Original Research

BTX Air Pollution in Zabrze, Poland

H. Pyta*

Institute of Environmental Engineering of the Polish Academy of Sciences,
ul. M. Skłodowskiej-Curie 34, 41-819 Zabrze, Poland,

Received: December 5, 2005
Accepted: April 14, 2006

Abstract

This paper presents results of monitoring of benzene and its alkyl derivatives (BTX) in ambient air. The measurements were performed in Zabrze, using an automatic analyzer. Concentrations of BTX from August–September 2001 and August–September 2005 were compared. The experiment of comparison was done to assess effects on air quality of the coking installation shutting down. The mean concentration of BTX significantly dropped. In general, neither the character of diurnal distribution of BTX concentrations nor the concentration maxima changed. Instead, in 2005, the share of low concentrations was greater and high BTX episodes were less frequent.

Keywords: air pollution, air quality monitoring, urban background, BTX, benzene

Introduction

Benzene and its alkyl derivatives (BTX) are especially harmful for human health, because of their toxic, mutagenic or carcinogenic properties [1]. In particular, benzene is characterized as a human carcinogen [2]. It has low acute toxicity but repeated exposure to high concentrations can cause effects on blood and blood-forming organs [3]. The most convincing evidence is found for the development of leukaemia as a result of benzene exposure [4]. Toluene and xylenes strongly affect the nervous system. They may induce brain function disturbances and problems with balance, vision, hearing and speech. They may also induce damage to kidneys or liver. Some studies suggest a connection between the brain tumours and toluene and xylenes exposure. However, the knowledge on the carcinogenicity of these pollutants is still insufficient [5].

Benzene and some other monocyclic aromatic hydrocarbons commonly occur in urban ambient air [6, 7,]. These air pollutants contribute to the formation of tropospheric ozone [8, 9]. They come mainly from combustion of liquid fuels in car engines, and also from combustion processes in energy production and domestic heating, and from such industrial sources as refineries or cokeries [10-13]. The emission of BTX from traffic is determined by driving conditions, car fleet and fuels composition [14]. Within a city the concentration of BTX might vary with a factor of 5 from street canyons to urban background areas [15]. According to measurements carried out in Germany in 1997, the mean annual concentrations of benzene were in the range of 3.7 to 16 μg/m^3 in the road's vicinity and in the range of 1.8 to 5.7 μg/m^3 in urban background conditions. The mean annual benzene concentration 10.2 μg/m^3 was noted near a cokery in Duisburg [10].

The legislation on vehicle emissions, fuel standards, solvent use, etc. has led to reductions in BTX emissions across the whole EU [5, 14]. The Air Quality Report of the first Auto-Oil Programme estimated a 56% reduction in urban emissions of benzene between 1990 and 2010 [10].

Two different methods are applied for monitoring BTX – manual sampling followed by analysis at a laboratory and automatic measurements *in situ* [14, 15]. An analysis of BTX is based on gas chromatography. The samples are taken with the use of sorption cartridges There are two ways of taking a sample: passive and active (pumped). The principle of passive sampling is diffusive uptake of BTX

*e-mail: pyta@ipis.zabrze.pl

on sorption cartridge, according to Fick's 1st law [17, 18]. Many different adsorbing materials and cartridge types are used, depending on the desorption method and sampling time [15, 19]. On-line BTX analyser is an automatic gas chromatograph with sampling unit, working with the time resolution of 15-60 min. Ambient air is sucked through a sorption tube and then the trapped compounds are injected into a chromatograph by thermal desorption, either directly or via a cryo-focusing trap [10, 20]. The automatic BTX measurements can also be performed along an optical path by means of differential optical absorption spectroscopy [21, 22]. However, this method is not in agreement with the standard EN 14662:2005 regarding the reference techniques of BTX monitoring.

Monitoring of BTX was not obligatory in urban areas till the Frame Directive 96/62/EC and its Daughter Directive 2000/69/EC came into force [23, 24]. In EU countries, the limit concentration of BTX in ambient air is determined only for benzene. The limit value of mean annual concentration of benzene for purposes of health protection is 5.0 μg/m^3. However, the 100% margin of tolerance, functioning as a provisional mitigation, is allowable till the end of 2005.

