Modern Levels of the Accumulation of Polychlorinated Diphenyls in the Objects of the Baikal Natural Territory

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Abstract

Concentrations of polychlorinated diphenyls (PCD) were measured in snow cover (10–520 ng/m^2), in the soil (0.3–45 ng/g of dry mass) of Pribaikalia and the southern lakeside, in bottom sediments of Lake Baikal and its tributaries (0.3–3.9 ng/g of dry mass), in Baikalian omul (*Coregonus autumnalis migratorious G.*, 25–41 ng/kg of damp mass). A conclusion concerning the background pollution of the atmosphere of Pribaikalia with PCD at present and the absence of intensive local sources of organic pollutants of this class at this territory is formulated. The concentrations of PCD in soil and bottom sediments remained almost unchanged during the years 1992–2006. The levels of PCD bioaccumulation in Baikalian omul are 3.5–10 times lower than the MPC. Determination of PCD was carried out with the help of gas chromatography-mass spectrometry with the intra-laboratory precision of 7–15 %.

INTRODUCTION

Synthesis of polychlorinated diphenyls (PCD) had been carried out since the 30s of the past century. However, at present their production is prohibited by a number of international agreements; the compounds of this class are included into the list of stable organic pollutants of natural objects. Total mass of PCD is considered to have achieved 2 mln t by the moment when their production was ceased; not less than 30 % of this amount had entered the environment [1, 2]. During the years 1992–1994, when working on a series of international projects [3], researchers detected relatively high PCD concentrations in the surface water of Lake Baikal (up to 0.6–1.3 ng/l) and in the fat of Baikal seal (3.3–11 μg/g); however, the source of PCD entering the Baikal Natural Territory (BNT) had not been detected.

The Irkutsk Region is among 12 regions of Russia where substantial amount of electrotechnical equipment containing PCD is concentrated [4]. Performance of this equipment followed by its utilization is one of the possible sources of PCD at the territory of Pribaikalia. Because of this, monitoring of PCD concentrations in natural objects with the help of modern analysis methods is important and urgent for the BNT as a model of a territory of sustainable development of universal importance.

In the present work, we describe the results of the investigation of snow cover and soil of southern Pribaikalia, bottom sediments of Lake Baikal and its tributaries, and Baikalian omul (*Coregonus autumnalis migratorious* G.); these investigations were carried out in order to evaluate modern levels of the accumulation of PCD in the natural objects of BNT. The choice of objects was based on their ability to accumulate PCD entering the environment *via* different channels and during different time intervals. The profiles and sampling sites were chosen taking into account the position of potential PCD sources and the directions of prevailing winds over the territory of Pribaikalia.

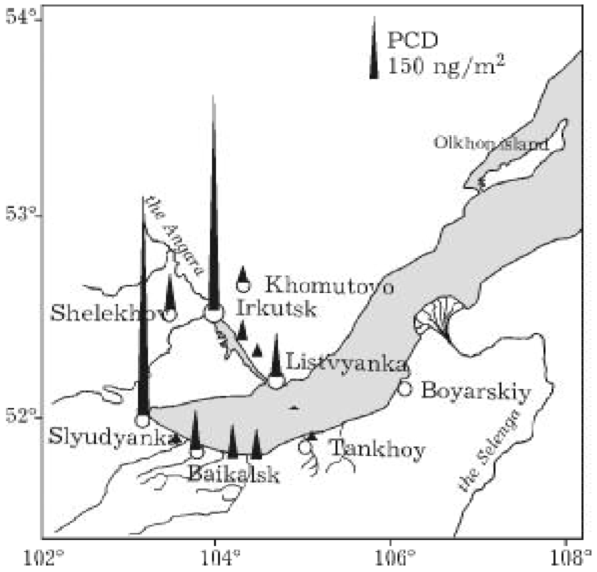

Fig. 1. Scheme of sampling sites and the levels of accumulation of polychlorinated diphenyls (PCD) in the snow cover of Southern Pribaikalia.

