Issue 2: November 2011

Dear reader,

The Perfood project has now reached its second half and some major results are becoming available. The project was evaluated in the meantime by an external panel who produced a midterm review. Some quotes from the review include: " ..the project is running well .. and being conducted in an efficient manner "; "Perfood at its mid-term has generated and will continue to produce original and highly relevant scientific knowledge on the factors that are influencing the PFC burden of our diet. ... Research on transfer pathways including lab studies (food packaging materials) and field experiments (cattle farm, vegetation) are considered as relevant and original ". The general conclusion of the reviewers was that the project has made good progress and achieved most of its objectives and technical goals for the period.

Of course we are pleased and proud with the outcome of the midterm review, that has reinforced our belief in the methodologies and approaches chosen for this project. Perfood members have been actively engaged in what we consider an instrumental paper for the terminology and understanding of per and polyfluorinated compounds, that will strengthen the communication between scientists and stakeholders. The paper in question has been published in the journal Integrated Environmental Assessment and Management, vol. 7:4, 2011, p. 513-541 (R.C. Buck et al.).

Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins

Robert C Buck,† James Franklin,*‡ Urs Berger,§ Jason M Conder,‖ Ian T Cousins,§ Pim de Voogt,#
Allan Astrup Jensen,†† Kurunthachalam Kannan,‡‡ Scott A Mabury,§§ and Stefan PJ van Leeuwen‖‖

†E.I. du Pont de Nemours & Co., Inc., DuPont Chemicals and Fluoroproducts, Wilmington, Delaware, USA
‡CLF-Chem Consulting, 3 Clos du Châtaignier, BE-1390 Grez-Doiceau, Belgium
§Department of Applied Environmental Science (ITM), Stockholm University, Stockholm, Sweden
‖ENVIRON International, Irvine, California, USA
#Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, Amsterdam, The Netherlands
††Nordic Institute for Product Sustainability, Environmental Chemistry and Toxicology (NIPSECT), Frederiksberg, Denmark
‡‡Wadsworth Center, New York State Department of Health, and Department of Environmental Health Sciences, School of Public
  Health, State University of New York at Albany, Albany, New York, USA
§§Department of Chemistry, University of Toronto, Toronto, Ontario, Canada
‖‖RIKILT—Institute of Food Safety, Wageningen, The Netherlands

Critical Review

ABSTRACT

The primary aim of this article 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. The overarching objective is to unify and harmonize communication on PFASs by offering terminology for use by the global scientific, regulatory, and industrial communities. 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. Terminology related to fluorinated polymers is an important aspect of our classification. Second, we provide a brief description of the 2 main production processes, electrochemical fluorination and telomerization, used for introducing perfluoroalkyl moieties into organic compounds, and we specify the types of byproducts (isomers and homologues) likely to arise in these processes. Third, we show how the principal families of PFASs are interrelated as industrial, environmental, or metabolic precursors or transformation products of one another. We pay particular attention to those PFASs that have 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 subfamilies of PFASs and 268 selected individual compounds, providing recommended names and acronyms, and structural formulas, as well as Chemical Abstracts Service registry numbers. Integr Environ Assess Manag 2011;7:513–541. © 2011 SETAC

Keywords: Perfluoroalkyl Polyfluoroalkyl Terminology Acronyms PFAS

The presence of fluorinated organic compounds in food packaging material has attracted big media interest in Denmark as a result of the outcomes of the Ph.D. thesis of Dr. Xenia Trier from Copenhagen University (http://ing.dk/artikel/124245-beviserne-mod-fluorstoffer-taarner-sig-op). Dr. Trier defended her thesis in September this year. Her work is closely related to the work in Work Package 5 of the Perfood project. Martin Schlummer, leader of Work Package 5 contributes to this Newsletter with an article about migration of fluorinated organics from food packaging into food.

Pim de Voogt
University of Amsterdam
Coordinator PERFOOD

How Poly- And Perfluoroalkyl Substances (PFAS) May Enter Our Food From Food Contact Materials (FCM)

By
Martin Schlummer, Ludwig Gruber, Romy Fengler, Dominik Fiedler, Gerd Wolz

The European Perfood project focusses on the occurrence of poly- and perfluorinated alkyl substances in food as well on their sources. On the environmental route PFAS may enter the food chains along various pathways starting from environmental compartments (water, air and soil). In addition however, PFAS are present in selected food contact materials [1] and, therefore, these are considered as relevant and significant sources of PFAS in food. Food contact materials (FCM) comprise packaging items as well as materials applied for cooking, baking and other types of food preparation.

