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Polychlorinated Biphenyl and Low Polybrominated Diphenyl Ether Transfer to Milk in Lactating Goats Chronically Exposed to Contaminated Soil

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This study investigated milk excretion kinetics of PCBs, tetra-BDE (BDE 47), and penta-BDE (BDE 99) in goats exposed to contaminated soil under controlled conditions. The animals were fed (80 days) with feed containing 5% of contaminated soil. During this exposure period, milk was analyzed weekly. At the end of the experiment the PCBs and PBDEs retained in hepatic and adipose tissues were also determined. The soil-milk carry over rates (CORs) of PCBs ranged from 6 to 62%. This result suggests that a large part of ingested soil-bound PCBs was recovered in milk. Significantly different levels between the congeners were reported in the tissues (fat, liver). BDE 47 and 99 excretions in milk achieved a plateau after 2 weeks of exposure, and their corresponding CORs were about 30%. These two congeners showed a significantly ($P < 0.05$) lower accumulation in the adipose tissue than the major PCB congeners. The concentrations of BDE 47 and 99 in the liver were the same as PCB concentrations. This result suggests that the low brominated congeners are submitted to the metabolism more extensively than the major PCBs.

Introduction

Polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) are persistent contaminants which contaminate environmental matrices. These ubiquitous anthropogenic substances may transfer to the food chain via animals exposed to environmental matrices (*1, 2*).

In dairy cattle, the main intake of these chemicals occurs via involuntary soil ingestion during grazing (*3*). Indeed, organic pollutants are known to accumulate in the organic matter of soil "memory effect of soil". PCB and PBDE concentrations in soil may reach 50 μg/kg in contaminated areas (*4*). Regarding soil ingestion by grazing animals, it appears that cows ingest up to 1000 g of soil per day (i.e., several μg of halogenated congeners daily), depending on numerous factors such as season, climate, or density of grass (*5*).

Previous studies performed in monogastric animals have revealed that soil significantly reduces the bioavailability of PCBs (*6*). In ruminants, only a few studies focused on the bioavailability of soil-bound PCBs and low brominated congeners. The question arising is to know whether the exposure of ruminants to soil bound congeners has to be taken into account when evaluating the safety of the animals and their products. In the available studies performed under controlled conditions, PCBs were generally administered to ruminants via contaminated oil or feed (*7, 8*). Regarding PBDEs, very few studies reported on their fate in lactating ruminants (*9*−*11*). As an example, the behavior of penta PBDE-mix formulation congeners (i.e., low degree of bromination) largely found in agricultural areas which received contaminated sludge, has been described (*11*). Thus, PCBs and PBDEs present in soil require a particular attention and their potential bioavailability need to be addressed in terms of risk assessment of the food chain.

This study aimed at 1) estimating the bioavailability of soil-bound PCBs and low brominated congeners and 2) comparing the behavior of low brominated congeners and PCBs in milk and in different tissues.

Materials and Methods

Preparation of Experimental Soil. Twenty kilograms of surface soil sampled on permanent grassland were collected from a dairy farm located in the North East of France where milk was found to be contaminated by PCBs (38 ng/g milk fat (*4*)) and banned from sale. This PCB contaminated soil has previously been characterized, showing PCB concentrations up to 20 ng/g. The initial source of soil contamination was probably a heavy PCB mixture with a prevalence of penta/hexa chlorinated congeners (close to an Aroclor 1254-type mixture) and minor components of light congeners (*12*). Based on their structure-toxic activity relationships a number of PCBs showing properties similar to dioxins are assigned to PCB dioxin-like, whereas other PCBs are classified as non-dioxin-like PCBs.

The PCB contaminated soil (calcaric cambisoil, FAO classification; 1.6% organic carbon (OC); distribution of particle size: 14% clay, 18% silt, and 68% sand; 95% dry weight) was collected from the superficial horizons (O and A). After a 20 day drying process at room temperature, i.e. 18−20 °C, the soil samples were ground with a laboratory jaw crusher (BB100, Kurt Retsch GmbH & Co. KG, Haan, Germany), sieved at 2 mm, homogenized and stored in closed glass containers prior to being spiked with low brominated congeners: tetra-BDE (BDE 47) and penta-BDE (BDE 99). The artificial spiking method used, including an aging process, is considered as a relevant way to contaminate soil with different families of contaminants (*13*−*15*). The choice of these PBDE congeners was made according to their potential high levels in agricultural soils, their occurrence, and their toxicity (*11, 16*). Indeed, these two congeners constitute the major congeners of the penta-BDE commercial formulation (Bromkal-70) used as flame retardants.

A fraction of soil (5 g) was placed in an automatic mixer-bowl in aluminum and spiked with BDE 47 (catalogue number 33670, Oekanal, 50 μg/mL in isoctane) and BDE 99 (catalogue number 33676, Oekanal, 50 μg/mL in isoctane) until final concentrations of 1.5 and 3 ng/g DM of soil, respectively. Soil was gradually added until reaching 20 kg during the 180

