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Contamination of the Caspian Sea ecosystem with organic pollutants

A. T. Lebedev, O. V. Poliakova, M. N. Repina &
N. S. Sokolov
Moscow State M.V.Lomonosov University,
Organic Chemistry Department,
119899 Moscow, Russia.

Abstract

The Caspian Sea is known to be the largest inland reservoir of salted water in the world. The square of the sea is 378000 km^2. However there were no reliable studies of its contamination during 15 years. Our preliminary study [1] showed that the levels of organochlorines in biota seriously decreased. Seventy-one samples of sediments were collected in October 2001 in the North part of the sea. US EPA method 8270 was used to analyze organic pollutants in the samples. Although the presence of all types of hazardous chemicals was checked, petroleum hydrocarbons and sulfur were the major ingredients. Since the amount of data was too large geo-informational approach was used for the development of the ecological maps of the Sea. The elaborated maps allowed to identify the main sources of penetration of organic pollutants into the sea.

1 Introduction

The Caspian Sea always 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 pollution with organic toxicants so far. According to the data published 15-20 years ago in the local press petroleum hydrocarbons, phenols, surfactants, organochlorine pesticides and PCB were pollutants of special concern. The levels of PCB, DDT with metabolites and other organochlorines in the caviar and tissues of sturgeons were in the region of hundreds ppm. High level of pollution at that time brought to histological problems e.g. stratification of the muscle tissues of sturgeons and weakening of the outer shell of caviar. The threat of disappearance of sturgeons became real. Since almost all resources of sturgeon species of the world are concentrated in the Caspian Sea the problem had been actively discussed in the mass media and various plans had been proposed for the improvement of the situation. However, due to the dramatic political changes in the country in 90th, there were no any studies on the pollution of the sea. However, the preliminary data obtained 2 years ago [1] demonstrated that the level of contamination of the sea with organochlorines seriously decreased.

The aim of the present study was to identify priority pollutants for the sea and to estimate their levels in sediments. For this purpose 71 samples of sediments were collected in October 2001 (Figure 1) 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 GC column.

2 Methods

Samples of sediments were analyzed according to the US EPA 8270 method. 30$\pm$5g of the material were twice extracted with 30ml CH_2Cl_2 in an ultrasonic bath. The extracts were combined, concentrated to 1 ml and transferred to a glass column packed with 5 ml of silica gel. Hexane (30ml) was used as an eluent. The eluate was concentrated to 1 ml and subjected to GC-MS analysis.

GC-MS analysis was carried out with Thermo SSQ 7000 mass spectrometer. Ionization energy - 70eV (electron impact ionization), fused silica capillary column HP-5 (30m), column temperature: 50°C(4 min) - 8°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), PCB (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 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.

