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PFAAs in matched milk and serum from *primipara* women

Summary

The aim of the study was to assess the association between serum and milk levels of perfluoroalkyl acids (PFAAs) in humans. Individual milk and serum samples from fifty (50) *primipara* women in Uppsala, Sweden, were collected in 2004, 2007, 2009, and 2011. PFAAs were analysed in milk and serum using in-house validated methods and quality control protocols. PFOS, PFOA and PFHxS were detected in 98-100% of the milk and serum samples in the concentration order PFOS>PFHxS>PFOA. PFBuS, PFHpA, and PFDA were detected in 12-64% of the milk and serum samples. PFNA and PFUnDA were detected at high frequency but low levels in serum and were consequently less frequently detected in milk. PFOS and PFHxS showed a stronger correlation between serum and milk levels compared to PFOA. The regression slope with 95% confidence interval was calculated to assess the association between serum and milk levels. The level of PFOS in milk is 1.4 ± 0.25% of the corresponding maternal serum level. For PFHxS the interval is 1.4 ± 0.33% and for PFOA 2.6 ± 1.1%. The temporal trends (2004-2011) observed are similar in serum and milk.

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Prepared by
Anna Kärrman, PhD
Jenna Davies, MSc
Samira Salihovic, PhLic.

MTM Research Centre
School of Science and Technology
Örebro University
701 82 Örebro, Sweden

Samples were provided by Sanna Lignell and Marie Aune at the National Food Agency, Uppsala, Sweden.

Contact:
Email: anna.karrman(at)oru.se
Phone: +4619301401

Materials and methods

Samples (50 serum and 50 milk) were collected in Uppsala, Sweden in 2004, 2007, 2009, and 2011 by The National Food Agency. All samples were from *primipara* women and were collected in glass bottles during the third week after delivery and stored in plastic containers at –20°C.

Names and abbreviations of all PFAAs are listed in Annex A. The milk samples were extracted using weak anion exchange, solid-phase extraction (Waters Oasis® WAX, Waters Corporation, Milford, USA) using a previously reported method (Kärrman et al. 2007). Internal standards ($^{18}O_2$PFHxS, $^{13}C_4$PFOS, $^{13}C_4$PFBA, $^{13}C_2$PFHxA, $^{13}C_4$PFOA, $^{13}C_5$PFNA, $^{13}C_2$PFDA, $^{13}C_2$PFUnDA, $^{13}C_2$PFDoA, Wellington Laboratories, Guelph, Canada) and 2 mL formic acid/water (1:1) were added to 1 mL milk. The solution was sonicated for 30 minutes and centrifuged at 9000 x g for 30 minutes. The supernatant was extracted on Oasis WAX and PFAAs were eluted with 2 mL 2% ammonium hydroxide in methanol, after washing the column with 2 mL sodium acetate buffer solution (pH 4) and 2 mL 40% methanol in water. Performance standards, $^{13}C_3$PFBA, $^{13}C_8$PFOA, $^{13}C_9$PFNA, $^{13}C_6$PFDA, $^{13}C_7$PFUnDA, $^{13}C_3$PFHxS, $^{13}C_8$PFOS (Wellington Laboratories, Guelph, Canada), and *7H*-PFHpA (ABCR, Karlsruhe, Germany) were added. After evaporation the final extract volume was 20 µL, then 30 µL 2mM ammonium acetate in water was also added. Milk extracts were injected (10 µL) on an Acquity UPLC Xevo TQ-S tandem mass spectrometer (Waters Corporation, Milford, USA) with an atmospheric electrospray interface operating in negative ion mode. The analytes were separated on an Acquity BEH C18 column (2.1 x 100 mm, 1.7 µm).

Serum samples were extracted using Ostro Sample Preparation 96-well plates, 25mg (Waters Corporation, Milford, USA). Serum (150 µL), 1% formic acid in acetonitrile (450 µL) and internal standards ($^{18}O_2$PFHxS, $^{13}C_4$PFOS, $^{13}C_4$PFBA, $^{13}C_2$PFHxA, $^{13}C_4$PFOA, $^{13}C_5$PFNA, $^{13}C_2$PFDA, $^{13}C_2$PFUnDA, $^{13}C_2$PFDoA, Wellington laboratories, Guelph, Canada) were mixed in the wells before filtration (Salihovic et al. 2012). The sample extract was then transferred to vials containing performance standards, $^{13}C_3$PFBA, $^{13}C_8$PFOA, $^{13}C_9$PFNA, $^{13}C_6$PFDA, $^{13}C_7$PFUnDA, $^{13}C_3$PFHxS, $^{13}C_8$PFOS (Wellington laboratories, Guelph, Canada), and *7H*-PFHpA (ABCR, Karlsruhe, Germany) and evaporated down to 250 µL using nitrogen. Finally, 750 µL 0.1 M formic acid in water was used to dilute the sample prior to the instrumental analysis. Serum analyses were performed on a Acquity UPLC Quattro Premier XE tandem mass spectrometer (Waters Corporation, Milford, USA) system by injecting 250 µL onto a C18 (2.1 ×20 mm, 2.5 µm) trap column connected to a C18 (2.1 ×100 mm, 7 µm) analytical column by a 6-port column switch valve. Analytes were analyzed on a MS/MS system run in electrospray ionization mode (ESI).

Quantification and quality assurance

Multiple reaction monitoring (MRM) was used and two product ions were monitored for each compound, when possible (Annex A). Milk samples were quantified using solvent calibration curves and isotope dilution, while serum samples were quantified using matrix-matched calibration curves; using calf serum and internal standards. A minimum of five-point calibration curve was used. The internal standard closest in retention time was used for those compounds that did not have a corresponding labeled internal standard (PFBS, PFDS, PFPeA, PFHpA). The ratio between the two product ions in the samples were calculated and compared to an authentic standard, and did not exceed 50%. The performance standard was used to assess the recovery of the internal standard. Recoveries of internal standards for milk and serum analysis are presented in Table 3. For acceptable recovery a limit of 50-120% was set. However for milk analysis using solvent standards, lower recoveries were obtained for the more hydrophobic compounds. Recoveries between 20 and 50% were decided to be reported as reliable since authentic internal standards were used for quantification; those results are however marked in the result tables. Samples with recoveries below 20% were not reported and are denoted as not quantified (NQ) in the result tables.

Procedural blanks were included in each extraction batch and treated the same way as the samples. Limit of detection (LOD) was calculated as mean concentration in blank samples with addition of three times the standard deviation. Quality control samples were included in each batch to assess reproducibility and accuracy. For milk analysis an interlaboratory study sample was used (Kärrman and Lindström 2013) and for serum the SRM 1957 from the National Institute of Standards and Technology (NIST) at the US Department of Commerce (Washington, USA) was used. Further quality control was the successful participation in the 2009/2010 interlaboratory studies on milk (Kärrman and Lindström 2013) and serum (Lindström et al. 2009) which both resulted in Z-scores <|2|.

