PCDD/Fs IN HUMAN MILK AND BLOOD SAMPLES FROM A CONTAMINATED REGION NEAR LAKE BAIKAL

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Introduction

In 1997, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) were found in Baikal seals at concentrations comparable with those found in seals from contaminated marine ecosystems such as the Baltic Sea[1]. Further study demonstrated that these compounds accumulate through the food chain in Lake Baikal[2], that the high levels are not the result of continental background arising from long range transport[3], and that the contamination is higher in the southern basin of the lake[4]. A study of PCDD/F inventories in soils indicated that the primary source of contamination had likely been airborne emissions originating from the vicinity of the industrial city of Usol'ye Sibirskoe located 110 km to the north of the southern tip of the lake[5]. Analysis of a number of food samples from this area provided evidence that this contamination continues to affect the food supply, as the PCDD/F levels were highest in milk from a dairy in Usol'ye[6].

Usol'ye S., with a population of 104,300, lies in the valley of the Angara River. This river drains Lake Baikal and the valley is home to a wide range of industry. The major industry in Usol'ye S. is the chemical factory Khimprom which was one of the centres of the chloralkali industry in the Soviet Union. The chemical complex lies to the west (upwind) of the city. Although there was no public knowledge of PCDD/F emissions from this facility, the heavy concentration of chlorine industry makes it a plausible candidate for the source of the local and regional contamination.

In a study of PCDD/F levels in the adipose tissue of 21 individuals living in the Angara River valley, the highest concentration (104 pg I-TE/g lipid) was found in the one volunteer in the cohort who lived in Usol'ye S.[7]. This man had also worked for many years at Khimprom. This, and the evidence of environmental contamination, led to concerns that workers from the Khimprom facility and/or inhabitants of Usol'ye S. could have elevated tissue levels of PCDD/Fs. In this study PCDD/F levels were determined in breast milk from 6 women from Usol'ye S. and in 8 women from Cheremkhovo, a city with a large coal mining and power generation industry that lies 60 km to the northwest of Usol'ye. In addition, PCDD/Fs were determined in the blood of 5 workers from Khimprom who also lived in Usol'ye S..

Methods

The milk samples were collected in accordance with the WHO guidelines for documenting background exposure. All of the women were between the ages of 16 and 25, had lived in either Usol'ye S. or Cheremkhovo all of their lives, and were nursing for the first time. The milk samples were collected by pumping into precleaned glass jars.

The blood samples were taken directly into precleaned glass jars containing heparin. The volunteers ranged in age between 25 and 59 and had been working in the chemical complex for periods ranging from 5 to 40 years.

All of the samples were frozen immediately following collection and were kept frozen at all times until work-up in the laboratories began. The 5 blood samples were analysed at the ERGO laboratory in Hamburg; 7 of the 8 milk samples from Cheremkhovo and one from Usol'ye S. were analysed at the Chemical and Veterinary State Laboratory in Münster, and the remaining sample from Cheremkhovo and 5 samples from Usol'ye S. were analysed at Health Canada. Published and externally validated methods were used by all laboratories[8-10]. The toxicity equivalents (TEs) were calculated using the TEFs proposed by the WHO in 1998.

