OCCURRENCE OF PCDD/Fs, PCBs, AND PBDEs IN FISH MEAL, FISH OIL AND FISH FEED IN NORTHERN EUROPE

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Abstract

We analyzed concentrations and congener profiles of polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (PBDEs) in 13 fish meal and five fish oil samples from Northern Europe. Concentrations of PCDD/Fs and dl-PCBs in seven fish feed samples were also analyzed. All TEQ concentrations of PCDD/Fs and sum concentrations of PCDD/Fs and dl-PCBs in fish meal, in fish oil and fish feed were below limit values of the EU. The ratio of TEQ-concentrations of PCDD/Fs and dl-PCBs in three Danish fish meal samples of four was one or higher, which is typical especially for the northern Baltic Sea. Ratios of TEQ-concentrations of PCDD/Fs to dl-PCBs close to one were also detected in Icelandic fish meal and oil. There was no correlation between concentrations of WHO-PCDD/F-TEQ and indicator PCBs in our samples. Sum concentrations of PBDEs ranged from 7.4 to 23.5 μg kg^{-1} fat in fish meal and 12.6 to 16.6 μg kg^{-1} fat in fish oil. The most common congeners were BDE 47 and BDE 100. In Polish and German fish meals and in one Danish fish meal the BDE-209 was the dominating congener among the measured PBDEs.

Introduction

World production of aquaculture products reached almost 52 million tonnes in 2006[1] and EU aquaculture production has been around 1.3 million tonnes per year[2]. Many undesirable organic compounds, such as PCDD/Fs, PCBs, and PBDEs are known to accumulate in fishery products. Fish feed may contain 50% to 70% of products of marine origin. Undesirable compounds in fish feed accumulate in cultivated fish[3]. Methods have been developed to clean PCDD/Fs and PCBs from fish oil and fish meal with activated carbon[4], supercritical CO_2-extraction[5] or by extraction and enzymatic treatment[6].

We studied the occurrence of PCDD/Fs, PCBs, and PBDEs in fish meal and fish oil. Concentrations of PCDD/Fs in seven fish feed samples were measured. We collected samples that originated from six Northern European countries (Denmark, Poland, Germany, Norway, Iceland, and Finland).

Materials and Methods

Five samples of fish oil and 17 samples of fish meal from years 2002, 2007, and 2008 were analysed for PCDD/Fs, PCBs and PBDEs. We also analysed concentrations of PCDD/Fs and dl-PCBs in seven fish feed samples from Denmark and Finland. Raw material for Finnish fish feed is imported from other, mainly European countries. Samples were taken in accordance with the Directive 76/371/EEC. After homogenisation samples were freeze dried and fat was extracted with a mixture of toluene and ethanol using an ASE (Accelerated solvent extractor, ASE 350) apparatus or Soxhlet-apparatus. The extraction solvent was changed to hexane and the fat percentage was determined gravimetrically. Samples were defatted on an acidic silica column and further purified with sulphuric acid and a miniature silica column. PCDD/Fs and PCBs were fractionated and purified on alumina and carbon columns. Analyses of PCDD/Fs, PCBs, and PBDEs were performed with HRGC/HRMS using SIR with a resolution of 10,000.

Results and Discussion

Of the fish meals, the highest concentrations of PCDD/Fs were detected in Danish products (Figure 1). The lowest levels of PCDD/Fs were detected in Polish, Icelandic and Norwegian fish meals. The highest concentrations of dl-PCBs were detected in Danish and Norwegian fish meals. There was no clear difference in concentrations of PCDD/Fs in fish oil between the countries. Norwegian fish oil showed the highest concentrations of dl-PCBs.

Concentrations of PCDD/Fs in fish feed in this study (0.61 to 1.36 ng WHO-PCDD/F-TEQ/kg (12% moisture)) (Table 1) were lower than the highest concentration of PCDD/Fs in dry fish feed measured in Finland detected in 2002[7] (4.72 ng TEQ kg^{-1} d.w. or 4.15 ng TEQ kg^{-1} (12% moisture)). All TEQ-concentrations of PCDD/Fs and the sum of PCDD/Fs and dl-PCBs in this study were below the limit values of the EU as set by Directive 2002/32/EC (Table 1).

