Pollution of the Lake Baikal Basin: Organochlorine Pesticides

OYUNA V. TSYDENOVA[1], VALERIY B. BATOEV[1], LUDWIG WEISSFLOG[2] and KLAUS-DIETER WENZEL[2]

[1]*Baikal Institute of Natural Management, Siberian Branch of the Russian Academy of Sciences, Ul. Sakhyanovoy 8, Ulan-Ude 670047 (Russia)*

[2]*UFZ-Umweltforshungszentrum,Permoserstrasse 15,D-04318 Leipzig (Germany)*

E-mail: vbat@binm.baikal.ru

(Received March 1, 2002)

Abstract

The organochlorine pesticides (OCPs) content in bottom sediments of main tributaries of the Lake Baikal was studied. Experimental data on the presence of hexachlorobenzene, DDT and its metabolites and hexachlorocyclohexane (HCH) isomers in sediments allowed estimating pathways of OCPs input to the Baikal basin.

INTRODUCTION

The recognition by UNESCO in 1996 of Lake Baikal as a site of the world natural heritage has become recognition of uniqueness of this lake by the international community. For conservation of the biological diversity of the Baikal it is necessary to establish the level of its pollution and determine the pathway of pollutants input. It should be given particular consideration to persistent organic pollutants (POPs) recognized as dangerous ecotoxicants. In May 1995, the Council of directors of UNEP assumed the resolution 18/32 on persistent organic pollutants, according to which a list of twelve hazardous POPs (polychlorinated biphenyls, dioxins, furans, aldrin, DDT, endrin, dieldrin, chlordane, hexachlorobenzene, mirex, toxaphene and heptachlor) was published [1]. In this regard, studies aimed at estimation of organochlorine pesticides (OCPs), including those from the list of 12, content in the ecosystem of the lake itself and its basin are important.

By today, estimation of some OCPs in water and biota of Lake Baikal has been carried out [2–5]. However, the basin of the lake (total area of 570 000 km^2) has been studied poorly. In order to estimate input of OCPs into the Baikal basin ecosystem, we have chosen sediments of some tributaries of the lake, since they absorb OCPs washed away by atmospheric precipitations from the basin territory. In this way, the sediments of tributaries are integral indicators of OCPs fall-outs in the basin.

EXPERIMENTAL

Sediments of the rivers Selenga, Uda, Khaim, Turka, Barguzin and Bolshaya Rechka that give about 70 % of the water inflow to the lake were studied. Samples were collected from the surface layer of sediments (down to 10 cm). Preparation of samples consisted in a double extraction of OCPs with solvents (hexane, acetone), purification of the obtained extracts with concentrated sulphuric acid and running through a column with florisil. In the obtained extracts, isomers of DDT (*p,p′*-DDT, *o,p′*-DDT), isomers of its metabolites (*p,p′*-DDE, *p,p′*-DDD, *o,p′*-DDE, *o,p′*-DDD), isomers of hexachlorocyclohexane (α-HCH, β-HCH, γ-HCH) as well as dieldrin, endrin and hexachlorobenzene (HCB) were estimated.

Identification and quantitative estimation of individual OCPs in samples of sediments were carried out at the Centre for Environmental Research (UFZ, Leipzig, Germany) and Baikal Institute of Natural Management, SB RAS. In the former case, the method of chromatomass-spectrometry (Hewlett-Packard HP 5890 gas chromatograph with a mass spectrometer HP 5971 and an autosampler HP 7673) was used. The analyzing components were separated on a 25 m long capillary column HP Ultra with the internal diameter of 0.32 mm. Helium was used as the carrier gas. The column temperature increased from 60 °C (exposure time 1 min) to 260 °C (exposure time 1 min) at the rate of 10 °C/min. Pesticide standards of Promochem (Wesel, Germany) were used.

In the latter case, the method of gas chromatography with electron-capture detection (Hewlett-Packard gas chromatograph HP 6800 with an electron-capture detector, a 30 m long capillary column HP 5 with the inner diameter of 0.32 mm, with helium as carrier gas). The column temperature increased from 80 °C (exposure time 1 min) to 190 °C (exposure time 1 min) at the rate of 30 °C/min, then to 280 °C (exposure time 1 min) at the rate of 6 °C/min and to 300 °C (exposure time 2 min) at the rate of 20 °C/min. Pesticide standards GSO 1855–99P, GSO 8024–99, OSO 113–04043–90, Hewlett-Packard No. 8500–6011 were used.

