MeFOSA, EtFOSA, PFOSA, MeFOSE, EtFOSE) as well as C_4, C_6, C_8, C_{10} PFSAs and C_4–C_{12}, C_{14} PFCAs. The instrumental analysis was performed using GC-MS and HPLC-ESI-MS/MS.

Results & Discussion
Atmospheric concentrations at the aeration tank were 2-19 times higher compared to the secondary clarifier, and 5-380 times higher than ambient background air concentrations. In the gas phase highest concentrations were found for ∑FTOHs (11000 pg m^{-3} at the aeration tank vs. 590 pg m^{-3} at the secondary clarifier), followed by ∑PFCA&PFSA (70 vs. 34 pg m^{-3}) and ∑FOSA&FOSE (43 vs. 16 pg m^{-3}). In the particulate phase ∑PFCA&PFSA was dominant (3900 vs. 1100 pg m^{-3}) with PFOS as the predominant compound (~90 % of the ∑PFCA&PFSA). Precursors (i.e ∑FOSA&FOSE: 70 vs. 11 pg m^{-3}, ∑FTOH: 25 vs. 2.5 pg m^{-3}) contributed only a small part of the ∑PFCs in the particulate phase. The aeration process in the aeration tank seems to lead to elevated atmospheric concentrations.
The particle associated fraction increased with increasing chain length for PFCAs (from 30 to 100%). PFSAs were predominantly bound to particles (~98%). Lower fractions on particles were found for FTOHs (~2%), FOSAs (~30%) and FOSEs (~60%). The detection of PFCAs and PFSAs in the passive air samplers and the good agreement between concentrations derived from high volume samples and passive samples confirmed the presence of PFCAs and PFSAs in the gas phase. However, sampling artifacts such as sampling of particles on the passive sampler must be considered.

Conclusions
WWTPs and in particular aeration tanks were shown to be a source for PFCs in the atmospheric gas and particle phase. The presence of PFCAs and PFSAs in the atmosphere promotes the hypotheses of their atmospheric transport.

Literature
Vierke, Lena; Ahrens, Lutz; Shoeib, Mahiba, Reiner, Eric J; Guo, Rui; Palm, Wolf-Ulrich; Ebinghaus, Ralf; Harner, Tom (accepted): Air Concentrations and Particle-Gas Partitioning of Polyfluoroalkyl Compounds at a Wastewater Treatment Plant. In: Env. Chem.

B11
Estimating physicochemical properties of poly- and perfluorinated alkyl substances (PFAS) with a quantum chemistry-based model

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Recently, concern about the presence of anthropogenically produced poly- and perfluorinated alkyl substances (PFAS) in the environment has arisen. However, the application of environmental fate models to understand the environmental distribution and ultimate fate of PFAS has been hindered by a lack of physicochemical property data. Experimental determination of PFAS properties is challenging and there are many compounds of potential interest. Therefore, computational methods are an attractive alternative for estimating properties of PFAS. In this work [1], we employed a quantum chemistry-based model, COSMOtherm, to estimate physicochemical properties for 130 individual PFAS, namely homologous series of saturated and unsaturated carboxylic acids, sulfonic and sulfinic acids, phosphonic and phosphinic acids, olefins, iodides, phosphate esters, sulfonamides/-ethanols, and saturated and unsaturated aldehydes with poly- and perfluorinated chain lengths from 4-14 carbons (including branched isomers for C_4–C_8 perfluorocarboxylic acids). The estimated physicochemical properties are interpreted using structure-property relationships and rationalised with insight into molecular interactions. Within a homologous series of linear PFASs with the same functional group, both air-water and octanol-water partition coefficient increase with increasing perfluorinated chain length, likely due to increasing molecular volume. For PFASs with the same perfluorinated chain length but different functional groups, the ability of the functional group to form hydrogen-bonds strongly influences the chemicals' partitioning behaviour. The partitioning behaviour of all theoretically possible branched isomers can vary considerably; however, the predominant isopropyl and monomethyl branched isomers in technical mixtures have similar properties as their linear counterparts (differences below 0.5 log units). Our property estimates provide a useful basis for further environmental modelling, but only with some caveats and limitations. To understand the overall partitioning behavior of PFAS in the real environment, further studies on phenomena such as the surfactant-like nature of PFAS, their acid dissociation ratio, and specific sorption of anions to organic matter are required.