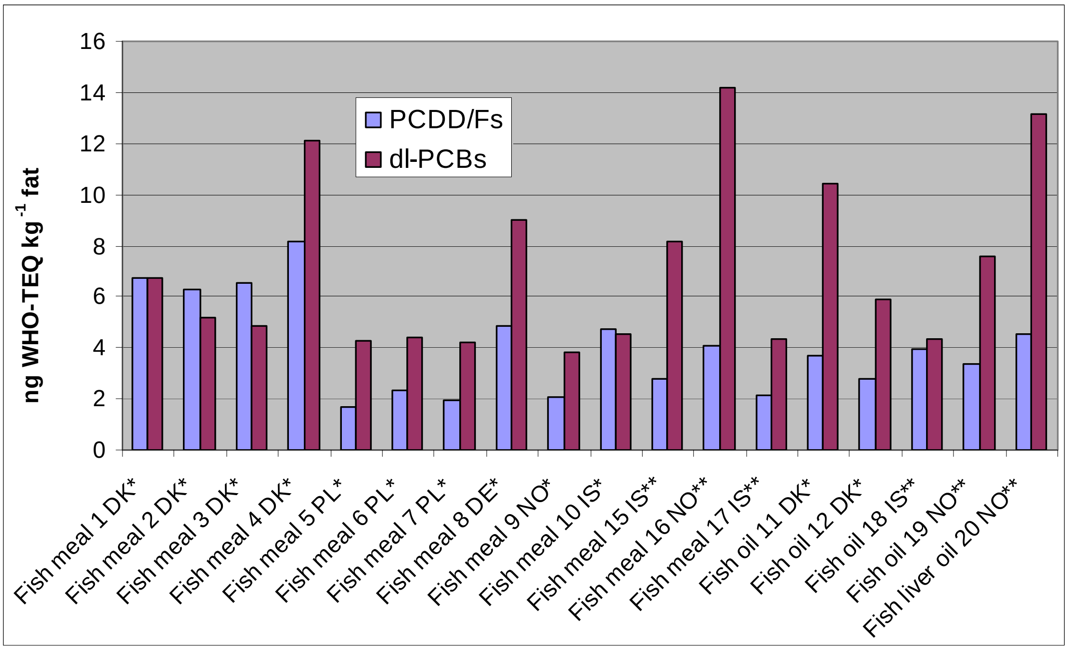

Figure 1. Concentrations of PCDD/Fs and dl-PCBs as WHO-TEQs in fish meal and fish oil samples from northern Europe sea area. For abbreviations of the countries, see Table 1.
* sampled in 2007 and 2008
** sampled in 2002

The ratio of PCDD/Fs to dl-PCBs was one or higher in three of the four Danish fish meal samples (Figure 1). The ratio was also close to one in one Icelandic fish oil and in one Icelandic fish meal sample. The ratio of PCDD/Fs to dl-PCBs of one or more is typical for fish from the northern Baltic Sea[8], but ratios close to one have also been reported in Icelandic fish meal[9].

Figure 2 shows the congener profile of PCDD/Fs in fish meal and fish oil samples. The 2,3,7,8-TeCDF was a major component in all samples. The 2,3,4,7,8-PeCDF was most abundant in Danish fish meals. The 2,3,4,7,8-PeCDF is a typical congener for Baltic sprat and Baltic herring[8,10]. Higher chlorinated PCDD/Fs (OCDD, OCDF) are not the major congeners in Baltic herring[8,10]. In our study, OCDD and OCDF were most abundant in Icelandic and Norwegian products, but also in one Danish fish meal sample.

The congener patterns of indicator PCB-congeners in our study were almost identical in all our samples with PCB 153 and PCB 138 the most abundant congeners (Figure 3). Our patterns were almost similar to patterns in small Baltic herring[10], in fish from Spain[11] and in Atlantic salmon[12].

Figure 4 shows the correlation between the concentrations of indicator PCBs and of WHO-PCDD/F-TEQ in our samples. There was a difference in this ratio between countries: the ratio of concentration of WHO-PCDD/F-TEQ to indicator PCBs was higher in Danish than in Polish fish meals. This probably indicates different areal sources and a difference in fish species composition in the raw material for fish meal and fish oil production. The poor correlation between the concentration of WHO-PCDD/F-TEQ and indicator PCBs (R^2=0.10) in our study suggests that indicator PCBs are not a suitable indicator for the concentration of PCDD/Fs in marine products.