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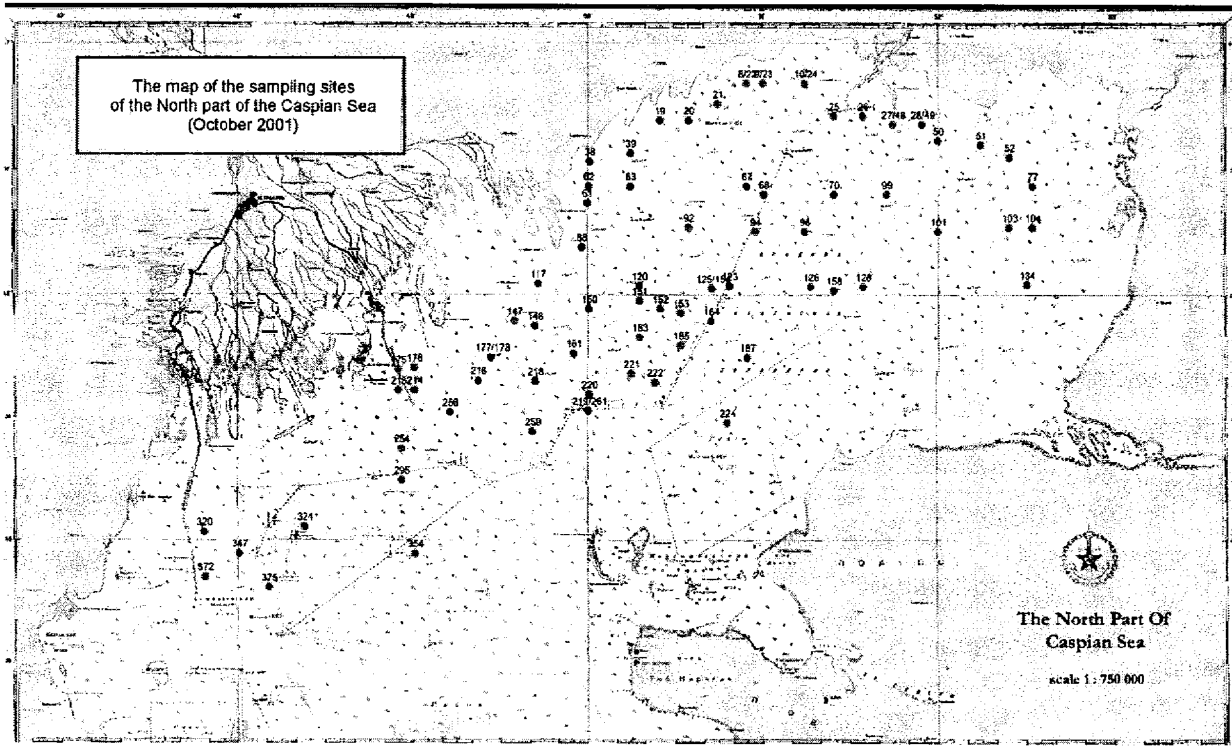

Fig 1: The map of the sampling sites of the North part of the Caspian Sea

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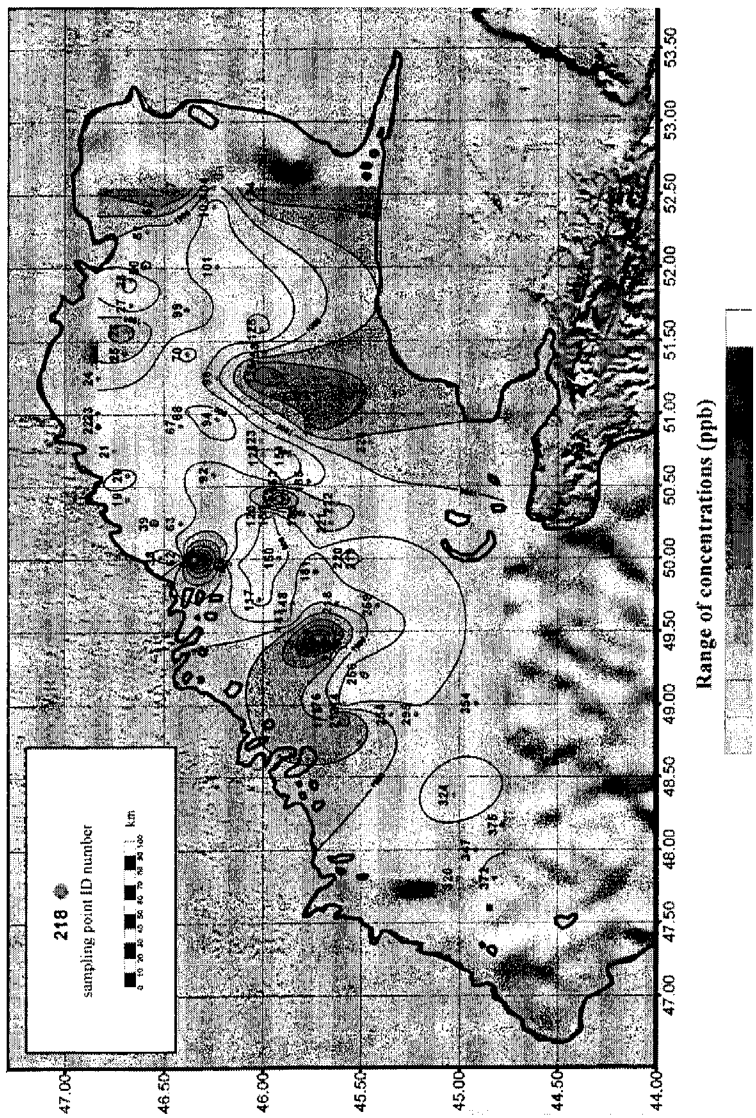

