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THE IMPACT OF ROAD TRAFFIC ON HYDROCARBON CONTENT IN THE SEDIMENTS OF THE ŠKOCJAN WETLAND

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ABSTRACT

Traffic is a very important source of hydrocarbons in the marine environment. In the present work the hydrocarbon content (polyaromatic and aliphatic) in the sediments of a coastal wetland, influenced by road traffic, are presented. The results of the analyses show higher concentrations of hydrocarbons in sediments from the area close to the highway. Polyaromatic hydrocarbons are primarily of pyrogenic origin, while aliphatic are mostly of petrogenic origin, indicating fresh inputs of these compounds from the road surface. The reduction of this impact should be an important goal in the revitalization of this protected wetland.

Key words: Škocjan wetland, traffic, pollution, aliphatic hydrocarbons, polyaromatic hydrocarbons, sediments

IMPATTO DEL TRAFFICO STRADALE SUL CONTENUTO DI IDROCARBURI IN SEDIMENTI DELLA ZONA UMIDA DI VAL STAGNON

SINTESI

Il traffico è una fonte molto importante di idrocarburi nell'ambiente marino. L'articolo presenta il contenuto di idrocarburi (poliaromatici e alifatici) nei sedimenti della zona umida costiera, sotto l'influenza del traffico stradale. I risultati delle analisi indicano concentrazioni più elevate di idrocarburi nei sedimenti dell'area prossima alla strada maestra. Gli idrocarburi poliaromatici sono principalmente di origine pirogenica, mentre quelli alifatici hanno un'origine petrogenica, il che indica apporti recenti di tali composti dalla superficie della strada. La riduzione di tale impatto dovrebbe essere di primaria importanza nella fase di rivitalizzazone di quest'area protetta.

Parole chiave: Val Stagnon, zona umida, traffico, inquinamento, idrocarburi alifatici, idrocarburi poliaromatici, sedimenti

INTRODUCTION

Hydrocarbons are compounds primarely composed of carbon and hydrogen. They are the major components of crude oil, fuels and lubricants. Polyaromatic hydrocarbons are also formed during the combustion of organic matter. As such they are important pollutants of the natural environment. They can also arise from natural sources (bacteria, plankton...). Different sources of the introduction of these compounds into the natural environment can be enumerated. The most important among them are oil seepage, oil spillage, traffic, urban runoff, waste water and sewage effluent, as well as atmospheric deposition (GESAMP, 1993). Road traffic is an important source of environmental pollution. Pollutants can arise from a variety of sources, including vehicle exhaust emissions (hydrocarbons, heavy metals, NOx, CO, SO_2, PEC...), vehicle lubricating system losses, vehicle fuel system losses, road surface degradation, degradation of automobile tyres, road surface cleaning/de-iceing and load losses from vehicles.

Determination of various sources of the introduction of such compounds into the marine environment as well as the concentrations of these compounds in the natural environment 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.

Hydrocarbons are hydrophobic compounds. Because of their low solubility in water, hydrocarbons tend to adsorb on organic or inorganic particles in the water column (Means *et al.*, 1980; Guzella & de Paolis, 1994; Quintero & Diaz, 1994). The enriched suspended matter settles 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 sediments are a better substrate for the assessment of the extent of pollution of the marine environment.

The aim of the present work is to assess the impact of road traffic on pollution by hydrocarbons in the protected area of the Škocjan wetland.

MATERIAL AND METHODS

Study area

The Škocjan wetland is the largest brackish wetland in Slovenia (about 122 ha, average depth 0.5 m). It is located on the margin of the city of Koper and surrounded by agricultural land (Fig. 1). Water circulation is very limited because of a very narrow connection to the sea