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B12
Inhalation anaesthetics and climate Change

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Isoflurane (HCFE-235da2, $CF_3CHClOCHF_2$), desflurane ($CF_3CHFOCHF_2$) and sevoflurane ($(CF_3)_2CHOCH_2F$), are halogenated organic compounds used for induction and maintenance of general anesthesia. Isoflurane entered broad clinical use in the early 1980's, followed by desflurane and sevoflurane a decade later. The volatile anesthetic gases are delivered via a system that mixes the anesthetic gas with a carrier gas (oxygen and nitrous oxide) in various concentrations. Exhaled gases flow through an absorber, most commonly, calcium hydroxide, which are used to remove carbon dioxide. Some gas may at the same time escape from the delivery system. Although the increasing abundance of CO_2 in our atmosphere is the main driver of the observed climate change, it is the cumulative effect of all forcing agents that dictates the direction and magnitude of the change, and many smaller contributors are also at play. Isoflurane, desflurane, and sevoflurane, are widely used inhalation anaesthetics.
We have measured the infrared spectra of these anaesthetics and conducted the first calculations of their contribution to radiative forcing of climate change which recognize the important fact that radiative forcing is strongly dependent on the wavelength of the absorption features.
Radiative efficiencies of 0.453, 0.469, and 0.351 W m^{-2} ppb^{-1} and global warming potentials (GWPs) of 510, 1620 and 210 (100 year time horizon) were established for isoflurane, desflurane, and sevoflurane, respectively.
Based on the derived 100-year GWPs, the average climate impact per anaesthetic procedure at the University of Michigan is the same as the emission of approximately 22 kg CO_2. We estimate the global emissions of inhalation anaesthetics have a climate impact which is comparable to that from the CO_2 emissions from 1 coal fired power plant or 1 million passenger cars.

B13
Degradation of 8:2 FTOH and formation of PFOA in laboratory experiments with brackish sea water

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It is well known that 1*H*,1*H*,2*H*,2*H*-perfluorodecanol also known as 8:2 FTOH is a precursor to more stable, toxic and less volatile perfluorooctanoic-acid (PFOA). At wastewater treatment plants (WWTP) greater PFOA concentrations have been observed in the effluent than in the influent. In the aquatic environment, numerous environmental parameters can affect on the speed and effectiviness of degradation of 8:2 FTOH and on the formation of PFOA. In this study the degradation of 8:2 FTOH in relation to the formation of PFOA was investigated with multiple different test configurations using brackish sea water. Degradation experiments were performed as closed bottle –type tests with abiotic controls, oxygen/pH controls and blank samples in selected experiments. These degradation tests were compared with activated sludge method, which was done according to OECD 310 (ready biodegradability, duration 28 days) method guideline with inocolum collected from a WWTP. Degradation experiments excluding OECD 310 were done at different temperatures in the range of 5-20 °C using coastal sea water from the western Gulf of Finland in the Baltic Sea. In the first experimental set-up, the impact of dissolved oxygen concentration was investigated with surface water. In the second set-up, oxygen-rich surface water and lower oxygen content bottom water from a basin were compared. The duration of first experiments was 45 days and that of the second experiments 60 days. Samples were taken periodically and the concentration of both 8:2 FTOH and PFOA was monitored. At the same time also pH and dissolved oxygen concentration in the control samples of the second set-up was measured. Analysis of samples for 8:2 FTOH and PFOA was performed with method developed for HPLC/MS and utilizing solid phase extraction (C18) for pretreatment. The results showed that 8:2 FTOH is rapidly degraded or removed from the liquid phase and the removal rate was found to be virtually constant regardless of the test setup or parameters within sample matrix. Also it was confirmed that microbial degradation leads to PFOA as in the abiotic control samples 8:2 FTOH could still be easily detected even after 30 days and at the same time no PFOA was detected. Even though the degradation of 8:2 FTOH was almost identical within different experimental set-ups, the differences came from the formation of PFOA which was at maximum roughly 10 % of the initial 8:2 FTOH concentration. Clear temperature-dependent formation of PFOA was observed in both experimental set-ups with faster formation at higher temperatures, while other parameters had no great impact.

