

MARZENA ZACIERA*, JOLANTA KUREK*, LIDIA DZWONEK*
BARBARA FEIST**, ALEKSANDER JĘDRZEJCZAK***

SEASONAL VARIABILITY OF PAHs AND NITRO-PAHs CONCENTRATIONS IN TOTAL SUSPENDED PARTICULATE MATTER IN AMBIENT AIR OF CITIES OF SILESIAN VOIVODESHIP

Polycyclic aromatic hydrocarbons (PAHs) are present in ambient air with their nitro-derivatives and hundreds of other organic compounds. PAHs and nitro-PAHs originate from Diesel and gasoline exhaust emission, and other sources of fuels combustion. These compounds are responsible for mutagenic activation of ambient air. Concentrations of PAHs, nitro-PAHs and dinitro-PAHs in total suspended particulate matter in air of Katowice, Sosnowiec and Zawiercie as well seasonal variability of their concentrations have been investigated. The method of solvent extraction of particulate matter, fractional organic extraction as well HPLC and GC/MS analyses were applied. Nitro-PAHs concentrations in ambient air in Poland are poorly researched, compared to foreign literature.

1. INTRODUCTION

Studies of particulate matter and gas phase of urban air performed by Air Pollution Research Center in California showed that polycyclic aromatic hydrocarbons (PAHs) and their derivatives are mainly responsible for mutagenic activity of ambient air. PAHs, nitro-PAHs and other polycyclic aromatic compounds are mainly adsorbed on particulate matter, and their smaller quantities may be found in the gas-phase. Nitrated polycyclic aromatic hydrocarbons are a group of about 200 various chemical compounds. Many of them are mutagenic in microbial mutagenicity bioassays as well in mutation assay using human cells, a lot of nitro-PAHs have carcinogenic effects in animal studies [3–7].

*Institute of Occupational Medicine and Environmental Health (IOMEH), ul. Kościelna 13, 41-200 Sosnowiec, Poland. Corresponding author M. Zaciera, e-mail: m.zaciera@imp.sosnowiec.pl

**University of Silesia, Chemistry Institute, ul. Szkolna 9, 40-006 Katowice, Poland.

***Sanitary and Epidemiological Station in Zawiercie, ul. 11 Listopada 15, 42-400 Zawiercie, Poland.

Compared to PAHs, some their nitro-derivatives gain an increased attention due to 200 000 times higher mutagenicity and 10 times higher carcinogenicity. Humans are exposed to nitro-PAHs and other coexisting air pollutants from various sources. No data exists concerning the influence of individual nitro-compounds on human body [7] but correlation between lung cancers and presence of PAHs and nitro-PAHs in air of industrialized regions was found [9].

Most studies on the problem of the presence of nitro-PAHs in atmospheric air related to the mutagenic effect of fractions containing nitro-PAHs. The results of these studies showed that the fraction containing nitro-PAH was characterized by the highest mutagenic activity [3, 10–13]. In IOMEH, the mutagenic activity of PAHs and nitro-PAHs fractions was studied. This study showed that nitro-PAHs fraction exhibit higher mutagenic activity. Nevertheless, the concentrations of nitro-PAHs were ten times lower in comparison to PAHs. Therefore a need to measure low concentrations of nitro-PAHs in the air exists because even in such concentrations these compounds can cause health hazard.

In some studies [2, 14–17, 23], nitro-PAHs concentrations in ambient air have been monitored in many countries such as USA, Brazil, Germany, Czech Republic, Slovakia, Austria, Sweden. In Poland, the levels of nitro-PAHs concentrations in ambient air were studied in the 90s of the twentieth century but only two of nitro-PAHs were determined in the summer season in several cities of the Silesian voivodeship [18–20]. Thus nitro-PAHs concentrations in ambient air in Poland are poorly researched; insufficient data exist about their dependence on the heating season.

The paper presents the results of measurements of PAHs and their nitro-derivatives concentrations, having been conducted for two years (2009–2010), in three cities of the Silesian voivodeship.

Some studies [7, 8, 21, 22] reported that the main source of exposure to nitro-PAHs in ambient air is emission from diesel engines and combustion from individual households. Therefore samplings were planned in such areas of cities where is a large vehicle traffic and individual heating with coal prevailed. In addition, the seasonal variability of concentrations of the compounds was tested and the influence of the heating season as well.

