Perfood Newsletter

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Dear reader,

I am very pleased to introduce to you the first PERFOOD news letter. In this first news letter you will find short articles on the latest developments in two different fields touched by the PERFOOD consortium. The first article concerning the assessment of perfluorinated chemicals within the EU and the second one on the behavior of perfluorinated chemicals during drinking water preparation processes.

On behalf of the PERFOOD consortium,

Pim de Voogt

THE RETROSPECTIVE INTAKE ASSESSMENT OF PERFLUORINATED CHEMICALS WITHIN THE EUROPEAN UNION

by
Brambilla Gianfranco

The diverse grade of intake, accounting for the geographical origin of food (water included) and for the different food habits among Countries may determine on regional basis a qualitative/quantitative differences in the intake of PFAS.

As first step of the WP6 activities, a restrospective assessment of the dietary exposure of the general European population, To this purpose, occurrence of the contaminants of interest in food and national average food consumption data were utilized. The national databases (updated at the end of 2009) from the following Countries representing North, West, East and South Europe, respectively, were collected: Belgium, Czech Republic, Germany, Italy, Nederland, Norway, Sweden, United Kingdom, and Europe[2]. Detailed food consumption databases were harmonised mostly according to the food categories indicated by EFSA[3].

Because the available data were not directly comparable, data grouping has been harmonised (mostly according to the indication of EFSA Datex Uunit), to match the food categories and sub-categories (see Table 1), and to get more comparable food consumption data from different Countries. This basically consisted on: a) some food items were classified under a different food group from that reported in the national database (i.e. all soft drinks were included among “water” group); b) the consumption of some composite food items, reported on wet weight, was expressed on dry weight: in the case of bread and tea, this meant to subtract the contribution of water; c) the expression of the data was harmonised and referred to a daily consumption for a 60 kg bw person.

As regards occurrence data of PFAS in food, in the first phase of the

project (retrospective assessment) only PFOS and PFOA were taken into consideration as for other perfluorinated substances the data available from the scientific literature were not sufficient for a sound exposure calculation. Databases used by EFSA for its opinion[4] on PFOS and PFOA were updated and integrated as former data were referred only to “Fish and fishery products” and “Drinking and surface water” categories, data for drinking water being mainly derived from environmental freshwater samples (87 %) and tap and bottled water contribution was limited to 17 % of the samples.

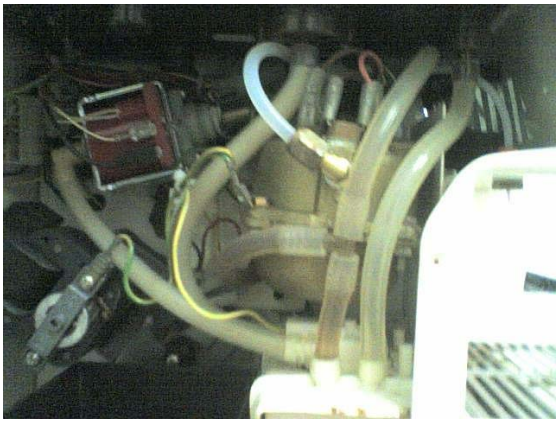
Therefore, peer-reviewed data coming from international publications and national reports on PFAS intake studies, available within the PERFOOD Consortium and referred to all food items, were added. However, because some samples of surface water were referred to sites under environmental pressure with no information about a possible water captation for drinking purposes, in our retrospective estimation we have considered only those values referred to tap water samples.

The “Fish and fishery products” occurrence data allowed a preliminary assessment about environment background differences on geo-referenced basis, that could affect the levels of contamination in wild fish, and possibly, the PFAS intakes in the different EU Countries. To this purpose, PERFOOD partners were classified into four geographical regions: Northern area (NO, SW), Central area (BE, NL), Eastern area (CZ, DE), and Southern area (IT). Such preliminary evaluation is reported in Table 2.

The retrospective assessment is summarised in Table 1 (occurrence) and Figures 1 and 2 for PFOA and PFOS intake, respectively,

Preliminary results indicate that the average intake on a deterministic basis in the selected EU countries is 22.8 and 8.18 ng/kg bw per day for PFOS and PFOA, respectively, against a PFOS TDI of 150 ng/kg bw per day and a PFOA TDI of 1500 ng/kg bw per day. This means an estimated Margin of Exposure (MOE) of 6.57 and 183, for PFOS and PFOA, respectively,

Evident regional/local differences of PFOS, PFOA levels among wild fish and seafood on geographical basis were observed (Table 2), though available data are based on few publications. These differences could be reflected in the outcomes from bio-monitoring studies[5] and will be deepened along with the increased representativeness of data.