EXPERIMENTAL

Snow was sampled at the end of the winter season (at the end of February and early in March) of the years 2005–2006 at the territory of Irkutsk, in the region of Shelekhov and Khomutovo settlement, in the points of the profile Irkutsk–Listvyanka, and at the southern lakeside (Fig. 1). Snow was sampled in the form of cores with the base area of 230 cm^2 over the whole depth of the snow cover (30–40 cm), two samples from each point were taken at a distance of about 50 cm from each other. Snow samples were put into polyethylene bags are kept in a freezing chamber at −18 °C before analysis. The soil samples were upper layer of ground 5 cm deep with the core base area of 400 cm^2. The samples of bottom sediments in the mouths of the tributaries of southern Baikal (May 2005): the upper layer to the depth of 5 cm and 40–60 cm^3 in volume was taken with the help of a syringe, two samples at each point, at a distance of about 25–50 and 1–2 m from the bank. The cores of bottom sediments in the southern, middle and northern hollows of Lake Baikal were taken with a benthos tube.

To determine PCD, snow samples were melted, the snow water was filtered through membrane filters (Toyo Roshi Kaisha Ltd., Japan), and the filters were dried at room temperature to the constant mass. Soil samples were dried, homogenized and sieved; the fraction with particle size not more than 74 μm was collected. An upper layer 3 cm thick was taken from the cores of bottom sediments. Solid residues obtained by filtering snow water and the soil samples (~7 g, precise weighed portion) were extracted with a mixture of *n*-hexane with acetone (volume ratio 1 : 1). The samples of bottom sediments (~10 g, precise weighed portion) were extracted with a mixture of methanol and methylene chloride (volume ratio 1 : 1), under ultrasonic treatment three times for 30 min. Before extraction, 10 μl of surrogate standard (4,4'-dibromodiphenyl, 50 ng/ml in *i*-propanol) was added.

To determine PCD in Baikalian omul (the Selenga population, bottom deep-sea morphoecoogical group, mature, fished in June 2006 in the Southern Baikal region), about 1 g (precise weighed portion) of homogenized fish muscles was sampled after removal of head, fins, skin, entrails, and backbone. After the addition of 10 μl of the surrogate standard, the weighed portion was boiled for 1 h in 50 ml of a 5 % solution of potassium hydroxide in 90 % aqueous methanol. The products of hydrolysis were extracted with *n*-hexane (twice).

The extracts of the suspended matter from snow water, soil, bottom sediments were purified by means of solid-phase extraction with the cartridges filled with silica gel 9500 mg, Discovery® SPE DSC-Si, Supelco, the USA), fish extract with the cartridge filled with phlorizil (500 mg, Sep-Pak® Vac 6cc, Waters, Ireland). The isolated PCD fractions were concentrated to the volume of about 0.15 ml, then 10 μl of the solution of 4-bromophenol (48 ng/μl in *n*-hexane, Fluka, Switzerland) and 10 μl of 2,2',4,4',5,5'-hexabromophenol (84 ng/μl in *n*-hexane, Ultra Scientific, the USA) were added.

Thus prepared samples were analysed using the Agilent 6890/5973N GC/MSD System (the USA) under the following conditions: column HP-5, 30 m, diameter 0.32 mm; temperature regime: 80 °C (2 min), 80–140 °C (5 °C/min), 140–240 °C (1 °C/min), 240–310 °C (10 °C/min) and 310 °C (15 min); temperature of injector: 290 °C, of quadrupole: 150 °C, the volume of sample introduced into the column: 2 μl. Detection was carried out in the mode of selective ion monitoring of two isotopic molecular ions for each group of congeners with the same degree of chlorination within time intervals corresponding to outlet of these groups from the column. The peaks of PCD on mass chromatograms were identified according to relative retention times and ratios of the areas of isotopic molecular ion peaks. Measurement of PCD was carried out using the internal standard. Calibration was performed with the mixtures of 8 congener PCD containing 2-chlorodiphenyl, 2,3-dichlorodiphenyl, 2,4,5-trichlorodiphenyl, 2,2′,4,4′-tetrachlorodiphenyl, 2,2′,3′,4,6-pentachlorodiphenyl, 2,2′,4,4′,6,6′-hexachlorodiphenyl, 2,2′,3,3′,4,4′,6-heptachlorodiphenyl, 2,2′,3,3′,4,5′,6,6′-octachlorodiphenyl (Supelco, the USA) within the mass range 1 to 100 ng. Calculation of the masses of congeners was carried out using the calibration equations: $m_{PCD} = km_{St}S_{PCD}/S_{St}$ where k is the calibration coefficient for each group of congeners with the same degree of chlorination; m_{PCD} is congener mass, ng; m_{St} is the mass of the surrogate standard, ng; S_{PCD} is the area of the peak of congener, rel. units; S_{St} is the area of the peak of the surrogate standard, rel. units.

