Persistent organic pollutants in soil and snow from the Lake Baikal Region, Russia

Alexander Mamontov[1], Elena A. Mamontova[1], Eugenia N. Tarasova[1], Mikhail I. Kuzmin[1], Michael S. McLachlan[2]

[1]A.P. Vinogradov Institute of Geochemistry, SB of RAS, Irkutsk
[2]Institute of Applied Environmental Research, Stockholm University, Stockholm

Introduction

Lake Baikal, located in east-central Asia, is a unique freshwater ecosystem; more than 2/3 of the species found there are endemic. Almost 20% of the earth's unfrozen surface freshwater is contained in its basin. During the last 20 years scientists have found high levels of PCBs in the Lake Baikal ecosystem that are comparable to those in Lake Superior and the Baltic Sea. The fish and water samples indicated that PCB contamination of Lake Baikal does not originate from background input and that contamination increases from north to south. A survey of PCB levels in 34 soil samples in 1997 indicated a steep and consistent gradient of over a factor of 1000 in PCB soil inventories moving from the southwest end of the lake towards the north and east[1]. The highest level was found in the industrial town Usol`e-Sibirskoe located 110 km to the northwest of the southern end of Lake Baikal. The purpose of this study was to more closely examine the soil concentration and the PCB levels in snow in the area around Usol`e-Sibirskoe in order to better localize the source of the contamination and evaluate the risk it poses to the local population. In addition, soil samples were gathered in regions which had not been covered in the original survey. They were also analyzed for hexachlorobenzene (HCB), hexachlorocyclohexane (HCH), and DDT plus metabolites.

Materials and methods

Sample collection. Soil and snow samples were collected at 80 and 32 sites, respectively, around Lake Baikal and in the Angara River valley from Lake Baikal to the town Taishet during the summer of 2001 and the winter and summer of 2002 (see Figure 1). The soil was sampled to a depth of 20-25 cm or to the bottom of the organic matter rich soil layer (A horizon), and the concentrations were calculated normalized to the cross-sectional area of the cores taken. All samples were transported to the institute and stored at -30^0C until analysis. For details of the soil sampling procedure see Mamontov [2]. Snow sampling was done during the last week February prior to the beginning of the snow melt. Samples (4-5 kg) were taken very cautiously with a steel shovel (10×10×5 cm) to the full depth of the snow cover (about 60 cm deep). The snow was transferred to a plastic container. The containers were sealed and transported to the laboratory for extraction. The concentrations were calculated normalized to the cross-sectional area of the area sampled.

Sample extraction and analysis. Soil. Before analysis all samples of soil were dried at room temperature to constant weight and then the fraction <2 mm was used for analysis. 3-120 g was placed in a Soxhlet extractor, surrogate standards (21.5 ng PCB 14 and 8.3 ng PCB 65) were added, and extraction proceeded with equal parts hexane and acetone for 12 h (about 90 cycles). Large molecules in the extract were separated by gel permiation chromatography (GPC) on Bio-Beads S-X3. This was followed by a column consisting of 3 g Al_2O_3 (activated at the 950^0C), 3 g silica gel (activated at the 400^0C) and 3 g Na_2SO_4. The fraction containing the PCBs was evaporated to 30 µl. *Snow*. The sample containers were transferred to a glass container which had been pre-cleaned by rinsing them three times with dichloromethane. The containers were left at room temperature until the snow had melted fully. Then the snow water was carefully mixed with a glass rod, and 0.9 L were transferred to a dark glass bottle. The melted snow samples (0.9 L water per sample) were mixed with surrogate standards (21.5 ng PCB 14 and 8.3 ng PCB 65) and extracted thrice using 20, 15, and 15 ml dichloromethane, respectively. The extracts were dried over Na_2SO_4 and cleaned up as described above, but without the GPC step.