Results and Discussion

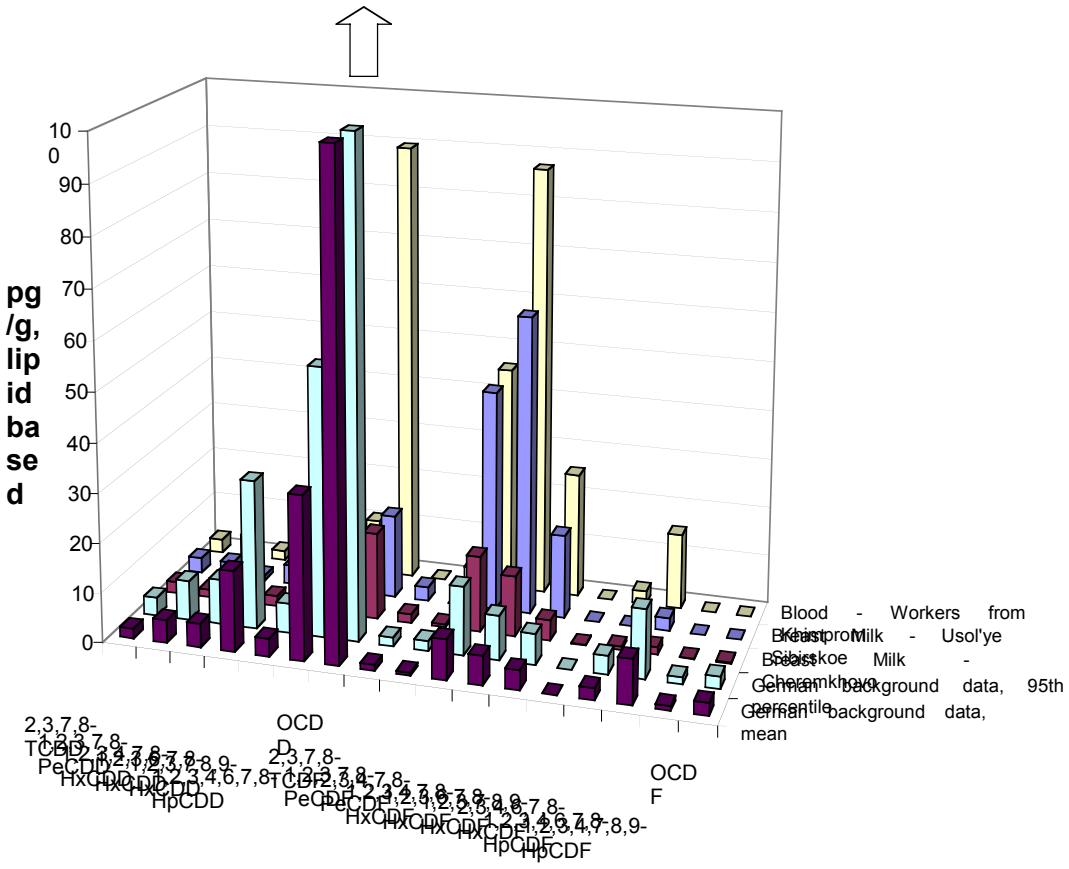
The results are summarised in Figure 1. The average concentrations of the 2,3,7,8-substituted congeners in each of the three sample groups (human milk from Cheremkhovo, human milk from Usol'ye S. and blood from Khimprom workers living in Usol'ye S.) are compared with the background contamination for the German population. The basis of comparison is a study of 59 blood samples collected in 1996 from individuals aged 18 – 30 years. The median and the 95th percentile are shown. A common basis of comparison for the milk and blood samples was chosen for the abstract to save space; with the exception of the higher chlorinated dioxins the lipid based concentrations in blood and milk from a given individual are generally similar[11].

The TE levels in the 8 human milk samples from Cheremkhovo were comparable with the levels found in Germany, with an average of 13 pg/g lipid. The TE levels in the human milk from Usol'ye S. averaged 37 pg/g lipid, which is considerably higher that the German background and nearly a factor of 3 higher than the levels measured in Cheremkhovo. This indicates that the inhabitants of Usol'ye S. were subjected to higher PCDD/F exposure.

The average TE concentration in the 5 workers from the Khimprom plant was 43 pg/g lipid, which is somewhat higher but comparable with the levels measured in the human milk samples from Usol'ye. There was a good correlation between the levels in blood and age, with a correlation coefficient of 0.97. This suggests that the somewhat higher levels measured in the Khimprom workers was not the result of occupational exposure, but rather the higher average age of the workers group (38 vs. 22). Due to the size of the Khimprom complex, it would have been a fortuitous coincidence if any of the 5 workers sampled had had working place contact with the hypothesised PCDD/F source.

The average concentration measured in the previous study of adipose tissue of 19 individuals from the city of Irkutsk and the surrounding area was 24 pg I-TE/g lipid[7]. Schecter et al. reported an average of 17.3 pg I-TE/g lipid for human milk collected from 4 individuals in Irkutsk in 1988/1989[12]. These concentrations lie between the levels in Cheremkhovo and Usol'ye. Irkutsk lies about 70 km to the southeast (down wind) of Usol'ye, and the study of soil inventories showed that the PCDD/Fs had been dispersed in this direction and accumulated in the soils in the Irkutsk area and beyond this around all of southern Lake Baikal[5].