Results

Table 1 presents the detection rate and concentration ranges of the individual PFAAs in serum and milk samples. Detailed presentation of the levels is found in Annex B. Levels of PFAAs are in the range of other studies reported (Thomsen et al. 2010, Glynn et al. 2012). PFOS, PFOA and PFHxS were detected in all milk and serum samples (except for PFOA in one milk sample) and at the highest levels PFOS>PFHxS>PFOA. PFBuS, PFHpA, and PFDA were detected in 12-64% of the milk and serum samples. PFUnDA was detected at low levels in 78% of the serum samples but in 0% of the milk samples. A similar situation was found for PFNA. The explanation for the non-detects in milk is likely the low transfer potential to milk in combination with low levels in serum which in the case of low serum levels results in difficulties to measure milk levels. Detection limits in the present studies were low and ranged in the area of single to double digit ppt (parts per trillion).

Linear regression was used to assess the relationship between PFOS, PFHxS and PFOA between milk and serum. The linear isomer of PFOS was chromatographically separated and used here to assess the relationship. Figures 1-3 illustrates the regression and the statistics are presented in Table 2. Based on the 95% confidence interval of the slope (average) the level of PFOS in milk is 1.1% - 1.6% (1.4%) of the corresponding maternal serum level. For PFHxS the interval is 1.1 - 1.7% (1.4%) and for PFOA 1.5 - 3.8% (2.6%). Hence, there is no statistical difference between the three PFAAs' transfer potential in this study, although PFOA has the highest average transfer. PFOA also showed a weaker correlation between serum and milk levels compared to PFOS and

PFHxS. Pearson's correlation coefficient was calculated as 0.9171 for PFOS, 0.7811 for PFHxS, and 0.5513 for PFOA. The results are in accordance with other reports. PFOS has been reported having a serum to milk relationship of 1.09% (Kim et al. 2011), and 1.4% (Thomsen et al. 2010). The same studies reported PFOA to 2.5% and 3.8%, respectively.

The matched serum and milk pairs were collected in different years between 2004 and 2011. Figures 4-9 illustrates the levels of PFOS, PFHxS, and PFOA in milk and serum divided into the different collection years. The temporal trends are similar in serum and milk; there is an clear decreasing trend for PFOS, a decreasing trend for PFOA that might however level off, and an increasing trend of PFHxS for the last years. The results here are confirmative of the time trend in pooled serum samples from Uppsala women presented by Glynn et al. (2012).

Also included in this report is the quality assurance taken in this study. Recoveries, precision and accuracy are demonstrated in Tables 3-5. Good recoveries were obtained for most compounds (Table 3). PFHxA averaged just under the set criteria of 50% in the milk analysis and was reported but marked for most of the milk samples. All samples were however under LOD. The most hydrophobic compounds (PFDoDA, PFTrDA, PFTDA) were difficult to analyze in the milk matrix and were therefore not reported. Based on the serum levels they are however not likely to be found in human milk. Good precision and accuracy was demonstrated for both methods. The serum samples were all run in one batch and precision is therefore given as repeatability (Table 4).

Table 1. Overview of PFAA[a] concentrations (ng/mL) in serum and milk collected 2004-2011.

SERUM	**PFBuS**	**PFHpA**	**PFHxS**	**L-PFOS**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTrDA**
Min	0.030	0.030	0.670	1.32	0.810	0.200	0.390	0.200	0.040	0.030
Max	0.170	0.250	22.1	20.2	4.54	1.67	1.01	0.850	0.080	0.190
Average	0.090	0.060	4.60	5.90	2.08	0.510	0.520	0.330	0.060	0.090
Median	0.070	0.050	3.76	5.27	1.90	0.460	0.460	0.300	0.060	0.080
% detection	20%	64%	100%	100%	100%	100%	20%	78%	8%	10%
MILK	**PFBuS**	**PFHpA**	**PFHxS**	**L-PFOS**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTrDA**
Min	0.014	0.015	0.013	0.024	0.060	0.028	0.021	<0.032	<0.007	<0.008
Max	0.392	0.020	0.451	0.354	0.220	0.079	0.097			
Average	0.138	0.017	0.073	0.094	0.119	0.038	0.046			
Median	0.028	0.017	0.055	0.085	0.106	0.035	0.038			
% detection	18%	12%	100%	100%	98%	30%	22%	0%	0% [b]	0%[b]

[a] Following compounds were detected in 0% of serum and milk samples: PFPeA (<0.001 in serum, <0.032 in milk), PFHxA (<0.03 in serum, <0.012 in milk), PFDS (<0.04 in serum, <0.009 in milk), PFTDA (<0.03 in serum, <0.031 in milk).

[b] Were analyzed in only 10% of the samples.

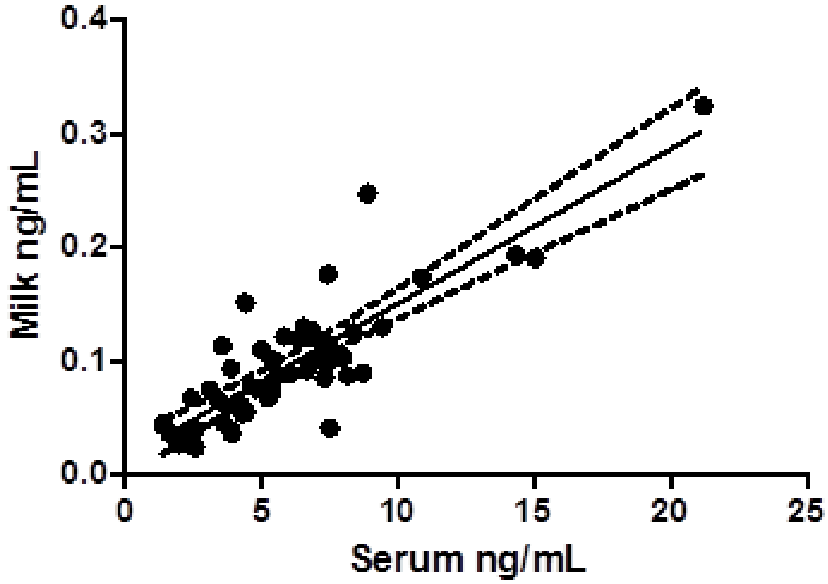

Figure 1. Linear regression of PFOS concentrations (ng/mL) in matched pairs (n=50) of milk and serum collected 2004-2011.