Table 1. Concentrations of PCDD/Fs and dl-PCBs in fish meal, fish oil and fish feed as WHO-TEQs in the Northern Europe and limit values for feed in the EU (Directive 2002/32/EC). Abbreviations for the countries of the origin of the products: DK: Denmark; PL: Poland; DE: Germany; NO: Norway; IS: Iceland; FI: Finland.

Sample	Year of sampling	Concentration ng WHO-TEQ kg^{-1} (12% moisture)			Limit value in the EU ng WHO-TEQ kg^{-1} (12% moisture)	
		PCDD/Fs	dl-PCBs	PCDD/Fs + dl-PCBs	PCDD/Fs	PCDD/Fs + dl-PCBs
Fish meal 1 DK	2008	0.89	0.88	1.77	1.25	4.5
Fish meal 2 DK	2007	0.81	0.66	1.47	1.25	4.5
Fish meal 3 DK	2008	0.80	0.60	1.40	1.25	4.5
Fish meal 4 DK	2008	0.90	1.33	2.23	1.25	4.5
Fish meal 5 PL	2008	0.32	0.81	1.12	1.25	4.5
Fish meal 6 PL	2008	0.39	0.74	1.13	1.25	4.5
Fish meal 7 PL	2007	0.29	0.62	0.91	1.25	4.5
Fish meal 8 DE	2007	0.46	0.85	1.31	1.25	4.5
Fish meal 9 NO	2008	0.26	0.49	0.76	1.25	4.5
Fish meal 10 IS	2007	0.51	0.48	0.99	1.25	4.5
Fish meal 15 IS	2002	0.26	0.75	1.01	1.25	4.5
Fish meal 16 NO	2002	0.08	0.29	0.37	1.25	4.5
Fish meal 17 IS	2002	0.19	0.38	0.57	1.25	4.5
Fish oil 11 DK	2008	3.26	9.20	12.5	6.0	24.0
Fish oil 12 DK	2008	2.44	5.21	7.65	6.0	24.0
Fish oil 18 IS	2002	3.46	3.79	7.25	6.0	24.0
Fish oil 19 NO	2002	2.94	6.67	9.60	6.0	24.0
Fish liver oil 20 NO	2002	3.98	11.6	15.6	6.0	24.0
Feed for fish 13 DK	2007	0.64	0.96	1.60	2.25	7.0
Feed for fish 14 DK	2007	0.48	0.63	1.10	2.25	7.0
Feed for fish 21 FI	2002	1.24	1.34	2.58	2.25	7.0
Feed for fish 22 FI	2002	1.36	1.37	2.73	2.25	7.0
Feed for fish 23 FI	2002	0.61	0.76	1.37	2.25	7.0
Feed for fish 24 FI	2002	0.83	1.17	2.00	2.25	7.0
Feed for fish 25 FI	2002	0.94	0.95	1.99	2.25	7.0

Concentrations of PBDEs in fish meal ranged from 7.4 to 23.5 µg kg^{-1} fat as upperbound (in Figure 5 concentrations are in lowerbound). This corresponds to approximately 4.7 to 11.5 µg kg^{-1} f.w. Our figures are higher than those reported in wild or farmed fish in different places around the world (≤ 4.1 µg kg^{-1} f.w.)[13] and similar or slightly higher than the results reported in Baltic fish (3.0 to 7.9 µg kg^{-1} f.w.)[14]. The highest concentration of PBDEs in our study was detected in a German fish meal. The predominant BDE-congener in almost all fish samples was BDE 47. It is a ubiquitous and most common compound of PBDEs measured in population globally[13]. Also BDE 100 and BDE 99 were present in all samples. These compounds are typical for the technical mixture of pentabrominated PBDE which is now abandoned in the EU. The BDE-209 was a dominant congener in the German sample, in one Danish sample, and in all Polish samples. It was almost absent in Norwegian and Icelandic fish meals. Information on occurrence of BDE 209 in fish is scarce. It was absent in the Belgian diet[15]. In Spain BDE-209 was present in a river environment due to local pollution sources and it was accumulated into fish[16].

