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ASSESSMENT OF DANGEROUS SUBSTANCES LEVEL OFF THE DANUBE MOUTHS

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ABSTRACT

The impurification source of the marine environment at the Danube mouths are the wastes transported by fluvial water from continental industries and aquatic transports.The pollution of marine waters can affect the quality of the phsical and chemical parameters of the ecosystem with effects on its dynamics, biodiversity, living resources and human activities.

The contamination of the marine environment is expressed by considering three groups of parameters : hydrocarbons (total hydrocarbons, polycyclic aromatic hydrocarbons (PAHs) and organochlorines compounds), heavy metals (Cd, Cu, Pb) and artificial radionuclides.

Here is discussed the level of contaminants in 2001 in comparison with 1996-1998 reference period.

The analytical results demonstrate the anthropogenic input in the marine environment in the area of fluvial discharge impact.The spatial and temporal variations in hydrocarbon and heavy metals pollution in the abiotic component of the marine ecosystem

influenced the bioaccumulation process of PAH, heavy metals and organochlorines compounds in biota.

KEY WORDS : Danube mouths, contaminants, hydrocarbons, heavy metals, artificial radionuclides

INTRODUCTION

The consequences of marine pollution are reflected in degradation of the physical and chemical quality of the ecosystem, accompanied by biological and social changes.

In the marine area influenced by Danube, the impurification source of marine environment is represented by fluvial waters, characterized by a substantial input of pollutants, resulted from anthropic activities carried out along the fluvial catchment area and naval transport.

The paper presents the results obtained in 2001 regarding:

- the levels of organic and mineral pollutants in sea water from the area influenced by fluvial discharges;
- the trend of the pollutants accumulation process, such as total hydrocarbons, heavy metals, organochlorinated pesticides, polyaromatic hydrocarbons and radionuclides, in the surface marine sediments and biota.

The contaminants level in 2001 was compared with the results obtained in reference period 1996-1998 .

MATERIAL AND METHODS

The sampling strategy of the abiotic samples for pollutants content determination has taken into account :

- the main hydrological and meteorological characteristics of the studied area;
- the spreading area of the pollutant load.

The study of the evolution of marine pollution process has been carried out by comparative analyses of the pollutants load in the main source – fluvial waters discharged through Sulina arm, with the seasonal levels determined in abiotic components from the marine zone influenced by Danube, and also in the southern direction, along the Romanian Black Sea coastal area (Fig. 1 and Table 1).

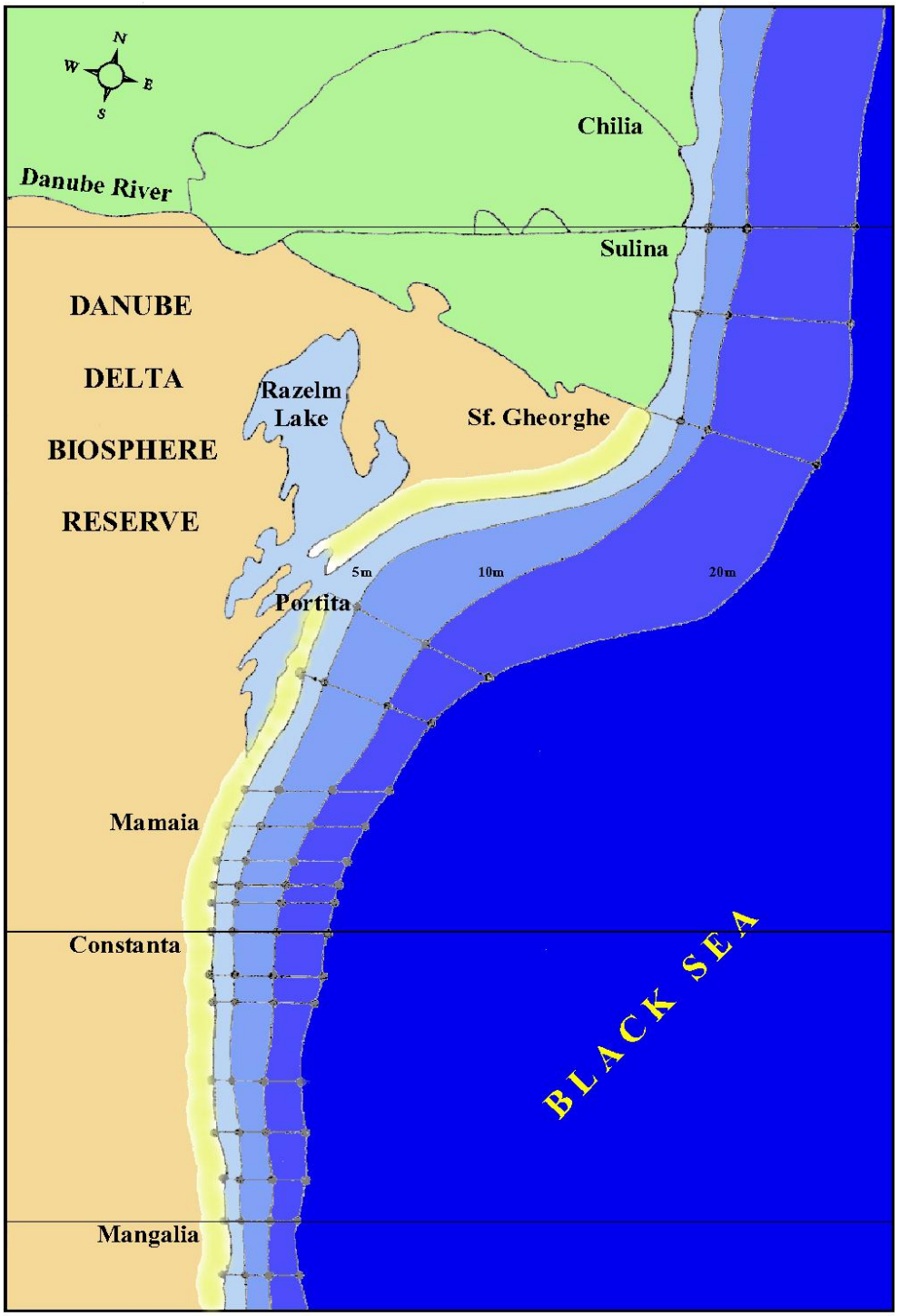


Figure 1. Romanian coastal zone

Table 1

The investigation system applied in 2001 for pollutants control in marine ecosystem components from the area influenced by Danube

