Automotive air pollution in Poznan from benzene: sources and reduction measures

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Abstract

Over the Copernicus Roundabout in Poznan, which is one of the largest cities in Poland, an automatic measuring system OPSIS has been installed to measure on-line the concentration of pollutants in the air. The Copernicus Roundabout is located in the city centre, close to the International Poznan Fair and near the main railway station Poznan Central. Five main streets cross here and the traffic congestion here is the greatest in the city. The concentration of benzene and aromatic hydrocarbons taken by OPSIS are at alarmingly high level close to permissible value or even exceeding it. Because of that the Department of Environment Protection of City Council in Poznan decided to create a special team of experts to examine and explain this phenomenon and find all possible solutions. The team's research proved that it is gasoline vehicles that are responsible for high concentration of benzene and aromatic hydrocarbons at the Copernicus Roundabout and at many other crossroads in Poznan.
This paper describes the results of the team's work, which are as follows: measurements of benzene and aromatic hydrocarbons concentration at chosen crossroads of Poznan, sources of benzene and aromatic hydrocarbons emission and the conditions that enable this emission to spread, the analysis of city traffic conditions promoting greater emission of benzene and aromatic hydrocarbons, the inspection of benzene and aromatic hydrocarbons content in gasoline available at Poznan filling stations, possible ways of reducing the benzene and aromatic hydrocarbons concentration in the air in the vicinity of crossroads with great intensity of city traffic.

1 Introduction

The emission of automotive pollution, as an extreme case of low emission, directly affects people, both participants of city traffic (automobile, bicycle or pedestrian traffic) and residents of regions in the vicinity of the road infrastructure, who are especially subject to a long-time exposure to pollutants. This effect is extremely troublesome in the city agglomeration as the specific town topography and climate conditions often cause a very serious limitation for the motor pollution dispersion area. As a resultant effect there are high levels of momentary and average pollution concentrations recorded in the staying and residence areas of a significant number of people.

Among the automotive pollutants, aromatic hydrocarbons, the mononuclear and polynuclear ones, are especially considered. It is benzene from among the mononuclear aromatics that is extremely toxic and has some carcinogenic, mutagenic, teratogenic and embryotoxic features. In practice there is no benzene emission from the biogenic sources. The main source of the anthropogenic emission of benzene are gasoline vehicles, i.e. mostly passenger cars (Fig.1).

In Poland the permissible values for the concentration of benzene in the air are specified in the Directive of the Ministry of Environmental Protection, Natural resources and Forestry of 24 April, 1998 and they are as follows: D_{30} = 20 $\mu g/m^3$, D_{24} = 10 $\mu g/m^3$, D_a = 2,5 $\mu g/m^3$.

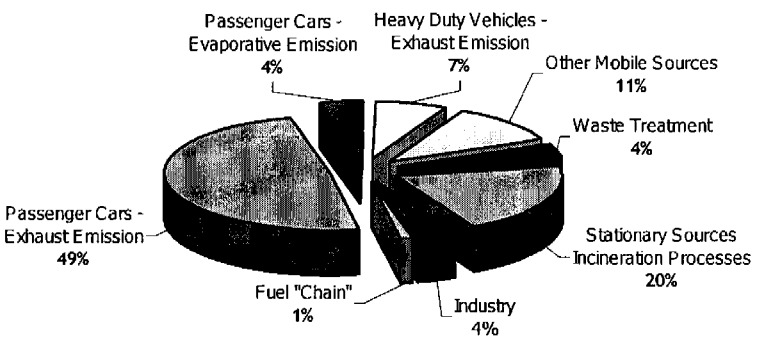


Fig. 1. Contribution of various sources to anthropogenic benzene emissions in Germany (reference year 1995) [6]

In the Directive 96/62/EC of the European Commission, benzene (as only one of the organic compounds) has been qualified as one of the priority pollutants discussed in the basic document which specifies the requirements on the evaluation and quality control of air. The Directive 00/69/EC (as approved on 16 November, 2000) specified the limit value D_a for benzene at a level of 5 $\mu g/m^3$ [3]. The present margin of tolerance relating to the concentration limit value of 5 $\mu g/m^3$, ranging up to 100%, will be

no more allowed in 2006 and subsequently it will be still reduced till the year 2010 when the limit value is assumed to be achieved in all union countries.

