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Ecological study of gas fields in the northern Adriatic

9. Heavy metals and macroconstituents in sea water

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In March 1986 the content of heavy metals and macroconstituents in sea water was analyzed in the IVANA field, as well as the content of heavy metals in fish and shellfish stretching from the IVANA field to cove Štinjan near Pula. The content of heavy metals in sea water is slightly increased whereas the concentration of heavy metals in organisms is within the limits of an unpolluted area. The analysis of macroconstituents showed that the sea water can be characterized as clean sea.

9.1. INTRODUCTION

Due to favorable physical and chemical properties, heavy metals are widely used in modern technology, which is the reason why they are more and more present at unwanted locations.

This mainly applies to human environment, where due to uncontrolled inflow of untreated waste, in time it accumulates in dangerous quantities, thus becoming a constant and direct threat to living organisms of a certain area.

Because of bioaccumulation, which understands multiplication of harmful effects through the food chain, very quickly they reach human beings. This is one of the basic reasons why concentration research is necessary in all parts of the ecosystem, so that the human environment may remain healthy and useful for future generations as well.

Although detailed insight into the biogeochemical cycle of each metal is needed for complete knowledge of the conditions in a certain area, our research is limited to sea water and certain organisms, that indicate whether the studied waters are truly endangered, or man himself as the consumer of such organisms.

The process of defining the actual content of microelements in sea water (which includes also heavy metals) is neither unique nor easy, since their concentrations are very low, which means that very sensitive analytical methods should be applied.

On the other hand, the sampling process, storing of samples and their pretreatment until analysis is the source of unwanted contamination that can bring about completely incorrect results. The significance of such a fact is visible when comparing the 1975 results with those of recent years, showing that the concentrations of certain metals differed for several orders of magnitude (UNEP/FAO/IAEA.-1986).

Obviously the reason for such differences is not the lower content of metals in sea water, but better developed sampling techniques, that is, elimination of contamination of samples before and during analysis, as well as more sophisticated analytical procedures.

9.2. MATERIALS AND METHODS

Sea water samples, both for analysis of trace elements and macroconstituents, were taken from the research ship "BIOS" with the centrifugal pump (EINHELL Typ GP 45 - made of plastic) , with which sea water from the desired depth (0.5 m under the surface and 2 m above the bottom) was taken through a polythene tube.

Water samples for the analysis of macroconstituent concentrations were stored in plastic vessels of 25 dm^3, that were previously washed in 1:1 HNO_3, and then rinsed with sea water samples.

Water samples for total mercury concentration analysis were put in the 1000 ml glass (Pyrex) bottles, previously cleaned in a streaming apparatus for cleaning glassware in nitric acid vapor (reflux), and then rinsed with double-distilled water and stored until sampling in polythene bags. Before pouring the samples into bottles, 20 cm^3 HNO_3 (65% supra-pur) was added into each bottle, and the samples were stored at the temperature of +4°C until analysis.

Samples for determining lead, cadmium, zinc and copper concentrations were stored in one liter polythene bottles, that were also carefully cleaned in the laboratory (soaked for several days in 1:1 HNO_3, washed in redistilled water, and stored in sealed PTF bags until sampling). Each sample was acidified with 0.5 cm^3 65% supra-pur HNO_3, stopped up with paraffin wax, sealed in a PTF bag and stored at +4°C temperature until analysis.

The metal concentrations (lead, cadmium, copper, zinc and iron) in marine organisms were determined after dry digestion at 450°C temperature, by the flame atomic absorption spectrometry (PRICE, 1972.).

Mercury concentrations in fish and shellfish tissue were determined following wet decomposition in a HNO_3-H_2SO_4 mixture, using the cold-vapor atomic absorption spectrophtometry (CVAAS) (GORSUCH, 1970).

Analysis of Na, K, Ca, Mg, Sr and Fe concentrations in sea water samples was performed using the method of flame atomic absorption spectrometry (by VARIAN Type AA5).

The total zinc, cadmium, copper and lead concentrations in sea water were determined electrochemically (anodic stripping voltammetry) by the standard addition method with the polarographic analyzer PAR M 374/M 303.

Mercury concentrations were determined using the CV AAS method (Cold-Vapor Atomic Absorption Spectrophotometry), with a double amalgamation on a gold absorber using as detector a laboratory Data Control (LDC), MERCURY MONITOR - model 1255 (FREIMANN et al. 1982).

