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Contamination of the Caspian Sea ecosystem with organic pollutants

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Abstract

The Caspian Sea is the largest inland reservoir of salted water in the world. In the last 30-40 years the Sea has been considered to be seriously polluted due to the drilling works of oil companies and notable pollution of the Volga, which brings into the Sea about 23 km^3 of waste waters annually. However there have been no reliable data on its contamination with organic compounds. To identify and quantify these contaminants water and biota samples were collected in 1999-2000. Quantitative determination of the priority pollutants from the US EPA list was accompanied with qualitative and semi quantitative analysis of all types of organic compounds passing through GC column. Petroleum hydrocarbons appeared to be the dominant organic contaminants of the Sea. Phthalates may be mentioned as another group of pollutants present in all the samples. Surprisingly only traces of persistent organochlorines were detected. Therefore a considerable decrease of the level of pollution during last 10 years may be marked. Comparing the levels of the toxicants along the trophic web it is obvious that zooplankton sample is the most polluted. This fact may be rationalized by the poor metabolic system of these aquatic organisms.

1 Introduction

The Caspian Sea is known to be the largest inland reservoir of salted water in the world. The square of the Sea is 371000 km^3. Another peculiarity deals with the fact that this watershed lies 28 m below the sea level. Two main sources of pollution of the sea are the Volga river and drilling works of the oil companies. Caspian sea has been considered to be seriously polluted. The Volga river brings into the Sea more than 23 km^3 of waste waters annually. However there were no reliable studies of its contamination with organic compounds so far. According to the data published in the 80th in local press petroleum hydrocarbons, phenols, surfactants and organochlorine pesticides were the priority pollutants for the Caspian Sea. High level of pollution at that time brought to histological problems e.g. stratification of the tissues of muscles of sturgeons and weakening of the outer shell of caviar. The treat of disappearance of sturgeons became real. Since almost all resources of sturgeon species of the world are concentrated in the Caspian Sea and taking into account that besides their extreme biological value sturgeons are the source of the famous all over the world dainties the problem actively discussed in the mass media and various plans were proposed for the improvement of the situation. However political changes at the beginning of the 90th led to the diminished attention to the problem of the Sea. There were no new data on the pollution of the Sea in the period between 1992-1997. The data published in 1998 and 1999 although covering few parameters demonstrated the decreased level of the Sea contamination [1,2]. The aim of the present study was to identify priority organic pollutants for the sea and to estimate their levels in water and biota. For this purpose water, zooplankton, sprat, sturgeon, beluga and a blubber of a 2-year old seal were collected in the autumn of 1999 and spring 2000 and after appropriate sample preparation were subjected to the GC-MS analysis. Quantitative determination of the priority pollutants from the US EPA list as well as PCB and organochlorine pesticides was accompanied with qualitative and semi quantitative analysis of all types of organic compounds passing through the GC column.

2 Methods

Water sample was analysed according to the US EPA 8270 method. The samples of zooplankton, shrimps, fish muscles, liver and caviar (4-5g) were mixed with 10g of anhydrous sodium sulfate and triply extracted with 100ml of 1:1 hexane/dichloromethane in an ultrasonic bath. The extract was concentrated to 1 ml and transferred to a glass column packed with 30 ml of a 50:1 mixture silica gel/activated carbon. Mixture of hexane/dichloromethane (1:1 80 ml) was used as an eluent. The eluate was concentrated (Quderna-Danish) to 1 ml and subjected to GC-MS analysis.

Caspian seal blubber sample (5g) was mixed with 10g of anhydrous sodium sulfate and triply extracted with 100 ml of 1:1 hexane/dichloromethane. The extract was concentrated to 1 ml and transferred to a glass column packed with layers of 10 ml silica gel, 10 ml of silica gel with 90% NaOH, 10 ml of silica gel, and 15 ml of conc. sulfuric acid/silica (upper layer). Hexane/dichloromethane

(1:1 100 ml) mixture was used as an eluent. The eluate was concentrated and transferred to a column packed with 30 ml of a 50:1 mixture silica gel/activated carbon. Hexane/dichloromethane (1:1 100 ml) mixture was used as an eluent. The eluate was concentrated (Quderna-Danish) 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°C(4 min) - 7°C/min - 300°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).