Fig 2: The map of the levels of hydrocarbons in sediments of the North Caspian Sea

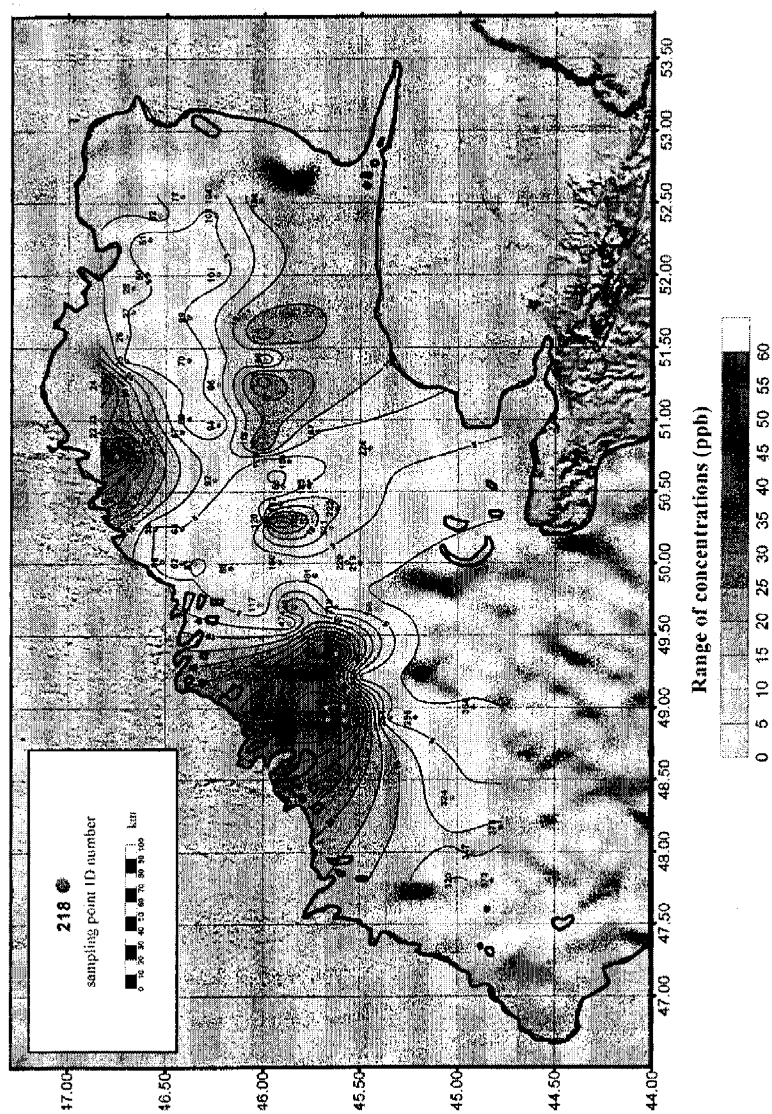

Fig 3: The map of the levels of alkylnaphthalenes in sediments of the North Caspian Sea

