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THE CONTAMINATION OF DATESHELL *(LITHOPHAGA LITHOPHAGA)* FROM THE EASTERN COAST OF THE ADRIATIC SEA BY POLYCYCLIC AROMATIC HYDROCARBONS

ONEČIŠĆENOST ŠKOLJKE PRSTAC *(LITHOPHAGA LITHOPHAGA)* SA ISTOČNE OBALE JADRANA POLICIKLIČKIM AROMATSKIM UGLJIKOVODICIMA

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Polycyclic aromatic hydrocarbons (PAH) in the dateshell *(Lithophaga lithophaga)* from a wide variety of different polluted and unpolluted habitats of the eastern coast of the Adriatic Sea have been detected. UV-fluorescence spectroscopy was used for the analysis. Emission spectra were scanned at the wavelengths from 350—510 nm and the results were expressed in chrysene and Kuwait oil equivalents.

The lower value determined in the investigated area was 0.41 μg/g dry weight in the Dugi otok island and the maximum was 20.41 μg/g dry weight determined in a locality near the port of Šibenik. The levels of PAH in shellfish *Lithophaga lithophaga* are closely related to land-based sources contamination of the Adriatic Sea. The background levels in the dateshell are about 1.0 μg/g.

INTRODUCTION

It is evident that in recent years the number of organic compounds entering the marine environment has increased. Most of them are present as a hydrocarbon mixture, which contains complex homologous and isomeric series of alkanes, olefins and aromatics. Among these the aromatic hydrocarbons, particularly the polycyclic ones (PAH), have drawn special attention because of their toxicity to marine organisms (Anderson et al., 1974; Moore and Dwyer, 1974) and to man through food web or environmental exposure.

This inputs of PAH, besides industrial wastewaters, could be also from shipping traffic, incidents, shipping losses, deposition from the atmosphere, from street run-off etc (Pavoni et al., 1987; Wakeham et al., 1970; McVeety, 1987).

Shellfish filter large amounts of sea water. At the same time they accumulate and concentrate water soluble fractions, oil in water dispersions and oil compounds which are adsorbed onto suspended matter.

The experiments made with exposed marine organisms to oil polluted sea water have proved that they accumulate in their tissues aromatic hydrocarbons and they remain for a long time, so they act as bioaccumulators. However, when the organisms are transported from polluted to unpolluted sites, the accumulated hydrocarbons are released rather quickly (2—60 days), depending on the type of organisms. The crab and fish eliminate PAH quicklier than shellfish, which means that shellfish have probably a lower detoxification system (Neff et al., 1976; Stegeman and Teal, 1973; Fossato, 1975).

It is well known that some PAH components are higly genotoxic so that there is a major concern for their occurrence in the marine environment (NRC, 1985).

The contents of PAH in bivalves from several coastal areas are well documented (Albaiges *et al.*, 1982; Ehrhardt, 1972; Fazio, 1971; Cahnmann and Kuratsune, 1957; Farrington *et al.*, 1983; Tavers *et al.*, 1988) while for the Adriatic Sea the information is very limited (Fossato and Siviero, 1974; Dujmov and Sučević, 1986 and 1989).

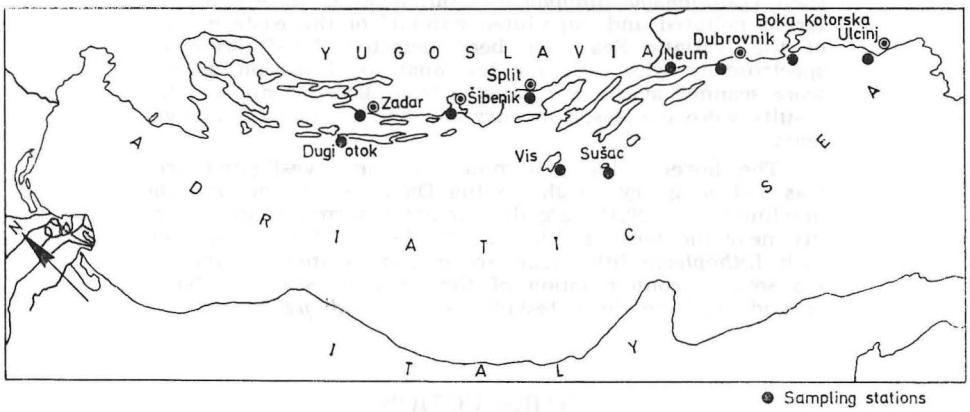

Fig. 1. Sampling locations

We report in this paper the contents of PAH in a shellfish dateshell *(Lithophaga lithophaga)* collected from ten localities on the eastern coast of the Adriatic Sea: Dugi otok (Sakarun), Zadar (Borik and Punta Mika), Šibenik (Solaris and Zlarin), Split (Kašjuni), Neum (Klek and Duboka), Dubrovnik (Gruž), Herceg Novi (Trašće), Ulcinj (Valdanos), Vis (Rukavac) and Sušac (Gradiška) (Fig. 1).