In Poland concentrations of BTX in ambient air have been measured systematically within the frame of the National Environment Monitoring Program since 2003. The measurements are mainly manual, most often done by using passive samplers. Until 2004 the automatic BTX analyzers worked only in Zabrze and Gdynia.

This paper presents results of automatic monitoring of benzene and its alkyl derivatives in ambient air of the central part of Upper Silesia. The measurements were performed in Zabrze, where beside the effects of emission from mobile sources, typical of urban sites, numerous episodes of high BTX concentrations occur due to presence of cokeries (Fig. 1).

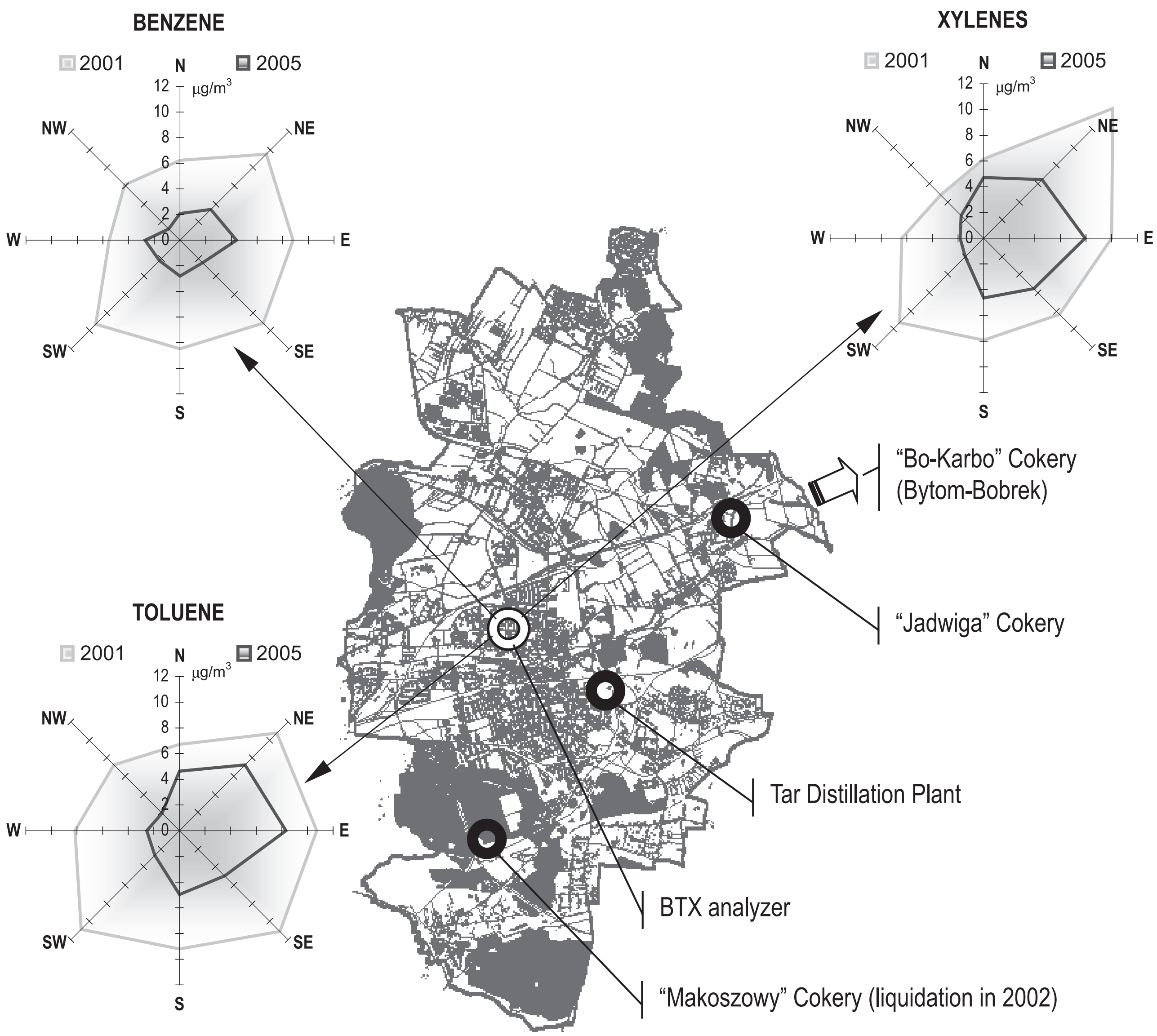

Fig. 1. Location of BTX analyzer and the main industrial sources of BTX emissions in Zabrze. The mean BTX concentrations for eight directions of wind.

Sampling and Analytical Method

The measurement station lies in the residential quarter of Zabrze (premises of Institute of Environmental Engineering, urban background conditions – Fig. 1). The sampling point is situated about 7 m above the ground and 170 m west of the busy road (Korfanty Ave.).

Concentrations of benzene, toluene and total xylenes (m,p- and o-xylene) from August–September 2001 and August–September 2005 are compared. These periods were chosen due to continuous, non-interrupted and simultaneous work of the BTX analyzer and meteorological station, both located at the same site. Selection of warm months allowed elimination of the effect of elevated BTX emissions due to higher fuel consumption in the heating season. In the former period the big cokery, "Makoszowy," was still functioning; the later one is the period three years after the shutdown of this cokery. The comparative analysis was conducted to assess the effects of liquidation of old cokery and modernization of existing coking plants, on air quality in Zabrze.

BTX were sampled and analyzed using automatic chromatograph AirmoBTX1000 (Chromatotec), consisting of the sampling unit, thermodesorber, analytical column MTX-5 and flame ionization detector (FID).