According to the retrospective occurrence and food consumption databases, prospective studies have been targeted to: 1) a sampling carried out on the regional basis with a full description of samples, with particular attention paid to the representativeness of tap water samples[6]; 2) reduce the uncertainties related to: poor information about occurrence of PFAS in some categories of raw and processed food, accounting also for their composition; 3) reduce the analytical uncertainties derived from inadequate LOQs, with respect to the food category consumption database,

thus allowing a more consistent use of left-censored data[7]. To this purpose minimum required LOQs have been proposed for each food category accounting for their relevance in contributing to the intake assessment with respect to the TDI values provided for PFOS and PFOA; 4) sampling and analysis of cauldrons of known composition to assess the contribution from packaging and processing system with respect to the background levels present in raw foods; 5) correlation between intake studies and biomonitoring evidences on pharmaco-toxicokinetics basis to evaluate the contribution of the diet to the aggregate exposure and the possible relevance of sources other than food (indoor dust, carpeting and clothing).

Food categories	PFOS					PFOA				
	N	LD (%)	mean	sd	range	N	LD (%)	mean	sd	range
01. Cereals & cereal products	9	78%	0.183	0.239	0.0017-*0.5* [a]	9	67%	0.246	0.221	0.005-*0.5*
02. Sweet products and substitutes	27	96%	0.021	0.096	*0.002-0.5*	25	96%	0.025	0.099	0.0014-*0.5*
03. Vegetables and pulses, fresh and processed	39	49%	0.556	1.64	0.00017-10	40	48%	0.589	0.860	0.0018-4.1
04. Potatoes, starchy roots and their products	11	55%	4.64	9.58	0.001-28	12	42%	0.698	0.768	0.0053-2.2
05. Fruit, fresh and processed	13	62%	0.150	0.251	*0.0085* -0.7	13	54%	0.390	0.445	*0.018* -1.6
06. Meat, meat products and substitutes	58	40%	0.973	1.45	*0.000745* -5.36	56	63%	0.753	1.99	*0.001* -11.4
07. Fish, seafood and their products	221	18%	12.7	27.8	0.013-230	144	58%	0.692	1.98	0.002-15
08. Eggs	16	44%	3.50	7.09	*0.01* -22	14	50%	0.867	1.34	*0.016* -5.0
09. Milk and dairy products	25	56%	0.351	1.02	0.0023-*5.0*	24	54%	0.062	0.139	*0.0005-0.5*
10. Fats (vegetable and animal)	4	100%	*0.142*	0.240	*0.015-0.5*	4	100%	*0.171*	0.225	*0.0015-0.5*
11. Miscellaneous	1	100%	*0.500*	—	—	1	100%	*0.500*	—	—
12. Water (ng/L)	26	58%	1.72	1.96	0.071-8.1	27	52%	1.75	1.59	0.400-6.8
13. Coffee, tea, infusions (ng/L)	1	100%	*<0.03*	—	—	1	0%	9.50	—	—
14. Alcoholic beverages	4	75%	*5.85*	4.87	*0.65-10*	4	75%	*19.2*	34.0	*0.4* -70

Table 1. PERFOOD statistical descriptors of PFOS and PFOA occurrence (ng/g whole weight) in EU food items based on samples obtained from 2001 onward. In italics the medium bound values ("0.5 × LD") derived from limits of determination.

Statistical descriptors	PFOS				PFOA			
	Central EU	East EU	North EU	South EU	Central EU	East EU	North EU	South EU
mean value	13.7	42.8	0.925	1.14	1.22	0.135	0.040	0.551
min	0.039	12.0	0.013	0.025	0.002	—	0.024	0.014
max	230	136	2.80	13.0	8.00	—	0.051	15.0

Table 2. PERFOOD statistical descriptors of PFOS and PFOA levels (ng/g whole weight) in EU fish and seafood grouped in the four EU macroareas.