2 Benzene pollution in air at transportation roads in Poznan

In 1993 the Provincial Inspectorate of Air Protection in Poznan (the fifth town in Poland, very significant centre of trade, science and culture) installed the OPSIS system for automatic measurements of air pollutants using the optical absorption spectroscopy method. The 24-hour measurements of such pollutants as sulphur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3), benzene (C_6H_6), toluene (C_7H_8), p-xylene (C_8H_{10}) and formaldehyde (CH_2O) are taken by this station. This system is also equipped with instruments which are able to measure the speed and direction of the wind and temperature as well. The measurements of pollution concentrations are carried out in the air over the Copernicus Roundabout, one of the most traffic loaded junctions in Poznan. The maximum capacity of this roundabout of 5500 vehicles per hour is being recorded for a significant part of every day and results in a lack of traffic fluency, traffic jams, and stoppages. The location of this roundabout in the city centre at the crossing of busy communication roads, namely Roosvelta – Głogowska and Sw. Marcin – Zwierzyniecka and Grunwaldzka as well, and close to main railway station Poznan Central is a reason for which independently on the wind direction (especially for slower winds) pollutions emitted elsewhere, also far from this roundabout, are being transmitted there.

The concentrations of benzene in the air recorded by the OPSIS system in 2000 were of alarmingly high levels [10]. The records of 24-hours concentrations of benzene (Fig. 2) and the average concentration values (Table 1) showed levels exceeding (for a complete time period) the permissible value. The relatively high concentration values averaged for one hour over the one month period were also recorded during night hours i.e. at time of a poor intensity of traffic. At the same time in the concentration records some distinct peaks for traffic rush hours and their season-dependence can be observed.

In connection with the alarmingly high concentrations of benzene in the air over the Copernicus Roundabout signalled by the OPSIS system the Department of Environmental Protection of City Council in Poznan decided to create in 2001 a special team of experts in order to perform the verification of the level of the benzene contamination in the air by the additional independent measurements of benzene concentrations at the selected communication junctions in Poznan. In November 2001 some independent measurements of the benzene concentration in air were taken in Poznan at the Copernicus Roundabout and Garbary street. These measurements were carried out by the laboratory of the Provincial Inspectorate of Air Protection (chromatography identification, sampling time of about 120 minutes) The results of these measurements are presented in Table 2.

The results of the independent examination showed the values similar to those recorded by OPSIS system, i.e. the average value of benzene concentrations at the Copernicus Roundabout was of 11,8 $\mu m/m^3$ (OPSIS – 13,91 $\mu m/m^3$ in November 2000). At the Garbary Street slightly higher concentration

