Results of the Assessment of the Western Black Sea Contamination Status in the Frame of the MISIS Joint Cruise *(A. Oros, V. Coatu, D. Secrieru, D. Țigănuș, D. Vasiliu, H. Atabay, C. Beken, L. Tolun, S. Moncheva, L. Bat)*	"Cercetări Marine" Issue no. 46 Pages 61-81	2016

RESULTS OF THE ASSESSMENT OF THE WESTERN BLACK SEA CONTAMINATION STATUS IN THE FRAME OF THE MISIS JOINT CRUISE

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ABSTRACT

The MISIS Joint Cruise, the main activity of the WP2 of the project MISIS (**M**SFD GUIDING **I**MPROVEMENTS IN THE BLACK **S**EA **I**NTEGRATED MONITORING **S**YSTEM), has aimed, among others, to collect additional data and produce homogeneous datasets based on a common sampling procedure and laboratory analysis of specific contaminants, as well as to provide useful information regarding the assessment of laboratories' performances in the Western Black Sea region. In addition, the expected results of the cruise could contribute to the improvement and revision of national monitoring strategies in the region, as well as to bring new knowledge in order to prepare the Articles 11 and 13 of MSFD by the EU countries in the region.

The cruise was carried out onboard R/V Akademik in the Western Black Sea, during 22-31 July 2013. The selected transects, Constanta, in the Romanian waters, Galata, in the Bulgarian waters, and Igneada, in the Turkish waters, were considered representative for the purposes of the projects. A total of 18 stations were performed (7 in RO waters, 6 in BG water, and 5 in the TR waters) covering the coastal, shelf and open waters. Wide range of contaminants: trace metals, and persistent organic pollutants (TPH, PAH, OCP, PCB) were analyzed in seawater (surface horizon) and sediments samples from all stations. Two intercomparison stations, one in the open waters and the second one in the coastal waters, were selected for contaminants in the sediments.

With respect to Directive 2008/56/EC Marine Strategy Framework Directive (MSFD)/ Descriptor 8, results from the MISIS Joint Cruise will promote further work toward

common understanding of good environmental status and will contribute to the development of Black Sea environmental targets in a harmonised approach.
Keywords: *Black Sea, MISIS cruise, heavy metals, organic pollutants, MSFD*

AIMS

Preventing and reducing inputs to the marine environment, with a view to phasing out pollution, is clearly stated as one of the main objectives of the Marine Strategy Framework Directive, in line with international commitments at global and regional level. Pollution by contaminants is one form of pollution of the marine environment and the aim of Descriptor 8 is to ensure that the levels of contaminants in the marine environment do not to give rise to pollution effects. Contaminants can arise from numerous anthropogenic sources such as land-based industrial activity, pollution by ships, atmospheric deposition, oil, gas and mineral exploration and exploitation and riverine inputs. It should be noted, however, that natural oceanographic and geological factors, including geothermal activity, can sometimes be responsible for elevated levels of some contaminants (such as heavy metals).

The assessment of achievement of Good Environmental Status (GES) under the Marine Strategy Framework Directive 2008/56/EC (MSFD) Descriptor 8 “Concentrations of contaminants are at levels not giving rise to pollution effects” should be based upon monitoring programmes covering the concentrations of chemical contaminants and also biological measurements relating to the effects of pollutants on marine organisms. The combination of conventional and newer, effect based, methodologies, with the assessment of environmental concentrations of contaminants provides a powerful and comprehensive approach. As the occurrence of adverse effects at various levels of organization (organism, population, community, and ecosystem) needs to be avoided, monitoring schemes should also indicate the approaching of critical values as early warning.

Therefore, for the purpose of implementing Descriptor 8 under the MSFD, three core elements of data assessment are recommended (1):

- Concentrations of contaminants in water, sediment and/or biota are below environmental target levels identified on the basis of ecotoxicological data;
- Levels of pollution effects are below environmental target levels representing harm at organism, population, community and ecosystem levels;
- Concentrations of contaminants in water, sediment and/or biota, and the occurrence and severity of pollution effects, should not be increasing.

The assessment following MISIS Joint cruise with respect to contaminants followed the criterion 8.1. Concentrations of contaminants, indicator 8.1.1. (Table 1).

Table 1. MSFD Criteria and indicators for contamination assessment following MISIS Joint Cruise, July 2013

Criterion	Indicator	Parameter	Assessment criteria
8.1. Concentrations of contaminants	8.1.1 Concentrations of contaminants measured in relevant matrix (such as biota, sediment and water) in a way that ensure comparability with the assessments under Directive 2000/60/EC	Heavy metals and persistent organic pollutants in seawater	The Environmental Quality Standard Directive (Directive 2008/105/EC, updated by Directive2013/39/EC) establishes requirements for the chemical status of surface waters including marine waters defining an Environmental Quality Standard (EQS);
		Heavy metals and persistent organic pollutants in sediments	Environmental Assessment Concentrations (EAC, OSPAR); Effect Range Low values (ERL,US EPA);

BACKGROUND

Available information on contaminants in the survey area

Romanian Black Sea waters

The state of the Romanian Black Sea marine ecosystem in terms of hazardous substances is assessed in the framework of the national monitoring programme by NIMRD on the basis of the following indicators:

- the presence of dangerous chemicals in surface seawater: total petroleum hydrocarbons (TPHs), heavy metals (HM), organo-chlorinated pesticides (OCPs), polyaromatic hydrocarbons (PAHs);

- contamination of marine sediments with hazardous chemicals: total petroleum hydrocarbons (TPHs), heavy metals (HM), organo-chlorinated pesticides (OCPs), polyaromatic hydrocarbons (PAHs);

- bioaccumulation of hazardous chemicals (HMs, OCPs) in marine molluscs.

Information on contamination is included in the report on the Initial assessment of the Romanian Black Sea waters (2), based on monitoring data generated between 2006-2011 from a network of 40 stations located on territorial waters, up to 30 nm distance from the shore, with a sampling frequency of 2 - 4 times / year.

