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HYDROCARBONS AND CHLORINATED HYDROCARBONS IN THE AIR IN THE GREATER SPLIT AREA

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The content of hydrocarbons and chlorinated hydrocarbons was examined in samples of air from the greater Split area. Organic pollutants were accumulated from the air by adsorption on Polysorb-10 and desorption with hot water vapour. Gaseous and liquid phases were analysed by gas chromatography. Hydrocarbon concentrations were within permissible limits and their effects on human health were negligible. There were marked differences between pollutant concentrations in air samples taken from the industrial zone, crossroads in the city centre and »clean« zones.

Key terms: air pollution, automobile traffic, gas chromatographic method, industrial facilities

Sources of organic pollutants in the atmosphere are of biogenic, geogenic and man-made origin. On a global scale, anthropogenic emission of organic substances is considerably lower than the biogenic one (1). However, in comparison with natural sources, anthropogenic emitters tend to concentrate over limited city areas.

Presently, a major source of pollution is car traffic. Its contribution to total hydrocarbon emission in the United States is reported to range from 53 to 63 per cent (2). In general, traffic-induced air pollution is likely to increase because of a growing number of motor cars, despite the measures taken for decreasing the toxicity of internal combustion engines. The hydrocarbon emission from various parts of motor cars with spark ignition is distributed as follows: over 50 per cent of the total amount of emitted compounds is due to exhaust gases, evaporation from tanks and carburetters accounts for about 20 per cent, and leakage from crankcases for another 25 per cent (3).

Exhaust gases are a multicomponent mixture consisting not only of the initial hydrocarbons present in fuel, but also of the products of their incomplete oxidation, thermal decomposition and other transformations. *Hampton and co-workers* (4) published a comprehensive list of volatile components comprising about 450 compounds. According to their report, methane, acetylene and C_2–C_3 alkanes, as destruction products, make more than 47 per cent of the total amount of hydrocarbons in exhaust gases, although they are not present in liquid fuel. Non-burned hydrocarbons, represented by benzene and

its homologues make 20 per cent, and C_4–C_8 alkanes about 13 per cent of the total amount.

Assessment of the contribution of automobile exhaust gases to urban air pollution presupposes comparison of the characteristics of the relative composition of light hydrocarbons in fuel, exhaust gases and urban air. As a parameter suitable for comparison the ratio (»r«) of the total content of aromatic hydrocarbons and that of alkanes has been proposed (5, 6):

$$r = \left(\sum_{4}^{12} C_nH_{2n-6}\right) / \left(\sum_{4}^{12} C_nH_{2n+2}\right)$$

Parameter »r« has the maximum value for exhaust gases, because alkanes burn more completely than aromatic hydrocarbons. In the air of four cities in Russia (3, 7) parameter »r« varies from 0.4 to 0.9 (for a gasoline mixture it is about 1.0, and for exhaust gases of a »Volga« car 2.6). This may imply that a major source of hydrocarbons emission into the air in Russian cities is the loss of fuel due to evaporation. Parameter »r« as calculated by authors in Western Europe and the United States (8, 9) is about 1.1 meaning that in those parts of the world exhaust gases are present in the atmosphere to a much greater measure.

The second most important anthropogenic source of organic pollutants in the atmosphere are industrial facilities. The amount of pollutants (hydrocarbons, halogenated compounds, polyaromatic hydrocarbons etc.) emitted into the atmosphere in the proximity of big factories can be very high. Finally, there are municipal sources of pollutants such as public buildings, power plants and water supplies, sewage purification plants and solid waste incinerators.

The aim of this investigation, which was planned as part of a long-term project, was to examine the content of selected hydrocarbons and chlorinated hydrocarbons in the air of the area encompassing the town of Split and its surroundings. The town is situated in the central part of the eastern Adriatic coast. It has a population of 206 000 and about 45 000 cars. Besides a great harbour storage of petrol products (butane for domestic use in the first place) and chemicals, major sources of pollution are polyvinyl chloride and cement industry.

