PCBs, HCHs and DDTs in cow's milk and soil of pasture from the Irkutsk Region, Russia

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Introduction

The main pathway of human exposure to organochlorine compounds is food, especially dairy products. Our previous investigations of PCDD/Fs and PCBs in food produced in the Irkutsk region showed that the average daily intake amounts to 88 pg PCDD/F TEQ per day and 95 pg PCB TEQ per day[1]. Thus the contribution of PCBs and PCDD/Fs to the total daily intake is 51.7 and 48.3 % respectively. Cow's milk contributes up to 24 % of the daily intake of PCBs, and is exceeded only by fish (64 %). It was shown also that PCDD/F and PCB levels in milk and the daily intake of these compounds depends on the distance of the farms from the largest PCB source in the Irkutsk Region located in the Usol'e-Sibirskoe area[1,2,3].

In the previous study milk samples were taken from dairies which collect milk from a lot of farms. The aim of the paper is to investigate the organochlorine contamination in milk from single farms and to see if this is related to the contaminant levels in soil from the farms' pastures.

Methods and Materials

Sampling. Cow's milk was sampled twice in 2003, during spring (April-May) and autumn (September). Samples were collected from 16 farms located around the suspected PCB source (see Fig. 1). In addition, in two cases where there were no farms in the area samples were taken from private households with several cows and pooled. Each farm had at least 97 cows, while the pooled samples from private households came from 5-8 cows. The milk was taken from the central milk container which contained the milk of all cows on the farm. It was collected in glass bottles, frozen, and stored at -30^{o}C until analysis.

Soil from summer pastures belonging to the same farms was sampled in the autumn of 2003. All farms had their own summer pastures except P-4(1), P-20 and P-21. Farm P-4(1) did not put their cows to pasture but instead fed them with feed purchased elsewhere. The cows from private households in P-20 and P-21 grazed freely throughout the village so there soil from pastures was not sampled. The top 5 cm layer of soil from pastures was sampled with a hand corer at 5 points, wrapped in aluminum foil, and stored at -30^{o}C until they were analyzed in the laboratory of the Institute of Geochemistry in Irkutsk.

PCB, HCH and DDT analysis. Soil samples were Soxhlet extracted in *n*-hexan:aceton (1:1) for 12 h. Milk samples were freeze-dried and the residue was taken up in *n*-hexan:aceton (1:1), after which the solvent was evaporated and the lipid weight was determined gravimetrically. An internal standard containing two PCB congeners (IUPAC numbers 14 and 65) was added to the solvent prior to beginning extraction of soil and to the milk prior to freeze-drying. The samples were cleaned up using two liquid chromatography columns: a gel chromatography column filled with bio-bead S-X3 and a silica gel / aluminum oxide column. The gel chromatography column was used twice for milk samples when content of lipids were high. The GC/ECD analyses were performed on a HP 5890A Series II using a 60 m DB-5ms capillary for PCBs and organochlorine pesticides.

α-HCH, γ-HCH, p,p'-DDT, p,p'-DDE, p,p'-DDD, o,p'-DDT and PCB congeners (IUPAC number) 31, 28, 52, 49, 48/47, 44, 74, 70, 95/66, 91, 84, 101/90, 99, 97, 87/115, 85, 110, 149,123, 118, 146, 153, 132/105, 138, 158, 187, 183, 180, 190/170) were quantified in the samples. Blanks were run with each batch of 10-12 samples.

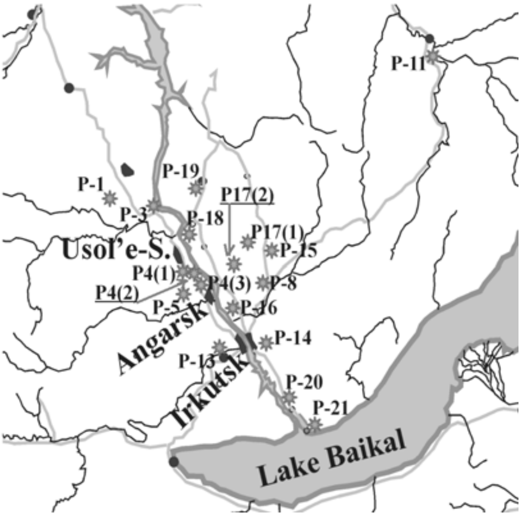

Figure 1: Sampling sites.

Results and Discussion

The results are presented in Table 1 and in Figures 2-4.