2. EXPERIMENTAL

Sampling locations. Air samples were collected in three cities in the region of Silesia: Katowice, Sosnowiec and Zawiercie. Both in Katowice and Sosnowiec, Polish cities of largest population, samples were collected in areas of high and compact buildings, the most of them being old buildings with individual heating with coal. In both cities, aspirators were situated in the centre of city near roads (ca. 1 m from the

road) with a significant volume of traffic, for example in Katowice it was situated near the roadway Katowice–Warsaw.

Zawiercie is characterized by a much smaller population thus the type and density of buildings are different from those in other two cities. Air samples were collected in area of sparse, low buildings comprising mainly heated with coal detached houses with gardens. There are also industrial facilities with their heating with coal or oil. In the surroundings there are areas of open space: the park, a small area of fallow lands, the railway line. Aspirator was situated near the road linking the city centre to the road 78 Chałupki–Chmielnik and road 791 Trzebinia–Myszków. Movement of vehicles on this road is much smaller than on the roads where samples were collected in Katowice and Sosnowiec.

Air sampling. The sample of total suspended particulate matter (TSP) was collected on glass fibre filters (11 cm in diameter) using Staplex high volume sampler model TFIA-2. The flow-rate was 1 m³/min. The total volume of sampled air was 350–660 m³. Filters with the collected urban dust were protected from light by wrapping in aluminum foil and stored in a freezer until sample analysis. In these studies, 10–12 samples were collected in every city, in each season.

Analysis of PAHs and nitro-PAHs. Particulate matter samples were extracted using Soxhlet apparatus with 100 ml of dichloromethane (DCM). The extract was fractionated on a glass column packed with silica gel using the following solvents: cyclohexane, dichloromethane in cyclohexane and dichloromethane (with different volumes for two fractions). Separated fractions contain: (1) – aliphatic hydrocarbons, (2) – PAHs, (3) – mononitro-PAHs, (4) – dinitro-PAHs [12, 17, 25]. Each eluate was evaporated to dryness. The following nine nitrated polycyclic aromatic hydrocarbons were determined: 9-nitroanthracene, 2-nitrofluorene, 1-nitropyrene, 3-nitrofluoranthene, 6-nitrochrysene 1,3-dinitropyrene, 1,6-dinitropyrene, and 1,8-dinitropyrene.

Polycyclic aromatic hydrocarbons were detected using AT 1200 high performance liquid chromatograph with a fluorescence detector. Nitrated polycyclic aromatic hydrocarbons were detected using a Varian 450 GC gas chromatograph interfaced with a 320 MS mass detector with electron ionisation GC/MS (EI). Limit of quantification for 480 m³ of air, for polycyclic aromatic hydrocarbons is 0.006-0.017 ng/m³, for the nitro-PAHs it is 0.003-0.014 ng/m³.

3. RESULTS AND DISCUSSION

Table 1 shows the average concentrations of polycyclic aromatic hydrocarbons and their nitro-derivatives in various seasons, the average air temperature and the number of days, from collecting sample days, in which the air temperature was lower than 10 °C.

Table 1

Mean concentrations of polycyclic aromatic hydrocarbons and their nitro-derivatives in ng/m³ in different seasons in Sosnowiec, Katowice and Zawiercie

