

Test report

61243-006-08N5163

Client: Environmental Protection Agency (EPA)
McCumiskey House
Richview
Clonskeagh Road
Dublin 14
Ireland

Order dated: July 22, 2008

Sample: Cow's milk samples, details see table

Sample-No.	Client's sample characterization	GfA sample No.
Sample 1 (B1, B2, B14)	Cow milk	8N5163.001
Sample 2 (A5, A8, A9)	Cow milk	8N5163.002
Sample 3 (A7, A15, A24)	Cow milk	8N5163.003
Sample 4 (A3, A20, A23)	Cow milk	8N5163.004
Sample 5 (A11, A19, A25)	Cow milk	8N5163.005

Testing: Analysis for polybrominated Diphenylethers (PBDE), polybrominated Biphenyls (PBBs), Hexabromocyclododecane (HBCD), Tetrabromobisphenol A (TBBPA) and polybrominated Dibenzofurans and Dibenzodioxins (PBDF/D).

Sampling: The samples were sent to GfA by the client.

Sample entry: July 24, 2008

Test method: **Sample preparation (BFRs)**
Pooling of three individual milk samples to a composite sample; Freeze drying; Homogenisation; Addition of $^{13}\text{C}_{12}$ -labelled internal PBDE standards ($^{13}\text{C}_{12}$ -TriBDE, $^{13}\text{C}_{12}$ -TetraBDE, $^{13}\text{C}_{12}$ -PentaBDE, $^{13}\text{C}_{12}$ -HexaBDE, $^{13}\text{C}_{12}$ -HeptaBDE, $^{13}\text{C}_{12}$ -DecaBDE), a $^{13}\text{C}_{12}$ -HBCD standard (γ -HBCD) and a $^{13}\text{C}_{12}$ -TBBPA standard to the dried sample material; ASE extraction of a representative sample amount by means of Hexane/Dichloromethane/Methanol; Gravimetric determination of the fat content after evaporation of the solvents.

PBDE, PBB and HBCD analysis:

Clean-up by liquid/solid chromatography; HRGC/LRMS analysis; Quantitative determination of PBDEs and PBBs by means of the internal $^{13}\text{C}_{12}$ -labelled PBDE standards and of HBCD by means of the $^{13}\text{C}_{12}$ -HBCD standard (Isotope dilution method).

TBBPA analysis:

Treatment of an extract portion by means of sulphuric acid; Derivatisation; HRGC/LRMS analysis; Quantitative determination by means of the internal $^{13}\text{C}_{12}$ -labelled TBBPA standard (Isotope dilution method).

Sample preparation (PBDF/Ds)

Pooling of three individual milk samples to a composite sample; Freeze drying; Homogenisation; ASE extraction of a representative sample amount by means of Hexane/Dichloromethane/Methanol. Addition of ten $^{13}\text{C}_{12}$ -labelled internal Tri- through HeptaBDF/D standards prior to extraction. Gravimetric determination of the fat content after evaporation of the solvents.

PBDF/D analysis:

For the PBDF/D analysis the solution was cleaned-up by multi-step liquid/solid chromatography. Prior to the gas chromatographic analysis, a further ^{13}C -labelled PCDF/D standard was added to the PBDF/D fraction for the determination of the recovery of the internal standards.

A capillary gas chromatograph (HRGC, HP 5890) equipped with a DB1 column coupled with a high resolution mass spectrometer (HRMS, VG-AutoSpec) was used for the PCDF/D analysis. The quantitative determination of native Tri- through HeptaBDF/Ds was achieved via the corresponding $^{13}\text{C}_{12}$ -labelled internal standards (Isotope dilution method; QMA504-205; DIN EN ISO/IEC 17025:2005 accredited method).

Start of testing: July 24, 2008

End of testing: November 24, 2008

Results: The results of the analysis of the samples are shown in the Tables 01 to 09.

