

HYDROCARBONS IN SEA WATER AND COASTAL SEDIMENTS OF THE SLOVENIAN PART OF THE GULF OF TRIESTE

Oliver BAJT

National Institute of Biology, Marine Biological Station, SI-6330 Piran, Fornače 41

ABSTRACT

In spite of the expected pollution of the marine environment of the Gulf of Trieste with hydrocarbons (heavy sea traffic, Ports of Koper, Trieste and Monfalcone), only a few data are available on the content of these compounds in sea water and sediment. This is the reason why the results regarding the content of hydrocarbons in sea water samples and surficial sediment from the southeastern part of the Gulf of Trieste are presented in this work. Aliphatic and polyaromatic hydrocarbons were determined with the method of gas chromatography after the extraction from sediment. In the samples of sea water, the hydrocarbons were determined spectrofluorometrically. In view of the semblance and concentration of certain hydrocarbons, the most probable sources of pollution in this part of the Gulf of Trieste with hydrocarbons were stipulated. The results indicate, on average, a significant pollution of the sea and surficial sediment with hydrocarbons. These are to a high extent of petrogenic and pyrogenic origin. A terrestrial input of natural hydrocarbons is also evident, which is in view of the fact that we are dealing with coastal water not unexpected at all.

Key words: hydrocarbons, Gulf of Trieste, pollution, marine sediments

IDROCARBURI IN ACQUA DI MARE E SEDIMENTI COSTIERI DELLA PARTE SLOVENA DEL GOLFO DI TRIESTE

SINTESI

Nonostante gli idrocarburi rappresentino un carico non indifferente per l'ambiente marino del Golfo di Trieste (visto l'intenso traffico marino, i porti di Capodistria, Trieste e Monfalcone ed il turismo nautico), scarseggiano i dati riguardanti il contenuto di queste sostanze nell'acqua di mare e nei sedimenti. Nell'articolo vengono presentati i risultati della ricerca effettuata sul contenuto di idrocarburi in campioni di acqua di mare e di sedimenti superficiali della parte sud-orientale del Golfo di Trieste. Gli idrocarburi alifatici e poliaromatici sono stati determinati con il metodo della cromatografia a gas, in seguito all'estrazione di questi dal sedimento. Nei campioni di acqua di mare gli idrocarburi sono stati determinati con la spettrofluorimetria. In base ai dati su presenza e concentrazione di determinati idrocarburi, sono state evidenziate le più probabili fonti di inquinamento da idrocarburi in questa parte del Golfo di Trieste. Sia per l'acqua di mare che per i sedimenti superficiali, i risultati in media indicano un rilevante inquinamento da idrocarburi. La gran parte di questi è di origine petrogenica e pirogenica. È stata inoltre registrata la presenza di idrocarburi naturali provenienti da terra ferma, dato prevedibile per le acque costiere.

Parole chiave: idrocarburi, Golfo di Trieste, inquinamento, sedimenti marini

INTRODUCTION

Hydrocarbons of natural and anthropogenic origin are widely distributed in the natural environment throughout the world. Different sources of introduction of these compounds into the natural environment can be stated. The most important among them are oil seepage, oil spillage, traffic, urban runoff, waste waters and sewage effluents, as well as atmospheric deposition (GESAMP, 1993). Knowledge of the various sources of the introduction of such compounds into the marine environment as well as the concentrations of these compounds in sea water, sediment and marine organisms is of crucial importance to adequately assess the state of the environment. This is especially important where extensive industrial activity or traffic might be expected.

Because of their hydrophobic nature and, as a consequence, of low solubility in water, hydrocarbons tend to adsorb on organic or inorganic particles in water column. The enriched suspended matter is settled down to the sediment surface. In the sediment phase, hydrocarbons are less subjected to physico-chemical or biological processes and may accumulate to higher levels. In this way the marine sediments often contain hydrocarbons of higher concentrations than those in the overlaying water (Landrum & Robbins, 1990).

Hydrocarbons, especially polyaromatic hydrocarbons (PAH), have been recognized as hazardous envi-

ronmental chemicals (GESAMP, 1993). They may act as narcotics to marine organisms, many of them are also carcinogenic and mutagenic (Donkin *et al.*, 1991; Simpson *et al.*, 1996) due to their metabolic transformation products. Many of marine organisms living in contaminated areas accumulate hydrocarbons (Baumard *et al.*, 1998). As a consequence, the elevated concentrations of these compounds in sea food could be harmful also for human health. These are important reasons for special attention devoted to this class of organic compounds.