A 750-ml sample of ambient air was automatically taken at the rate of 50 ml/min. Volatile compounds were adsorbed on Carbotrap B bed. The sampling system comprised three sorption tubes. Two tubes worked alternately – while the desorption from one of them occurred, the second one was sorbing pollutants. The thermal desorption of analyte lasted 3 min at 300°C.

Quantitative determination was performed with FID. The temperature of the analytical column was changing from 45 to 140^{o}C and the terminal temperature of the column was maintained for 2 min. The flow-rate of carrier gas (hydrogen) in the column was 0.5 ml/min. The temperature of the detector was 150^{o}C. Determined compounds were identified by their retention times using the external standard method (the mixture of gas standards). The detection limit was 0.3 µg/m^3 for benzene and 0.4 µg/m^3 for toluene and xylenes [25].

Table 1. Description statistics for a series of measurements of BTX concentrations (15 min. data). Zabrze, August–September 2001 and August–September 2005.

Statistical parameter	Benzene	Toluene	m,p-Xylene	o-Xylene	Total BTX
August–September 2001					
Mean [µg/m^3]	8.1	9.3	6.9	1.6	25.9
Std. Deviation [µg/m^3]	10.4	10.4	12.6	2.3	30.5
Minimum [µg/m^3]	<0.3	<0.4	<0.4	<0.4	<0.4
Maximum [µg/m^3]	145.4	100.7	212.1	29.3	332.7
Date of maximum occurrence	2001-08-01 02:42	2001-08-01 21:25	2001-08-01 22:27	2001-08-01 22:27	-
Number of benzene concentrations greater than limit value 5 µg/m^3	2152	-			
Number of benzene concentrations greater than double limit value 10 µg/m^3 *(limit value + margin of tolerance)*	899	-			
Number of measurements	3990				
August–September 2005					
Mean [µg/m^3]	2.8	5.0	3.5	1.2	12.6
Std. Deviation [µg/m^3]	4.8	10.7	8.0	2.5	21.9
Minimum [µg/m^3]	<0.3	<0.4	<0.4	<0.4	<0.4
Maximum [µg/m^3]	113.7	200.6	133.4	33.0	234.8
Date of maximum occurrence	2005-08-05 01:11	2005-09-05 23:41	2005-08-05 20:06	2005-09-05 02:26	-
Number of benzene concentrations greater than limit value 5 µg/m^3	695	-			
Number of benzene concentrations greater than double limit value 10 µg/m^3	241	-			
Number of measurements	4064				

Results and Discussion

In Table 1, 15 min concentrations of benzene, toluene and xylenes (m-, p- and o-xylene), are presented. The standard deviations, means, minima and maxima of BTX concentrations are computed for two two-month periods: August–September 2001 and August–September 2005.