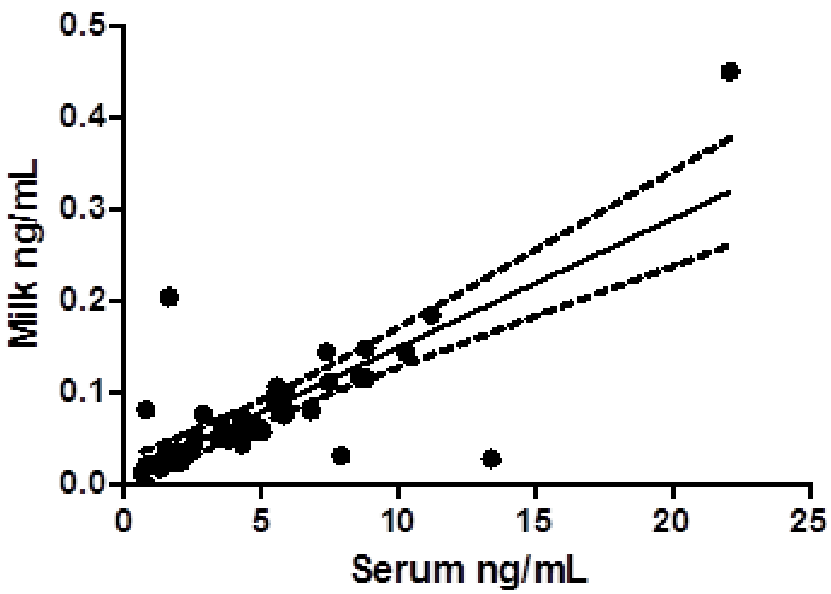

Figure 2. Linear regression of PFHxS concentrations (ng/mL) in matched pairs (n=50) of milk and serum collected 2004-2011.

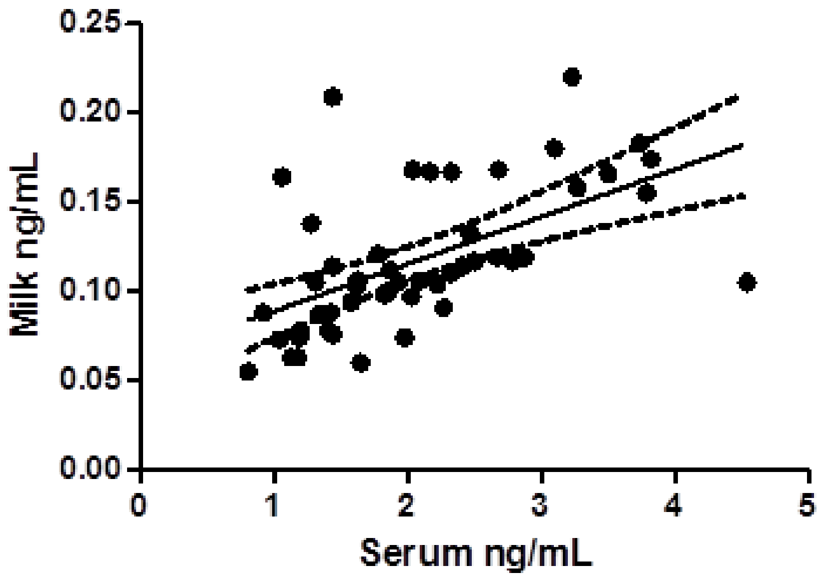

Figure 3. Linear regression of PFOA concentrations (ng/mL) in matched pairs (n=50) of milk and serum collected 2004-2011.

Table 2. Linear regression statistics of three PFAAs in matched pairs (n=50) serum and milk collected 2004-2011.

	PFHxS	L-PFOS	PFOA
Slope	0.01407	0.01363	0.02648
95% CI	0.01081 - 0.01734	0.01114 - 0.01612	0.01544 - 0.03753
R^2	0.6103	0.7168	0.3266

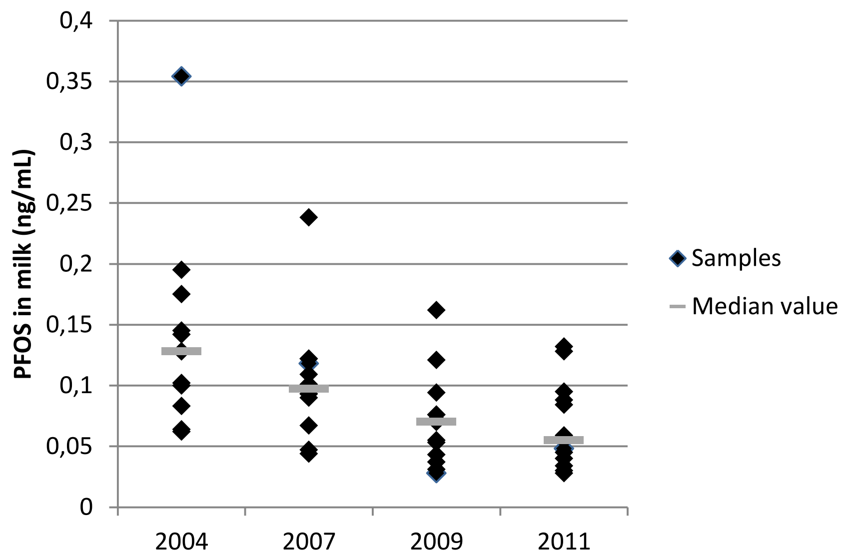

Figure 4. Concentrations of PFOS in individual milk samples (ng/mL) spanning different years.

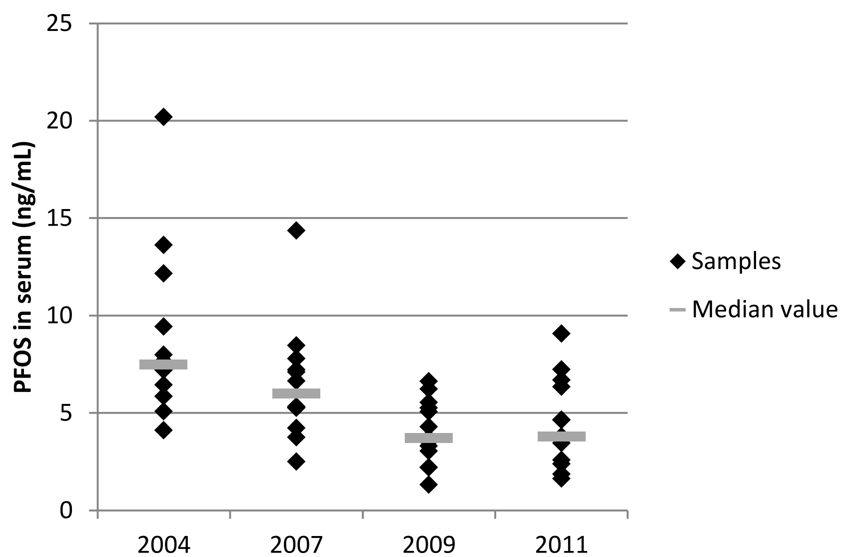

Figure 5. Concentrations of PFOS in individual serum samples (ng/mL) spanning different years.

