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Traffic-Generated Air Pollution with Volatile Organic Compounds in Kraków and its Environs

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Abstract

The content of volatile hydrocarbons in the atmospheric air in Kraków as well as in the country in the vicinity of the A-4 motorway was determined. The air was sampled to canisters made of electropolished stainless steel. Determinations of hydrocarbons were performed on a gas chromatograph equipped with a cryogenic trap and flame-ionization detector. The contribution of traffic to air pollution with volatile hydrocarbons both in built-up and open areas in the vicinity of busy motorways was estimated.

Keywords: hydrocarbons, air pollution, gas chromatography

Introduction

Due to their harmful effect on both human health and the quality of crops as well as their particular role played in photochemical generation of oxidants taking place in the atmosphere with the participation of nitrogen oxides under the influence of sunlight, hydrocarbons are air pollutants attracting special attention pollution [1]. They require a continuous monitoring of their concentrations and structures. The above has been a great stimulus to worldwide research on hydrocarbons in pollution.

Hydrocarbons in the atmosphere are both of natural and anthropogenic origin [2,3]. While the natural sources of hydrocarbons are dispersed all round Earth relatively evenly, antropogenic ones are commonly concentrated in small areas. This is why their impact is perceived as more harmful [4]. The most significant antropogenic sources of hydrocarbons are exhaust gases emitted from vehicles. To that add hydrocarbons evaporating from liquid fuels. The emitted compounds are dispersed in the air and spread over long distances. The measured level of imission depends on the level of emission, and their magnitude is influenced by factors such as the location of the emitter, topography of the area, meteorological conditions and reactivity of the emitted compounds [1,5]. The highest concentrations of hydrocarbons are observed in big cities, where traffic is heavy and its flow is slow, and the limited space reduces considerably the process of air self-cleaning. By contrast, outside built-up areas the masses of air can move freely and there is no accumulation of contaminants observed [6,7].

The dispersing of contaminants, of those generated by traffic in particular, is a complex process [8-10]. Mathematical modeling is commonly used for the description of the process. At present a number of ready-made packets are available [11,12], with use of which the surface areas of traffic-generated contamination can be calculated. In the above models some of the input data are difficult to estimate, which can account for the fact that

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the error of the results obtained is sometimes very high. However, for decisions (especially those to be made under critical ecological circumstances) their utility cannot be questioned [5].

In Kraków both the local and transit traffic go through the city centre. This worsens the quality of the ambient air not only along the streets in question but also in the whole of the city, as has been demonstrated by the air monitoring system in the city. According to the results collected, the air in Trzech Wieszczów Av. is the one most contaminated in the city centre with carbon oxide, nitrogen dioxide, dust and lead in dust.

This research is a continuation of our previous work [13], in which we presented how concentrations of hydrocarbons change along the distance from the source of emission and we demonstrated unambiguously the effect of the traffic on quality of the ambient air. In this work we continue to analyze the data with an attempt to assess the quantitative contribution of the traffic to the air pollution with hydrocarbons. The starting point for the interpretation are the concentrations of hydrocarbons measured along the roads of heavy traffic in Kraków and its environs, and the tunnel measurements performed in Sydney [14] and Vancouver [15]. Such measurements have not been performed in Poland to date.

Materials and Methods

The American EPA T0-14 method of hydrocarbon determination in ambient air [16] was adapted. Air was sampled with use of the SUMMA® passivated canisters, 6 dm^3 in volume, made of electropolished stainless steel. The canisters were evacuated to about 10^{-3} mm Hg pressure prior to sampling. The canisters were equipped with Nupro SS-4H valves, and were protected against dust while sampling by placing a filter paper on their inlets. Having been filled with the air samples, the canisters were transported to the lab and installed to the analytical set-up. 160 cm^3 air were subjected to cryogenic preconcentration in a trap cooled with liquid nitrogen followed by thermal desorption. From there the sample was transported with a carrier gas to a chromatographic column, where the compounds were separated and detected by a flame-ionization detector. The compounds were identified based on their retention times and Kovatč retention indexes at the programmed temperature. The method of external standard was employed - a calibration mixture consisting of 27 hydrocarbons of concentrations between 5 and 72 ppbV in nitrogen was used. The details of the calibration procedure and of determinations were presented in [13,17]. The technical parameters of chromatographic analysis of ambient air performed with use of the Varian Star 3600CX gas chromatograph are presented in Table 1.