The stack-bar charts (Fig. 2) present 24h concentrations of the sum of BTX. The horizontal line is drawn at 5 μg/m³ – the limit value for annual benzene concentrations.

The short-time concentrations of BTX and 24h concentrations of total BTX were significantly lower in 2005 than in 2001. The mean concentrations of benzene, toluene and xylenes dropped from 8.1 μg/m³, 9.3 μg/m³ and 8.5 μg/m³ in 2001 to 2.8 μg/m³, 5.0 μg/m³ and 4.7 μg/m³ in 2005, respectively. Benzene concentration decreased most. The mean concentration of benzene was about three times lower in 2005 than in 2001. The number of 15 min benzene concentrations exceeding limit value was also about three times lower in 2005. Benzene concentrations higher than the doubled limit value were about four times scarcer in 2005 than in 2001.

The low BTX concentrations were more frequent and episodes of elevated BTX concentrations were less frequent in August–September 2005.

Air quality improvement was also confirmed by passive measurements performed in Zabrze near the point of automatic BTX monitoring. These measurements yielded mean annual concentrations of benzene in 2002, 2003 and 2004 at levels 9.6 μg/m³, 5.4 μg/m³ and 4.1 μg/m³, respectively [26, 27]. According to the passive measurements performed at the same point in the period July-December 2005, the mean benzene concentration amounted to 3.96 μg/m³. The results of our measurements carried out in the same period by two main crossings in the city showed the following mean values of benzene concentrations: 7.44 μg/m³ (Teatralny Sq.) and 7.41 μg/m³ (Korfanty Ave. – Wolności St.).

In Fig. 3, diurnal distributions of concentrations of benzene, toluene and xylenes in the analyzed periods are presented. In general, diurnal variability of BTX concentrations matches the variability of concentrations of the main air pollutants and is caused by changes of the thermodynamic parameters of the mixing layer. The morning and evening peaks of concentration occur, but hours of their occurrence change over a year (in winter higher concentrations occur in later hours). Within 24 hours, three peaks of BTX concentrations occur. The first peak is about 3:00 a.m., the second one occurs at 7:00 a.m. (morning rush hour), the third and the highest one is observed from