B14
Fluorotelomer alcohol biodegradation pathways

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Extensive aerobic biodegradation studies have been conducted in numerous matrices using both cold and 14C radiolabelled 8:2 and 6:2 Fluorotelomer Alcohol to elucidate their biotransformation pathways. Interestingly, whilst both 8:2 and 6:2 FTOH follow similar biotransformation routes and result in substantial irreversibly bound residues, the short-chain 6:2 alcohol degrades faster and more extensively with mineralization of multiple –CF2- groups. These results suggests that there may be biodegradation pathways that lead to trifluoroacetic acid. Meticulous analyses have revealed new insights in to the precise step-wise transformations that occur. This paper will present the current state of knowledge regarding biodegradation pathways and explore what additional studies may help us learn more.

B15
Atmospheric Chemistry of $CF_3CH_2OCH_3$

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Recognition of the adverse environmental impact of chlorofluorocarbon (CFC) release into the atmosphere has led to an international effort to replace these compounds with environmentally acceptable alternatives. One central issue is to develop CFC alternatives with low global warming potentials (GWPs). There are several strategies to increase reactivity towards OH radicals and thereby decrease the atmospheric lifetime and GWP. Two classes of new CFC alternatives are unsaturated fluorinated hydrocarbons and hydrofluoroethers (HFEs). HFEs are compounds which have been developed to replace CFCs in applications such as the cleaning of electronic equipment, heat transfer agents, and carrier fluids for lubricant deposition. Smog chamber/FTIR techniques were used to study the atmospheric chemistry of $CF_3CH_2OCH_3$. Prior to its large-scale industrial use an assessment of the atmospheric chemistry, and hence environmental impact, of $CF_3CH_2OCH_3$ is needed. To address this need the atmospheric chemistry of $CF_3CH_2OCH_3$ was investigated: Kinetics of the reactions with chlorine atoms and hydroxyl radicals to provide information on atmospheric lifetimes, the atmospheric oxidation mechanism, and degradation products, and global warming potential (GWP).

B16
Development of a method to combine the extraction of both PFCs and legacy-POPs from human serum.

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Background
Animal studies have shown that perfluorinated compounds (PFCs) are easily absorbed by oral intake, inhalation and to a smaller extent through dermal contact. The elimination of the PFCs is in general considered very slow with average human serum half-lives of 8.8 years for PFHxS, 5.4 years for PFOS and 3.8 years for PFOA. However, the PFCs are not bioaccumulated in the fatty tissue as most of the legacy persistent organic pollutants (legacy-POPs). Instead the PFCs are distributed to liver and kidney through the bloodstream. In vitro studies have indicated that PFCs and legacy-POPs both affect the sex hormone receptor functions. The aim of the present study is to develop a method to combine the extraction of both PFCs and legacy-POPs from human serum. This method will be used to determine the total mixture effect of sex hormone receptor functions.

Methods
A method for extracting legacy-POPs from human serum was developed by Philip S. Hjelmborg et al. [1]. This method includes a solid phase extraction (SPE) and a solvent extraction followed by normal-phase high-performance liquid chromatography (NP-HPLC). The method was tested and modified with the aim for application to extract PFCs as well as legacy-POPs in the same SPE-HPLC run.

Results
The SPE-HPLC legacy-POP method in its original form was found not to be fit for the extraction of PFCs. The SPE-HPLC method however showed promissing results by an omission of the solvent extraction shows promissing results. Further adjustments of the HPLC method are required.

Conclusion
The SPE-HPLC method for legacy-POP serum extraction was not applicable to include PFC extraction. Some minor adjustments of the method may however have a positive influence on the extraction recovery of PFCs.

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Session C: Exposure, toxicity and regulation

C01
Perfluoro acrylates as surface refining agents for paper and board: investigations on their resistance at higher temperature