Remarks: The results of the analyses of the samples were verified by means of duplicate analysis.

Tab. 01: Results of the analysis of composite milk samples for PBDEs; the results refer to the fat-weight and to the fresh-weight

Client's sample characterisation	Sample 1 (B1, B2, B14)		Sample 2 (A5, A8, A9)	
GfA Sample No.	8N5163.001		8N5163.002	
Unit	ng/kg fresh-weight	ng/kg fat-weight	ng/kg fresh-weight	ng/kg fat-weight
PBDEs				
2,2',4-TriBDE (BDE-17)	< 0,1	< 3,0	< 0,1	< 3,0
2,4,4'-TriBDE (BDE-28)	< 0,1	< 3,0	< 0,1	< 3,0
2,2',4,5'-TetraBDE (BDE-49)	< 0,3	< 5,0	< 0,3	< 5,0
2,3',4',6-TetraBDE (BDE-71)	< 0,3	< 5,0	< 0,3	< 5,0
2,2',4,4'-TetraBDE (BDE-47)	1,8	46,3	1,2	32,4
2,3',4,4'-TetraBDE (BDE-66)	< 0,3	< 5,0	< 0,3	< 5,0
3,3',4,4'-TetraBDE (BDE-77)	< 0,3	< 5,0	< 0,3	< 5,0
2,2',4,4',6-PentaBDE (BDE-100)	0,3	6,9	0,3	6,9
2,3',4,4',6-PentaBDE (BDE-119)	< 0,3	< 5,0	< 0,3	< 5,0
2,2',4,4',5-PentaBDE (BDE-99)	1,9	49,1	1,4	36,4
2,2',3,4,4'-PentaBDE (BDE-85)	< 0,3	< 5,00	< 0,3	< 5,0
3,3',4,4',5-PentaBDE (BDE-126)	< 0,3	< 5,00	< 0,3	< 5,0
2,2',4,4',5,6'-HexaBDE (BDE-154)	< 0,5	< 10,0	< 0,5	< 15,0
2,2',4,4',5,5'-HexaBDE (BDE-153)	1,6	41,2	< 0,5	< 15,0
2,2',3,4,4',5'-HexaBDE (BDE-138)	< 0,5	< 10,0	< 0,5	< 10,0
2,2',3',4,4',5,6'-HeptaBDE (BDE-183)	< 2,50	< 50,0	< 2,50	< 50,0
DecaBDE (BDE-209)	< 50,0	< 1000	< 50,0	< 1000
Sum of PBDEs (excl. LOQ)	5,6	143,5	2,9	75,7
HBCD (Sum of α-, β- and γ-HBCD)	< 20	< 500	< 20	< 500
TBBPA	< 20	< 500	< 20	< 500

< : Concentration below the indicated limit of quantification (LOQ)

ND: Not determined since none of the corresponding congeners was above the LOQ

Tab. 02: Results of the analysis of composite milk samples for PBDEs; the results refer to the fat-weight and to the fresh-weight

