An Assessment of Contamination of the Selenga River Basin by Chlorinated Phenols

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Abstract

The concentrations of chlorinated phenols (CP) have been determined in superficial water of Selenga River and its basic tributaries, which provide for 53 % of the Baikal Lake drainage. It has been found that a level of contamination of the Selenga River basin by CP is relatively low and the total CP content comprises 0.36–1.85 mg/l. The presence of CP in natural water is caused mostly by the local anthropogenic and natural sources, for identification of which the use of the ratios of net concentrations of 2,4,5- and 2,4,6-trichlorophenols and 2,4- and 2,6-dichlorophenols, together with 2,4,5- and 2,4,6-trichlorophenols and 2-chlorophenol is suggested.

INTRODUCTION

Chlorinated phenols (CP) are toxic, organic contaminants that enter aquatic ecosystems with sewage and wastes from the pulp-and-paper and chemical industry, and with the residential sewage [1], and also as a result of spontaneous chlorination of natural organic matter [2].

An increasing number of chlorine atoms in benzene ring, as is known, raises the toxicity of CP, their stability against decomposition, and the capability for bioaccumulation [3]. Chlorophenols are the precursors of more dangerous ecotoxicants, dioxins [4]. Pentachlorophenol (PCP) and 2,4,6-trichlorophenol possess mutagen and carcinogenic properties [5], and PCP is additionally the most stable and toxic contaminant among CPs. According to the United Nations Environment Program (UNEP), in 2003, pentachlorophenol is included into the list of stable organic contaminants [6].

In Russia, 2-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol (4 class of hazard), and PCP (2 class of hazard) are standardized in the water bodies of household and amenity water use, and also in the water bodies of commercial fishing importance [7, 8]. According to the worked out "List of the substances harmful for the Baikal Lake ecosystem", CPs fall into the category of "extra hazardous" substances, the presence of which in Baikal water and in its tributaries is inadmissible [9]. Meanwhile, Baikal receives CP with sewage from the Baikal integrated pulp and paper mill (BIPPM) located directly on the lake bank. These CP are derived from lignine at a stage of pulp bleaching with chlorine [10]. CP content of the cleansed sewage from BIPPM varies mostly within the limits of 1–10 mg/l [10], but can be as great as 21 mg/l [11]. Chlorophenols are detected also in the bottom silt of southern water area of the Baikal Lake, inside the BIPPM influence zone [12].

There were no any studies performed previously in the Baikal Lake water-collecting area into CP contamination of aquatic ecosystems and the sources of their ingress. To analyse CP ingress in the Baikal basin, we chose superficial waters of the Selenga River and its main tributaries, which provide for 53 % drainage of the lake [13], and also the Baikal

TABLE 1

CP content of aqueous samples, mg/l

Station number	Stations of sampling	Compound				
		2-CP	SDCP	STCP	PCP	SCP
1	The Selenga River, the settlement of Naushki	0.35	0.21	0.16	0.13	0.85
2	The same, the settlement of Novoselenginsk	0.29	0.34	0.04	0.08	0.75
3	The same, 20 km downstream of Ulan Ude	0.95	0.76	0.01	–	1.72
4	The same, the village of Kabansk	0.40	0.53	0.92	–	1.85
5	The Same, the settlement of Murzino	0.48	0.69	0.63	–	1.80
6	Delta of Selenga River, the Middle arm	0.39	1.19	0.11	–	1.69
7	The same, Kharauz arm	0.43	0.58	0.76	–	1.77
8	The same, Lobanovskaya arm	0.39	N/d	0.15	–	0.54
9	The same, Kolpinnaya arm	N/d	1.33	0.05	–	1.38
10	Uda River, 0.5 km upstream from the mouth	0.28	0.74	0.01	–	1.03
11	Dzhida River	0.24	0.39	0.11	–	0.74
12	Chikoy River	0.31	N/d	0.05	–	0.36
13	Tyemnik River	0.31	N/d	0.28	–	0.59
14	The Baikal Lake, 100 m downstream of BIPPM sewage discharge	0.47	1.11	0.03	0.25	1.86
15	Aeration pond of BIPPM	0.30	2.38	0.09	2.99	5.76

Note. Here and in Table 2, N/d means no data, dash means the compound is not detected in the sample.

