THE GLOBAL DISTRIBUTION OF PCBs, ORGANOCHLORINE PESTICIDES, POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS USING BUTTER AS AN INTEGRATIVE MATRIX

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1. Summary

A total of 138 samples of butter were collected during 1998 and 1999 from retail outlets (mainly supermarkets) in 24 countries worldwide. A sub-set of 63 samples representing 23 of the countries were analysed for PCBs and a number of chlorinated pesticide residues at the University of Lancaster, UK (as previously reported by Kalantzi *et al.* 2000). A further sub-set of 25 butter samples, representing all 24 countries included, were selected for analysis of dioxins, furans and dioxin-like non-*ortho* PCBs by the Central Science Laboratories, York, UK.

Butter ∑PCB concentrations varied by a factor of ~60 in 63 samples from 23 countries (Kalantzi *et al.* 2000). They were highest in European and North American butter and lowest in southern hemisphere (Australian, New Zealand) samples, consistent with known patterns of historical global usage and estimated emissions. Congener-specific concentrations in butter reflected differences in the propensity of PCB congeners to undergo long range atmospheric transport from global source regions to remote areas. HCB distributions were consistent with the relatively even distribution of this compound in the global atmosphere. Concentrations of p,p-DDT, p,p-DDE and HCH isomers all varied over many orders of magnitude in the butter samples, with highest levels in areas of current use (e.g. India and south/central America for DDT; India, China and Spain for HCH).

With the exception of the sample from Spain, which yielded by far the highest concentrations, levels of dioxins and furans (I-TEQ and WHO-TEQ) in the samples fell within a range similar to values reported previously for European butters and other dairy products. Other than the Spanish butter, highest values were recorded for samples from the Netherlands and Italy. Outside Europe, butters from India, China and Tunisia also showed relatively high levels of dioxin contamination. Dioxin-like non-*ortho* PCBs made particularly significant contributions to overall TEQ in butters from Germany, Italy, the Czech Republic, Tunisia, India and Argentina. Although overall TEQs were generally highest in butters from European countries, elevated levels were also apparent in the industrialising regions of Asia (India and China) and Latin America (particularly Argentina).

On the basis of levels of PCBs and pesticides recorded, Kalantzi *et al.* (2000) concluded that:-

"*…butter is sensitive to local, regional and global scale spatial and temporal atmospheric trends of many POPs and may therefore provide a useful sampling medium for monitoring purposes. However, to improve the quantitative information derived on air concentrations requires an awareness of climatic and livestock management factors which influence air-milk fat transfer processes*".

In a similar manner, butter may also represent a useful matrix to obtain a representative description of regional patterns of dioxin/furan distribution. Given the relatively low mobility of these compounds, however, the possible significance of specific dioxin sources in close proximity to the provenance of the butters may be even greater in this case.

2. Introduction

The current development of a United Nations Environment Programme protocol to control releases of persistent organic pollutants (POPs) (Rodan *et al.* 1999) highlights the need to develop reliable monitoring programmes with which to assess the effectiveness of global source reduction measures. This study was designed to evaluate the possibility of using butter to assess regional/global scale distribution of POPs.

Dairy products have been used previously to assess local and regional variability in POP residue contamination within Europe (e.g. Ramos *et al.* 1999 for Spain, MAFF 1997 for UK) and the US (Lorber *et al.* 2000). The high fat content of butter (approximately 80%) and highly lipophilic properties of POPs, coupled with the relationships between atmospheric deposition, food intake and milk fat contaminant concentrations in cattle which have previously been reported (McLachlan 1996, Thomas *et al.* 1998a, 1999), suggest that butter may represent a valuable integrative matrix of regional POP contamination levels. Furthermore, the global availability of locally-produced butter may render it a useful and relatively consistent environmental matrix for use in the determination of POP distribution patterns on a more global basis.

A total of 138 butter samples were obtained through retail outlets in 24 countries around the world during 1998 and 1999. A sub-set of 63 samples (from a total of 23 countries) were forwarded to the University of Lancaster, UK, for analysis of PCBs and selected organochlorine pesticides and breakdown products (HCHs, HCB, DDT, DDE, DDD and chlordane). These data have previously been reported by Kalantzi *et al.* (2000) and are summarised below. A further sub-set of 25 butter samples (two from USA, one from each of the other 23 countries included in the study) were selected for analysis of dioxins, furans and dioxin-like non-*ortho* PCBs by the Central Science Laboratories, York, UK.

3. Materials and Methods

Butter samples were collected from 24 countries of origin with the assistance of staff from national and regional offices of Greenpeace worldwide. All butter samples were initially transported from their countries of origin to the Greenpeace Research Laboratories, University of Exeter, UK, from which they were forwarded on for analysis. 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. Care was taken to ensure that the butter samples analysed were prepared from milk from the country of origin in every case, and not from imported milk.

Samples for PCBs and pesticide residue analysis were taken from the following countries, with the number of separate samples from each country given in brackets: Austria (1), Australia (5), Brazil (4), Canada (6), China (1), Czech Republic, (1), Denmark (2), Germany (1), India (1), Israel (1), Italy (1), Japan (1), Mexico (3), Philippines (3), S. Africa (2), Spain (3), Sweden (3), Thailand (1), Netherlands (1), New Zealand (1), Tunisia (1), UK (2) and USA (18). In the case of dioxin analyses, six samples were selected from the Americas (Argentina, Brazil, Mexico, Canada and two from USA), nine from Europe (Austria, Czech Republic, Denmark, Germany, Italy, Netherlands, Spain, Sweden, UK), two from the Eastern Mediterranean (Israel and Tunisia), seven from the Asia-Pacific region (India, Thailand, Philippines, China, Japan, Australia and New Zealand), and one from South Africa.