Bulgarian Black Sea waters

The information about sea water and sediment pollution is scarce. Monitoring of pollutants was carried out in Bulgarian Black Sea area irregularly during last decade. Until now a chemical monitoring (for priority and specific substances) of coastal waters in context of EU Water Framework Directive 2000/60/EC (WFD) has not carried out. Some data was collected in the frame of scientific projects or screening in regard to WFD implementation. Most of published data in literature is for heavy metals (3, 4, 5, 6).

Turkish Black Sea waters

In a recent work to support the future implementation of WFD and MSFD in the Turkish coastal and marine waters, a supporting feasibility and assessment study has been conducted considering the GES descriptors of MSFD and the ongoing monitoring activities. Within the scope of D8, evaluations on sediments were made (7, 8, 9).

MATERIALS AND METHODS

The study area for contamination state was the Western Black Sea, three transects from the Romanian, Bulgarian and Turkey waters. Map of sampling stations and stations coordinates and depths are presented on Table 2 and Fig.1. Water samples for pollutants were collected from the surface layer (more precise, 1 m below the surface) from the 5 l Niskin bottles of the Rosette System. About 1 liter seawater was transferred into glass bottles, which were stored at refrigerator temperature until their subsequent analysis in laboratory. NIMRD analysed the pollutants in water at all stations. Sediment samples for pollutants were taken using a Van Veen sampler grab, from the surface undisturbed layer. GEOECOMAR collected sediment samples from all transects, for granulometry and heavy metals, and NIMRD collected samples from all transects for persistent organic pollutants (POPs). The samples were stored frozen and analysed subsequently in laboratory. Details on specific seawater and sediment pollutants analysed, methods and responsible institutions are presented in the Table 3.

Table 2. List of sampling stations, coordinates and depths

Station	Transect	Lat, ºN	Long, ºE	Bottom depth, m	Type	Date
M 01	Constanta	44°10.000	028°47.000	33.3	coastal	23.07.13
M 02	Constanta	44°10.000	029°.08.000	47.0	shelf	23.07.13
M 03	Constanta	44°10.000	029°.20.000	54.0	shelf	23.07.13
M 04	Constanta	44°10.000	029°.40.000	64.7	shelf	24.07.13
M 05	Constanta	44°04.800	030°.11.900	101.0	shelf	24.07.13
M 06	Constanta	43°55.000	030°.22.100	495.0	open waters	24.07.13
M 07	Constanta	43°47.800	030°.42.900	1000.0	open waters	25.07.13
M 12	Galata	43°10.000	028°.00.000	23.2	coastal	26.07.13
M 11	Galata	43°10.000	028°.20.000	39.9	shelf	26.07.13
M 10	Galata, inter-comparison	43°10.000	028°.30.000	76.1	shelf	26.07.13
M 09	Galata	43°10.000	028°.40.000	92.7	shelf	27.07.13
M 08	Galata	43°10.000	029°.00.000	1169	open	27.07.13

					waters	
M 13	Inter-comparison	42°44.232	029°.20.599	2018	open waters	28.07.13
M 14	Igneada	42°00.252	028°.48.773	1124	open waters	29.07.13
M 15	Igneada	41°56.173	028°.34.350	101.0	shelf	29.07.13
M 16	Igneada	41°53.830	028°.22.760	75.6	shelf	29.07.13
M 17	Igneada	41°51.235	028°.06.772	53.3	shelf	29.07.13
M 18	Igneada,inter-comparison	41°49.795	028°.00.275	27.2	coastal	30.07.13

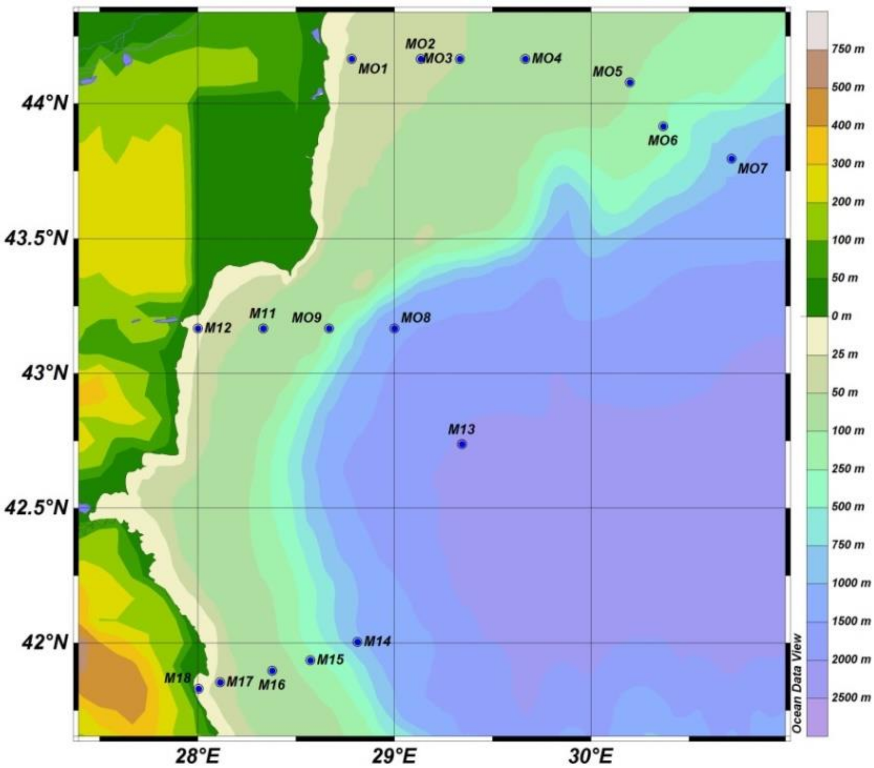


Fig. 1. Map of study area

Table 3. Specific pollutants analysed in seawater and sediment sampled in July 2013 during MISIS cruise, analytical methods and responsible institutions