Lake, in the part which is downstream from the BIPPM sewage discharge and aeration pond that is the destination point for the cleansed sewage from BIPPM.

EXPERIMENTAL

Sampling of superficial water from the Selenga River was made from the Mongolian border (the settlement of Naushki) up to the Baikal Lake, including the delta of Selenga River and its main tributaries, the rivers Uda, Dzhida, Tyemnik, and Chikoy. Sample preparing consisted in CP bromination in acidic medium (derivatization), removing the excess of bromine with sodium thiosulphate solution, and extraction concentrating of formed bromine-derivatives of chlorophenols by means of toluene [14]. The obtained extracts were analyzed in Hewlett-Packard HP 6890 gas chromatograph (an electron-capture detector with a microcell, HP 5 capillary column, 30 m in length, with inner diameter of 0.32 mm). Conditions of gas chromatographic determination were as follows: a temperature of the evaporator of 250 °C, a temperature of the detector of 330 °C; gas-carrier was helium; boosting the detector with nitrogen, 60 ml/min, without the stream separation. A temperature of a column thermostat was increased from 40 °C (dwell time of 2 min) up to 70 °C (dwell time of 1 min) with the rate of 30 °C/min, then up to 200 °C (dwell time of 3 min) with the rate of 20 °C/min, and up to 255 °C (dwell time of 1 min) with the rate of 20 °C/min.

The following chlorophenols were determined in extracts: 2-chlorophenol (2-CP), dichlorophenol isomers (2,4-DCP and 2,6-DCP), trichlorophenol isomers (2,4,5-TCP and 2,4,6-TCP), and pentachlorophenol. The concentration of CP was calculated by standard addition method. CP standards manufactured by JSC "Science and Production Association Ekros" (St. Petersburg) were used.

RESULTS AND DISCUSSION

Table 1 lists the results of CP determination in superficial natural water and in the water of BIPPM aeration pond.

2-CP. The concentration of 2-CP in all samples does not exceed the MPC for water of the water bodies of household and amenity water

use (1.0 mg/l) [7], but is over the MPC for water of the water bodies that are of commercial fishing importance (0.1 mg/l) [8]. The maximum concentration of 2-CP (0.95 mg/l) was observed in the sample taken from the Selenga River, 20 km downstream of Ulan Ude, which was comparable to its content in the Gdansk gulf (Poland) (0.80 mg/l), which receives CP, mainly, of anthropogenic origin [15]. In the other aqueous samples, the concentration of 2-CP varies from 0.24 to 0.48 mg/l. This is at a level of 2-CP content in the rivers of Northern sea water-collecting area (0.50 mg/l) [16] and the Netherlands (0.60 mg/l) [3], and is lower than its content in the rivers of the southern hemisphere (1.21–8.88 mg/l) (Republic of South Africa) [17]. It should be noted that higher than usual content of 2-CP (up to 0.48 mg/l) in Selenga water is typical both for near-the-delta area (a settlement of Murzino), and for the river delta as such (arms Middle, Kharauz, and Lobanovskaya), and it is comparable to its content in the water of the Baikal Lake in the part, which is downstream from the BIPPM sewage discharge (0.47 mg/l), and aeration pond (0.30 mg/l). The tributaries of Selenga River contain 2-CP in the lower concentration, an average of which is 0.28 mg/l.