The aim of the present work was to determine the content of hydrocarbons in surficial sediments and sea water in the southeastern (Slovenian) part of the Gulf of Trieste and to try to identify the origin of these compounds in this region. Despite several potential sources of pollution with hydrocarbons in this area only data for other parts of the Adriatic Sea are available (Dujmov & Sučević, 1989; Guzzella & de Paolis, 1994).

MATERIAL AND METHODS

Study area

The investigated area in the southeast of the Gulf of Trieste is part of the Northern Adriatic (Fig. 1). The marine environment along the coast is affected by pollution from different sources since this area is one of the most urbanized in the Northern Adriatic.

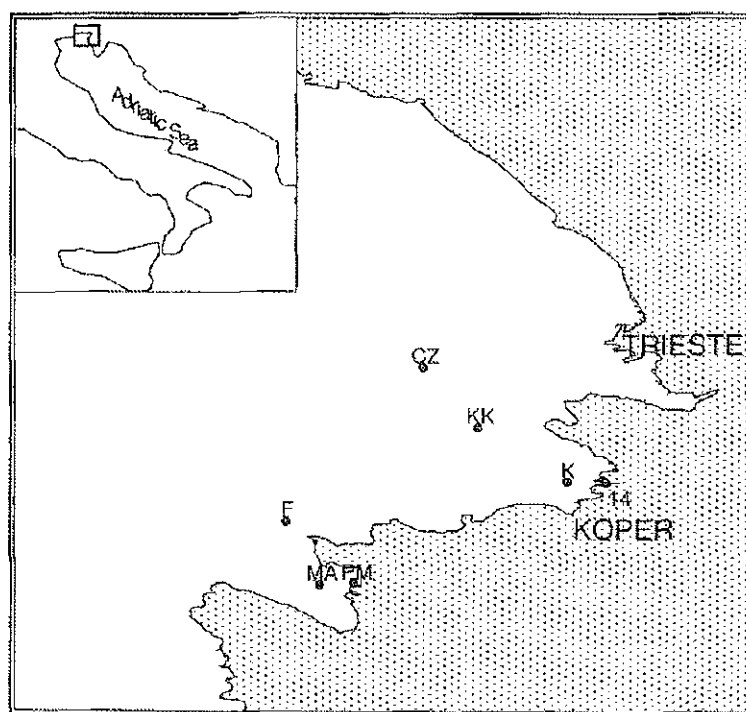


Fig. 1: Sampling sites within the investigated area.
Sl. 1: Vzorčevalna mesta na preiskovanem območju.

The estimated quantity of petroleum carried by ships to the three ports (Koper, Trieste, Monfalcone) in the Gulf of Trieste is about 30 millions tons per year. Beside the intensive maritime traffic, the nautical tourism is also well developed (3 marinas). Moreover, the marine environment within the studied area receives waste waters from several sewage treatment plants and fresh water from rivers, carrying also waste waters of the local industry, as well as waters draining rather large agricultural areas. Coastal waters in this part of the Gulf of Trieste are used for some other economically important activities, like tourism, fisheries and mariculture. According to the above mentioned facts, the knowledge about the state of marine environment in this part of the Adriatic Sea is thus very important.

Material and methods

"Distilled in glass" quality hexane, methanol and methylene chloride (Fluka) were used for extraction of hydrocarbons. All other chemicals used throughout this work were of analytical grade and purchased from Merck (Germany). Na₂SO₄, Silica, Alumina and extraction thimbles were precleaned by Soxhlet extraction with methanol and hexane (8 hours). Hg was rinsed several times with hexane.

Samples of water were collected in 3 l precleaned (methanol, hexane) bottles at 1 m depth. Hydrocarbons were extracted with 100 ml of hexane and, additionally, twice with 50 ml of hexane. The hexane phase was dried with Na₂SO₄ and concentrated on rotary evaporator at ambient temperature to about 5 ml. Concentration of hydrocarbons was determined spectrofluorometrically using a Turner 430 spectrofluorometer. The excitation and emission wavelengths were 310 and 360 nm, respectively. Calculations were made on chrysene standard basis.