	SEAWATER POLLUTANTS						
Parameters	**Heavy metals (HM)**	**Total petroleum hydrocarbons (TPH)**	**Poly-aromatic hydrocarbons (PAH)**	**Organo-chlorine pesticides (OCP)**	**Poly-chlorinated biphenyls (PCB)**	**Total organic carbon (TOC)**	
Responsible:							
NIMRD	X (RO, BG, TR transects)	X (RO, BG, TR transects)	X (RO, BG, TR transects)	X (RO, BG, TR transects)	X (RO, BG, TR transects)	X (RO, TR transect)	
GEOECOMAR	-	-	-	-	-	-	
TUBITAK	-	-	-	-	-	-	
Methods	GF-AAS	Fluorescence method	GC-MS	GC-ECD	GC-ECD	TOC Analyzer	
	SEDIMENT POLLUTANTS						
Parameters	**Heavy metals (HM)**	**Total petroleum hydrocarbons (TPH)**	**Poly-aromatic hydrocarbons (PAH)**	**Organo-chlorine pesticides (OCP)**	**Poly-chlorinated biphenyls (PCB)**	**Total organic carbon (TOC)**	**Grain size**
Responsible:							
NIMRD	X (inter-calibration)	X (inter-calibration; RO, BG, TR transects)	X (inter-calibration; RO, BG, TR transects)	X (inter-calibration; RO, BG, TR transects)	X (inter-calibration; RO, BG, TR transects)		
GEOECOMAR	X (inter-calibration; RO, BG, TR transects)					X (RO, BG, TR transects)	X (RO, BG, TR transects)
TUBITAK	X (inter-calibration; TR transect)		X (inter-calibration samples)				
Methods	GF-AAS F-AAS X-ray fluorescence spectroscopy ICP-MS	Fluorescence method	GC-MS	GC-ECD	GC-ECD	Titration method (Gaudette,1974).	Laser difractometry

RESULTS AND DISCUSSION

Seawater

Heavy metals concentrations in surface seawater collected during July 2013 from all transects were found to be rather low, being comparable and included within typical ranges reported for Black Sea coastal or open waters (Table 4).

Generally, a slight decreasing gradient from coastal to open sea was noticed for most analysed metals, with the exception of lead and chromium, but with no statistically significant differences (Fig. 2).

These measurements from July 2013 indicated a low level trace metal pollution of marine waters, concentrations of cadmium, lead and nickel being much below recommended EQS from European Legislation (Directive 2013/39/EU).

Table 4. Comparative data on heavy metals in seawater of the Black Sea region

	Cu (µg/L)	Cd (µg/L)	Pb (µg/L)	Ni (µg/L)	Cr (µg/L)
MISIS cruise, July 2013 (RO, BG, TR transects) (total metals)	0.65 (0.10-2.99)	0.20 (0.05 - 0.76)	2.45 (1.16-3.70)	4.38 (0.14-12.38)	2.54 (1.14-6.06)
IA RO Transitional, Coastal and Marine Waters (2006-2011) (total metals) (2)	10,02	0,99	3,78	3,65	3,84
RO Coastal and Marine waters (2013 Monitoring data) (total metals)	1,14 (0,37 - 4,14)	0,56 (0,16 - 2,87)	2,40 (0,04 - 7,04)	1,42 (0,24 - 8,13)	2,45 (0,37-10,34)
Ukrainian coastal Black Sea waters (total metals) (10)	0.40 - 3.00	0.05 - 0.15	1.00 - 9.30		
BG coastal Black Sea waters (4)	0.60 - 0.85	0.018 - 0.026	0.40 - 0.87	0.61 - 0.82	
BG coastal Black Sea waters (6)		0.84 - 0.97	1.70	3.8 - 5.9	
TR coastal Black Sea waters (total metals) (11)	7.75	1.68	8.08	8. 33	5.82
W Black Sea (dissolved metals) (12)	1.78	0.016	0.037	0.94	
NW Black Sea (dissolved metals) (13)	1.19 – 218.11	0.15–1.59		0.23 – 11.15	

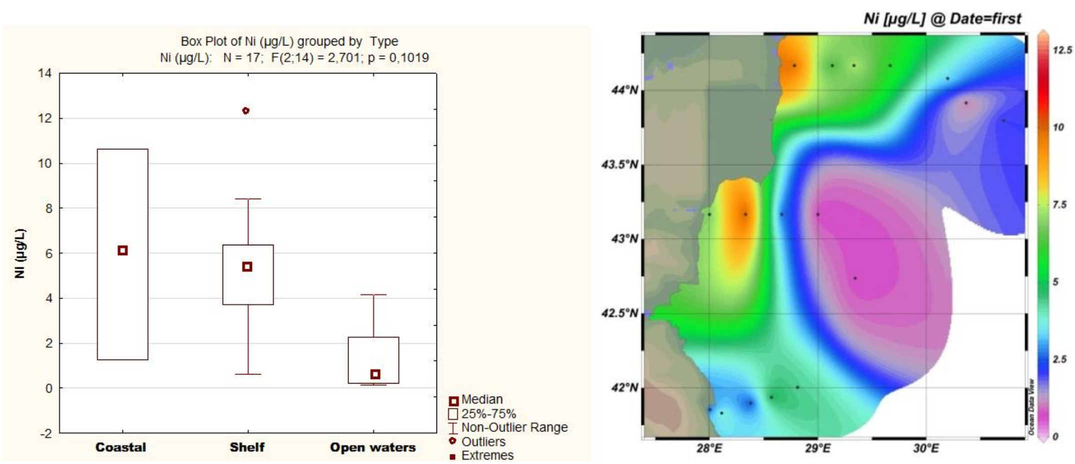
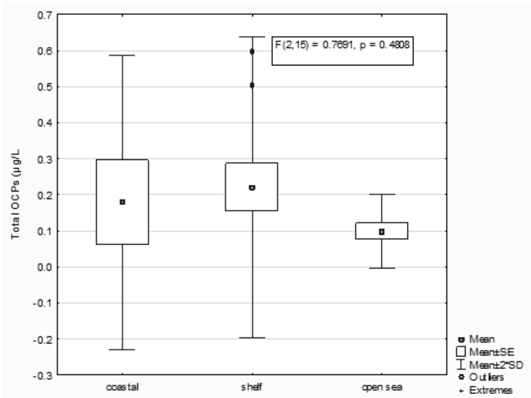