2,4-DCP and 2,6-DCP. The total content of DCP isomers in water of Selenga River and its tributaries, as is the case with 2-CP, does not exceed the maximum concentration limit according to HN 2.1.5.689–98 (2.0 mg/l) [7], but is higher than MPC for water of the water bodies that are of commercial fishing importance (0.1 mg/l) [8]. Higher than usual concentrations of DCP are detected in water of Selenga River, 20 km downstream of Ulan Ude (0.76 mg/l), and that of Uda River, 0.5 km upstream from the mouth (0.74 mg/l). In the delta of Selenga River, the maximum concentrations of DCP isomers (0.58–1.33 mg/l) are observed, which are comparable with DCP contamination level of water of the Baikal Lake taken at the location downstream from the point of BIPPM sewage discharge (1.11 mg/l). This is lower than their content in the water of, for example, Uvodskoye water reservoir (the city of Ivanovo) (up to 2.1 mg/l) [18], and the rivers of Great Britain (up to 2.0 mg/l) [19]. The concentrations of DCP isomers in the rest aqueous samples correlate with the data on DCP content of natural waters in the Netherlands (0.33 mg/l) [3], Poland (0.20–0.60 mg/l) [15], and Japan (0.20 mg/l) [20].

2,4,5-TCP and 2,4,6-TCP. TCP isomers are found in all aqueous samples studied. 2,4,6-TCP is considered to be the most widespread CP of natural origin among those observed by now in the non-polluted lake and river waters saturated by humic substances in Sweden and Finland [3, 21, 22]. Therefore, TCP presence in the water of Selenga River near the border with Mongolia (0.16 mg/l), in Tyemnik River (0.28 mg/l), and Chikoy River (0.05 mg/l) can be caused by its production, mainly, as a result of natural chlorination of humic substances dissolved in water. The maximum concentrations of TCP isomers are detected in water samples from Selenga River taken in the regions near the village of Kabansk and the settlement of Murzino (0.92 and 0.63 mg/l, respectively), from Kharauz arm in the river delta (0.76 mg/l). This is caused predominantly by natural sources, since these concentrations tangibly exceed TCP content of Baikal water downstream from the BIPPM sewage discharge and aeration pond (an anthropogenic source). The content of TCP in the samples taken from Selenga River, 20 km downstream of Ulan Ude, and from Uda river, 0.5 km upstream from the mouth, is lower, and it does not exceed the MPC for the water of water bodies of commercial fishing importance (0.1 mg/l) [8]. The data obtained are comparable to the levels of TCP contamination for natural waters of the Netherlands (0.32–0.74 mg/l) [3], Sweden (0.01 mg/l) [21], Italy (0.04 mg/l) [23], and Portugal (from 0.02 mg/l) [24].

PCP. PCP is detected in the water of Selenga River near the border with Mongolia (the settlement of Naushki) and in the area of Novoselenginsk settlement at a rate of 0.13 and 0.08 mg/l, respectively, which is comparable to the background PCP content in the natural waters of Canada (up to 0.05 mg/l) [25], in the water of Rotorua Lake (New Zealand) (0.01–0.34 mg/l) [26] and is within the MPC for water of the water bodies of commercial fishing importance (0.5 mg/l) [8]. The maximum PCP content is found in the water of BIPPM aeration pond (2.99 mg/l).

TABLE 2

Ratios of CP content in the samples under investigation

Ratio	Station numbers														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
STCP/SDCP	0.76	0.12	0.01	1.74	0.91	0.09	1.31	N/d	0.04	0.01	0.28	N/d	N/d	0.03	0.04
STCP/2-CP	0.46	0.14	0.01	2.30	1.31	0.28	1.77	0.38	N/d	0.04	0.46	0.16	0.90	0.06	0.30
2-CP/SDCP	1.67	0.85	1.25	0.75	0.70	0.33	0.74	N/d	N/d	0.38	0.61	N/d	N/d	0.42	0.13

As is known, anthropogenic sources of CP ingress into the aquatic ecosystems are represented by industrial and residential sewage. Chlorophenols are formed in chlorine disinfection of drinking water and upon using antiseptics in medicine [3, 5]. In addition, CPs enter ecosystems as a result of disinfection of the equipment at the food factories and as a result of domestic use of chlorine-containing agents for bleaching and cleansing. We reason that relatively high CP content of the sample from station 3 (20 km downstream from Ulan Ude) is caused by its introduction as a result of sewage infiltration from urban disposal plants. Agricultural application of phenolic pesticides, which yield CP as intermediate products of their decomposition, also can be responsible for the dispersed ingress of these ecotoxicants in the aquatic ecosystems as a result of washout of their residual quantities from the ground [25].