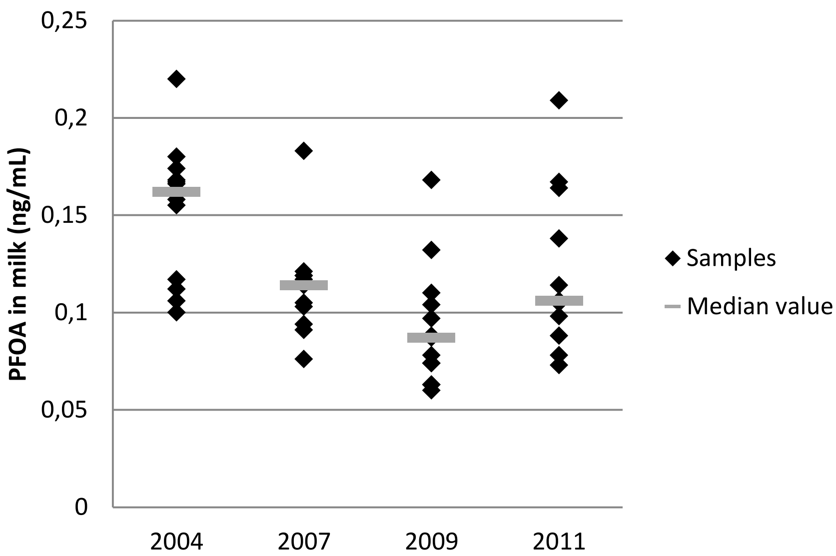

Figure 6. Concentrations of PFOA in individual milk samples (ng/mL) spanning different years.

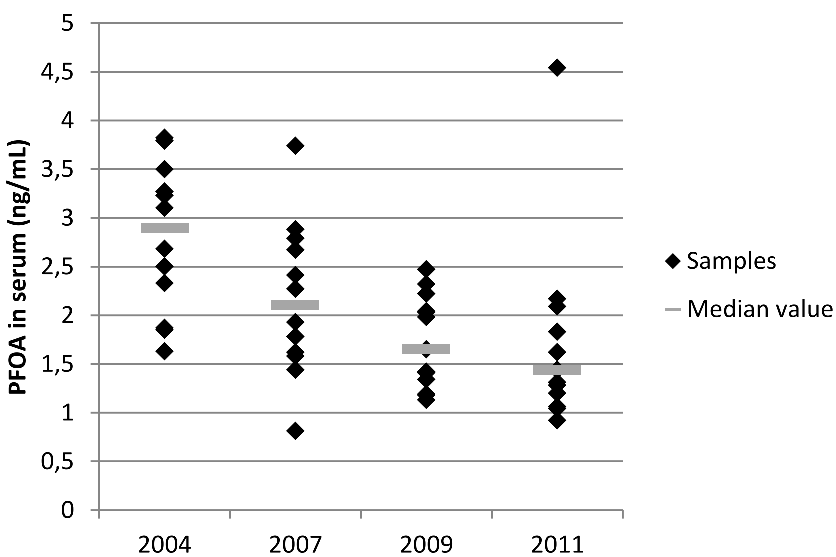

Figure 7. Concentrations of PFOA in individual serum samples (ng/mL) spanning different years.

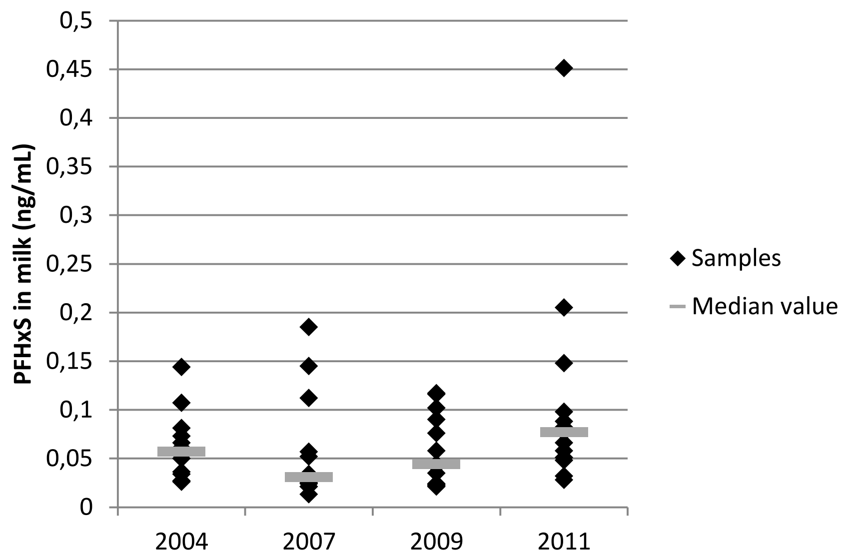

Figure 8. Concentrations of PFHxS in individual milk samples (ng/mL) spanning different years.

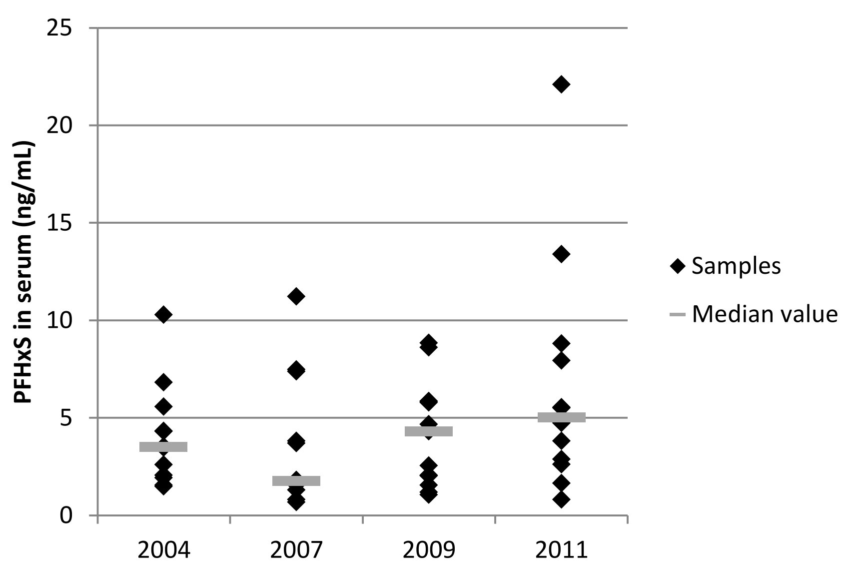

Figure 9. Concentrations of PFHxS in individual serum samples (ng/mL) spanning different years.

Table 3. Internal standard recoveries in serum (n=50) and milk (n=50) samples. All samples are presented here however samples with <20% are removed from the result tables (NQ), and samples with recoveries 20-50% are marked.

SERUM	**C^{13}PFHxA**	**O^{18}PFHxS**	**C^{13}PFOS**	**C^{13}PFOA**	**C^{13}PFNA**	**C^{13}PFDA**	**C^{13}PFUnDA**	**C^{13}PFDoDA**
Average	80.7	102	102	102	98.6	101	91.8	64.5
MILK	**C^{13}PFHxA**	**O^{18}PFHxS**	**C^{13}PFOS**	**C^{13}PFOA**	**C^{13}PFNA**	**C^{13}PFDA**	**C^{13}PFUnDA**	**C^{13}PFDoDA**
Average	43.9	87.7	77.5	82.0	72.7	22.8	52.7	16.2

Table 4. Accuracy and repeatability of serum PFAA analysis (ng/mL) by analyzing a reference serum sample[1)].

