

# The Global Distribution of PCBs and Organochlorine Pesticides in Butter

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In this study we explored the use of butter as a sampling matrix to reflect the regional and global scale distribution of PCBs and selected organochlorine pesticides/metabolites in air. This was because persistent organic pollutants (POPs) concentrate in dairy fats, where concentrations are controlled by feed intake (primarily from pasture/silage), which is in turn primarily controlled by atmospheric deposition. Butter  $\Sigma$ PCB concentrations varied by a factor of  $\sim 60$  in 63 samples from 23 countries. 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. Concentrations in butter reflected differences in the propensity of PCB congeners to undergo long range atmospheric transport from global source regions to remote areas and the relatively even distribution of HCB 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). We conclude 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.

## Introduction

"Persistent organic pollutants" (POPs) are compounds which, because of their vapor pressures and partitioning behavior under ambient conditions, are persistent and mobile in the environment and bioaccumulate in foodchains (1). Concern about their potential toxicity, propensity for long-range atmospheric transport (LRAT), and the suggestion that they may undergo global scale redistribution (1, 2) to condense and accumulate in colder regions has resulted in international measures to ban or restrict the use and/or release of POPs (1-3). To test the current theories on global distillation and

cold condensation of POPs (2, 4) and to obtain input data for regional/global models of their fate (e.g. refs 5-7), it is necessary to have data on their atmospheric distribution. Ideally, this should relate to samples taken in different parts of the world simultaneously and analyzed by a standardized procedure (2, 4), to help overcome the natural variability which affects air concentrations and systematic differences between the analytical procedures of different laboratories. However, making direct measurements of air concentrations in several parts of the world simultaneously would require a huge financial outlay on active air sampling equipment and presents major logistical problems. There is, therefore, considerable incentive to devise a sampling strategy which allows "indirect" measures of air concentrations to be made. Furthermore, the current development of a United Nations Environment Program protocol to control POPs (3) highlights the need to develop reliable monitoring programs and data sets with which to assess the effectiveness of global source reduction measures and to observe their decline in the environment. Possibilities include the development, validation, and deployment of a reliable and robust passive air sampling technique (e.g. refs 8 and 9) or the use of surrogate measures of air concentrations. An example which falls into the latter category is the collection and analysis of vegetation samples, such as pine needles or tree bark (10-12), but this approach is hampered by species differences and other confounding factors which can make data interpretation difficult (13).

As another possible sampling medium, we wished to test the use of butter to assess the regional/global scale distribution of POPs. Dairy products have been used previously to assess local and regional variability in POP residue contamination, for example in Mexico (14), Spain (15, 16), Austria (17), Slovakia (18), the U.K. (19), and the U.S. (20). As a global sampling medium we reasoned that (1) POPs are lipophilic and accumulate in butter, which is typically  $\sim 80\%$  fat. This makes detection and analysis relatively straightforward. (2) It is known from detailed studies that milk fat concentrations are controlled by the cow's feed intake. Grazing dairy cows predominantly feed on herbage, and the POP concentrations of herbage are, in turn, controlled by atmospheric deposition (21-28). (3) Air-milk fat transfer factors (with the units  $m^3$  air/g lipid) have been measured and reported for some POPs (e.g. ref 27). Once these are known and defined, it becomes possible to estimate air concentrations supplying the dairy foodchain. (4) Because cows ingest large quantities of herbage (typically 12 kg dry matter/day) and milk from a herd is thoroughly mixed at the farm and dairy, milk fat provides an excellent medium for integrating the loading in air. For example, 1 g of milk fat contains the equivalent mass of PCB-170 as  $650 m^3$  air, and under typical U.K. conditions a cow yields 100 g milk fat/day. (5) Butter can be easily obtained, sampled, and stored. (6) Finally, human exposure to POPs in typical western diets is strongly influenced (and often dominated) by ingestion of milk, meat, and dairy products (29). Hence, butter concentrations can also provide data of interest from an exposure perspective.

Butter samples were therefore obtained from different countries around the world and analyzed for PCBs and selected organochlorine pesticides and breakdown products (HCHs, HCB, DDT, DDE, DDD, and chlordane) in this study. The data are discussed here in the context of regional/global usage of these POPs and their global distribution, fate, and transport. We also comment further on the usefulness of butter as a sampling medium which provides an integrated surrogate of air concentrations.