Besides the priority pollutants from the US EPA list other organic compounds present in sufficient quantity to give a detectable peak in the chromatogram in total ion current were tentatively identified and quantified. In fact precisely these compounds (first of all hydrocarbons) appeared to be the major organic pollutants of the Sea. NIST and WILEY computer libraries of mass spectra were used for the qualitative identification of these compounds. Quantitative results were obtained by comparison of the chromatographic peaks of a component and of the closest by retention time internal standard in the chromatogram in total ion current. The response factors in all these cases were equal one.

Results and discussion

The results obtained are summarized in Table 1. Actually, only few compounds from the US EPA list of priority pollutants were detected. Petroleum hydrocarbons are definitely the dominant organic pollutants of the sea. This fact proves the opinion that petroleum industry is the main source of the sea contamination. Table 1 demonstrates that 33 of 40 detected pollutants are hydrocarbons. The range of unbranched alkanes (C_{10}-C_{20}) allows to conclude that petroleum fuels are the main pollutants of the sea. The representative array of alkylbenzenes and tetralines supports this conclusion. It is worth mentioning that only the low molecular weight polycyclic aromatic hydrocarbons were present in the samples while their heavier analogs were absent. This observation proves once more that these toxicants are ingredients of oil. Zooplankton appeared to be the most contaminated specie among the others. This phenomenon can be rationalized by the fact that the higher metabolic rates in the higher representatives of the food web permit to metabolize easily these compounds, which are not highly persistent. Concentration of the petroleum hydrocarbons in water sample is very close to the limit accepted in Russia, as the maximal allowable concentration (MAC) value for hydrocarbons is 0.05ppm. However it is possible to conclude that the level of contamination notably decreased during the last 10 years, since in 1970-1990, when similar data had been collected at regular basis, concentration of petroleum hydrocarbons had been in the range 0.25-0.4 ppm.

Phthalates may be mentioned as another group of organic pollutants present in all the samples. Two mostly widespread representatives of this group for Russian environment (bis-(2-ethylhexyl)-phthalate and dibutylphthalate) were detected in sufficient quantities. Maximal allowable concentration of these chemicals for water in Russia is 1 ppb. Thus even water sample contains hazardous concentrations of phthalates, while their levels in biota are of definite concern. Surprisingly only traces of persistent organochlorines were detected even in the seals (highest section of the food web). This fact remarkably distinguishes the Caspian Sea (considered to be very contaminated) from the lake Baikal (considered to be very clean). The levels of polychlorinated biphenyls and DDT with metabolites in the Siberian seals from the Baikal [1,2] were 1-2 orders of magnitude higher. The traces of DDE and the absence of DDT in the blubber of seals demonstrate that DDT after its prohibition in 1980 was not applied in European part of Russia in contrast to Siberia [3,4]. Nitrotoluene and chloronitrobenzene were two other compounds worth mentioning.

It is necessary to mention the absence of phenols in the analyzed samples. Since this group of chemicals had been previously declared to be one of the major concern for the Caspian Sea, a special attention was paid to the detection of phenols. However even traces of these compounds were absent.

Comparing the levels of the detected toxicants along the trophic web of the sea it is obvious that zooplankton samples are the most polluted. This fact may be rationalized by the poor metabolic system of these aquatic organisms. The present results completely match these obtained 2 years ago during similar study of the Baikal [1,2].

The results obtained allow to declare that the level of contamination of the Caspian Sea considerably decreased during the last 10 years. These conclusions proved the previous results of our colleagues from Astrakhan [1,2], obtained in 1997-1999. Another fact in favor of these conclusion involves the ending of the processes of stratification of tissues in the sturgeons. The reason of this phenomenon may engage the overall decrease of the industry in Russia after the split of the Soviet Union. The use of pesticides for agriculture was also significantly decreased due to prohibition of the most hazardous (although effective) of them and inability of the farmers to by new ones due to their financial difficulties.

Conclusions

1. Petroleum hydrocarbons are the dominant organic contaminants of the Caspian sea.
2. Phthalates is another group of contaminants, which may be treated as priority pollutants for the sea.
3. Only traces of persistent organochlorines were detected in the Caspian seals (highest section of the food web).
4. The level of contamination of the Caspian Sea decreased significantly during the last 10 years.

References

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Table 1. Concentrations of priority pollutants (ppm) in the Caspian samples.