Sample ID	**PFPeA**	**PFBuS**	**PFHxA**	**PFHpA**	**PFHxS**	**L-PFOS**	**PFDS**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTrDA**	**PFTDA**
SRM1957 (1:1)	< 0.010	< 0.004	< 0.030	0.240	2.87	9.67	< 0.040	3.42	0.630	0.210	0.150	< 0.020	< 0.020	< 0.030
SRM1957 (1:2)	< 0.010	< 0.004	< 0.030	0.240	2.89	9.79	< 0.040	3.42	0.650	0.210	0.190	< 0.020	< 0.020	< 0.030
SRM1957 (1:3)	< 0.010	< 0.004	< 0.030	0.240	2.88	9.55	< 0.040	3.40	0.620	0.200	0.120	< 0.020	< 0.020	< 0.030
SRM1957 (1:4)	< 0.010	< 0.004	< 0.030	0.230	2.86	9.66	< 0.040	3.40	0.630	0.210	0.170	< 0.020	< 0.020	< 0.030
Average	--	--	--	0.240	2.88	9.67	--	3.41	0.630	0.210	0.160	--	--	--
SD	--	--	--	0.0	0.0	0.1	--	0.0	0.0	0.0	0.0	--	--	--
%RSD	--	--	--	2.9	0.4	1.0	--	0.3	1.7	1.9	14.8	--	--	--
Reference value[1)]	--	--	--	0.31	--	10.6[2)]	--	5.00	0.88	0.39	0.17	--	--	--

[1)] NIST, National institute of standards and technology. U.S. Department of Commerce
[2)] Riddell et al., 2009

Table 5. Accuracy and reproducibility of milk PFAA analysis (ng/mL) by analyzing a reference milk sample[1)] on six different days.

Sample ID	**PFPeA**	**PFBuS**	**PFHxA**	**PFHpA**	**PFHxS**	**L-PFOS**	**PFDS**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTrDA**
130111	<0.032	<0.435	<0.012	<0.015	0.088	0.097	<0.009	0.140	<0.028	<0.019	<0.007	<0.008	<0.031
130115	<0.032	<0.327	<0.012	<0.015	0.088	0.092	<0.009	0.143	<0.028	<0.019	<0.007	<0.008	<0.031
130118	<0.032	<0.209	<0.012	0.018	0.091	0.089	<0.009	0.158	0.034	<0.019	NQ	NQ	NQ
130121	<0.032	<0.021	<0.012	<0.015	0.097	0.087	<0.009	0.164	<0.028	<0.019	NQ	NQ	NQ
130123	<0.032	<0.012	<0.012	<0.015	0.091	0.090	<0.009	0.158	<0.028	<0.019	NQ	NQ	NQ
130103	<0.032	NA	<0.012	<0.015	0.074	0.083	<0.009	0.120	<0.028	<0.019	<0.007	<0.008	<0.031
Average	--	--	--	--	0.088	0.090	--	0.147	--	--	--	--	--
Min	--	--	--	--	0.074	0.083	--	0.120	--	--	--	--	--
Max	--	--	--	--	0.097	0.097	--	0.164	--	--	--	--	--
Std Dev	--	--	--	--	7.5	4.2	--	16.3	--	--	--	--	--
RSD (%)	--	--	--	--	8.5	4.7	--	11.1	--	--	--	--	--
Reference value[2)]	--	--	--	8	0.080	0.103[3)]	NA	0.166	0.068	--	--	--	--

[1)] 2009 worldwide proficiency testing sample "milk S".
[2)] Kärrman and Lindström, 2013. Values are compared here if more than 5 laboratories contributed to the consensus value in the proficiency testing.
[3)] Reported as "PFOS"

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APPENDIX A

Name, abbreviation and multiple reaction monitoring (MRM) transitions for UPLC/MS/MS analysis of PFAAs. The quantification trace is indicated in bold.

Name	Abbreviation	MRM Transition
Perfluorobutane sulfonic acid	PFBS	299.2 > 79.8 **299.2 > 98.85**
Perfluorohexane sulfonic acid	PFHxS	399.1 > 79.85 **399.1 > 98.9** 399.1 > 168.8
n-Perfluorooctane sulfonic acid	L-PFOS	498.9 > 79.85 **498.9 > 98.85** 498.9 > 129.9
Perfluorodecane sulfonic acid	PFDS	599.0 > 79.7 **599.0 > 98.7**
Perfluoropentanoic acid	PFPeA	**263.2 > 218.9**
Perfluorohexanoic acid	PFHxA	313.25 > 119.0 **313.25 > 269.25**
Perfluoroheptanoic acid	PFHpA	363.18 > 168.8 **363.18 > 319.0**
Perfluorooctanoic acid	PFOA	413.1 > 169.1 **413.1 > 369.2**
Perfluorononanoic acid	PFNA	462.99 > 219 **462.99 > 419**
Perfluorodecanoic acid	PFDA	513.05 > 168.8 **513.05 > 469.15**
Perfluoroundecanoic acid	PFUnDA	563.0 > 269.1 **563.0 > 519.1**
Perfluorododecanoic acid	PFDoDA	613.01 > 168.9 **613.01 > 569.0**
Perfluorotridecanoic acid	PFTrDA	662.90 > 168.96 **662.90 > 619.0**
Perfluorotetradecanoic acid	PFTDA	712.9 > 168.97 **712.9 > 669.0**
$^{13}C_2$- perfluorohexanoic acid	^{13}C-PFHxA[a]	**315.25 > 270.25**
$^{13}C_4$- perfluorooctanoic acid	^{13}C-PFOA[a]	**417.1 > 372.2**
$^{13}C_5$- perfluorononanoic acid	^{13}C-PFNA[a]	**468.0 > 423**
$^{13}C_2$- perfluorodecanoic acid	^{13}C-PFDA[a]	**515.05 > 470.15**
$^{13}C_2$- perfluoroundecanoic acid	^{13}C-PFUnDA[a]	**565 > 520.1**
$^{13}C_2$- perfluorododecanoic acid	^{13}C-PFDoDA[a]	**615.01 > 570**
$^{18}O_2$- perfluorohexane sulfonic acid	^{18}O-PFHxS[a]	**403.1 > 102.9**
$^{13}C_4$- perfluorooctane sulfonic acid	^{13}C-PFOS[a]	**502.9 > 98.85**
$^{13}C_8$- perfluorooctanoic acid	$^{13}C_8$-PFOA[b]	**421.1 >376.2**
$^{13}C_8$- perfluorooctane sulfonic acid	$^{13}C_8$-PFOS[b]	**506.9 > 98.85**
7H-dodecafluoroheptanoic acid	*7H*-PFHpA[b]	**345.03 > 281**

[a] Used as internal standard, i.e. is added before extraction

[b] Used as performance standard, i.e. added after extraction and before instrumental analysis

APPENDIX B

Table B1. PFAA concentrations (ng/mL) in serum samples from Sweden, 2004-2011.