Fig. 2. Distribution of nickel (µg/L) in coastal, shelf and open sea waters from the Romanian, Bulgarian and Turkish area, July 2013

Concentrations of **organochlorine pesticides (OCP) -** nine individual compounds (HCB, lindane, heptachlor, aldrin, dieldrin, endrin, p,p'DDE, p,p'DDD and p,p'DDT) **and polychlorinated biphenyls (PCB)** - seven individual compounds (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180) in water were higher or comparable with those reported in the Black Sea region in previous researches (2, 6, 13). The BS waters were dominated by the presence of lindane and cyclodiene, which often exceeded the threshold values set out by Directive 2013/39/EU. Except PCB 52, the values measured for other PCBs compounds were low or under detection limit.

There is an obvious difference between open sea area and waters closer to shore where the anthropic influence is stronger (Fig. 3).



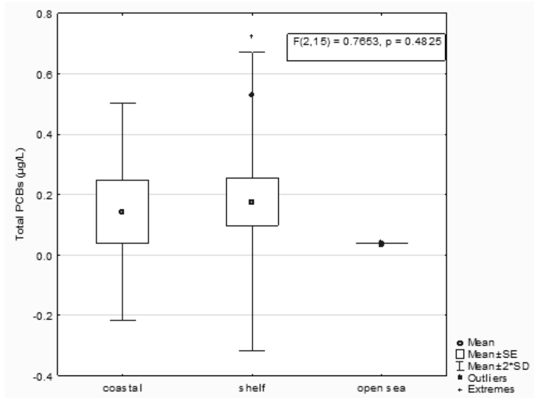


Fig. 3. Box plots of ∑OCPs (µg/L) and ∑PCBs (µg/L) in coastal, shelf and open sea waters from the Romanian, Bulgarian and Turkish area, July 2013

The concentrations of **total petroleum hydrocarbons (TPH)** in seawater ranged between 82.5 and 221.6 (µg/l) with an average of 147.4 (µg/l), with 83% samples with low TPH values <200 µg/l. (Fig. 4). The distribution of concentrations in coastal, shelf and open waters did not point out statistically significant differences between the means. The average total TPH concentration (µg/l) calculated as 147.4 ± 40.5 is comparable with the mean value of 103 ± 64.0 reported for the Black Sea waters in 1992 - 2006 (14).

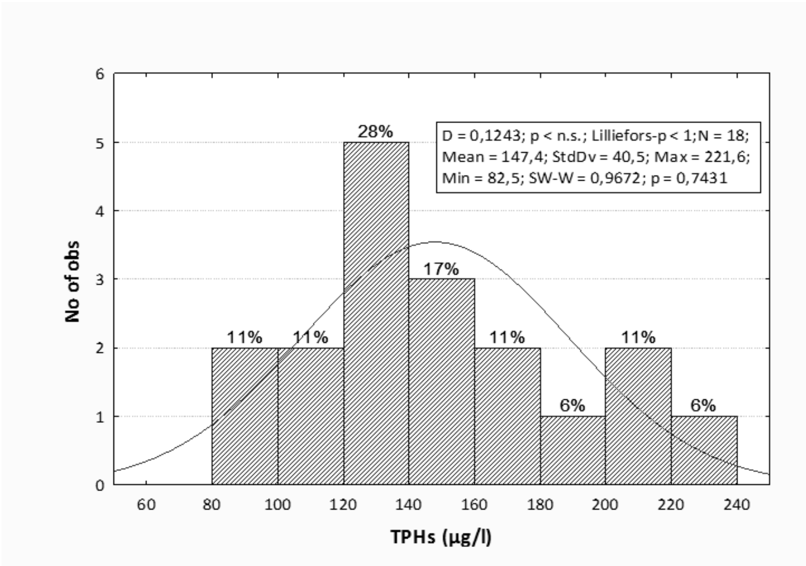


Fig. 4. Histogram of TPHs (µg/l) in waters from the Western Black Sea, including the Romanian, Bulgarian and Turkish transect, July 2013

The **total polycyclic aromatic hydrocarbons - Σ_{16}PAH** (µg/l) content in water samples ranged from 0.339 to 2.107, with a mean of 0.690 ± 0.400. Of the total PAHs, the petroleum (2-3 rings) PAHs contributed to about 75%, while pyrolytic (4-6 aromatic rings) PAHs accounted for 25%. Naphthalene and phenanthrene were found as the most dominant compounds, with average distribution of 34% and 18 % of the total PAHs in the Western Black Sea waters. The statistical analysis of data shows significant differences ($p < 0.05$) between the mean value of the total Σ_{16}PAH (µg/l) in coastal waters (1.290 ± 0.707) and shelf (0.586 ± 0.138), and open sea (0.520 ± 0.146) waters (Fig. 5). Highest abundance of total PAHs compound in coastal waters were dominated by 2-3 rings PAHs, characteristic for discharges, oil and oil product spill (Fig. 6). In comparison to assessment criteria, values exceeding the maximum allowable concentration set by Directive 39/2013/EU were determined for benzo[k]fluoranthene, benzo[a]pyrene) and anthracene.