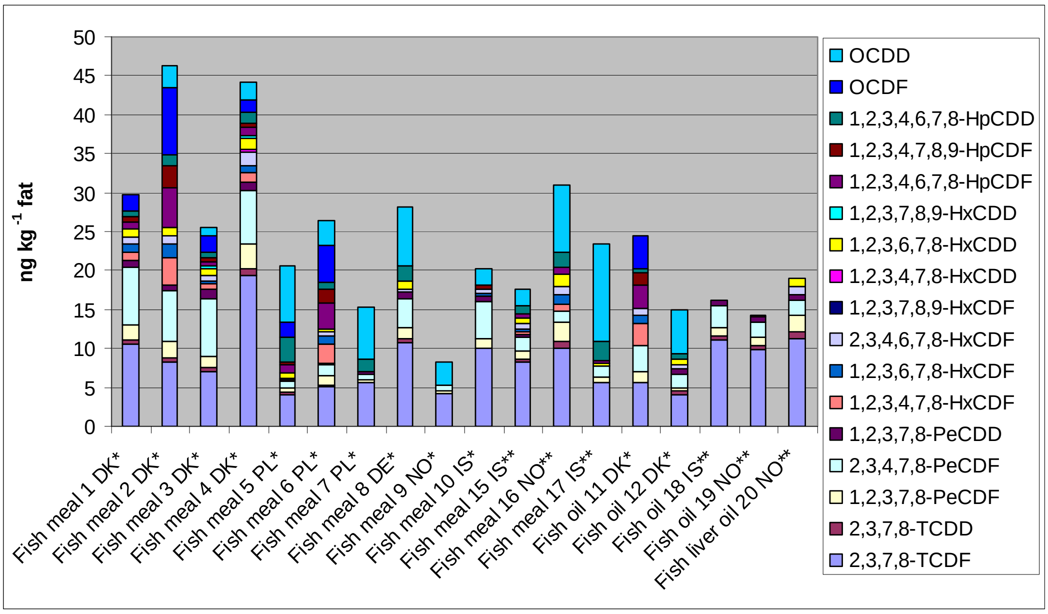

Figure 2. Congener profiles of PCDD/Fs in fish meal and fish oil samples from the northern Europe sea area. For abbreviations of the countries, see Table 1.
* sampled in 2007 and 2008
** sampled in 2002

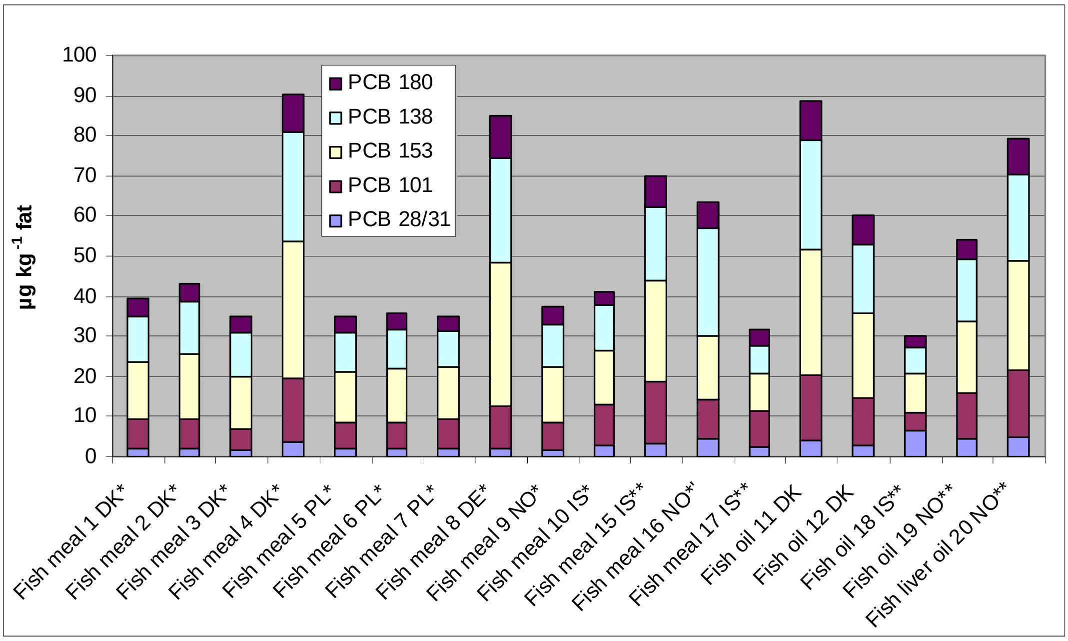

Figure 3. Congener profiles of indicator PCBs in fish meal and fish oil samples from the northern Europe sea area. For abbreviations of the countries, see Table 1.
* sampled in 2007 and 2008
** sampled in 2002