METHODS

Sampling location

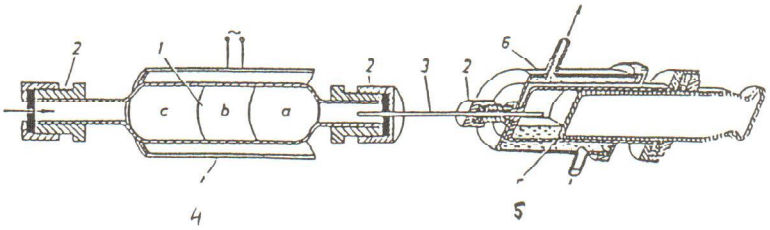
Sampling was carried out at eight locations (Table 1): crossroads in the city centre (locations 1, 2, 3), industrial zone (locations 4, 5), »clean« locations (locations 6, 7) and the island of Vis (location 8). The latter was taken as a referent place because of minimal anthropogenic sources of organic pollutants. Measurements took place in June and July 1992, from 10 to 12 a.m., at the temperature of 26–32 °C, with the wind of mild intensity and different direction.

The method of accumulation of organic pollutants from the air

Samples were prepared by the method of Isidorov (3, 10) using thermal desorption with displacement of the sorbate with superheated water vapour instead of inert gas. The advantages of the method are its rapidity, the possibility of determining unstable compounds without their decomposition at a relatively low desorption temperature, and

upon leaving the heated sorption tube, and in combination with air displaces hydrocarbons from sorbent pores, forming a two-phase liquid-gas system. The distribution of desorbed compounds between the two phases is determined by ratio $C_L/C_G=K$, where C_L and C_G are respective concentrations of compounds in the liquid and gas. »K« is partition coefficient which, for dilute solutions, only depends on the temperature. Hence, poorly soluble substances with low »K« values are accumulated in the gaseous phase, and well soluble substances are accumulated in the aqueous phase. This method of sample preparation is particularly suitable for analysis of low alcohols and carbonyl compounds against the background of predominant hydrocarbons.

In our experiments ten litres of air were collected on Polysorb-10 sorption tubes with a Desaga GS 312 (velocity 0.5–1.0 litre per minute). Desorption of hydrocarbons from the tubes was achieved with water vapour at 200 °C, according to the scheme shown in Figure 1 (11, 12).



1 – sorption tube, 2 – union nut, 3 – steel needle,
4 – oven, 5 – syringe, 6 – thermostating jacket

Figure 1. *Scheme for desorption process by superheated water vapour in a variable volume device*

In small portions, 2 ml of water was injected into the sorption tube, heated to 220 °C and connected to a vapour receiver of variable volume by a steel needle. The receiver was a 10 ml medical syringe. The syringe plunger was pushed by water vapour and the air coming from the sorbent pores, and after desorption the pressure in the syringe became equal to atmospheric pressure. After desorption the syringe receiver was disconnected from the sorption tube, and the gas was sampled for analysis through the rubber septum.

Gas chromatographic analysis

After the desorption process, hydrocarbons and chlorinated hydrocarbons, from C_4 to C_8, in the gaseous phase, were analysed by gas chromatography on a Perkin Elmer Sigma 2000 gas chromatograph equipped with an LCI-100 laboratory computing integrator.

Operating conditions:

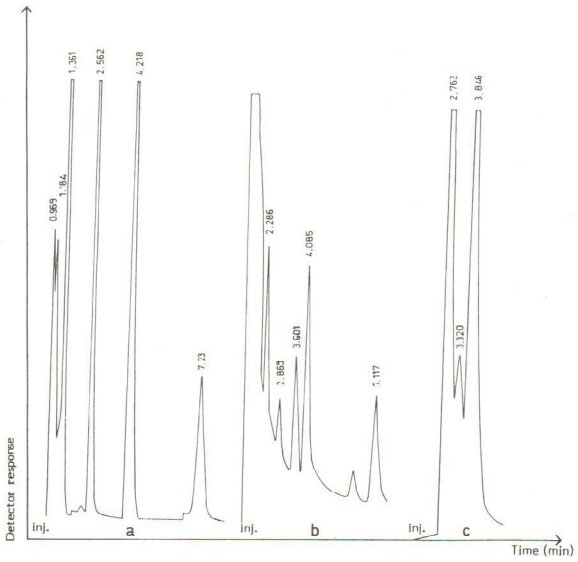
a) n-C_4H_{10} (butane), i-C_4H_{10} (isobutane), C_5H_{12} (pentane), C_6H_6 (benzene), C_7H_8 (toluene) and C_8H_{10} (o-, m-, and p-xylene).