Client's sample characterisation	Sample 3 (A7, A15, A24)		Sample 4 (A3, A20, A23)	
GfA Sample No.	8N5163.003		8N5163.004	
Unit	ng/kg fresh-weight	ng/kg fat-weight	ng/kg fresh-weight	ng/kg fat-weight
PBDEs				
2,2',4-TriBDE (BDE-17)	< 0,1	< 3,0	< 0,1	< 3,0
2,4,4'-TriBDE (BDE-28)	< 0,1	< 3,0	< 0,1	< 3,0
2,2',4,5'-TetraBDE (BDE-49)	< 0,3	< 5,0	< 0,3	< 5,0
2,3',4',6-TetraBDE (BDE-71)	< 0,3	< 5,0	< 0,3	< 5,0
2,2',4,4'-TetraBDE (BDE-47)	0,9	27,9	1,3	33,8
2,3',4,4'-TetraBDE (BDE-66)	< 0,2	< 5,0	< 0,2	< 5,0
3,3',4,4'-TetraBDE (BDE-77)	< 0,2	< 5,0	< 0,2	< 5,0
2,2',4,4',6-PentaBDE (BDE-100)	0,2	5,1	< 0,3	< 5,0
2,3',4,4',6-PentaBDE (BDE-119)	< 0,3	< 5,0	< 0,3	< 5,0
2,2',4,4',5-PentaBDE (BDE-99)	0,8	24,2	1,1	29,0
2,2',3,4,4'-PentaBDE (BDE-85)	< 0,3	< 5,0	< 0,3	< 5,0
3,3',4,4',5-PentaBDE (BDE-126)	< 0,3	< 5,0	< 0,3	< 5,0
2,2',4,4',5,6'-HexaBDE (BDE-154)	< 0,5	< 15,0	< 0,5	< 15,0
2,2',4,4',5,5'-HexaBDE (BDE-153)	< 0,5	< 15,0	< 0,5	< 15,0
2,2',3,4,4',5'-HexaBDE (BDE-138)	< 0,5	< 15,0	< 0,5	< 15,0
2,2',3',4,4',5,6'-HeptaBDE (BDE-183)	< 2,5	< 50,0	< 2,5	< 50,0
DecaBDE (BDE-209)	< 50,0	< 1000	< 50,0	< 1000
Sum of PBDEs (excl. LOQ)	2,0	57,2	2,4	62,8
HBCD (Sum of α-, β- and γ-HBCD)	< 20	< 500	< 20	< 500
TBBPA	< 20	< 500	< 20	< 500

< : Concentration below the indicated limit of quantification (LOQ)

ND: Not determined since none of the corresponding congeners was above the LOQ

Tab. 03: Results of the analysis of a composite milk sample for PBDEs; the results refer to the fat-weight and to the fresh-weight

Client's sample characterisation	Sample 5 (A11, A19, A25)	
GfA Sample No.	8N5163.005	
Unit	ng/kg fresh-weight	ng/kg fat-weight
PBDEs		
2,2',4-TriBDE (BDE-17)	< 0,1	< 3,0
2,4,4'-TriBDE (BDE-28)	< 0,1	< 3,0
2,2',4,5'-TetraBDE (BDE-49)	< 0,3	< 5,0
2,3',4',6-TetraBDE (BDE-71)	< 0,3	< 5,0
2,2',4,4'-TetraBDE (BDE-47)	1,9	50,6
2,3',4,4'-TetraBDE (BDE-66)	< 0,3	< 5,0
3,3',4,4'-TetraBDE (BDE-77)	< 0,3	< 5,0
2,2',4,4',6-PentaBDE (BDE-100)	0,3	8,4
2,3',4,4',6-PentaBDE (BDE-119)	< 0,3	< 5,0
2,2',4,4',5-PentaBDE (BDE-99)	1,6	36,8
2,2',3,4,4'-PentaBDE (BDE-85)	< 0,3	< 5,0
3,3',4,4',5-PentaBDE (BDE-126)	< 0,3	< 5,0
2,2',4,4',5,6'-HexaBDE (BDE-154)	< 0,5	< 15,0
2,2',4,4',5,5'-HexaBDE (BDE-153)	1,0	28,1
2,2',3,4,4',5'-HexaBDE (BDE-138)	< 0,5	< 15,0
2,2',3',4,4',5,6'-HeptaBDE (BDE-183)	< 2,5	< 50,0
DecaBDE (BDE-209)	< 50,0	< 1000
Sum of PBDEs (excl. LOQ)	4,8	123,9
HBCD (Sum of α-, β- and γ-HBCD)	< 20	< 500
TBBPA	< 20	< 500

< : Concentration below the indicated limit of quantification (LOQ)

