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Accumulation of the persistent organic pollutants in the food chain of the lake Baikal

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Abstract

Lake Baikal is the deepest and oldest freshwater lake in the world. It contains 20% of the world's resource of fresh water (23 000 km3), more than all five of the North American Great Lakes together. Its unusual size (700 km long,20-40 km wide and 1600m deep) makes evaluation of its state of health particularly difficult. In the last twenty years potential pollution of the lake has caused controversy not only in Russia but throughout the world.

To study the present state of its contamination with organic pollutants the samples of water, snow, sediments, phytoplankton, zooplankton, sponges, plants, algae, fish, eggs of birds and blubber of seals were collected in 1997-1998. In each case sample preparation was followed by the GC-MS analysis. Together with semivolatile priority pollutants on the US EPA list, the presence of organochlorine pesticides and polychlorinated biphenyls was checked.

There was pronounced bioaccumulation of persistent organochlorine compounds along the trophic chain, leading to substantial residues of organochlorines in seals. An important point revealed involves the fact that the ratio of DDT to its metabolites is high enough to suggest there is a primary source of entry of this chemical into the lake even though its use is banned in Russia. On the other hand concentrations of polycyclic aromatic hydrocarbons (PAH) appeared to be maximal for the lower levels of the food chain: zooplankton and phytoplankton.

Introduction

Lake Baikal is the deepest and oldest freshwater lake in the world. It contains 20% of the world's resource of fresh water (23 000 km^3), more than all five of the North American Great Lakes together. Its unusual size (700 km long, 20-40 km wide and 1600m deep) makes evaluation of its state of health particularly difficult. In the last twenty years potential pollution of the lake has caused controversy not only in Russia but throughout the world. Two major sources of the lake's contamination are the Trans-Siberian Railway and the Selenga river which drains industrial and domestic effluents from a vast industrialized area south-east of the lake into the lake. Another well known source of contamination is a pulp and paper mill plant in Baikalsk. However, in the last years its negative influence on the lake has considerably decreased due to new purification facilities and due to recession of industry in general for Russia in 1990's. Now the plant works at only 10% of its capacity. Nevertheless the water in Baikal remains quite pure. It is impossible to detect any toxicants in water samples even using the newest instrumentation. GC-MS analysis demonstrated the levels of PAHs, organochlorines or other priority pollutants below ppt values. Thus the present approach involves the study of biota samples containing higher levels of contamination due to bioaccumulation effect.

A number of studies carried out in 1980-1990th[1] revealed notable contamination of the Baikal's fauna. However these results were obtained by various groups using different analytical tools and different plant or animal species. In all these studies only few individual toxicants were analyzed.

At the first stage of the present study the eggs of the 15 species of birds nesting in the delta of Selenga river were collected. The concentration of semivolatile priority pollutants (US EPA list) were measured in the lyophilized matter of these eggs[2]. The results demonstrated that the most important pollutants for the lake were PAH, while the fish-eating birds were less contaminated than invertebrate-eating species.

Results and discussion

The health of the water basin may be estimated by studying the condition of its principal food chain. In the case of Baikal this food chain is a short one:

phitoplankton - zooplankton - fish - seal.

Together with seals, birds constitute the upper level of the food web of the lake. Continuing the study started earlier[2,3] the corresponding samples of sediments, algae, sponges, aquatic plants, various fish species were collected in 1997-1998. GC-MS was used to detect the presence of semivolatile organic pollutants (US EPA list), PCB and organochlorine pesticides (including p,p'-DDT and its metabolites) which were found to be the principal organic pollutants for the lake[2-4]. Only a few semivolatile priority pollutants other than polycyclic aromatic hydrocarbons (PAH) were detected in the samples, while their appearance in various samples seems to be only occasional. Similarly, of the organochlorine pesticides, only p,p'-DDT and its metabolites were detected in significant quantities. The data for PAH, PCB and DDT with metabolites, present in all the samples studied are summarized in the Tables 1,2 and 3. The accumulation of pollutants in the food web is obvious, but there is a difference between PAHs and persistent organochlorines.

Table 1.Concentrations of PAH and persistent organochlorine pollutants in the environmental samples from the Baikal (ng/g dry weight).