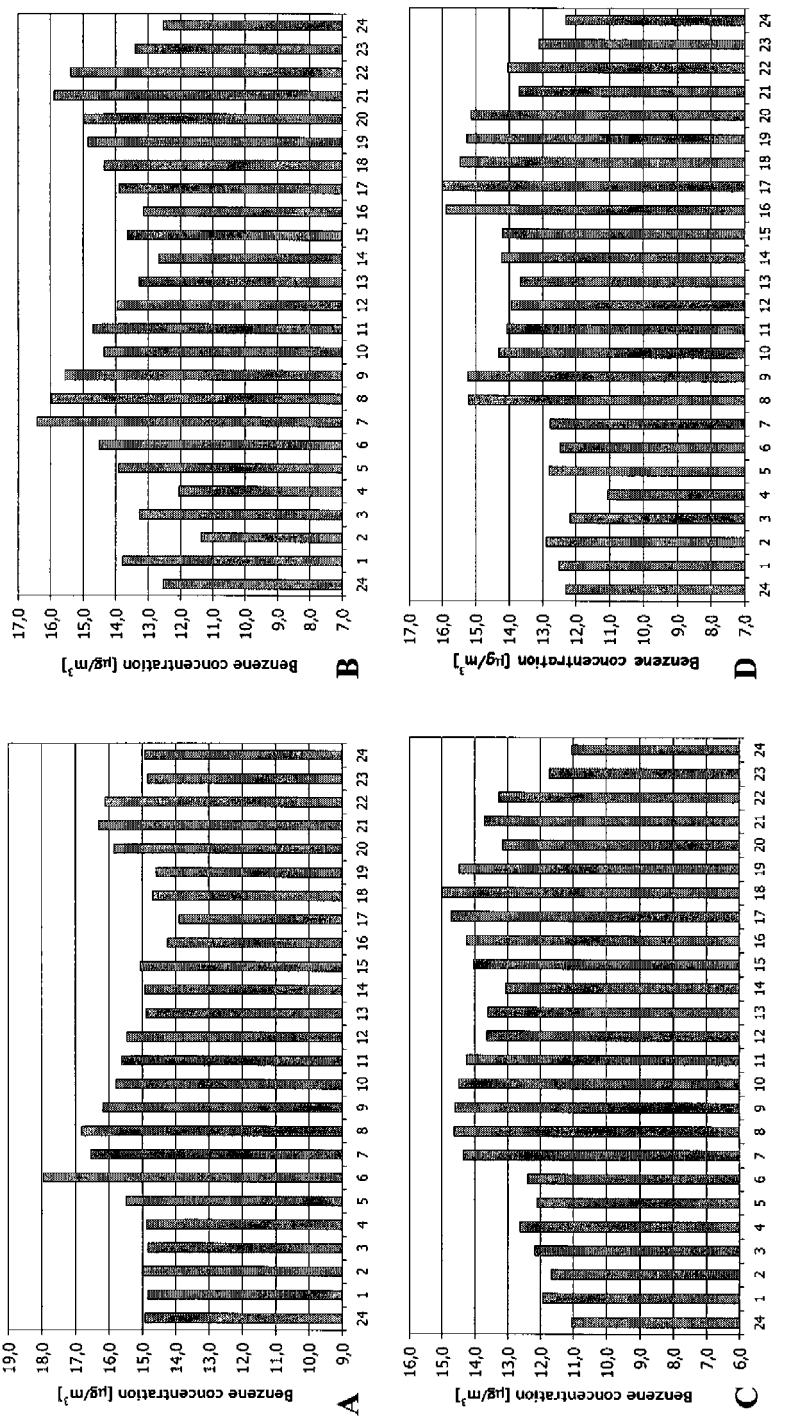


Fig. 2. Twenty-four hours benzene concentrations in the month of: (A) – May, (B) – September, (C) – October, (D) – November, taken by automatic measuring system OPSIS over the Copernicus Roundabout in Poznan in the year 2000

Table 1. The 30-min benzene concentrations in 2000 according to OPSIS [10]

Month	S_{30} av. [μm/m^3]	S_{30} min.[μm/m^3]	S_{30} max.[μm/m^3]
May	15,36	0,50	34,4
June	14,21	0,10	24,2
July	14,96	0,40	22,6
August	12,92	0,50	24,6
September	14,11	1,20	29,8
October	13,47	0,30	23,3
November	13,91	0,80	23,2
December	11,81	0,40	20,6

Table 2. The results of measurements of benzene concentrations at the transportation routes in Poznan taken in November, 2001 [7]

Location	Date	Time	Air temp. [°C]	Direction of the wind	Traffic flow [veh./h]	**Benzene concentr. [μg /m^3]**	Comments
Garbary Street	13.11.	14.55-16.15	5,6	N	1090	**20,7**	
Copernicus R.	13.11.	14.15-16.15	7,0	N	2736	**15,0**	
Copernicus R.	13.11.	16.15-18.15	7,0	N	2867	**23,3**	
Garbary Street	15.11.	14.30-16.30	1,4	S	1253	**5,6**	Strong wind
Copernicus R.	15.11.	14.10-15.45	1,4	W	2580	**7,6**	
Copernicus R.	15.11.	15.50-17.30	1,4	W	2924	**6,6**	
Garbary Street	20.11.	15.00-17.30	6,0	S	1145	**11,7**	
Copernicus R.	20.11.	15.30-17.00	6,0	W	2647	**8,5**	
Copernicus R.	20.11.	17.10-18.30	6,0	W	2789	**9,5**	

value (12,7 μm/m^3) than at the Copernicus Roundabout was recorded and probably to a certain extent it resulted from the specific "tunnel" arrangement of this street. The potential summation of local and transmitted pollutions is a factor which can significantly affect the pollution concentration values. However, at the same time at the increased wind velocity the effect of the roundabout ventilation ability itself can lower the concentration values. There are reasons to assume that the results of measurements taken at the heavy traffic roads of poor ventilation degree (street tunnels) could show higher benzene concentration values, especially at the unfavourable directions of wind.
As high concentrations of benzene in the air at the transport roads in Poznan were proved by the verification measurements, the group of experts created by the Department of Environment Protection of City Council started their research work in order to find an explanation of the mechanism of the existing phenomenon and develop the potential preventive measures. The work of this group led to the conclusion that high concentrations of benzene in air resulted chiefly from the exhaust gas emission from the gasoline vehicles. The explanation of this effect is discussed in the following part of this paper.