Glass column, 2 m x 3.2 mm i.d., filled with 9% Tween-80 on Chromosorb W-HP, 0.16–0.20 mm; detector flame ionisation; temperatures: column 70 °C, injector 120 °C, detector 250 °C; carrier gas nitrogen 27.3 ml/min.

b) CH_2Cl_2 (dichloromethane), $CHCl_3$ (chloroform), CCl_4 (carbon tetrachloride), C_2HCl_3 (trichloroethylene) and C_2Cl_4 (tetrachloroethylene). Stainless steel column, 3 m x 3.2 mm i.d., filled with 10% SE-30 on Chromosorb W-HP, 0.16–0.20 mm; detector electron capture; temperatures: column 100 °C, injector 150 °C and detector 300 °C; carrier gas nitrogen 27.3 ml/min.

c) CH_3OH (methanol), C_2H_5OH (ethanol) and CH_3COCH_3 (acetone). These compounds were measured in the liquid phase after the desorption process, under the same conditions as hydrocarbons from group a).

Figure 2 shows chromatograms of standard mixtures of all the three groups of compounds.



Retention time (min):

0.969	$n\text{-}C_4H_9$	2.286	CH_2Cl_2	2.762	CH_3COCH_3
1.184	$i\text{-}C_4H_9$	2.869	$CHCl_3$	3.320	CH_3OH
1.361	C_5H_{10}	3.601	CCl_4	3.846	C_2H_5OH
2.562	C_6H_6	4.085	C_2HCl_3		
4.218	C_7H_8	7.117	C_2Cl_4		
7.23	C_8H_{10}				

Figure 2. *Chromatograms of standard mixtures of all three groups of air pollutants*

RESULTS

We analysed three groups of hydrocarbons in the air of the greater Split area applying the gas chromatographic method with corresponding columns and measurement condi-

Table 1. *Selected organic pollutants in the air of the greater Split area*

LOCATION	HYDROCARBONS ($\mu g/m^3$)						CHLORINATED HYDROCARBONS ($\mu g/m^3$)				
	$n\text{-}C_4H_{10}$	$i\text{-}C_4H_{10}$	$C5H_{12}$	C_6H_6	C_7H_8	C_8H_{10}	CH_2Cl_2*	$CHCl_3$	CCl_4	C_2HCl_3	C_2Cl_4
1. Chemical school	187.4	142.3	47.3	54.3	74.8	40.8	-	13.7	2.2	5.1	18.9
2. Council House	174.2	385.5	0	43.0	24.2	0	25.4	12.8	3.5	2.1	1.7
3. Medical faculty	161.4	119.9	19.4	22.4	51.1	0	-	10.0	1.9	5.6	1.7
4. Solin - St. Kajo	716.4	390.8	0	32.8	21.4	0	-	31.2	8.7	22.5	5.2
5. Kaštel Sućurac	646.4	489.4	142.1	54.9	201.4	55.0	-	35.5	6.6	28.6	2.4
6. Marjan hill	316.7	37.2	32.9	0	0	0	-	11.4	1.0	7.7	2.7
7. Zenta bay	156.9	50.4	0	0	0	0	17.9	16.0	1.5	4.9	1.4
8. Island Vis	104.4	87.5	0	0	0	0	10.5	18.2	0.7	5.2	0

* Very often it was not possible to distinguish this signal from the signal of the air and light products.
All results are average values of three measurements.
Period: June-July 1992, time: 10-12 a.m., temperature: 26-32 °C, wind: mild, different directions.
Locations: crossroads in the city centre (1 to 3); industrial zones (4 to 5); clean city zones (6 to 7); referenced location (8).

tions. Results for the selected aliphatic and aromatic hydrocarbons and chlorinated hydrocarbons are presented in Table 1.