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TABLE 1. Levels of PCBs and PBDEs in All Constituents of Diet and Milk, As Determined by GC-HRMS at Steady State (45 d)[h]

	concentration, pg/g DM				average contribution of soil in the ingestion of PCB			
compounds	control feed (fixed ingestion)	contaminated concentrate (measured ingestion)	hay (fixed ingestion)	quantities of PCBs ingested ($n = 3$), pg/day	pg/day	%	mean concentration in milk ($n = 3$), pg/g fat	mean individual COR ($n = 3$), %
PCB 77	1.5	22.0	3.2	26453 ± 509	21750	82	13 ± 1	6[g]
PCB 81	0.1	0.1	0.1	244 ± 2	92	38		
PCB 126	0.2	5.4	0.4	5928 ± 124	5285	89	25 ± 1	47[b,c]
PCB 169	0.1	0.1	0.1	191 ± 2	84	44		
total of the nonortho-PCBs	1.8	27.9	3.8	33123	27537		40 ± 4	
PCB 105	6.4	81.5	16.1	102949 ± 1883	80435	78	504 ± 15	57[a]
PCB 114	1.0	2.9	1.7	5522 ± 67	2863	52		
PCB 118	16.11	175.32	43.17	232259 ± 4000	173000	72	1200 ± 100	59[a]
PCB 123	0.6	4.9	1.8	7150 ± 112	4799	67	12 ± 1	21[f]
PCB 156	1.8	26.1	4.1	31706 ± 603	25780	81	165 ± 9	62[a]
PCB 157	0.3	7.5	1.1	8852 ± 174	7440	84	41 ± 7	52[a,b]
PCB 167	0.8	12.7	2.3	15681 ± 294	12564	80	64 ± 1	48[b,c]
PCB 189	0.1	1.0	1.3	2388 ± 24	1035	43		
total of the mono-ortho-PCBs	26.5	312.1	81.6	416010	307902		1995 ± 175	

	concentration, ng/g DM				average contribution of soil in the ingestion of PCB			
compounds	control feed (fixed ingestion)	contaminated concentrate (measured ingestion)	hay (fixed ingestion)	quantities of PCBs ingested ($n = 3$), ng/day	ng/day	%	mean concentration in milk ($n = 3$), ng/g fat	mean individual COR ($n = 3$), %
PCB 28	0.03	0.02	0.03	79 ± 0.4	17	19		
PCB 52	0.03	0.02	0.02	67 ± 0.4	18	25		
PCB 101	0.03	0.08	0.03	139 ± 1.9	83	57		
PCB 138	0.02	0.24	0.06	322 ± 5.5	236	70	1 ± 0.1	36[d,e]
PCB 153	0.04	0.23	0.16	425 ± 5.4	230	51		
PCB 180	0.01	0.04	0.03	76 ± 0.9	38	47		
total of the non-dioxin-like-PCBs	0.16	0.63	0.33	1110	623		3.4 ± 0.3	
PBDE 28	0.002	0.002	0.000	5 ± 0.0	2	41		
PBDE 47	0.03	0.14	0.02	188 ± 3	142	73	0.4 ± 0.05	30[e]
PBDE 99	0.02	0.18	0.01	211 ± 4	175	81	0.5 ± 0.08	30[e]
PBDE 100	0.01	0.01	0.00	17 ± 0.2	9	49		
PBDE 153	0.00	0.00	0.01	12 ± 0.1	4	33		
PBDE 154	0.00	0.00	0.00	7 ± 0.1	4	46		
PBDE 183	0.01	0.01	0.02	27 ± 0.2	7	22		
total of the PBDEs	0.07	0.35	0.06	468	343		1 ± 0.1	

[a] Mean values with similar letter did not differ significantly ($P > 0.05$). [b] Mean values with similar letter did not differ significantly ($P > 0.05$). [c] Mean values with similar letter did not differ significantly ($P > 0.05$). [d] Mean values with similar letter did not differ significantly ($P > 0.05$). [e] Mean values with similar letter did not differ significantly ($P > 0.05$). [f] Mean values with similar letter did not differ significantly ($P > 0.05$). [g] Mean values with similar letter did not differ significantly ($P > 0.05$). [h] The dry weights (DW) of feed and hay were about 88 and 92%, respectively.

min mixing. Deionized water was then added to the soil to bring its moisture to approximately 80% of its field capacity. The soil was stored in six glass flasks which were tightly capped and placed in the dark at 21 ± 2 °C during 40 d to allow physical and chemical binding. After 7 and 28 d the soil was dried (at 21 °C during 7 d) and wetted again (80% of its field capacity), in order to increase the sequestration of the two PBDEs (*13*−*15*). At the end of the 40 d aging, the soil was finally dried, homogenized, and stored in tinted closed glass containers at −20 °C.

Manufacture of the Experimental Feed. The uncontaminated feed was based on corn, alfalfa, wheat, soybean, mineral mix, and sunflower oil and formulated in order to meet the needs of the milk producing animals (*17*). Contaminated feed was obtained by mixing contaminated soil with uncontaminated feed at the rate of 5% in order to facilitate the ingestion by goats. The amount of soil added in feed was estimated in order to mimic soil quantities ingested by ruminants (in this case, 0.8 g/kg of live weight per day) (*5*).

Six samples of the mixed feed used to contaminate the animals were collected and analyzed. Feed sampling was achieved using a trier sampler on a horizontal plane following a diagonal movement in order to sample feed from each part of the package. Table 1 indicates PCB and PBDE concentrations in feed. As expected, the PCB profile in contaminated feed reflected the profile found in soil sampled.