MATERIALS AND METHODS

The bivalves (cca 5 cm lenght) were collected from 1 m depth by diver with aqualung. The fleshy part was separated and homogenized in a blender type »Waring« before freeze drying. The analitical procedure consisted in saponification of the sample with 6N NaOH aq. solution during 18 hours at 30°C. The mixture was extracted five times with ethyl ether, the combined extracts dissolved in hexane and put on top of a column, filled with alumina (top) and silica (bottom). The aluminium oxide 90 active, acidic, was prepared by heating at 350°C for 12 hours and partly deactivated adding 5 pet cent distilled water by weight. The silica gel 60 (0.063—0.200 mm) was heating at 120°C for 8 hours and partly deactivated with 2 per cent water by weight. Three portions were eluted: I with 20 ml of hexane, II with 20 ml of hexane--methylene chloride (9:1), III with 40 ml hexane-methylene chloride (8:2). After concentration and dilution the sample was analysed by UV-flourencence (I O C / U N E P / C S I C, 1984).

The emission spectra of fractions II and III were scanned from 330 to 530 nm with an excitation wavelength of 310 nm. The contents of PAH were calculated from the fluorencence intensity measured at 360 nm and were expressed as chrysene and Kuwait oil equivalents.

The relation between wet weight and dry weight was also determined. For this purpose a few grams of wet sample was dried at 105°C till constant weight.

RESULTS AND DISCUSSION

The PAH contents in dateshell are presented in Table 1. The most polluted shellfish was from the locality of Šibenik (Solaris) where the contents of PAH were 20.41 μg/g chrysene equivalents and 239.46 μg/g Kuwait oil eguivalents. The next one is the Split area with PAH contents of 6.57 μg/g chrysene equivalents and 77.32 μg/g Kuwait oil equivalents and then Boka Kotorska Bay with 5.63 μg/g chrysene equivalents or 66.26 μg/g Kuwait oil equivalents basis. The minimum PAH value was observed in the offshore island Dugi otok (0.41 μg/g dry weight chrysene equivalents and 5.46 Kuwait oil equivalents).

This spatial distribution of PAH contents in organisms from the eastern coast of the Adriatic Sea is in connection with the known origin of pollution on the investigated industrial zones such as Zadar with about 120.000 inhabitants, Šibenik with 80.000, Split about 250.000 and the touristic place Dubrovnik with about 67.000 inhabitants, a number which in summer time grows up significantly.

In Fig. 2 are shown the typical emission spectra for dateshell living in the area situated out of direct influence of industrial and urban waste waters, whereas in Fig. 3 are presented the spectra of the samples collected near Split, which is the largest town in the coastal area, the more industrialized and consequently with higher traffic activity.

From the profile of the emission spectra it is also possible to identify the sources of aromatic compounds, because the compounds which are of petroleum have their maximum emission at wavelenghts from 340 do 400 nm,

Table 1. The PAH contents in shellfish *Lithophaga lithophaga* sampled in June 1987 on the eastern coast of the Adriatic Sea (μg of chrysene and Kuwait oil equivalent/g dry tissue)

Localities	Fraction II		Fraction III		Total		Wet weight
	Chrysene	Kuwait oil	Chrysene	Kuwait oil	Chrysene	Kuwait oil	Dry weight
Dugi otok							
Sakarun	0.06	1.03	0.35	4.43	0.41	5.46	—
Zadar							
Borik	0.39	4.72	2.50	29.40	2.89	34.15	5.9
Punta Mika	2.01	24.28	0.99	12.32	2.01	36.60	3.9
Šibenik							
Solaris	4.14	48.69	16.27	48.69	20.41	239.46	2.3
Zlarin	4.21	49.49	1.12	13.37	5.33	62.86	4.5
Split							
Kašjuni	0.24	2.95	6.33	74.37	6.57	77.32	3.7
Vis							
Rukavac	0.65	7.89	0.88	10.46	1.53	18.35	6.0
Neum Klek							
Klek	0.07	0.96	0.99	11.74	1.06	12.70	4.4
Duboka	0.46	5.58	0.80	9.62	1.26	15.20	5.0
Sušac							
Rt Gradiška	0.16	2.29	0.84	10.30	1.00	12.59	4.1
Dubrovnik							
Gruž	0.87	10.42	0.84	10.06	1.71	20.48	6.0
Boka Kotorska							
Trašće	0.26	3.27	5.36	62.99	5.63	66.26	—
Ulcinj							
Valdanos	0.30	3.76	2.33	27.49	2.63	31.25	4.0

