CONCENTRATIONS OF POLYCHLORINATED DIBENZO-P-DIOXINS, POLYCHLORINATED DIBENZOFURANS AND DIOXIN-LIKE PCBS IN THREE SAMPLES OF BUTTER FROM THE BALTIC REGION OF THE RUSSIAN FEDERATION

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Greenpeace Research Laboratories Technical Note 08/2001

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1. Summary

Concentrations of dioxins and dioxin-like PCBs were determined for three samples of butter sourced from the Baltic region of the Russian Federation. Dioxin concentrations, expressed both on the basis of individual congener concentrations and WHO-TEQ, fell broadly within the range previously reported for European butters. The highest concentration (1.34 pg/g lipid) was found in one of the two butter samples drawn from the Leningradskaj area (St Petersburg). The contribution to overall TEQ from the non-*ortho* PCBs was greater than that from dioxins in all three Russian butters. The range of total TEQs (1.18-3.25 pg/g lipid) was again similar to the range previously reported for European butters, noting however that only the butter previously analysed from Spain contained higher concentrations than the most contaminated butter from Leningradskaj. Indeed, the concentration of non-*ortho* PCBs was greater in this sample than in any of the European butters, and on a global basis was surpassed only by the single sample previously analysed from Tunisia.

2. Introduction

Three samples of butter from the Baltic region of the Russian Federation were forwarded the Greenpeace Research Laboratories for analysis of dioxins/furans and dioxin-like (*ortho* and non *ortho* PCBs):-

BT01016	Leningradskaj area	Gatchina
BT01017	Leningradskaj area	St Petersburg
BT01018	Kaliningradskaj area	Poleski

Concentrations of dioxins and PCBs are reported below, and compared against concentrations previously determined for butters from Europe and other regions of the globe by Santillo *et al.* (2000).

3. Materials and Methods

Samples were frozen as soon as possible following collection and were kept frozen during transportation and for storage (at -20^{o}C) prior to analysis. Quantitative determination of dioxins and furans was conducted by Central Science Laboratories (CSL, UK) according to the following methodology.

Small sub-samples were excised from the centre of the butter portions and freeze dried for a period of approximately 2 weeks before extraction. Methods used for the extraction and analysis of samples were as previously published by Krokos *et al.* (1997), using acceptance criteria developed by Ambidge *et al.* (1990). Samples were exhaustively extracted using mixed organic solvents, following grinding and spiking with ^{13}C-labelled analogues of target compounds. Extracts were cleaned using adsorption chromatography and quantified using high resolution gas chromatography/ high resolution mass spectrometric detection. Additional chromatographic confirmation was conducted for the PCDDs and PCDFs. All analyses and results are UKAS accredited.

Further details of methods and analytical hardware used can be provided on request.

4. Results and Discussion

Concentrations of individual dioxin congeners for the three butters are shown in Table 1, along with concentrations relating to the butter samples from European countries which were analysed in a previous study (Santillo *et al.* 2000).

Dioxin concentrations (both of individual congeners and WHO-TEQ for humans and mammals) in the three Russian butters fell broadly within the range previously reported for European butters *i.e.* 0.28-1.34 pg/g lipid WHO-TEQ compared to 0.10-1.46* pg/g lipid WHO-TEQ for 8 European butters analysed previously (*excluding the butter from Spain, which yielded an exceptionally high value of 4.8 pg/g lipid). Concentrations in one of the butters from the Leningradskaj area (BT01016, Gotchina) and in the butter from Kaliningradskaj area (BT01018, Poleski) yielded dioxin WHO-TEQs towards the lower end of the European range (0.31 and 0.28 pg/g lipid respectivel). Indeed, of the 9 European butter samples analysed by Santillo *et al.* (2000), only the sample from Sweden showed lower levels of contamination. In contrast, the second sample from Leningradskaj area (BT01017, St Petersburg) contained higher levels, closer to those concentrations previously reported in the butter samples from Italy and the Netherlands.

As far as the authors can verify, the only previously reported data for dioxin concentrations in butter from the Russian Federation are those published by Maystrenko *et al.* (1998) for butter samples collected in the Republic of Bashkortostan in 1996 (mean 0.43 pg I-TEQ/g lipid). This mean value is of the same order as those recorded in the current study.