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## Materials and Methods

Commercial butter samples were collected from 22 different countries during the latter part of 1998 and early 1999, from shops in their respective country of origin and delivered frozen to Lancaster University. Care was taken to ensure that the butter samples were prepared from milk from the country of origin and not from imported milk. Samples 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 (2), S. Africa (2), Spain (3), Sweden (3), Thailand (1), Netherlands (1), New Zealand (1), Tunisia (1), U.K. (2), and U.S.A. (18). A total of 63 samples were therefore analyzed. The samples were stored at  $-20^{\circ}\text{C}$  until their analysis.

The extraction method used was based on a previously tested and validated PCB method (30). However, the second stage of the cleanup procedure was altered 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 sulfate was added. Approximately 50 mL of hexane was added, the sample boiled for 10 min and then cooled, and a subsample was taken for fat determination. The remaining sample was spiked with recovery standards and evaporated to approximately 5 mL. It was then applied to a 25 mm i.d. column containing 15 g of acidified silica gel (2:1 silica gel: acid by weight) and eluted with 150 mL of hexane. It was then evaporated to 1 mL under a gentle stream of nitrogen and applied to a silica fractionation column (9 mm id), packed with 3 g of silica (activated at  $350^{\circ}\text{C}$ ). The sample was eluted with 33 mL of hexane (for PCBs) and 15 mL of hexane:DCM (1:1) (for OC pesticides). Fifty microliters of dodecane containing internal standards was added to both fractions, and the samples were reduced to 50  $\mu\text{L}$  and analyzed by GC-MS.

All solvents used were of HPLC or glass-distilled grade. Silica gel (Merck, 0.063–0.200 mm) was activated at  $450^{\circ}\text{C}$  overnight for the acid silica chromatography and at  $350^{\circ}\text{C}$  overnight for the silica fractionation chromatography. The latter was then stored at  $125^{\circ}\text{C}$  until use. Sodium sulfate was baked at  $450^{\circ}\text{C}$  overnight, and all sorbents were stored in sealed containers in a desiccator after activation.

Gas chromatography was performed on a Fisons GC8000 series gas chromatograph equipped with a 50 m CPSil8 0.25 mm i.d. capillary column (Chrompak), fitted with a retention gap (2 m long, 0.53 mm i.d. FSOT column with a methyl stationary phase). Two microliters of sample was injected by a Fisons AS800 autoinjector, with the injection port at  $250^{\circ}\text{C}$  in splitless mode. Carrier gas was helium, and the flow rate 1 mL/min. The oven program was as follows:  $100^{\circ}\text{C}$  for 2 min,  $20^{\circ}\text{C min}^{-1}$  to  $140^{\circ}\text{C}$ ,  $4^{\circ}\text{C min}^{-1}$  to  $200^{\circ}\text{C}$ ,  $200^{\circ}\text{C}$  for 13 min,  $4^{\circ}\text{C min}^{-1}$  to  $300^{\circ}\text{C}$ ,  $300^{\circ}\text{C}$  for 10 min. The quadrupole MS was set in selected ion recording mode (SIR or SIM), with an EI+ source, a source temperature of  $250^{\circ}\text{C}$ , interface temperature of  $300^{\circ}\text{C}$ , and electron energy of 70 eV. The instrument was tuned on PFTBA. The following PCB congeners were screened (those italicized were regularly detected): PCB 18, 31, 28, 52, 49, 41/64, 74, 70, 99, 123, 118, 114, 105, 149, 153, 138, 183, 180, 170, 203.

## Results and Discussion

**PCBs. General Comments on Congener Composition.** Table 1 shows mean concentrations and ranges for  $\Sigma\text{PCB}$  and selected individual PCB congeners (28, 52, 118, 105, 153, 138, 180, and 170) for each country. As expected, congeners PCB-138, PCB-153, PCB-180, and PCB-118 were the most abundant in the butter samples, followed by PCB-170, PCB-99, PCB-74, and PCB-152 (in decreasing order of abundance). This

mixture has been noted previously and reflects the fact that 4,4'-chlorine substitution confers resistance to metabolism in mammalian systems (21, 26). It is also noteworthy that some of the tri- and tetrachlorinated congeners (PCB-18, PCB-31, PCB-28, and PCB-49) and some of the higher chlorinated ones (PCB-105 and PCB-149) were detected only at very low levels, close to the method detection limit. These congeners are known to be relatively easily metabolized by cows (21, 26).