3 Emission of benzene from vehicles in city traffic conditions

3.1 Engine operating conditions during urban driving

City traffic has many specific features which differentiate it from the long distance or motorway one. Its main features are frequent changes in load and

rotational speed of vehicle engines, i.e. non-stationary operating conditions resulting from very changeable traffic conditions – frequent starting (crossroads), accelerating followed by slowing-down (braking), stopping and again start moving. A great percentage of engine operation at idling in a total engine operation time is the next feature of the urban traffic.

A low speed of travelling is another distinctive feature characteristic for urban driving. This speed is legally limited for safety reasons. However, small average speed experienced in city traffic result chiefly from a great congestion caused by the transportation road systems solutions which are inadequate in relation to the traffic intensity and cause breaks in driving and consequently traffic jams and stoppages.

The city driving is also characteristic because of its beginning from starting the cold engine vehicle which is followed by a lasting for some time drive with the non-warmed up engine. In cities most vehicles are only periodically operated i.e. they are used in order to get home from a place of work or for shopping etc. During their several hour long inter-drive breaks the vehicles are parked outdoors and they reach the ambient temperature. In such a situation their restartings are cold engine startings which are again followed by warming-up phases of engine operation. Taking into account that urban driving are short (approx. 5 km average), performed at low load and a long time operation at idling, it can be stated that during such driving the nominal operating temperatures cannot be reached by some of the engines [2].

These most important features of urban traffic mentioned above are disadvantageous when a car engine operation is considered. They disturb the fuel combustion process in the engine and cause the improper operation of many of its systems. The incorrectness of the engine operation connected with some special features of urban traffic manifests itself in the reduced driving abilities of the engine, increased fuel consumption and increased exhaust emissions, mostly products of the incomplete combustion. The exhaust emissions in the unsteady operating conditions which are typical for urban traffic, is many times higher than the emission in case of the steady state operation [8].

3.2 The chemical and physical features of the engine work cycles resulting in the hydrocarbons emission

More than 200 hydrocarbons (HC) have been identified in car engine exhaust gas and among them the simple aromatic hydrocarbons are met in the largest amount. The presence of hydrocarbons in vehicle exhaust results from an incomplete fuel combustion. The incomplete combustion of hydrocarbons in the engine can be caused mainly by the following reasons:

- a lack of oxygen (global, local),
- misfiring,
- oil consumption,
- fuel and oil evaporation.

The global deficiency of oxygen occurs when the combustion chamber is supplied with a rich fuel mixture ($\lambda < 1$) i.e. with the fuel mixture comprising too much fuel in relation to the stoichiometric composition ($\lambda = 1$). In case of

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Diesel engines a rich air-fuel mixture is not existing, however, for spark ignition engines the rich air-fuel mixture is being dosed at the moments of the increased power demand, i.e. first of all during the acceleration that often occurs in conditions of the urban driving. Another situation during urban driving leading to the global enrichment of a fuel mixture occurs when braking the vehicle with use of engine load. Such enrichment is caused by the intensive grabbing of fuel absorbed on walls of the intake manifold due to an increase of the negative pressure in the intake system as a result of a throttle backing. According to [4] the hydrocarbons emission produced by braking the vehicle with use of engine load is composed largely of aromatic hydrocarbons.
In case of spark-ignition engines a local deficiency of oxygen is caused by non-homogeneity of mixture in a combustion chamber. Non-homogeneity of air-fuel charge occurs when too poor turbulence of charge occurs in a combustion chamber. Such operating conditions are characteristic for an engine running at a low speed, and especially at idling, that is in a situation often experienced in urban traffic. According to [9], xylenes are dominant components of the HC emission from the spark-ignition engines in idle running conditions and their concentration is of about 150 ppm (m/m).
The dilution of charge with exhaust gas remaining from the earlier cycle is conductive to misfiring as high exhaust pollution brings about the incombustibility of mixture. This effect intensifies when the engine load decreases due to a throttle backing and is the most intensive at idle running.
When considering the HC emission from vehicles the emission of these chemical compounds by fuel and lubrication oil evaporation should be taken into account. Only very small amounts of hydrocarbons are emitted in such a way by the diesel vehicles, however, in case of gasoline vehicles this evaporative emission can be of even 30% of total hydrocarbons emission. The main sources of such emission are the supplying and fuel systems and the crankcase venting system as well. The highest emission is recorded from the old carburettor vehicles which are not equipped with fuel vapour absorbers. As their fuel systems are not hermetic they can emit the hydrocarbons even when their engines are stopped. It is worth noticing that the evaporative emission is also determined by the composition of gasoline and any reduction of benzene content results in a decrease of this emission level.