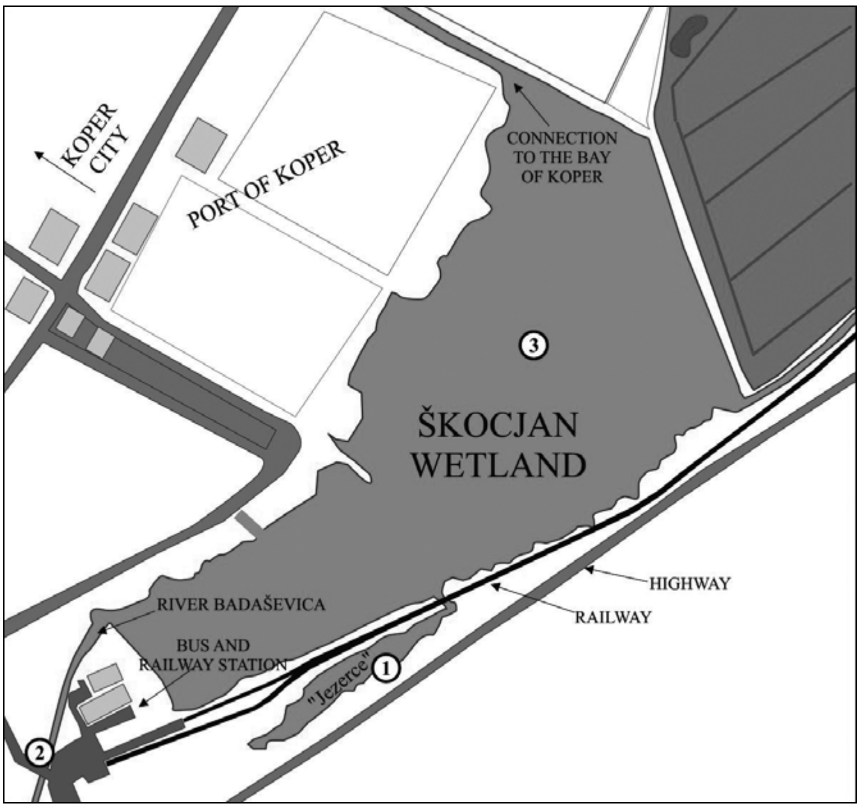

Fig. 1: Location of sampling sites within the investigated area.
Sl. 1: Vzorčevalna mesta na preiskovanem območju.

in the port of Koper. The importance of this lagoon with its surroundings is its rich flora and fauna which boast a number of rare or endangered species. The fate of this area in the past was connected to the industrial development of this area, especially the expansion of the Port of Koper. In the last ten years this area has become a national nature reserve and a special protected area Natura 2000. Many activities were undertaken to re-establish and protect this important wetland.

The wetland receives runoff waters ("Jezerce") from the highway which passes at its south-eastern part. The traffic on this highway is quite intensive, especially in the summer period, when many tourists pass by. The average number of vehicles per day is approaching 45,000 with more than 40,000 cars and around 4,000 trucks. On its southern flank the main bus and railway stations of the city of Koper are located. Runoff waters are introduced into the Badaševica River and consequently into the Škocjan wetland.

For comparison, a reference site (R) was chosen in the Stjuža lagoon in Strunjan. The natural conditions in this lagoon are similar to the investigated wetland (depth, limited circulation, fresh water inflow, sediment composition), with no significant sources of pollution by hydrocarbons (Čermelj *et al.*, 2000).

The sediment in the wetland is grey to dark grey, in some parts even black and with a strong odour of H_2S. It is composed mainly of clayey silt and silty clay, mostly homogeneous in the surficial 10 cm layer. The sediment is characterized by rather high contents of organic C (1–5%) and total N (0.1–0.7%), indicating important eutrophication processes (Čermelj *et al.*, 2000).

Experimental

"For residue analyses" quality hexane, methanol and methylene chloride were used for extraction. All other chemicals were of analytical grade. Extraction thimbles, silica, alumina and sodium sulphate were precleaned with methanol and hexane.

Sediment samples were collected in stainless steel tubes by a scuba diver. Sampling sites are presented in figure 1. The upper 1cm layer of each sediment sample was taken for analysis.

After freeze-drying, the samples were extracted in a Soxhlet apparatus with hexane and methylene chloride (50:50) for 8 hours. The solutions were dried with Na_2SO_4, concentrated in a rotary evaporator and additionally under an N_2 stream. After sulphur removal with activated Cu and additional concentration, the partition of hydrocarbons was performed using column chromatography (Silica, Alumina). Concentrated extracts were analyzed using an HP 5890 gas chromatograph equipped with an FI detector and an HP 3396 integrator. The HP Ultra 2 column (25 m x 0.32 mm, 0.17 μm film thickness) was used for analyses. Quantitative determinations were achieved using both internal and external standards. The analytical procedure is described in detail in UNEP reference methods (UNEP/IOC/IAEA, 1992).