PCBs. The sum of all quantified PCB congeners varies from 3.9 (P-3) to 44 (P-15) ng/g lipid weight (LW) in spring milk, from 1.5 (P-11) to 49 (P-4(3)) ng/g LW in autumn milk and from 0.75 (P-11) till 8.9 (P-4(2)) ng/g dry weight (DW) in soil from pastures. Levels of PCBs in soil don't exceed the Russian sanitary standard (0.06 mg/kg)[4]. Usually all PCB congeners were found in pasture soil except PCB-48/47, 70 and 84. In milk tri- and tetra-chlorinated PCBs were determined in several samples while hexa- and hepta-chlorinated PCBs were found in all samples.

In order to compare the level of total PCBs in soil and cows' milk, it is necessary to eliminate as much as possible the factors which influence the PCB pattern when the chemical are transferred between these two matrices. Assuming that soil ingestion is a major source of PCB exposure to the cows, metabolism is the major process influencing the transmission of the PCBs to milk. Therefore, the ∑PCB was calculated just from those congeners known to be persistent in the cow, namely PCB-74, 99, 85, 118, 153, 138, 158, 183, 180, and 190/170[5].

The distribution of PCBs in soil and milk is presented in Figure 2. The highest levels in soil were found in pasture P-4(2) located south-east of Usol'e-Sibirskoe. The concentrations decreased 2.3 times going from Usol'e-Sibirskoe (P-4(2)) to Irkutsk (P-14). The lowest PCB level was found in soil from pasture P-11, which had 11 times lower levels than the most contaminated soil (P-4(2)). The distribution of PCBs in soil from pastures is similar to the distribution measured in a parallel study in non-agricultural soils (sampled layer 0-20 cm) [6]. The PCB levels in pasture soils were usually lower than in the non-agricultural soils (except P-3), which might be due to the cultivation of the pastures and the resulting deep mixing of the soils.

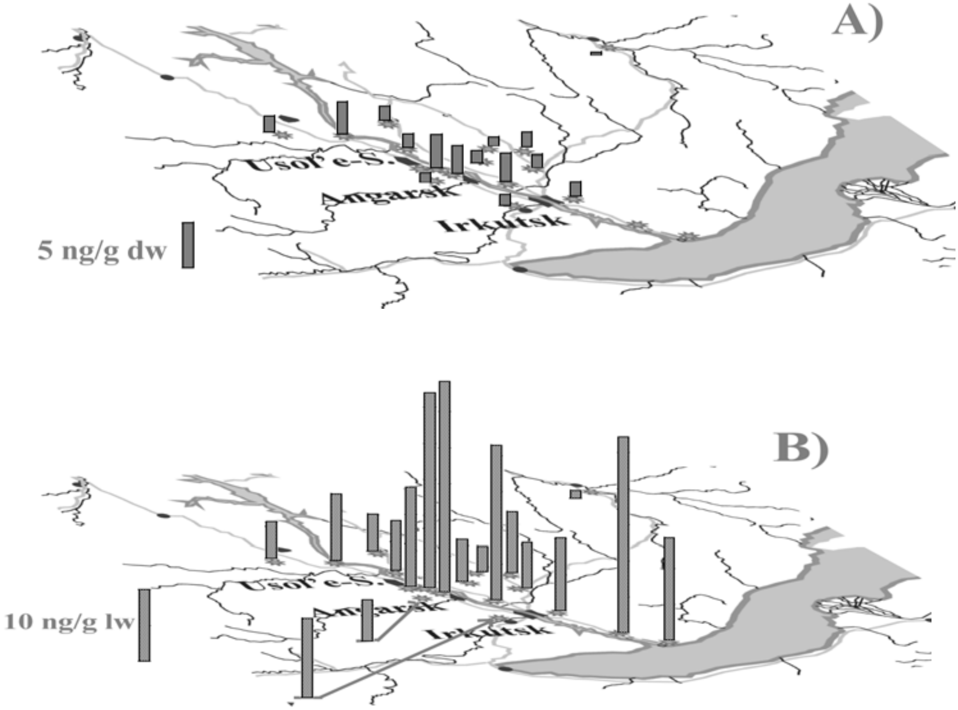

Figure 2: The distribution of PCBs in pasture soil (A) (ng/g dw) and in autumn cow's milk (B) (ng/g lw).

The distribution of PCBs in spring milk among the farms differs from the distribution in autumn milk. The farms can be divided in two groups. The first group includes 9 farms where autumn PCB levels were higher than spring concentrations. The second group also includes 9 farms where spring PCBs levels in milk were higher than autumn levels. Higher concentrations in spring can result from the winter feed and potential sources of PCBs in the barns. Some farms purchase additional feed from elsewhere if the feed crop is poor. Thus it is better to use autumn milk to examine influence of local contamination on PCB levels in cow's milk. An excellent correlation between PCB levels in pasture soil and PCB levels in autumn milk was obtained ($r^2 = 0.80$), which suggests that the level of feed contamination is closely linked to if not caused by the soil contamination (Fig. 3). No correlation was found between PCB levels in soil and spring milk ($r^2 = 0.03$).