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Perfluoroalkylated substances (PFAS) represent a class of environmental contaminants that comprise a vast array of chemical entities being without exception of anthropogenic origin. Due to their special physico-chemical properties, which differ significantly from those of other halogenated compounds, they are extremely persistent against biodegradation or non-biological disintegration. Attributable to their chemical resistance, PFAS are widely used for an enormous assortment of consumer goods, including household products. In addition PFAS are also utilised as additives and coatings of contact materials for food like paper and cardboard. The physico-chemical properties of PFAS, such as their hydrophobicity and oleophobicity make them ideal substances applied as finishing components for paper and cardboards in this area. Examples for such applications comprise sandwich wrappings, microwavable popcorn bags and cup cake liners as well as fast food containers like pizza boxes. Although paper and cardboard surface treatments with PFAS are only indirect sources for the contamination of food with perfluorinated substances, these materials represent potential sources of oral exposure for consumers. However, the exact contribution of perfluorinated packaging materials to the overall perfluoro-contamination of food and beverages is currently not well characterised.
In 2010 the European Commission had taken account of this situation and recommended "Member States should monitor during 2010 and 2011 the presence of perfluoroalkylated substances in food".
An increasingly important and rather new substance class used for this purpose are perfluoro acrylates. Their molecular weight ranges from 30000 up to four million Dalton.
In this study we looked into the thermal stability of three different perfluoro acrylates by means of thermogravimetric analysis (TGA). In addition, gases released from the sample were identified by coupling of Fourier-Transform-Infrared (FT-IR) spectroscopy to the TGA instrumentation. The results show, that despite the chemical inertness of perfluoro acrylates not all acrylates are thermally stable at higher temperatures and therefore suitable as refining agents for baking paper. Thus, the precise knowledge on the degradation pattern of perfluoro acrylates will be highly valuable for both manufacturers and risk assessors alike.

C02
Detection of FTOHs in indoor air of work places

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Fluorotelomer alcohols (FTOH) are volatile polyfluorinated compounds, and they are considered as precursor compounds of persistent perfluorinated carboxylic acids (PFCA), since they may degrade into PFCA both, biologically and abiotically. Thus FTOH may contribute to the overall exposure of human towards PFCA, especially PFOA.
FTOH are present in or released from high molecular polyfluorinated compounds, which are used as water and grease repellents on surfaces of consumer products. Due to the comparably high vapor pressures of FTOH an emission from consumer products into indoor air is expected.
The Federal Environment Agency of Germany initiated an analytical screening project for per- and polyfluorinated compounds (PFC) in consumer products in 2009. Part of this project was an investigation of indoor environments with special exposure to PFC containing consumer products.
In this study indoor air samples from 11 workplaces were drawn and analyzed for FTOH. Sampling sites were located in offices, kitchen, shops selling floorings, sports goods and outdoor textiles, two work places with focus on metal processing and automotive painting as well as in passenger car. As proposed by Jahnke et al.[1] 15-25 m³ of indoor air were trapped on Isolute ENV+ SPE cartridges, previously spiked with labeled internal standards. FTOH were eluted with acetone and analyzed by GC-CI-MS.
In addition 5 textile samples were put in an emission test chamber with two ports; one connected to the surrounding air, the other connected to an SPE cartridge and an air pump. 3 m³ of air was drawn through the chamber and the emitted FTOH were trapped and analyzed like the indoor air samples.
Results reveal 6:2- 10:2 FTOH levels in both, indoor air and emission samples. 4:2 concentrations were below the LOD of 40 pg/m³. The sum of 6:2-, 8:2- and 10:2-FTOH in air of the investigated workplaces was below 2 ng/m^3 in both bureaus and the kitchen. Higher levels were obtained in the car interior, at the metal processing and car painting places and in the shops. The highest indoor air level of 390 ng/m³ 6:2-, 8:2- and 10:2-FTOH was found in a shop selling outdoor textiles.
Air emitted from outdoor textiles investigated in the emission chambers contained up to > 600 ng/m³ with 8:2 FTOH being the dominating congener.
Presented data are in good agreement with recently published data on German indoor air[2] and are an indication for a significant FTOH emission from consumer products into indoor air. The significance of the obtained FTOH exposure in indoor and workplace environments for the human PFCA burden, however, depends on uptake rates and degradation rates which are not well known in humans.