Compound	Sosnowiec				Katowice				Zawiercie			
	Sp	S	A	W	Sp	S	A	W	Sp	S	A	W
	<i>n</i>											
	10	11	11	11	12	11	11	12	10	10	10	10
Phenanthrene	2.11	1.51	1.00	3.50	1.58	1.36	0.61	3.77	1.46	0.76	0.81	1.36
Anthracene	0.26	0.09	0.25	0.69	0.16	0.10	0.11	0.84	0.07	0.06	0.29	0.32
Fluoranthene	2.63	0.87	2.46	9.24	1.95	0.96	0.73	8.74	0.48	0.86	2.37	4.13
Pyrene	2.14	0.60	2.36	7.24	1.70	0.60	0.65	8.36	0.34	0.55	2.59	3.03
Benzo(a)anthracene	1.76	0.52	2.46	8.03	1.27	0.55	0.73	8.21	0.30	0.46	2.90	3.58
Chrysene	1.28	0.80	1.76	6.41	1.58	0.82	0.79	5.26	0.44	0.53	1.97	2.64
Benzo(b)fluoranthene	2.05	0.85	1.25	6.26	1.56	0.97	0.81	4.96	0.44	0.51	1.47	1.69
Benzo(k)fluoranthene	0.61	0.24	0.62	1.67	0.44	0.29	0.24	1.71	0.46	0.16	0.93	0.91
Benzo(a)pyrene	2.99	1.09	3.41	9.91	2.18	0.96	1.12	10.82	0.58	0.76	3.76	3.89
Dibenzo(ah)anthracene	0.55	0.17	0.76	0.75	0.25	0.16	0.08	1.17	0.11	0.16	1.04	0.58
Benzo(g,h,i)perylene	0.91	0.37	3.79	2.97	0.42	0.44	0.54	4.49	0.16	0.23	4.68	2.47
Indeno(1,2,3-c,d)pyrene	1.34	0.57	1.13	3.62	1.08	0.31	0.44	2.94	0.28	0.36	1.19	1.62
Sum of PAHs	18.62	7.68	21.26	60.29	14.17	7.53	6.82	61.27	5.12	5.40	24.00	26.22
2-Nitrofluorene	0.18	0.05	0.58	1.83	0.33	0.11	0.18	1.66	0.05	0.05	0.28	0.49
9-Nitroanthracene	0.13	0.06	1.01	2.40	0.34	0.09	0.25	2.59	0.04	0.05	0.79	0.60
3-Nitrofluoranthene	0.09	0.06	0.24	0.25	0.09	0.16	0.11	0.22	0.05	0.04	0.15	0.14
1-Nitropyrene	0.01	0.01	0.02	0.05	0.01	0.01	0.01	0.03	p.o.	p.o.	0.03	p.o.
6-Nitrochrysene	p.o.	p.o.	p.o.	0.03	0.01	p.o.	p.o.	0.08	p.o.	p.o.	0.01	p.o.
Sum of mononitroPAHs	0.41	0.18	1.86	4.55	0.70	0.37	0.55	4.57	0.14	0.15	1.26	1.23
1,3-Dinitropyrene	p.o.	p.o.	0.02	0.02	p.o.	p.o.	p.o.	p.o.	p.o.	p.o.	p.o.	p.o.
1,6-Dinitropyrene	0.02	0.02	0.04	0.02	0.03	0.02	0.04	0.04	p.o.	p.o.	0.03	0.02
1,8-Dinitropyrene	p.o.	p.o.	0.02	0.02	0.02	0.01	0.02	0.02	p.o.	p.o.	p.o.	p.o.
Sum of dinitroPAHs	0.03	0.03	0.08	0.06	0.05	0.05	0.06	0.06	0.02	0.02	0.04	0.03
Air temperature [°C]	21.50	23.80	10.40	-1.50	12.30	23.60	11.70	-1.00	18.90	24.80	9.00	9.20
Days with <i>t</i> < 10 °C	0.00	0.00	4.00	11.00	2.00	0.00	3.00	12.00	0.00	0.00	7.00	5.00

Sp – spring, S – summer, A – autumn, W – winter.

The average concentration of polycyclic aromatic hydrocarbons and their nitro-derivatives being the highest in winter exceeded the levels in summer 5–8 times. Relatively high concentrations of 9-nitroanthracene, which similarly as 3-nitrophenanthrene, is formed mainly during combustion of coal [8], also prove emissions from households to participate in air pollution in winter.

A similar relationship was noted during the monitoring concentrations of PAHs and nitro-PAHs using passive samplers in Poland in 1999–2000. The concentrations of studied compounds were 10 times higher in winter than in summer. Similar dependence has not been found in any of four project countries, probably due to PAHs emission from individual households heated with coal, characteristic of Poland [23].

High concentrations of 2-nitrofluorene, whose main source is emission from diesel engines [8, 24], also proved right choice of sampling sites situated near roads with high traffic density.

The concentrations of PAHs in Zawiercie were 2–4fold lower than in other cities under investigation, and the concentration of 2-nitrofluorene and 9-nitroanthracene were tenfold lower. In Zawiercie, mean concentration of sum of PAHs in autumn is comparable to that in winter but the average temperatures in autumn and winter were similar 9.0–9.2 °C. In addition, there were more days in autumn where the temperature decreased below 10 °C (7 days) than in winter (5 days).

The Silesian Voivodeship is one of the region, where the highest levels of air pollutants are noticed. In recent years, it was associated with the presence of many industrial plants, old technologies and low attention to environmental protection. Nowadays, the industry has been restructured, and each plant has a duty to minimize pollutants emissions, the ambient air is polluted mainly by toxic exhaust from vehicles and individual heating home.

