DETERMINATION OF SOME ORGANIC AND INORGANIC POLLUTANTS FROM THE BLACK SEA COAST

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Abstract

Black Sea's pollution by organic and inorganic pollutants is very frequency due to the fact that in the sea water there are discharged some waste waters (industrial or home originated) and river waters with a high pollutants concentration. Persistent organochlorine pesticides (OCPs) and polycyclic aromatic hydrocarbons (PAHs) are a major issue of research in order to investigate their environmental occurrence, biochemical and toxic effects, human exposure and health risk assessment. For the determination of the selected OCPs and PAHs in Black Sea water, samples were analized by Gas Chromatography with Mass Spectrometer Detector (GC-MS) and by Gas Chromathography with Electron Capture Detector (GC-ECD). To the best of our knowledge, these data were the first reported in water samples of Black Sea. Many researchers discuss the presence of these pollutants in Black Sea but most of them present their results on the OCPs and PAHs contamination in sediments or aquatic organisms. The content of some microelements (Mn, Cr, Mo, Ni) which are potentially hazardous to the environment and human health, from the Black Sea was determined using inductively coupled plasma atomic emission spectrometry (ICP-AES).The experimental results shown by comparision with the literature date that the presence of inorganic contaminants is not a dangerous factor due to normally less concentration.

Keywords Surface water, Seawater, Black Sea, Polycyclic aromatic hydrocarbons, Organochlorine pesticides, heave metals, GC–MS, GC–ECD, ICP-AES

Introduction

In recent decades, many investigations reports have been documented that organic contaminants like organochlorine pesticides and polycyclic aromatic hydrocarbons (OCPs and PAHs) might be transported widely through atmosphere and eventually polute all over the world. Such a worldwide spread and transition is expected to affect the current status of global contamination and pose a threat to human beings and wildlife, particulary marine mammals (1-2), mussels (3) and fishes (4). Nowadays there is an increasing concern over the potential hazardous effects that OCPs and PAHs may have on human health. OCPs are one of the most persistent organic pollutants present in the environment. So, the toxicity, potential bioaccumulation and non-biodegradability of these compounds represent risks to the environment in respect of human health. On the other hand, PAHs are a group of compounds whose mutagenic and/or carcinogenic effects are well known. Furthermore, the relationship between PAH in aqueous media and carcinogenicity is less well established (5). The determination of trace metal pollutants, like Cr, Mn, Mo, Ni, in seawaters is of great importance because they are involved in biological cycles and they are potentially hazardous to the environment and human health. Because of the high sensitivity, wide dynamic range and relative freedom from interferences, inductively coupled plasma atomic emission spectrometry (ICP-AES) has been used for the determination of trace metal pollutants in seawater samples.

In this paper, OCPs and PAHs were analyzed for the first time in water samples from the Black Sea, to the best of our knowledge. Many researchers discuss the presence of these contaminants in the Black Sea, but most of them present their results on the OPCs and PAHs contamination in sediments

or marine organisms [6-9]. Seawater samples were analyzed by Gas Chromatography with Mass Spectrometer Detector (GC–MS) and by Gas Chromatography with Electron Capture Detector (GC–ECD) for the determination of the organic contaminants and for determination of trace metal pollutants samples were analysed by ICP-AES technique, between January and March 2002.

Methods

Chemical and reagents Standards of OCPs and PAHs: p,p'- DDT, p,p'- DDE, p,p'- DDD, Dieldrin, Aldrin, Endrin, Acenaphthene (Ace), acenaphthylene (Acy), fluorene (F), naphthalene (Np), anthracene (An), fluoranthene (Fl), phenanthrene (Ph), benzo[α]anthracene (B[α]An), benzo[k]fluoranthene (B[k]Fl), chrysene (Chry), pyrene (Py), benzo[ghi]perylene (B[ghi]Pe), benzo[α]pyrene (B[α]Py), dibenzo[α,h]anthracene dB[α,h]An, indeno[1,2,3–cd]pyrene (I[1,2,3–cd]Py), were supplied by International Atomic Energy Agency, Monaco laboratory.Three usual sorbent materials of variable polarities (silica gel, florisil and aluminium oxide) were assayed for preconcentration step. Silica gel 60 (0.2 – 0.5 mm) and aluminium oxide 90 (0.063 – 0.200 mm) were obtained from Merck, Darmstadt, Germany. Florisil (60 – 100 mesh) was obtained from Fluka (packed in Switzerland). As eluents were assayed two organic solvents: n-hexane, supplied by Merck, Darmstadt, Germany and dichlormethane supplied by J.T. Baker. All reagents used for trace metal determination were of analytical reagent grade (Merck). Deionised water was used for the preparation of all solutions. All metal stock solutions (1000 mg/l) were prepared by dissolving the appropriate amounts of the metals or compounds in dilute acids (1:1) and then diluting them with deionised water.