Parameter / sample	Total hydrocarbons ✧ ❁	Heavy metals ✧ ❁	Pesticides ✧ ❁	PAHs ✧ ❁	Radionuclides ❁
Sulina					
Depth 20m	x x	x x	x x	x x	x
Depth 40m	x x	x x			
Mila 9					
Depth 20m	x x	x x	x x	x x	x
Depth 40m	x x	x x			
Sfantu Gheorghe	x x	x x	x x	x x	x
Depth 20m	x x	x x			
Depth 40m					
Portita					
Depth 20m	x x	x x	x x	x x	x
Depth 40m	x x	x x			
Chituc					
Depth.20m	x x	x x	x x	x x	x
Depth.40m	x x	x x			x
Constanta					
Depth 20m	x x	x x	x x	x x	x
Depth 50m	x x	x x	x x	x x	x
Mangalia					
Depth 20m	x x	x x	x x	x x	x
Depth 50m	x x	x x	x x	x x	x

✧ seawater sample ❁ sediment sample

Table 2

Analytical methods for determination of concentrations

Parameter	Analytical method
Total hydrocarbons	Spectrophotometric detection in UV domain, 230 - 270 nm by HEWLETT PACKARD 8453 equipment.Calibration with *Danube Reference Oil* [1,2,3,6]
Polyaromatic hydrocarbons	Detection by Hewlett Packard 5890 gas cromatograph, with mass spectrometer detector [7,8]
Organochlorinated pesticides	Detection by Hewlett Packard 5890 gas cromatograph, with electron capture detector [7,8]
Heavy metals	Investigation by atomic absorbtion spectrometry, using an ATI-UNICAM Z939, with Zeeman correction device[4,5]
Radionuclides	Gamma spectrometric detection, using a high resolution system with GeHP semiconductor detector, according to IAEA(1989)

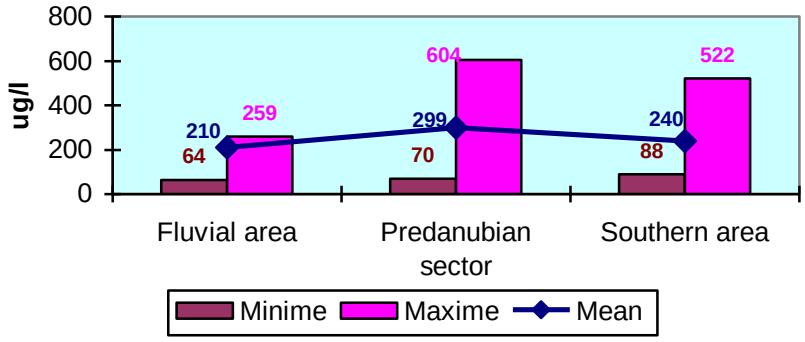
RESULTS AND DISCUSSIONS

The investigations carried out in 2001 concerning contaminant levels in seawater and surface sediments from the area influenced by Danube have identified pollutants such as petroleum hydrocarbons, heavy metals, polyaromatic hydrocarbons and organochlorinated pesticides, resulted from fluvial discharge.

Total hydrocarbons content

Total hydrocarbons content analysis in seawater samples collected in 2001 from marine area influenced by Danube indicated the presence of petroleum pollutant in all investigated samples, in concentrations between 64.9 - 259μg/l in fluvial waters and within the limits of 11.3 - 604 μg/l in transitional waters (Fig. 2).

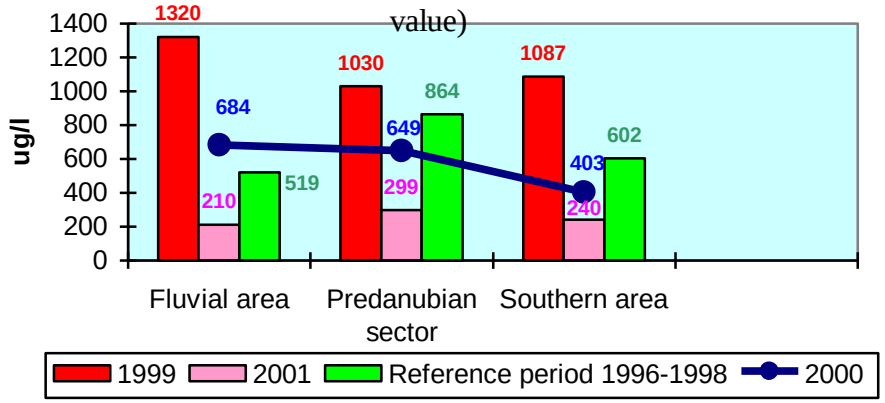
Fig.2. Total petroleum hydrocarbons in sea water samples collected in 2001



Spatial distribution of the average concentration values determined in transitional water collected from 20 m and 40 m depths along the Romanian Black Sea coast reflects the fluvial discharges input, with a concentration decreasing tendency southwards (Fig. 2).

The average load of total hydrocarbons content established in seawater samples collected from Sulina – Chituc, of 299 μg/l, increased with 19.7%, compared with the average content of the samples from the southern littoral zone between Constanta and Mangalia (Fig.2).