Table 2 summarises the relative concentrations of a number of key congeners in the Russian samples, compared to those for butters from other locations from our previous study (Santillo *et al.* 2000) and from other published work (Malisch 1998, Malisch *et al.* 2000, Malisch 1998, Ramos *et al.* 1998). The broad congener pattern for the Russian butters appears comparable to that for the European butters analysed previously.

Table 3 summarises the contribution to total WHO-TEQ from dioxins/furans and non-*ortho* PCBs in each of the Russian butters compared to those previously reported from the other butter samples analysed in our previous study (Santillo *et al.* 2000). In all three cases, the contribution to overall TEQ from non-*ortho* PCBs in the Russian samples was greater than that from the dioxins. Indeed, the concentration of non-*ortho* PCBs was greater in the sample from St Petersburg (BT01017) than in any of the European butters, and on a global basis was surpassed only by the single sample previously analysed from Tunisia. Total (dioxin/furan + non-*ortho* PCB) WHO-TEQs for the three butters fell within the same broad range as those for the European butters analysed in our previous

study, noting however that only the butter previously analysed from Spain (Santillo *et al.* 2000) contained higher concentrations than the most contaminated butter from Leningradskaj (BT01017).

Data for *ortho* PCBs are also available for the three Russian butters; these have not been included in this brief analysis, however, as comparable data are not yet available for the butters analysed in our previous study. Inclusion of the contribution from *ortho* PCBs in the calculation would increase total WHO-TEQs for the Russian butters by 15-25% (to the range 1.40-3.74 pg/g lipid).

References

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Country of origin	Austria	Czech Rep.	Denmark	Germany	Italy	Netherlands	Spain	Sweden	UK	Leningrad-skaj area	Leningrad-skaj area	Kaliningrad-skaj area
Sample code	**B8018**	**B8061**	**B8058**	**B8064**	**B8034**	**B8001**	**B8019**	**B8011**	**B8115**	**BT01016**	**BT01017**	**BT01018**
Dioxins												
2,3,7,8-TCDD	0.07	0.08	0.11	0.07	0.25	0.43	0.20	<0.05	0.09	0.07	0.18	<0.06
1,2,3,7,8-PCDD	0.21	0.15	0.17	0.14	0.31	0.43	0.39	<0.04	0.36	0.08	0.40	0.09
1,2,3,4,7,8-HCDD	0.11	0.09	0.08	0.11	0.12	0.16	0.14	<0.03	0.14	<0.04	0.13	<0.04
1,2,3,6,7,8-HCDD	0.24	0.19	0.17	0.22	0.26	0.26	0.29	0.07	0.32	0.05	0.17	0.08
1,2,3,7,8,9-HCDD	0.11	0.12	0.07	0.11	0.13	0.12	0.15	<0.02	0.24	<0.04	0.14	<0.04
1,2,3,4,6,7,8-HpCDD	0.43	0.39	0.27	0.45	0.46	0.42	0.38	0.15	0.57	0.11	0.32	0.11
OCDD	1.14	0.54	0.45	0.36	0.66	0.64	0.27	0.27	0.47	<0.75	0.96	1.11
Furans												
2,3,7,8-TCDF	0.04	<0.02	0.03	<0.04	0.05	<0.04	0.41	<0.04	0.04	<0.06	0.16	0.07
1,2,3,7,8-PCDF	<0.02	0.03	<0.02	<0.04	0.05	0.04	0.21	<0.04	0.04	<0.07	0.11	<0.07
2,3,4,7,8-PCDF	0.35	0.63	0.33	0.50	0.56	0.78	7.73	0.15	0.34	0.27	1.11	0.29
1,2,3,4,7,8-HCDF	0.15	0.3	0.14	0.25	0.56	0.53	0.94	0.07	0.18	0.10	0.48	0.11
1,2,3,6,7,8-HCDF	0.12	0.18	0.11	0.20	0.32	0.34	0.55	0.06	0.16	0.09	0.46	0.08
2,3,4,6,7,8-HCDF	<0.02	0.18	<0.02	<0.01	0.33	<0.01	<0.02	<0.01	<0.02	<0.04	<0.04	<0.04
1,2,3,7,8,9-HCDF	0.12	<0.01	0.11	0.19	<0.01	0.55	0.81	0.05	0.15	<0.08	0.40	0.10
1,2,3,4,6,7,8-HpCDF	0.10	0.14	0.11	0.16	0.38	0.50	0.17	0.06	0.12	<0.05	0.15	<0.05
1,2,3,4,7,8,9-HpCDF	0.02	0.03	<0.01	<0.02	0.09	<0.02	0.04	<0.02	<0.01	<0.04	<0.04	<0.04
OCDF	0.10	0.05	<0.06	<0.06	0.19	0.31	0.07	<0.06	<0.06	<0.67	<0.67	<0.67
WHO-TEQ	**0.55**	**0.66**	**0.52**	**0.57**	**1.03**	**1.46**	**4.80**	**0.10**	**0.75**	**0.31**	**1.34**	**0.28**