Animals. To fulfill the objectives of this study, it was necessary to use lactating ruminants. In order to limit the use of animals, several measures were taken: lactating goats

were used as a model for ruminants, their number was limited, and the experimental period was strictly adjusted to the purposes of the study. Three Alpine multiparous goats (*Capra hircus*, 65 ± 7 kg body weight, second month postpartum) from the Nancy University experimental farm (Domaine Experimental de la Bouzule, Champenoux, France) were used. The animal protocol was in accordance with the general directive no. 1986/609/CEE on animal care used in EU. The animals were placed in adequate animal housing facilities (Agreement by Prefecture 54, décret no. A-54-547-15) and given an adaptation period of 2 weeks within individual boxes at an average day temperature of 22 °C, under natural light conditions. During the experiment the animals were milked twice a day, and milk yields were individually recorded. The goats were fed with meadow hay, water, and mineral salt ad libitum. During the adaptation period, they received 2 kg of an uncontaminated commercial feed. Overall, the distribution ration met the nutritional requirements of goats yielding 3500 ± 900 mL of milk.

Experimental Design. Control milk samples were collected twice before starting the oral exposure period to the contaminated feed. After the adaptation period, each animal received 1 kg of contaminated feed during 80 successive days. During the whole exposure period, individual milk samples were collected at 7 day intervals. Immediately after sampling, milk samples were transferred into 100 mL glass bottles and kept frozen at −20 °C until analysis. At the end of the experimental period, animals were euthanasized (Pentobarbital, Ceva santé animale, Libourne, France). Afterward, fat from the adrenal area and liver were sampled. All the samples were collected in plastic bags and stored at −20 °C before lyophilization and analysis.

During the experimental period 15 samples of grass and uncontaminated feed were taken (one sample each week), pooled, and ground to produce a significant control sample for analytical purposes.

To assess the contribution of soil in the contamination of goats, a global characterization of PCBs and PBDEs was undertaken for each feed matrix. Based on a feeding regime of 1 kg per day of each uncontaminated and contaminated feed (measured data) and approximately 1 kg per day of hay, the congeners quantities of the various orally ingested feeds compared with total intake of PCBs and PBDEs were calculated. Water and air contamination were not investigated because inhalation and water drinking are considered of negligible importance in PCBs and PBDEs intake (*18*).

Chemical Analysis. Methods of analysis of PCBs have already been reported by Costera et al. (*19*). Analyses of PCBs and PBDEs were carried out according to the requirements of the quality assurance parameters of the Commission Directive 2002/69/EC and 2002/70/EC of July 2002. Moreover, analyses were performed at LABERCA (Nantes, ENV) upon an accredited system ISO 17025. All the analytical methods used have been validated and accredited according to ISO 17025. Furthermore, this research project was conducted under a certified system ISO 9001 v. 2000 standard.

The analysis of BDEs and PCBs was performed by GC-HRMS. The instrumental conditions and a list of the ions monitored are presented in the Supporting Information (SI).

Measures of Biotransfer. In order to distinguish the congeners for which soil was the major contributor, two criteria were applied. First, the concentrations of congeners had to be at least five times higher than the initial concentration in uncontaminated feed. Second, the contribution of the soil contaminants had to be above 2/3 of total oral ingestion. Thus, the congeners with values under these thresholds were not considered further.

The transfer of chemicals from feed to milk fat is usually characterized by the BioConcentrations Factors (BCFs) and Carry Over Rates (CORs) (*18, 20*). All of these descriptors assume that animals have reached the steady state. The terms are defined by the following equations in which the units have been modified to fit with the concentrations usually encountered in studies dealing with PCBs and PBDEs

$$\mathrm{BCF} = C_{\mathrm{MF}} / C_{\mathrm{feed}}$$

where C_{MF} is the concentration in milk fat (pg/g), and C_{feed} is the concentration in the dry matter of the feed (pg/g).

$$\mathrm{COR} = 100{*}\mathrm{Ex}_{\mathrm{milk}} / I$$

where COR is the proportion of daily ingested pollutant which is excreted in milk per day (%), $\mathrm{Ex}_{\mathrm{milk}}$ is the amount excreted in milk (pg/d), and I is the intake of the considered congener (pg/d).

The two transfer coefficients were calculated using data from the same sampling time at steady state.

Statistical Analysis. Data of BCFs (liver and fat tissues) and CORs (milk) were statistically analyzed using the software StatBox version 6.5 (GrimmerSoft, Paris, France) with an analysis of variance model (ANOVA) in total randomization with one studied factor (congeners, PCBs: 9; PBDEs: 2) and repetitions (goats: 3).

Individual BCF and COR values were compared using a Bonferroni t test and significance was declared at $P < 0.05$.

Results

Contribution of Ingested Matrices on PCB and PBDE Exposure. PCB and PBDE concentrations in the contaminated feed are given in Table 1. For the following congeners: dioxin-like PCBs (DL-PCBs) 77, 118, 126, 105, 123, 156, 157, and 167, non-dioxin-like PCBs (NDL-PCBs) 138, BDE 47 and 99, exposure via contaminated soil was at least five times higher than contribution via uncontaminated feed and represented at least 2/3 of the total oral ingestion (Table 1).

For PCBs 81, 169, 114, and 189 (DL-PCBs), PCB 28, 52, 101, 153, and 180 (NDL-PCBs), and BDE 28, 100, 153, 154, and 183 (PBDEs), hay and uncontaminated feed contributed to more than 57% of total exposure of the animals (Table 1). For PCB 153 (major NDL-PCB), the soil contributed only 51% of the amounts of PCB 153 ingested by the animals. Thus, these congeners were not further considered.