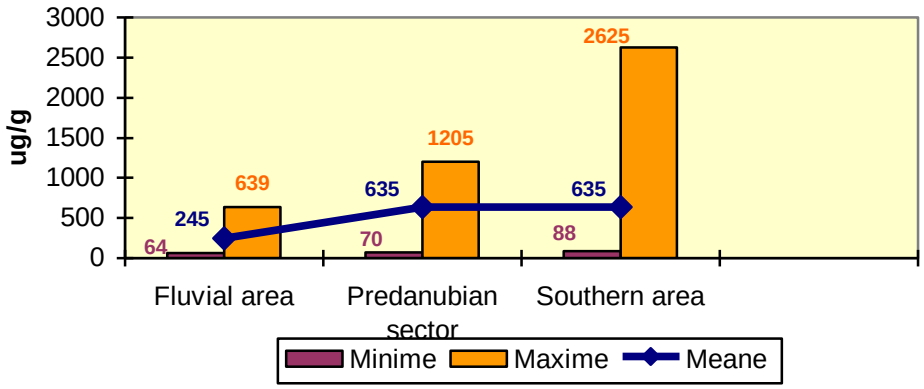
Fig.3.Temporal distribution of oil content in sea water samples collected between 1996 and 2001(average value)



In 1999 were identified the highest values for total hydrocarbons in seawater; compared with those determined in 2001, these values were 6.2 times higher in fluvial water, 3.4 times higher in transitional water from predanubian sector and 4.5 times higher in coastal water from the southern part of the littoral (Fig. 3).

Regarding the accumulation of petroleum pollutant in surface sediments, in 2001 the petroleum pollutant content varied between 70 and 2625 μg/g (Fig.4).

Fig.4 Total petroleum hydrocarbons in sediment samples collected in 2001

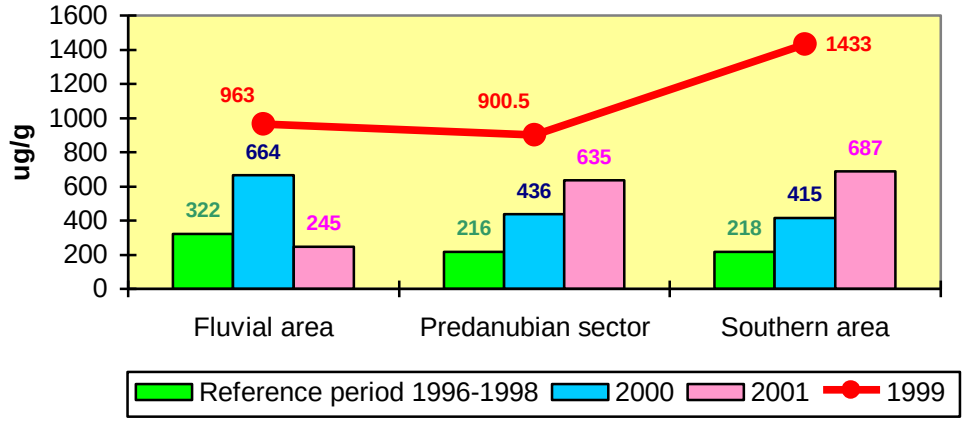


The pollutant spreading process in southern direction, with an increased accumulation in the southern zone of the Romanian littoral, has been identified.

Temporal distribution pattern of the average concentrations observed between 1996 and 2001 shows in 1999 the highest contamination level with hydrocarbons of the marine sediments from the area under the influence of the Danube.

In comparison with the results obtained in the reference period 1996-1998, in 2001 was registered a decreasing of the total hydrocarbons content in seawater from the area under the influence of the Danube, about 2,6 times lower; this is compensated by an increasing of the petroleum pollutant accumulation in the surface sediments, where was observed a load of 2,9 times higher in pre-danubian sector and 3,1 times higher loads in the southern zone of the costal area (Fig.5).

Fig.5 Temporal distribution of oil content in sediment samples collected between 1996 and 2001 (average values)



Heavy metals content

The investigations carried out in 2001 in order to evaluate trace metals concentration l in the abiotic components of the marine ecosystem in the area under the influence of Danube have shown a significant load of Cd, Cu, Mn and Pb, concentration values being specific for each element and characteristic for prelevation stations (Tables 3, 4).

Table 3

Trace metal concentrations in seawater samples collected in 2001 from marine area under the influence by Danube (μg/l)

Investigation Area	Cu m - M	Cu M*	Cd m - M	Cd M*	Mn M*	Pb m - M	Pb M*
Fluvial water	0.54 – 5.8	2.9	0.02 – 1.15	0.58	2.39	0.18 – 9.53	4.86
Pre-danubian sector	0.16 – 8.86	4.6	0.04 - 1.64	0.52	5.16	0.03- 32.8	14.6
Southern area	0.39 – 13.4	4.41	0.03 - 0.66	0.25	9.3	0.02 – 44.1	20.4

m-minimum value, M- maximum value, M* - mean value

Table 4

Trace metal concentrations in sediment samples collected in 2001 from marine area under the influence by Danube (μg/g)

Investigation Area	Cu m - M	Cu M*	Cd m - M	Cd M*	Mn M*	Pb m - M	Pb M*
Fluvial water	43.7 –131.2	87.4	3.8 - 24.9	14.3	121	81.8-147.2	114
Pre-danubian sector	49.2 –124.3	82.7	8.27- 34.2	21.9	96.2	69.7-120.2	87.3
Southern area	24.3–124.3	86.9	3.1- 17.8	10.6	96.2	34.9-130	86.9

m-minimum value, M- maximum value, M* - mean value

The spatial distribution pattern of the concentrations reflects the fluvial waters input, which contributes to the contamination of the bottom sediments underneath the water column.

Between 1996 and 2001, trace metals content determined in abiotic samples from the marine zone under the influence by Danube showed a wide variation range, due to the anthropogenic input (Fig. 6, 7, 8, 9, 10, 11).