		SERUM (ng/mL)													
MTM Sample ID	**National Food Agency ID**	**PFPeA**	**PFBuS**	**PFHxA**	**PFHpA**	**PFHxS**	**L-PFOS**	**PFDS**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTrDA**	**PFTDA**
Samples from 2004:															
DL04027: 01	05424533	< 0.010	< 0.004	< 0.030	0.04	1.54	20.18	< 0.04	3.50	1.67	1.01	0.85	0.08*	< 0.02*	< 0.03*
DL04027: 02	05424534	< 0.010	< 0.004	< 0.030	0.03	3.47	7.28	< 0.04	1.87	0.30	< 0.39	0.28	< 0.02	< 0.02	< 0.03
DL04027: 03	05424531	< 0.010	< 0.004	< 0.030	0.06	1.48	5.85	< 0.04	1.85	0.30	< 0.39	< 0.03	< 0.02	< 0.02	< 0.03
DL04027: 04	05424527	< 0.010	0.04	< 0.030	0.07	2.60	9.43	< 0.04	3.23	0.35	< 0.39	0.25	< 0.02	< 0.02	< 0.03
DL04027: 05	05424523	< 0.010	< 0.004	< 0.030	0.04	5.57	7.20	< 0.04	2.33	0.43	< 0.39	0.25	< 0.02	< 0.02	< 0.03
DL04027: 06	05424524	< 0.010	< 0.004	< 0.030	0.11	6.82	6.44	< 0.04	2.50	0.57	0.39	0.28	< 0.02	< 0.02	< 0.03
DL04027: 07	05424522	< 0.010	0.05	< 0.030	0.08	4.32	12.16	< 0.04	2.68	0.47	< 0.39	0.35	< 0.02	< 0.02	< 0.03
DL04027: 08	05424518	< 0.010	0.09	< 0.030	0.06	10.28	7.66	< 0.04	3.10	0.58	< 0.39	0.34	< 0.02	< 0.02	< 0.03
DL04027: 09	05424519	< 0.010	0.06	< 0.030	0.25	3.54	7.99	< 0.04	3.27	0.36	< 0.39	0.23	< 0.02*	< 0.02*	< 0.03*
DL04027: 10	05424582	< 0.010	< 0.004	< 0.030	0.05	4.30	13.62	< 0.04	3.79	0.52	< 0.39	0.32	< 0.02	< 0.02	< 0.03
DL04027: 11	05424511	< 0.010	0.03	< 0.030	0.05	1.93	5.07	< 0.04	1.63	0.28	< 0.39	< 0.03	< 0.02*	< 0.02*	< 0.03*
DL04027: 12	05424508	< 0.010	< 0.004	< 0.030	0.04	2.06	4.11	< 0.04	3.82	0.75	0.55	0.22	< 0.02	< 0.02	< 0.03
Samples from 2007:															
DL12008: 01	5424411	< 0.010	< 0.004	< 0.030	0.06	3.70	6.63	< 0.04	2.67	0.78	0.47	0.45	< 0.02	0.08	< 0.03
DL12008: 02	5424415	< 0.010	< 0.004	< 0.030	0.05	1.80	7.09	< 0.04	2.88	0.67	0.44	0.26	< 0.02	< 0.02	< 0.03
DL12008: 03	5424414	< 0.010	< 0.004	< 0.030	0.06	1.56	5.25	< 0.04	1.93	0.48	< 0.39	0.23	< 0.02	< 0.02	< 0.03
DL12008: 04	5424416	< 0.010	< 0.004	< 0.030	0.04	7.38	7.21	< 0.04	1.62	0.36	< 0.39	0.31	< 0.02	0.07	< 0.03
DL12008: 05	5424420	< 0.010	< 0.004	< 0.030	< 0.03	1.30	7.79	< 0.04	2.27	0.88	< 0.39	< 0.03	< 0.02	< 0.02	< 0.03
DL12008: 06	5424422	< 0.010	< 0.004	< 0.030	0.07	11.22	14.36	< 0.04	3.74	0.43	< 0.39	0.25	< 0.02*	< 0.02*	< 0.03*
DL12008: 07	5424423	< 0.010	< 0.004	< 0.030	0.10	3.81	8.46	< 0.04	2.79	0.77	0.49	0.40	< 0.02	< 0.02	< 0.03
DL12008: 08	5424424	< 0.010	< 0.004	< 0.030	<0.03	0.67	2.49	< 0.04	1.44	0.40	< 0.39	0.32	< 0.02	< 0.02	< 0.03