Table 1. Congener-specific concentrations of dioxins and furans for three butter samples from the Russian Federation, compared to levels for nine European countries (Santillo *et al.* 2000). nd – not detected; nq – not quantified (detected but at below limits of quantification, i.e. <3 x limit of detection)

	2,3,7,8-TCDD	1,2,3,7,8-PCDD	1,2,3,4,6,7,8-HpCDD	OCDD	OCDF
This study – Russian Federation	nd-0.18	0.08-0.40	0.11-0.32	nd-1.11	nd
Europe[1]	nd-0.43	nd-0.43	0.15-0.57	0.27-1.14	nd-0.31
Mediterranean[1]	0.05-0.12	0.13-0.31	0.63-2.55	1.10-2.10	nd-0.11
Americas[1]	nd-0.06	0.09-0.19	0.09-3.04	0.22-4.07	0.02-0.17
Asia-Pacific[1]	nd-0.13	nd-0.25	0.09-0.84	0.41-3.14	0.08-0.22
South Africa[1]	nd	0.07	0.33	0.77	0.04
Germany 1993-96[2]	nd-0.26	nd-0.48	0.22-2.12	0.75-4.76	nd-0.67
Germany 1998[3]	0.36-0.62	0.37-0.52	0.41-0.79	0.59-0.84	0.28-0.50
Netherlands 1998[4]	0.9	0.64	0.42	0.45	0.16
Spain 1998[5]	nd-1.11	nd-1.08	0.58-3.09	1.35-26.6	nd-3.18

Table 2. Concentration ranges for selected dioxin and furan congeners in samples from the current study compared to those reported for butters from Europe by Santillo *et al.*(2000)[1], Malisch (1998)[2], Malisch *et al.* (2000)[3], Malisch (1998)[4] and Ramos *et al.* (1998)[5].

	WHO-TEQ (pg/g lipid)		
	dioxin	**non-*ortho*-PCBs**	**sum**
Europe			
Austria	0.55	0.99	1.54
Czech Rep.	0.66	1.80	2.46
Denmark	0.52	0.37	0.89
Germany	0.57	1.51	2.08
Italy	1.03	1.14	2.17
Netherlands	1.46	0.85	2.31
Spain	4.80	0.74	5.54
Sweden	0.20	0.51	0.71
UK	0.75	0.35	1.10
Russian Federation			
Leningradskaj	0.31	0.87	1.18
Leningradskaj	1.34	1.91	3.25
Kaliningradskaj	0.28	1.20	1.48
Mediterranean			
Israel	0.50	0.49	0.99
Tunisia	0.91	2.58	3.49
Americas			
Argentina	0.36	0.92	1.28
Brazil	0.28	0.39	0.67
Mexico	0.50	0.21	0.71
USA#1	0.27	0.13	0.40
USA#2	0.54	0.23	0.77
Canada	0.35	0.21	0.56
Asia-Pacific			
China	1.01	0.65	1.66
India	0.79	1.01	1.80
Japan	0.40	0.20	0.60
Philippines	0.09	0.01	0.10
Thailand	0.16	0.21	0.37
Australia	0.56	0.19	0.75
New Zealand	<0.01	0.07	0.07
Africa			
South Africa	0.18	0.17	0.35

Table 3: summary of contributions from dioxins/furans and non-*ortho*-PCBs to total WHO-TEQs for all 28 samples (including data from Santillo *et al.* 2000).