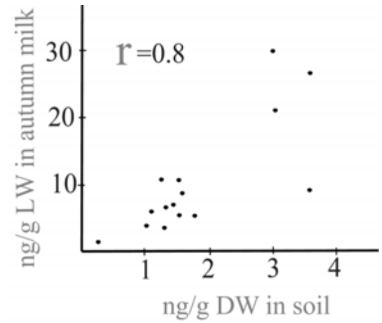

Figure 3. Correlation between PCB levels in pasture soil and PCB levels in autumn milk.

The highest levels of PCB in autumn cow's milk were determined in farms located between Angarsk and Usol'e-Sibirskoe. It is interesting that farm P-4(1), which is located close to Usol'e-Sibirskoe but doesn't have its own pasture (instead relying on feed harvested in a distant area) has lower levels than the neighboring farm P-4(2).

The autumn milk with the highest PCB level was from a farm located near Angarsk. This farm also had amongst the higher soil concentrations. Although the highest soil levels were measured a little closer to Usol'e, some variability can be expected due to the condition of pasture. The PCB levels in autumn milk decrease by a factor of 2 on a transect from Angarsk to Listvyanka on Lake Baikal. The lowest PCB level was found in autumn milk from the remote farm P-11, which was 26 times lower than at the most contaminated farm.

The milk sample from site P-20 close to Lake Baikal shows surprisingly high PCB levels. This was a site where village cows (as opposed to a farm) were sampled. The higher levels may be the result of the few number of cows sampled or the fact that the cows pasture freely in an inhabited area.

Interestingly the milk from the farm P-18 and soil from their pasture located opposite Usol'e-Sibirskoe factories on the other shore of the Angara river didn't contain high levels relative to other farms nearby (P-4(2) / P-18 = 2.5 for pasture and 3.9 for autumn milk). This can be explained by the prevailing wind direction (from north-west to south-east) that take emissions from Usol'e-Sibirskoe around this area.

In general the PCB levels in milk from farms sampled in 2003 were similar or a little higher than in milk collected from dairies (Irkutsk, Angarsk, Usol'e-Sibirskoe) in August of 1997 and analyzed in the laboratory of the University of Bayreuth (Germany).

HCHs and DDTs. The levels of HCH and DDT and their metabolites vary widely both in soil and milk samples (Table 1, Fig. 4), but all values are under the Russian sanitary standard (1.25 mg/kg LW in cow's milk and 0.1 mg/kg DW in soil for HCH and 1.0 mg/kg LW in cow's milk and 0.1 mg/kg DW in soil for DDT)[5,7]. The high mean level of HCH in spring milk is due to high concentrations in three samples of milk from P-1 (241), P-17(1) (214 ng/g LW) and P-17(2) (93). High DDT levels were found in one of the spring milk samples too (P-17(2) = 23 ng/g LW).

The α- and γ-HCH levels obtained for pasture soil near Irkutsk is comparable to or smaller than in samples collected in 1992 from agricultural fields near Irkutsk and analyzed by Iwata et al. (0.019-6.1 ng/g DW)[8]. On the other hand, the DDT levels found in soil from the same pasture (76.7 ng/g DW) are higher than the values found by Iwata et al. (0.34-28 ng/g DW)[8]. The levels of both

∑HCH and ∑DDT in soil found in our investigation are lower than were found in 2000 on agricultural fields in the Irkutsk Region by the Department of Hydrometeorology and Monitoring of the Environment[9]. That study indicated that the most polluted areas are fields around Irkutsk, particularly with regard to DDT (mean value was equal to 0.07-0.10 of the sanitary standard, while the maximum was equal to 1.30-3.59 of the sanitary standard for ∑DDT; mean for ∑HCH was equal to 0.02 of the sanitary standard)[9].

The contribution of α-HCH to ∑HCH was higher in milk samples (52-99 %) than in soil samples (58-77 %). The contribution of p,p'-DDT to ∑DDTs amounted to 52.4 % (16-73 %) in soil, while in milk samples p,p'-DDE made up the largest part of ∑DDT (89 % on average). This results from metabolism of the compounds in cows [5].