Table 1. Characteristic of gas chromatograph Varian Star 3600CX.

Element of chromatograph	Operation parameters
Chromatographic column DB-1 ID 0.32 mm, length 30 m., film 3 mm (J&W Scientific, USA)	flow rate of a carrier gas (helium) 2.5 cm^3min^{-1} temperature program: initial temperature: -60°C for 6 min temperature increment: 5°C/min to 20 or 40°C followed by 8°C/min to 180°C
Cryogenic trap (SPT)	temperature of preconcentration: -175°C time of preconcentration: 4 min desorption temperature:120°C
FID detector	operation temperature: 250°C gas flow rates: 'make-up': 27.5 cm^3min^{-1} hydrogen: 30 cm^3min^{-1} air: 300 cm^3min^{-1}
Electromagnetic valvesfour- and ten-ways	valves operation temperature: 160°C

Sampling Sites

The results of measurements presented in this work were performed in 1997-1999. The air samples were collected in Kraków and in the vicinity of the A-4 motorway connecting Kraków and Katowice. The flow of traffic is 1200-1800 vehicles per hour on the A-4 and 3000-4000 in Trzech Wieszczów Av. at rush hour. The samples were taken at 1.5 m above ground level. The sampling sites were chosen in a way to collect comprehensive information on the VOC levels produced by the traffic and on their levels in places distant from the source of pollution. Samples were taken in spring and autumn, only on rainless days. Over 200 samples were analyzed in the years 1997-1999.

Results and Discussion

VOC Levels Studied in Atmospheric Air

The method of determination of volatile organic compounds allowed us to identify about 60 compounds in atmospheric air, but the number of peaks in the obtained chromatograms indicated the presence of over 150 compounds at levels higher than the method detection limit, i.e. higher than 0.2 $\mu g/m^3$. The content of the volatile organic compounds in the air at the motorway was in the range 40-430 $\mu g/m^3$ and that in the center of Kraków 50-2000 $\mu g/m^3$, 20-30% of that corresponded to unidentified compounds. The highest concentrations were determined in the samples collected at the edge of the roadways. The frequency of the occurrence of given concentrations both for the city of Kraków and for the area outside the city is presented in Figures 1a and 1b. It was observed that for both areas VOC concentrations assumed the values from the upper range of the noted. concentrations considerably more rarely than lower values.

The study of the distribution of VOCs outside the built-up area of Kraków and outside the city demonstrated that the concentrations of the majority of the compounds

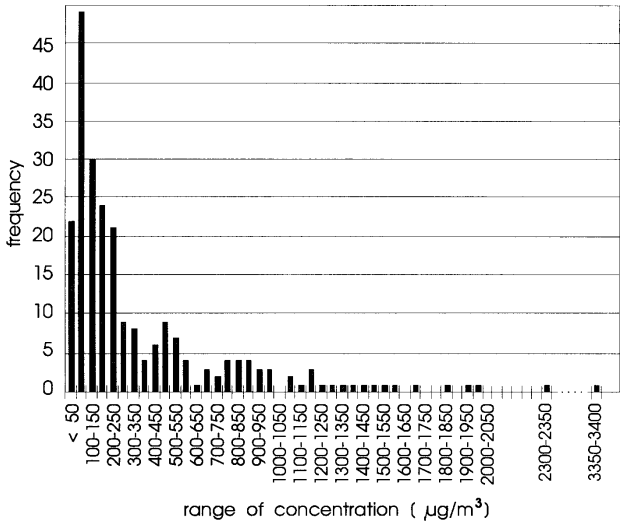

Fig. 1a. Frequency of occurrence of the overall concentration of the identified compounds for all the samples collected in Kraków.