Such FCM may contain PFAS when fluorine based coatings were applied in order to equip the FCM with water or oil repellent properties. Such coatings may be made of fluoropolymers such PTFE (Teflon™) or they are built by not fluorinated polymers (acrylates, polyesters, etc.) with side groups basing on perfluorinated sulfonamide derivatives, fluorotelomer alcohols (FTOH) or fluorotelomer thiols (FTSH). In addition non polymeric fluorinated surfactants are applied in FCM, which base on phosphate esters of fluorotelomer alcohols, thiols and derivatives. A prominent examples of these fluorinated surfactants are PAPs (polyfluoroalkyl phosphate esters), which have been identified in popcorn bags, fast food wraps and other FCM [1].

Therefore, one work package of the Perfood project deals especially with the interactions of food and FCM. Initially, FCM from the European market were screened for the presence of fluorine, in order to identify those FCM, which contain intentionally added amounts of fluorine based coatings. As screening tools sliding spark spectroscopy, wave length dispersive x-ray fluorescence analysis and DART-MS were applied. More sophisticated approaches based on the deliberation of volatile fluorinated species from surface treated FCM by headspace or purge&trap sampling and detection by GC-MS or GC-EPED [2].

The FCM screening revealed that in all studied countries (D, NL, N, B, I, Gr) the majority of investigated samples was fluorine negative (Fig. 1). However, in specific product groups as butter wraps, sandwich papers, baking papers (including such to prepare muffin papers) and cardboard boxes, a significant number of samples were

fluorine positive. The highest fluorine value was obtained with P&T-GC-EPED for a butter wrap with 1888 ng fluorine per dm². [2]

In a further survey 47 of the fluorine positive samples were subjected to a specific PFAS analysis [3]. 6:2 FTOH, 8:2 FTOH and 10:2 FTOH were identified in all fluorine positive samples at levels ranging from 9 to 39500 ng/g, whereas 4:2 FTOH where only quantified in about 25% of the samples (maximum value 54 ng/g). Concentrations of perfluorinated carboxylates (PFCA) were considerably lower and ranged from LOD (<1) to 619 ng/g PFOA, LOD (<1) to 1500 ng/g PFNA, and LOD (<1) to 390 ng/g PFDA. These ranges are well comparable to previously reported levels in food contact materials. Perfluorinated sulfonic acids (PFSA) were not found in any sample at levels above 1 ng/g. This may indicate at a switch from FOSE-based coatings to FTOH containing macromolecules in industrial practice.
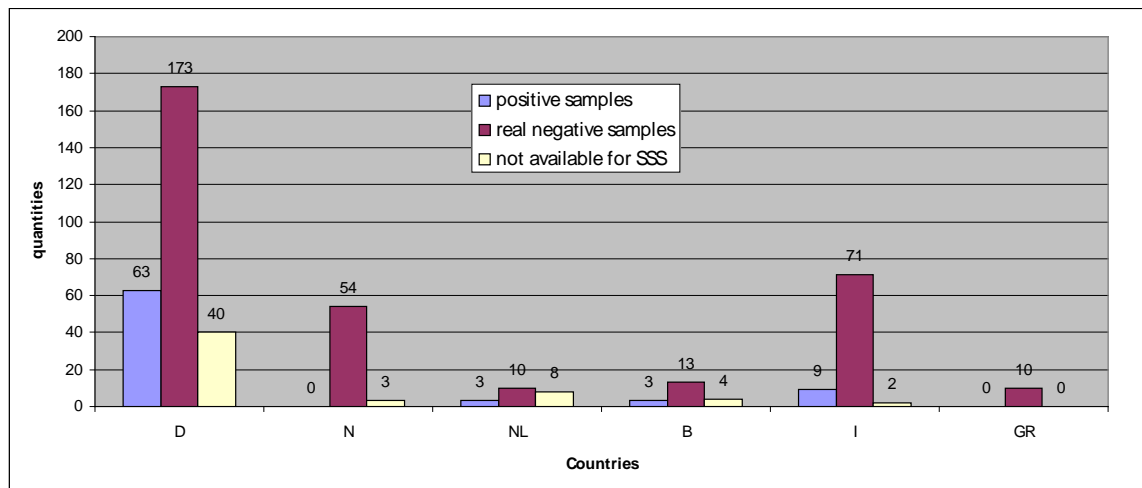

Fig.1: Quantities of fluorine positive and negative samples from 6 European countries.