**General Comments on the Levels.**  $\Sigma\text{PCB}$  concentrations in the butter samples varied between 230 and 14 100 pg/g, with the lowest in the samples from Australia/New Zealand and the highest in the sample from the Czech Republic, a factor of 60 difference between the highest and lowest samples. 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 (9, 10). Our only sample from North Africa (Tunisia) also contained elevated PCB concentrations of 11 800 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 or from hazardous waste repositories. Overall, European butter samples contained consistently higher concentrations than samples from the U.S. Samples from the Southern Hemisphere consistently contained the lowest PCB concentrations. These trends are consistent with those observed for surface soils (31).

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,  $\Sigma\text{PCB}$  ranges for Brazil ( $n = 4$ ) were 380–1700 pg/g, for Australia ( $n = 5$ ) 230–1900 pg/g, for Canada ( $n = 6$ ) 460–3800 pg/g, and for the U.S.A. ( $n = 18$ ) 410–3500 pg/g. Butter from the U.S. east coast contained higher PCB concentrations than samples collected from the west coast or the Midwest—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 in the U.S. (20). Highest TEQ values in this survey occurred in milk from the more urban southeast than the rural southwest. A recent survey of butter samples from Spain ( $n = 36$ ) also found a high degree of variability in PCBs concentrations between regions, with levels ranging from 0.75 to 150 ng/g wet weight (15).

There is evidence that concentrations of PCBs in butter and dairy products have been declining significantly in Europe since the early 1980s (17, 32), in line with observations from several different environmental media (29). For example, our data for German butter (8740 pg/g fat) was much lower than that reported by Furst (mean = 31 800 pg/g) in the early 1990s (33). Similarly, our Spanish data (4400–6200 pg/g) was significantly lower than that reported in the early 1990s (34). These observations reflect the declines in regional air concentrations over the last couple of decades (35, 36).

**Variations in Congener Composition and a Consideration of Global Distribution Processes.** Wide variations in PCB concentrations are also reflected in the congener composition of individual samples. Figure 1 illustrates this point, showing spatial differences and variations with latitude for PCB congeners 28, 74, and 138. Highest concentrations of every PCB congener analyzed were found in samples collected from northern hemisphere temperate latitudes (ca.  $30^{\circ}$ – $60^{\circ}\text{N}$ ). This is the area of the globe with the greatest historical production and use of PCBs (37). Samples from the southern hemisphere consistently contained much lower concentrations. The difference in the range of concentrations globally was greatest for the higher chlorinated congeners, as illustrated by Table 2. For example, concentrations of PCB-

TABLE 1: Concentrations of Selected PCB Congeners and Organochlorine Pesticides in butter Samples (pg/g lipid)<sup>a</sup>