The highest concentration values for heavy metals in abiotic elements collected from pre-danubian sector between 1996 and 2001 were determined in 1999, just after the Jugoslavian conflict.

In 1999 were registered average values 2.5 times higher for Cu, 4.8 times higher for Cd and 6.3 times higher for Pb, in sea water, comparing with reference period 1996-1998; in sediments the values were increased with 34% for Pb, 42% for Cu and 69% for Cd.

Fig.6 Temporal distribution of Cu concentrations in sea water samples collected between 1996 and 2001(average values)

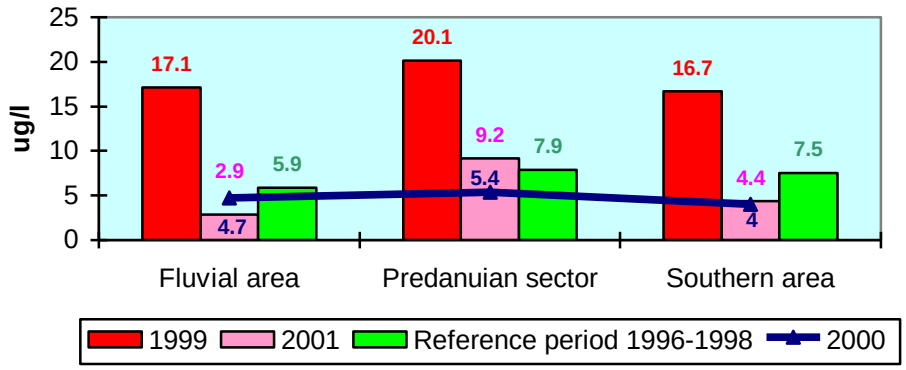


Fig.7 Temporal distribution of Cd concentrations in sea water samples collected between 1996 and 2001(average values)

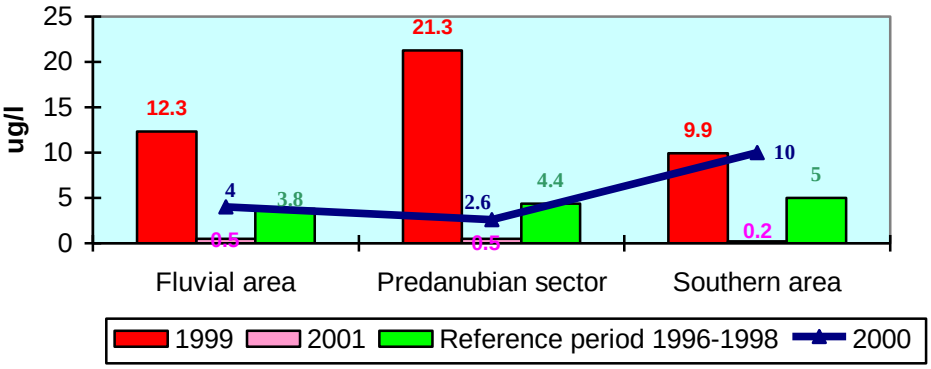


Fig.8 Temporal distribution of Pb concentrations in sea water samples collected between 1996and 2001(average values)

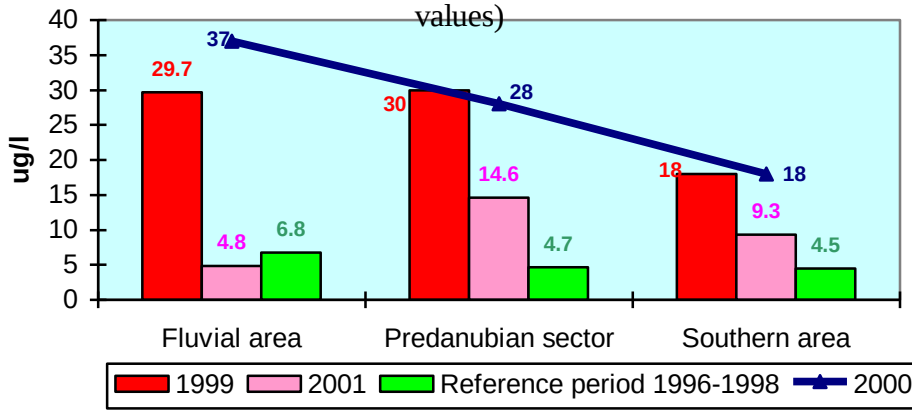


Fig.9 Temporal distribution of Cd concentrations in sediment samples collected between 1996and 2001 (average values)

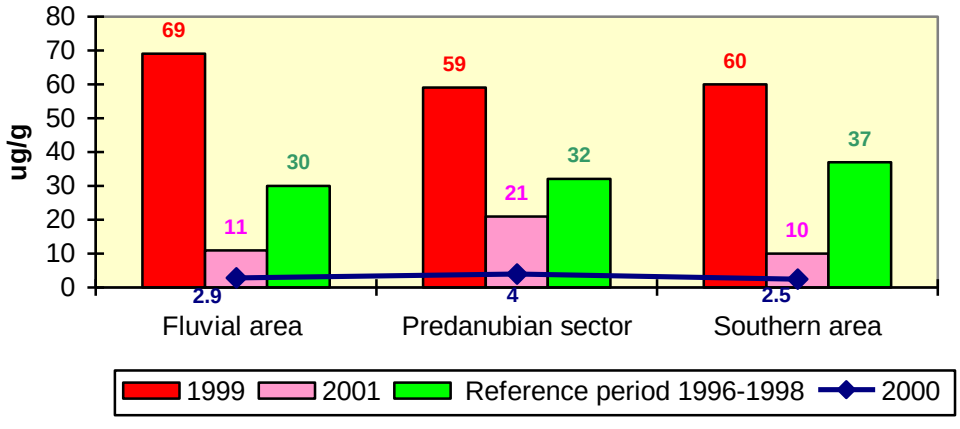


Fig.10 Temporal distribution of Cu concentrations in sediment samples collected between 1996 and 2001 (average values)