Transfer of PCBs and PBDEs from Contaminated Feed to Milk. Concentrations of individual congeners in milk are given in Table 1. The PCB profile in milk presents a huge difference from that found in feed. Indeed, contribution of NDL-PCB congeners reached 71% of total feed contamination and only 60% in milk. PCB 153 was the major congener in milk accounting for more than 24% of total PCB levels. It was followed by PCB 118 and 138, with 18 and 15% of total PCB levels, respectively. Nonortho and mono-ortho PCBs (DL-PCBs) contributed for 33 and 7%, respectively. The contribution of BDE 47 and 99 to the sum of PBDEs in contaminated feed and milk showed the same percentage of 92 and 91%, respectively.

Figure 1 illustrates the enrichment kinetic of PCBs and PBDEs in milk. It indicates that steady state was achieved for all studied congeners after 2 weeks. CORs of PCBs and low brominated congeners were calculated at 45 d of exposure. PCB CORs from soil to milk ranged from 6 to 62% and reached 30% for BDE 47 and BDE 99 (Table 1). The CORs of PCB 118, 157, 156, and 105 were found to be the highest. PCB 77 presented the lowest COR.

Liver and Fat Bioaccumulation of PCBs and PBDEs. Figure 2 shows PCBs and low brominated levels in liver (2a) and in fat (2b) after 80 days of exposure. BCFs of PCBs and low brominated congeners indicated different levels and patterns in liver and fat tissue. PCB 138 (NDL-PCBs) presented the same pattern as the major mono-ortho PCBs (without

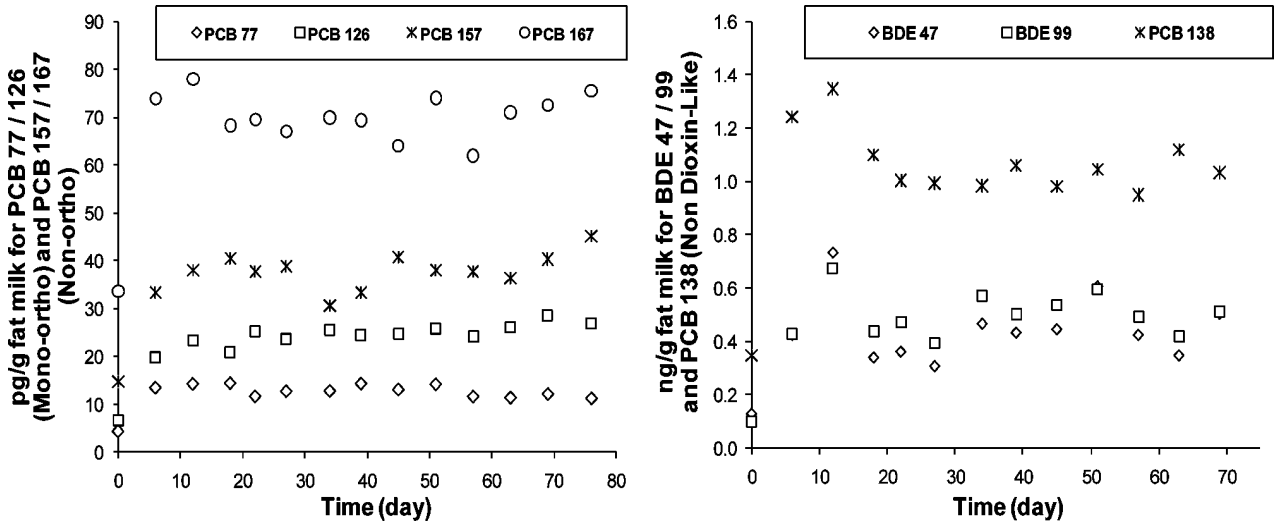

FIGURE 1. Excretion kinetics of some studied compounds (DL-PCB, NDL-PCB, and PBDE) in milk.

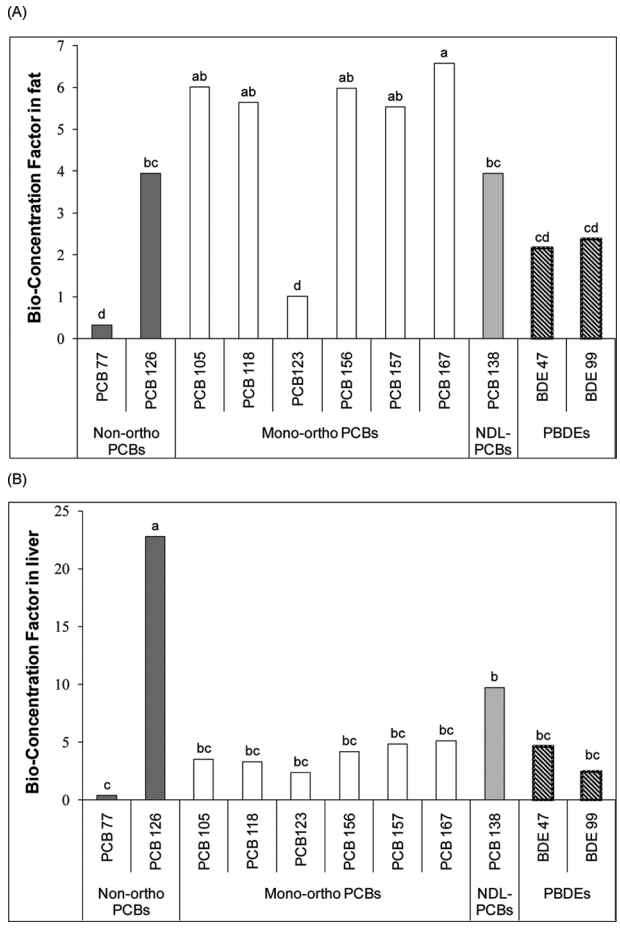

FIGURE 2. BioConcentration Factors for PCBs ($n = 9$) and PBDE ($n = 2$) in fat (A) and liver (B) obtained at the steady state in the lactating goats.