	28	52	118	105	153	138	180	170	sum PCB	pp-DDT	op-DDT	pp-DDE	op-DDE	pp-DDD	op-DDD	sum DDT	a-HCH	b-HCH	g-HCH	sum HCH	HCB
<b>Austria (n = 1)</b>																					
mean	nd	20	780	110	1330	2140	830	440	6810	120	30	1340	nd	50	nd	1540	1220	350	1910	3480	5070
range																					
<b>Australia (n = 5)</b>																					
mean	50	40	120	40	110	180	140	80	740	780	180	5350	nd	180	nd	5960	60	240	260	310	600
range	40–50		70–220	30–80	40–250	70–350	30–330	20–130	230–1870	590–910	-	1440–12350	nd	70–350	nd	1440–13780	-	30–610	130–410	0–860	410–920
<b>Brazil (n = 4)</b>																					
mean	nd	nd	110	50	120	300	90	140	1060	590	nd	2980	nd	670	30	4250	nd	290	1840	2330	520
range	nd	nd	30–160	20–90	90–150	180–370	60–110	10–450	380–1680	190–1310	nd	1090–7050	nd	50–1600	20–50	1330–10000	nd	120–510	430–4480	840–4830	340–900
<b>Canada (n = 6)</b>																					
mean	80	30	360	70	190	370	120	50	1680	170	nd	5580	nd	100	nd	5770	nd	60	1020	1210	980
range	40–120	20–40	100–910	10–200	60–430	110–860	30–290	10–140	460–3810	50–450	nd	380–16820	nd	60–140	nd	380–16920	nd	20–130	480–1610	130–2100	810–1220
<b>Brazil (n = 4)</b>																					
mean	nd	nd	430	nd	220	440	150	80	1790	2440	nd	37030	170	1710	140	41490	nd	14540	2420	36100	6150
range																					
<b>Czech Republic (n = 1)</b>																					
mean	40	nd	740	110	2660	4180	3020	1330	14090	1180	nd	15660	nd	420	20	17280	490	250	1030	1770	6240
range																					
<b>Denmark (n = 2)</b>																					
mean	nd	30	390	30	490	810	310	140	3050	NA	NA	2270	NA	NA	NA	2380	NA	NA	NA	680	2555
range	nd		350–430		490–500	790–830	290–330	120–160	2840–3250	NA	NA	1720–2820	NA	NA	NA	1930–2820	NA	NA	NA	0–1350	-
<b>Germany (n = 1)</b>																					
mean	nd	20	720	60	1680	2930	1250	580	8740	NA	NA	1690	NA	NA	NA	1690	NA	NA	NA	nd	3278
range																					
<b>India (n = 1)</b>																					
mean	110	nd	890	250	390	860	270	130	4510	25230	nd	146080	80	75860	1630	248880	98040	108280	16440	222760	630
range																					
<b>Israel (n = 1)</b>																					
mean	nd	nd	800	180	400	730	350	160	3570	1260	50	19300	nd	270	nd	20890	1030	1170	1390	3590	1000
range																					
<b>Italy (n = 1)</b>																					
mean	70	34	960	160	1350	2230	1230	450	7660	NA	NA	5070	NA	NA	NA	5070	NA	NA	NA	nd	4715
range																					
<b>Japan (n = 1)</b>																					
mean	nd	nd	110	50	60	120	nd	10	600	210	nd	2650	nd	110	nd	2970	1300	910	630	2840	1720
range																					
<b>Mexico (n = 3)</b>																					
mean	30	nd	180	30	110	250	110	60	1180	1360	20	99520	nd	310	40	101220	340	1760	770	2860	1110
range	20–30	nd	90–250	20–50	60–150	140–340	70–150	50–80	670–1580	340–2030	-	9820–176520	nd	150–460	30–50	10330–178590	120–590	230–2550	470–1230	1580–3690	420–1880
<b>Philippines (n = 2)</b>																					
mean	nd	30	60	10	60	110	40	20	520	2290	100	68530	nd	420	nd	71290	740	370	170	910	920
range	-				50–60	90–120	30–50	20–30	470–570	320–4250	-	7360–129700	nd	100–740	nd	7780–134790		80–660	90–260	340–1490	600–1240
<b>S. Africa (n = 2)</b>																					
mean	nd	80	80	10	110	210	140	50	4160	920	40	5810	nd	160	nd	4020	740	1000	730	2480	720
range										380–1450	30–40		nd	80–230	nd	1730–6310	590–890	740–1270	510–960	1840–3120	
<b>Spain (n = 3)</b>																					
mean	30	nd	640	110	890	1360	1000	440	5470	700	30	3900	nd	300	nd	4920	4920	1680	12470	19070	2630
range		nd	420–940	80–160	680–1010	1090–1600	810–1190	350–490	4380–6230	600–860	30–40	3240–5070	nd	270–360	nd	4160–6220	810–12250	770–2700	9780–17600	11610–32550	2540–2740
<b>Sweden (n = 3)</b>																					
mean	50	40	410	80	580	1040	410	170	3610	270	40	3210	nd	120	40	3630	410	270	930	1610	1380
range	30–70	30–40	310–540	60–100	500–660	910–1210	380–430	80–230	3030–3920	150–340		1090–6480	nd	60–190		1300–7010	220–530	120–410	720–1320	1220–2200	830–1700
<b>Thailand (n = 1)</b>																					
mean	30	30	170	10	170	260	140	70	1210	250	60	3520	nd	120	nd	3950	200	280	2010	2490	830
range																					
<b>Netherlands (n = 1)</b>																					
mean	80	nd	770	100	960	1510	600	290	5620	2730	nd	6290	nd	2460	nd	11470	nd	340	3130	4010	3200
range																					
<b>New Zealand (n = 1)</b>																					
mean	nd	nd	40	nd	30	nd	nd	20	230	1750	nd	95450	nd	480	20	97710	nd	160	440	600	640
range																					
<b>Tunisia (n = 1)</b>																					
mean	30	nd	830	140	2440	3330	2580	1090	11810	1250	200	6110	nd	240	nd	7800	2370	2330	1710	6410	2340
range																					
<b>U.K. (n = 2)</b>																					
mean	nd	30	550	60	500	870	336	150	3370	130	20	2220	nd	70	nd	2390	520	260	3080	3860	2120
range	nd		440–660	10–110	400–610	660–1080	280–390	120–170	2830–3910	90–170		2020–2410	nd		nd	2110–2670	410–630	110–410	1470–4700	2210–5520	1580–2660
<b>U.S.A. (n = 18)</b>																					
mean	90	50	420	90	260	470	200	150	2250	630	100	24070	nd	300	30	23610	380	420	780	1330	900
range	30–180	20–120	10–730	30–170	80–410	120–720	50–390	40–390	410–3490	80–1560	20–220	1620–140380	nd	60–1670	20–30	23610–141260	290–570	20–1250	320–1590	0–2170	690–1390