Koistinen *et al.*[10] reported concentrations of PCDD/Fs and dl-PCBs in Baltic herring from the northern Baltic Sea of 6.3 to 24.4 ng WHO-PCDD/F-TEQ kg^{-1} f.w. and of 4.0 to 9.5 ng WHO-PCB-TEQ kg^{-1} f.w. These correspond to approximately 27 to 90 ng WHO-PCDD/F-TEQ kg^{-1} (12% moisture) and 15 to 36 ng WHO-PCB-TEQ kg^{-1} (12% moisture). Concentrations reported in this study in fish meals were 1/10 to 1/300 of those reported in Baltic herring by Koistinen *et al.*[10].

The presence of 2,3,4,7,8-PeCDF and a ratio of PCDD/Fs and dl-PCBs close to one that were detected in Danish fish meal samples, are typical for the Baltic Sea[6]. The presence of BDE-209 in some of our samples suggests that they may contain fish from rivers or estuaries. It is likely that our fish meal and fish oil samples contain many fish species from different fishery regions.

Fish oil and fish meal can be cleaned of PCDD/Fs and PCBs by supercritical extraction, by activated carbon[4,5], or by extraction and enzymatic treatments[6]. These methods may remove up to 94% of TEQs in fish oil[4,5]. It is possible that part of the raw material for some of our samples originated from the northern Baltic Sea and they have been treated using cleaning methods. Cleaning may have an influence on the congener profile of the studied compounds or on the ratio of PCDD/Fs and PCBs. Efficacy of these methods on other compounds such as PBDEs may still be questioned[4].

Acknowledgments

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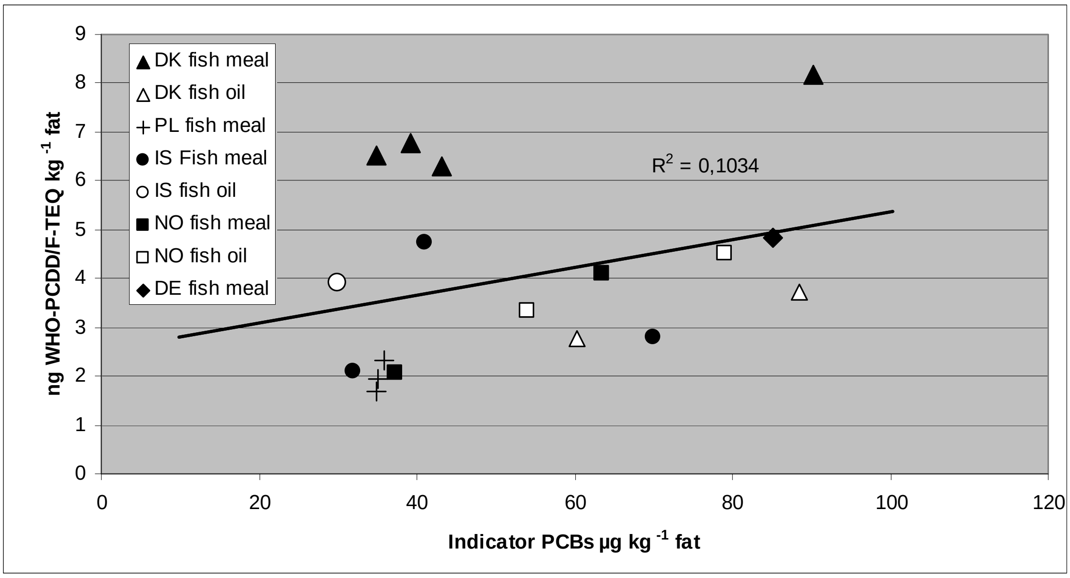

Figure 4. Correlations between concentrations of indicator PCBs and of WHO-PCDD/F-TEQ in fish meal and fish oil samples from northern Europe sea area. For abbreviations of the countries, see Table 1.