3.1 Preparation and analysis of samples for PCBs and pesticide residues

The extraction method used was based on that previously published by Thomas *et al.* (1998b) for PCBs, with an alteration to the second stage of the clean-up procedure to allow for the concurrent analysis of organochlorine (OC) pesticides. About 1.7 g of butter was weighed into a flask and 5 g of sodium sulphate added. Approximately 50 ml of hexane were added and the sample boiled for 10 minutes, then allowed to cool and a sub-sample taken for lipid determination. The remaining sample was spiked with recovery standards and evaporated to approximately 5 ml, before clean-up using an activated acid silica gel column and concentration under a gas stream. Extracts were analysed using gas chromatography/mass spectrometry with an EI+ source. The following PCB congeners were screened (those underlined were regularly detected): PCB 18, 31, <u>28, 52, 49</u>, 41/64<u>, 74, 70, 99, 123, 118, </u>114, <u>105, 149, 153, 138, 183, 180, 170, 203</u>.

3.2 Preparation and analysis of samples for dioxins/furans and non-*ortho* PCBs

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

Data presented below for PCBs and chlorinated pesticide residues have been published previously by Kalantzi *et al.* (2000). The discussions presented below are a summary of those presented in that paper. Data for PCDDs and PCDFs are reported below for the first time.

4.1 PCBs

Mean concentrations and ranges for ∑PCB (sum of 21 congeners) are shown in Table 1. ∑PCB concentrations varied from 230 to 14,090 pg/g lipid, with lowest concentrations in samples from Australia and New Zealand and the highest in the sample from the Czech Republic. A factor of 60 separates the highest and lowest PCB concentrations found. Elevated concentrations in Eastern Europe could reflect the fact that PCB production and use stopped somewhat later in this region than the rest of Europe (Calamari *et al.* 1991, Ockenden *et al.* 1998). Our only sample from North Africa (Tunisia) also contained elevated PCB concentrations of 11,810 pg/g, again possibly reflecting a more recent cessation of production and/or use in this country. Higher levels in some countries might also relate to greater losses from aging or obsolete electrical equipment of from hazardous waste repositories. It should be noted, however, that data for single samples only were available for the Czech Republic and Tunisia.

Overall, European butter samples contained consistently higher concentrations than samples from the US. Samples from the Southern Hemisphere consistently contained the lowest PCB concentrations. These trends are consistent with those observed for surface soils (Ockenden *et al.* 1999).

Within-country variability in PCB concentrations was quite high, particularly for the larger countries, reflecting large differences in urbanization and industrialization within broad geographical regions. For example, ∑PCB ranges for Brazil (n=4) were 380-1680 pg/g, for Australia (n=5) 230-1870 pg/g, for Canada (n=6) 460-3810 pg/g and for the USA (n =18) 410-3490 pg/g. Butter from the U.S. east coast contained higher PCB concentrations than samples collected from the west coast or the mid-west – presumably reflecting the greater industrial activity and population density of the east coast states. The geographical variability found in this study is supported by a national survey of milk carried out by Lorber *et al.* (1998) in the US. Highest TEQ values in this survey occurred in milk from the more urban southeast than the rural southwest.

4.2 The organochlorine pesticides

4.2.1 DDT and its breakdown products

∑DDT (p,p’-DDT, o,p’-DDT, p,p’-DDE and p,p’-DDT) was quantified in butter fat at concentrations between 410 and 249,000 pg/g, comprised primarily of p,p’-DDE and p,p’-DDT. Concentrations of p,p’-DDT varied enormously (over 3 orders of magnitude) between 80-25,200 pg/g, with elevated levels reflecting the significance of present use on contemporary foodchain accumulation. India had the highest p,p’-DDT concentrations in butter, presumably as a result of ongoing substantial use for malaria control. The highest DDT:DDE ratios recorded in the current study, indicative of more recent use of DDT formulations, were found in butter collected from Central/South America, India, Tunisia, Spain, a single sample from the US west coast and 2 samples from Australia, generally in line with countries where more recent or even ongoing DDT usage is known or suspected.

4.2.2 HCHs

Concentrations of the 3 isomers in butter varied markedly from country to country, with ∑HCH ranging from 310 to 222 760 pg/g. Concentrations of each isomer were highest in butter samples from India, followed by China and Spain. Again this likely reflects recent or current manufacture and/or use of HCH formulations, or possibly ongoing releases of HCH isomers from waste repositories. The $\alpha : \gamma$ HCH ratio, a indicator of current technical HCH application, was particularly high in India, China and the Philippines, implying either that technical HCH is still in use in these countries or that present concentrations are being influenced by past use of technical HCH.

4.2.3 HCB

Concentrations of HCB showed a much narrower range (i.e. a more even distribution) than observed for other OCs, with concentrations varying over a factor of ~18, between 340-6,240 pg/g. HCB is one of the most volatile POPs, similar to some of the light PCB congeners. It is therefore relatively well mixed in the atmosphere and more readily dispersed from source regions (Calamari *et al.* 1991). Some regional variation was apparent, however, with particularly high levels recorded in samples from the Czech Republic, Austria, China and Brazil.

4.3 PCDDs and PCDFs

4.3.1 Europe

Data for 17 dioxin/furan congeners are reported for all 11 samples drawn from Europe and the Mediterranean region in Table 2 (pg/g lipid). Recent data for four butters from the Freiburg region of Germany, for a single butter from the Netherlands (Malisch *et al.* 2000) and for eight butters from Spain (Ramos *et al.* 1998) are also included for comparison, along with mean values reported by Malisch (1998) for a total of 222 samples of butter collected in Germany between 1993 and 1996. Data for samples from the Americas, Asia-Pacific region and South Africa are given in Table 3. In all cases, TEQ values have been calculated on the basis of internationally accepted toxicity equivalence factors as reported by van den Berg *et al.* (1998). Wherever possible, two sets of TEQs are calculated, using standard I-TEFs and TEFs as revised by the World Health Organisation (WHO-TEQs). I-TEQs are calculated for purposes of comparison with previously published data for which congener profiles are unavailable.

With the exception of the samples from Spain, dioxin concentrations (expressed as I-TEQs) for the current sample set (0.10-1.24 pg/g lipid) were in the same range as those reported by Bluthgen *et al.* (1996) from a study of 204 butter samples from Germany in 1995 (0.28-1.19 pg/g TEQ) and by Ramos *et al.* (1998) for 8 samples from Spain (mean 1.09 pg/g). The Spanish butter included yielded dioxin concentrations well in excess of those recorded for all other samples in the current study (4.61 pg I-TEQ/g lipid), almost 4 times the next highest value recorded. The predominance of the 2,3,4,7,8-PCDF congener in this sample indicates a rather distinct source of dioxin contamination in this butter, although it is not possible to deduce anything further regarding likely origins of such contamination at this stage. Given that only one sample was analysed, of course, it is also not possible to determine whether this pattern of contamination is representative of Spanish butters in general, although the high levels and somewhat unusual profile certainly warrants further investigation.