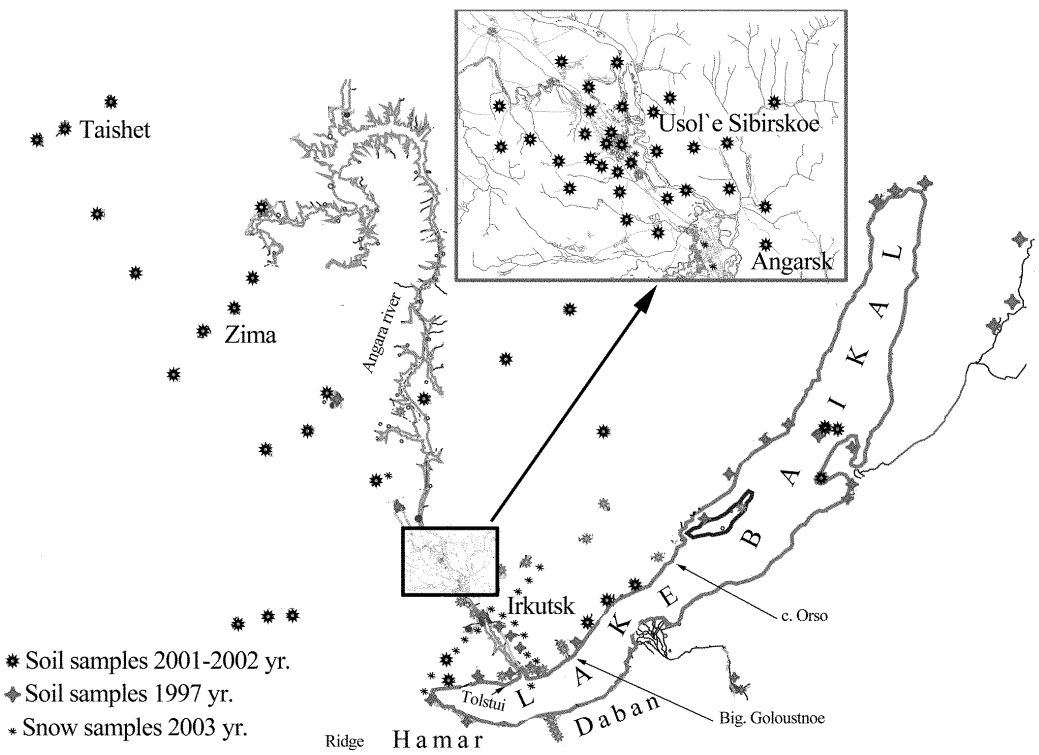

Figure 1: Soil and snow sampling sites.

The POPs were analyzed using gas chromatography with a ^{63}Ni electron-capture detector (GC-ECD). The Hewlett – Packard 5890 series II GC was equipped with a 0.25 µm × 60 m DB-5 capillary column (J&W Scientific). The carrier gas was He and the make-up gas was N_2. The

temperatures of the detector and the injector were 320^{0}C and 270^{0}C, respectively. The temperature program was: start at 90^{0}C (2 min hold), increasing to 170^{0}C at 22^{0}C/min and then increasing to 280^{0}C at a rate 1.32^{0}C/min (17 min hold).

Method recoveries were determined using spiked samples. They lay between 0.8 and 1.2 for most analytes, the only exceptions being HCB (0.73) and DDD (1.61) in soil and PCB 28 (1.37) in snow.

PCB-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 (IUPAC number) were determining in all samples. Furthermore a-, b-, and g-HCH, HCB, p,p-DDT, p,p-DDE, and p,p-DDD were found in almost all samples.

Results and Discussion

PCB. The concentration of the sum of all PCB congeners (ΣPCB) in soil varied from 0.92ng/g (5.4 ng/cm^2) up to 530 ng/g (3200 ng/cm^2) in the area of Usol`e-Sibirskoe and from 0.45 ng/g (3.4 ng/cm$^2$) in the area of Cape Orso up to 32 ng/g (133 ng/cm$^2$) in the village Listvenichnoe. The greatest concentrations were found in a zone in the northeast of Usol`e-Sibirskoe which included the chemical complex «Chimprom», a waste dump, and the eastern part of the city. The pattern of pollution suggests that industrial wastes in the dump site are the source of pollution.

The regions of elevated contamination extended lengthways along the Angara River (see Figure 2). Moving at right angles to the valley, the concentration PCB decreased by more than two orders of magnitude within 5-10 km. Moving along the river valley, one must travel 20-40 and more kilometers to see a similar decrease in concentration. The most contaminated areas extend along the Angara River from the town of Zima up to the northern slopes of the ridge Hamar Daban in the Baikal reserve.