3.3. Vehicles equipped with catalysts

There are catalysts installed in the exhaust systems of modern cars in order to reduce the pollutant emissions from exhaust gas. It is obvious that when the catalyst is used the hydrocarbons emission decreases, however, it is also symptomatic that composition of hydrocarbons changes (Table 3). It results from a varied catalysts capabilities of oxidising the individual groups of hydrocarbons. The unsaturated hydrocarbons, i.e. acetylene hydrocarbons (alkynes) and olefins undergo the oxidation most easily. The saturated hydrocarbons (paraffines) are most hardly oxidised – their percentage share in hydrocarbons in exhaust gas after passing the catalyst nearly doubles. The aromatic hydrocarbons have an intermediate capability to be subject to the catalytic combustion process in the

catalyst and their contribution to the HC emission from the spark-ignition engines, with and without catalysts, is similar. It is worth noticing that the catalyst efficiency is dependent on the catalyst operating temperature. The catalyst starts the effective oxidation of hydrocarbons having reached the so called light-off temperature which for hydrocarbons is usually of about 250 – 300°C and rises as the catalysts ages. Below this temperature its efficiency significantly drops and only more reactive hydrocarbons (unsaturated) can be still oxidised or the catalytic combustion process generally ceases. The catalyst temperature depends on the exhaust gas temperature which in turn is conditioned by engine loads. In urban driving conditions i.e. at low engine loads and a serious contribution of idling the catalyst temperature is often too low for performing the catalytic combustion process for less reactive hydrocarbons, benzene for instance, in the effective way.

Table 3. The comparison of average composition of hydrocarbons in exhaust gas emission from spark-ignition engines with or without catalysts [5]

	Percentage share of individual hydrocarbons in total HC emission			
	Paraffins	Olefins	**Aromatics**	Acetylene
Without catalyst	33	27	**32**	8
With catalyst	57	15	**26**	2

The recombination of hydrocarbons can also take place in the catalyst. For the problems discussed here the process of alkylobenzene-to-benzene conversion is of special importance. The simplest alkylobenzenes are basic components of the hydrocarbons in exhaust gas emission from spark-ignition engines, so there are plenty of substrates to form benzene.

In the process of benzene formation in the catalyst the dealkylation of alkylobenzenes takes place. This dealkylation process is performed in the same way as the one in a combustion chamber which was earlier discussed, however, it can be more intensive as it proceeds in the presence of the three-way catalyst.

The process of dealkylation can be performed in the most effective way in presence of water vapour, and especially of hydrogen. Hydrogen exists in exhaust gas in case of a rich mixture of fuel i.e., for example, while accelerating a car (in general, in transient operating conditions of spark-ignition engines. The dealkylation is the most effective at temperature of 400 – 500°C, but it already starts below the light-off temperature of the catalyst [9]. The mentioned facts prove that during urban driving there are same conditions which are promotions for the formation of benzene in the vehicle's catalyst.

3.4 The cold engine starting and warming-up phase

In fact every urban driving starts from the cold engine starting and its succeeding warming-up phase. It is a car engine's operation period (especially in case of spark-ignition engines)for which the highest emission of hydrocarbons occurs. It is caused by a low vehicle and engine temperature that induces many disadvantageous effects resulting in high emission of hydrocarbons. They are, first of all, instability of combustion process and low efficiency of catalytic