Contamination of the butter from Germany in the current study, at 0.5 pg/g I-TEQ, was somewhat lower than the range reported by Malisch *et al.* (2000) for random butter samples collected in Germany in the same year (1.00-1.41 pg/g lipid, see Table 2). All samples were collected during the period when dioxin contaminated citrus pulp from Brazil had been incorporated into cattle feeds (Malisch 2000). The differences in levels between that for Germany in the current study and the data of Malisch *et al.* (2000) may simply reflect regional differences in the extent to which contaminated feed had been used in Germany. Much of the difference in TEQs is attributable to elevated 2,3,7,8-TCDD and 1,2,3,7,8-PCDD in the samples reported by Malisch *et al.* (2000), again indicative of a specific dioxin source. Prior to this contamination event, concentrations in German dairy products had, on average at least, been lower and decreasing over time. Average concentrations for German butter sampled over the period 1986-1991 and 1993-1995 were 1.1 pg I-TEQ/g lipid (Beck *et al.* 1992) and 0.64 pg I-TEQ/g lipid (Malisch 1998) respectively, the latter much closer to the value recorded for the single sample in the current study. Even so, the maximum I-TEQ for the 1993-1995 period was 2.00 pg/g lipid, clearly indicating significant sample-sample variation in contamination even within a relatively small country.

Relatively few data are available for other countries. Theelen *et al.* (1993) reported an average of 1.8 pg I-TEQ/g lipid for butter samples collected in the Netherlands in the early 90's, while Malisch (2000) reported 1.97 pg/g in a single sample collected from the Netherlands during the citrus pulp contamination event in 1998. The single sample from the Netherlands analysed in the current study, also collected during 1998, also yielded dioxin levels significantly above those recorded in other European samples (1.24 pg I-TEQ/g lipid). In both cases, and in common with the congener profiles for the German butters analysed by Malisch *et al.* (2000), tetra- and penta- dioxins were the greatest contributors to TEQ. This was evident also for the single sample from Italy analysed in the current study (0.87 pg I-TEQ/g lipid).

The lowest value reported for Europe was in butter from Sweden (0.10 pg I-TEQ/g lipid). Levels for Austria, Denmark, Czech Republic, Germany and UK all fell within the range 0.44-0.57 pg/g. Levels in the Italian butter (0.87 pg/g) were relatively high, though well below the range reported by Berlincioni *et al*. (1992) for three butter samples collected in Italy in the early 1990's (1.1-8.4 pg I-TEQ/g lipid). This possibly reflects a downward trend in dioxin contamination of dairy products through the decade (although Berlincioni *et al.*, 1992, note that their data may be slightly overestimated). In the UK, mean levels for dairy products (including butter) have been reported to have fallen from 3.4 pg/g lipid in 1982 to 0.75 pg/g lipid in 1992 (MAFF 1997). The level in the UK butter in the current study (0.57 pg I-TEQ/g lipid) appears consistent with such a trend.

The single sample analysed in this study from the Czech Republic appears to provide the first data regarding butter contamination from this region (0.58 pg I-TEQ/g lipid). Slightly lower values were reported by Maystrenko *et al.* (1998) for butter samples collected in the Republic of Bashkortostan (Russian Federation) in 1996 (mean 0.43 pg I-TEQ/g lipid). Overall, however, very few data are available on levels of dioxins in any matrices in Eastern Europe and the Rusian Federation.

4.3.2 Eastern Mediterranean

Samples from Israel and Tunisia yielded dioxin concentrations of a similar order to those recorded in the majority of European butters, perhaps reflecting the significant degree of industrialisation of these nations. The Israeli butter contained especially high levels of hepta- and octa-chlorinated dioxins. Again few other data are available for comparison, although much higher values were reported by Rainer and Magdi (1996) for butters from various regions of Egypt (mean 7.69 pg I-TEQ/g lipid). A key feature of the data in this latter study, however, was substantial regional variation within Egypt. The potential significance of this cannot be determined in the current study, given the single samples available in each case, but nevertheless should not be underestimated.

Calculation of TEQs on the basis of the revised WHO-TEFs (Table 2) yield slightly higher values for the majority of samples both for the current study and for those data reported by Malisch (1998), Malisch (2000) and Malisch *et al.* (2000). Nevertheless, comparison of the WHO-TEQs which result reveal much the same trends.

4.3.3 Americas

Both I-TEQs and WHO-TEQs fell within a more restricted, and slightly lower, range in samples from North and South America (e.g. 0.20-0.53 pg I-TEQ/g lipid) compared to those from Europe (Table 3). Highest and lowest dioxin levels for this region corresponded to the two butters from USA, again illustrating the significance of regional variation within countries. Butters from Mexico, Argentina and Brazil contained dioxins at levels on a par with those in the US and Canadian butters. Although these concentrations were not amongst the highest recorded worldwide, they may well, nevertheless, reflect the increasingly industrialised nature of these Latin American nations. The dioxin congener profile of the Mexican butter showed some similarities to those for the two US butters, with notably high concentrations of hepta- and octa-chlorinated dioxins.

4.3.4 Asia-Pacific (and South Africa)

The range of dioxin concentrations recorded was somewhat greater across the Asia-Pacific region, with relatively low levels in butters from the Philippines and Thailand (0.09 and 0.13 pg I-TEQ/g lipid respectively) and relatively high concentrations in those from India and China (0.69 and 0.90 pg/g respectively). Although all four countries support a variety of industrial activities, the differences in butter contamination may reflect a greater extent of industrialisation in India and China than in the other parts of Asia sampled. Clearly it is not possible to speculate further on temporal and spatial trends in this region on the basis of available data. What is clear, however, is that levels of dioxin contamination in butters from both India and China were higher than those determined for many of the European butters (see above) and for the samples from Australia (0.44 pg/g) and Japan (0.33 pg/g). Lower levels in these latter two industrialised nations may result from greater investment in pollution abatement technologies, particularly in comparison with the rapidly industrialising nations.