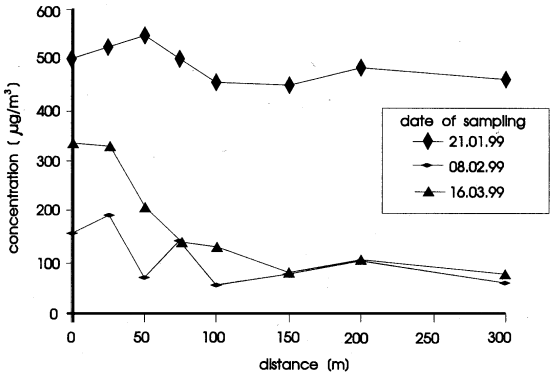

Fig. 2. Examples of the overall concentration of the identified compounds in different distance from the source of pollution.

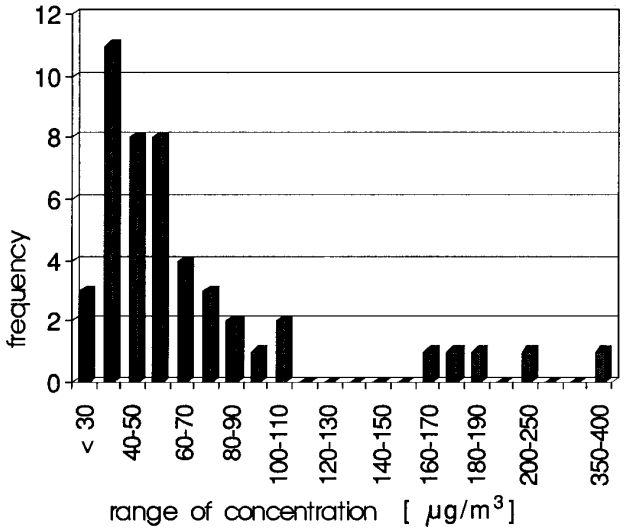

Fig. 1b. Frequency of occurrence of the overall concentration of the identified compounds for all the samples collected outside Kraków in the vicinity of the motorway.

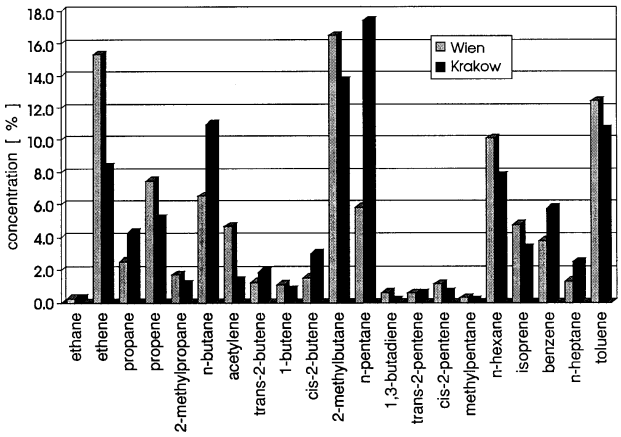

Fig. 3. Percentage by weight of selected hydrocarbons in the air sampled in Kraków and Vienna (100% is the sum of all the concentrations of the compounds presented in this Figure).

decreased with distance from the source of pollution. Different concentration-distance correlations were obtained. In several cases the Gaussian fall of concentration with distance was observed and in other cases the correlation was pulsatory (Fig. 2). Seinfield [1,18] showed that the imission is a random variable, dependent on both meteorological conditions and the magnitude of emission. It is therefore possible that after assuming its maximum value, the concentration falls to a lower value.

All the samples of air collected in different sampling sites along the streets of heavy traffic in Kraków had similar compositions. The samples collected elsewhere (e.g. in parks), however, had considerably different concentration profiles. To illustrate this the mean values of the concentrations of the compounds identified in three areas are comprised in Table 2. The standard deviations of concentrations are printed in italics and the number of samples are presented at the end of the table. The median values were also calculated and for all compounds in the three places they were smaller than the mean values.