Results of hydrogencarbonate contents were obtained by volumetric determination (titration with HCl), and the total CO_2 by gravimetric method (adsorption on natron lime).

Sulfate concentrations were also determined by gravimetric method (as $BaSO_4$).

Fluorides were determined with ionselective electrode (ORION M9609/M701) by means of the standard addition method (SD ± 0,02 mg kg^{-1}).

Table 9.3.1. Concentration of heavy metals in sea water samples in March 1986

Station	Hg	Cd	Pb	Cu	Zn	Fe
	(ng/kg)				(µg/kg)	
1 surface	0.14	30	60	70	1.06	190
bottom	0.30	40	70	80	1.61	190
2 surface	1.60	<10	120	50	0.54	190
bottom	4.00	10	30	160	0.65	190
3 surface	0.48	15	30	370	1.81	170
bottom	1.60	<10	290	310	0.84	200
4 surface	<0.05	20	60	50	0.72	170
bottom	0.22	20	100	60	0.83	170

9.3. RESULTS AND DISCUSSION

9.3.1. Heavy metals

Content of heavy metals in sea water samples from the studied area (gas field IVANA) are shown in Table 9.3.1.

The analysis of the vertical distribution of heavy metals in the water column reveals that most heavy metal concentrations in samples from the bottom is greater than that of the surface samples (exceptions are Cu and Zn at station 3, and Pb at station 2).

Their horizontal distribution reveals increased mercury concentrations at station 2, and lead, copper, zinc and iron concentrations at station 3. However, the distribution of cadmium differs, higher values were recorded at stations 1 and 4.

Since until now there have been no reliable data on the natural concentrations of a certain metal in the studied area, the increased concentrations of each metal, that is the level of possible pollution, may be determined only by comparing data of other authors. Therefore, the mean values of Cd, Pb, Cu and Zn are presented, based on the calculations of repeated measurements at 40 stations in the Adriatic Sea in 1980 (BRANICA et al. 1985), in the northern Adriatic in 1984 (BRANICA et al. 1986), and ranges of those metals measured in the Mediterranean (UNEP/FAO/IAEA 1983, 1986) (Table 9.3.2)

Table 9.3.2. Mean values of concentrations of certain heavy metals in surface sea water samples

Area	Cd	Pb	Cu	Zn
		(ng/dm³)		
Adriatic sea 1980. (BRANICA et al. 1986)	7	71	240	3700
Nord Adriatic 1984 (BRANICA et al. 1985)	<4	24	90	520
Mediterranean R 1979-84	5-90	18-950	30-3000	100-86000
$\bar{X}$±SD (UNEP/FAO/IAEA)	17 ± 7		210 ± 70	400 ± 160

Table 9.3.3. Heavy metal concentrations in fish (Mullus barbatus) *and musssels* (Mytilus galloprovincialis) *in the studied area Platform Panon*

Organisme /date	Sampling place	Concetration (mg/kg)					
		Pb	Cd	Cu	Zn	Fe	Hg
Fish/ 06.12.1985.	IVANA field (on the profile to cove Štinjan) near Pula	0.04	<0.01	0.37	6.48	11.2	0.104
14.03.1986.	IVANA field	0.11	<0.01	-	-	-	0.076
Mussels/ 06.12.1985.	Cove Štinjan near Pula	0.81	0.107	0.39	19.9	21.3	0.082
07.12.1985.	IVANA field Platform Panon	0.53	0.117	1.03	9.3	23.7	0.133
14.03.1986	Cove Štinjan near Pula	1.00	0.054	-	-	-	0.176
14.03.1986	IVANA field Platform Panon	0.30	0.033	-	-	-	0.103

By comparing our values (Table 9.3.1.) with the concentration values from Table 9.3.2, the following may be concluded:
-Cadmium concentrations at all the IVANA field stations are from 2 to 10 times greater than the concentrations reported for the northern Adriatic, although they are in agreement with the ranges reported for the Mediterranean.
- Lead concentrations (with the exception of the surface value at station 2 and bottom value at station 3) are in agreement with the results for surface samples in the Adriatic.
-Copper and zinc concentrations (with the exception of station 3) vary within the range for the northern Adriatic and the Adriatic Sea.
- The measured mercury concentrations, although there are no comparable data for this area, range within the limits of the natural concentration of this metal in sea water.
-Therefore, in spite of the small number of analyzed samples, it may be concluded that heavy metal content in sea water samples in the studied area is slightly greater compared to other parts of the Adriatic.