The butter from New Zealand contained only 4 of the 17 dioxin/furan congeners quantified at levels above limits of detection. Those residues determined did not give rise to a significant TEQ value, in common with the generally low levels reported for the other POPs measured (PCBs and pesticide residues) in that butter. The butter from South Africa contained detectable levels of dioxins, though at 0.15 pg I-TEQ/g lipid, within the lower range recorded worldwide.

4.3.5 Dioxin/furan congener profiles

Dioxin/furan congener profiles for many of the samples included in the current study shared some characteristics with those reported by Malisch (1998) for butters collected from Germany between 1993 and 1996 (Table 4). Somewhat less similarity was apparent, however, to those profiles reported by Malisch (2000) and Malisch *et al.* (2000) for butters from Germany and the Netherlands collected in 1998. In the latter cases, the consistent differences may reflect the specific profile of the contamination of the citrus pulp which likely contributed to the dioxin burden of the butters from Germany and the Netherlands (Table 4). For example, concentrations of 2,3,7,8-TCDD and 1,2,3,7,8-PCDD were notably higher in the 1998 German and Dutch samples than in the majority of those included in the current study. The butter from the Netherlands (B8001) was a notable exception (see Table 2), perhaps also reflecting a contaminated feed source. Although mean I-TEQs for the eight Spanish butters analysed by Ramos *et al.* (1998) were substantially lower than that recorded for Spain in the current study, congener profiles illustrate much higher concentrations of OCDD and OCDF in those butters (Table 4) than in the single Spanish sample included in the current study.

In the current study, relatively high concentrations of HpCDD were recorded in butters from Mexico, USA and Israel, and of OCDD for Mexico, USA, Israel, China, India and Australia, suggestive of similar sources in these samples. Further analysis of congener profiles for the samples from Europe, the Americas and the Asia-Pacific region will be presented in a subsequent paper, and may give further insight into local and regional patterns and might yield valuable information with regard to the identification of possible sources in each case.

4.3.6 Non-*ortho* PCBs

Including non-*ortho* PCBs into the calculation of WHO-TEQs has a marked effect on overall TEQs for some samples (including those from the Czech Republic, Germany, Tunisia and Argentina), and relatively little impact on TEQ for other samples (including Spain, Mexico, USA and the

Philippines), in which dioxins/furans accounted for by far the greater contribution (Table 5, Figures 1-3). In the case of the Czech Republic, non-*ortho* PCB concentrations (as WHO-TEQs) were almost three times higher than dioxin/furan TEQs (Figure 1), as may be expected from the relatively high PCB concentrations determined by Kalantzi *et al.* (2000) for these samples. Similarly for the Tunisian butter, non-*ortho* PCBs contributed substantially to TEQ.

Combined WHO-TEQs (dioxins/furans and non-*ortho* PCBs) were highest for Spain (5.54 pg WHO-TEQ/g lipid), largely because of the high contribution from dioxins. As a result of contributions from the non-*ortho* PCBs, however, these high levels were also approached by the Tunisian butter (3.49 pg/g) and to a lesser extent by butters from the Czech Republic, Germany, Italy and the Netherlands. Countries from other regions showing relatively high combined TEQs included Argentina, China and India (Table 4). Lowest concentrations were again recorded for the samples from New Zealand (0.07 pg WHO-TEQ/g lipid) and the Philippines (0.10 pg/g lipid). Within Europe, lowest values corresponded to butters from Sweden and Denmark (0.71 and 0.89 pg/g respectively).

5. Conclusions

On the basis of results presented for PCBs and pesticide residues in butter, and their general reflection of known global patterns of contaminant distribution, Kalantzi *et al.* (2000) conclude that butter may provide a convenient matrix with which to monitor such spatial and temporal trends of POPs. These authors stress, however, a number of factors which are likely to exert a significant influence on the validity of this conclusion by affecting the manner in which contaminant levels in butter lipid relate to rates of deposition of contaminants on pastureland.

Overall, European butter samples contained consistently higher concentrations than samples from the US. Samples from the Southern Hemisphere consistently contained the lowest PCB concentrations. Within Europe, particularly high values were recorded in butter from the Czech Republic, which may reflect relatively recent use of PCB formulations, substantial ongoing generation as byproducts from industrial processes, or generally high levels of environmental contamination resulting from historic or ongoing uncontrolled releases.

Within individual countries, particularly large countries, PCB levels showed substantial variation from butter to butter, probably reflecting relative proximity of source regions of butter to centres of population and industrial activity. Nevertheless, it was evident on a global basis that highest PCB concentrations were generally found in butter samples collected from temperate latitudes in the Northern Hemisphere.

Levels of pesticide residues in butter also showed trends which may be expected from existing knowledge relating to ongoing use and/or historical contamination. Levels of DDT were particularly high in butter samples from India. Ratios of DDT:DDE were notably high in India and in Central and South America, indicative of more recent or contemporary use of DDT formulations (probably for malaria vector control) in these areas. Butter samples from India also yielded the highest levels of HCH contamination, along with samples from China and Spain. Moreover, high $\alpha : \gamma$ HCH ratios are suggestive of a greater use of technical HCH grades, as opposed to lindane, in India, China and the Philippines. The relative propensity of α and β isomers in these regions could also result from releases from wastes arising from the manufacture and purification of lindane (the γ isomer), however.

Concentrations of dioxins/furans in the majority of the butter samples analysed fell within a similar range to those commonly reported for European butters. The Spanish butter was a notable exception, showing dioxin levels substantially in excess of those in butters from other European countries. Interpretation of the data in terms of regional variations are somewhat limited, of course, by the inclusion of only a single sample for all but one of the 24 countries. It is not possible, for example, to state conclusively that the concentrations determined represent an average level for each of the countries included in the study. Substantial regional variation in contamination levels may clearly be expected within countries, dependent on proximity of the butter's source region to centres of population and industrial development in each case. Nevertheless, some interesting differences are apparent from the data available and would seem to justify further study.