RESULTS AND DISCUSSION

Concentrations of aliphatic hydrocarbons are presented in Table 1. Very high concentrations were observed at station 1, which is close to the highway and receives runoff water from the highway. The concentrations were also higher at station 2, which is situated close to the Koper bus station. Concentrations of hydrocarbons in the middle of the wetland were very low. These concentrations were even lower when compared to the reference site R.

Tab. 1: Content of aliphatic hydrocarbons in sediment samples (ng/g dry sediment).
Tab. 1: Vsebnost alifatskih ogljikovodikov v vzorcih sedimenta (ng/g suhega sedimenta).

Aliphatic hydrocarbons	1	2	3	R
C-17	427	29	2	82
Pristane	85	87	<1	<1
C-18	270	147	<1	<1
Phytane	69	144	<1	<1
C-14 do C-34	41750	1876	44	464
Total aliphatic hydrocarbons	**42807**	**2283**	**46**	**546**

There are different parameters used for the determination of the origin of aliphatic hydrocarbons. The most frequently used parameter is the ratio between the "unresolved complex mixture – UCM" and resolved aliphatic hydrocarbons (Gogou *et al.*, 2000; Commendatore & Esteves, 2004). The UCM is usually considered as a mixture of degraded compounds from oil in the natural environment. It is determined as a background signal in the GC chromatogram. Higher values of this ratio (>10) are indicative of chronic/degraded contamination (Tolosa *et al.*, 2005). The calculated ratios presented in Table 2 reveal significant fresh contamination with hydrocarbons at sampling site 1. The ratio at sampling site 2 shows a prevailing degraded fraction of aliphatic hydrocarbons, but even this does not mean that this area is not affected with fresh inputs in lower amounts. The obtained very high UCM/resolved ratio for the central part of the wetland is an indication of a much degraded area.

The second parameter usually used is the "carbon preference index-CPI" which is a ratio between the contents of aliphatic hydrocarbons with an even number of carbon atoms and those with an odd number of carbon atoms in the range C-27 to C-30. Petrogenic hydrocarbons show values around 1, while those of vascular plants and uncontaminated sediments range from 3 to 6 (Wakeham, 1996; Gogou *et al.*, 2000; Wang *et al.*, 2007).

Tab. 2: Values of parameters used for the determination of the origin of aliphatic hydrocarbons.
Tab. 2: Vrednosti parametrov za določanje izvora alifatskih ogljikovodikov.

Parameter	1	2	3	R
CPI	1.3	2.3	2.5	3.8
UCM/Resolved	8	68	203	12

The CPI at site 1 is close to 1. This is an indication of fresh input of petroleum hydrocarbons. At all other sites the CPI is higher than 2, confirming the more degraded mixture of hydrocarbons or an important source of natural aliphatic hydrocarbons of terrestrial origin in the Badaševica River mouth. This different distribution pattern is also presented in figure 2, showing the typical distribution of aliphatic hydrocarbons in the higher fraction for fresh input (chromatogram A) and that for degraded petroleum hydrocarbons and/or hydrocarbons of terrestrial origin.