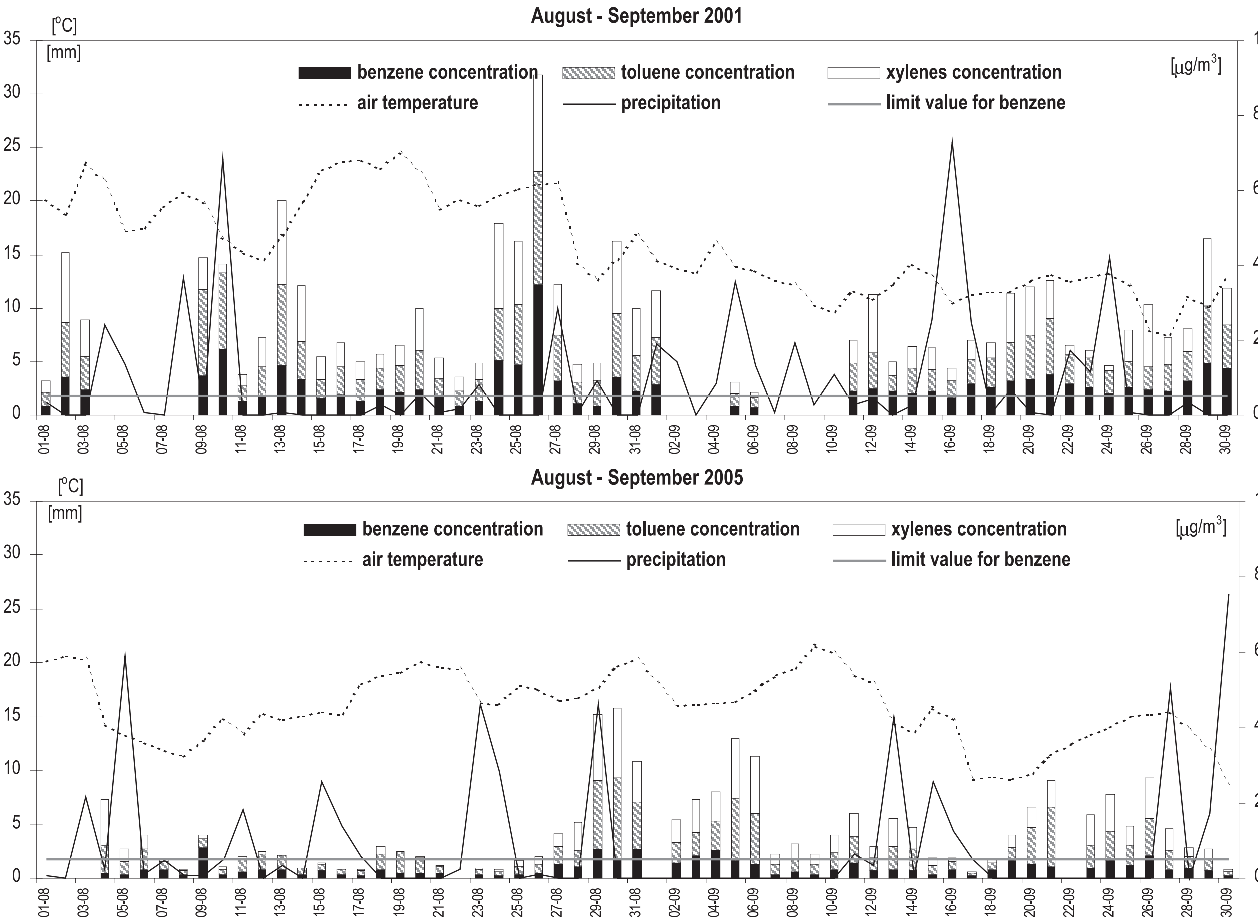

Fig. 2. BTX concentrations, air temperature and precipitation (24h data). Zabrze, August – September 2001 and August – September 2005.

9:00 to 11:00 p.m. The lowest concentrations occur in the afternoon, exactly in the period of the maximum wind velocity. The shapes of diurnal distribution curves of concentrations of toluene and xylenes in the analyzed periods are very similar. The diurnal variability of benzene concentration in 2005 was slightly weaker. Lower BTX concentrations in the evening, in the night and early morning in August–September 2005, especially for benzene, were due to higher wind speed.

The mean concentrations of BTX are presented in Fig. 1 in dependence on eight wind directions. Within August-September 2001, the highest BTX concentrations were noted when the northeast and southwest winds were blowing; slightly lower concentrations occurred for the east, southeast and south winds. High concentrations of BTX for the northeast, east, southeast and south winds may be explained by the effects of the coking plant, neighbouring busy road (east) and the city centre (southeast). Probably, high concentrations of BTX brought by the southwest winds are caused by the presence of an area of urban green, situated in the way of south winds and lying between the measuring point and the "Makoszowy" cokery. Weak winds carry polluted air along the railroad towards a quarter of low buildings lying southwest from the measuring point and bringing the pollutants to the measuring point from there. For faster southwest winds (> 1 m/s) concentrations of BTX are distinctly lower than for the south winds (Table 2). Concentrations of BTX in August-September 2005 were clearly lower. The highest BTX concentrations were observed for winds blowing from the northeast and west, and also from the southeast. The results for winds with velocities greater than the mean value 1 m/s (Table 2) prove that decreasing BTX concentrations are due mainly to liquidation of cokery in the southern part of Zabrze. In 2001, the highest mean BTX concentrations were noted for the northeast, east,