Proportional contributions of non-*ortho* PCBs to combined WHO-TEQ were by far the greatest in the Tunisian and Czech butters, as may be expected from the relatively high total PCB concentrations determined for these samples. Again potential local sources of PCBs deserve investigation, but the exceptional contribution from the PCBs possibly reflects historical or contemporary industrial sources.

In relation to the Americas, both highest and lowest dioxin TEQs were recorded for samples from the US, though significant levels were also found in butters from Mexico, Argentina and Brazil. Including non-*ortho* PCBs, the highest TEQ for the Americas was recorded for the Argentinean butter, with lower values for the other countries in the region. Possible regional sources of PCBs clearly deserve further investigation.

Samples of butter drawn from Asia showed markedly different levels of dioxin and non-*ortho* PCB contamination depending on origin. Butters from India and China contained dioxins at levels similar to the more contaminated samples from Europe, though substantially below those for the Spanish butter sampled. Other Asian butters, specifically those from Thailand and the Philippines, contained among the lowest levels recorded in the current study. While the Australian butter yielded dioxin concentrations of a similar order to those from many European countries, dioxins in the butter from New Zealand did not give rise to a significant TEQ.

The differences apparent in the data set with respect to total concentrations and congener profiles clearly warrant further investigation on an individual country basis. Nevertheless, as Kalantzi *et al.* (2000) note, the results of this global survey indicate the utility of butter as a representative matrix for use in the monitoring of spatial and perhaps temporal trends in the distribution of persistent organic pollutants (POPs).

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	Sum PCB	Sum DDT	SumHCH	HCB
Austria (n = 1)				
Mean	6810	1540	3480	5070
Range	-	-	-	-
Australia (n = 5)				
Mean	740	5960	310	600
Range	230-1870	1440-13780	0-860	410-920
Brazil (n = 4)				
Mean	1060	4250	2330	520
Range	380-1680	1330-10000	840-4830	340-900
Canada (n = 6)				
Mean	1680	5770	1210	980
Range	460-3810	380-16920	130-2100	810-1220
China (n=1)				
Mean	1790	41490	36100	6150
Range	-	-	-	-
Czech Republic (n = 1)				
Mean	14090	17280	1770	6240
Range	-	-	-	-
Denmark (n = 2)				
Mean	3050	2380	680	2555
Range	2840-3250	1930-2820	0-1350	-
Germany (n = 1)				
Mean	8740	1690	nd	3278
Range	-	-	-	-
India (n = 1)				
Mean	4510	248880	222760	630
Range	-	-	-	-
Israel (n = 1)				
Mean	3570	20890	3590	1000
Range	-	-	-	-
Italy (n = 1)				
Mean	7660	5070	nd	4715
Range	-	-	-	-
Japan (n = 1)				
Mean	600	2970	2840	1720
Range	-	-	-	-
Mexico (n = 3)				
Mean	1180	101220	2860	1110
Range	670-1580	10330-178590	1580-3690	420-1880

Table 1: Concentrations of selected PCB congeners and organochlorine pesticides in the butter samples (pg/g lipid): page 1 of 2

	Sum PCB	Sum DDT	SumHCH	HCB
Philippines (n = 2)				
Mean	520	71290	910	920
Range	470-570	7780-134790	340-1490	600-1240
S. Africa (n = 2)				
Mean	4160	4020	2480	720
Range	-	1730-6310	1840-3120	-
Spain (n = 3)				
Mean	5470	4920	19070	2630
Range	4380-6230	4160-6220	11610-32550	2540-2740
Sweden (n = 3)				
Mean	3610	3630	1610	1380
Range	3030-3920	1300-7010	1220-2200	830-1700
Thailand (n = 1)				
Mean	1210	3950	2490	830
Range	-	-	-	-
Netherlands (n = 1)				
Mean	5620	11470	4010	3200
Range	-	-	-	-
New Zealand (n = 1)				
Mean	230	97710	600	640
Range	-	-	-	-
Tunisia (n = 1)				
Mean	11810	7800	6410	2340
Range	-	-	-	-
UK (n = 2)				
Mean	3370	2390	3860	2120
Range	2830-3910	2110-2670	2210-5520	1580-2660
USA (n = 18)				
Mean	2250	23610	1330	900
Range	410-3490	410-141260	0-2170	690-1390

Table 1 (cont.): Concentrations of selected PCB congeners and organochlorine pesticides in the butter samples (pg/g lipid): page 2 of 2

Country of origin	Austria	Czech Rep.	Denmark	Germany	Italy	Netherlands	Spain	Sweden	UK	Israel	Tunisia	Germany 1998[1]	Netherlands 1998[2]	Spain 1998[3]	Germany 1993-1996[4]
Sample code	**B8018**	**B8061**	**B8058**	**B8064**	**B8034**	**B8001**	**B8019**	**B8011**	**B8115**	**B8005**	**B8037**	**Range of 4 samples**	**Single sample**	**Range of 8 samples**	**Mean of 222 samples**
Dioxins															
2,3,7,8-TCDD	0.07	0.08	0.11	0.07	0.25	0.43	0.20	<0.05	0.09	0.05	0.12	0.36-0.62	0.9	nd-1.11	0.08
1,2,3,7,8-PCDD	0.21	0.15	0.17	0.14	0.31	0.43	0.39	<0.04	0.36	0.13	0.31	0.37-0.52	0.64	nd-1.08	0.21
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	0.13	0.09	0.11-0.14	0.19	nd-1.63	0.14
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	0.67	0.29	0.26-0.36	0.31	nd-1.33	0.36
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	0.18	0.12	0.11-0.13	0.14	nd-0.67	0.15
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	**2.55**	0.63	0.41-0.79	0.42	0.58-3.09	0.69
OCDD	1.14	0.54	0.45	0.36	0.66	0.64	0.27	0.27	0.47	**2.1**	1.10	0.59-0.84	0.45	1.35-26.6	1.37
Furans															
2,3,7,8-TCDF	0.04	<0.02	0.03	<0.04	0.05	<0.04	0.41	<0.04	0.04	<0.02	0.05	0.05-0.06	0.08	nq-0.75	0.04
1,2,3,7,8-PCDF	<0.02	0.03	<0.02	<0.04	0.05	0.04	0.21	<0.04	0.04	0.04	0.06	0.05-0.06	0.06	nq-0.32	0.03
2,3,4,7,8-PCDF	0.35	0.63	0.33	0.50	0.56	0.78	7.73	0.15	0.34	0.24	0.63	0.54-0.70	0.98	nd-2.06	0.59
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	0.29	0.35	0.40-0.59	0.7	nq-0.93	0.29
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	0.21	0.32	0.25-0.35	0.53	nq-0.94	0.25
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	0.15	<0.01	0.34-0.49	0.51	nq-1.27	0.23
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	<0.01	0.27	<0.05	<0.03	nq-3.10	0.01
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	0.4	0.21	0.27-0.42	0.31	nq-1.33	0.17
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	0.05	<0.02	0.06-0.09	0.05	nd-0.63	0.02
OCDF	0.10	0.05	<0.06	<0.06	0.19	0.31	0.07	<0.06	<0.06	0.11	<0.06	0.28-0.50	0.16	nd-3.18	0.09
WHO-TEQ	**0.55**	**0.66**	**0.52**	**0.57**	**1.03**	**1.46**	**4.80**	**0.10**	**0.75**	**0.50**	**0.91**	**1.18-1.67**	**2.29**	**-**	**-**
I-TEQ	**0.45**	**0.58**	**0.44**	**0.50**	**0.87**	**1.24**	**4.61**	**0.10**	**0.57**	**0.43**	**0.75**	**1.00-1.41**	**1.97**	**1.09**	**0.64**