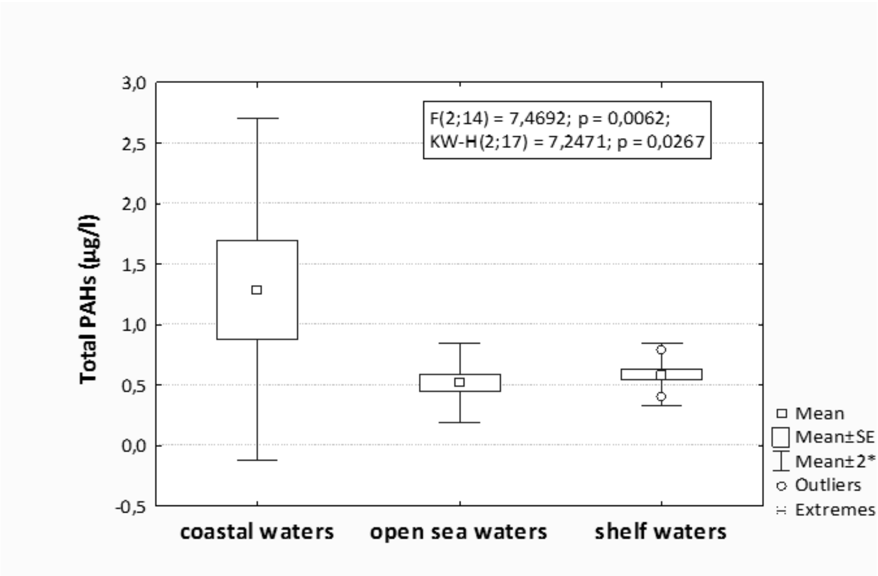
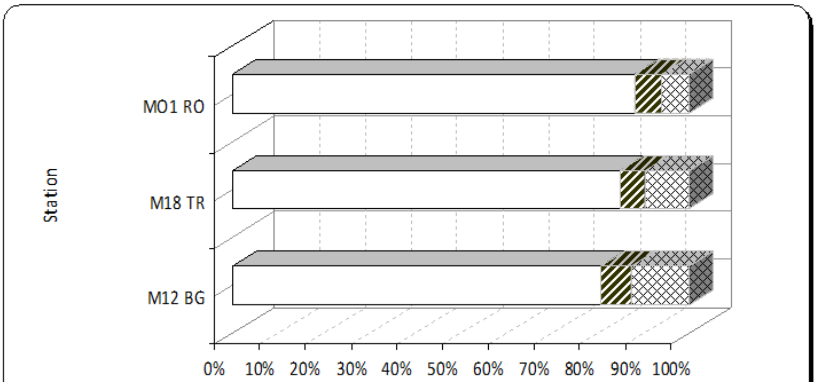


Fig. 5. Distribution of the polycyclic aromatic hydrocarbons - Σ_{16}PAH (µg/l) in seawater from the Western Black Sea, July 2013



	M12 BG	M18 TR	M01 RO
PAH(5-6 rings)	0,117	0,082	0,127
PAH(4 -rings)	0,060	0,047	0,123
PAH(2-3 rings)	0,737	0,722	1,858

Fig. 6. Distribution of PAHs in coastal waters from the Western Black Sea, according to the number of aromatic rings

Sediments

Following detailed **grain size analyses**, the cumulated percentages of sandy, silty and clayey fractions were used to sedimentologically classify the sediments according to Sheppard (Table 4).

Table 4. Sediment composition in terms of sand-silt-clay and Sheppard's classification

Sample	Grain size composition			Shepard class
	Sand %	Silt%	Clay %	
M 01	7.40	71.94	20.66	Clayey silt
M 02	0.47	78.68	20.85	Silt
M 03	10.09	65.94	23.97	Clayey silt
M 04	7.48	69.69	22.84	Clayey silt
M 05	0.82	65.19	33.99	Clayey silt
M 09	0.00	76.65	23.35	Silt
M 11	4.91	74.92	20.17	Clayey silt
M 12	16.10	70.12	13.78	Sandy silt
M 15	10.29	65.98	23.73	Clayey silt
M 16	6.96	72.77	20.27	Clayey silt
M 17	3.19	79.17	17.64	Silt
M 18	73.94	20.94	5.12	Silty sand

With the exception of the coarser sediments from stations M12 and M18, all the rest were characterized by the dominance of the fine fraction (from fine silt to fine clay), usually representing ≈60% from the sediment composition, with a maximum of 85% in station M05.

The dominance of the fine clayey-siltic sediments, confirmed by the median diameter values, varying between 6.45 φ and 7.45 φ, indicates as the main sedimentary process the deposition of suspensions. For the sediments with higher sand percentages (stations M12 and M18), the higher values of the median diameter (5.44 φ and 2.95 φ) indicate a more energetic environment.

The **chemical characterization** of the sediments shows a rather high compositional variability (Table 5).

Table 5. Main statistical parameters of the distribution of the inorganic chemical components of sediment in MISIS stations

Component	C_{mediu}	C_{median}	s	K	Sk	C_{Min}	C_{Max}	C_v, %	n
$CaCO_3$, %	26.56	17.79	17.145	-1.218	0.887	11.22	53.60	64.55	13
TOC, %	1.55	1.56	0.766	-0.375	-0.058	0.11	2.78	49.54	13
Fe_2O_3, %	4.49	5.09	1.477	-1.423	-0.606	2.27	6.23	32.90	13
TiO_2, %	0.35	0.31	0.276	-1.215	0.163	0.03	0.84	78.21	13

Mn, µg/g	745.7	642.8	306.53	0.534	1.007	349	1425	41.11	13
Rb, µg/g	93.5	101	36.14	-1.369	-0.400	31	141	38.64	13
Zr, µg/g	162.6	148	55.19	7.083	2.482	121	327	33.93	13
Ba, µg/g	398.4	398	92.78	0.147	0.396	250	589	23.29	13
Sr, µg/g	514.1	349	296.17	-1.303	0.646	215	1028	57.61	13
Ni, µg/g	39.36	41.63	14.63	-1.277	-0.328	15.7	57.8	37.17	13
Co, µg/g	8.94	8.58	2.608	-0.817	-0.183	4.371	12.82	29.16	13
Cr, µg/g	63.6	66.3	18.57	-1.634	-0.087	38	88	29.19	13
V, µg/g	46.0	39	25.49	-0.139	0.520	5	91	55.38	13
Cu, µg/g	30.99	28.15	13.259	-1.396	0.214	13.76	50.31	42.78	13
Pb, µg/g	26.32	23.57	10.538	-0.052	0.425	9.21	45.18	40.04	13
Zn, µg/g	55.69	57.03	19.99	-1.313	-0.009	26.1	85.6	35.89	13
Cd, µg/g	0.236	0.247	0.0950	-0.452	-0.374	0.057	0.386	40.29	13

- C - concentration; - s - standard deviation; - K - kurtosis;
- Sk - skewness; C_v - coefficient of variation

As expected, higher coefficients of variation (>50%) characterized the biogenic components (calcium carbonate, TOC, strontium), highly redox sensitive elements (V – C_v=55% and Mn – C_v=41%) as well as some technophyllic metals (Cu, Pb, Cd – coefficients of variation around 40%).