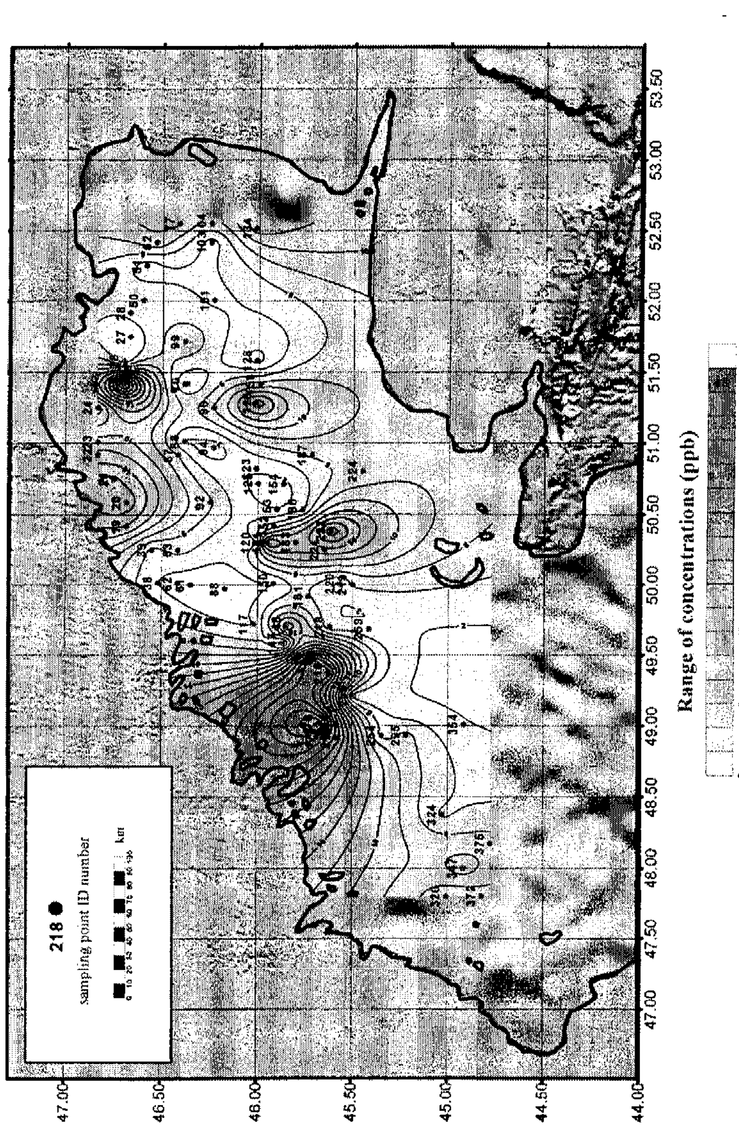

Fig 4: The map of the levels of polycyclic aromatic hydrocarbons in sediments of the North Caspian Sea

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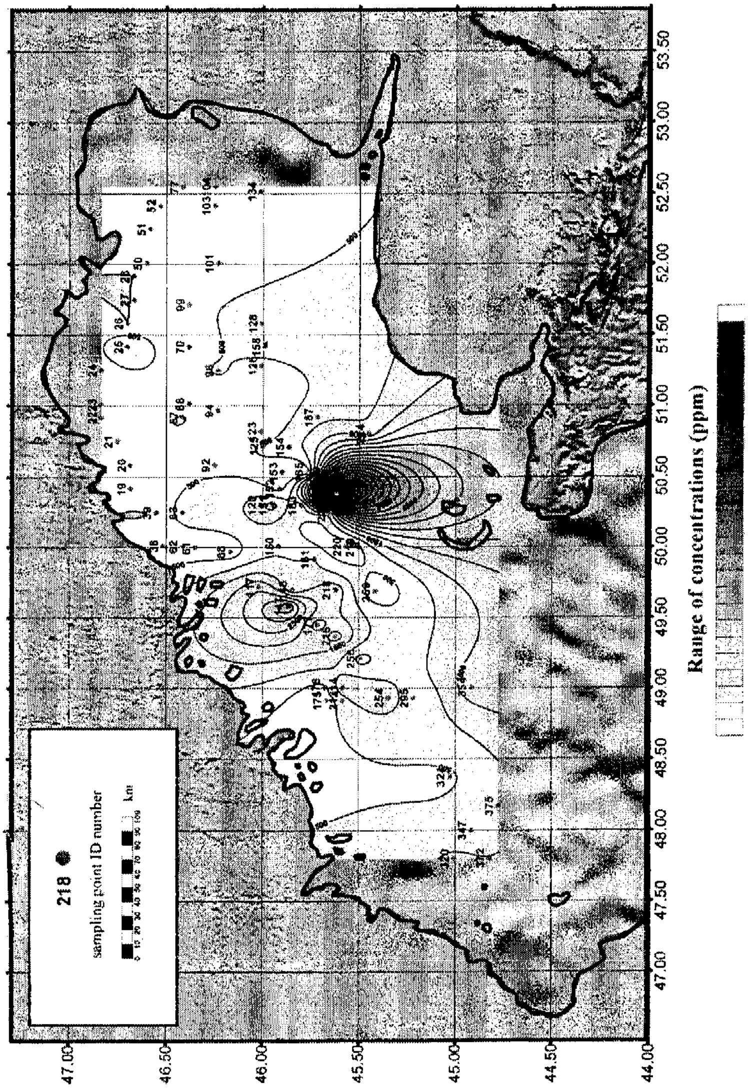