DL12008: 09	5424426	< 0.010	< 0.004	< 0.030	<0.03	0.81	5.28	< 0.04	1.78	0.67	< 0.39	< 0.03	< 0.02	< 0.02	< 0.03
DL12008: 10	5424430	< 0.010	< 0.004	< 0.030	0.04	7.47	4.22	< 0.04	1.58	0.37	< 0.39	0.27	< 0.02	< 0.02	< 0.03
DL12008: 11	5424429	< 0.010	< 0.004	< 0.030	0.08	1.71	5.33	< 0.04	2.41	0.37	< 0.39	0.29	< 0.02	< 0.02	< 0.03
DL12008: 12	5424433	< 0.010	< 0.004	< 0.030	0.05	1.71	3.75	< 0.04	0.81	0.24	< 0.39	< 0.03	< 0.02*	< 0.02*	< 0.03*
Samples from 2009:															
DL12008: 13	5424303	< 0.010	< 0.004	< 0.030	<0.03	1.54	1.32	< 0.04	1.13	0.20	< 0.39	< 0.03	< 0.02	< 0.02	< 0.03
DL12008: 14	5424305	< 0.010	< 0.004	< 0.030	<0.03	2.02	2.20	< 0.04	1.34	0.31	< 0.39	< 0.03	< 0.02*	< 0.02*	< 0.03*
DL12008: 15	5424308	< 0.010	0.14	< 0.030	0.05	4.31	5.06	< 0.04	1.65	0.37	< 0.39	0.22	< 0.02	< 0.02	< 0.03
DL12008: 16	5424309	< 0.010	< 0.004	< 0.030	<0.03	8.60	6.62	< 0.04	2.47	0.66	0.45	0.48	< 0.02	< 0.02	< 0.03
DL12008: 17	5424317	< 0.010	< 0.004	< 0.030	0.04	1.06	6.23	< 0.04	1.42	0.78	< 0.39	< 0.03	< 0.02*	< 0.02*	< 0.03*
DL12008: 18	5424318	< 0.010	< 0.004	< 0.030	<0.03	5.85	3.04	< 0.04	1.41	0.42	< 0.39	< 0.03*	NQ	NQ	NQ
DL12008: 19	5424319	< 0.010	0.04	< 0.030	<0.03	4.66	3.51	< 0.04	1.18	0.52	< 0.39	0.32	< 0.02*	< 0.02*	< 0.03*
DL12008: 20	5424323	< 0.010	< 0.004	< 0.030	<0.03	2.05	3.70	< 0.04	1.98	0.45	< 0.39	0.26	< 0.02*	< 0.02*	< 0.03*
DL12008: 21	7134072	< 0.010	< 0.004	< 0.030	0.06	5.78	3.31	< 0.04	2.22	0.45	< 0.39	0.23	< 0.02	< 0.02	< 0.03
DL12008: 22	7134065	< 0.010	< 0.004	< 0.030	0.05	2.54	5.54	< 0.04	2.32	0.57	< 0.39	0.34	< 0.02	< 0.02	< 0.03
DL12008: 23	7134051	< 0.010	0.17	< 0.030	0.08	5.85	4.28	< 0.04	2.04	0.53	< 0.39	0.42	0.05	0.09	< 0.03
DL12008: 24	7231310	< 0.010	< 0.004	< 0.030	<0.03	1.19	2.21	< 0.04	1.19	0.30	< 0.39	0.24	< 0.02	< 0.02	< 0.03
DL12008: 25	7231301	< 0.010	< 0.004	< 0.030	0.05	8.83	5.26	< 0.04	2.03	0.38	< 0.39	0.38	< 0.02	< 0.02	< 0.03
Samples from 2011:															
DL12008: 26	7225381	< 0.010	< 0.004	< 0.030	<0.03	2.62	6.69	< 0.04	1.44	0.58	0.39	0.34	< 0.02	< 0.02	< 0.03
DL12008: 27	7225388	< 0.010	< 0.004	< 0.030	<0.03	5.03	3.80	< 0.04	1.83	0.69	0.44	0.30	< 0.02	< 0.02	< 0.03
DL12008: 28	7225386	< 0.010	< 0.004	< 0.030	<0.03	5.50	4.65	< 0.04	1.62	0.59	< 0.39	0.28	< 0.02	< 0.02	< 0.03
DL12008: 29	7225389	< 0.010	< 0.004	< 0.030	<0.03	1.65	2.38	< 0.04	1.44	0.41	< 0.39	< 0.03	< 0.02*	< 0.02*	< 0.03*
DL12008: 30	7225390	< 0.010	< 0.004	< 0.030	<0.03	13.39	7.23	< 0.04	4.54	0.47	< 0.39	0.55	0.07	0.19	< 0.03
DL12008: 31	7225391	< 0.010	< 0.004	< 0.030	<0.03	4.73	9.06	< 0.04	2.09	1.09	0.59	0.40	< 0.02	< 0.02	< 0.03
DL12008: 32	7225393	< 0.010	< 0.004	< 0.030	0.04	2.88	1.86	< 0.04	0.92	0.25	< 0.39	0.20	< 0.02	< 0.02	< 0.03
DL12008: 33	7507598	< 0.010	*na	< 0.030	0.06	5.54	4.64	< 0.04	1.31	0.55	< 0.39	0.23	0.04	0.03	< 0.03

DL12008: 34	7225392	< 0.010	*na	< 0.030	< 0.03	3.81	2.58	< 0.04	1.20	0.25	< 0.39	0.20	< 0.02	< 0.02	< 0.03
DL12008: 35	7507597	< 0.01	0.14	< 0.03	0.06	22.09	6.34	< 0.04	2.17	0.57	< 0.39	0.50	< 0.02*	< 0.02*	< 0.03*
DL12008: 36	7507590	< 0.01	< 0.004	< 0.03	<0.03	0.81	1.63	< 0.04	1.04	0.33	< 0.39	0.61	< 0.02	< 0.02	< 0.03
DL12008: 37	7507591	< 0.01	< 0.004	< 0.03	0.03	7.93	3.45	< 0.04	1.06	0.36	< 0.39	0.36	< 0.02	< 0.02	< 0.03
DL12008: 38	7507584	< 0.01	0.09	< 0.03	0.04	8.81	3.75	< 0.04	1.28	0.56	< 0.39	< 0.03	NQ	NQ	NQ

NQ Not quantified due to quality reasons
NA Not analyzed due to technical difficulties
***** Recovery of internal standard >20% but <50%

Table B2. PFAA concentrations (ng/mL) in milk samples from Sweden, 2004-2011.

							MILK (ng/mL)								
MTM Sample ID	**National Food Agency ID**	**PFPeA**	**PFBuS**	**PFHxA**	**PFHpA**	**PFHxS**	**L-PFOS**	**PFDS**	**PFOA**	**PFNA**	**PFDA**	**PFUnDA**	**PFDoDA**	**PFTrDA**	**PFTDA**
							Samples from 2004:								
DL04027: 13	HF 20040001	<0.032	<0.021	<0.012*	<0.015	0.027	0.354	<0.009	0.166	0.039	<0.019	<0.032	NQ	NQ	NQ
DL04027: 14	HF 20040002	<0.032	<0.021	<0.012*	<0.015	0.050	0.128	<0.009	0.112	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL04027: 15	HF 20040005	<0.032	<0.021	<0.012*	<0.015	0.026	0.062	<0.009	0.100	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL04027: 16	HF 20040018	<0.032	0.028	<0.012*	<0.015	0.053	0.142	<0.009	0.220	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL04027: 17	HF 20040019	<0.032	<0.021	<0.012*	<0.015	0.107	0.175	<0.009	0.167	0.033	<0.019	<0.032	NQ	NQ	NQ
DL04027: 18	HF 20040020	<0.032	<0.021	<0.012*	<0.015	0.081	0.083	<0.009	0.117	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL04027: 19	HF 20040022	<0.032	0.026	<0.012*	<0.015	0.073	0.145	<0.009	0.168	0.031	<0.019	<0.032*	NQ	NQ	NQ
DL04027: 20	HF 20040023	<0.032	0.019	<0.012*	<0.015	0.144	0.100	<0.009	0.180	0.028	<0.019	<0.032*	NQ	NQ	NQ
DL04027: 21	HF 20040024	<0.032	NA	<0.012*	0.020	0.066	0.128	<0.009	0.158	<0.028	<0.019*	<0.032*	NQ	NQ	NQ
DL04027: 22	HF 20040047	<0.032	NA	<0.012*	<0.015	0.061	0.195	<0.009	0.155	<0.028	<0.019	<0.032*	NQ	NQ	NQ
DL04027: 23	HF 20040048	<0.032	0.014	<0.012*	<0.015	0.036	0.102	<0.009	0.106	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL04027: 24	HF 20040050	<0.032	<0.012	<0.012*	<0.015	0.034	0.064	<0.009	0.174	<0.028	<0.019	<0.032	NQ	NQ	NQ
							Samples from 2007:								
DL12008: 39	H0700010	<0.032	<0.435	<0.012*	<0.015	0.057	0.118	<0.009	0.119	<0.028	0.038	<0.032	NQ	NQ	NQ