PCB 167). The mono-ortho PCB 123 and nonortho PCB 77 showed the lowest accumulation ($P < 0.05$) in fat, whereas PCB 126 presented the same pattern of accumulation as the major mono-ortho PCBs.

BDE 47 and BDE 99 presented identical accumulations in fat tissue ($P > 0.05$). No statistical difference ($P > 0.05$) between retention of low brominated congeners and PCBs 138, 123, 77, and 126 was found. These congeners present lower accumulation in the adipose tissue than the other PCB congeners. Indeed, the BCF of both BDE congeners ranged between 2 to 3. In liver, BDE 47 had accumulated ($P > 0.05$) at a similar level when compared to BDE 99; on the other hand, its BCF was statistically not dissociable from the BCFs found for most of the other PCBs. PCB 126 showed the highest BCF ($P < 0.05$).

Discussion

Transfer of Soil-Bound PCBs and Low Brominated Congeners from Contaminated Feed to Milk. Before the distribution of contaminated feed, milk samples were found to be slightly contaminated with NDL-PCBs (up to 1 ng/g milk fat). Hay was found to be the major fixed factor affecting the background PCB concentration in milk.

In this work we focused especially on congeners for which the contaminated soil contributed to more than 66% of PCB intake. The same dominant congeners transferred to ruminant milk were also reported in previous studies focusing on other contaminated matrices than soil (*19, 21*). Table 1 shows a strong disparity in CORs between congeners: PCBs with highest CORs ≥ 50% (e.g., PCB 118) were followed by PCBs with medium CORs ≥ 20 to ≤50% (e.g. PCBs 138 and 126) and PCBs with low transfer rates ≤10%. The lowest CORs were obtained for the tetra-chlorinated congener 77, reflecting probably its high metabolization rate as previously suggested in mammals (*22*). The CORs of PCBs in milk (Table 1) are in the same range as those reported for polychlorinated dioxins/furans which do not exceed 66% (*23*). In this study, the milk PCB levels reached 2.7 pg WHO-I-TEQ DL-PCB/g fat, and this value was close to the EU tolerance limit of 3 pg TEQ/g fat authorized.

The CORs observed for BDE 47 and 99 were in the same range as PCB 138 and may be associated with a medium metabolism. No clear correlation between CORs and the chlorination degree of PCBs was observed. For example, with the same pentachlorination the CORs decreased from 57% for PCB 105 to 21% for PCB 123. In the same way, no evident correlation could be made between the substitution at both para-positions (4 and 4′) of PCBs and their moderate or major CORs. In contrast, some authors (*19, 21*) have suggested a correlation between CORs and para-position substitution in PCBs.

The ratio "milk fat/adipose tissue" pollutant concentration versus the log K_{ow} is plotted in Figure S1 in the Supporting Information (SI). It appeared that the "milk fat/adipose tissue" concentration ratio depended on the log K_{ow} of the congeners. This ratio remained higher than 1 for most of the congeners whatever the log K_{ow} considered in this study. This result indicates that the concentration found in milk fat was higher than the concentration in fat tissue and suggests that the

TABLE 2. Comparison of Carry Over Rates (%) Reported for PCBs

	contaminated matrix			
compounds	present study soil (controlled conditions with goats)	Costera et al. (*19*) hay (controlled conditions with goats)	Thomas et al. (*18*) pasture (field study with cows)	Kerst et al. (*7*) grass (field study with cows)
Nonortho-PCBs				
PCB 77	6	10	nd[a]	2
PCB 126	47	55	nd[a]	40
Mono-Ortho-PCBs				
PCB 105	57	90	0	28
PCB 118	58	85	100	33
PCB 123	21	18	nd[a]	9
PCB 156	62	78	76	20
PCB 157	52	82	nd[a]	24
PCB 167	48	52	91	21
Non-Dioxin-Like-PCBs				
PCB 138	36	55	74	nd[a]

[a] nd: not determined.

partitioning equilibrium between these two compartments is in favor of milk (sorption properties of the two tissues are similar since both are made up of triglycerides), and a similar mechanism occurs for low brominated congeners. PCB 77 presented a highest ratio of 1.7.

A "milk fat/adipose tissue" ratio different from 1 may be explained by congeners having log K_{ow} < 7. Indeed, with PBDEs and PCBs with higher log K_{ow}, Kierkegaard et al. (*9*) found that this ratio was strongly reduced. For example, the concentrations of higher PBDEs (hepta to deca) were 9−80 times higher in the adipose tissue than in milk fat, with the difference increasing with the degree of bromination (*9*). On the other hand, opposite results were found in eggs for PCDD/Fs with a high degree of chlorination (*24*).

Moreover, regarding the literature, the congeners with log K_{ow} lower than 7 are supposed to have no specific affinity to fatty compartments and no difficulty to cross the biological barrier during the transfer process (*9, 10*). However, the more chlorinated and, therefore, the more lipid-soluble PCB (log K_{ow} > 7.5) congeners are supposed to be less efficiently transferred from fat to the circulatory stem and from there to milk, than less chlorinated ones (*25*).