RESULTS AND DISCUSSION

Hexachlorobenzene

The pesticide was approved for use till 1990. As commercial products, hexathiuram (30 % HCB) and gammahexane (30 % HCB) were used in agriculture for the treatment of seeds, in forestry and in public utilities. HCB is formed also as a by-product in organochlorine synthesis, in ferrous and non-ferrous metallurgy, and in pulp-and-paper industry.

HCB concentrations in sediments of the Lake Baikal tributaries (Table 1), of the lake (5–160 pg/g [2]) and of Arctic seas (5–1500 pg/g [6]) are comparable. HCB has a relatively high vapor pressure (about 10^{-2} Pa) [7], and due to this it is distributed rather uniformly in the northern hemisphere as a result of global transport.

TABLE 1

Content of organochlorine pesticides in sediments of the Baikal tributaries

Compound	Content, pg/g of dry mass
HCB	3.7–8.8
n,n′-DDT	102–621
n,n′-DDE	22–86
n,n′-DDD	12–385
o,n′-DDT	200–261
o,n′-DDE	13–15
o,n′-DDD	23–34
ΣDDX	135–1594
Dieldrin	not detected
Endrin	»
α-HCH	470–3523
β-HCH	469–516
γ-HCH	170–606
ΣHCH	640–4598

Dieldrin, endrin

In sediments of tributaries of the lake these pesticides have not been detected. Dieldrin was used in very small doses (the years of active use were 1966–1967), and endrin has not been used in Russia. In the Baikal region, dieldrin and endrin have not been used. In the countries where they have been used, their presence in ecosystems is noticeable. In China (Hongkong), in sediments of sea gulfs the dieldrin content amounts to 500–19 400 pg/g [8].

DDT

The dangerous toxicant, pesticide DDT, is prohibited for production and use in Russia since 1970. The half-life period of DDT in ecosystems is 18–20 years. Nowadays, the bulk of DDT would have converted to metabolites DDD and mainly DDE. At present, in European countries the DDT/DDE ratio is usually less than one (*e.g.*, 0.06–0.07 [9]).

TABLE 2

Content of organochlorine pesticides in sediments of rivers and fresh water lakes in countries of the northern hemisphere

Pesticide	Canada [15]	Greenland [6]	Lake Baikal [2]	Baikal tributaries*	China [13]
HCB	80–1800	<100	5–160	3.7–8.8	–
ΣDDX	50–5000	<300	14–2700	135–1594	100–14 500
ΣHCH	50–3000	<300	19–120	640–4598	200–101 400

*Data of this study.

Our studies demonstrate that in sediments of the Baikal tributaries the DDT/DDE ratio is 4.2–7.2 for *p,p′*-DDX and 15.3–17.4 for *o,p′*-DDX.

It is noteworthy that a peculiarity of the Lake Baikal is abnormal DDT/DDE ratio in water (0.23–5) and sediments of the lake (0.1–4) [2]. The high DDT/DDE ratios in the water and sediments of Lake Baikal and its tributaries indicate the fact that DDT is entering the ecosystem. In our opinion, the main source of DDT input into the Baikal basin ecosystem is the transport over the atmosphere from the countries that produce and use DDT at present. These are India and China. According to estimations of the World Wildlife Foundation (WWF), for the control of malaria in India about 10 000 t DDT is produced and used every year. As for China, data on this are not available (not presented officially); however, according to experts“ estimates, the volume of production there is no less [10]. An indirect confirmation of the present DDT input to the Lake Baikal basin is the data for 1988–1996 on DDT flux in the Yenisei river (the Angara, the only river that originates from Lake Baikal is its tributary). The total DDT discharge amounted to 21.4 t, DDE 9.3 t (DDT/DDE ratio is 2.3). For comparison, let us note that the Volga has received during the same period 8.6 t of DDT and 7.2 t of DDE (DDT/DDE ratio is 1.2) and the Amur received 10.2 t of DDT and 10.2 t of DDE (DDT/DDE = 1) [11].

In China (including Hongkong), DDT and its metabolite content in sediments reaches very high values (Table 2, the highest concentration is 1803 mg/kg [12]). The DDT/DDE ratio in the sediments of Chinese rivers reaches value of 11.1 [13].

Although the majority of countries (over 80) have signed the convention for prohibition of DDT production and use, in India and China this pesticide is used at present for spraying indoors and in the sites of accumulation of gnats, malaria transmitters, and for agricultural pest control. Since DDT has the capacity to evaporate (vapor pressure of about $2\ 10^{-3}$ Pa [14]), and is well absorbed by soil particles, it becomes involved in the air mass transfer processes. We suppose that the source of DDT for the Baikal basin is transboundary air transport. Let us note that the countries that produce and use DDT are situated geographically closely to the Baikal basin which, in Mongolia, extends almost to the border with China.