4. CONCLUSIONS

- Concentrations of polycyclic aromatic hydrocarbons and their nitro-derivatives in the winter season were found to be higher 5–8 times than those in other seasons.
- Concentrations of 2-nitrofluorene and 9-nitroanthracene in the air of urban areas were relatively high compared to the concentrations of other nitro-PAHs. The main source of emissions of 2-nitrofluorene, possibly carcinogenic to humans, is emission from diesel engines. 9-nitroanthracene is formed mainly from coal combustion.
- In all seasons, concentrations of dinitro-PAHs were at a similar level of pg/m^3 .

ACKNOWLEDGEMENTS

This study was supported by the Polish Ministry of Science and Higher Education as a research project No. N N404 028535 in the years 2008–2011.

REFERENCES

- [1] Research Note No. 94-22 – *Mutagenic activity of air pollutants*, California Environmental Protection Agency, 1994.
- [2] ATKINSON R., AREY J., *Environ. Health Perspect.* 1994, 102 (4), 117.
- [3] BAMFORD H.A., BEZABEH D.Z., SCHANTZ M.M., WISE S.A., BAKER J.E., *Chemosphere*, 2003, 50, 575.
- [4] MÖLLER L., *Environ. Health Perspect.* 1994, 102 (4), 139.
- [5] *Report on Carcinogens*, 11th Ed., U.S. Department of Health and Human Services, Public Health Service, National Toxicology Program.
- [6] *IARC Monographs on the Evaluation of Carcinogenic Risks to Humans*, Vol. 46, *Diesel and Gasoline Engine Exhaust and Some Nitroarenes*, WHO, 1998.
- [7] MAKHNIASHVILI I., *Bezpieczeństwo pracy*, 2003, 3 (In Polish).
- [8] *Selected Nitro- and Nitro-oxy-polycyclic Aromatic Hydrocarbons*; Environmental Health Criteria 229, WHO, Geneva 2003.
- [9] TALASKA G., UNDERWOOD P., MAIER A., LEWTAS J., ROTHMAN N., JAEGER M., *Environ Health Perspect.*, 1996, 104 (5), 901.
- [10] STRANDELL M., ZAKRISSON S., ALSBERG T., WESTERHOLM R., WINQUIST L., RANNUNG U., *Environ. Health Perspect.*, 1994, 102 (4), 85.
- [11] ČERNA M., POCHAMNOVA D., PASTORKOWA A., ŠMID J., BINKOVA B., *Bacterial mutagenicity of fractionated organic material adsorbed on urban air particles*, [In:] *Impact of Air Pollution on Human Health*, R.J. Šram (Ed.), Academia, Praga, 2001.
- [12] OSTBY L., ENGEN S., MELBYE A., EIDE I., *Arch. Toxicol.*, 1997, 71, 314.
- [13] EIDE I., JOHNSEN H.G., *Environ. Health Perspect.*, 1998, 106 (3), 1373.
- [14] SCHAUER CH., NIESSNER R., PÖSCHL U., *Anal. Bioanal. Chem.*, 2004, 378, 725.
- [15] YAFFE D., COHEN Y., ATEY J., GROSOVSKY A.J., *Risk Analysis*, 2001, 21 (2), 275.
- [16] CASTELLS P., SANTOS F.J., GALCERAN M.T., *J. Chromatogr.*, 2003, 1010, 141.
- [17] LENICEK J., SEKYRA M., BEDNARCOVA K., BENES I., SIPEK F., *Intern. J. Environ. Anal. Chem.*, 2000, 77 (4), 269.
- [18] WARZECHA L., STRÓZYK M., *Chem. Anal.*, 1998, 43, 807.
- [19] WARZECHA L., *Chem. Anal.*, 1993, 38, 303.
- [20] TYRPIEŃ K., WARZECHA L., BODZEK D., *Chem. Anal.*, 1994, 39, 389.
- [21] BEZABEH D.Z., BAMFORD H.A., SCHANTZ M.M., WISE S.A., *Anal. Bioanal. Chem.*, 2003, 375, 381.
- [22] AREY J., *Environ. Health Perspect.*, 2004, 112 (8), 812.
- [23] SODERSTROM H., HAJŠLOVÁ J., KOCOUREK V., SIEGMUND B., KOCAN A., OBIEDZINSKI M.W., TYSKLIŃD M., BERGQVIST P.A., *Atmosph. Environ.*, 2005, 39, 1627.
- [24] ZACIERA M., MNISZEK W., KUREK J., *Archives Environ. Prot.*, 2009, 35 (4), 35.
- [25] MIELŻYŃSKA D., SIWIŃSKA E., KAPKA L., *Mutagenic effect of particulate matter as an indicator of air quality*, Institute of Occupational Medicine and Environmental Health, 2002 (in Polish).