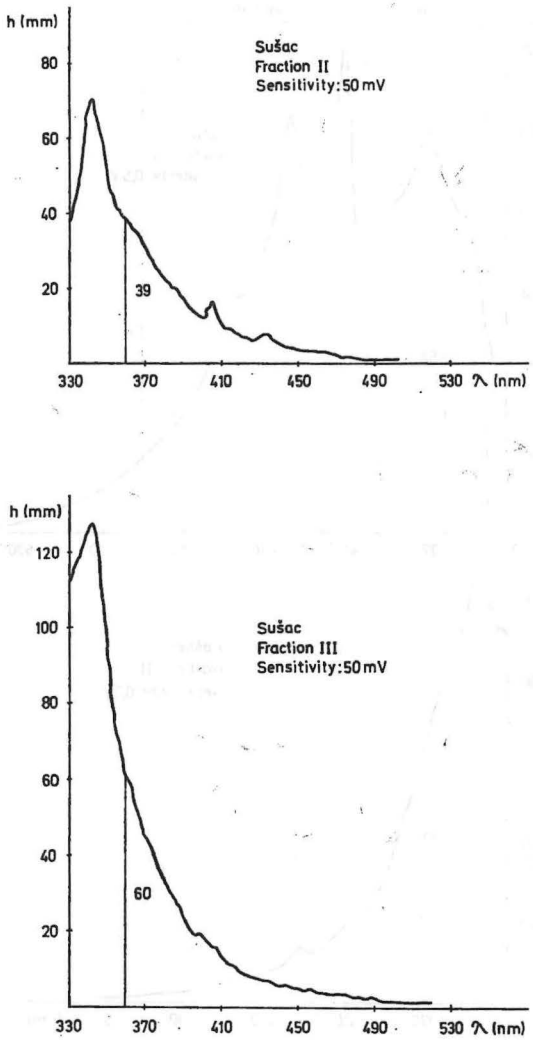

Fig. 2. Emissions spectra of fractions II and III of shellfish *Lithophaga lithophaga* from Sušac locality

and the more condensed which usually are of pyrolitic origin have maximum emission at 400—480 nm. The spectra obtained in our investigation reflect that marine organisms accumulate most aromatics with 2 to 4 rings (petroleum origin) although in the urban and industrial areas a pyrolitic component can also be recognized.

There is a little number of published data about the levels of PAH in shellfish from the eastern coast of the Adriatic Sea. P i c e r (1987) cited

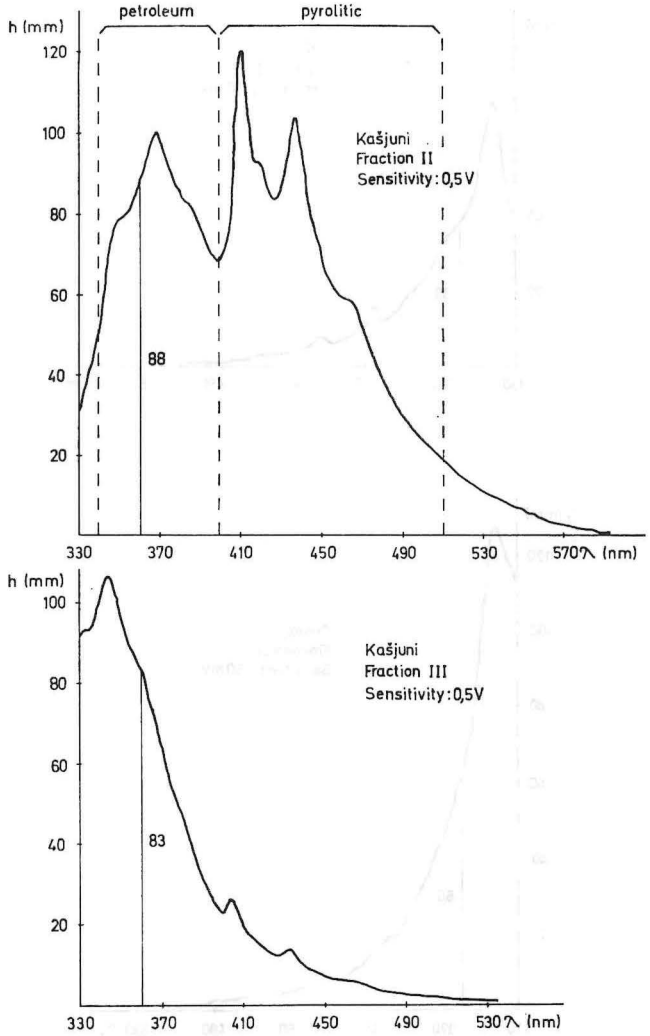

Fig. 3. Emission spectra of fractions II and III of shellfish *Litpophaga lithophaga* from Split erea (Kašjuni)