Compound name	Sedi-ments	Algae	Sponges	Aquatic plants	Phyto plankton	Zoo plankton
Naphthalene	100	150	100	65	1700	570
1-Methylnaphthalene	6	34	4	26	500	140
2-Methylnaphthalene	2	29	8	30	330	130
Biphenyl	3	123	20	320	200	3400
Acenaphthylene	7	-	-	20	30	40
Acenaphthene	2	60	-	3	70	500
Fluorene	-	-	-	4	100	70
Phenanthrene	40	90	130	100	1600	850
Anthracene	7	25	5	3	200	140
Fluoranthene	8	12	40	160	20	1100
Pyrene	6	14	20	90	20	400
Benzo[a]anthracene	-	-	-	-	200	80
Chrysene	-	-	-	230	-	-
Benzo[b]flouranthene	-	-	-	-	60	-
p,p'-DDT	15	-	-	-	-	-
p,p'-DDD	-	-	-	-	-	-
p,p'-DDE	-	-	-	-	-	-
Tetrachlorobiphenyls	-	-	-	-	-	-
Pentachlorobiphenyls	-	-	-	-	-	-
Hexachlorobiphenyls	-	-	-	-	-	-
Heptachlorobiphenyls	-	-	-	-	-	-
Octachlorobiphenyls	-	-	-	-	-	-

The highest concentrations of PAH were found in zooplankton and phytoplankton. These data nicely correlate with these of Stegeman[5] conclusions who reported marked accumulation of PAHs in invertebrates, largely due to the low rates of biotransformation in them. The same conclusion has been drown for these compounds in marine food chains [6]. Such accumulation was not found in fish who are able to rapidly metabolize them. The difference in levels of these toxicants for predatory fish and other fish species (excluding *Comephorus baikalensis*) is not significant (see Table 2). The obtained results support the hypothesis proposed at the early stage of this project [2,3]. The amount of fat in fish is an important factor in determining concentrations of lipophiles on the basis of whole body weight. The PAH levels in *Comephorus baikalensis* are an order of magnitude higher than in other fish species. The most important feature distinguishing *Comephorus baikalensis* from other species is the amount of fat. In fact 40% of the weight of this fish is fat which is about 4 times higher than in other fish species and because of its lipophilicity PAH reaches relatively high levels *in Comephorus baikalensis*. The levels of these compounds increase also from fish to seals, probably due to higher amount of fat in the latter (lipophilicity effect). In this case even the higher rates of metabolism did not improve the situation.

Table 2. Concentrations of organic priority pollutants in the fish muscles samples from the Baikal (ng/g wet weight).

Compound name	Carp	Perch	Pike	Coregonus autumnalis	Comephorus baicalensis
Naphthalene	10	5	5	5	360
1-Methylnaphthalene	5	-	-	5	66
2-Methylnaphthalene	7	-	-	8	120
Biphenyl	2	-	-	3	22
Acenaphthylene	-	-	-	2	14
Acenaphthene	-	-	-	-	12
Fluorene	3	2	-	2	46
Phenanthrene	17	8	16	19	110
Anthracene	-	1	-	-	10
Fluoranthene	8	7	14	15	120
Pyrene	12	4	22	19	120
Benzo[a]anthracene	-	-	-	2	16
Chrysene	3	2	3	6	12
Benzo[b]flouranthene	-	-	-	-	-
p,p'-DDT	-	-	-	-	170
p,p'-DDD	-	-	-	-	23
p,p'-DDE	-	-	-	-	260
Tetrachlorobiphenyls	7	-	23	16	130
Pentachlorobiphenyls	26	-	61	21	690
Hexachlorobiphenyls	6	-	4	1	350
Heptachlorobiphenyls	-	-	-	-	-
Octachlorobiphenyls	-	-	-	-	-

On the other hand PCB, as well as p,p'-DDT and its stable metabolites such as p,p'-DDE and p,p'-DDD, are more persistent than PAHs, even mammals cannot metabolize them rapidly. As a result there is a marked increase in the levels of these compounds moving from invertebrates to seals. Actually, the measured levels of these organochlorines in Baikal seals are close to those in Baltic seals [7]. This phenomenon is quite intrigueing , since the contamination of water in Baikal and in Baltic sea is incomparable. It is hardly possible also to find any rule in levels of organochlorines for seals rather than the fact that the older are the species the higher are the levels of those toxicants.

It is again worth mentioning that lipofilicity of these pollutants is an extremely important factor in accumulation. For example the levels of PCBs in *Comephorus baicalensis*, which constitutes 90% of the food ratio of seals, are 20-50 times higher, then in other fish species. The reason of this phenomenon may be rationalized, in part, similarly than in the case of PAH by the fact that *Comephorus baicalensis* consists of 40% of fat, notably exceeding that of other fish species. Another possible reason might be a lower rate of metabolism in this fish, which lives rather deep in colder water.