CORs of BDE 47 and 99 present higher levels of transfer in milk (30%, Table 1) when compared to PBDEs such as BDE 209 which presents a lower transfer to milk estimated at less than 0.2% (*9*). Thus, in contrast to previous results (*9*), this study indicates for the first time a potential risk of human exposure to lower PBDEs via dairy products.

Bioavailability of Soil-Bound PCBs. Assuming steady state conditions, CORs of PCBs were used to estimate the oral bioavailability of soil-bound PCBs in goats. Three studies from the literature provide PCB CORs from contaminated feed without contaminated soil (Table 2).

The PCB CORs reported in this study were higher than those reported by Kerst et al. (*7*) and in the same range as those shown by Thomas et al. (*18*). Interestingly, CORs obtained with soil-bound PCBs are very close to those of Costera et al. (*19*) which were the most relevant data available for this comparison. Indeed, Costera et al. (*19*) performed a study using contaminated hay in very similar conditions to ours (lactating goats, duration of exposure). CORs of the PCB from both studies were in the same range for all the congeners (Table 2). Therefore, it seems that the bioavailability of PCBs is not really affected by the soil matrix (1.6% OC and 14% clay). This result is in line with results of Hoogenboom et al. (*26*), which reported no effect of soil on bioavailability of PCBs in eggs. Fries et al. (*6*) showed a limited but significant reduction (10 to 20% for three PCBs) of oral bioavailability when PCBs were bound to soil (5% organic matter; 10% clay) in rats. In contrast in vitro investigation performed on a monogastric model reported the same conclusion, with a reduction of the PCB mobilized fraction of 67% (*27*).

Biodegradation and Bioaccumulation Process. For each studied congener, BCF values were in the same range as those reported in the literature (*24, 28*). Persistence (bioconcentration) of PCBs in mammals and fish organisms is characterized by three features: lipophilicity, chlorination degree, and stereochemistry (*29*). It has been observed in cows that high chlorinated PCBs are likely to be bioaccumulated (Figure 2). The main characteristic which is commonly related to the metabolism of PCBs is the presence of meta/para vicinal hydrogen and to a lesser extent, ortho/meta vicinal hydrogen atoms. For example, PCB congeners without ortho/meta or meta/para vicinal H atoms are highly persistent and difficult to metabolize (*30, 31*). These authors (*30, 31*) proposed a PCB classification (group 1, group 2, and group 3) according to the presence of meta/para and ortho/meta hydrogen atoms. PCB167 BCF (group 1) in fat is considered to be high because this congener is the most persistent due to the absence of vicinal H atoms. They are followed by PCBs 118, 138, 105, 157, and 156 (group 2), which present vicinal H atoms in ortho/meta positions combined with a chlorine atom in the ortho position, suggesting an intermediate value of BCF and a partial metabolization. The congener which does not follow the characteristics of group 2 is PCB 123, which has two vicinal H atoms in the ortho/meta position combined with one ortho chlorine substitution; it seems to be highly eliminated in goats. Finally, the less abundant congeners (group 3) belong to easily metabolized PCBs which have vicinal H atoms in ortho/meta positions (PCBs 77 and 126). It has to be noted that BCF of PCB 126 in fat was in the same range as BCFs of congeners from group 2. Among the two nonortho coplanar congeners, PCB 77 is known to be more biodegradable than PCB 126 (*32*). Indeed, PCB 77 is less transferred to milk compared to PCB126, and this result is also associated with reduced bioconcentration levels in the different sampled tissues as already observed by Thomas et al. (*30*).

However, it appears that this classification (group 1, group 2, and group 3) is not always sufficient to explain the metabolism patterns observed in Figure 2 (for example BCF of PCB123 differed markedly from group 2 BCFs). Thus, other factors than presence or absence of vicinal H atoms in ortho/meta and meta/para positions might play an important role in the metabolism of PCBs in goats. Some authors have pointed out that ortho Cl-substitutions also play a part in the biotransformation in marine mammals (*33*). Other authors have suggested that less chlorinated PCBs are less persistent in cows than more highly chlorinated ones regardless of the Cl position (*34*).

In the liver, the PCB 126 BCF was particularly high when compared to its BCF value in the fat tissue. This result was already observed in other studies (*35*−*37*), where the hepatic concentration was 5-fold higher than the concentration in fat tissue. These authors explained the specific hepatic sequestration of PCB 126 by the inducible binding protein (CYP1A2) (*16*).

PCB138 BCFs was 2-fold higher in the liver than in fat tissue of goats unlike what has been reported by Lyche et al. (*37*). Such a variation may be explained by the fat content of the liver (from 7 to 14%) or anterior PCB exposure of the animals. Among 50 congeners of PCBs (PCB 126 was not investigated), the dominant presence of PCB 153 in the liver followed by PCB 138 (40 and 20%, respectively) was previously demonstrated by Hoshi et al. (*34*) in cows.

In the lactating goats, BDE 47 and BDE 99 were retained to a low extent in the hepatic and fat tissues, in the same range as PCB 77. On the one hand, these data seem in contradiction with the fact that the PBDE congeners are known to be higher metabolized than PCBs (*9*). On the other hand, it was expected that BDE 99 would be metabolized to BDE 47 following the observations with higher PBDEs in cows (strong debromination), but this metabolism did not occur (*9*). Indeed, in ruminal conditions, it appears that BDE 99 was not submitted to the same metabolism of debromination reported in the carp (*38*) or for the higher PBDEs in cows (*9*).