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C03
Perfluorinated compounds in human breast milk from the Czech Republic: results of a pilot

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Human breast milk is an important source for infants because it contains a large number of nutritional substances, growth and immune factors. However, as far as mothers are exposed to harmful environmental pollutants, they may be transferred into human milk thus breastfeeding can be a potential route of postnatal exposure for infants.
The aim of this study was *(i)* to develop and validate a broad scope method for analysis of altogether 25 PFCs: 13 perfluorocarboxylic acids (PFCAs), 4 perfluorinated sulfonates (PFSAs), 3 perfluorinated phosphonic acids (PFPAs), 3 perfluorinated sulfonamides (FOSAs), 2 perfluorinated sulfoamidoethanols (FOSEs); sample preparation step based on extraction with acetonitrile and a dispersive solid phase clean-up step followed by ultra-performance liquid chromatography (UPLC) coupled to a tandem mass spectrometric detection (MS/MS) with electrospray ionisation (ESI), for detail see Lacina et al.[1], *(ii)* to apply this method for examination of the occurrence of PFCs in the set of 50 breast milk samples collected in the Czech Republic, *(iii)* to estimate PFCs daily intakes and risk indexes (RIs) according to EFSA guidelines (European Food Safety Authority) for the first 6 month of infants´ life.
Only 7 PFCs were detected in human breast milk samples. Branched isomers of perfluorooctane sulfonate (PFOS) were separated from linear isomer of PFOS and quantified as a sum for total content and together with perfluorooctanoic acid (PFOA) were found in all samples. Concentration of branched PFOS and linear PFOS ranged from 1 to 63 pg/ml and 7 to 114 pg/ml, respectively. Concentration of PFOA ranged from 12 to 128 pg/ml. Perfluorononanoic acid (PFNA) and perfluorodecanoic acid (PFDA) were detected in more than 86% of the samples at mean concentrations 7 and 4 pg/ml. The total concentration of PFCs in human breast milk ranged from 29 to 405 pg/ml. Both PFCs pattern and their levels are comparable with other world studies on the occurrence of PFCs in human breast milk. Based on the estimated body weight and milk intake, the average and highest daily intakes of total PFCs by infants were 20 and 74 ng/kg bw, respectively. RIs calculated for breast milk samples did not exceed the maximum limit (RI=1) recommended by EFSA[2].

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C04

Perfluorinated alkyl substances in whole blood and plasma; an assessment in maternal and umbilical cord samples from two communities in Russia and Uzbekistan.

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Perfluoro alkylated substances (PFAS) are ubiquitous in the Arctic environment, however the knowledge about the PFAS concentrations in the Russian Arctic is scarce. From two communities, Norilsk in the Russian Arctic and Urgench in Uzbekistan, the concentrations of PFAS in full blood and plasma from delivering women and the umbilical cord were sampled right after delivery.

Having the opportunity to analyse both full blood and plasma from the same individual could give valuable information about the distribution of PFAS between the two matrixes. Previously Kärrman[1] reported for five adults a difference in distribution of PFOSA compared to the ionic PFAS. Ionic PFAS such as PFOS and PFOA bind to albumin in plasma/serum, whereas neutral compounds as PFOSA will also distribute to the neutral fraction.

Comparing the two communities, the samples from Norilsk had a higher concentration of PFAS than samples from Urgench. In the samples from Urgench, the majority of the samples had a concentration close to the detection limit or below 1 ng/mL for both PFOS and PFOA. All other compounds were below the detection limit.
From Norilsk we had 14 paired samples, 7 maternal and 7 umbilical cords. For PFOS, PFOA, PFHxS and PFOSA the highest concentrations were found in maternal samples, independent of sample matrix. The distribution between full blood and plasma varied. In plasma PFOS was the dominating compound followed by PFOA, PFHxS and PFOSA, however in whole blood the PFOSA concentration was above the PFHxS concentration, but still below PFOS and PFOA.

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C05
Temporal trends in perfluoronate exposure in a US population exposed to raised levels of PFOA through drinking water