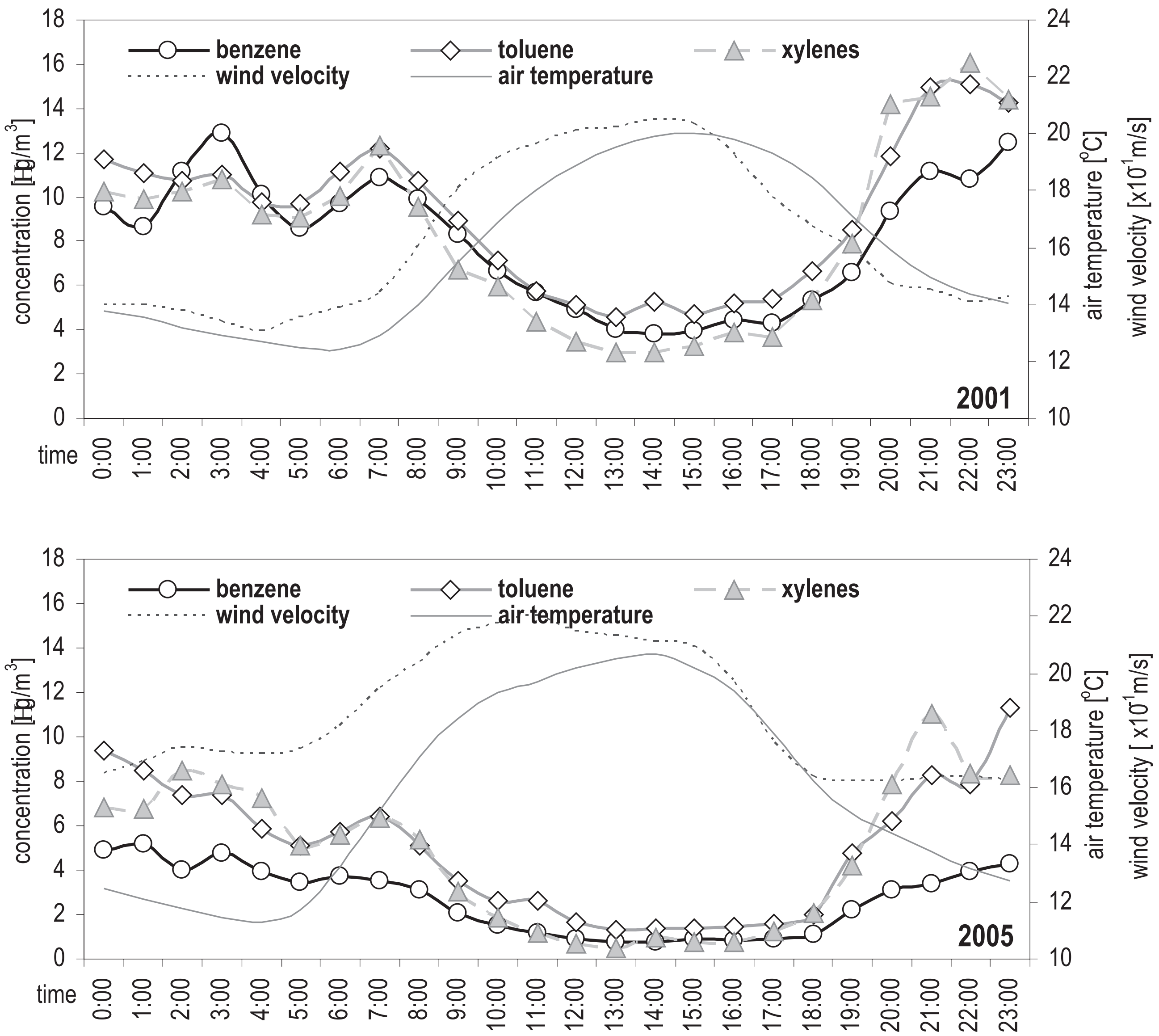

Fig. 3. Diurnal distributions of BTX concentrations, wind velocity and air temperature (1h data). Zabrze, August–September 2001 and August–September 2005.