exhaust emission control systems. The HC emission intensity from the engine during its initial warming-up phase is nearly 1000 times higher than during the engine's thermal stability period. After warming-up phase the HC emission from the hot engine can be as low as a background level.
During the cold starting the walls of the inlet system combustion chamber are cold (they have an ambient temperature) that significantly limit the evaporation of fuel. To ensure the fuel vapour amount needed to start the engine, additional fuel for enriching the air-fuel mixture has to be dosed. During starting and the first cycles of operation the air-fuel ratio is about 8 to 15 times higher than the stoichiometric one [1]. It is obvious that in such conditions (high deficiency of oxygen) only a small part of supplied fuel is being combusted and most often in an incomplete way. The remaining fuel is thrown out to the exhaust system or is kept in a liquid form (fuel film) in the inlet manifold or combustion chamber causing an uncontrolled enrichment of fuel mixture that leads to an increase of the hydrocarbons emission. After starting, the enrichment of fuel mixture still proceeds for time of several decades of seconds (the enrichment level decreases as the engine warms up) in order to ensure the stable engine operating conditions and good driveability.
If even there is a catalyst installed in the vehicle's exhaust system it does not perform its function at the initial phase of engine operation as it has too low temperature. The catalyst reaches the relevant light-off temperature needed for its effective operation only after a several kilometre long driving that follows the cold starting. Taking into account the fact that the urban drives are short it often happens that the catalyst is not able to start its operation. The frequent rich mixture operation negatively affects the catalyst durability and causes an increase of its light-off temperature.
In order to limit the HC emission during the starting and warming-up periods it should be aimed to reach the nominal operating temperature as soon as possible. The best warming-up the engine and catalyst takes place when the engine is operated under load. The specificity of urban driving with a significant percentage of idling and the engine operation at low load is not promotions for the warming-up process.

4 Summing-up and conclusions

- The dominant source of benzene emission in Poznan are gasoline vehicles; this emission mostly comes from exhaust gas and, to smaller degree, from gasoline and oil evaporation,
- The significantly higher benzene emission from the vehicles in the urban traffic conditions is caused by some disadvantageous features of vehicle engine operating conditions connected with a specificity of such traffic, namely:
  - ✓ Transient engine operating conditions – a lack of the traffic fluency, frequent accelerating and slowing down,
  - ✓ Significant percentage of engine operation at idling and low load,
  - ✓ Frequent engine starting (usually cold),
  - ✓ Significant percentage of driving with engine which has too low temperature,

- ✓ The extended time of reaching by exhaust emission control system the temperature necessary for the effective operation.

- Cars without catalysts and with damaged or worn out catalysts make a significant contribution to the benzene emission.

As a significant reduction of benzene pollution in the air in Poznan and other towns in Poland is necessary, the undertaking of the following actions is considered to be suitable, namely:

- ✓ Reduction of benzene and aromatic hydrocarbons content in gasoline at least to a level which is obligatory in the European Union countries,
- ✓ Promotion of gas fuelled vehicles (propane-butane, natural gas), which are free of benzene and other aromatic hydrocarbons,
- ✓ A detailed inspection of technical conditions of vehicles during the registration surveys, especially of the effectiveness of the catalytic exhaust emission control system (catalyst + exhaust gas oxygen sensor).

References

[1] Bielaczyc P., Merkisz J., Pielecha J.: Stan cieplny silnika spalinowego a emisja związków szkodliwych. Wydawnictwo Politechniki Poznańskiej, Poznan 2001.

[2] Bielaczyc P.: Analiza wpływu fazy rozruchu i nagrzewania się silnika ZI na emisję toksycznych składników spalin. Praca doktorska. Politechnika Poznańska 2000.

[3] Directive 00/69/EC of the European Parliament and the Council of 16 November 2000 relating to limit values for benzene and carbon monoxide in ambient air.

[4] Frey R., Nagel H., Franzen J., Rikeit: Time-resolved measurements of individual hydrocarbons in automotive exhaust at transient engine operation. SAE Technical Paper 951053.

[5] Heywood J.B.: Internal Combustion Engine Fundamentals. McGraw-Hill Book Company, Series in mechanical engineering USA 1988.

[6] Lenz H.P., Cozzarini C.: Emissions and Air Quality. Society of Automotive Engineers Press 1999.

[7] Merkisz J., Bagienski Z., Kozak M.: Przeprowadzenie badań i sporządzenie opinii naukowej dotyczącej przyczyn wykazywania podwyższonych stężeń benzenu w pomiarach zanieczyszczeń powietrza na Rondzie Kaponiera w Poznaniu. Praca wykonana na zlecenie Wydziału Ochrony Środowiska Urzędu Miasta Poznania, Poznań 2001.

[8] Merkisz J.: Ekologiczne problemy silników spalinowych t.2. Wydawnictwo Politechniki Poznańskiej, Poznań 1999.

[9] Nagel H. i in.: On-line Analysis of Individual Aromatic Hydrocarbons in Automotive Ehhaust: Dealkylation of the Aromatic Hydrocarbons in the Catalytic Converter. SAE Technical Paper 971606.

[10] Wyniki pomiarów stężeń zanieczyszczeń powietrza nad Rondem Kopernika w Poznaniu w 2000 r. Wojewódzka Inspektorat Ochrony Środowiska w Poznaniu; materiały nie publikowane.