Figure 1: Average concentrations in the 3 groups of analysed samples compared with the German background in blood from 1996



All of the samples including those from Cheremkhovo showed a PCDD/F congener pattern that differed distinctly from that commonly found in western industrialised areas. Schecter et al. observed this in their early study of milk from Irkutsk[12]. This pattern is characterised by comparatively low values of the higher chlorinated dioxins that typically lay close to or below the minimum levels measured in the German background study, accompanied by very elevated levels of 2,3,4,7,8-Cl_5DF, 1,2,3,4,7,8-Cl_6DF and 1,2,3,6,7,8-Cl_6DF. Of particular note was the unusual ratio of the 2,3,7,8-substituted Cl_6DF congeners to each other: on average 28:9:1 (1,2,3,4,7,8 : 1,2,3,6,7,8 : 2,3,4,6,7,8). The environmental contamination of this region also shows the same pattern, namely high levels of lower chlorinated PCDFs, low levels of higher chlorinated PCDDs,

and the unusual Cl_6DF isomer ratios. The pattern in the samples has many similarities to the pattern in the PCDD/F contamination present in commercial PCB mixtures[5], and the environment has also been shown to be contaminated with PCBs from an atmospheric source originating in the same area[5]. It also has similarities to the pattern reported for wastes from the chloralkali industry, although there are also distinct differences[13]. It has not yet been possible to identify the source.
The results of this study thus support the hypothesis that the contamination of the local population with PCDD/Fs is linked to a source in the Usol'ye S. area that has contaminated the environment throughout the Lake Baikal region. This link between environmental contamination and human levels is facilitated by the extensive dependence on locally produced food.

Acknowledgements
We thank the volunteers for their willingness to participate in the study and to donate samples.

References

1. Tarasova E.N., Mamontov A.A., Mamontov A.E., Klasmeier J. and McLachlan M.S.; *Chemosphere* **1997**, 34, 2419-2427.
2. Mamontov A.A., Mamontova E.A., Tarasova E.N., Pastukhov M.V., Lutz H. and McLachlan M.S. *Organohalogen Compounds* 1997, 32, 272-277.
3. Mamontov A.A., Mamontova E.A., Tarasova E.N. and McLachlan M.S.; *Organohalogen Compounds* **1998**, 39, 323-326.
4. Mamontov A.A., Mamontova E.A., Tarasova E.N., McLachlan M.S. and Anoshko P.N.; *Organohalogen Compounds* **1998**, 39, 319-322.
5. Mamontov A.A., Mamontova E.A., Tarasova E.N. and McLachlan M.S.; *Organohalogen Compounds* **1998**, 39, 327-330.
6. Mamontova E.A., Mamontov A.A., Tarasova E.N. and McLachlan M.S.; *Organohalogen Compounds* **1998**, 38, 135-138.
7. Mamontova E.A., Mamontov A.A., Tarasova E.N. and McLachlan M.S.; *Organohalogen Compounds* **1998**, 38, 131-134.
8. Päpke O., Ball M., Lis Z.A., Scheunert K.; *Chemosphere* **1989**, 19, 941-948.
9. Ryan J.J., Lau B.P.-Y. and Boyle M. Chapter 3.16, pp.583-602, in *Biological Mass Spectrometry: Present and Future*; Eds. T. Matuso, R.M. Caprioli, M.L. Gross and Y. Seyama, **1994**.
10. Stephens R., Rappe C., Hayeard D., Nygren M., Startin J., Esboll A., Charle J. and Yrjänkeikki E.; *Anal. Chem.* **1992**, 64, 3109-3117.
11. Päpke O.; *Environ. Health Persp.* **1998**, 106/Sup. 2, 723-731.
12. Schecter A., Fürst P., Fürst C., Groebel W., Kolesnikov S., Savchenkov M., Beim A., Boldonov A., Trubitsun E. and Vlasov B.; *Chemosphere* **1990**, 20, 927-934.
13. Rappe C., Glas B., Kjeller L.-O., Kulp S.E., de Wit C. and Melin A.; *Chemosphere* **1990**, 20, 1701-1706.