Table 2. The mean and maximum concentrations of BTX for eight directions of wind blowing at velocity greater than 1 m/s (30 min. data). Zabrze, August–September 2001 and August–September 2005.

Period	Statistical parameter	Wind direction							
		N	NE	E	SE	S	SW	W	NW
Benzene concentration									
August – September 2001	Mean [μg/m³]	4.6	7.7	6.9	6.1	6.0	3.6	3.9	2.6
	Maximum [μg/m³]	19.6	116.6	13.3	14.1	26.6	7.0	7.1	10.5
August – September 2005	Mean [μg/m³]	0.8	2.3	3.6	1.4	1.3	0.9	1.3	0.7
	Maximum [μg/m³]	1.7	21.6	23.9	9.2	12.5	4.5	17.2	2.8
Toluene concentration									
August – September 2001	Mean [μg/m³]	4.9	7.2	7.3	6.9	5.6	4.9	6.0	3.6
	Maximum [μg/m³]	51.1	37.4	13.9	18.1	33.5	10.7	11.4	10.0
August – September 2005	Mean [μg/m³]	1.3	3.9	3.9	3.4	2.2	1.8	2.0	1.2
	Maximum [μg/m³]	2.8	103.7	19.3	15.5	9.5	8.4	12.6	7.7
Xylenes concentration									
August – September 2001	Mean [μg/m³]	4.2	9.8	6.2	4.6	5.0	4.1	5.0	2.4
	Maximum [μg/m³]	79.4	119.2	15.6	14.7	114.9	17.8	8.0	7.0
August – September 2005	Mean [μg/m³]	0.7	2.0	4.8	3.7	1.8	1.0	1.3	1.3
	Maximum [μg/m³]	4.0	28.1	58.0	26.8	11.3	4.9	31.2	21.4

southeast and south winds, the maximum concentration occurred for the northeast and south winds. In 2005, the highest mean BTX concentrations were noted during the northeast, east and southeast winds, and the maximum concentration occurred for the east and northeast winds.

Conclusions

The mean benzene concentration in August–September 2005 was about three times lower than in August–September 2001. The mean concentrations of toluene and xylenes in 2005 were about two times lower than in 2001. In general, neither the character of diurnal distribution of BTX concentrations nor the concentration maxima changed. Instead, there occurred lower BTX concentrations and high BTX concentration episodes were less frequent in 2005 than in 2001 (Table 1).

Obviously, the main reason for the decrease of BTX concentrations was liquidation of a cokery in the southern part of Zabrze and modernization of the rest of coking plants (Fig. 1, Table 2).

The results of automatic and passive measurements confirm the absence of risk of occurrence of benzene concentration higher than the standard 10 μg/m³ (limit value + margin of tolerance), valid till 2005, in Zabrze. But exceeding the limit value 5 μg/m³ (health protection standard) may be expected. Thus, it should be stated that air quality is still not satisfactory in Zabrze.

References

1. SIEMIŃSKI M., Environmental Health Risk, 269, (in Polish), PWN, Warszawa **2001.**
2. SNYDER R., HEDLI C.C, An overview of benzene metabolism, Environ. Health Perspec., **104** (6), 1165, **1996**.
3. WHO Regional Office for Europe, Monitoring Ambient Air Quality for Heath Impact Assessment., WHO Regional Publications, European Series No. **85**, 107, **1999**.
4. WHO Regional Office for Europe, Air Quality Guidelines for Europe. Second Ed., WHO Regional Publications, European Series No. **91**, 62, **2000**.
5. BONO R., BUGLIOSI E.H., SCHILIRO T., GILLI G., The Lagrange Street story: the prevention of aromatics air pollution during the last nine years in a European city, Atm. Environ., **35** Supplement No.1, S107, **2001**.
6. PILIDIS G. et al., BTX measurements in a medium-sized European city, Atm. Environ., **39**, 6051, **2005**.
7. THIJSSE T.R., OSS R.F., LENSCHOW P., Determination of source contributions to ambient volatile organic compounds concentrations in Berlin, J. Air and Waste Manage Assoc., **49**, 1394, **1999**.
8. CARTER W. P., Development of ozone reactivity scales for volatile organic compounds, J. Air and Waste Manage. Assoc., **44**, 881, **1994**.
9. FINLAYSON-PITTS B. J., PITTS J. N., Atmospheric chemistry of tropospheric ozone formation: scientific and regulatory implications, Air and Waste, **43**, 1091, **1993**.