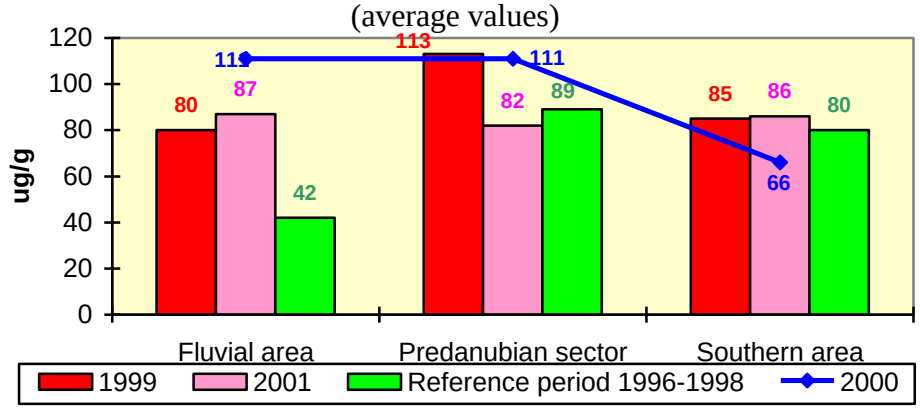
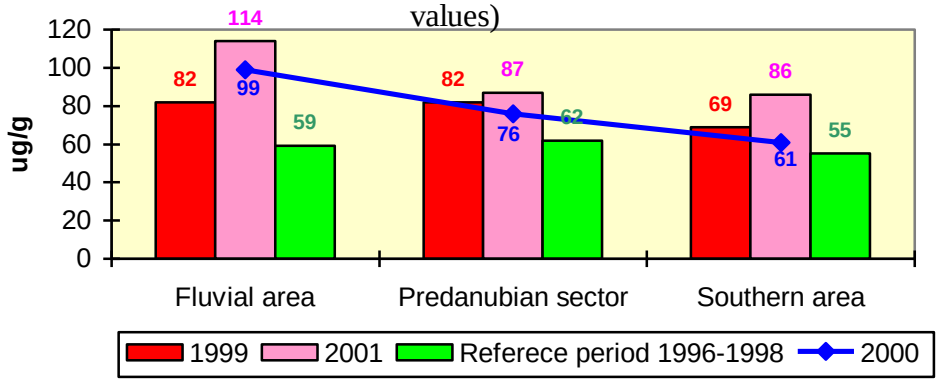


Fig.11 Temporal distribution of Pb concentrations in sediment samples collected between1996 and 2001(average values)



In comparison with the results registered in the reference period 1996-1998, the investigations carried out in 2001 showed some variations of trace metal concentrations, which were specific for each element in the three studied areas, as follows:

- in water from fluvial area was observed a decrease of 6.5 times in Cd concentrations, 2 times of Cu concentrations and 1.4 times of Pb concentrations, whereas in sediments a decrease of 2.1 times of Cd content and an increase of 2 times of Cu content and 1.9 times for Pb were registered;

- in transitional water of the predanubian sector Sulina – Portita a 8.4 time decrease in Cd concentrations and a 3.1 time increase in Pb

concentrations have been observed;

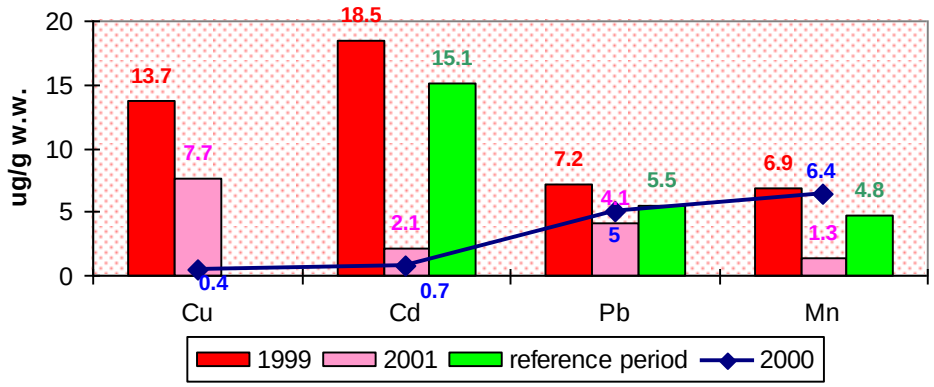
- in sediments of the predanudian sector 1.5 times higher level of Pb was registered;

- in the southern zone, Constanta – Mangalia, coastal water had a level of Cd diminished by 20 times and a level of Pb by 2 times higher , whereas in the sediments a reduction of Cd content by 3.5 times and a higher level of Pb by 1.5 times higher was registered.

The analyses of metals in marine organisms (fish and mussels) sampled in 2001 from Portita – 2 Mai underlined the presence of Pb, Cd, Cu and Mn in specific concentrations for each ion, species and collecting area as follows:

- Cu concentration varied between 6,46 µg/ww and 8,74 µg/ww in *Sprattus sprattus* and between 3,61 µg/ww and 6,42 µg/ww in *Mytilus galloprovincialis* (Fig. 12, 13);

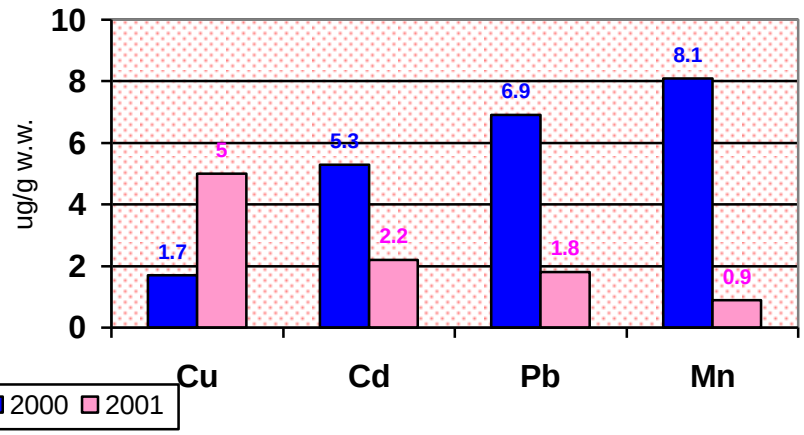
Fig.12.Temporal distribution of metalic ions in sprat samples collected in 1997-2001 period(averages values)