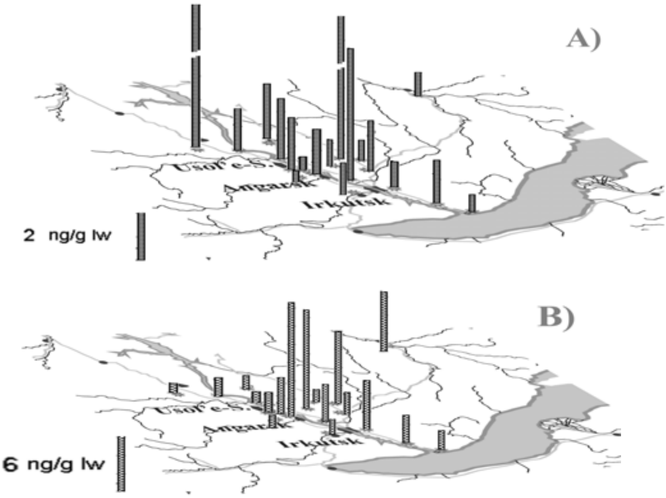

Figure 4: Distribution of HCH (A) and DDT (B) in autumn milk (ng/g lw).

The distribution of ∑DDT and ∑HCH in spring milk among the farms differs from the distribution in autumn milk. There were also two groups of farms: those where autumn levels were higher than spring concentrations, and vice versa.

No correlation was found between ∑HCH levels in pasture soil and its levels in either autumn milk (r^2= - 0.13) or spring milk (r^2= - 0.11). A moderate correlation between the sum of DDT and DDE levels in pasture soil and its levels in autumn milk was obtained (r^2 = 0.54), but if the two highest concentrations of DDT in soil were ommited from the calculations, the correlation coefficient decreased to – 0.11. This suggests that these compounds come to the cow's milk from a source other than pasture soil.

In contrast to the PCB distribution in soil and in milk, the HCH and DDT distributions don't suggest a single regional source. The presence of the compound in each area depends on the history of its use in that area.

Table 1: Levels of HCHs and DDT and their metabolites and their contribution to ∑HCH and ∑DDT in cow's milk and soil from pastures.

	Cow's milk, spring, %	N	Cow's milk, autumn, %	N	Pasture, %	N
% lipids	4.8 (3.2-9.5)	18	4.2(2.9-6.4)	18	-	
α-HCH	88 (53-99)	18	91 (79-99)	18	69 (59-77)	17
γ-HCH	12 (0.6-47)	18	8.5 (0.6-20)	18	31 (22-41)	16
∑ HCHs,%	100	18	100	18	100	17
∑ HCHs, ng/g lw,ww	**32 (0.5-241)**	**18**	**3.6 (0.5-28)**	**18**	**0.3 (0.02-0.9)**	**18**
p,p'-DDE	83 (18-99)	18	87 (60-97)	18	33 (16-74)	16
p,p'-DDD	5.8 (2.1-19)	10	3.2 (0.9-10)	11	1.4 (0.5-33)	14
o,p'-DDT	5.2 (1.3-19)	5	4.4 (2.5-7.3)	4	12 (2.6-46)	13
p,p'-DDT	14 (1-60)	16	10 (1.5-30)	17	52 (16-74)	15
∑ DDTs,%	100	18	100	18	100	17
∑ DDTs, ng/g lw,ww	**3.8 (0.5-23)**	**18**	**3.9 (1-12)**		**11 (0.05-99)**	**17**

Acknowledgements

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References

1. Mamontova E.A., Tarasova E.N., Mamontov A.A., McLachlan M.S. and Litvinstev A.N. (2003) Ecological Chemistry 12(1), 47-56.
2. Mamontova E.A., Mamontov A.A., Tarasova E.N. and McLachlan M.S. (1998) Organohalogen Compounds 38, 135-139.
3. Mamontova E.A., Mamontov A.A. and Tarasova E.N. (2000) Organohalogen Compounds 48, 260-263.
4. McLachlan M.S. (1993) J. Agric.Food Chem. 41, 474-480
5. POPs Regulatory Actions and Guidelines concerning persistent organic pollutants. (1998) UNEP chemicals, Geneva, 267
6. Kuzmin M.I., Mamontov A.A., Mamontova E.A., Tarasova E.N. and MacLachlan M.S. (2004) Organohalogen Compounds (submitted)
7. Hygienic requirements for quality and safety of primary products and food. Sanitary regulations and standards (SanPiN 2.3.2.560-96)
8. Iwata H., Tanabe S., Ueda K., Tutsukawa R. (1995) Environ. Sci. Technol. 29, 792-801.
9. State report "About condition of environment in the Irkutsk Region in 2000". (2001) Irkutsk: Oblmashinform, 384 p.