The PCB congener composition varied widely between contaminated areas and background sites. The fraction of the more volatile PCBs was greater in the remote regions compared to the area of maximal concentration. In the contaminated zone the fraction of the higher chlorinated congeners is actually greater than in the technical PCB mixture (Sovol), providing further evidence that the lighter chlorinated congeners are revolatilizing and being transported to more remote areas. The results of this study are consistent with the results of the earlier work from 1997. In Table 1 the PCB levels at two locations that were sampled in both 1997 and 2002 are compared. In general there is good agreement for most congeners. The lower chlorinated congeners generally showed lower concentration in the more recent samples, which may be the result of ongoing volatilization from these contaminated soils.

Over a period of 4 months (November until the end of February), the snow accumulated < 0.1 % of the PCB already contained in the underlying soil in ground for the strongly polluted regions and about 1 % for regions remote from zones of the sources. The PCB levels in snow were higher in Usol`e-Sibirskoe, Irkutsk, and Angarsk (see Figure 3). This may be related to emissions from electrical transformers. All elevated concentrations observed outside of cities were at locations near to high-voltage electricity lines.

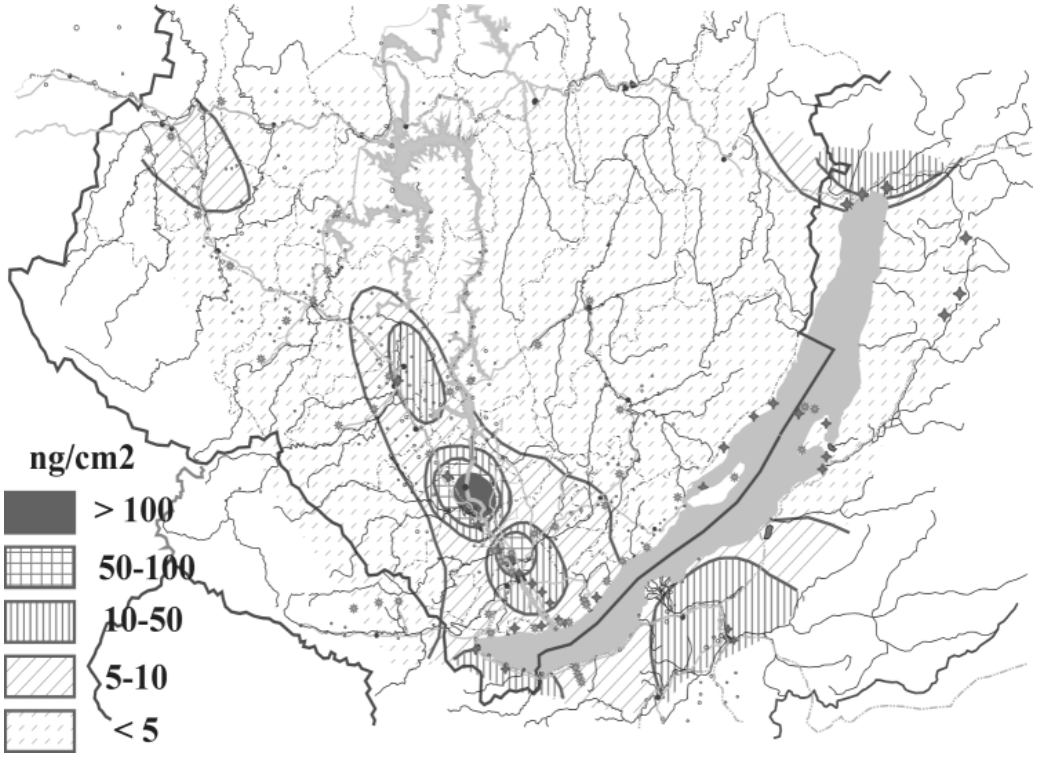

Figure 2: Map showing the distribution of $\Sigma 8PCB_{(28+52+101/90+153+138+180+99+118)}$ in soil in the Irkutsk region.

Table 1: Comparison of the levels of 8 PCB congeners in two contaminated soils that were sampled and analyzed in both 1997 and 2002.

ng/cm^2	Usol`e-Sibirskoe, 1997	Usol`e-Sibirskoe, 2002	Angarsk, 1997	Angarsk, 2002
PCB 28	11	n.d.	1.4	0.6
PCB 52	45	26	4.6	2.6
PCB 101/90	140	95	13	14.7
PCB 99	66	42	8.3	7.1
PCB 118	54	136	4.8	14.9
PCB 153	260	142	19	12.7
PCB 138	260	234	19	20.2
PCB 180	89	73	4.8	4.8

n.d. –not determined.