- Cd concentration varied between 1,23 µg/ww and 3,87 µg/ww in *Sprattus sprattus* and between 1,48 µg/ww and 3,33 µg/ww in *Mytilus galloprovincialis*;

- Pb concentration varied between 1,28 µg/ww and 6,12 µg/ww in *Sprattus sprattus* and between 1,22 µg/ww and 2,62 µg/ww in *Mytilus galloprovincialis* (Fig. 12, 13).

Fig.13 Temporal distribution of metalic ions in *Mytilus galloprovincialis* collected between 2000 and 2001 (average values)



Comparing with concentrations detected in the reference period, in 2001 a decrease of metals bioaccumulation in *Sprattus sprattus* of 7,5 times for Cd; 1,3 times for Pb and 3,6 times for Mn was observed.

Polyaromatic hydrocarbons content (PAHs)

The investigations carried out in 2001 for qualitative and quantitave determination of polyaromatic hydrocarbons in the abiotic elements of the marine environment from the area under the influence of the Danube showed the presence of this pollutant especially naphthalene, anthracen, fluorene and pyrene derivatives (Tables 5, 6; Fig. 14).

Table 5

Polyaromatic hydrocarbons concentrations (PAHs) in sea water samples collected in 2001 from the area under the influence by Danube (ng/l)

Parameters	Fluvial area	Predanubian sector	Southern area
Naphthalene	0 –15,5	9,2 - 23,9	19,5 - 30,5
Acenaphthylene	0	0 - 0,57	0 - 44
Acenaphthene	0,5	0 - 1,7	0,55 - 0,88
Fluorene	0,39 – 0,5	0 - 54	0,44 - 0,55
Anthracen	0	0	0 - 0,55
Benzo[ghi]perylene	0,19	0	0
Indeno[1,2,3,-c,d]pyrene	0,19 - 0,5	0 - 0,57	0

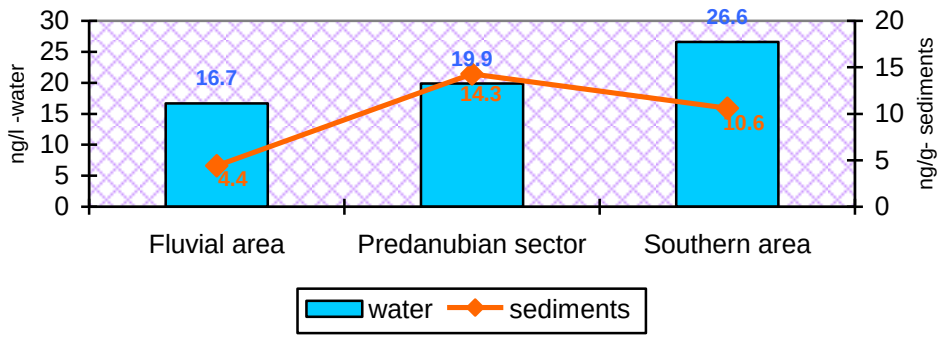
The significant content of PAHs, determined in coastal water and sediment samples collected from the southern zone of the coastal area, reflects not only the cummulative effect produced by fluvial discharge, but also the urban and industrial anthropogenic input.

Table 6

Polyaromatic hydrocarbons concentrations (PAHs) in sediments sample collected in 2001 from the area under the influence by Danube (ng/g)

Parameters	Fluvial area	Predanubian sector	Southern area
Naphthalene	0	10,4-11,11	5,2-5,5
Acenaphthylene	0,19	0-0,2	0,05-4,8
Acenaphthene	0,39	0,18-0,22	0,12-0,5
Fluorene	0,39	0-0,22	0,51-1,2
Phenanthrene	0	0- 0,19	0,9 -1,2
Anthracene	0	0-0,22	0,18-0,5
Fluoranthene	0	0	0,2-0,25
Benzo[a]anthracene	1,95	0 –5,5	0
Crysene	1,56	0-3,9	0
Benzo[ghi]perylene	0,195	0	0
Indeno[1,2,3,-c,d]pyrene	0,195	0	0

Fig.14 Spatial distribution of total PAHs content in abiotic samples collected in 2001 (average values)

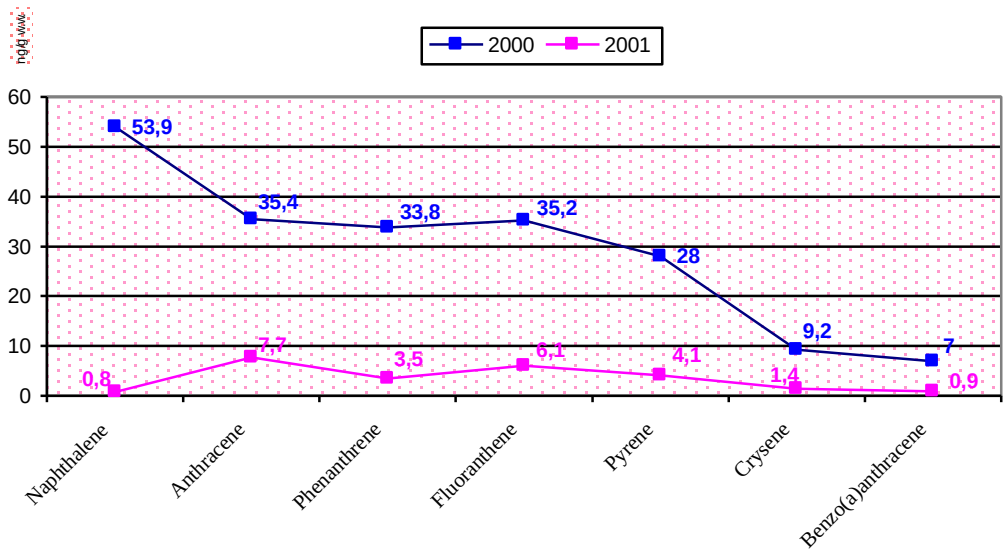


The investigations identified a pollutant spreading process in north-south direction, the number of identified compounds being reduced along with the increasing of distance from fluvial zone, but accompanied with an accumulation tendency.