Under the experimental conditions applied no measurable concentrations of low alcohols and acetone were found being below the established detection limits of 25 $\mu g/m^3$ for methanol, 15 $\mu g/m^3$ for ethanol and 15 $\mu g/m^3$ for acetone.

DISCUSSION

Among the investigated compounds aliphatic hydrocarbons are the less toxic pollutants. According to Russian authors the threshold limit value in the city air is 200 mg/m^3 for butane and 100 mg/m^3 for pentane (13, 14). In big Russian cities the average butane and pentane concentrations are 117 $\mu g/m^3$ and 139 $\mu g/m^3$, respectively (7). High concentrations of butane and i-butane in our experiments, exceeding average values for the big cities in Russia, are very likely a consequence of pollution from a gas distribution station situated in the Split industrial zone. That could explain an unexpected presence of both pollutants even on the top of Marjan hill in Split, which is considered to be a clean location.

Concentrations of benzene and its homologues in the air are of even greater concern because of their carcinogenic properties. However, the threshold limit values for benzene and homologues are very high and differ from country to country. For example in Germany the threshold limit value for benzene is 3 mg/m^3 and for toluene and o-, m- and p-xylene 20 mg/m^3 (13). In Russia the respective values are considerably lower, 0.6 mg/m^3 for benzene and toluene and 0.2 mg/m^3 for o-, m- and p-xylene (13, 14).

Table 2 shows average values of benzene and its homologues in selected big cities of the world (7).

Table 2. *Average concentrations of benzene, toluene and o-, m- and p-xylene in the air of some big cities (μg/m^3)*

Compound	Los Angeles (*Ref. 15*)	Zürich (*Ref. 16*)	Haag (*Ref. 17*)	Berlin (*Ref. 18*)	London (*Ref. 19*)	Petersburg (*Ref. 10*)
Benzene	52	188	46	51	319	104
Toluene	152	160	93	102	180	111
o-, m-, p-Xylene	142	93	116	53	123	114

Our results show that the analysed toxic pollutants were present only at the crossroads and in the industrial zone of the Split area. Their concentrations were below the average values measured in the big cities worldwide from 1970 to 1980. In the other city zones no measurable contents of the pollutants were detected suggesting that most inhabitants were not at risk from contact.

The investigated chlorinated hydrocarbons make a minor part of organic pollutants. Our findings are in accordance with the results reported by other authors (6, 7). For example, the trichloroethylene concentration reported for Berlin is 1–33 μg/m^3 (18), and that measured in Paris 9–36 μg/m^3 (19). The content of tetrachloroethylene in Berlin is reported to be 0.7–47 μg/m^3 (18), and in Zürich up to 74 μg/m^3 (16). Those concentrations are much lower than the threshold limit value for chlorinated hydrocarbons (1–30 mg/m^3) (13) and are considered to have no significant adverse effects on human health.

The low level of chlorinated hydrocarbons and absence of difference between concentrations at various locations in the Split area are considered to be a consequence of the global distribution of these pollutants indicating no significant effects from traffic or other pollution sources in the town.

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Sažetak

UGLJIKOVODICI I KLORIRANI UGLJIKOVODICI U ZRAKU SPLITA I OKOLICE

Sadržaj ugljikovodika i kloriranih ugljikovodika ispitan je u uzorcima zraka iz Splita i okolice. Organski onečišćivači akumulirani su iz zraka adsorpcijom na polimeru Polisorb-10 i desorpcijom pomoću vruće vodene pare. Plinovita i vodena faza analizirane su metodom plinske kromatografije. Koncentracije ugljikovodika bile su unutar dopuštenih granica a učinci na ljudsko zdravlje zanemarivi. Koncentracije u uzorcima zraka iz industrijske zone, raskršća u gradskom središtu i »čistih« područja uočljivo su se razlikovale.

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Ključne riječi: automobilski promet, industrijska postrojenja, onečišćenje zraka, plinska kromatografija