Fig 5: The map of the levels of sulfur in sediments of the North Caspian Sea

Geo-informational system approach was used to estimate the pollution of the sediments in the various regions of the sea. The data of sputnik altimetry (water and surface) were used as the map basement. The basement is constructed in rectangular coordinates. The covering of the sea and surface was elaborated using shaded relief technology with the eastern lightning. To develop the maps of pollution with various chemicals on the prepared basement the program media Surfer and Adobe Photoshop were used. The calculation of matrixes was achieved by kriging with the step 0,01° in both directions.

Results and discussion

More than 300 individual compounds were identified in the samples. Thus the array of the information obtained was extremely large. Table 1 summarizes the results obtained for the major groups of pollutants identified. To be able to present and use this information in the proper way the Geo-Informational Systems approach was used. Due to the constructed maps the main sources of the penetration of chemicals into the sea became rather obvious (figures 2-6). Since the mapping is quite a time consuming process the identified compounds were grouped according to their structures. Happily, all these chemicals belong to several classes of organic substances.

The most important group of contaminants engages petroleum hydrocarbons. Representatives of alkanes, naphthenes, alkylnaphthalenes, alkylbenzenes, and PAH constituted a major portion of the organic matter identified. Since an ecological parameter Maximal Allowable Concentration (MAC) exists for the sum of petroleum hydrocarbons we developed the ecological map of pollution of the Caspian Sea based on the total amount of hydrocarbons detected. The levels of the total amounts of hydrocarbons in the sea sediments were in the range 0.4 - 6 ppm (Table 1). Three regions could be mentioned as the most polluted: the territory accepting the effluents of the Volga and Ural Rivers and the Central part of the Ural Borozdina hollow (Figure 2). To check the spread of smaller, but more hazardous, groups of hydrocarbons separate maps were elaborated covering pollution with alkylnaphthalenes and PAH. The levels of alkylnaphthalenes in the sea sediments were in the range 0.1-66 ppb (Figure 3), while the regions of the sea attached to the deltas of the Volga and Ural Rivers appeared to be the most contaminated. The sediments from Ural Borozdina hollow were slightly less polluted. Among 13 PAH the levels of the low molecular weight representatives were considerably higher than the levels of PAH with 4 and 5 cycles. This fact proves that crude oil and oil fuels are the principal source of the sea contamination with PAH. The levels of the sum of PAH were in the range 0.2-34 ppb (Figure 4), while the maximal level of benz(a)pyrene reached 0.2 ppb. The region attached to the delta of the Volga River was the most polluted.

Caspian oil and gas are enriched with sulfur. Rather large heaps of elemental sulfur could be seen on the banks of the Volga River in its delta. Due to this fact analyzed sediments contained very high levels of elemental sulfur. Several samples contained up to 1% sulfur. These samples were collected in the southwest part of the Ural Borozdina hollow (figure 5). The region attached to the Volga Delta was slightly cleaner (about 0.1-0.3%).