Sediment samples were collected using a gravity core sampler (Meischner & Rumohr, 1974) at seven sites along the Slovenian part of the Gulf of Trieste (Fig. 1). The upper 1cm layer of each sediment sample was taken for analysis. After freeze drying, the samples were extracted in Soxhlet apparatus with hexane and methylene chloride (50:50) for 8 hours. The solution was concentrated on rotary evaporator and additionally under nitrogen stream. After sulfur removal with mercury and additional concentration, partition of hydrocarbons was performed with column chromatography (Silica, Alumina). Concentrated extracts were analyzed using a HP 5890 gas chromatograph equipped with FI detector and HP 3396 integrator. The HP Ultra 2 column (25 m x 0.32 mm, 0.17 µm film thickness) was used for analysis. C-32, n-octadecene and 9,10-dihydroanthracene were used as internal standards. Quantification was performed with external standards.

RESULTS AND DISCUSSION

Concentrations of hydrocarbon in sea water are presented in table 1. These results show somewhat higher concentrations of hydrocarbons only at sites 14 (Port of Koper) and PM (Portorož Marina), most probably due to the pollution from ships and boats.

Tab. 1: Content of total hydrocarbons in sea water (in chrysene equivalents).

Tab. 1: Vsebnost celotnih ogljikovodikov v morski vodi (v ekvivalentih krizena).

Sampl. site/ date	K (µg/l)	KK (µg/l)	14 (µg/l)	PM (µg/l)	MA (µg/l)
June	0.03	0.02	0.24	0.20	0.07
September	0.04	0.20	0.28	0.38	0.17
November	0.06	0.15	0.23	0.20	0.10
December	0.15	0.14	0.26	0.36	0.20

The amount of hydrocarbons in sea water at other sampling sites, compared with the results from the middle and southern Adriatic sea (Dujmov & Sučević, 1989), could be considered as relatively low.

Concentrations of aliphatic hydrocarbons in sediment samples are presented in table 2. The highest concentrations were obtained at stations 14 inside the Port of Koper, PM at the entrance of Portorož Marina, K in the middle of the Bay of Koper and CZ in the center of the Gulf of Trieste. Pollution from boats and ships appears as most probable the source of hydrocarbons at these locations. Moreover, site 14 is located in the estuary of the Rižana river and as such influenced by fresh water inputs, bringing also waste waters from the sewage treatment plant of the city of Koper. Different sources of the elevated concentrations of hydrocarbons in the Bay of Koper could be presumed. Among them, the influence of the port of Koper, the direct influence of the runoff from the coastal road between Koper and Izola (Faganeli *et al.*, 1997) and atmospheric inputs (city of Koper) (Faganeli *et al.*, 1997) could be important sources of pollution in this bay. The content of hydrocarbons in surficial sediments in the center of the Gulf of Trieste (site CZ) seems to be dependent on the transport processes of particles on which hydrocarbons are associated, sedimentation and sorptive preservation on mineral surfaces in mostly pelitic sediments (Hedges & Keil, 1995). On the other hand, the lowest amount of hydrocarbons at the site F is most probably related to the lower degree of adsorption, since the sediment is mostly composed of silty sand (Ogorelec *et al.*, 1991).

Tab. 2: Aliphatic hydrocarbons in sediment samples (ng/g dry weight).

Tab. 2: Alifatski ogljikovodiki v vzorcih sedimenta (ng/g suhe teže).

	CZ	14	PM	K	KK	MA	F
n-heptadecane	21	17	18	7	5	8	5
Pristane	12	10	3	5	<1	<1	<1
n-octadecane	25	22	20	26	7	18	9
Phytane	17	15	10	17	<1	10	<1
n-C14 to n-C34	193	182	216	117	71	78	49
Resolved aliphatics	268	246	267	197	83	114	63
UCM* (µg/g)	1.73	2.45	1.97	2.85	1.42	0.57	0.93
Total aliphatic (µg/g)	2.00	2.70	2.24	3.05	1.50	0.68	0.99

*UCM unresolved complex mixture

Concentrations of PAH, presented in table 3, followed a similar pattern of distribution to aliphatic hydrocarbons. Only concentrations at site PM were exceptionally high, with significant diversity of detected PAH.