The calculated masses were summed up for each group of congeners with the same chlorination degree and for all the identified PCD compounds. The PCD content of each sample was determined two times; the result was represented as an average value of two measurements.

The reagents used for analyses were n-hexane, grade 1 (Kriokhrom Co., St. Petersburg), acetone of ch.d.a. reagent grade (pure for analysis) (EKOS-1, Moscow), methylene chloride of kh.ch. grade (chemically pure), methanol of ch.d.a. grade, sipropanol of kh. ch. grade. Blank experiments were carried out to check the PCD background at the laboratory and the purity of the solvents and instruments used.

RESULTS AND DISCUSSION

Levels of accumulation of PCD in natural objects

Under the conditions of East Siberia distinguished by clearly exhibited anticyclonic atmospheric circulation during the winter season, the snow cover as a test object allows one to discover the sources of pollutants on the basis of the levels of their accumulation at the controlled territory. According to the data of monitoring of the territory of Southern Pribaikalia (seasons 2004–2006), the accumulation of ΣPCD (the sum of the detected polychlorinated diphenyls) in the snow cover is distinguished by the low and rather uniform surface density in non-inhabited regions (~40 ng/m^2). An increase in the level of accumulation of these pollutants was detected at the territory of towns and settlements. For instance, the maximal accumulation of PCD was observed in the snow cover of the central districts of Irkutsk (up to 520 ng/m^2). The level of ΣPCD accumulation decreases to 20–90 ng/m^2 at the outlying districts and at a distance of 20 km from the city boundary to the south-east or at a distance of 20 km to the north-west. The concentration of ΣPCD in snow samples did not exceed 85 ng/m^2 at the points of the profile from Irkutsk to Listvyanka village coinciding in direction with the dominating winds in Pribaikalia, and also at the southern side of Lake Baikal. The low surface density of ΣPCD in the snow cover over the lake ice (≤10 ng/m^2) is likely to be connected with the shorter period of their accumulation due to the later formation of a stable ice cover.

Investigation of the samples of snow water revealed the presence of PCD only in the suspended solid particles (2–270 ng/g), so PCD compounds get accumulated during the snow-melting period at the ground, in bottom sediments of rivers and other water bodies. Unlike for snow cover, these natural objects belong to the conservative matrices accumulating the pollutants and conserving the information on atmospheric pollution during a long period of time. Along with accumulation, such processes as biodestruction and chemical transformations occur simultaneously in these matrices, thought he rates of these processes are low. For example, the half-life of PCD in soil reaches 45 years [5]. This time interval may be much longer for East Siberia distinguished by a long winter period.

The level of ΣPCD accumulation in soil samples taken at the territory of Pribaikalia is 0.3 to 45 ng/g of dry mass; rather clear correlation is observed between the levels of their accumulation in the snow cover and in soil (r = 0.965) (Fig. 2). This fact points to a long-range atmospheric transport to the territory of Prib-

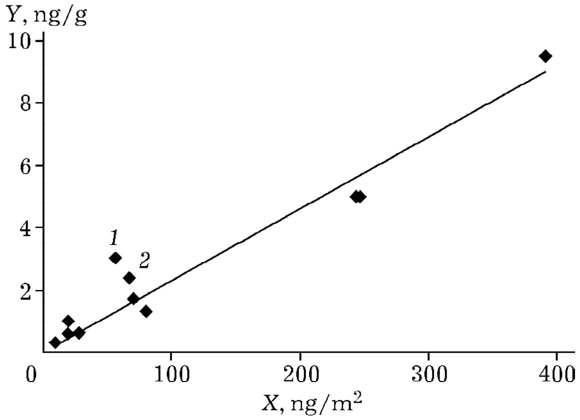

Fig. 2. Interdependence of the levels of PCD accumulation in snow cover (X) and soil (Y) of Southern Pribaikalia (r = 0.967): *1* – the mouth of the Snezhnaya River, *2* – the mouth of the Khara-Murin River.