The parameters K (Kurtosis) and Sk (Skewness) define the aspect of the frequency distribution curve of the component concentration, with K defining the peakedness and Sk the symmetry of the curve. For a normal (gaussian) distribution the curve is mesokurtic (K=0) and symmetric (Sk=0). It is interesting that the distribution of all the technophyllic metals may be accepted as normal, which might be an indication of little to no metal pollution.

Investigated components of terrigenous origin are introduced into the Black Sea mainly through the North-Western Rivers, in both dissolved and particulate forms, with the Danube being the main contributor. Diffuse discharge and atmospheric input play probably a significant part in determining the sediment total concentrations for some heavy metals (Cd, Pb, Ni).

Interesting are the statistically positive correlations of TOC with many terrigenous components (Ba, Rb, Zn, Ni, Mn, Pb, Cu, Cd) (Fig.7), despite the biogenic marine origin of the organic matter.These strong associations (Ba, Ni, Pb, Cu, Cd) are probably explained by a combination of factors - biogenic inputs of metals, the organic matter being a good concentrator, the dependence of TOC concentration of the fine fraction of sediment, the main source of terrigenous components and, possibly, the dependence of manganese nodules formation on a highly reducing environment in the sediment below the uppermost layer.

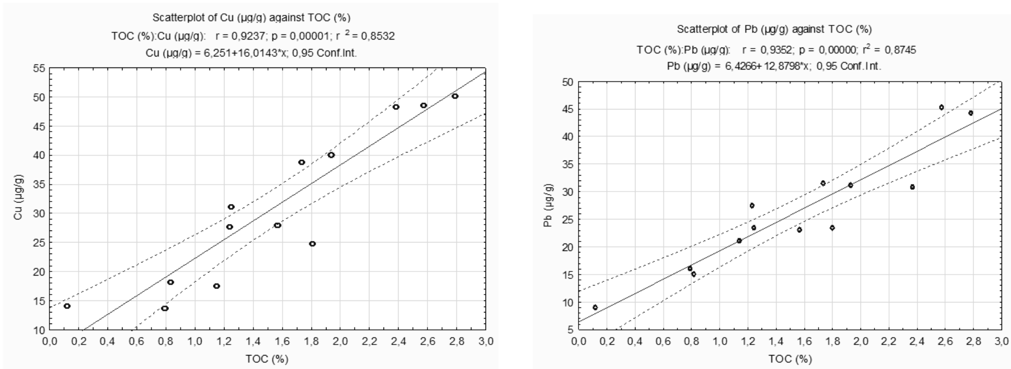


Fig. 7. Correlation of TOC (%) against Cu and Pb content (µg/g) in sediments from the MISIS cruise

A comparison with available environmental quality standards and sediment quality guidelines (Table 6) showed that the concentrations of most metals were below the established limits. Frequent exceeding of the limits were identified for Ni and Cu, but a further analysis using Rb as a normalizing element demonstrated that this is mostly the result of a higher natural background. The excessive enrichments of Ni and Cu in station M05 were demonstrated as being the result of metal concentration in shallow water manganese nodules.

Based on these result it may be affirmed that metal contamination of sediments does not represent a problem for the investigated area. However, again due to the limited number of samples, this affirmation is rather uncertain and needs further confirmation.

Table 6. National quality criteria for metals in sediments, actual metal concentrations and other quality guidelines (µg/g)

Metal	**Ord. 161/2006**	**Actual range**	**Actual mean**	**ERL[1]**	**PEL[1]**	**Upper Crust[2]**
Cadmium	0,8	0.06 - 0.39	0.24	1.2	4.21	0.1
Chromium	100	38 - 88	63.6	81	160	69
Copper	40	13.8 - 50.3	31.0	34	108	39
Lead	85	9.2 - 45.2	26.3	46.7	112	17
Zinc	150	26.1 - 85.6	55.7	150	271	67
Nickel	35	15.7 - 57.8	39.4	20.9	42.8	55

ERL - effects range low; PEL - probable effects level
[1] - (15); [2] - (16)

Organochlorine pesticides (OCP) and polychlorinated biphenyls (PCB) concentrations determined in sediment samples are presented in Table 7 and 8, where ∑OCPs (µg/kg dry weight) is the concentration of the nine individual compounds (HCB, lindane, heptachlor, aldrin, dieldrin, endrin, p,p'DDE, p,p'DDD and p,p'DDT) and ∑PCBs (µg/kg dry weight) is the concentration of the seven individual compounds (PCB 28, PCB 52, PCB 101, PCB 118, PCB 153, PCB 138, PCB 180).

Except for some extreme values obtained in the case of PCBs, the other chlorinated contaminants were comparable with previous data obtained in the Black Sea region (14, 18). The results were compared to Environmental Assessment Criteria (EACs) proposed by OSPAR as a means for assessing the significance of concentrations of hazardous substances in the marine environment and if EACs were not available with Effects Range Low (ERLs) developed by the United States Environmental Protection Agency for assessing the ecological significance of sediment concentrations (17). P, p' DDE and lindane exceeded the ERLs value in 3 samples. The concentrations of HCB and dieldrin were below the ERLs values in all samples. Except PCB 153 and PCB 180, the others PCBs exceeded EACs values in some samples. (Table 7; Table 8).