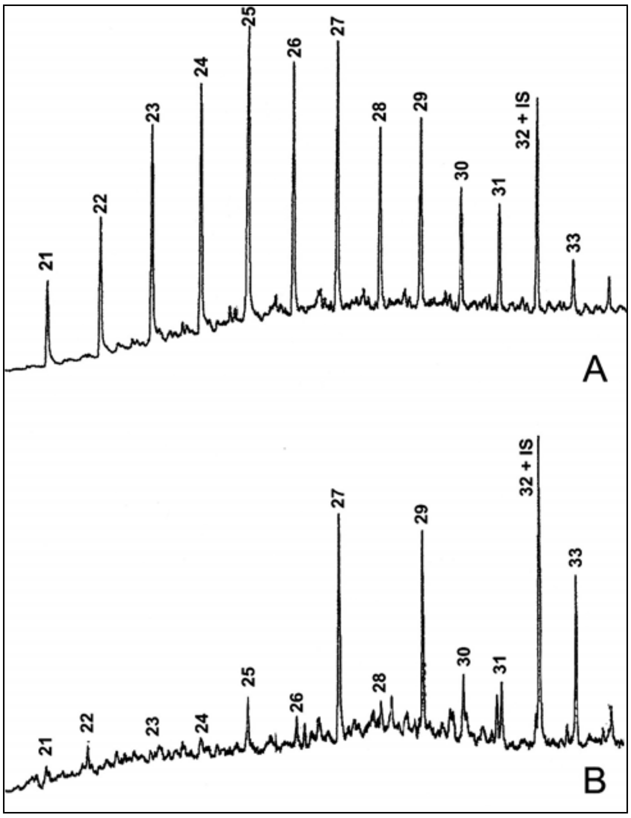

Fig. 2: The chromatograms of the aliphatic hydrocarbon fraction at the sites 1 (A) and 2 (B).
Sl. 2: Kromatograma frakcije alifatskih ogljikovodikov na mestih 1 (A) in 2 (B).

A similar pattern of distribution, but with less significant differences, was also obtained in the case of polyaromatic hydrocarbons (Tab. 3). Their concentrations were about two times higher at sampling site 1 in comparison to sampling site 2. Concentrations of all the determined polyaromatic hydrocarbons at station 3 were below the detection limit of the analytical procedure. The content of these compounds at the reference site was rather low. Concentrations of polyaromatic hydrocarbons, as well as aliphatic hydrocarbons, are in good correlation with the amount of organic C in the sediment samples. The highest content of organic carbon was determined at sampling site 1 (5.13%), it decreased to 3.80% at sampling site 2 and further to 1.11% at site 3 (Čermelj *et al.*, 2000). This correlation indicates rather important interactions of hydrocarbons with organic matter in sediment samples.

The most abundant polyaromatic hydrocarbons are phenanthrene, 1-methylphenanthrene, anthracene, fluoranthene, pyrene, chrysene and benzo[b]fluoranthene. The concentartions of polyaromatic hydrocarbons presented in Table 3 show the prevalence of highly condensed or high molecular weight hydrocarbons (HMW) compared to low molecular weight hydrocarbons (LMW). The calculated ratio (LMW/HMW) is shown in Table 4. For both sites (1 and 2) the ratio is below 1, indicating higher amounts of 4, 5 and 6-ring polyaromatic hydrocarbons. This is characteristic for a pyrogenic (burning of fossil fuels) source of these compounds (Sporstol *et al.*, 1983; Culotta *et al.*, 2006).

This source is also confirmed by a high fluoranthene/pyrene ratio and a low phenanthrene/anthracene ratio. The first ratio (Fl/Py) is usually higher than 1 for polyaromatic hydrocarbons derived from combustion processes, while the Ph/An ratio is significantly lower than 30 for pyrogenic derived hydrocarbons (de Luca *et al.*, 2005; Culotta *et al.*, 2006).

The third ratio presented in Table 4 (Me-Phe/Phe) also reveals the contribution of a petrogenic source of polyaromatic hydrocarbons (Zakaria *et al.*, 2002; Yim *et al.*, 2007). Alkylated compounds are more abundant in crude oil, while the parent compounds are derived during combustion processes. Ratios higher than 2 are significant for a petrogenic source of polyaromatic hydrocarbons.

The above results show that the Škocjan wetland is, in general, only moderately polluted with hydrocarbons. It is usually difficult to distinguish different pollution sources. In the presented case some influence of atmospheric deposition, urban runoff and maritime traffic could contribute to the pollution by hydrocarbons (city of Koper, port of Koper). This contribution is rather small in comparison to that of the road traffic. This is evident

Tab. 3: Concentrations of polyaromatic hydrocarbons in sediment samples.
Tab. 3: Koncentracije poliaromatskih ogljikovodikov v vzorcih sedimenta.