DL12008: 40	H0700013	<0.032	<0.435	<0.012	<0.015	0.025	0.093	<0.009	0.119	<0.028	<0.019	<0.032*	NQ	NQ	NQ
DL12008: 41	H0700012	<0.032	<0.435	<0.012*	<0.015	0.034	0.101	<0.009	0.105	<0.028	0.024	<0.032*	NQ	NQ	NQ
DL12008: 42	H0700026	<0.032	<0.435	<0.012	<0.015	0.145	0.122	<0.009	0.103	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 43	H0700021	<0.032	NA	<0.012*	<0.015	0.021	0.090	<0.009	0.091	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 44	H0700025	<0.032	<0.435	<0.012	0.015	0.185	0.238	<0.009	0.183	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 45	H0700023	<0.032	<0.435	<0.012	<0.015	0.052	0.122	<0.009	0.117	<0.028	0.031	<0.032	NQ	NQ	NQ
DL12008: 46	H0700024	<0.032	<0.435	<0.012*	<0.015	0.013	0.044	<0.009	0.076	<0.028	0.023	<0.032	NQ	NQ	NQ
DL12008: 47	H0700028	<0.032	<0.435	<0.012	<0.015	0.021	0.109	<0.009	0.121	<0.028	0.048	<0.032*	NQ	NQ	NQ
DL12008: 48	H0700031	<0.032	<0.435	<0.012	<0.015	0.112	0.067	<0.009	0.094	0.079	0.052	<0.032	NQ	NQ	NQ
DL12008: 49	H0700030	<0.032	<0.435	<0.012*	<0.015	0.027	0.093	<0.009	0.114	<0.028	<0.019	<0.032*	NQ	NQ	NQ
DL12008: 50	H0700033	<0.032	<0.327	<0.012*	<0.015	0.024	0.047	<0.009	<0.055	<0.028	0.037	<0.032	<0.007	<0.008	<0.031
Samples from 2009:															
DL12008: 51	H0900003	<0.032	<0.327	<0.012*	<0.015	0.022	0.028	<0.009	0.063	<0.028	0.051	<0.032	<0.007	<0.008	<0.031
DL12008: 52	H0900004	<0.032	NA	<0.012*	<0.015	0.035	0.031	<0.009	0.087	<0.028	<0.019	<0.032*	NQ	NQ	NQ
DL12008: 53	H0900005	<0.032	<0.327	<0.012	<0.015	0.044	0.072	<0.009	0.060	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 54	H0900006	<0.032	0.392	<0.012*	<0.015	0.117	0.162	<0.009	0.132	<0.028	0.089	<0.032	<0.007	<0.008	<0.031
DL12008: 55	H0900007	<0.032	0.365	<0.012*	<0.015	0.021	0.121	<0.009	0.088	<0.028	0.097	<0.032	<0.007	<0.008	<0.031
DL12008: 56	H0900008	<0.032	<0.327	<0.012*	<0.015	0.076	0.055	<0.009	0.078	<0.028	<0.019	<0.032	<0.007	<0.008	<0.031
DL12008: 57	H0900009	<0.032	<0.327	<0.012	<0.015	0.058	0.053	<0.009	0.063	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 58	H0900028	<0.032	<0.327	<0.012	<0.015	0.024	0.076	<0.009	0.074	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 59	H0900094	<0.032	<0.327	<0.012*	<0.015	0.090	0.043	<0.009	0.104	<0.028	0.021	<0.032	NQ	NQ	NQ
DL12008: 60	H0900095	<0.032	<0.327	<0.012*	<0.015	0.042	0.094	<0.009	0.110	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 61	H0900167	<0.032	0.344	<0.012*	<0.015	0.102	0.070	<0.009	0.168	0.049	<0.019	<0.032	NQ	NQ	NQ
DL12008: 62	H0900203	<0.032	NA	<0.012*	<0.015	0.023	0.037	<0.009	0.074	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 63	H0900204	<0.032	<0.209	<0.012*	<0.015	0.116	0.076	<0.009	0.097	0.035	<0.019	<0.032	NQ	NQ	NQ
Samples from 2011:															
DL12008: 64	H1100003	<0.032	<0.209	<0.012*	<0.015	0.051	0.048	<0.009	0.114	0.042	<0.019	<0.032*	NQ	NQ	NQ

DL12008: 65	H1100028	<0.032	<0.209	<0.012*	<0.015	0.058	0.128	<0.009	0.098	0.033	<0.019	<0.032	NQ	NQ	NQ
DL12008: 66	H1100029	<0.032	NA	<0.012*	0.017	0.088	0.059	<0.009	0.106	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 67	H1100030	<0.032	<0.209	<0.012*	<0.015	0.205	0.040	<0.009	0.209	0.030	<0.019	<0.032	NQ	NQ	NQ
DL12008: 68	H1100082	<0.032	<0.209	<0.012*	<0.015	0.028	0.095	<0.009	0.105	0.035	<0.019	<0.032	NQ	NQ	NQ
DL12008: 69	H1100083	<0.032	<0.209	<0.012*	<0.015	0.066	0.132	<0.009	0.106	0.037	<0.019	<0.032	NQ	NQ	NQ
DL12008: 70	H1100085	<0.032	<0.209	<0.012	0.017	0.077	0.028	<0.009	0.088	<0.028	<0.019	<0.032	NQ	NQ	NQ
DL12008: 71	H1100086	<0.032	<0.209	<0.012*	0.017	0.098	0.084	<0.009	0.105	0.036	<0.019	<0.032	NQ	NQ	NQ
DL12008: 72	H1100087	<0.032	<0.209	<0.012*	0.016	0.048	0.030	<0.009	0.078	<0.028*	<0.019*	<0.032*	NQ	NQ	NQ
DL12008: 73	H1100089	<0.032	0.025	<0.012*	<0.015	0.451	0.088	<0.009	0.167	0.033	<0.019*	<0.032*	NQ	NQ	NQ
DL12008: 74	H1100090	<0.032	<0.021	<0.012*	<0.015	0.082	0.034	<0.009	0.073	<0.028	<0.019*	<0.032*	NQ	NQ	NQ
DL12008: 75	H1100091	<0.032	0.035	<0.012*	<0.015	0.032	0.045	<0.009	0.164	<0.028*	<0.019*	<0.032*	NQ	NQ	NQ
DL12008: 76	H1100273	<0.032	<0.021	<0.012*	<0.015	0.148	0.055	<0.009	0.138	0.036*	<0.019*	<0.032*	NQ	NQ	NQ

NQ Not quantified due to quality reasons
NA Not analyzed due to technical difficulties
***** Recovery of internal standard >20% but <50%