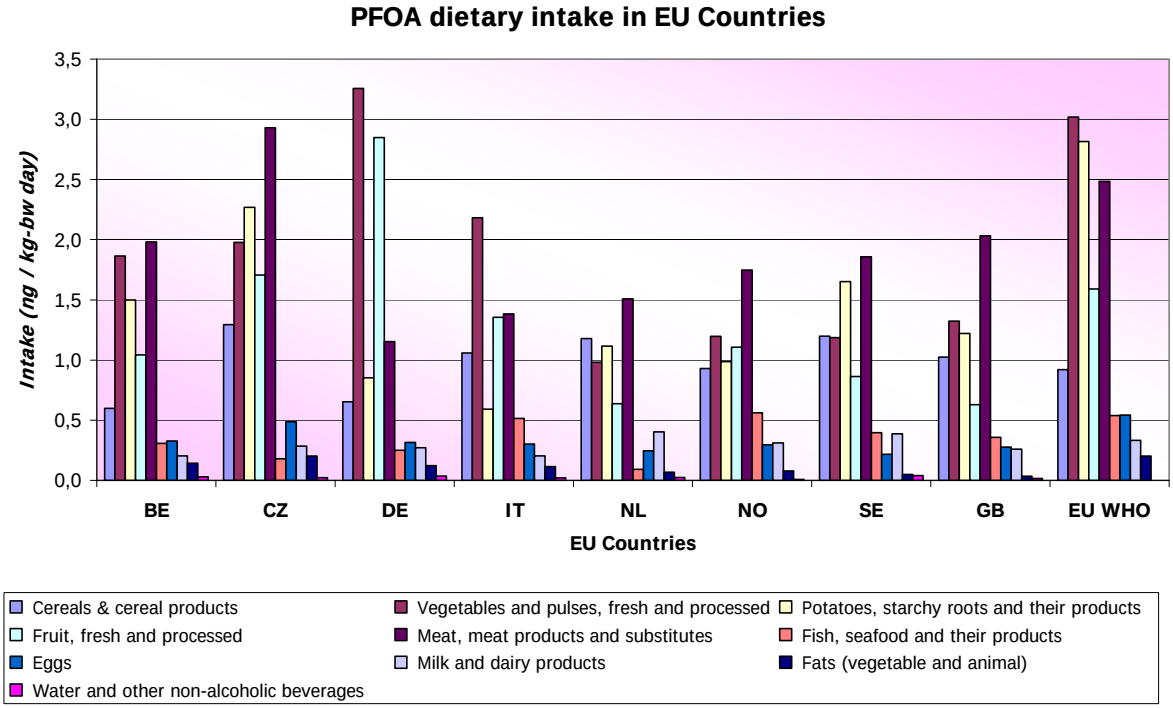


Figure 1. PFOA preliminary dietary intake in European countries. The contributions of the food categories "Sweet products and substitutes" and "Fats (vegetable and animal)", less than 0.5 %, are not reported. Among the EU average data, the consumption of "Water and non-alcoholic beverages" is missing.