aikalia as the main source of PCD in this region. One can see in Fig. 2 that the unpopulated regions at the southern side of Lake Baikal in the mouths of the Snezhnaya and the Khara-Murin rivers are distinguished by the higher level of PCD accumulation in soil than that observed in the mouths of the Utulik and the Pereyemnaya. This phenomenon is likely to be connected with the spatial features of the airborne income of pollutants in Southern Pribaikalia [6]. Points for two regions of Irkutsk (Solnechny microdistrict, the territory around the heat and electric power plant No. 2) and for Sluidyanka falling out of this dependence are not shown in Fig. 2. For Irkutsk, in the former case, a higher concentration of PCD in soil (45 ng/g of dry mass) should be related to a local emission as a result of the accident at the transformer substation. In the second case, the high levels of PCD accumulation in soil and in snow cover in the centre of the city are likely to be connected with the arrival of these compounds from a local source, and also with the relief of this part of the city. It is known [7, 8] that the lowered relief of the city centre leads tot eh maximal accumulation of pollutants in the atmosphere during the cold season, followed by the precipitation of these compounds onto the underlying surface, which determines the high level of their accumulation in this region.

The features of atmospheric precipitation at the southern side of Lake Baikal may promote water pollution in the case if air masses come from the industrial zone of Pribaikalia. Atmospheric precipitation, accumulation of

TABLE 1

Concentrations of polychlorinated diphenyls in natural objects of the Baikal Natural Territory, 2005–2006

Sampling region	Snow cover,			Soil,	Bottom sediments,
	ng/m^2	ng/l	ng/m^2 per week	ng/g of dry mass	ng/g of dry mass
Irkutsk	10–520	2.0–17	0.7–3.4	5.0–45	–
Shelekhov	20–88	1.6–6	1.3–5.9	0.6–0.8	–
Khomutovo village	27	0.7	1.8	0.6	–
Profile: Irkutsk–Listvyanka village	15–78	0.4–2.2	1.3–5.3	0.5–4.0	–
Slyudyanka	545	38	36	1.3	–
Listvyanka	84	3.0	5.6	0.3	–
Mouths of rivers at the southern lakeside:					
the Utulik	10	0.7	0.7	0.3	31
the Khara-Murin	67	3.0	4.5	2.4	0.6
the Snezhnaya	56	6.0	3.7	3.0	0.5
the Solzan (within the boundaries of Baikalsk)	70	9.0	4.4	1.7	2.1
the Pereemnaya (the region of Tankhoy village)	10	0.3	0.7	0.3	0.5
Lake Baikal:					
southern hollow	–	–	–	–	0.8–3.9
middle hollow	–	–	–	–	0.3–1.5
northern hollow	–	–	–	–	0.6–1.0

pollutants at the slopes of the Khamar-Daban Ridge and subsequent flow of PCD from the water-collecting basin to the southern hollow of the lake determine the level of their accumulation in the bottom sediments of the tributaries of the lake. However, one can see in Table 1 that the accumulation of PCD in the bottom sediment samples taken in the mouths of the tributaries of Lake Baikal and in soil at the southern side of the lake is comparable and close to the background level, which points to the minimal contribution from the regional transport into the pollution of this region with PCD. The high ΣPCD content (up to 30 ng/g of dry mass) detected in the bottom sediments of the Utulik with respect to the level of accumulation in soil (0.3 ng/g of dry mass) and the minimal level of accumulation in snow cover (≤10 ng/m^2) is likely to be due to the emission from a local source but not to regional transport, especially if we take into account the qualitative composition of the detected congeners.