It is commonly believed that every city has its characteristic concentration profile (fingerprint) dependent on local pollution, intensity of traffic, fuel and climatic conditions. However, studies of ambient air performed in Kraków and Vienna [17] show that bigger discrepancies appear between the concentration profile of hydrocarbons in one city in places of different utility than between the concentration profile in the places of similar character in

Table 2. The mean values of the concentrations and the standard deviations of the compounds identified in the area of Trzech Wieszczów Av., the A-4 motorway and in the recreational sites, i.e. parks and Błonia. All values in μg/m^3.

Compounds	Trzech Wieszczów Av.		recreational sites		A-4 mororway	
	concentration	standard deviation	concentration	standard deviation	concentration	standard deviation
ALKANE						
ethane	12.3	*11.5*	5.0	*2.8*	3.2	*1.4*
propane	18.5	*12.9*	4.1	*3.1*	2.0	*1.3*
2-methylpropane	11.3	*7.9*	2.4	*2.5*	0.9	*0.7*
n-butane	23.3	*16.4*	4.9	*4.5*	2.1	*1.6*
3-methylbutene	13.7	*11.2*	4.0	*3.5*	2.7	*3.0*
2-methylbutane	34.7	*25.7*	12.6	*10.9*	7.7	*8.9*
n-pentane	17.8	*13.5*	2.8	*2.4*	1.4	*1.4*
2,2-dimethylbutane	4.0	*3.0*	0.9	*1.1*	0.3	*0.1*
cyklopentane	0.6	*0.2*	0.5	*0.2*	2.0	*0.7*
2,3-dimethylbutane	9.9	*8.9*	2.0	*1.5*	1.4	*1.1*
2-methylpentane	12.9	*10.0*	2.9	*2.0*	1.5	*1.9*
3-methylpentane	7.5	*6.9*	1.5	*1.9*	0.5	*0.3*
n-hexane	10.4	*9.2*	1.9	*1.9*	1.0	*1.3*
methylcyclopentane	0.9	*1.0*	0.6	*0.3*	0.5	*0.5*
2,4-dimethylpentane	7.6	*6.4*	0.8	*0.7*	0.6	*0.6*
cyclohexane	6.7	*9.5*	1.2	*1.9*	7.2	*10.8*
2-methylhexane	8.0	*7.5*	1.5	*1.2*	1.6	*1.9*
2,3-dimethylpentane	2.8	*2.0*	1.3	*2.5*	0.6	*0.3*
3-methylhexane	7.9	*6.4*	1.8	*1.3*	2.0	*4.8*
2,2,4-trimethylpentane	6.9	*5.9*	1.0	*1.1*	1.4	*2.8*
n-heptane	10.6	*10.0*	1.7	*2.7*	0.5	*0.5*
methylcyclohexane	5.5	*5.6*	1.1	*1.8*	0.5	*0.3*
2,3,4-trimethylpentane	3.7	*3.0*	0.9	*0.7*	0.8	*1.8*
2-methylheptane	4.6	*4.2*	0.8	*0.6*	1.8	*6.4*
3-methylheptane	2.8	*6.1*	1.6	*3.7*	2.8	*7.0*
n-octane	3.7	*3.9*	3.1	*5.2*	1.8	*2.5*
n-nonane	1.1	*0.9*	0.9	*0.9*	1.0	*0.4*
ALIPHATIC NONSATURATED HYDROCARBONS						
ethylene	30.7	22.9	6.1	4.3	3.0	2.0
acetylene	30.2	22.9	4.5	2.8	1.6	1.3
propene	14.0	9.9	2.2	2.0	1.0	0.7
1-butene	9.5	12.7	2.9	9.3	0.7	0.4
1,3-butadiene	5.8	4.4	2.7	2.7	2.3	3.6
trans-2-butene	3.1	2.2	1.6	3.5	0.7	0.8
cis-2-butene	3.0	2.3	0.6	0.3	0.7	0.6
1-pentene	4.7	5.8	0.7	0.7	0.6	0.5
isoprene	4.0	4.1	0.8	0.6	0.5	0.2
trans-2-pentene	4.3	4.7	0.6	0.4	0.3	0.1
cis-2-pentene	2.2	2.3	0.3	0.1	0.4	0.5

Table 2. continues on next page.