<sup>a</sup> nd = below limit of detection. NA = not available due to analytical difficulties.

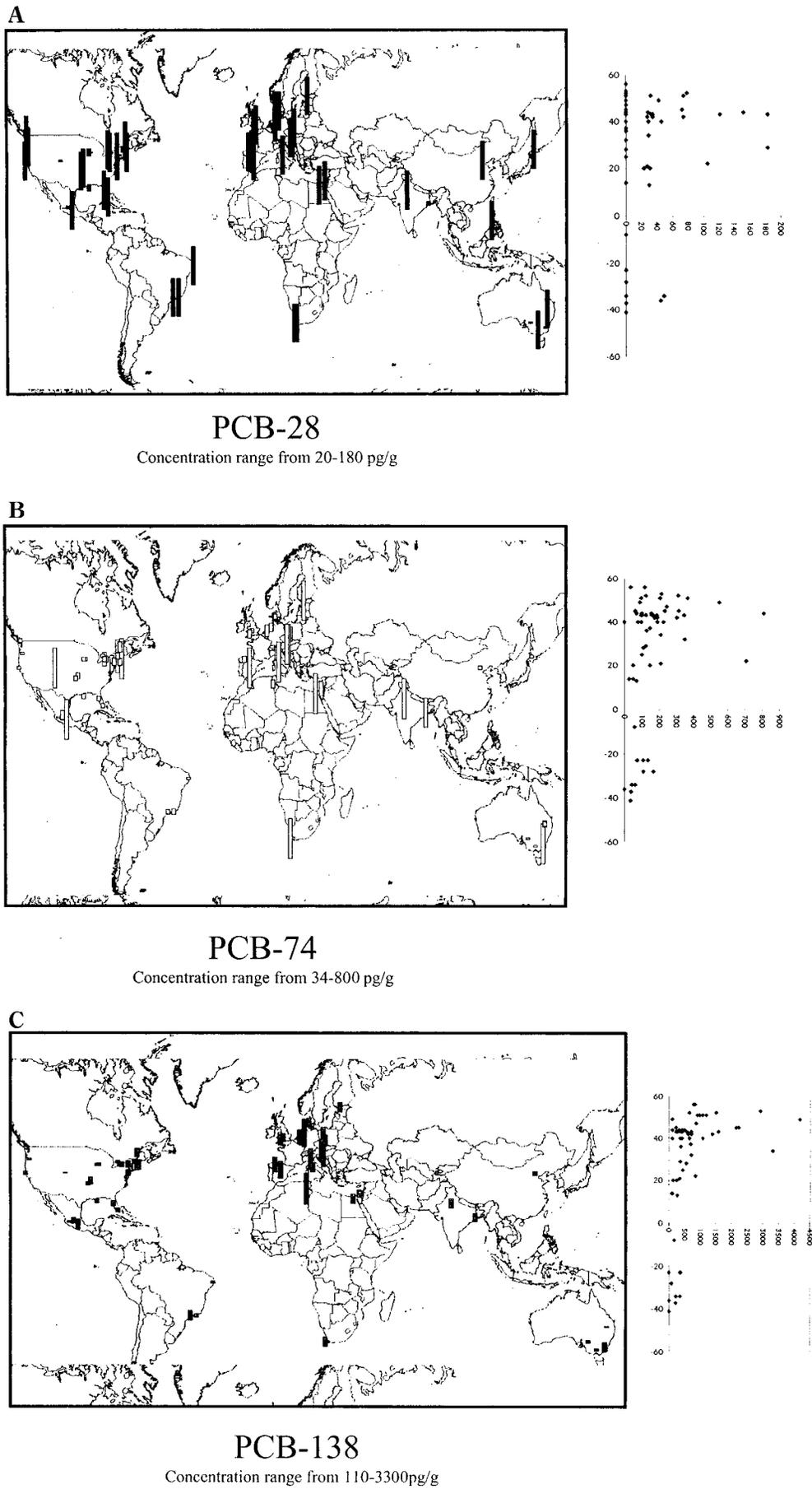


FIGURE 1. Global and latitudinal distribution of PCB congeners in butter: A. PCB-28, B. PCB-74, and C. PCB-138.

**TABLE 2: Maximum and Minimum Concentrations (pg/g lipid) and the Ratio of These Values for Selected PCB Congeners**

PCB congener	maximum	minimum	ratio
28	180	20	9
52	120	20	6
118	960	40	24
138	3330	110	30
153	2440	30	81
170	1090	20	55
180	2580	40	65

28 in butter varied by only a factor of 9 globally, compared to a factor of 81 for PCB-153.

European samples contained higher proportions of higher chlorinated congeners (PCB-138, PCB-153, and PCB-180) reflecting proximity to source regions of PCBs. In contrast, samples from more remote regions (e.g. Australia, the Philippines, some samples from Canada and Brazil) contained higher proportions of lighter (tetra- and pentachlorinated) congeners reflecting differences in compound susceptibility to LRAT. These observations on the global distribution of PCB congeners in butter reflect some key features of global POP behavior. First, as we noted earlier, the highest concentrations are detected in samples from areas of the globe where production and use was greatest. Ninety percent of the global usage (and primary atmospheric emissions) occurred in north temperate latitudes, particularly in Europe (37). Following emission to atmosphere, PCBs can be subject to LRAT, away from the area of production and use. However, there are differences in the "characteristic travel distances" of different congeners (38, 39). In general, lighter congeners can undergo greater long range transport, because they are less readily deposited by dry gaseous and particulate deposition (2, 4, 38, 39). In addition, once they have been deposited to terrestrial systems and water bodies, lighter congeners have a greater propensity to undergo secondary emission, volatilizing to air again and being subject to further LRAT (1, 9, 10, 35). As a consequence, lighter congeners have become better mixed in the atmosphere than heavier congeners (9, 10). However, the results of this butter survey