ND: Not determined since none of the corresponding congeners was above the LOQ

Tab. 04: Results of the analysis of composite milk samples for PBBs; the results refer to the fat-weight and to the fresh-weight

Client's sample characterisation	Sample 1 (B1, B2, B14)		Sample 2 (A5, A8, A9)	
GfA Sample No.	8N5163.001		8N5163.002	
Unit	ng/kg fresh-weight	ng/kg fat-weight	ng/kg fresh-weight	ng/kg fat-weight
PBBs				
2,2',5,5'-TetraBB	< 0,2	< 5,0	< 0,2	< 5,0
Total other TetraBB	ND	ND	ND	ND
Total TetraBB	ND	ND	ND	ND
2,2',4,5,5'-PentaBB	< 0,3	< 8,0	< 0,3	< 8,0
Total other PentaBB	ND	ND	ND	ND
Total PentaBB	ND	ND	ND	ND
2,2',4,4',5,5'-HexaBB	< 0,4	< 10,0	< 0,4	< 10,0
Total other HexaBB	ND	ND	ND	ND
Total HexaBB	ND	ND	ND	ND
HeptaBB	< 1,0	< 25,0	< 1,0	< 25,0
Total other HeptaBB	ND	ND	ND	ND
Total HeptaBB	ND	ND	ND	ND
OctaBB	< 2,0	< 50,0	< 2,0	< 50,0
Total OctaBB	ND	ND	ND	ND
NonaBB	< 2,0	< 50,0	< 2,0	< 50,0
Total NonaBB	ND	ND	ND	ND
DecaBB	< 3,0	< 60,0	< 3,0	< 60,0

< : Concentration below the indicated limit of quantification (LOQ)

ND: Not determined since none of the corresponding congeners was above the LOQ

Tab. 05: Results of the analysis of composite milk samples for PBBs; the results refer to the fat-weight and to the fresh-weight

Client's sample characterisation	Sample 3 (A7, A15, A24)		Sample 4 (A3, A20, A23)	
GfA Sample No.	8N5163.003		8N5163.004	
Unit	ng/kg fresh-weight	ng/kg fat-weight	ng/kg fresh-weight	ng/kg fat-weight
PBBs				
2,2',5,5'-TetraBB	< 0,2	< 5,0	< 0,2	< 5,0
Total other TetraBB	ND	ND	ND	ND
Total TetraBB	ND	ND	ND	ND
2,2',4,5,5'-PentaBB	< 0,3	< 8,0	< 0,3	< 8,0
Total other PentaBB	ND	ND	ND	ND
Total PentaBB	ND	ND	ND	ND
2,2',4,4',5,5'-HexaBB	< 0,4	< 10,0	< 0,4	< 10,0
Total other HexaBB	ND	ND	ND	ND
Total HexaBB	ND	ND	ND	ND
HeptaBB	< 1,0	< 25,0	< 1,0	< 25,0
Total other HeptaBB	ND	ND	ND	ND
Total HeptaBB	ND	ND	ND	ND
OctaBB	< 2,0	< 50,0	< 2,0	< 50,0
Total OctaBB	ND	ND	ND	ND
NonaBB	< 2,0	< 50,0	< 2,0	< 50,0
Total NonaBB	ND	ND	ND	ND
DecaBB	< 3,0	< 60,0	< 3,0	< 60,0

< : Concentration below the indicated limit of quantification (LOQ)

ND: Not determined since none of the corresponding congeners was above the LOQ

Tab. 06: Results of the analysis of a composite milk sample for PBBs; the results refer to the fat-weight and to the fresh-weight