2-methyl-2-butene	2.2	*3.1*	0.4	*0.3*	0.4	*0.2*
cyclopentene	2.8	*2.1*	0.5	*0.4*	0.4	*0.2*
4-methyl-1-pentene	3.0	*5.0*	1.0	*0.8*	0.4	*0.2*
2-methyl-1-pentene	5.3	*9.6*	0.5	*0.3*	0.4	*0.1*
trans-2-hexene	1.2	*0.9*	0.4	*0.5*	0.6	*0.6*
cis-2-hexene	1.1	*0.9*	0.5	*0.5*	3.2	*7.2*
alpha-pinene	4.0	*3.0*	4.2	*6.5*	5.7	*4.2*
beta-pinene	9.7	*11.0*	5.0	*4.0*	1.4	*0.8*
AROMATIC HYDROCARBONS						
benzene	30.9	*21.8*	11.9	*11.2*	11.5	*28.4*
toluene	76.6	*65.9*	8.1	*7.9*	3.5	*4.5*
ethylbenzene	20.0	*21.1*	2.0	*2.6*	0.8	*1.2*
p,m-xylene	52.5	*54.3*	4.8	*5.9*	2.2	*3.7*
styrene	3.7	*3.4*	1.8	*3.4*	0.9	*1.2*
o-xylene	25.7	*26.4*	3.7	*3.0*	1.7	*1.2*
isopropylbenzene	0.6	*0.5*	4.5	*4.8*	0.7	*0.6*
n-propylbenzene	5.5	*5.1*	1.8	*2.1*	3.2	*3.5*
1,3,5-trimethylbenzene	6.7	*6.3*	1.9	*2.3*	0.9	*0.7*
1,2,4-trimethylbenzene	23.8	*23.0*	3.5	*6.6*	1.1	*1.4*
Summary of identyfied hydrocarbons	895.7		167.0		100.4	
number of samples	70 (in 17 days)		50 (in 12 days)		30 (in 6 days)	

the two cities. Figure 3 shows that the percentage concentrations of a number of compounds are similar in both Kraków and Vienna. The discrepancy in concentration appeared, however, for a few compounds, e.g. ethene, *n*-butane and *n*- pentane. But it was shown in [17] that the differences in concentrations were brought about by different analytical procedures used. Two different columns of dissimilar selectivity were used for separation of hydrocarbons (DB-1 in Kraków and GS-Alumina Plot in Vienna) and the air was sampled with the use of canisters and sorption tubes respectively. The influence of sampling methods and different gas chromatographic systems on the determination of concentrations of volatile hydrocarbons was described in the mentioned work in detail.

Estimation of the Contribution of Traffic to Air Pollution

Taking into consideration the above remarks the estimation of the contribution of traffic to air pollution was done for two areas: one in the city center (i.e. for the area of Trzech Wieszczów Av.) and the other one for the area outside the city (i.e. the A-4 motorway). The literature data of the tunnel studies carried out in 1996 and 1998 in Sydney [14] and in Vancouver [15], respectively, were employed in the calculations. In these studies the levels of hydrocarbons were measured in the air in the tunnels over the motorways of heavy traffic. Such measurements are one of the ways to determine hydrocarbon emissions besides dynamometric studies. The fact that normally in urban areas acetylene appears exclusively from traffic was helpful in the estimation (other hydrocarbons can be produced by other sources) [19]. In the calculations the mean concentrations of individual hydrocarbons were normalized towards the percentage of acetylene obtained in the tunnel studies. Traffic and other antropogenic and biogenic sources produce the concentrations of hydrocarbons determined in both areas: Trzech Wieszczów Av. and A-4 motorway. By subtracting the concentrations of the compounds taken from the tunnel studies from the normalized concentrations, and re-calculating them back to concentrations in the air, the concentrations produced by non-traffic sources were obtained. For the compounds for which the normalized concentrations were lower than those obtained from the tunnel studies it was assumed that these concentrations come exclusively from traffic.

The calculations performed using the Sydney tunnel data revealed that in the area of Trzech Wieszczów Av. 2/3 of the mass of hydrocarbons come directly from traffic (Table 3). Among compounds coming from other sources in the highest concentrations appeared aromatic hydrocarbons, i.e. toluene, xylenes, 1,2,4-trimethylbenzene

Table 3. The way of calculation of hydrocarbons concentration of both traffic and non-traffic origin.