An important point revealed involves the fact that the ratio of DDT to its metabolites is high enough (see Table 3) to suggest there is a primary source of entry of this chemical into the lake even though its use is banned in Russia. Similar conclusion concerning DDT in Siberia were done by H.Nakata [4,6].

Table 3. Concentration of PAH and persistent organochlorine pollutants in the seal samples from the Baikal (ng/g wet weight).

Compound name	juvenile 3 months	female 7 years	male 9 years	male 10 years
Naphthalene	170	240	710	450
1-Methylnaphthalene	8	41	100	100
2-Methylnaphthalene	8	53	260	150
Biphenyl	44	90	100	160
Acenaphthylene	12	6	34	10
Acenaphthene	3	5	78	14
Fluorene	16	17	98	61
Phenanthrene	180	140	230	240
Anthracene	-	4	5	6
Fluoranthene	74	17	73	63
Pyrene	90	8	60	36
Benzo[a]anthracene	-	25	8	10
Chrysene	-	15	6	8
Benzo[b]flouranthene	-	-	-	-
p,p'-DDT	870	5520	25330	6220
p,p'-DDD	140	150	1860	2630
p,p'-DDE	1190	2090	53550	500
Tetrachlorobiphenyls	-	-	15320	-
Pentachlorobiphenyls	620	4580	21134	5330
Hexachlorobiphenyls	1000	5070	25900	5720
Heptachlorobiphenyls	90	2560	7250	2200
Octachlorobiphenyls	-	600	1470	200

Materials and methods

All the samples analysed were collected in the Baikal in 1997. Fish muscles samples (4-5g) were mixed with 10g of anhydrous sodium sulfate and extracted

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with 50ml of 1:1 hexane/dichloromethane in an ultrasonic bath. The extract was concentrated to 1 ml and transfered to a glass column packed with silica gel. 98:2 Hexane/dichloromethane (80 ml) mixture was used as eluent. The eluate was concentrated (Quderna-Danish) to 1 ml and subjected to GC-MS analysis.

Seal (Phoca sibirica) blubber samples (2-3g) were mixed with 10g of anhydrous sodium sulfate and extracted with 50 ml of 1:1 hexane/dichloromethane in an ultrasonic bath. The extract was concentrated to 1 ml and transferred to a glass column packed with silica gel and sulfuric acid/silica gel from the bottom. 98:2 Hexane/dichloromethane (80 ml) mixture was used as eluent. The eluate was washed with sodium bicarbonate solution, dried over anhydrous sodium sulfate and concentrated to 1 ml prior to injection into GC-MS instrument.

The samples of sediments, plants and invertebrates were dried at room temperature, milled into powder, and extracted with 50 ml of 1:1 hexane/dichloromethane in an ultrasonic bath. The extract was concentrated to 1 ml and transferred to a glass column packed with silica gel. 98:2 Hexane/dichloromethane (80 ml) mixture was used as eluent. The eluate was concentrated to 1 ml and subjected to GC-MS analysis.

GC-MS analysis was carried out with HP 5973 (Hewlett-Packard) mass spectrometer. Ionization energy - 70eV (electron impact ionization), fused silica capillary column HP-5 (30m), column temperature: $50^{o}C$(4 min) - $7^{o}C$/min - $300^{o}C$ (10 min), scanning mass range 25-550 dalton. Perdeuterated naphthalene, phenanthrene and chrysene were used as internal standards for quantitation. Response factors and retention times of the pollutants of interest were calculated on the basis of standard mixtures: base-neutral extractable standards on US EPA list (HP 8500-5998), PCBs (Supelco 4-8246), and organochlorine pesticides (Supelco 4-8858).

Conclusions

1. Aquatic plants, invertebrates, fish and seals collected in the Baikal appeared to be rather contaminated with PAH, PCB and DDT. The levels of PCB and DDT with metabolites in seals are comparable with those for the Baltic sea.
2. There is a pronounced bioaccumulation of persistent organochlorines along the food chain of the lake.
3. Polycyclic aromatic hydrocarbons are detected at highest levels in phyto and zoo plankton due to low rates of metabolism. Relatively low levels are found in fish which metabolize them more rapidly. In case of seals the amount of fat brings to new increase of the levels of these compounds.
4. There is an unknown source of penetration of DDT, prohibited in Russia, into the lake.

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