Table 7. Concentrations of individual and total OCPs (∑OCPs) (µg/kg dry weight) in sediment samples from the Romanian, Bulgarian and Turkish area, July 2013

Stations	HCB	Lindane	Heptachlor	Aldrin	Dieldrin	Endrin	p,p' DDE	p,p' DDD	p,p' DDT	∑ OCPs
MO1(RO32m)	<0.300	<0.300	<0.200	<0.200	<0.200	<0.300	0.711	<0.200	<0.200	2.611
MO2(RO47m)	<0.300	<0.300	<0.200	<0.200	<0.200	<0.300	1.727	<0.200	<0.200	3.627
MO3(RO52m)	<0.300	<0.300	<0.200	<0.200	<0.200	<0.300	0.509	<0.200	<0.200	2.409
MO4(RO65m)	<0.300	<0.300	<0.200	<0.200	<0.200	<0.300	2.214	<0.200	<0.200	4.114
MO5(RO100m)	2.504	4.868	1.421	<0.200	0.494	<0.300	11.438	0.985	0.583	22.793
MO9(BG92m)	<0.300	<0.300	0.200	<0.200	0.200	<0.300	1.786	<0.200	<0.200	3.686
MO10(BG77m)	4.349	4.661	2.577	0.287	2.401	0.397	7.401	2.533	15.679	40.285
MO11(BG40m)	<0.300	<0.300	<0.200	2.854	<0.200	<0.300	0.984	<0.200	<0.200	5.539
MO12(BG23m)	3.056	<0.300	<0.200	<0.200	<0.200	<0.300	2.678	<0.200	<0.200	7.334
MO15(TR101m)	<0.300	<0.300	<0.200	<0.200	<0.200	<0.300	0.641	<0.200	<0.200	2.541
MO16(TR75.6m)	<0.300	<0.300	<0.200	<0.200	<0.200	<0.300	1.961	<0.200	<0.200	3.861
MO17(TR54m)	<0.300	<0.300	<0.200	<0.200	<0.200	<0.300	0.738	<0.200	<0.200	2.638
MO18(TR27m)	<0.300	<0.300	0.506	0.526	0.903	1.544	0.788	3.170	1.854	9.890
ERL*(µg/kg)	20.00	3.000	-	-	2.00	-	2.20	-	-	-

* ***ERL*** *- Effects Range Low were developed by the United States Environmental Protection Agency for assessing the ecological significance of sediment concentrations. Concentrations below the ERL rarely cause adverse effects in marine organisms (17)*

Table 8. Concentrations of individual and total PCBs (∑PCBs) (µg/kg dry weight) in sediment samples from the Romanian, Bulgarian and Turkish area, July 2013

Stations	PCB 28	PCB 52	PCB 101	PCB 118	PCB 153	PCB 138	PCB 180	∑ PCBs
MO1(RO32m)	2.74	0.63	7.06	0.56	0.61	<0.70	1.92	14.23
MO2(RO47m)	1.42	28.16	10.63	11.46	5.08	14.06	3.47	74.29
MO3(RO52m)	24.80	59.03	24.43	1.07	0.68	14.86	6.07	130.95
MO4(RO65m)	1.28	7.55	1.52	0.09	<0.60	<0.70	<0.30	12.03
MO5(RO100m)	<0.40	139.87	<0.60	<0.40	<0.60	<0.70	<0.30	142.87
MO9(BG92m)	13.58	30.40	3.66	<0.40	<0.60	<0.70	0.94	50.28
M10(BG77m)	<0.40	1.62	1.09	0.60	0.80	4.79	2.49	11.79
M11(BG40m)	<0.40	5.08	1.21	<0.40	<0.60	<0.70	1.65	10.05
M12(BG23m)	<0.40	82.98	1.48	1.05	<0.60	5.49	1.01	93.02
M15(TR101m)	<0.40	<0.30	2.56	7.26	3.00	<0.70	<0.30	14.52
M16(TR75.6m)	<0.40	<0.30	0.71	<0.40	<0.60	<0.70	<0.30	3.41
M17(TR54m)	<0.40	12.79	1.98	<0.40	<0.60	<0.70	0.49	17.35
M18(TR27m)	<0.40	1.77	<0.60	<0.40	<0.60	<0.70	0.45	4.92
EAC*(µg/kg)	1.7000	2.7000	3.0000	0.6000	40.0000	7.9000	12.0000	-

*** **EAC** - Environmental Assessment Criteria represent the contaminant concentration in the environment below which it can be assumed that no chronic effects will occur in marine species, including the most sensitive species (17)*

The data on **total petroleum hydrocarbons (TPHs)** indicate that 69 % of samples fall in the range of 100 - 200 (µg/g dw). The Western Black Sea area is only moderately contaminated by petroleum hydrocarbons, oil inputs are shown to be low and comparable to relatively uncontaminated areas on a worldwide basis (Table 9). A major contribution to the region could be associated with inputs through the River Danube.

Table 9. Worldwide concentrations of total hydrocarbons in sediments (µg/g dry weight)

Area	TPHs (µg/g d.w.)	References
Antarctica (pristine)	< 0.5	19
Rhone River, France, Mediterranean Sea	25–170	20
Oman Gulf	6–22	21
Saudi Arabia, Gulf	19–671	21
Victoria Harbour, Hong Kong	60–646	22
Kuwait, Gulf	40–240	23
Saudi Arabia, Gulf	11–6900	23
Black Sea	7–153	24
New York Bight, USA	35–2900	25
Bosphorus, Black Sea, Turkey	12–76	23
Sochi, Black Sea, Russia	7.6–170	23
Odessa, Black Sea, Ukraine	110–310	23
Coastline, Black Sea, Ukraine	2.1–6.6	23
Danube Coastline, Black Sea, Ukraine	49–220	23
Southern Black Sea Shelf, Turkey	0.3–363	26
Western Black Sea	**74.5- 328**	**In this study (2013)**

Results of total of **polycyclic aromatic hydrocarbon (PAHs)** analyses were expressed as **$\sum_{16}$PAHs** (µg/kg dry weight) - is the sum of the sixteen determined PAHs, **LMW/HMW** - the ratio of low molecular weight PAHs (2-3 rings) to high-molecular weight PAHs (4-6 rings), **CPAHs%** - the carcinogenic PAHs percentage to the total PAHs and **B(a)Peqv** - the total equivalent of toxicity by benzo(a) pyrene (µg/kg dw).