Compound	Tunnel studies - mean concentration values [µg/m³]	Trzech Wieszczów Av. [µg/m³]				
		mean concentration values	concentration normalized towards acetylene	substracts column 4 from 2	imission from non-traffic sources	imission from traffic sources
1	*2*	*3*	*4*	*5*	*6*	*7*
ethylene	8.3	33.9	8.6	0.3	1.1	32.8
acetylene	8.9	34.9	8.9	0.0	0.0	34.9
ethane	2.6	12.0	3.0	0.4	1.6	10.4
propene	6.9	15.7	4.0	-2.9	0.0	15.7
propane	5.8	18.6	4.7	-1.1	0.0	18.6
1-butene	1.3	10.5	2.7	1.4	5.3	5.2
1.3-butadiene	1.5	6.9	1.7	0.3	1.1	5.7
n-butane	5.2	24.1	6.1	1.0	3.8	20.3
trans-2-butene	0.9	3.6	0.9	0.0	0.0	3.6
cis-2-butene	0.8	3.7	0.9	0.1	0.6	3.1
2-methylbutane	8.5	41.9	10.6	2.2	8.5	33.3
n-pentane	3.3	20.1	5.1	1.8	7.1	13.0
2-methylpentane	3.4	14.8	3.8	0.3	1.2	13.5
3-methylpentane	2.2	9.5	2.4	0.2	0.7	8.9
n-hexane	2.1	12.1	3.1	1.0	3.8	8.3
methylcyclopentane	1.3	2.5	0.6	-0.7	0.0	2.5
2,4-dimethylpentane	0.5	8.3	2.1	1.6	6.2	2.1
benzene	6.9	33.3	8.5	1.6	6.2	27.1
2- + 3-methylhexane	3.0	18.0	4.6	1.5	6.0	12.0
n-heptane	0.9	12.7	3.2	2.3	9.1	3.6
methylcyclohexane	0.7	6.5	1.6	1.0	3.9	2.6
toluene	12.3	88.3	22.4	10.1	39.9	48.4
ethylbenzene	1.7	26.2	6.6	4.9	19.4	6.8
p,m-xylene	6.5	66.5	16.9	10.4	41.0	25.5
o-xylene	2.4	32.2	8.2	5.8	22.8	9.4
1,3,5-trimethylbenzene	0.5	12.5	3.2	2.7	10.5	2.1
1,2,4-trimethylbenzene	1.5	28.6	7.3	5.8	22.9	5.7
Total	100.0	598.0	151.9	51.9	222.6	375.4
Percentage					37 %	63 %

and ethylbenzene. In considerably lower concentrations from other sources appeared aliphatic hydrocarbons, and among those were found mainly 6-carbon hydrocarbons.

If, however, the calculations were based on data from [15], the amount of traffic-generated hydrocarbons in the area of Trzech Wieszczów Av. was estimated to be 80%. In that work a higher number of compounds was identified and therefore in the calculations 40 hydrocarbons could be taken into account. Among the hydrocarbons emitted by non-traffic sources again aromatic hydrocarbons were prevalent.

Analogous calculations were done for the air around the A-4 motorway, and the results are presented in Figures 4a and 4b. Similarly to the area of Trzech Wieszczów Av., the traffic-generated concentrations of hydrocarbons calculated on the basis of the data of the tunnel study performed in Vancouver were higher than those based on the Sydney data. In the first case it was found that about 50% of hydrocarbons in the atmospheric air above the A-4 motorway are produced by vehicles and in the second case that the percentage of these contaminants in the air is lower and equal to 30%.