that the values of content PAH in the mussels from the locality of Šibenik lie in the limit from 1.9 to 19.5 μg/g wet weight Kuwait oil equivalents or 9.21 to 1.69 μg/g chrysene equivalents, while Dujmov and Sučević (1986) in the same shellfish (mussels) collected from a pillar of the drilling platform in the northern part of the Adriatic Sea found that contents of PAH were 4.36 μg/g dry weight crysene equivalents. Fossato *et al.* (1979) determined two representative aromatic compounds in mussels from the La-

goon of Venice (north-west Adriatic), benzo(a)pyrene and perylene. Lee *et al.* (1972) found that the mussel *Mytilus edulis* has the ability to benzo(a)pyrene from the sea water even when this is a very trace components The natural background levels of PAH in mussels are still largely unknown. According to Risebrough *et al.* (1983) levels of total hydrocarbons (aliphatics and aromatics) less than 10 μg/g (dry weight) are representative for relatively unpolluted areas.

However, Mackie *et al.* (1980) indicated the total PAH concentration in mussels varies 50 to 140 μg/g wet weight as unpolluted and these 1930 to 2850 μg/g wet weight as heavily polluted.

The PAH concentrations determined on the stations from the open sea represent background levels for this sort of shellfish in the Adriatic.

CONCLUSIONS

The PAH contents in shellfish *Lithophaga lithophaga* from the eastern Adriatic coast range from 1 to 20 μg/g dry weight chrysene equivalents. The higher values are found in the nearshore localities which are under direct influence of the land-based sources of pollutants.

The background contents of PAH for the open Adriatic Sea are about 1 μg/g dry weight. This bivalve can be used as a sentinel organism in monitoring studies.

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REFERENCES

Albaigés, J., A. Gallifa, J. Grimalt and M. Soler. 1982. Hydrocarbons in biota samples from the Western Mediterranean. VIes Journées Étud. Pollutions CIESM, 215—218.

Anderson, J. W., J. M. Neff, B. A. Cox, H. E. Tatem and G. M. Hightower. 1974. Caracteristics of dispersions and water-soluble extracts of crude and refined oils and their toxicity to estuarine crustaceans and fish. Mar. Biol., 27: 75—88.

Cahmann, H. J. and M. Kuratsune. 1957. Determination of polycycic aromatic hydrocarbons in oysters collected in polluted water. Analyt. Chem., 29: 1312—1317.

Dujmov, J. and P. Sučević. 1986. Report on the environmental studies — Gas field Ivana (Northern Adriatic). Institute of Oceanography and Fisheries, Split. Studies and Reviews, 78.

Dujmov, J. and P. Sučević. 1989. Contents of polycyclic aromatic hydrocarbons in the Adriatic Sea determined by UV-fluorescence spectroscopy. Mar. Pollut. Bull., 20: 405—409.

Ehrhardt, M. 1972. Petroleum hydrocarbons in oysters from Galveston Bay. Envir. Pollut., 3: 257—271.

Farrington, J. W., E. D. Goldberg, R. W. Risebrough, J. H. Martin and V. T. Bowen. 1983. US Mussel Watch 1976—1978: An overview of the trace metal, DDE, PCB, hydrocarbon and artificial radionucleide data. Environ. Sci. Technol., 17: 490—496.

Fazio, T. 1971. Analysis of oyster samples for polycyclic hydrocarbons. In: Proceedings of the 7th National shellfish sanitation workshop. Food and drug administration, Division of shellfish sanitation, Washington, pp. 238—243.

Fossato, U. V. 1975. Elimination of hydrocarbons by mussels. Mar. Pollut. Bull., 6: 7—10.

Fossato, V. U. and E. Silviero. 1974. Oil pollution monitoring in the Lagoon of Venice using the mussel *Mytilus galloprovincialis*. Mar. Biol. 25: 1—6.