Polyaromatic hydrocarbons	**1**	**2**	**3**	**R**
Naphthalene	18	9	<1	3
1-mehylnaphthalene	<1	<1	<1	<1
1-ethylnaphthalene	<1	<1	<1	<1
Acenaphthene	18	<1	<1	2
Acenaphthylene	<1	<1	<1	<1
2,3,6-trimethylnaphthalene	<1	<1	<1	<1
Phenanthrene	55	37	<1	15
Anthracene	42	19	<1	<1
Fluorene	29	<1	<1	<1
2-methylphenanthrene	61	6	<1	<1
1-methylphenanthrene	172	115	<2	<2
Fluoranthene	122	188	<1	<1
Pyrene	84	54	<1	<1
3,6-dimethylphenanthrene	<2	<2	<2	<2
Perylene	9	5	<1	<1
1-methylpyrene	<1	<1	<1	<1
Chrysene	155	50	<1	<1
Benzo[k]fluoranthene	55	13	<1	<1
Benzo[b]fluoranthene	123	29	<1	<1
Benzo[e]pyrene	3	6	<1	<1
Benzo[a]pyrene	39	8	<1	<1
Benzo[a]anthracene	41	34	<1	<1
Total polyaromatic hydrocarbons	**1026**	**573**		**20**

from the elevated concentrations of hydrocarbons in the area affected by road runoff. Comparison of hydrocarbon content in sediments from these areas of the Škocjan wetland with other parts of the Slovenian sea, even the port of Koper, shows concentrations of a few times higher (Bajt, 2000; Notar *et al.*, 2001). These observations certainly show the important impact of road traffic on pollution of the wetland, but for a better assessment of its extent some additional study should be undertaken, including the transformation and sink of hydrocarbons in such a specific environment.

Tab. 4: Values of parameters used for the determination of the origin of polyaromatic hydrocarbons.
Tab. 4: Vrednosti parametrov za določanje izvora poliaromatskih ogljikovodikov.

Parameter	**1**	**2**
LMW (ng/g)	395	186
HMW (ng/g)	631	387
LMW/HMW	0.63	0.48
Me-Phenanthrenes/Phenanthrene	4.24	3.27
Fluoranthene/Pyrene	1.45	2.90
Phenanthrene/Anthracene	1.31	1.95

CONCLUSIONS

Results of the present study show the significant impact of road traffic on the Škocjan wetland, a protected area, in terms of hydrocarbons content in sediments. Higher concentrations were found in the "Jezerce" part, which directly receives runoff water from the highway. The area near the bus and railway station is less polluted. The central part of wetland is a much degraded area. Concentrations of hydrocarbons are low, even compared with concentrations at the reference site. These low concentrations are probably due to intensive microbial and photochemical degradation, as well as bioaccumulation in rich vegetation. Aliphatic hydrocarbons are mostly of petrogenic origin (fuels) with some contribution from terrestrial derived compounds (freshwater inputs). The origin of polyaromatic hydrocarbons is mostly pyrogenic (combustion of fuels), with even some petrogenic origin evident. The obtained concentrations of hydrocarbons at sites 1 and 2 are rather high and could be connected to traffic pollution. The reduction of this impact should be an important goal in the revitalization of this protected wetland.

VPLIV CESTNEGA PROMETA NA VSEBNOST OGLJIKOVODIKOV V ŠKOCJANSKEM ZATOKU

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POVZETEK

Promet je pomemben vir onesnaževanja morskega okolja z ogljikovodiki. V pričujočem delu so predstavljene vsebnosti ogljikovodikov (alifatskih in poliaromatskih) v sedimentu obalnega mokrišča, ki je pod vplivom cestnega prometa. Rezultati analiz kažejo povišane koncentracije ogljikovodikov v sedimentu na področju v bližini avtoceste. Poliaromatski ogljikovodiki so večinoma pirogenega izvora, alifatski ogljikovodiki pa so večinoma petrogenega izvora, kar kaže na sveže onesnaževanje s ceste. Zmanjšanje vpliva cestnega prometa na onesnaževanje Škocjanskega zatoka bi moralo biti med prednostnimi nalogami njegove revitalizacije.

Ključne besede: Škocjanski zatok, promet, onesnaževanje, alifatski ogljikovodiki, poliaromatski ogljikovodiki, sedimenti

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