Tab. 3: Polyaromatic hydrocarbons in sediment samples (ng/g dry weight).

Tab. 3: Poliaromatski ogljikovodiki v vzorcih sedimenta (ng/g suhe teže).

	CZ	14	PM	K	KK	MA	F
Naphthalene	9	4	5	3	<1	6	<1
1-methylnaphthalene	<1	<1	<1	<1	<1	<1	<1
1-ethylnaphthalene	<1	<1	<1	<1	<1	<1	<1
Acenaphthene	<1	3	6	<1	<1	<1	<1
Acenaphthylene	<1	3	<1	<1	<1	<1	<1
2,3,6-trimethylnaphthalene	<1	<1	<1	<1	<1	<1	<1
Phenanthrene	8	<1	45	17	10	6	<1
Anthracene	5	<1	14	14	7	3	<1
Fluorene	6	72	10	6	6	<1	3
2-methylphenanthrene	18	11	15	19	13	8	<1
1-methylphenanthrene	23	4	<2	21	6	<2	4
Fluoranthene	8	7	87	24	14	4	6
Pyrene	5	3	75	39	22	10	<1
3,6-dimethylphenanthrene	<2	3	<2	<2	<2	<2	<2
Perylene	<1	12	3	<1	<1	<1	<1
1-methylpyrene	<1	<1	8	6	<1	<1	<1
Chrysene	<1	<1	64	13	4	<1	<1
Benzo[a]pyrene	<1	<1	46	<1	<1	<1	<1
Benzo[e]pyrene	13	<1	53	<1	<1	<1	<1
Benzo[a]anthracene	<1	<1	44	<1	<1	<1	<1
Resolved aromatic	86	113	484	162	82	31	13

Hydrocarbons may originate from different sources: biogenic, petrogenic and pyrogenic (La Flamme & Hites, 1978; Lipiatou & Saliot, 1991). A particular area may be affected from different sources of pollution and in such cases it is difficult to adequately distinguish between natural and mixed anthropogenic inputs. Different diagnostic criteria, such as unresolved/resolved hydrocarbons ratio, carbon preference index and PAH distribution pattern are used to determine the source of pollution (Bouloubassi & Saliot, 1993). Applying these criteria, some conclusions may be assumed about the investigated area. UCM was the major component of the aliphatic hydrocarbon fraction, higher than 80% (Tab. 2) at all sampling sites. It consists of branched and cyclic hydrocarbons (Gough & Rowland, 1990) and is usually related to degraded petroleum residues (Farrington & Tripp, 1977).

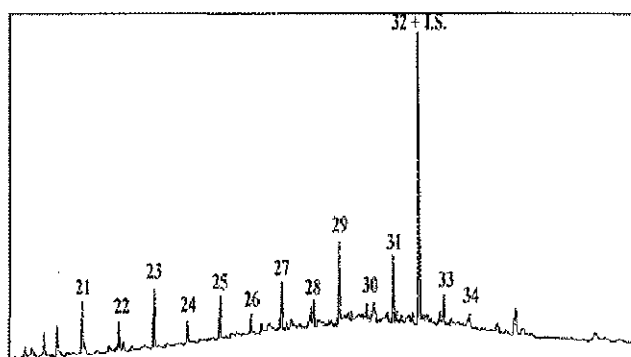


Fig. 2: Chromatogram of long-chain aliphatic hydrocarbon fraction (C₂₁-C₃₄) at site 14.

Sl. 2: Kromatogram višjemolekularne frakcije alifatskih ogljikovodikov (C₂₁-C₃₄) na mestu 14.

The compositional profile of n-alkanes showed a predominance of long-chain homologues (C₂₁ - C₃₄). An elevated odd to even carbon number preference was detected especially at stations K and 14 (Fig. 2). Such distribution pattern of n-alkanes reveals the importance of terrestrial inputs in the study area (Saliot, 1981). The predominance of n-heptadecane, the hydrocarbon associated with phytoplankton (Saliot, 1981), was not observed. This reflects most probably the labile character of short-chain n-alkanes and a moderate productivity in the study area (Fonda Umani *et al.*, 1990). The presence of isoprenoid hydrocarbons pristane and phytane (Tab. 2) confirms the algal (Boehm, 1980) and anthropogenic (Anderlini *et al.*, 1981) origin, respectively.