Fossato, U. V., C. Nasci and F. Dolci. 1979. 3, 4 — Benzopyrene and perylene in mussels. *Mytilus* sp. from the Laguna Veneta, north east Italy. Mar. Environ. Res., 2: 47—53.

IOC (UNEP) CSIC. 1984. Intercalibration exercise for oil and petroleum hydrocarbons. Barcelona, 11—17 November, 1974.

Lee, R. F., R. Sauerheber and A. A. Benson. 1972. Petroleum hydrocarbons: uptake and discharge by a marine mussel *Mytilus edulis*. Science, 177: 344—346.

Mackie, P. R., R. Hardy, K. J. Whittle, C. Bruce and A. S. Mc Gill. 1980. The tissue hydrocarbon burden of mussels from various sites around the Scottish coast. In: Polynuclear aromatic hydrocarbons: Chemistry and biological effects, Batelle Press, Columbus, Ohio, pp. 379—393.

Mc Veety, B. D. 1987. Atmospheric deposition of polycycic aromatic hydrocarbons to water surfaces: A mass balance approach. ASFA, 2, 17 (11): 119 (abstract).

Moore, S. F. and R. L. Dwyer. 1974. Effects of oil on marine organisms a critical assessment of published data. Wat. Res., 8: 819—827.

NRC (National Research Council). 1985. Oil in the sea. Iputs, fats and effects. National Academy Press, Washington, 601 pp.

Neff, J. M., B. A. Cox, D. Dixit and J. W. Anderson, 1976. Accumulation and release of petroleum-derived aromatic hydrocarbons by four species of marine animals. Mar. Biol., 38: 279—289.

Pavoni, B., A. Sfriso and A. Marcomini. 1987. Concentration and flux profiles of PCBs, DDTs and PAHs in a dated sediment core from lagoon of Venice. Mar. Chem., 21: 25—35.

Risebrough, W. R., B. W. De Lappe, W. Walker, B. R. T. Simoneit, J. Grimalt, J. Albaigés, J. A. G. Regueiro, A. Ballester and M. Fernandez. 1983. Application of the mussel watch concept studies of the distribution of hydrocarbons in the coastal zone of the Ebro Delta. Mar. Pollut. Bull., 14: 181—187.

Stegeman, J. J. and J. M. Teal. 1973. Accumulation, release and retention of petroleum hydrocarbons by the oyster *Crassostrea virginica*. Mar. Biol., 22: 37—44.

Tavers, T. M., V. C. Rocha, C. Porte, D. Barcels, and J. Albaigés. 1988. Application of the Mussel Watch concept in studies of hydrocarbons, PCBs and DDT in the Brazilian bay of Todos a Santa (Bahia). Mar. Pollut. Bull., 19: 575—578.

Wakeham, S. G., Cs. C. Schaffner and W. Giger. 1980. Polycyclic aromatic hydrocarbons in recent lake sediments — II. Compounds derived from biogenic precursors during early diagenesis. Geochim. cosmochim acta, 44: 415—429.

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KRATKI SADRŽAJ

U posljednje vrijeme zbog naglog urbanog i industrijskog razvoja znatno se povećava broj organskih spojeva koji ulaze u morsku sredinu. Među njima posebna pažnja se posvećuje aromatskim ugljikovodicima zbog njihove visoke toksičnosti i stabilnosti koje pokazuju akumulirajući se u tkivima morskih organizama.

U ovom radu po prvi put su za Jadran izneseni podaci o razini koncentracija ovih spojeva u školjki prstac *(Lithophaga lithophaga)*. Uzorci su sakupljeni uzduž istočne obale Jadrana. Tkivo školjaka je liofilizirano a analize su se izvodile tehnikom UV-fluorescentne spektroskopije preporučene od međunarodnih organizacija UNEP i IOC. Snimani su emisijski spektri niže i više aromatske frakcije na valnim duljinama od 290 do 540 nm, pri konstantnoj valnoj duljini ekscitacije od 310 nm. Količina aromatskih ugljikovodika izračunata je na valnoj duljini od 360 nm prema standardima krizenu i Kuvajtskom ulju. Minimalna vrijednost od 0.41 μg/g nađena je na postaji Dugi otok, dok je maksimalna određena na lokalitetu Solaris blizu Šibenika i iznosi 20.41 μg/g suhog tkiva. Prema dobivenim rezultatima količine PAH, uočena distribucija je u skladu sa poznatim kopnenim izvorima zagađenja. Također se na osnovu istih rezultata može utvrditi da »background« koncentracija PAH u prstacima Jadranskog mora iznosi 1,0 μg/g suhe težine.