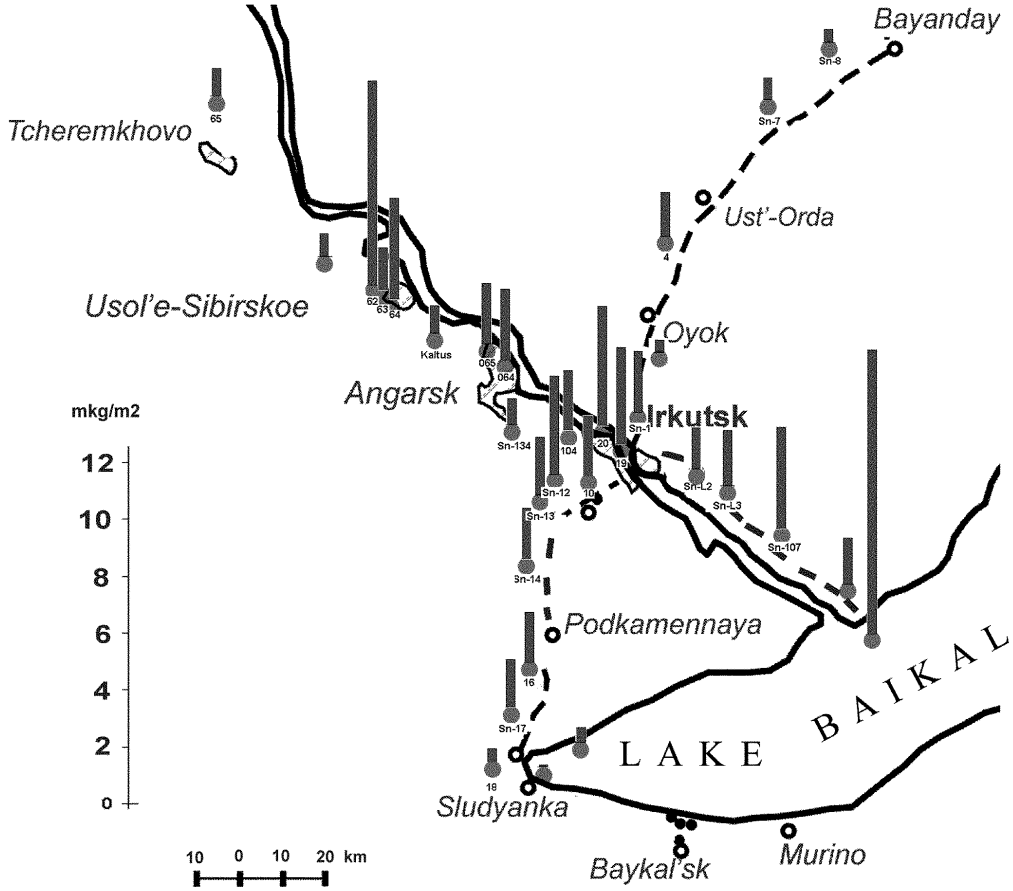

Figure 3: PCB levels in snow samples.

The range in the ΣPCB in snow cover was a factor of 15, from 0.04 ng/cm^2 up to 0.61 ng/cm^2. The high levels found in snow from the Baikal ice (1 ng/cm^2) was probably a consequence of snow drifting.

The congener composition of the PCB in snow close to the sources was characterized by a higher proportion of the more chlorinated congeners than in technical PCB (Sovol). The congener composition in the snow and soil was similar in background areas and contained a greater proportion of the more volatile PCBs.

The calculation of the annual flux of PCB to soil from the atmosphere on the basis of the snow data is not possible owing to the big distinctions between the stationary winter and dynamical

summer periods[3]. During the summer the emissions of PCB from stationary industrial combustion sources will be much lower while at the same time emissions due to forest fires and volatilization from soil will become more important. The seasonal cycle of PCBs between the atmosphere and the terrestrial environment in this area requires further research.

The levels of HCHs, DDTs and it metabolites in soil and snow cover (Table 2) varied widely. No consistent spatial pattern was observed. The highest levels of HCB in soil were found at sites with high levels of ash from forest fires. In snow cover HCB showed the greatest concentration in cities.

Table 2: Concentration of HCHs, DDTs and it metabolites in soil and snow cover.

	Snow (ng/cm^2)	**Soil (ng/cm^2)**
HCHs	0.00071-0.039	0.035-5.3
HCB	0.00027-0.024	0.28-183
DDTs	0.00025-0.062	0.39-460

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