Tissular distribution and CORs of BDE 47 and 99 showed similar orders of magnitude to those of PCBs from group 2 (partially metabolized). Moreover, these data support the fact that BDE 47 presented the same kinetic of transfer into milk as BDE 99. A different kinetic pattern was observed in the chicken (*39*).

Supporting Information Available

Figure S1 (fat and adipose tissue concentration ratio of PCBs and BDEs 47/99 vs log K_{ow}) and information on the analytical conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Matscheko, N.; Tysklind, M.; De Wit, C.; Bergek, S.; Andersson, R.; Sellström, U. Application of sewage sludge to arable land-soil concentrations of polybrominated diphenyl ethers and polychorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls, and their accumulation in earthworms. *Environ. Toxicol. Chem.* **2002**, *21* (12), 2515–2525.

(2) Darnerud, P. O.; Eriksen, G. S.; Jóhannesson, T.; Larsen, P. B.; Viluksela, M. Polybrominated diphenyl ethers: Occurence, dietary exposure, and toxicology. *Environ. Health Perspect.* **2001**, *109* (1), 49–68.

(3) Fries, G. F. A review of the significance of Animal food products as potential pathways of human exposures to dioxins. *J. Anim. Sci.* **1995**, *73* (6), 1639–1650.

(4) Rychen, G.; Jurjanz, S.; Toussaint, H.; Feidt, C. Dairy ruminant exposure to persistent organic pollutants and excretion to milk. *Animal* **2008**, *2* (2), 312–323.

(5) Laurent, C.; Feidt, C.; Laurent, F. Contamination des sols. *EDP sciences/ADEME France* **2005**, 1–215.

(6) Fries, G. F.; Marrow, G. S.; Somich, C. J. Oral bioavailability of aged polychlorinated biphenyl residues contained in soil. *Bull. Environ. Contam. Toxicol.* **1989**, *43* (5), 683–690.

(7) Kerst, M.; Waller, U.; Reifenhäuser, W.; Körner, W. Carry-over rates of dioxin-like PCB from grass to cows' milk. *Organohalogen Compd.* **2004**, *66*, 2240–2244.

(8) Lyche, J. L.; Oskam, I. C.; Skaare, J. U.; Reksen, O.; Sweeney, T.; Dahl, E.; Farstad, W.; Ropstad, E. Effects of gestational and lactational exposure to low doses of PCBs 126 and 153 on anterior pituitary and gonadal hormones and on puberty in female goats. *Reprod. Toxicol.* **2004a**, *19* (1), 87–95.

(9) Kierkegaard, A.; Asplund, L.; De Wit, C. A.; McLachlan, M. S.; Thomas, G. O.; Sweetman, A. J.; Jones, K. C. Fate of higher brominated PBDEs in lactating cows. *Environ. Sci. Technol.* **2007**, *41*, 417–423.

(10) Kierkegaard, A.; de Wit, C. A.; Asplund, L.; McLachlan, M. S.; Thomas, G. O.; Sweetman, A. J.; Jones, K. C. A mass balance of tri-hexabrominated diphenyl ethers in lactating cows. *Environ. Sci. Technol.* **2009**, *43* (7), 2602–2607.

(11) Law, R. J.; Allchin, C. R.; de Boer, J.; Covaci, A.; Herzke, D.; Lepom, P.; Morris, S.; Tronczynski, J.; de Wit, C. A. Levels and trends of brominated flame retardants in the European environment. *Chemosphere* **2006**, *64* (2), 187–208.

(12) Frame, G. M.; Cochran, J. W.; Bøwadt, S. S. Complete PCB congener distributions for 17 aroclor mixtures determined by 3 HRGC systems optimized for comprehensive, quantitative, congener specific analysis. *J. High Resolut. Chromatogr.* **1996**, *19* (12), 657–668.

(13) Kottler, B. D.; Alexander, M. Relationship of properties of polycyclic aromatic hydrocarbons to sequestration in soil. *Environ. Pollut.* **2001**, *113* (3), 293–298.

(14) White, J. C.; Kelsey, J. W.; Hatzinger, P. B.; Alexander, M. Factors affecting sequestration and bioavailability of phenanthrene in soils. *Environ. Toxicol. Chem.* **1997**, *16* (10), 2040–2045.

(15) White, J. C.; Quiñones-Rivera, A.; Alexander, M. Effect of wetting and drying on the bioavailability of organic compounds sequestered in soil. *Environ. Toxicol. Chem.* **1998**, *17* (12), 2378–2382.

(16) Frederiksen, M.; Vorkamp, K.; Thomsen, M.; Knudsen, L. E. Human internal and external exposure to PBDEs - A review of levels and sources. *Int. J. Hyg. Environ. Health* **2009**, *212* (2), 109–134.

(17) INRA. Alimentation des bovins, ovins et caprins; Tables Inra 2007. *Edition Quae*; **2007**; 1−307.

(18) Thomas, G. O.; Sweetman, A. J.; Jones, K. C. Input-output balance of polychlorinated biphenyls in a long-term study of lactating dairy cows. *Environ. Sci. Technol.* **1999a**, *33* (1), 104–112.

(19) Costera, A.; Feidt, C.; Marchand, P.; Le Bizec, B.; Rychen, G. PCDD/F and PCB transfer to milk in goats exposed to a long-term intake of contaminated hay. *Chemosphere* **2006**, *64* (4), 650–657.