Marine bottom sediments can be classified into three categories (27), depending on the total content of PAHs: slightly polluted (ΣPAHs<250 µg/kg dw), polluted (ΣPAHs from 250 to 500 µg/kg dw), highly polluted (ΣPAHs >500 µg/kg dw). Our results allow the classification of sediments as slightly polluted (54%) and highly polluted (46%) and comparable to different coastal areas of the Black Sea (Table 10).

Table 10. Comparison of PAH concentrations in sediments (μg/kg dry weight) from different coastal areas of Black Sea

Area Survey	Total PAHs	References
Abyssal, Black Sea	200–1200 (Σ28 PAHs)	24
Danube River mouth, Black Sea	2400 (Σ28 PAHs)	24
Danube River	10–3700 (Σ4 PAHs)	28
Bosphorus, Black Sea, Turkey	13.8–531 (Σ17 PAHs)	23
Sochi, Black Sea, Russia	61.2–368 (Σ17 PAHs)	23
Odessa, Black Sea, Ukraine	66.9–635 (Σ17 PAHs)	23
Coastline, Black Sea, Ukraine	7.2–126 (Σ17 PAHs)	23
Danube Coastline, Black Sea, Ukraine	30.5–608 (Σ17 PAHs)	23
Istanbul Strait, Turkey	2.1-3152 (Σ16 PAHs)	29
Marmara Sea	144 (Σ16 PAHs)	29
Istanbul Strait, Turkey	0.4–1703 (Σ8PAHs)	30
Southern Black Sea Shelf, Turkey	13–2342 (Σ15 PAHs)	31
The estuarine coast of Danube, Ukraine	329-1093 (Σ16 PAHs)	32
Western Black Sea	**26 -1841 (Σ16 PAHs)**	**In this study (2014)**

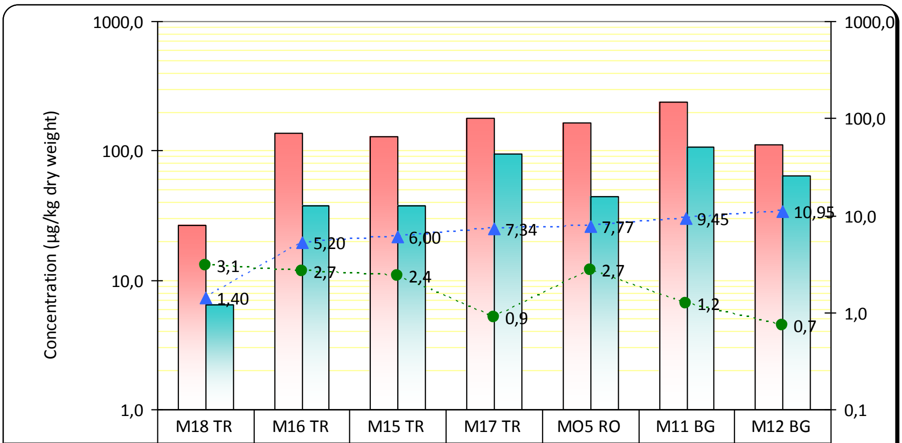
The abundance ratio of two- and three ring hydrocarbons (LMW) to four- to six-ring hydrocarbon (HMW) PAHs is commonly used ratio to help in distinguishing the petroleum and pyrolytic sources (33, 34). The data indicate that petroleum origin PAHs pollution was observed at stations on the Romanian transect, whereas pyrolitic origin PAHs pollution was dominant at stations on the Bulgarian transect, and a mixture of pyrolytic and petrogenic PAHs in the sediments on the Turkish transect, Igneada, with a slightly petroleum predominance was noticed (Fig. 8).

PAH results of the sediment analyses were compared to the ERL - Effects Range Low values for assessing the ecological significance of sediment concentrations. Effects Range (ER) values were established by the US National Oceanic and Atmospheric Administration (NOAA) as sediment quality guidelines. Most of the individual PAH concentrations did not exceed the ERL values, except naphthalene and phenanthrene concentrations in some stations.

According to the total content of PAHs, the total equivalent of toxicity by benzo(a) pyrene- B(a) Peqv and ERL values, the sediments from the Western Black Sea can be classified as:

-slightly polluted (54%) with ΣPAHs < 250 μg/kg dw and low level of toxicity - the total B(a) Peqv (μg/kg dw) < 10; individual PAH concentrations do not exceed the ERL value;

-highly polluted (46%) with ΣPAHs > 500 μg/kg dw, with naphthalene and phenanthrene concentrations that exceed the ERL values at some stations, indicating a petroleum pollution; high level of toxicity the total B(a) Peqv (μg/kg dw) > 10, but do not exceed ERL values for individual carcinogenic PAHs.



	M18 TR	M16 TR	M15 TR	M17 TR	MO5 RO	M11 BG	M12 BG
∑16PAHs	26,4	138,3	128,1	177,8	165,4	237,6	112,7
CPAH	6,5	37,8	37,8	94,3	44,5	106,7	64,8
B(a)Peqv	1,40	5,20	6,00	7,34	7,77	9,45	10,95
LMW/HMW	3,1	2,7	2,4	0,9	2,7	1,2	0,7

Fig. 8. Examples of slightly polluted sediments at stations on the Romanian, Bulgarian and Turkish transect, the sum of 16 PAHs, by 7 carcinogenic PAHs, B(a)Peqv (µg/kg dw) and LMW/HMW

CONCLUSIONS

New data on a wide range of contaminants (HM, TPH, PAH, OCP, PCB) in seawater and sediments from the Western Black Sea were obtained following MISIS Joint Cruise, July 2013, thus contributing to further integrated assessments of the Black Sea state of environment.

With respect to Directive 2008/56/EC Marine Strategy Framework Directive (MSFD)/ Descriptor 8, results from the MISIS Joint Cruise will promote further work toward common understanding of good environmental status and will contribute to the development of Black Sea environmental targets in a harmonised approach.

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