Concentrations of PFAS picture the migration potential of a given PFAS from the studied FCM. For safety considerations, however, it is important to know which share of the detected PFAS migrates into food at realistic conditions. In general, migration is controlled by food contact conditions (temperature, time), FCM properties (thickness, initial concentration, and diffusion coefficient) and the interaction of FCM and compound (distribution coefficient FCM-food). Considering the FCM types with highest shares of fluorine positive samples, migration conditions vary significantly: Butter, e.g., is exposed to butter wraps at refrigerated temperatures over longer times, whereas muffins are exposed to muffin papers over 10-15 minutes at temperatures above 150°C.

Therefore, migration studies included fridge and room temperatures for packaging items, heating temperatures of 80°C for short term packaging (fast food) and oven temperatures for baking aids. Besides realistic food items as butter, sandwich, muffin, food simulants (MeOH, olive oil, Tenax™) were tested. After the food contact, all food items, simulants and FCM were analyzed for FTOH, PFCA and PFSA [4].

3

A first result of these migration studies was that classical food simulants as olive oil, isooctane or methanol are inappropriate models for food items. Olive oil and isooctane significantly underestimate "real" migration, methanol overestimates it by far. Highest but realistic migration was obtained for the food item butter. Secondly, levels of PFOA in investigated food items increased only slightly after the migration contact. This indicates at rather low migration rates. In contrast, the migration contact raised the FTOH levels in FCM exposed food. Migration 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 points to low migration rates [4].

Migration of FTOH, however, increased with increasing temperatures and durations of the migration experiments. At baking temperatures, migration values even exceeded the migration potential, i.e. the total amount present in the original packaging, by far. This is a strong evidence for 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 (compare Fig 2) [5].
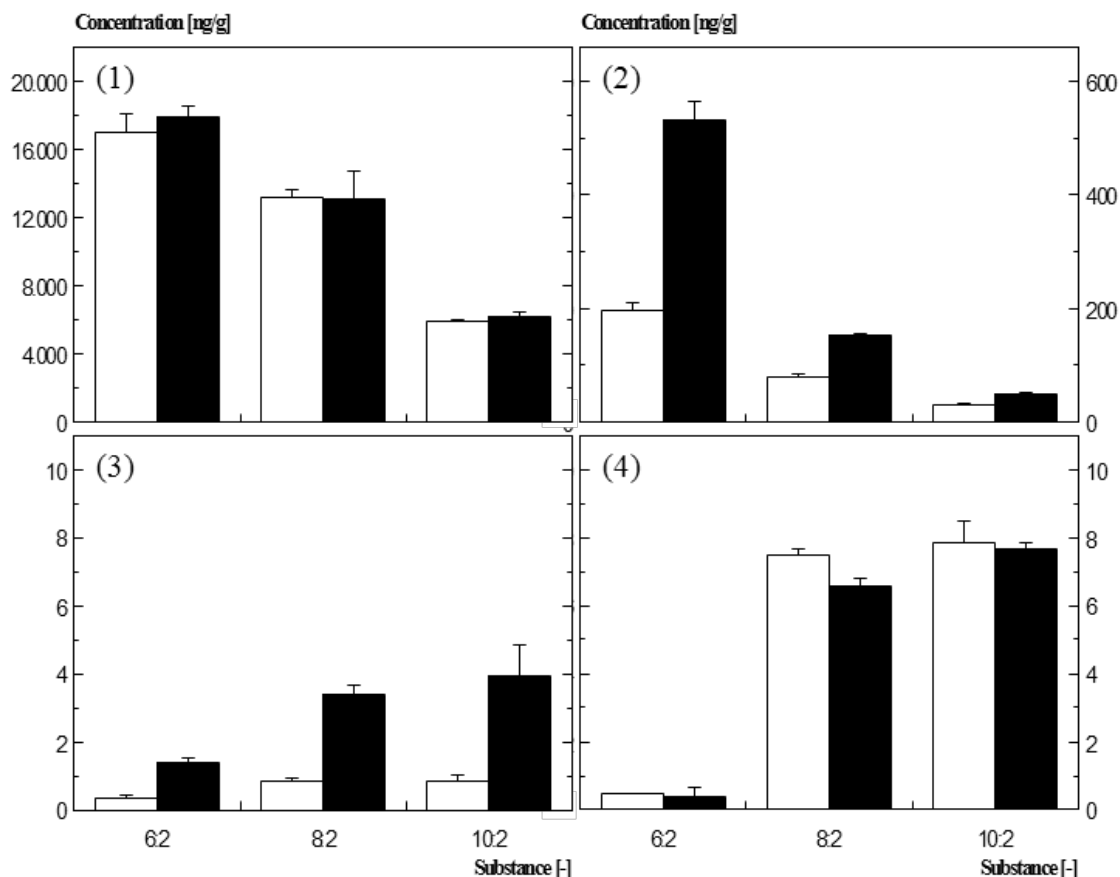
Fig 2: Investigation of a temperature-induced production of 6:2-, 8:2- and 10:2-FTOH in pure muffin paper (1), butter previously in contact with muffin paper at 120 °C for 15 min (2), pure butter 1 (3), pure butter 2(4). White bars show the not thermally treated samples, black bars the heated ones.