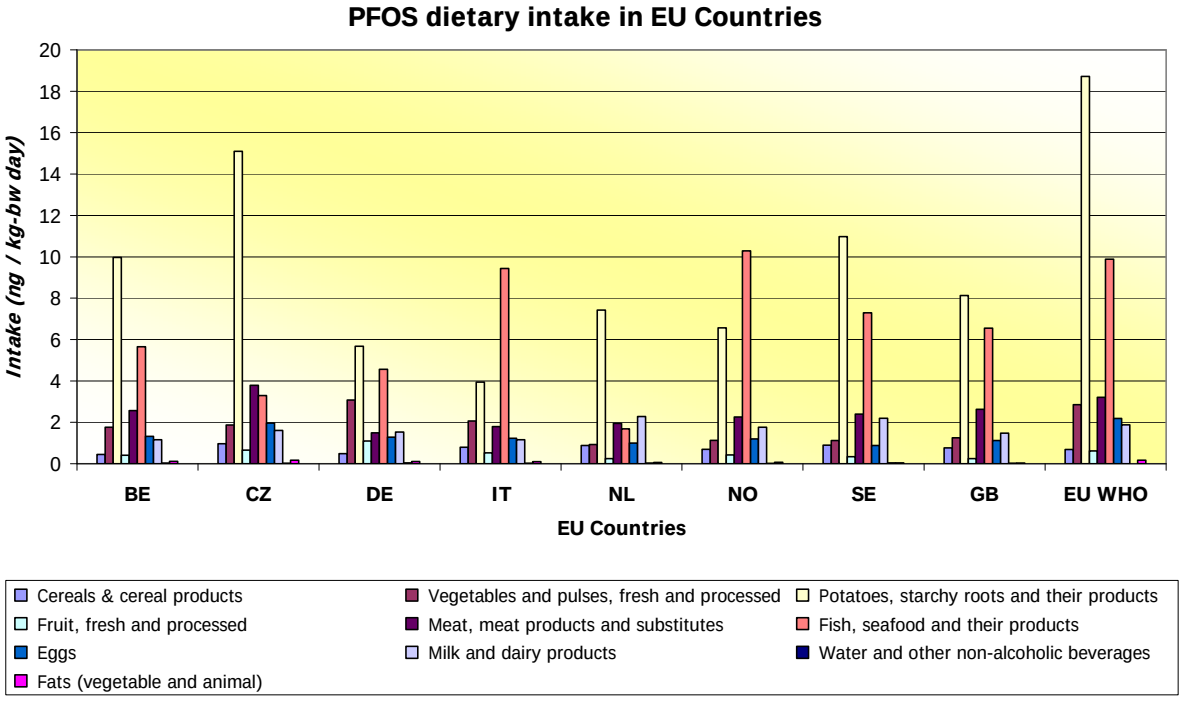


Figure 2. PFOS preliminary dietary intake in European countries. The contributions of the food categories "Sweet products and substitutes" and "Fats (vegetable and animal)", less than 0.5 %, are not reported. Among the EU average data, the consumption of "Water and non-alcoholic beverages" is missing

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References:

1. EU COMMISSION RECOMMENDATION of 17 March 2010 on the monitoring of perfluoroalkylated substances in food.
2. WHO (2003). GEMS/FOOD Regional Diets. Regional per capita consumption of raw and semi-processed agricultural commode-ties.
3. EFSA (European Food Safety Authority) 2009. "EFSA Concise European Food Consumption Database"; General principles for the collection of national food consumption data in the view of a pan-European dietary survey. *The EFSA Journal* 2009; 7:1435.
4. EFSA (European Food Safety Authority) 2008. Opinion of the Scientific Panel on Contaminants in the Food chain on Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and their salts, *The EFSA Journal* 2008; 653:1.
5. De Felip et al., *Chemosphere*, accepted.
6. EFSA (European Food Safety Authority) 2010. Standard sample description for food and feed. *The EFSA Journal* 2010; 8:1457.
7. EFSA (European Food Safety Authority) 2010. Management of left-censored data in dietary exposure assessment of chemical substances. *The EFSA Journal* 2010; 8:1557.

OCCURRENCE AND BEHAVIOR OF PFASS IN THE DRINKING WATER PRODUCTION CHAIN

by
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The behavior of polyfluoralkyl substances (PFASs) in the water cycle from raw source water to finished drinking water was assessed by taking samples from influents and effluents of the several treatment steps used in a drinking water production chain. Special interest was taken in the behavior of PFASs in the dune infiltration treatment step.

Perfluoroalkyl substances have been detected in drinking water at concentrations typically in the low ng/L range, with occasionally higher concentrations (lower µg/L level) in some contaminated areas. 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 [1], information is needed about their presence in drinking water and their removal during treatment processes.

The relationship between PFASs in source water and drinking water was shown in several studies by sampling both the influent of the treatment and the produced finished drinking water. A positive correlation between the two concentrations has been observed, with levels detected in the raw water sometimes identical to that in the produced drinking water. It is important to understand the role of individual treatment step in the removal of PFASs in the treatment process in order to assess the problem of PFASs contamination [2].

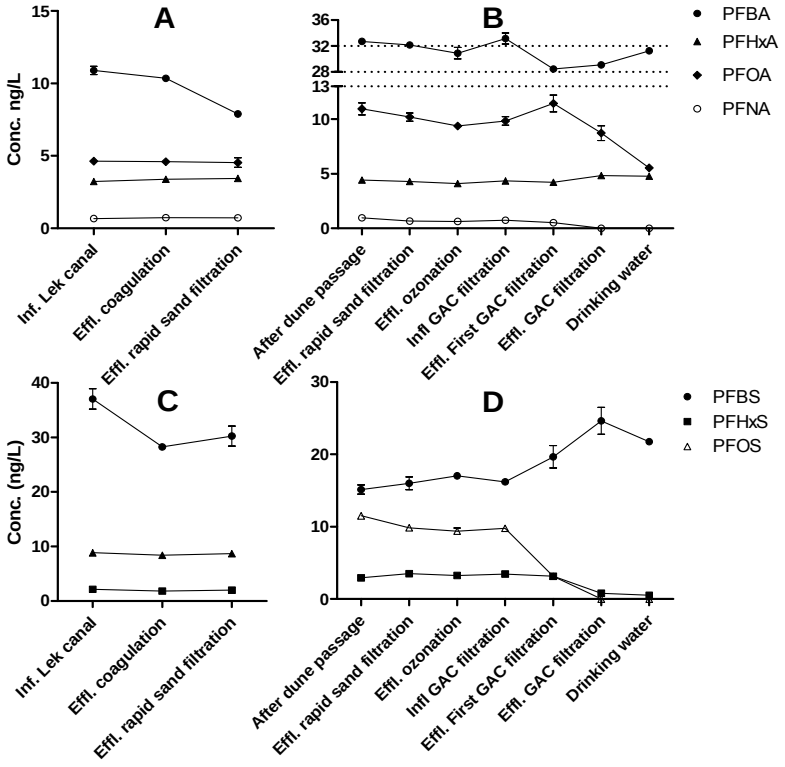
Recent studies in one of the biggest drinking water production plants in the Netherlands have contributed significantly to the understanding of the behavior of perfluorinated compounds at the process scale. The different treatment steps consisted of intake, coagulation, rapid sand filtration, dune passage, aeration, rapid sand filtration, ozonation, pellet softening, granular activated carbon (GAC) filtration, slow sand filtration and finished water. Part of the samples was taken taking hydrological retention times into account [3].