Client's sample characterisation	Sample 5 (A11, A19, A25)	
GfA Sample No.	8N5163.005	
Unit	ng/kg fresh-weight	ng/kg fat-weight
PBBs		
2,2',5,5'-TetraBB	< 0,2	< 5,0
Total other TetraBB	ND	ND
Total TetraBB	ND	ND
2,2',4,5,5'-PentaBB	< 0,3	< 8,0
Total other PentaBB	ND	ND
Total PentaBB	ND	ND
2,2',4,4',5,5'-HexaBB	< 0,4	< 10,0
Total other HexaBB	ND	ND
Total HexaBB	ND	ND
HeptaBB	< 1,0	< 25,0
Total other HeptaBB	ND	ND
Total HeptaBB	ND	ND
OctaBB	< 2,0	< 50,0
Total OctaBB	ND	ND
NonaBB	< 2,0	< 50,0
Total NonaBB	ND	ND
DecaBB	< 3,0	< 60,0

< : Concentration below the indicated limit of quantification (LOQ)

ND: Not determined since none of the corresponding congeners was above the LOQ

Tab. 07: Results of the analysis of composite milk samples for PBDF/Ds; the results refer to the fat-weight and to the fresh-weight

Client's sample characterisation	Sample 1 (B1, B2, B14)		Sample 2 (A5, A8, A9)	
GfA Sample No.	8N5163.001		8N5163.002	
Fat content [%]	3,6		3,6	
Unit	pg/g fresh-weight	pg/g fat-weight	pg/g fresh-weight	pg/g fat-weight
PBDF				
238-TriBDF ^b	< 0,007	< 0,21	< 0,004	< 0,11
2378-TetraBDF ^b	< 0,002	< 0,05	< 0,001	< 0,03
12378-PentaBDF ^b	< 0,003	< 0,09	< 0,001	< 0,04
23478-PentaBDF ^b	< 0,003	< 0,08	< 0,001	< 0,04
123478-/123678-HexaBDF ^{a, b}	< 0,02	< 0,52	< 0,003	< 0,08
1234678-HeptaBDF ^b	< 0,02	< 0,52	< 0,01	< 0,27
PBDD				
237-TriBDD ^b	< 0,007	< 0,21	< 0,004	< 0,11
2378-TetraBDD ^b	< 0,002	< 0,05	< 0,001	< 0,03
12378-PentaBDD ^b	< 0,005	< 0,14	< 0,002	< 0,05
123478/123678-HexaBDD ^{a, b}	< 0,03	< 0,78	< 0,01	< 0,41
123789-HexaBDD ^b	< 0,04	< 1,15	< 0,01	< 0,41
WHO-PBDD/F-TEQ excl. LOQ [c]	ND	ND	ND	ND
WHO-PBDD/F-TEQ incl. LOQ [d]	0,02	0,49	0,01	0,19

< : Concentration below the indicated limit of quantification (LOQ)

ND: Not determined since none of the corresponding congeners was above the LOQ

[a] : Not separated on DB1 as GC stationary phase

[b] : Maximum value, coelution with other isomers cannot be excluded

[c] : TEQ-value calculated by including the quantified congeners only

[d] : TEQ-value calculated by including the non-quantified congeners by taking the full value of their LOQ

[e] : Higher detection limit due to interferences

Tab. 08: Results of the analysis of composite milk samples for PBDF/Ds; the results refer to the fat-weight and to the fresh-weight

Client's sample characterisation	Sample 3 (A7, A15, A24)		Sample 4 (A3, A20, A23)	
GfA Sample No.	8N5163.003		8N5163.004	
Fat content [%]	3,8		3,6	
Unit	pg/g fresh-weight	pg/g fat-weight	pg/g fresh-weight	pg/g fat-weight
PBDF				
238-TriBDF ^b	< 0,01	< 0,36	< 0,004	< 0,11
2378-TetraBDF ^b	< 0,001	< 0,03	< 0,001	< 0,03
12378-PentaBDF ^b	< 0,002	< 0,06	< 0,001	< 0,04
23478-PentaBDF ^b	< 0,002	< 0,05	< 0,001	< 0,04
123478-/123678-HexaBDF ^{a, b}	< 0,03	< 0,72	< 0,008	< 0,21
1234678-HeptaBDF ^b	< 0,03	< 0,90	< 0,20 ^e	< 5,60 ^e
PBDD				
237-TriBDD ^b	< 0,01	< 0,36	< 0,004	< 0,11
2378-TetraBDD ^b	< 0,0009	< 0,02	< 0,001	< 0,03
12378-PentaBDD ^b	< 0,007	< 0,18	< 0,001	< 0,04
123478/123678-HexaBDD ^{a, b}	< 0,05	< 1,35	< 0,01	< 0,41
123789-HexaBDD ^b	< 0,05	< 1,35	< 0,01	< 0,41
WHO-PBDD/F-TEQ excl. LOQ [c]	ND	ND	ND	ND
WHO-PBDD/F-TEQ incl. LOQ [d]	0,02	0,58	0,01	0,25