Sampling All of the surface seawater samples were collected in 1L glass bottles capped with glass caps for organic pollutants determination and for inorganic pollutants samples were collected in Teflon bottles. The seawater samples were collected from six sites on the Black Sea Coast: (1) Midia; (2) Mamaia; (3) Constantza Harbour; (4) Agigea; (5) Costinesti; (6) Vama Veche. Fig. 1 shows the positions of sampling sites and the location of the Black Sea Romanian coast. The collection of the seawater samples was made from the surface, approximately to 10 m from the coast. The sample stations were selected on the basis of the different factors, which influence the quality of water, such as Năvodari, Constantza and Mangalia cities, where important maritime and industrial activities are developing. The sample stations covered the whole Romanian coast of the Black Sea. Samples were filtered to remove particulate material and kept refrigerated at 4°C away from light prior to extraction, which was done within 24h. The extracts were analyzed before two weeks of collection.

Extraction of organic pollutants Liquid–liquid extraction and solid–phase extraction are the most known techniques used for recovery and preconcentration of PAHs from water samples. All of the water samples were handled by liquid-liquid extraction (LLE) with hexane in the separatory funnel. All glassware was thoroughly cleaned and rinsed with acetone and then hexane before use. These samples were condensed using rotary evaporator and then the sulfur-containing compounds were removed with elemental copper using ultrasonication bath. Aliphatic and aromatic fractions were separated using a chromatographic column packed with aluminium oxide and silica-gel, 5 g activated at 400° C and pesticides were separated using a chromatographic column packed with florisil, 5 g activated at 110° C, as described in EPA method 8270C and 3600C. These fractions were eluted with n-hexane and n-hexane-dichlormethane (3:1), respectively. The column material was not allowed to become dry and the eluate was dried over anhydrous Na_2SO_4 and washed with diclormethane. Then the fractions were reduced to 1 ml in the Kuderna–Danish apparatus and adequacte volumes of the final extracts were injected. The analysis of the extracts was achieved using 9,10 dihidroanthracene and trichlorobiphenyl as internal standards.

Instrumentation Analysis of OCPs was performed using a gas chromatograph Hewlett Packard model 5890, equipped with an Electron Capture Detector (ECD), a split/splitless injector operated in splitless mode and a fused–silica capillary chromatographic column HP–5 (Hewlett Packard)

30m×0.32mm×0.25μm film thickness. These results were confirmed by gas chromatography-mass spectrometry. A 1 μl aliquot of the extract was manually injected with a syringe. The temperature for injector and detector were 250°C and 300°C, respectively. The temperature column was programmed as follows: from 60°C (hold 1 min at 60°C) to 300°C at 20°C/min (hold 10 min at 300°C). The carrier gas was Helium (purity 99.999%) at a flow rate of 1.36ml/min. ECD conditions: temperature 300°C, nitrogen (make-up) 60 ml/min, split/splitness inlet vent – 17.14mL/min. Chromatographic analysis of PAHs was performed on a Hewlett Packard gas chromatograph model 5890, directly connected to a Hewlett Packard 5972 Mass Selective Detector. The instrument was operated with electron impact ionization. A 0.5 μl aliquot of the extract was manually injected with a syringe. The temperature for injector and detector were 250°C and 280°C, respectively. The temperature column was programmed as follows: from 60°C (hold 1 min at 60°C) to 280°C at 20°C/min C (hold 10 min at 280°C). Helium was used as a carrier gas at a flow rate of 1.36ml/min.

A "Spectroflame P" apparatus provided by Spectro Company, Germany analyzed the seawater samples. The instrumental components and operating conditions in the ICP-AES measurements are summarized in table 1 [10,11]. For each sample three determinations were performed and average results were reported.

Table 1. Instrument systems and operating conditions of the ICP-AES

Plasma conditions	
Rf. frequency	27.12 Hz
Rf. power	2.5 Kw
Outer gas	Ar 17 l/min
Intermediate gas	Ar 1 l/min
Carrier gas	Ar 1 l/min
Observation height	18 mm above work coil
Plasma's temperature	8000-9000 K

Results and discussion

Results obtained for the 6th OCPs with GC-MS technique are listed in Table 2. OCPs were detected in 9 of 18 samples. The predominant one was dieldrin and the higest concentration was 0.391 μg/l. OCPs concentrations were not especially high in comparison to levels reported from surface water of Bering Sea and Chuckhi Sea (12).