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There is growing concern about human exposure to polyfluroalkyl chemicals (PFCs) and its potential human health effects. PFCs have been used increasingly since the 1950s in commercial applications, including surfactants, lubricants, paper and textile coatings, polishes, food packaging, and fire-fighting foams. Direct industrial emissions are estimated to be the main source of these compounds to the environment, though PFCs can also result from the breakdown of fluorinated telomers. The combination of widespread presence and long half life of PFCs led to voluntary and regulatory exposure control measures. Their production has been banned or reduced worldwide, leading to their decreased concentrations in the ecosystem. Biomonitoring data for these PFCs in the exposed population are needed to assess whether reduced environmental exposure affect human exposures to these compounds.
A chemical plant in the Mid-Ohio Valley near Parkersburg, West Virginia has used PFOA in the manufacture of fluoropolymers since 1951. In 2001, a group of residents from the West Virginia and Ohio communities surrounding the plant filed a class action lawsuit alleging health damage from drinking water supplies drawing on PFOA-contaminated groundwater. The settlement of the class action lawsuit included a baseline survey in 2005–2006 that gathered data from a large number of people from 6 contaminated water districts surrounding the plant, including measurement of 10 PFCs in serum. As a part of the ongoing C8 Science Panel Community Study for the same exposed population, PFCs were again measured in 2010 for a sub-set of the original study population. We present here the change in serum concentrations of 10 PFCs measured in 2010 and 2005-2006 (N=69 participants).
Serum PFC concentrations were determined using liquid-chromatography separation with detection by tandem mass spectrometry. The detection limit (LOD) for all the PFCs was 0.5 ng/mL except PFHxS and PFOS (LOD= 1.0 ng/mL). The average change in PFC concentrations was obtained excluding the observations below LOD and the outliers.
We detected PFOA and PFOS in >98% of the paired sample and PFNA and PFHxS in >75% of them. PFDA and PFUnA were detected in 4 and 1 paired sample, respectively. PFPeA, PFHxA, PFHpA and PFDoA concentrations were <LOD for all the paired samples.
The median decrease (N) and the Spearman correlation (rho) between 2005-2006 and 2010 serum samples were 58.5% for PFOA (N=64), rho=0.89; 40.1% for PFOS (N=63),rho=0.82; 43.9% for PFNA (N=50),rho=0.59 and 35.7% for PFHxS (N=53),rho=0.84. For the paired samples with PFDA (N=4) and PFUnA (N=1) concentrations >LOD, the decrease was 36.4% and 66.9%, respectively.
Exposure to PFOA in this community had largely stopped at or soon after the first survey and other PFC exposures have also being largely reduced. These findings confirms the downward time trend of PFCs in human serum, with levels similar to those observed in different populations except for the fact that this population had a very high PFOA exposure compared to others.

C06
Per- and polyfluorinated compounds in consumer products

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Per- and polyfluorinated chemicals (PFC) have inimitable properties. They are very stable, e.g. are resistant to biotic and abiotic breakdown, and are water and grease repellent. Therefore, they are used in numerous industrial applications, such as in paper- and packaging as well as textile industry. The manufacture, use, and disposal of consumer products is an important source for exposure into the environment. The persistence of PFCs, however, is problematic for the environment. A number of PFCs can be fund ubiquitously in the environment. Findings in remote regions, in human blood and breast milk are of very high concern.
The most frequently detected PFCs are perfluorooctansulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). Both of these compounds are persistent, toxic and bioaccumulative.
While the marketing and use of PFOS is prohibited with few exceptions in the EU since June 27, 2008 there is no substance specific regulation for PFOA.
Available data on PFCs in consumer products are scarce to date. Hence, more data are needed in order to get an overview on recent PFC loads and to evaluate if these data implicate further measures against PFOA with respect to a regulation according to REACH. Therefore, the Federal Environment Agency of Germany initiated an analytical screening project in 2009.
Perfluorinated sulfonic (C_4, C_6-C_8, C_{10}-PFSA) and carboxylic acids (C_4–C_{14}-PFCA) and fluorotelomer alcohols (4:2, 6:2; 8:2 and 10:2 FTOH) were analyzed in 118 consumer products including textiles (outdoor materials), carpets, cleaning and impregnating agents, leather samples, baking and sandwich papers, paper baking forms and ski waxes. PFCA and PFCA were analysed by LC-ESI-MS/MS, whereas FTOH were detected by GC-CI-MS.
The results show that there are consumer products with low or negligible PFSA- and PFCA-contents, such as the cleaning agents or baking and sandwich papers tested. On the other hand, high PFC levels were identified in ski waxes, leather samples, outdoor textiles and some baking papers. Moreover, the PFOS concentrations in most of the leather and carpet samples as well as some textile samples tested exceeded the regulatory threshold value of 1 µg/m^2 PFOS according to the European PFOS regulation.