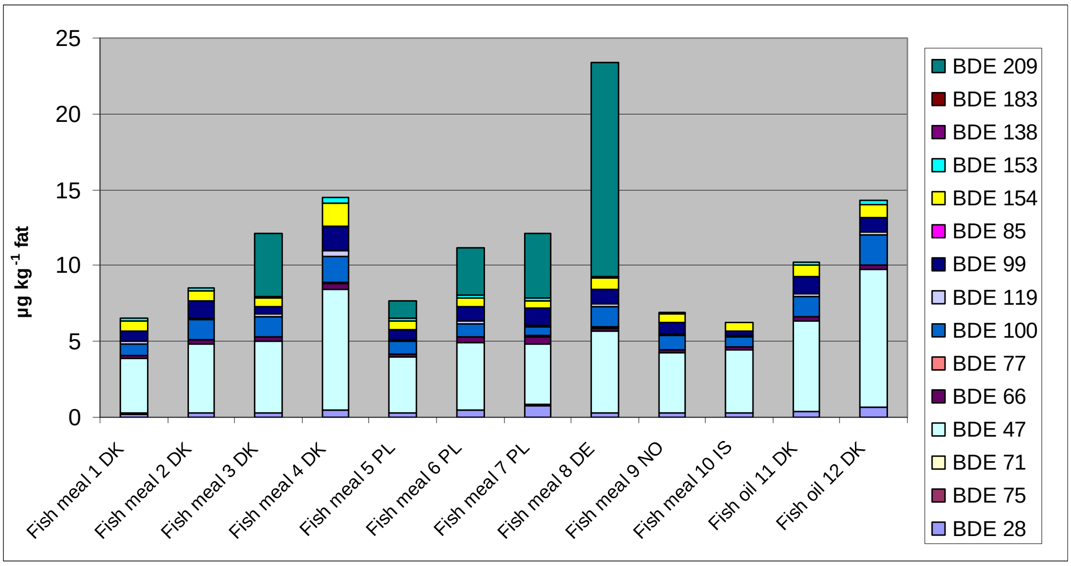

Figure 5. Concentrations of PBDEs in samples of fish meal and fish oil from northern Europe sea area. All samples were sampled in 2007 and 2008. For abbreviations of the countries, see Table 1.

References

1. European Commission, Fisheries, Common Fisheries Policy, Aquaculture and processing, Aquaculture, 2009 (http://ec.europa.eu/fisheries/cfp/aquaculture_processing/aquaculture_en.htm)
2. Europa-website 2009. (http://europa.eu/rapid/pressReleasesAction.do?reference=MEMO/09/161&type=HTML&aged=0&language=EN&guiLanguage=fr)
3. Isosaari P., Vartiainen T., Hallikainen A. and Ruohonen K. *Chemosphere* 2002;48:795
4. Usydus Z., Szlinder-Richert J., Polak-Juszczak L., Malesa-Ciećwierz M. and Dobrzański Z. *Chemosphere* 2009;74:1495
5. Kawashima A., Watanabe S., Iwakiri R. and Honda K. *Chemosphere* 2009;75:788.
6. Baron C.P., Børresen T. and Jacobsen C. *J Agric Food Chem* 2007;55:1620
7. Isosaari P., Kiviranta H., Øyvind L., Lundebye A-K., Ritchie G., and Vartiainen T. *Environ Toxicol Chem* 2004;23:1672.
8. Kiviranta H. Ph.D.-thesis. National Public Health Institute, Finland. 2005.
9. Asmundsdottir A.M., Auðunsson G.A. and Gunnlaugsdottir, H. Undesirable substances in seafood products - Results from the monitoring activities in 2004. IFL Project Report 33 - 05. 2005.
10. Koistinen J., Kiviranta H., Ruokojärvi P., Parmanne R., Verta M., Hallikainen A. and Vartiainen T. *Environ Poll* 2008;154:172.
11. Bocio A., Domingo J.L., Falcó G., Llobet J.M. *Environ Int* 2007;33:170.
12. Jacobs M.N., Covaci A. and Schepens P. *Environ Sci Technol* 2002;36:2797
13. Hites A.R., Foran J.A., Schwager S.J., Knuth B.A., Hamilton M.C. and Carpenter D.O. *Environ Sci Technol* 2004;38:4945
14. Isosaari P., Hallikainen A., Kiviranta H., Vuorinen P.J., Parmanne R., Koistinen J. and Vartiainen T. *Environ Pollut* 2006;141:213
15. Voorspols S., Covaci A., Neels H. and Schepens P. *Environ Int* 2007;33:93.
16. Eljarrat E., Labandeira A., Marsh G., Raldúa D and Barcelo D. *Chemosphere* 2007;69:1278.