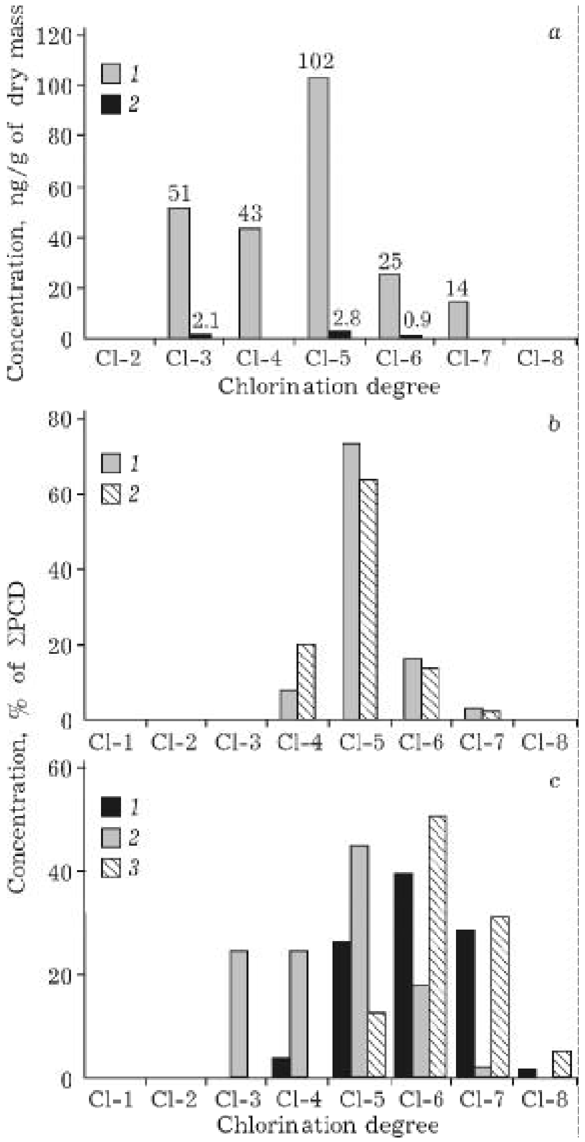

Fig. 3. Group composition of PCD congeners: *a* – in the suspended particles in snow cover (*1* – Irkutsk, *2* – points of the profile Irkutsk–Lisvyanka village); *b* – in bottom sediments of Southern Baikal (*1*) and in omul from the Selenga (*2*); c – in bottom sediments of the Utulik River (*1*) and in technical mixtures “Arokhlor 1254” (*2*) and “Arokhlor 1260” (*3*).

Group composition of congeners in the natural objects of Pribaikalia

The samples of snow cover collected at the regions with the maximal accumulation of PCD exhibit prevalence of pentrachlorodiphenyls (up to 50 % of the mass of the identified congeners). As a consequence of a decrease in the mass of the accumulated PCD, the number of the detected congeners decreases (from 15 to 4), mainly due to tetra- and heptachlorodiphenyls because their concentrations in the samples become below the detection limit (Fig. 3, *a*). This kind of the qualitative composition of PCD including tri-, penta- and hexachlorodiphenyls is also conserved in the points along the profile from Irkutsk to Listvyanka village; only the redistribution of congener ratios varies. The qualitative composition of PCD congeners in snow samples from the southern lakeside differs by the higher nonuniformity and includes one to four groups of isomers depending on sampling site.

Congeners with higher chlorination degree (5 to 8 chlorine atoms in a molecule) than that for snow prevail in the soil of urban districts. Only penta- and hexachlorodiphenyls were detected in the samples collected at the territory of Pribaikalia and at the southern lakeside.

In bottom sediments of the tributaries of the southern Baikal, the PCD compounds are represented by tetra- and pentachlorodiphenyls, while the upper layer of bottom sediments contains also hexa- and heptachlorodiphenyls in addition to the indicated compounds. It should be noted that the group composition of PCD in the bottom sediments of Lake Baikal is almost the same as that in Baikalian omul (see Fig. 3, *b*) and depicts the composition of PCD polluting the water of Lake Baikal at present. Unlike for bottom sediments of Lake Baikal and the sediments in other tributaries of the southern Baikal, the bottom sediments of the Utulik River contain a broader range of PCD congeners similar to their group composition in technical mixtures "Arokhlor", which confirms the assumption of a local source of these ecotoxic compounds (see Fig. 3, *c*).

Estimation of the level of pollution of BNT natural objects with polychlorinated diphenyls at the present stage

The data on the accumulation of PCD in natural objects, collected during the years 1992–1996 [9–11], and the results of the present investigation allow us to carry out a comparative estimation of the levels of BNT pollution with PCD at the present stage. It was established that the flux of PCD to the snow cover in Southern Pribaikalia, averaged over the winter season, decreased by a factor of 10 and more. This is an evidence of a substantial decrease in atmospheric pollution (Fig. 4). With the average PCD fluxes on snow cover of the territory of Irkutsk and Slyudyanka (up to 36 ng/m^2 per week) and at the lakeside (0.7–5.3 ng/m^2 per week), the pollution of the atmosphere is close to the background level. These data are comparable with the estimated values for the regions of high-mountain lakes of West Europe where the corresponding PCD fluxes are 1.8 (the Tatry) to 38 ng/m^2 per week (the Alps) [12].