Table 2. Concentrations of OCPs in surface water of the Black Sea during January – March 2002

Sample time	Pesticides (μg/l)	Midia	Mamaia	Constantza Harbor	Agigea	Costinesti	Vama Veche
January	p,p'-DDT	-	-	-	-	-	-
	p,p'-DDE	-	-	-	0.048	-	-
	p,p'-DDD	-	-	-	-	-	-
	Dieldrin	0.082	-	-	-	0.008	-
	Aldrin	-	-	-	-	-	-
	Endrin	-	-	-	-	-	-
February	p,p'-DDT	-	-	-	-	-	-
	p,p'-DDE	-	0.080	-	-	-	-
	p,p'-DDD	-	-	-	-	-	-
	Dieldrin	0.391	0.069	-	-	0.065	-
	Aldrin	-	-	-	-	-	-
	Endrin	-	-	-	-	-	-
March	p,p'-DDT	-	-	-	-	-	-
	p,p'-DDE	-	-	-	-	-	-
	p,p'-DDD	-	-	-	-	-	-
	Dieldrin	0.216	-	0.006	-	-	0.102
	Aldrin	-	-	-	-	-	-
	Endrin	-	-	-	-	-	-

The most often detected compound was Np, which was detectable in 15 of the 18 samples and levels ranged between 0.020 - 0.600 µg/l (Table 3). Analyses of coastal waters taken from throughout the region indicate that levels of PAHs are much lower than concentrations measured in coastal waters from North Atlantic and coastal waters of Rhode Island (13,14). Highest concentrations of PAHs (0.600 µg/l for Np in March) were associated with wastewater discharges, shipping activity and discharges from the river Danube (9, 15). This river flows into the Black Sea after it crosses eight countries in its way.

Table 3. Concentrations of PAHs in surface water of the Black Sea during January – March 2002

Sample time	Station	Np	Acy	Ace	F	Ph	Chry	B[α]Py	I[1,2,3-cd]Py
January	Midia	0.155	-	-	-	-	-	-	-
	Mamaia	0.234	-	-	-	-	-	-	-
	Constantza	0.250	0.004	0.010	-	-	-	-	-
	Agigea	0.095	-	0.009	-	-	-	-	-
	Costinesti	0.067	-	-	-	-	-	-	-
	Vama Veche	-	-	-	-	-	0.057	-	-
February	Midia	0.020	0.004	0.010	-	-	0.031	-	0.008
	Mamaia	0.300	0.005	0.008	-	-	-	-	0.005
	Constantza	0.200	-	0.009	0.003	0.003	-	0.003	0.005
	Agigea	-	0.004	0.007	0.004	-	-	-	-
	Costinesti	0.288	0.006	0.004	0.004	-	-	-	-
	Vama Veche	0.423	0.004	0.017	0.006	-	-	0.006	-
March	Midia	0.162	0.004	-	-	0.004	-	0.004	0.004
	Mamaia	0.260	-	0.034	0.016	0.006	-	-	0.008
	Constantza	0.600	-	0.008	0.008	0.008	-	0.008	0.006
	Agigea	0.365	-	0.001	0.005	-	-	0.005	0.001
	Costinesti	0.147	-	0.042	0.005	-	-	0.005	0.004
	Vama Veche	-	0.004	0.033	-	-	-	-	0.006

The occurrence of Cr, Mn, Mo and Ni in surface water of the Black Sea during January and March 2002 is summarized in Table 4. For each seawater sample three determinations were performed and average results were reported.

Tabel 4. Determination of Cr, Mn, Mo and Ni in seawater samples by ICP-AES

Element	λ (nm)	Concentration (µg/L)					
		Midia	Mamaia	Constantza Harbor	Agigea	Costinesti	Vama Veche
Cr	267.711	3.60	5.46	5.34	2.98	4.65	4.06
Mn	257.600	7.90	18.16	2.75	5.24	5.66	10.42
Mo	203.844	11.8	7.22	6.58	17.06	27.60	12.62
Ni	231.603	18.60	19.58	12.58	18.34	3.29	11.70

For these pollutants (organic and inorganic) there were observed some variations for the same site. This is a consequence of the enormous flow rate of the river Danube and its seasonal variability. Danube is the main important pollution agent of the Black Sea because wastewaters from ferrous, chemical, mechanical plants and oil refineries were discharged into the river (15).

Conclusions
The concentration of PAHs ranged from 0.001 to 0.600 µg/l as individual PAHs, for OCPs ranged from 0.006 to 0.391 µg/l, for Cr ranged from 2.98 to 5.46 µg/l, for Mn ranged from 2.75 to 18.16 µg/l,

for Mo ranged from 6.58 to 27.60 μg/l and for Ni ranged from 3.29 to 19.58 μg/l in water of the Black Sea.

By examination of the experimental results and by comparison with the literature data, it is possible to conclude that OCPs, PAHs, Cr, Mn, Mo and Ni pollution presently is not a dangerous factor due to normally less concentration.

The distribution profiles of these contaminants in water suggest that there are a number of sources contributing to total contamination including wastewater discharged in Danube by Metallurgical Industrial Centers, flow characteristics, domestic and wastewaters discharged into the sea from large cities and industries, domestic sewage and oil spills from cargo ships and storage tanks, the quality of sea and river transport.

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