clearly show that the global distribution of PCBs in the air over terrestrial systems remains most strongly influenced by general proximity to source regions. We have seen the same trends in a global survey of surface soils from rural/remote locations (31). We interpret these observations as evidence that the "wholesale" global distribution of PCBs via LRAT and cold condensation (1, 2) is severely tempered by their slow release from areas of use and the strong affinity that these compounds have for surface soil.

**Relationship of Butter Concentrations to Air Concentrations.** Given a knowledge of the transfer factors for individual PCB congeners from air to cows milk, tentative predictions of air concentrations from concentrations in butter can be made. Data observed for grazing cows in the U.K. (27) were as follows ( $m^3$  air/g lipid): PCB-28, 3.2; PCB-118, 400; PCB-153, 260; PCB-138, 380; PCB-180, 540; PCB-170, 650. It should be emphasized that these values apply to temperate latitudes, with livestock feeding on pasture/silage that dominates their PCB intake (25). Under warmer conditions, the air-pasture partitioning is likely to lead to less efficient transfer to the terrestrial foodchain (24), while in some countries soil ingestion/fodder crops may be more important as components of the livestock diet/PCB intake (25).

To illustrate, applying the transfer factors above to the average concentrations of PCB-153 and PCB-138 in U.K. butter (500 and 870 pg/g lipid, respectively) yields estimated

air concentrations of 1.9 and 2.3 pg/ $m^3$ . Daily air concentrations of these two congeners measured at a semirural U.K. site in 1994 were <1.5–12 (1.7) and <1.2–5.7 (1.5) pg/ $m^3$ , respectively (40), in good agreement with levels calculated above. Applying the same transfer factors to the New Zealand butter data (where climatic conditions and livestock management regimes are generally similar to those in the U.K.) suggests air concentrations for PCB-153 (PCB-138 was not detected in the New Zealand sample) would be 10–20-fold lower, at ca. 0.1–0.2 pg/ $m^3$ . Rural New Zealand air data for this congener is generally in the range 0.1–0.5 pg/ $m^3$  (41).