Table 2. Congener-specific concentrations of dioxins and furans for individual butter samples from nine European and two Mediterranean countries, compared to data reported for samples from Germany, the Netherlands and Spain by Malisch *et al.* (2000)[1], Malisch (2000)[2], Ramos *et al.* (1999)[3] and Malisch (1998)[4]. nd – not detected; nq – not quantified (detected but at below limits of quantification, i.e. <3 x limit of detection)

	AMERICAS						ASIA-PACIFIC & SOUTH AFRICA							
Country of origin	**Argentina**	**Brazil**	**Mexico**	**USA#1**	**USA#2**	**Canada**	**China**	**India**	**Japan**	**Philippines**	**Thailand**	**Australia**	**New Zealand**	**South Africa**
Sample code	**MI8052**	**B8027**	**B8008**	**B8044**	**B8056**	**B8106**	**B8023**	**B8042**	**B8073a**	**B8068**	**B8071**	**B8077**	**B8067**	**B8105**
Dioxins														
2,3,7,8-TCDD	<0.02	<0.02	0.06	<0.02	0.06	<0.05	0.08	0.11	0.05	0.05	<0.05	0.13	<0.02	<0.02
1,2,3,7,8-PCDD	0.09	0.11	0.14	0.1	0.19	0.14	0.23	0.2	0.13	<0.02	0.08	0.25	<0.02	0.07
1,2,3,4,7,8-HCDD	0.03	<0.01	0.09	0.13	0.18	0.10	0.09	0.07	0.05	0.06	<0.03	0.16	<0.02	0.03
1,2,3,6,7,8-HCDD	0.14	0.12	0.54	0.4	0.89	0.27	0.27	0.25	0.11	0.16	0.09	0.28	<0.02	0.11
1,2,3,7,8,9-HCDD	0.05	0.06	0.17	0.2	0.24	0.11	0.10	0.09	0.09	0.07	0.05	0.21	<0.01	0.06
1,2,3,4,6,7,8-HpCDD	0.09	0.29	**3.04**	**1.77**	**2.96**	0.54	0.52	0.72	0.15	0.25	0.17	0.84	0.09	0.33
OCDD	0.22	0.48	**4.07**	**1.74**	**3.19**	0.32	**3.14**	**1.7**	0.19	0.68	0.90	**2.9**	0.41	0.77
Furans														
2,3,7,8-TCDF	<0.02	0.1	0.07	<0.02	<0.04	<0.04	0.06	0.13	0.36	<0.02	<0.04	0.05	<0.02	<0.02
1,2,3,7,8-PCDF	0.03	<0.01	<0.01	<0.01	<0.04	<0.04	0.07	0.09	<0.02	<0.01	<0.04	<0.01	<0.02	<0.01
2,3,4,7,8-PCDF	0.33	0.19	0.28	0.07	0.13	0.14	0.94	0.67	0.24	<0.01	0.11	0.19	<0.01	0.12
1,2,3,4,7,8-HCDF	0.19	0.11	0.17	<0.01	0.24	0.11	0.69	0.31	0.12	<0.01	0.05	<0.01	<0.02	0.12
1,2,3,6,7,8-HCDF	0.15	0.09	0.09	0.1	0.13	0.09	0.53	0.26	0.12	<0.01	0.04	<0.01	<0.02	0.08
2,3,4,6,7,8-HCDF	0.22	0.08	0.11	0.09	<0.01	<0.01	<0.01	0.2	<0.02	0.05	<0.01	0.06	<0.02	0.07
1,2,3,7,8,9-HCDF	<0.01	<0.01	<0.01	<0.01	0.12	0.08	0.41	<0.01	0.11	<0.01	0.04	<0.01	<0.02	0.02
1,2,3,4,6,7,8-HpCDF	0.11	<0.01	0.22	0.33	0.48	0.12	0.32	0.25	0.08	0.08	0.09	0.05	0.04	0.09
1,2,3,4,7,8,9-HpCDF	0.02	<0.01	0.04	0.05	0.04	<0.02	0.04	<0.01	<0.01	<0.01	<0.02	<0.01	<0.01	<0.01
OCDF	0.02	0.05	0.07	0.11	0.17	<0.06	0.19	0.13	<0.06	0.05	0.22	0.04	0.08	0.04
WHO-TEQ	**0.34**	**0.26**	**0.50**	**0.25**	**0.44**	**0.22**	**1.01**	**0.79**	**0.40**	**0.09**	**0.16**	**0.56**	**<0.01**	**0.18**
I-TEQ	**0.29**	**0.21**	**0.43**	**0.20**	**0.53**	**0.29**	**0.90**	**0.69**	**0.33**	**0.09**	**0.13**	**0.44**	**<0.01**	**0.15**

Table 3. Congener-specific concentrations of dioxins and furans for butter samples from five countries of the Americas (North and South), seven countries of the Asia-Pacific region and South Africa.