This may be due to the fact that this part of the Adriatic receives greater quantities of these metals from the industrially developed Italian north.

Since there are no greater departures of our results from the stated values, it may be concluded that for now, the sea water in the studied area is not polluted with such heavy metals. Heavy metal concentrations (lead, cadmium, copper, zinc and iron) were determined in some marine organisms as well. These were samples of fish *(Mullus barbatus)* and mussel *(Mytilus galloprovincialis)*.

The obtained results are presented in Table 9.3.3., and show that the concentrations of analyzed heavy metals are also within the limits of an unpolluted area.

9.3.2. Content of macroconstituents in sea water

Within the framework of research of chemical characteristics of sea water in the IVANA field, contents of principal sea water components or the so-called macroconstituents were analyzed. According to the definition by Cuklin (RILEY and SKIRROW, 1975) these are cations and anions that considerably affect sea water salinity, that is the concentrations of >1 mg kg^{-1} -in the sea. Results of these analyses are given in Table 9.3.4.

In all samples HCO_3 ranged from 0.162-0.165 g kg^{-1}, whereas Br ranged from 0.069 - 0.075 g kg^{-1}.

Since the mentioned macroconstituents in sea water are always present in specific permanent ratios to salinity (conservative constituents), the comparison of measured concentrations with the values from Table 9.3.5. reveals the possible departures from the usual chemical content of sea water.

No concentration anomalies were recorded in our case, which is another proof that, according to chemical parameters, the sea water in the studied area may still be characterized as unpolluted.

Table 9.3.4. Concentration of macroconstituents in sea water samples - IVANA field (March 1986)

Station	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	SO_4^{2-}	F^-	CO_3
	g kg^{-1}						mg kg^{-1}	total
1 surface	12.50	0.427	1.315	0.420	0.009	2.931	1.30	0.120
bottom	12.42	0.430	1.315	0.420	0.008	2.929	1.31	0.121
2 surface	12.42	0.425	1.318	0.415	0.008	2.931	1.30	0.156
bottom	12.50	0.425	1.321	0.415	0.009	2.928	1.28	0.154
3 surface	12.58	0.420	1.321	0.415	0.009	2.916	1.26	0.153
bottom	12.83	0.425	1.321	0.415	0.008	2.904	1.25	0.139
4 surface	12.59	0.430	1.351	0.420	0.008	2.924	1.29	0.140
bottom	12.58	0.420	1.321	0.420	0.008	2.916	1.29	0.153

Table 9.3.5. Concentration of macroconstituents in sea water of different salinity (RILEY and SKIRROW, 1975)

Salinity ‰	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	SO_4^{2-}	F^-
			g kg^{-1}			mg kg^{-1}	
36	11.08	0.410	1.331	0.424	0.008	2.789	1.30
37	11.39	0.422	1.368	0.435	0.008	2.867	1.30
38	11.70	0.433	1.405	0.447	0.009	2.944	1.40
39	12.00	0.445	1.442	0.459	0.009	3.022	1.40

9.4. CONCLUSION

The content of heavy metals and macroconstituents in sea water was determined for the IVANA field, and heavy metal concentrations in fish and shellfish from samples collected on the profile: cove Štinjan (Pula) - IVANA field.

The concentrations of most metals are higher in bottom samples than in surface samples. In spite of the small number of analyzed samples, it may be concluded that in comparison with other locations in the Adriatic, the heavy metal concentrations (cadmium, lead, copper, zinc) in the IVANA field are slightly increased, probably due to the highly industrialized northern part of Italy. Heavy metal concentrations in organisms are within the limits of an unpolluted area.

The analysis of macroconstituents showed no concentration anomalies which is another proof that, according to chemical parameters, the sea water in the studied area may be characterized as clean sea.

9.5. REFERENCES

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Ekološka studija plinskih polja u sjevernom Jadranu

Sadržaj teških metala i makrokonstituenata u morskoj vodi

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KRATKI SADRŽAJ

U ožujku 1986. g. određen je za polje Ivana sadržaj teških metala i makrokonstituenata u morskoj vodi, a na potezu od polja Ivana - uvala Štinjan kod Pule, maseni udio teških metala u ribama i školjkama. Sadržaj teških metala u morskoj vodi je nešto povećan, a u organizmima je u granicama za nezagađena područja. Analiza makrokonstituenata je pokazala da morska voda posjeduje karakteristike čistog mora.