An independent study was conducted by Hajslova et al. [6], who prepared muffins in muffin papers with known amounts of PAPs. The authors were able to show, that mono-, di-, and tri-PAPs migrated from the FCM into the muffins. Furthermore, the amount of migrated di-PAPs exceeded the amounts of di-PAPS originally present in the muffin papers. These indicate at a net production of di-PAPS, most probably from tri-PAPs. This reaction would deliberate FTOH and would state the above described net production of FTOH during muffin preparation [5]. However, further studies are needed to understand the complex interactions of FTOH and PAPs in high temperature migration experiments [6].

The fate of FTOH and larger precursor molecules in food is not yet investigated. Once migrated into the food item FTOH may be partly volatilized upon food preparation or in the cooling phase after the baking process. In animal tests with rats large precursor molecules as PAPS have been shown to be absorbed into the gut and to be degraded into FTOH and PFOA, both in the intestine and blood [7]. Thus, even if direct migration of perfluorinated carboxylates and sulfonates from FCM may be small, the above described mechanisms may lead to an indirect FCM related human exposure, especially for perfluorinated carboxylates [8].

Acknowledgements

References

1. Begley, T. H., White, K., Honigfort, P., Twaroski, M. L., Neches, R., & Walker, R. A., Perfluorochemicals: Potential sources of and migration from food packaging. Food Additives and Contaminants 2005, 22, (10), 1023 – 1031.
2. Wolz, G., Gruber, L., Ewender, J., Fiedler, D., & Schlummer, M. (2010). Development of screening methods for fluorinated coatings of food contact materials and other everyday commodities. Organohalogen Compounds 2010, 72, 1173-1176.
3. Wolz, G., Schlummer, M., Gruber, L., Fiedler, D., Levels of perfluorinated carboxylic acids (PFCA), perfluorinated sulfonic acids (PFSA), and fluorinated telomers (FTOH) identified in paper-based food contact materials from the german market. Organohalogen Compounds 2010, 72, 1310-1313.
4. Gruber, L., Tentschert, J., Migration of poly- and perfluorinated compounds from food contact materials into food. 3rd International Workshop on Anthropogenic Perfluorinated Compounds, June 15-17, 2011, Amsterdam, The Netherlands
5. Fengler, R., Schlummer, M., Gruber, L., Fiedler, D., Weise, N., Migration of Fluorinated Telomer Alcohols (FTOH) from Food Contact Materials into Food at Elevated Temperatures. 31st International Symposium on Halogenated Persistent Organic Pollutants, August 21-25, Brussels, Belgium.
6. Hajslova J, Lacina O, Pulkrabova J, Vaclavik L., ood Contact Materials: Source of PFCs in Human Diet. 31st International Symposium on Halogenated Persistent Organic Pollutants, August 21-25, Brussels, Belgium.
7. D'eon, J. C., Mabury, S. A., Production of perfluorinated carboxylic acids (PFCAs) from the biotransformation of polyfluoroalkyl phosphate surfactants (PAPS): exploring routes of human

contamination. Environ Sci Technol 2007, 41(13), 4799–4805.

8. D'eon, J. C., Mabury, S. A., Exploring Indirect Sources of Human Exposure to Perfluoroalkyl Carboxylates (PFCAs): Evaluating Uptake, Elimination, and Biotransformation of Polyfluoroalkyl Phosphate Esters (PAPs) in the Rat. Environmental Health Perspectives 2011, 119(3), 344–350.