10. European Commission on Air Quality, Council directive on ambient air quality assessment and management working group on benzene: position paper on benzene, 8, 16, **1998**.
11. MURENA F., VORRARO F., Vertical gradients of benzene concentration in a deep street canyon in the urban area of Naples, Atm. Environ. **37**, 4853, **2003**.
12. DE SANTIS F. et al., Monitoring the air quality around an oil refinery through the use of diffusive sampling, Anal. Bioanal. Chem., **378,** 782, **2004**.
13. PFEFFER H., BREUER L., BTX measurements with diffusive samplers in the vicinity of a cokery: comparison between ORSA-type samplers and pumped sampling, J. Environ. Monit., **2**, 483, **2000**.
14. PALMGREN F., HANSEN A. B., BERKOWICZ R., SKOV H., Benzene emission from the actual car fleet in relation to petrol composition in Denmark, Atm. Environ., **35** Supplement No.1, S35, **2001**.
15. SKOV H., LINDSKOG A., PALMGREN F., CHRISTENSEN C.S., An overview of commonly used methods for measuring benzene in ambient air, Atm. Environ., **35** Supplement No.1, S141, **2001**.
16. WIDEQVIST U. et al., Comparison of measurement methods for benzene and toluene, Atm. Environ., **37**, 1963, **2003**.
17. NAMIEŚNIK J., JAMRÓGIEWICZ Z. (eds.), Physicochemical methods of environmental pollutants control, pp. 385, (in Polish), WNT, Warszawa 1998.
18. BROWN R.H., Monitoring the ambient environment with diffusive samplers: theory and practical considerations, J. Environ. Monit., **2**, 1, **2000**.
19. WRIGHT M.D., PLANT N.T., BROWN R.H., Diffusive sampling of VOCs as an aid to monitoring urban air quality, Environ. Monit. Assess., **52**, 57, **1998**.
20. YAMAMOTO N., OKAYASU H.; MURAYAMA S., MORI S., HANAHASHI K., SUZUKI K., Measurement of volatile organic compounds in the urban atmosphere of Yokohama, Japan, by an automated gas chromatographic system, Atm. Environ., **34**, 4441, **2000**.
21. KOURTIDIS K. et al., Benzene, toluene, ozone, NO_2 and SO_2 measurements in an urban street canyon in Thessaloniki, Greece, Atm. Environ., **36**, 5355, **2002**.
22. PETRAKIS M., PSILOGLOU B., KASSOMENOS P.A., CARTALIS C., Summertime measurements of benzene, toluene and xylene in Athens using a Differential Optical Absorption Spectroscopy system, J. Air and Waste Manage Assoc., **53**, 1052, **2003**.
23. Council Directive 96/62/EC of 27 September 1996 Official Journal of the European Union L296, 21 November **1996**.
24. Directive 2000/69/EC of 16 November 2000. Official Journal of the European Union L313, 13 December **2000**.
25. CZAPLICKA M., KLEJNOWSKI K., Determination of volatile organic compounds in ambient air. Comparison of methods, J. Chromatogr. **976**, 369, **2002**.
26. PYTA H., BŁASZCZYK J., KLEJNOWSKI K., KRASA A.: Benzene air pollution in the Silesian Region, Arch. Environ. Prot. **31**, 25, **2005**.
27. KUBICKA L., Ambient Air Quality, (in Polish), Ekologia, **28,** (2), 45, **2005**.