Naturally, CPs are formed as a result of active chlorine (a product of enzymatic and photolytic oxidation of chloride-ions) interaction with phenols, which are the constituents of humic substances (mostly humic and fulvic acids) [2, 4, 21, 22]. Active chlorine and initial phenols, in their turn, can stem from anthropogenic factors. CP generation occurs also during decomposition of natural chlorinated fulvic acids, the formulation of which includes, in particular, 4-hydroxychlorobenzoic and 4-hydroxydichlorobenzoic acids [27]. CPs are also produced by some kinds of soil mushrooms, lichens, and by insects [28]. In particular, 2,4-dichlorophenol is synthesized as a hormone of growth by soil fungus *Penicillium* sp. [29]; chloro- and dichlorophenols are produced by fungus *Caldariomyces fumago* [30]. A sexual hormone 2,6-dichlorophenol is found in some kinds of Ixodoidea parasites [31]; 2,4,6-trichlorophenol also represents the product of activity of soil microorganisms [22, 32].

To identify the sources of ingress of organic contaminants, the definite ratios between the concentrations of compounds are applied, which suggest the nature of their origin [33]. A similar attempt of identification of sources of CP ingress can be mounted using the results of the present work. A starting point can be the samples of stations 14 and 15 (the influence zone of BIPPM and aeration pond of BIPPM), where a nature of CP is obviously anthropogenic. As may be seen from Table 2, the values of STCP/SDCP and STCP/2-CP ratios are 0.01–1.74 and 0.01–2.30, respectively. The low values are also typical of the sampling stations located downstream of Ulan Ude along the Selenga River (station 3), upstream from the mouth of Uda river (within the city limits of Ulan Ude, station 10), and downstream of the BIPPM sewage discharge (station 14), where the nature of CP is anthropogenic. The ratio 2-CP/SDCP in this case cannot be the requisite criterion. Consequently, it can be inferred that when STCP/SDCP < 0.1 and when STCP/2-CP < 0.1, the anthropogenic sources of ingress of chlorophenols dominate. On the contrary, the maximum values of STCP/SDCP and STCP/2-CP ratios are found for the sampling stations, which are located in the Selenga Delta and in the near-the-delta region of the river in the neighbourhood of Kabansk village (station 4) and the settlement of Murzino (station 5). This can be indicative of the predominance of natural CP sources. Consequently, it can be assumed that when STCP/SDCP > 0.1 and when STCP/2-CP > 0.1, the natural sources of CP ingress become dominant.

The preceding permits the concentration ratios STCP/SDCP and STCP/2-CP to be

suggested as a criterion for identification of the nature of CP sources.

Unlike mono-, di-, and trichlorophenols, PCP can be exclusively of an anthropogenic origin [34]. An atmospheric transfer, in our opinion, provides the source of PCP ingress into the ecosystem of Selenga River, although we cannot rule out a local ingress with waste from woodworking manufacturers.

CONCLUSIONS

Results of the research of water contamination by CP and the analysis of ratios between CP concentrations for identification of sources of their ingress into aquatic ecosystems allow the following conclusions to be drawn:

– The level of CP contamination of natural waters in the Selenga River water-collecting area is relatively small; the total content of CP under investigation is in the range of 0.36–1.85 mg/l.

– CP delivery with the sewage from BIPPM shows a local nature and does not make the significant contribution to CP pollution of the Baikal Lake basin.

– The presence of 2-CP and isomers of DCP in the natural water saturated by humic substances is caused both by the delivery from anthropogenic sources, and from natural ones.

– The higher than usual content of 2,4,5-TCP and 2,4,6-TCP in the water of the Selenga River delta and in the near-the-delta region is caused by predominantly natural sources.

– Concentrations of PCP in natural water are low and are comparable with the background values.

– STCP/SDCP and STCP/2-CP concentration ratios enable an assessment of the nature of CP sources.

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