In the source water, taken in at the Lek canal (a confluent of the Rhine), the most abundant PFAS were PFBA (Pefluorobutanoic acid) 52 ng/L, PFBS (Perfluorobutane Sulfonate) 42 ng/L, PFOS (perfluorooctane sulfonate) 10 ng/L and PFOA (perfluorooctanoic acid) 5.1 ng/L. Coagulation and rapid sand filtration did not remove PFASs, although a decreasing trend was observed for PFBA and PFBS (**Error! Reference source not found.**).

After pretreatment (coagulation and rapid sand filtration) the water was filtered by infiltration in the dune area. The evolvement of PFC concentrations in Rhine water and rain water during dune water infiltration processes over a transect in the dune area showed interesting patterns: Concentrations of PFBS were found up to 37 ng/L in infiltrated river water. The concentrations of PFBS found in infiltrated river Rhine water were significantly higher than in infiltrated rain water. For PFHxS the opposite was found: infiltrated rain water contained more than infiltrated river water. The concentrations of PFOA, PFHxA, PFHpA, PFBS, PFOS and PFHxS in infiltrated river water showed an increasing trend with decreasing age of the water [4].

During post treatment aeration, rapid sand filtration, ozonation and pellet softening did not remove PFAS (Figure 1). However, longer chained PFAS such as PFNA and PFOS were readily removed by the GAC treatment step and their GAC effluent concentrations were <LOQ. More polar shorter chain PFAS (especially PFBA and PFBS) were not removed by GAC and their concentrations remained constant through treatment. A decreasing removal capacity was observed with increasing carbon life time. The finished water contained 26 and 19 ng/L of PFBA and PFBS. Other PFAS were present in concentrations below 4.2 ng/L. The concentrations observed are no reason for concern for human health whatsoever as margins to existing guidelines are sufficiently large.

Figure 1 . Concentrations of perfluoroalkyl carboxylic acids and perfluoroalkane sulfonic acids (ng/L) (sampled in September 2010) during water pre-treatment in Nieuwegein (A and C), and during water post-dune infiltration treatment at Leiduin (B and D). The figure is based on a virtual body of water followed along its pathway though the plant, taking into account hydrologic retention times (HRT) (except for drinking water as it is taken from a large reservoir), error bars represent the standard deviation of the duplicate analysis.



References:

1. Vestergren, R.; Cousins, I. T., Tracking the Pathways of Human Exposure to Perfluorocarboxylates. *Environmental Science & Technology* 2009, *43*, (15), 5565-5575.
2. Eschauzier, C.; Voogt, d. P.; Brauch, H. J.; Lange, F. T., *Review: Polyfluorinated alkylated substances (PFAS) in the European drinking water environment: from raw water to tap water*. Submitted to The Handbook of Environmental Chemistry: Fluorinated Surfactants and Transformation Products.
3. Eschauzier, C.; Beerendonk, E.; Scholte-Veenendal, P.; Voogt, d. P., Impact of treatment processes on the occurrence of perfluoroalkyl acids in the drinking water production chain. *Submitted to ES&T*.
4. Eschauzier, C.; Haftka, J.; Stuyfzand, P. J.; De Voogt, P., Perfluorinated compounds in infiltrated river rhine water and infiltrated rainwater in coastal dunes. *Environmental Science and Technology* 2010, *44*, (19), 7450-7455.

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