**The Organochlorine Pesticides. DDT and Its Breakdown Products.**  $\Sigma$ DDT (pp'-DDT, op'-DDT, pp'-DDE, and pp'-DDT) was quantified in butter fat at concentrations between 410 and 250 000 pg/g. The two most abundant DDT isomers were pp'-DDE and pp'-DDT, with much lower levels of pp'-DDD. Concentrations of pp'-DDT varied enormously (over 3 orders of magnitude) between 80 and 25 000 pg/g, with elevated levels reflecting the significance of present use on contemporary foodchain accumulation. India had the highest pp'-DDT concentrations in butter, presumably as a result of ongoing substantial use for malaria control.

The ratio of pp'-DDT:pp'-DDE provides an indication of how recently DDT formulations have been released to the environment, with the ratio decreasing over time as the DDT degrades. The highest DDT:DDE ratios recorded in the current study (0.2–0.3) were found in butter collected from Central/South America, India, Tunisia, Spain, a single sample from the U.S. west coast, and two samples from Australia, generally in line with countries where more recent or even ongoing DDT usage is known or suspected. All other butter samples had ratios an order of magnitude lower, between 0.02 and 0.08.

Generally in Europe, North America, and the temperate industrial regions of the northern hemisphere DDT use has been banned since the 1970/1980s. Use continues in parts of Asia and Africa as well as in Central and South America.

Concentrations of the breakdown product, pp-DDE, also showed a huge range in concentrations (380–180 000 pg/g), with the highest values in Mexican, Indian, and some southern U.S. butters in agreement with a previous global study on vegetation (10).

**HCHs.** HCHs have been commercially available as either technical HCH, consisting of 55–70%  $\alpha$ -HCH and 10–18%  $\gamma$ -HCH, or as lindane (pure  $\gamma$ -HCH). Voldner and Li (42) estimated total cumulative use of technical grade HCH and lindane to be 550 000 and 720 000 t, respectively. Subsequent calculations by Li et al. (43) estimated total cumulative world consumption of HCH as high as 6 million tonnes. China, India, and the former Soviet Union represented the largest producers and users of HCH in the 1980s. The vast majority of HCH used today is in the form of the  $\gamma$  isomer. There is concern, however, that this isomer can be transformed into isomers that exhibit greater persistence. As the most metabolically stable isomer,  $\beta$ -HCH is the predominant isomer accumulating in human tissues.

Concentrations of the three isomers in butter varied between 60 and 98 000 pg/g for  $\alpha$ -HCH, 20–110 000 pg/g for  $\beta$ -HCH, and 88–18 000 pg/g for  $\gamma$ -HCH. Concentrations of each isomer were highest in butter samples from India, followed by China and Spain. This is not surprising, considering the extensive use of technical HCH in both India and China and high contemporary lindane use/past use in Spain. The  $\alpha$ : $\gamma$  HCH ratio is often used to provide evidence of current technical HCH application. Ratios >4 were found in samples from 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.

**HCB.** HCB is a byproduct of some industrial chlorination processes, and emissions may therefore reflect overall activity of the chemical industry in a given country. Nevertheless, 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 and 6200 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 (10). Some regional variation was apparent, however, with particularly high levels recorded in samples from the Czech Republic, Austria, China, and Brazil.

**Final Remarks.** Butter obviously provides a convenient matrix with which to monitor spatial and temporal trends in the atmospheric concentrations of various POPs. However, it is important to bear in mind that several factors other than air concentrations can influence the concentrations of compounds in butter. Most notable among these are the stage of the animal's lactation cycle (25; 28); seasonality/temperature dependency in air–pasture transfer of POPs (24); the influence of dietary supplements/soil ingestion/livestock management regime on the POPs concentrations in dairy products (25); compound metabolism (21); and the possibility that samples may become contaminated in the dairy/food processing or mixed at the dairy with milk from other regions. Nonetheless, we envisage that—with suitable controls, safeguards, and further research—butter could be used by governments and international agencies as a convenient matrix with which to monitor the regional/global distribution of POPs and the effectiveness of international measures to reduce their emissions to atmosphere under national emission control legislation and international POPs treaties (1, 3, 44).

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## Supporting Information Available

The full data set are included as Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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