Studies for PAHs identification in marine organisms with economic importance collected along the Romanian coastal area between Chituc and Mangalia showed the presence of policyclic aromathic compounds in sprat and mussel tissues, their diversity and abundance being characteristic for each species and area (Table 7).

In sprat samples 13 PAHs compounds and in mussels 11 PAHs compounds were identified, the variable concentrations depending of the collecting area.

Fig. 15. Temporal distribution of PAHs concentrations in Mytilus galloprovincialis samples collected between 2000and 2001 (average values)



Organochlorinated hydrocarbons content

The investigations regarding the establishment of the contamination level with organochlorinated pesticides in sea water and surface sediments from the marine area under the influence of the Danube focused on the most frequently used chlorinated pesticides: α hexachlorciclohexan, ϒ hexachlorciclohexan or lindan, β hexachlorciclohexan, DDT and metabolites, (DDD, DDE) , Aldrin, Endrin and Dieldrin (Tables 8, 9).

Table 7

Polyaromatic hydrocarbons concentrations (PAHs) in biotic samples collected in 2001 from the area under the influence by Danube (ng/g.w.w.)

Compounds	Concentrations ng/g.w.w.	
	Sprattus	***Mytilus***
Naphthalene	1,9 – 7,11	0 – 2,5
Acenaphthylene	0,26 - 0,77	0 – 0,11
Acenaphthene	0,78 – 9,42	0-0,19
Fluorene	2,12 – 3,9	0,13- 1,6
Phenanthrene	1,28 – 5,53	1,08 – 13,4
Anthracene	0 – 4,02	0,74 – 8,32
Fluoranthene	0	0,32 – 9,57
Pyrene	0 – 1,94	0 – 6,61
Crysene	0 – 3,06	0 – 1,27
Benzo[a]anthracene	0,16 - 4,1	0 – 1,64
Benzo(a)pyrene	0 – 0,18	0 – 0,29
Benzo(ghi)perylene	0 – 37,7	0
Dibenzo(a,h)anthracene	0 - 0,61	0
Indeno[1,2,3,-c,d]pyrene	0,03 – 0,12	0

Table 8

Organochlorinated hydrocarbons (ng/l) in seawater samples collected in 2001 from the area under the influence by Danube

Parameter	Fluvial area	Predanubian sector	Southern area
HCB	22,9	25,2 – 49,5	14,2 – 42,8
Lindan	1145,5	0 – 612,5	0 - 5,2
Dieldrin	20,1	0 – 17,5	0

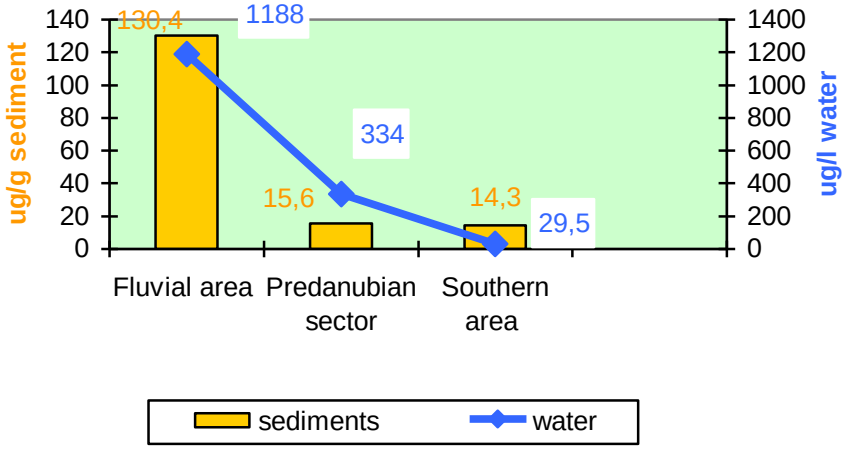
Table 9

Organochlorinated hydrocarbons (ng/g) established in sediment samples collected in 2001 from the area under the influence by Danube

Parameter	Fluvial area	Predanubian sector	Southern area
HCB	51.75	4,8 – 20,5	12
Lindan	5	1,5 – 4,5	9,7
Aldrin	25.64	0	0
Dieldrin	30.14	0	22
Endrin	18	0	0

The study of spatial distribution of concentrations indicated a pollutants spreading in the southern direction, the samples from the southern zone (Constantza-Mangalia) having 38 times lower concentrations compared with the fluvial area (Fig.16).