Distribution of PAHs in surficial sediments within the study area revealed similar origin of hydrocarbons. The ratio of alkylated PAH homologues to parent compounds (especially for phenanthrene) was higher than 1 at all stations (except the station PM). This is an indication of fresh petroleum pollution (Blumer & Youngblood,

1975). The lower ratio alkylated/parent PAHs was calculated only for sediments in Portorož Marina (PM), indicating the predominance of combustion derived PAHs (Blumer & Youngblood, 1975). The appearance of pyrene, fluoranthene, benzo[a]pyrene and benzo[e]pyrene at higher concentrations at sampling site PM confirms the prevalent pyrogenic origin of hydrocarbons (Sporstol *et al.*, 1983). Fluoranthene and pyrene were detected in higher amounts in comparison to other sampling sites also at stations K and KK. This is an indication of pyrogenic pollution, originating probably from the Port and City of Koper (atmospheric deposition). The situation in the Port of Koper, regarding the appearance of PAHs, is somewhat surprising. The rather low concentrations of PAHs are most probably due to maintenance dredging and higher microbial degradation, due to elevated number of bacteria from sewage treatment plant, especially in the summer period (Faganeli *et al.*, 1988). Perylene, a biogenic aromatic

hydrocarbon (Saliot, 1981), was detected at lower concentration in the Port of Koper. This could be a confirmation for terrestrial input, presumed already from the aliphatic hydrocarbon distribution.

In conclusion, the southeastern part of the Gulf of Trieste is, regarding pollution with hydrocarbons, a considerably polluted area. Hydrocarbons in surficial sediments in the investigated area are mostly of petrogenic and pyrogenic origin. Some terrestrial influence is also evident in the Port of Koper and in the middle of the Bay of Koper.

ACKNOWLEDGEMENTS

The present investigation was part of the national monitoring program "The quality of sea water and control of pollution in Slovenia", sponsored by Ministry of Environment and Civil Engineering of Slovenia and UNEP MEDPOL program.

OGLJIKOVODIKI V MORSKI VODI IN SEDIMENTU OBALNEGA MORJA SLOVENSKEGA DELA TRŽAŠKEGA ZALIVA

Oliver BAJT

Nacionalni inštitut za biologijo, Morska biološka postaja, SI-6330 Piran, Fornače 41

POVZETEK

Ogljikovodiki, alifatski in PAH-i, so bili določeni v površinskem sedimentu slovenskega dela Tržaškega zaliva. Analize so bile opravljene s plinsko kromatografijo. Vzorci morske vode z istega področja so bili analizirani spektrofotometrično.

Koncentracije raztopljenih/suspendiranih ogljikovodikov v morski vodi so razmeroma nizke. Le v Luki Koper in Marini Portorož so bile koncentracije nekoliko povišane, najverjetneje zaradi direktnega onesnaževanja z ladjami in čolnovi. Najvišje koncentracije alifatskih ogljikovodikov v površinskem sedimentu so bile izmerjene v Luki Koper, Marini Portorož ter sredi Tržaškega in Koprškega zaliva. Na razporeditev ogljikovodikov vplivajo, poleg direktnega onesnaževanja z ladjami in čolnovi, tudi transportni procesi in procesi sedimentacije. Ti procesi so še posebno pomembni v obeh omenjenih zalivih. Razporeditev PAH-ov je bila podobna kot v primeru alifatskih ogljikovodikov. Koncentracije v Marini Portorož so bile izrazito višje, visoka pa je bila tudi raznolikost določenih PAH-ov. Povišana vsebnost PAH-ov je bila določena tudi v Luki Koper in sredi Koprškega zaliva. Izvor ogljikovodikov je bil določen po različnih kriterijih, v literaturi opisanih v te namene. V Marini Portorož prevladujejo ogljikovodiki pirogenega izvora, na drugih vzorčnih mestih pa lahko sklepamo na mešani petrogeni in pirogeni izvor ogljikovodikov. V koprškem pristanišču in sredi Koprškega zaliva je opazen tudi kopenski vnos obravnavanih snovi, najverjetneje z vodami reke Rižane.

Ključne besede: ogljikovodiki, Tržaški zaliv, onesnaževanje, morski sediment

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