C07
The toxicology of 6:2 fluorotelomer sulfonate (C6F13CH2CH2SO3-, 6:2 FTSA)

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6:2 Fluorotelomer sulfonate, C6F13CH2CH2SO3-, 6:2 FTSA, has been reported in the environment. It may originate from its direct use or from degradation of precursor substances in the environment. The acute aquatic toxicity to fish, invertebrates and algae have been determined. In a 90-day early life-stage rainbow trout study, the NOEC was 2.62 mg/l based on mean, measured concentrations and first day of hatching. The LOEC (lowest observed effect concentration) and MATC (maximum acceptable toxicant concentration) for the same endpoint were 4.85 and 3.56 mg/L, respectively. A guideline study (OECD TG 305) that included the addition of a dietary exposure conducted under GLP was conducted to evaluate the bioconcentration and bioaccumulation potential 6:2 FTSA. Exposure conditions included a dilution water control, 1 ug/L and 10 ug/L aqueous exposures and a 10 ug/kg dietary exposure with a 56 day uptake phase followed by a 28 day depuration phase. Tissue residues of the test substance in whole fish were evaluated at multiple time points during both study phases. The test results indicated that the bioconcentration and bioaccumulation potential of the test substance is low and substantially less than any existing regulatory triggers. Similarly, the acute oral, dermal and inhalation toxicity, genotoxicity and repeated dose toxicity in rats have been studied. This paper will present the results of these studies and compare them with study data for perfluorooctane sulfonate, C8F17SO3-, an eight perfluorinated carbon sulfonate and perfluorohexane sulfonate, C6F13SO3-, a six perfluorinated carbon sulfonate.

C08
Level and temporal trend of perfluoroalkyl acids in Greenlandic Inuit

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Perfluoroalkyl acids (PFAAs) have been detected in human blood, breast milk, and umbilical cord blood from different countries and regions globally. In Greenland increasing PFAAs concentrations have been observed during 1982-2006 in ringed seals and polar bears. However, until now no data have been reported on human levels of PFAAs in Greenlandic Inuit. We have determined the level and temporal trend of selected PFAAs in the serum of Greenlandic Inuit.

Methods
Serum PFAA levels of 284 Inuit from different Greenlandic districts were determined using liquid chromatography-tandem mass spectrometry with electrospray ionization. The temporal time trend of serum PFAAs in Inuit from Nuuk during 1998-2005 was studied, and the correlation between serum PFAAs and legacy persistent organic pollutants (POPs), mainly obtained via marine food, was explored.

Results
PFOS, PFOA and PFHxS were the most prevalent PFAAs in all districts. Serum PFAA levels were higher in Inuit from Nuuk than in non-Nuuk districts. Within the same district higher levels were observed in males. An age dependent increasing trend of PFAA levels was observed for Nuuk Inuit during 1998-2005. For the pooled gender data no significant association of PFAAs and sum of legacy POPs was observed for Nuuk, whereas significant positive correlations was found for pooled non-Nuuk data. For females, significant positive correlations were observed between PFAAs and legacy POPs in general, but no correlations were found for males. Our data indicate that sources other than seafood intake might contribute to the observed higher PFAA levels in Nuuk Inuit compared to the pooled non-Nuuk districts.

C09
PFOS, PFOA and PFBS induce chicken hepatic fatty acid oxidation in chicken eggs

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In this study a new method for toxicity testing is presented which can be used for studies of environmental pollutants on fatty acid oxidation in avian models. In the current study the method has been used to study the effects of the perfluoroalkyl acids (PFAA) perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluorobutane sulfonate (PFBS) on the developing chicken embryo. Chicken eggs were incubated at 37.5°C and injected with a water solution of PFOS, PFOA or PFBS on day four of incubation. On day ten of incubation chicken embryos were dissected and the livers were incubated *in vitro* with media containing tritium labeled palmitic acid. The ß-oxidation of palmitic acid was measured by liquid scintillation counting of the media to measure the amount of tritiated water created by the metabolic processes. All of the tested chemicals showed induction of the hepatic fatty acid oxidation. The highest induction was 59% and was seen for PFOS at 0.3µg/g. The mechanisms behind the induction are not known but could be due to the structural similarity between these PFAAs and fatty acids or coupled to effects on membrane permeability. The lowest observed effect level (LOEL) was 0.1µg/g PFOS. Several of the doses in this study are below environmental levels found in bird eggs which indicate that effects of this kind could be present in some bird populations. Birds in the wild are not exposed to single PFAAs but mixtures of PFAAs and other pollutants. It is not known how mixtures of PFAAs affect this system. There may be additive or synergistic effects. It is reasonable to expect that the effects observed in this study also are occurring in wild populations of birds.