HCH

The pesticide HCH was found in sediments of all rivers, and its concentration was one order of magnitude higher than in the sediments of the Lake Baikal (α-HCH concentration is 6–54 pg/g, for β-HCH is 10–56 pg/g, for γ-HCH is 3–9 pg/g [2]). In sediments of the Selenga and Barguzin rivers in whose valleys HCH has been used [11], the concentration of HCH metabolites is higher. According to our data, the α-HCH/γ-HCH ratio is 2.2–5.8, and that of α-HCH/β-HCH is 6.8–7.5. These figures correspond to the technical HCCH mixture used in Russia, in which the α-HCH fraction made up 55–70 %, β-HCH 5–14 %, and γ-HCH 9–13 % [16]. Proportions of isomers in the same sample of sediments of the Lake Baikal also correspond to the mentioned technical HCH mixture, the content of HCH isomers was increasing in the samples taken near the mouth of the Selenga river in the southern part of the lake [2]. Therefore, on the basis of the data of [2] and our data, it is possible to hypothesize that the sources of HCH are local.

CONCLUSIONS

Experimental data on the presence of OCP in sediments of tributaries of the Baikal permit estimating the sources of OCPs penetration into the lake basin. In our opinion, the OCPs entering the Lake Baikal ecosystem are mainly of the following origin:

– global air transport (HCB);

– transboundary air transport from neighboring countries (DDT);

– local input (HCH).

The current contribution of the dangerous pesticide DDT to the Baikal basin really threatens the biodiversity conservation of the unique lake due to accumulation of DDT in food chain. Although the DDT concentration in the Lake Baikal water is close to background levels for Arctic regions (11 pg/l [2], (87 ± 37) pg/l for the sum of DDT group compounds), in the Baikal seal (top predator of the food chain) the DDT content is already as high as 4.9–160 mg/kg lipid weight [3]. One of causes of the mass death of seals during the morbillivirus epizootic in 1988 is believed to be an excessive accumulation of organochlorine compounds in seal organisms resulting in decreased immunity and incapacity of resisting the viral infection [17].

Acknowledgement

The authors express their acknowledgement to the Ministry of Education, Science and Arts of the Saxony State (Germany) for its financial support.

REFERENCES

1 J. Buchchini, Proc. Subregional Awareness Raising Workshop on Persistent Organic Pollutants (POPs), St. Petersburg, Russian Federation, 1–4 July 1997, Moscow, 1998, p. 29.
2 H. Iwata, S. Tanabe, K. Ueda, R. Tatsukawa, *Environ. Sci. Technol.*, 29 (1995) 792.
3 H. Nakata, S. Tanabe, R. Tatsukawa *et al.*, *Ibid.*, 29 (1995) 2877.
4 J. R. Kucklick, H. R. Harvey, P. H. Ostrom *et al.*, *Environ. Tox. and Chemistry*, 15 (1996) 1388.
5 J. R. Kucklick, T. F. Bidleman, L. L. McConnell *et al.*, *Environ. Sci. Technol.*, 28 (1994) 31.
6 M. Cleemann, F. Riget, G. B. Paulsen *et al.*, *Sci. Total Environ.*, 245 (2000) 173.
7 H. Fidler, Proc. Subregional Awareness Raising Workshop on Persistent Organic Pollutants (POPs), St. Petersburg, Russian Federation, 1–4 July 1997, Moscow, 1998, p. 253.
8 B. R. Richardson, G. J. Zheng, *Chemosphere*, 39 (1999) 913.
9 O. Gil, C. Vale, *Aquatic Ecology*, 33 (1999) 263.
10 Farm Chemicals Handbook 2001, Meister Pro Information Resources, 2001.
11 A. V. Zhulidov, J. V. Headley, D. F. Pavlov *et al.*, *Chemosphere*, 41 (2000) 838.
13 S. W. Flower, *Marine Environ. Res.*, 29 (1990) 1.
14 Ying Wu, Jing Zhang, Qing Zhou, *Environ. Pollut.*, 105 (1999) 143.
15 F. Ya. Rovinskiy, L. D. Voronova, M. I. Afanasyev *et al.*, Fonovy monitoring zagryazneniya ekosistem sushi khlororganicheskimi soyedineniyami, Gidrometeoizdat, Leningrad, 1990.
16 D. C. G. Muir, N. P. Grift, W. L. Lockhart *et al.*, *Sci. Total Environ.*, 160/161 (1995) 447.
17 V. P. Lobov, G. A. Efimov, Pestitsidy, Gostekhizdat USSR, Kiev, 1963.
18 M. A. Grachev, O sovremennom sostoyanii ekologicheskoy sistemy ozera Baikal, Irkutsk, 1999.