< : Concentration below the indicated limit of quantification (LOQ)

ND: Not determined since none of the corresponding congeners was above the LOQ

[a] : Not separated on DB1 as GC stationary phase

[b] : Maximum value, coelution with other isomers cannot be excluded

[c] : TEQ-value calculated by including the quantified congeners only

[d] : TEQ-value calculated by including the non-quantified congeners by taking the full value of their LOQ

[e] : Higher detection limit due to interferences

Tab. 09: Results of the analysis of a composite milk sample for PBDF/Ds; the results refer to the fat-weight and to the fresh-weight

Client's sample characterisation	Sample 5 (A11, A19, A25)	
GfA Sample No.	8N5163.005	
Fat content [%]	3,7	
Unit	pg/g fresh-weight	pg/g fat-weight
PBDF		
238-TriBDF ^b	< 0,006	< 0,15
2378-TetraBDF ^b	< 0,001	< 0,04
12378-PentaBDF ^b	< 0,002	< 0,06
23478-PentaBDF ^b	< 0,002	< 0,06
123478-/123678-HexaBDF ^{a, b}	< 0,009	< 0,24
1234678-HeptaBDF ^b	< 0,07 ^e	< 1,91 ^e
PBDD		
237-TriBDD ^b	< 0,006	< 0,15
2378-TetraBDD ^b	< 0,001	< 0,04
12378-PentaBDD ^b	< 0,003	< 0,08
123478/123678-HexaBDD ^{a, b}	< 0,02	< 0,56
123789-HexaBDD ^b	< 0,02	< 0,56
WHO-PBDD/F-TEQ excl. LOQ [c]	ND	ND
WHO-PBDD/F-TEQ incl. LOQ [d]	0,01	0,31

< : Concentration below the indicated limit of quantification (LOQ)

ND: Not determined since none of the corresponding congeners was above the LOQ

[a] : Not separated on DB1 as GC stationary phase

[b] : Maximum value, coelution with other isomers cannot be excluded

[c] : TEQ-value calculated by including the quantified congeners only

[d] : TEQ-value calculated by including the non-quantified congeners by taking the full value of their LOQ

[e] : Higher detection limit due to interferences

November 24, 2008

 Dr. R. Grümping

Remark: The test results relate only to the items tested. Extracts of the report shall not be reproduced without written approval of the GfA mbH.

Environmental Protection Agency (EPA)
Mr. Colman Concannon
McCumiskey House
Richview
Clonskeagh Road
Dublin 14

Ireland

November 24, 2008

Our ref.:

61243-006

 P02-139-Kr
Please include in all correspondences

Your ref.: ./.
Project manager: Dr. R. Grümping / Dipl.-Ing. M. de Hoogd
Direct dial: -154 / -243

**Analysis of 5 composite cow's milk samples for brominated flame retardants (BFRs) and PBDF/Ds;
Your order PO 018588 dated July 22, 2008**

Dear Mr. Concannon,

Enclosed please find our test report concerning the investigations mentioned above.

If you have any questions please don't hesitate to contact us.

Best regards

Dr. R. Grümping