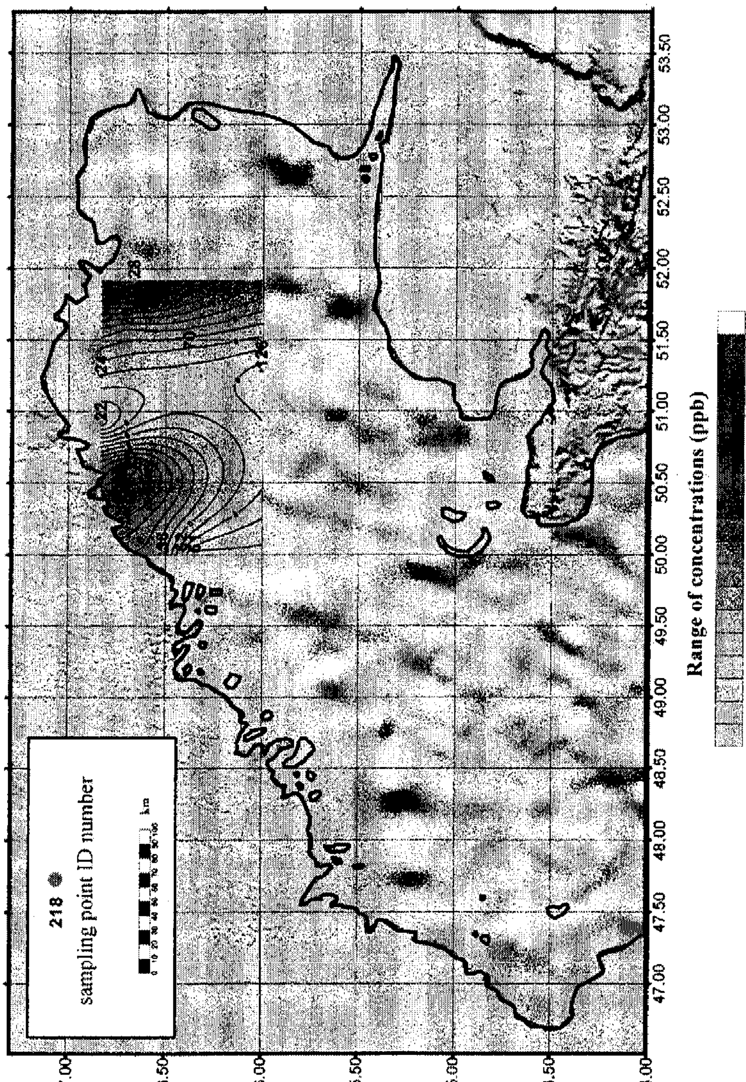

Fig 6: The map of the levels of DDT in sediments of the North Caspian Sea

Organochlorine compounds were detected only in the several samples. It is worth mentioning, that PCB, which had been considered as priority pollutants in 80^{th}, were not detected at all. This result supports previous data on the very low level of PCB in the tissues and blubber of fish and seals [1]. This is a pleasant fact demonstrating that these hazardous chemicals were totally destructed due to the self-purification processes in the sea, while new portions of them do not penetrate the sea. Among organochlorines DDT with metabolites, hexachlorobenzene and HCH including lindane are the most hazardous. The constructed map of the sea pollution clearly revealed that organochlorines were coming to the sea only with the effluents of the Ural River. Since the levels of DDT are not lower than the levels of its metabolites it is possible to conclude that this prohibited pesticide is still applied in the Ural River basin (figure 6).

Table 1: The range of levels of the pollutants in the sediments of the Caspian Sea

Group of pollutants	Range of levels
Petroleum hydrocarbons	400 – 5,700 ppb
Alkylnaphthalenes	0,1 – 61.1 ppb
PAH	0,2 – 34.0 ppb
Sum of HCH	0 – 1.95 ppb
Hexachlorobenzene	0 – 0.12 ppb
DDT	0 – 0.87 ppb
DDT with metabolites	0 – 0.92 ppb
Sulphur	0 – 13,800 ppm

Conclusions

1) Petroleum hydrocarbons remain the principal pollutants of the Caspian Sea. The main sources of penetration of these chemicals into the sea are the effluents of the Volga and Ural Rivers. The higher levels of the low molecular weight PAH in comparison to PAH with 4 and 5 cycles proves that crude oil and oil fuels are the principal source of the sea contamination with PAH.
2) Organochlorines (DDT with metabolites, BHC and hexachlorobenzene) come to the sea only with the effluents of the Ural River. DDT prohibited in early 80^{th} is still used in the Ural River regions. Chlorophenols and PCB were not detected.
3) Elemental sulphur is an anthropogenic pollutant presenting in the sediments of the sea at the highest level (up to 1%).

References

[1] O. V. Poliakova, A. T. Lebedev, N. K. Karakhanova, A. V. Funtov, V. S. Petrosyan; in "Water pollution V", Ed. P. Anagnostopoulos and C. A. Brebbia, WIT Press 1999, p. 419-426.