(20) Fries, G. F.; Paustenbach, D. J.; Mather, D. B.; Luksemburg, W. J. A congener specific evaluation of transfer of chlorinated dibenzo-*p*-dioxins and dibenzofurans to milk of cows following ingestion of pentachlorophenol-treated wood. *Environ. Sci. Technol.* **1999**, *33* (8), 1165–1170.

(21) Sewart, A.; Jones, K. C. A survey of PCB congeners in U.K. cows' milk. *Chemosphere* **1996**, *32* (12), 2481–2492.

(22) Van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunström, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; et al. Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife. *Environ. Health Perspect.* **1998**, *106* (12), 775–792.

(23) Khan, Z. I.; Hussain, A.; Ashraf, M.; Ashraf, M. Y.; McDowell, L. R.; Huchzermeyer, B. Copper nutrition of goats grazing native and improved pasture with the seasonal variation in a semiarid region of Pakistan. *Small Rumin. Res.* **2007**, *67* (2−3), 138–148.

(24) Pirard, C.; De Pauw, E. Uptake of polychlorodibenzo-p-dioxins, polychlorodibenzofurans and coplanar polychlorobiphenyls in chickens. *Environ. Int.* **2005**, *31* (4), 585–591.

(25) Espeland, O.; Kleivane, L.; Haugen, S.; Skaare, J. U. Organochlorines in mother and pup pairs in two Arctic seal species: Harp seal (Phoca groenlandica) and hooded seal (Cystophora cristata). *Mar. Environ. Res.* **1997**, *44* (3), 315–330.

(26) Hoogenboom, L. A. P.; Kan, C. A.; Zeilmaker, M. J.; Van Eijkeren, J.; Traag, W. A. Carry-over of dioxins and PCBs from feed and soil to eggs at low contamination levels - Influence of mycotoxin binders on the carry-over from feed to eggs. *Food Addit. Contam.* **2006**, *23* (5), 518–527.

(27) Hack, A.; Selenka, F. Mobilization of PAH and PCB from contaminated soil using a digestive tract model. *Toxicol. Lett.* **1996**, *88* (1−3), 199–210.

(28) Hoogenboom, L. A. P.; Kan, C. A.; Bovee, T. F. H.; Van Der Weg, G.; Onstenk, C.; Traag, W. A. Residues of dioxins and PCBs in fat of growing pigs and broilers fed contaminated feed. *Chemosphere* **2004**, *57* (1), 35–42.

(29) Borlakoglu, J. T.; Walker, C. H. Comparative aspects of congener specific PCB metabolism. *Eur. J. Drug Metab. Pharmacokinet.* **1989**, *14* (2), 127–131.

(30) Thomas, G. O.; Sweetman, A. J.; Jones, K. C. Metabolism and body-burden of PCBs in lactating dairy cows. *Chemosphere* **1999b**, *39* (9), 1533–1544.

(31) McLachlan, M. S. Mass balance of polychlorinated biphenyls and other organochlorine compounds in a lactating cow. *J. Agric. Food Chem.* **1993**, *41* (3), 474–480.

(32) Jiménez, O.; Jiménez, B.; Gonzalez, M. J. Isomer-specific PolyChlorinated Biphenyl determination in Cetaceans from the Mediterranean sea: Enantioselective occurence of Chiral Poly-Chlorinated Biphenyl congeners. *Environ. Toxicol. Chem.* **2000**, *19* (11), 2653–2660.
(33) Boon, J. P.; Everaarts, J. M.; Kastoro, W. W.; Razak, H.; Sumanta, I.; Surmarno; Nelissen, P. H.; Stefels, J.; Hillebrand, M. T. J. Cyclic organochlorines in epibenthic organisms from coastal waters around East Java. *Neth. J. Sea Res.* **1989**, *23* (4), 427–440.
(34) Hoshi, H.; Minamoto, N.; Iwata, H.; Shiraki, K.; Tatsukawa, R.; Tanabe, S.; Fujita, S.; Hirai, K.; Kinjo, T. Organochlorine pesticides and polychlorinated biphenyl congeners in wild terrestrial mammals and birds from Chubu region, Japan: Interspecies comparison of the residue levels and compositions. *Chemosphere* **1998**, *36* (15), 3211–3221.
(35) Huwe, J. K.; Smith, D. J. Laboratory and on-farm studies on the bioaccumulation and elimination of dioxins from a contaminated mineral supplement fed to dairy cows. *J. Agric. Food Chem.* **2005**, *53* (6), 2362–2370.
(36) Chen, C. Y.; Hamm, J. T.; Hass, J. R.; Birnbaum, L. S. Disposition of polychlorinated dibenzo-p-dioxins, dibenzofurans, and non-ortho polychlorinated biphenyls in pregnant long evans rats and the transfer to offspring. *Toxicol. Appl. Pharmacol.* **2001**, *173* (2), 65–88.
(37) Lyche, J. L.; Skaare, J. U.; Larsen, H. J. S.; Ropstad, E. Levels of PCB 126 and PCB 153 in plasma and tissues in goats exposed during gestation and lactation. *Chemosphere* **2004b**, *55* (4), 621–629.
(38) Stapleton, H. M.; Letcher, R. J.; Baker, J. E. Debromination of polybrominated diphenyl ether congeners BDE 99 and BDE 183 in the intestinal tract of the common carp (Cyprinus carpio). *Environ. Sci. Technol.* **2004**, *38* (4), 1054–1061.
(39) Pirard, C.; De Pauw, E. Absorption, disposition and excretion of polybrominated diphenyl ethers (PBDEs) in chicken. *Chemosphere* **2007**, *66* (2), 320–325.

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