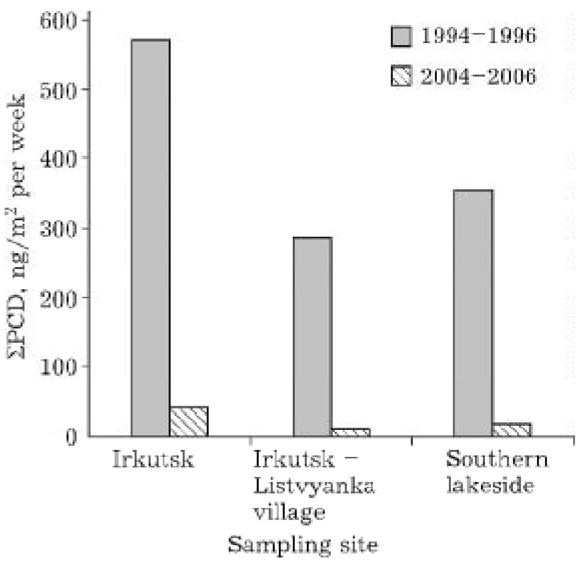

Fig. 4. PCD fluxes onto the snow cover of the Baikal Natural Territory, calculated according to the data of monitoring during the years 1994–1996 [11] and 2004–2006.

The PCD content in the soil of the Baikal region was 1.4–92 ng/g of dry mass in 1992 [9]. The data of the present work show that the level of soil pollution with PCD in Southern Pribaikalia remained almost unchanged during the past decade; at present, it is 0.3–45 ng/g of dry mass. This value is comparable with the pollution of the corresponding territories in West Europe and in America: Winnipeg – 6.7 to 15 ng/g [13], Mexico – 0.5 to 11.0 ng/g [14], unpopulated regions of Sweden – up to 2.3 ng/g [15]. In Russia, the highest PCD content in soil was detected in Serpukhov at the territory of the capacitor plant where capacitors were filled with PCD: $2 \cdot 10^6$ ng/g [16]. The PCD content in the soil of central regions of Russia is estimated as 0.2 ng/g [2].

The levels of PCD accumulation and biological concentrating in the bottom sediments of the lake and in Baikalian omul confirm the purity of Lake Baikal and demonstrate the absence of intense arrival of these organic pollutants into its water. According to [9], ΣPCD in the bottom sediments of Lake Baikal in 1992 was 0.08–6.1 ng/g and remained almost unchanged till present (0.3–3.9 ng/g, see Table 1). In the sediments of the lakes in Central Finland, situated far from industrial centres, ΣPCD varies within the range 0.05–2.54 ng/g of dry mass [17], in the bottom sediments of lakes in the southern part of Sweden it varies from 0.5 to 82 ng/g [18]. It should be noted that the level of PCD bioaccumulation in Baikalian omul, which is ascribed to a valuable species of food fish, did not increase and equals 25–41 ng/g of live mass, or 0.75–1.4 μg/g of lipids. This is 10 times smaller than the level of accumulation in herring fished in the Baltic Sea or in the Atlantic Ocean near the western coast of Sweden [19]. According to the data of [10], PCD content in omul in 1994 was 9.3–211 ng/g of live mass or 0.73–1.6 μg/g of lipids.

CONCLUSION

According to the data of the complex investigation of the objects of the Baikal Natural Territory, it is concluded that intense local and regional sources of PCD are absent at the BNT, while the contribution from the region transport of PCD to the area of the Baikal water is insignificant. The level of accumulation of the soil in Pribaikalia, bottom sediments of Lake Baikal and its tributaries, Baikalian omul with PCD at the present stage is comparable with the world background level. Up to 10-fold decrease of PCD fluxes from the surface layer of the atmosphere to snow cover in comparison with the data of monitoring performed during the years 1994–1996 was detected. This is an evidence of a substantial decrease in the degree of atmospheric pollution. The degree of PCD accumulation in the soil at the territory of Irkutsk, an industrial centre of East Siberia, and Slyudyanka, a large railway junction at he southern side of Lake Baikal, is comparable with the pollution of the corresponding territories in West Europe and in America.

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