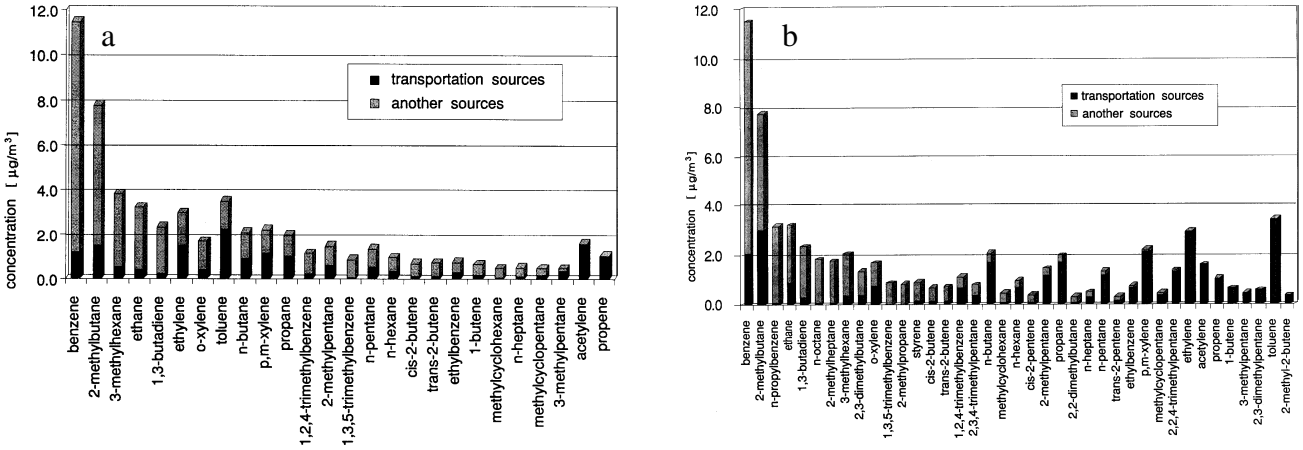

Fig. 4. The mean values of the concentrations of the hydrocarbons identified in the area of the A-4 motorway, classified as traffic-generated and others, in the order of decreasing concentration coming from other sources: a)calculations based on the data from the Sydney study; b) calculations based on the data from the Vancouver study.

Benzene and 2-methylbutane were the compounds coming mainly from sources other than traffic in the studied rural areas, in both methods of calculations.

The difference between the calculated contributions of traffic and of other sources to the measured imission of hydrocarbons on the basis of two different tunnel studies is for both Trzech Wieszczów Av. and the A-4 motorway of the same magnitude, i.e. nearly 20%. It seems that this discrepancy arose among others from different kinds of vehicles driven in Sydney and Vancouver and different kinds of fuels used in the two cities. It is difficult to judge if Sydney or Vancouver simulates Kraków conditions better and, consequently, which estimate of traffic contribution to pollution is better. The presence of negative values in column 5 in Table 3 might be connected with the errors of the concentration but also might be the size of discrepancy between the literature model and polish conditions. In such an approach the better fitting was for the Sydney data.

Conclusions

- A big number of volatile organic compounds occur in ambient air in Kraków and its environs. The presence of at least 150 of C_2-C_{12} compounds was stated at the concentration above 0.2 µg/m^3 (the method detection limit).
- Traffic constitutes a considerable thread to humans and to the natural environment. The normative concentration of benzene was exceeded both in Kraków and around the A-4 motorway[20]. It is a very worrying situation because of the carcinogenic and mutagenic character of benzene. But an alarming situation is found in the center of the city were a lot of people are exposed to the high concentration of toxicants.
- The profiles of hydrocarbon concentration in air around the source of contamination are differential and depend on meteorological and architectural conditions. Motorways running outside cities are less harmful regarding the pollution of the air, as the contaminants undergo quicker distribution and, practically, their accumulation does not occur.
- Traffic plays a decisive role in the overall imission of hydrocarbons in Kraków – its contribution was estimated at 63-80% according to used model calculations. The contribution of traffic to the contamination of air in the open areas outside Kraków is smaller than in the city center, it was estimated at about 40 %. The rest of hydrocarbons are coming from other antropogenic and biogenic sources.
- The high level of VOC concentrations might cause the contamination of soils and waters in the vicinity of the roads. Moreover, traffic worsens the comfort of life by producing noise and vibrations. The impact of motorways on the natural environment varies and depends on the contaminants and part of the environment concerned.

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