The production of Certified Reference Material for PFAS in fish and water

By
Jana Weiss and Ike van der Veen

Within-laboratory validation characteristics such as precision, accuracy, and robustness need to be determined. One important tool for evaluating accuracy is the use of certified reference materials (CRMs) but the availability of CRMs for many organohalogen micropollutants is limited. Some CRMs are available for classical lipophilic compounds like polychlorinated biphenyls, organochlorine pesticides and dioxins in food items such as milk powder, fish and fish oil. Recent feasibility studies evaluated the production and certification of CRMs for brominated flame retardants in fish (EU-BROC) and sterilized milk, pork, fish, fish oil and feed (EU-DIFFERENCE). These studies showed that it is possible to successfully produce matrix-type CRMs while keeping the physical state of the sample matrix intact. This is very important as the CRM should closely approximate real sample matrices. In line with these past experiences, and the lack of CRMs for PFAS, the PERFOOD consortium decided to create two CRMs. The two matrices selected were water and fish which is in line with the aim of PERFOOD (I.e. food related exposure), and as well are two sources of exposure to humans.

In December 2010 the Joint Research Centre (JRC) Institute for Reference Material and Measurements (IRMM) expressed their interest to collaborate with PERFOOD in the production line of the two CRMs. The role of IRMM is to become the responsible party for the storage and sales of the materials. Due to their expertise in the field they have been given valuable advice in the production. Representatives from IRMM, Håkan Emteborg and Jean Charoud-Got came to control and assist the fish and water RM production performed at IVM and KWR respectively.

Below is a demonstration of the work needed for a preparation of such a large sample volume and the importance to follow a well-defined protocol to ensure homogeneity and stability of the material. All equipment used during the production was thoroughly cleaned and material used for storage was tested regarding its stability after freezing/unfreezing and absorption test to material.

Fish – A total of 80 kg of frozen pike-perch fillet from the Dutch rivers Nieuwe Merwede and Amer and was delivered to IVM the 15th of November 2011 (Figure 1). The samples were homogenized one week later with the aid of a Stephan cutter of 40 L (Figure 2).

Figure. 1

Due to the large volume of sample the homogenization was done over three batches and repeatedly (4 times) equally divided into the final containers. For an equal dividing the portions were weighted. The total homogenization in the cutter was more than 2 hours before the correct particle size was reached (non-fibrous

Figure 2

particles <2mm, and fibers <5x1 mm, visually measured by isopropanol addition at IVM (Figure 3). In addition, two subsamples were taken out for particle size determination at IRMM. After particle size confirmation a total of 1249 jars was filled manually and numbered (Figure 4).
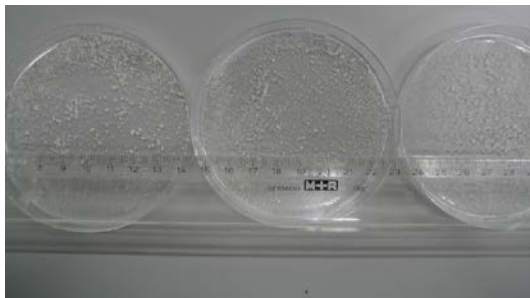

Figure 3

The jars were sterilized by autoclave (45 min, 120°C, 1.4 bar, Figure 5) and cooled to room temperature before the jars were labeled with labels provided by IRMM. The jars were transported to

Figure 4

IRMM who will store the material at room temperature and will keep jars apart for stability tests at different temperatures (Figure 6).

Figure 5

Water – The water CRM was prepared at KWR the 23rd of November 2011. A total of 650 L of drinking water was

Figure 6

collected from Nieuwegein (the tap) into a clean stainless steel barrel. The material was spiked with a PFAS

mixture due to low natural levels. The spike solution (10 ml) was added to a volumetric flask of 10 L. This flask was used 65 times and hence well rinsed. Four times during the sampling was 0.4 liter of drinking water taken out as control blank (no added spike solution). After the filling of the barrel the total bulk of 650 L was stirred for three hours. A sample of 0.4 L was taken out for PFAS analysis.

The next day the material was stirred for 1 h before the portioning of 0.4 L into plastic bottles of 0.5 L. Bottles were labeled immediately after filling, strictly following the filling sequence (labels supplied by IRMM). After the PFAS concentration was confirmed by IVM the bottles were transported to Isotron Nederland B.B for sterilization by gamma irradiation (25kGy). After sterilization all bottles were transported to IRMM to be stored at -20 °C and some bottles will be kept apart at different temperatures for stability tests.

The whole process took around one week and was very labor intensive. The IRMM partner was satisfied with the procedure and quality of the produced material. Now the homogeneity of the materials will be tested, the PFAS concentrations will be investigated in the material and the stability will be evaluated. The certification of the material is planned to be finished in December 2012. The material will be available for purchase via IRMM.