Fig.16. Spatial distribution of organochloride pesticides in abiotic samples collected in 2001



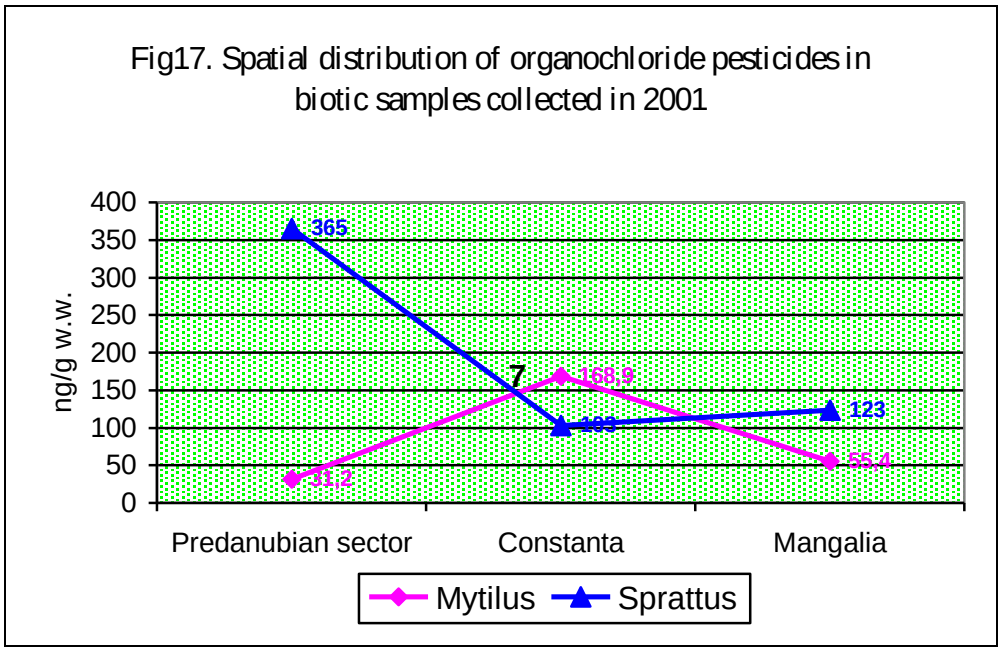
Studies for organochlorinated pesticides identification in marine organisms with economical importance collected in 2001 between Chituc and Mangalia showed the presence of organochlorinated pesticide compounds in sprat and mussel tissues , their diversity and abundance being characteristic for each species and area.

Table 10

Organochlorinated hydrocarbons (ng/g.w.w.) in biotic samples collected in 2001 from the area under the influence by Danube

Compound	**Concentrations ng/g.s.w.w.**	
	Sprattus	***Mytilus***
HCB	0 –3,1	0 – 0,44
Lindan	9,89 – 24,2	0 – 21,7
p-p DDE	1,19 – 158,2	3,95 – 90,9
M-p DDD	4,14 – 53,9	0 – 18,6
o-p DDT	11,7 – 188,5	2,74 – 46,3
Dieldrin	0 – 2,08	0 – 1,36
Endrin	0 - 9,59	0 – 3,6

The spatial distribution of total pesticides detected in sprat samples between March and May 2001 noted the highest level of bioaccumulation in fish collected from Chituc, which was 3.3 times higher compared with that detected in samples collected in Mamaia Bay and 2.9 times higher compared with that in samples collected from Mangalia (Fig. 17).



Radioactivity impact

During 2001, beta global indicators and Cs-137 have been found in abiotic and biotic samples.

The results showed beta global concentration values between 235 and 968 $Bq.Kg^{-1}$ dry weight (dw) in surface sediments and between 59 and 147 $Bq.Kg^{-1}$ wet weight (ww) in marine organisms.

Maximum values were registered in the northern sector of the littoral (Sulina, Sf. Gheorghe, Portita, Chituc) (Table 11).

Cs-137 in concentrations ranged between 54 and 120 $Bq.Kg^{-1}$ dw in surface sediments and between 1 and 2 $Bq.Kg^{-1}$ ww in mollusks and fish.

The tendencies registered in 2001 agree with the general observations from the last period: a low Cs-137 content in sea water and marine organisms, ans its relative high accumulation in surface sediments.

Table 11

Radioactivity level of marine components

collected from the area influenced by Danube in 2001

Nr. crt.	Sample	Beta global indicators	^{137}Cs
Sediments Bq.Kg^{-1} dry weight			
1	**Sulina**	**235+18**	**50.7±1.3**
2	**Sf. Gheorghe**	**406 - 855**	**42.6±1.2**
3	**Portita**	**649 - 968**	**17.1 - 4.5**
4	**Chituc**	**529 - 870**	**20.7 - 120**
5	**Constanta**	**439 - 627**	**14.2 - 17**
6	**Mangalia**	**668**	**21**
Marine organisms Bq.Kg^{-1} wet weight.			
Mya arenaria		59±3	1.46
Merlangius merlangus euxinus		86 - 92	1.52
Sprattus sprattus		77 - 147	
Trachurus mediterraneus		125	

CONCLUSIONS

According to the analytical results obtained in abiotic elements collected in 2001 from marine area under the influence of Danube, petroleum pollutants, heavy metals, polyaromatic hydrocarbons and organochlorinated pesticides have been identified, in relation with fluvial discharge, as follows:

- petroleum pollutant input from fluvial waters in 2001 is about 201.3 µg/l (average value). Spatial and temporal distribution of the average hydrocarbon concentrations follows a descending pattern for the hydrocarbon pollution process of sea water, along the Romanian Black Sea coastal area,in north-south direction;

- abiotic components from the area under the influence of Danube are characterized by a significant content of Cu, Cd and Pb, due to the fluvial input;

- in abiotic elements of the marine environment from the area under the influence of Danube were identified 8 PAH compounds in sea water and 7 in sediments, derivatives of naphthalene, anthracene, phenanthrene, pyrene, due to fluvial input;

- in abiotic elements of the marine environment from area under the influence of Danube were determined 3 types of organochlorinated pesticides: HCB, Lindan and Dieldrin;

- in the fluvial zone, organochlorinated pesticides content is 4.06 times higher in water samples and 8.9 times higher in sediments, compared with the southern zone;

- radiometric determinations carried out in 2001 in abiotic and biotic samples collected from the area under the influence of Danube showed the same tendency as in the last years, namely a low level for Cs-137 in water and marine organisms.

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