Compounds	Water	Zoo-plankton	Sprat	Seal	Sturgeon			Beluga (young male)		Beluga (male)		Beluga (female)	
					liver	Muscle	caviar	liver	muscle	liver	muscle	liver	muscle
Octane	0.002				0.1	0.3	0.04						
Nonane	0.003				0.2	0.2	0.05						
Decane	0.006	21.2		0.6	0.2	0.4	0.05	1.1	0.4	0.5	0.6	0.5	0.4
Undecane	0.007	15.6	1.9	0.6	0.1	0.2	0.03	1.2	0.4	0.6	0.8	0.5	0.6
Dodecane	0.003	11.3	0.7	0.8	0.2	0.1	0.03	1.5	0.5	0.4	0.7	0.8	0.4
Tridecane	0.003	10.6	0.6	0.5	0.2	0.2	0.04	0.8	0.2	0.5	0.4	0.5	0.5
Tetradecane	0.005	10.0	1.5	0.9	0.2	0.4	0.07	0.9	0.4	0.7	1.0	1.4	1.2
Pentadecane	0.004	7.8	0.8	1.7	0.1	0.4	0.15	0.3	0.2	0.8	3.0	0.3	0.4
Hexadecane		8.7	1.4	0.9	0.1	0.6	0.06	0.4	0.1	1.0	2.9	0.7	0.6
Heptadecane		8.6	9.5	4.3	0.1	0.6	0.05	0.5	0.3	1.9	2.2	1.5	0.6
Octadecane		6.2	6.4	3.1	0.3	0.5	0.13	0.4	0.2	0.7	1.6	0.7	0.6
Nonadecane		9.9	8.0	2.6	0.6	0.5				1.8	1.2	0.8	0.8
Eicosane			7.9	2.2						2.0		0.4	
Heneicosane			4.6										
Docosane			3.6										
Σ Unbranched alcanes	0.033	155.5	46.9	18.2	2.3	4.4	0.7	10.2	2.2	10.9	14.4	8.1	6.1
Σ Branched alcanes		274.3	74.0	31.1	14.7	1.1	9.4	10.2	8.1	16.7	48.5	23.7	9.0
Benzene, C3		44.3		0.7				0.2	0.2	0.3	0.4	1.5	1.0
Benzene, C4		43.3	1.7	1.6					0.2	2.4	5.6	5.6	0.6
Benzene, C5			0.9	0.5						0.01	0.1	0.03	0.03
Benzene, C6										0.01			0.01
Benzene, C7													0.01
Σ Alkylbenzenes		42.0	2.6	2.8				0.2	0.4	2.7	6.1	7.1	1.7

Table 1. Concentrations of priority pollutants (ppm) in the Caspian samples (continuing)

Compounds	Water	Zoo-plankton	Sprat	Seal	Sturgeon			Beluga (young male)		Beluga (male)		Beluga (female)	
					liver	Muscle	caviar	liver	muscle	liver	muscle	liver	muscle
Tetrahydronaphthalene									5.7				0.1
Decahydronaphthalene		440.1								2.1	4.6	2.7	11.9
Trimethyl-2,3-digidroindene								8.7		0.4			
Trimethyl-2,3-digidroindene (isom)								3.4		0.4			
Trimethyl-2,3-digidroindene (isom)				5.0				9.3		0.6			
Naphthalene	0.005	0.5	1.4	2.2				1.2		0.4	0.6	0.6	0.4
1-Methylnaphthalene	0.001	0.1	0.2	0.3						0.2	0.1	0.1	0.1
2-Methylnaphthalene	0.003	0.1	0.1								0.05		
1-Ethylnaphtalene		12.5	0.1	0.2						0.01	0.02	0.02	
1,2-Dimethylnaphtalene		1.4	0.02	0.2						0.04	0.02	0.03	0.3
Phenanthrene		0.3	0.1	1.6			0.1			0.1			
Fluoranthene				0.02	0.5								
Σ Hydrocarbons	0.042	931.3	125.3	61.6	17.5	5.5	10.2	43.2	16.4	34.6	74.5	42.6	29.8
1-Chloro-4-nitrobenzene				2.0					2.3	1.0	0.04	0.1	0.6
4-Nitrotoluene				0.9									
p,p-DDE				1.11				0.3		1.4			
Pentachlorobiphenyl				0.03									
Pentachlorobiphenyl (isom.)				0.03									
Dibutyl phthalate	0.005	134.0	0.9	84.5	1.1	1.5	0.2		7.8	5.3	6.1	7.6	7.0
Bis-(2-ethylhexyl)phthalate	0.004	273.0	17.3	197.5			7.5		48.2	9.0	13.0	9.7	10.1