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

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

	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
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 5: summary of contributions from dioxins/furans and non-*ortho*-PCBs to total WHO-TEQs for all 25 samples

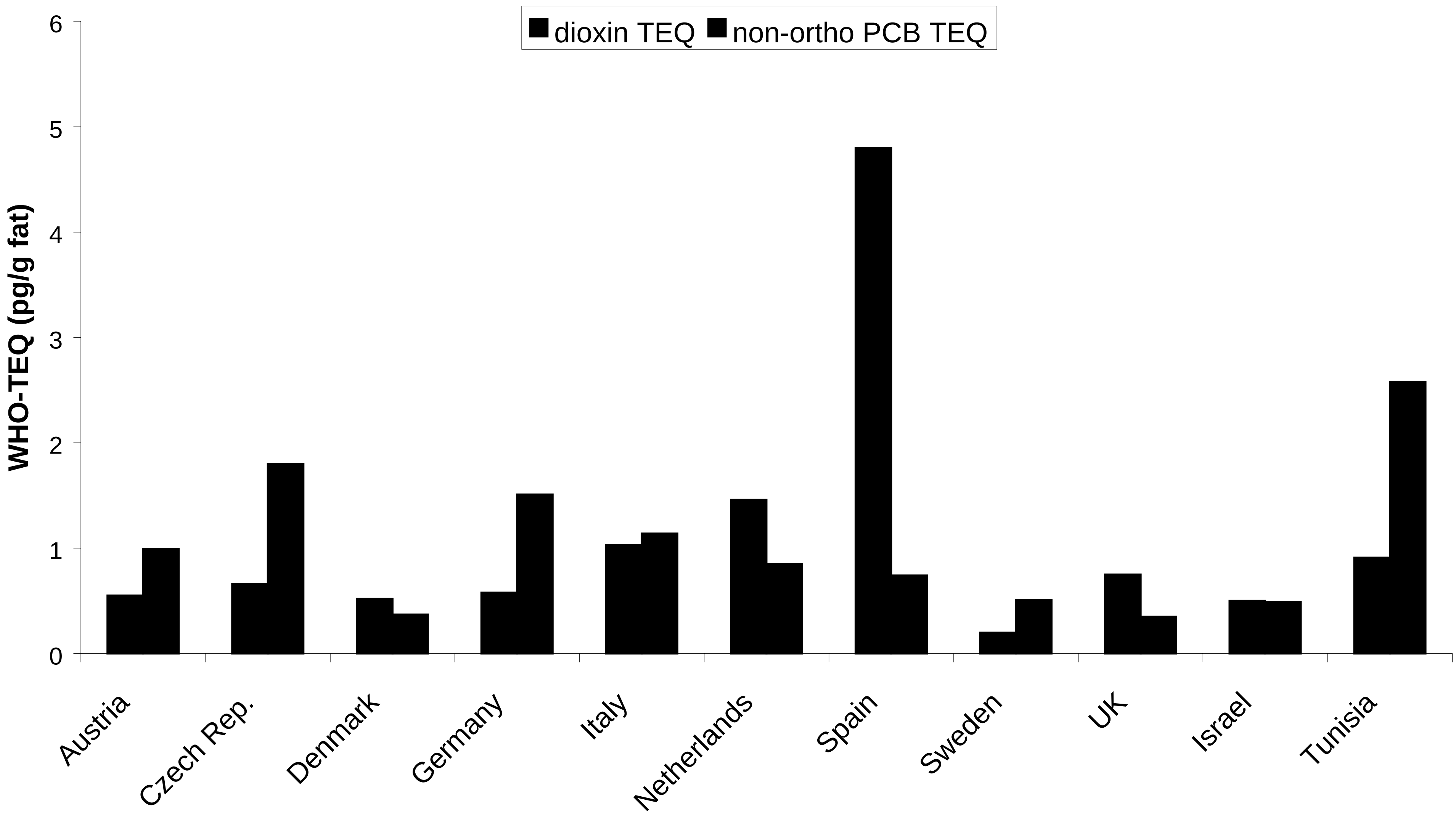

Figure 1. Contribution from dioxins/furans and non-*ortho* PCBs to total WHO-TEQs for the 11 samples from Europe and the Mediterranean.

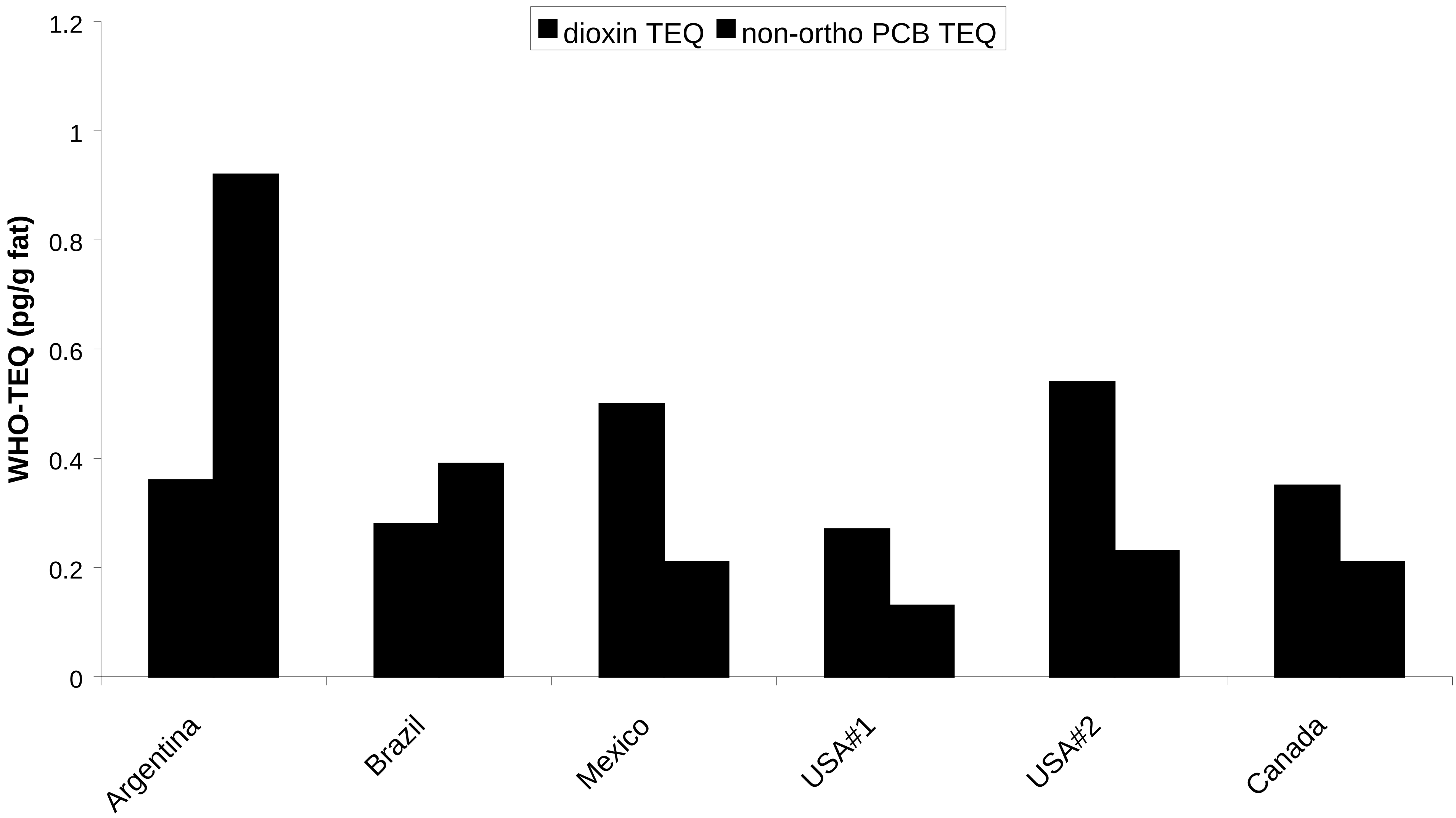

Figure 2. Contribution from dioxins/furans and non-*ortho* PCBs to total WHO-TEQs for the 6 samples from the Americas.

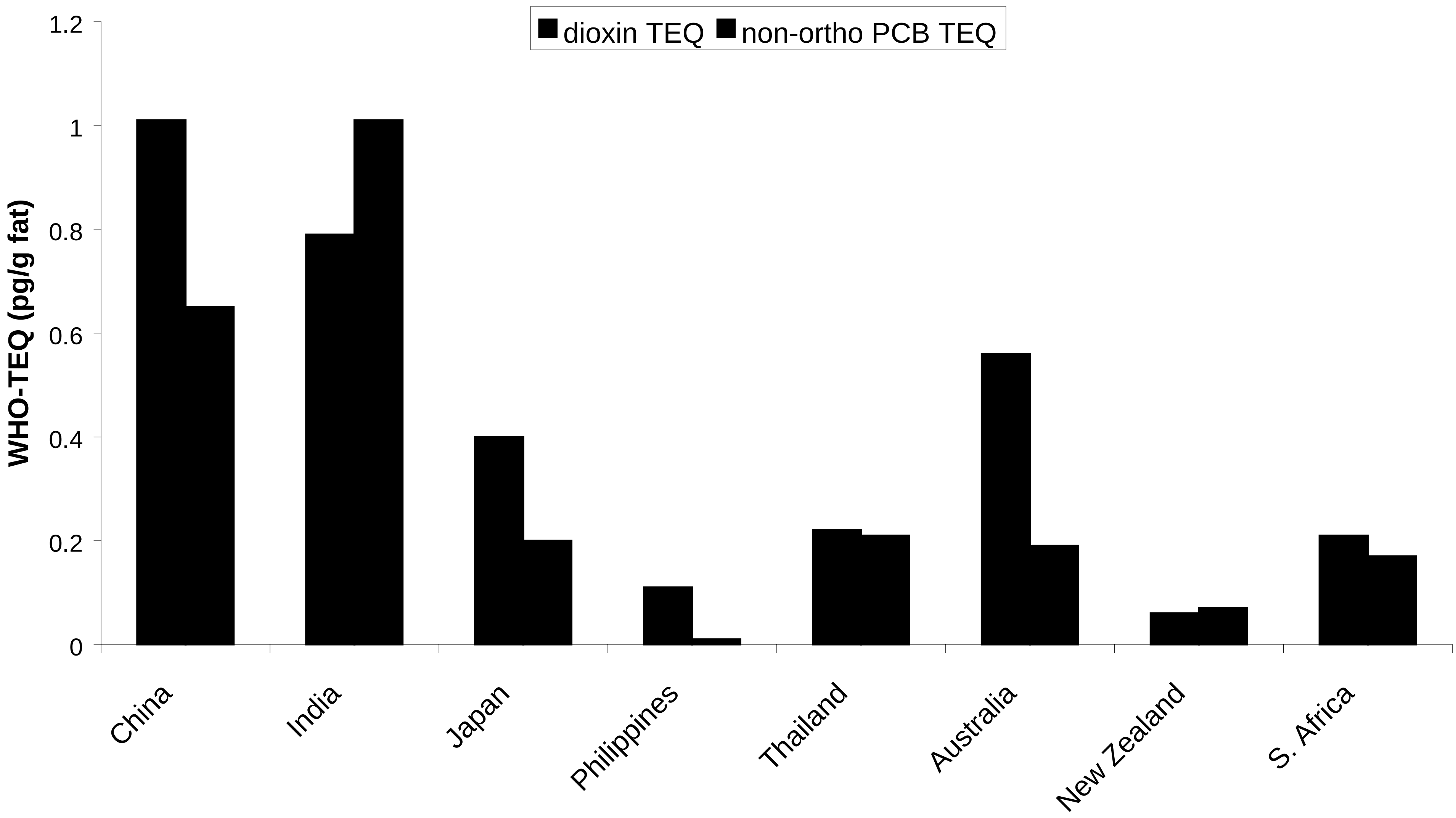

Figure 3. Contribution from dioxins/furans and non-*ortho* PCBs to total WHO-TEQs for the 7 samples from the Asia-Pacific region, plus the single sample from South Africa.