ARCHIVES OF ENVIRONMENTAL PROTECTION
vol. 35 no. 4 pp. 35 - 43 2009
PL ISSN 0324-8461

ENVIRONMENTAL LEVELS OF NITRO-PAHs IN TOTAL SUSPENDED PARTICULATE MATTER IN UPPER SILESIA (POLAND)

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Keywords: Nitro-PAHs, total suspended particulate matter (TSP), ambient air particulate.

Abstract: Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) may be formed during combustion of Diesel and gasoline fuel and may be produced in gas-phase reactions of polycyclic aromatic hydrocarbons (PAHs) with oxides of nitrogen. These compounds can form a significant fraction of the mainly direct-acting mutagenic compounds present in extracts of ambient air particles. Using own analytical method of nitro-PAHs determination, concentrations of total PAHs, nitro- and dinitro-PAHs in urban and non-urban area of three cites of Upper Silesia in Poland were measured. The dependence between concentration of PAHs and nitro-PAHs in urban and non-urban area as well as their distribution depending on roadway distance were searched. The study showed a significant influence of road transport on the levels of nitro-PAHs concentration.

INTRODUCTION

Nitrated polycyclic aromatic hydrocarbons (nitro-PAHs) can be numbered among the most dangerous chemical substances for human health due to their mutagenic and carcinogenic potency [22, 25]. These compounds are mainly produced during a gasoline and diesel fuel combustion. They are also formed during a nitration of PAHs by nitric acid or through addition of nitrogen monoxide or dioxide to PAH free radicals [1, 8]. Many of them are highly persistent in the environment; however, their concentrations are low (compared to unsubstituted PAHs). Nitro-PAHs are adsorbed onto airborne particles and can be transported for long distances from their original source. Inhalation of particulate matter is the main way of exposure to nitro-PAHs. Compared to PAHs, their nitro derivatives gain an increased attention due to 200000 times higher mutagenic and 10 time's higher carcinogenic properties. Such predominant mutagenic potency of nitro-PAHs is visible even at their environmental trace levels in bioassays utilizing human cells [2, 7, 8].

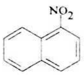
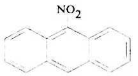
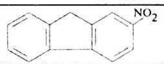
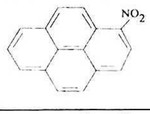
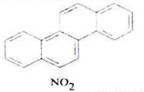
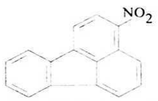
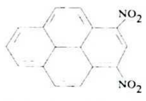
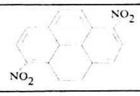
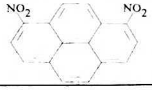
Many three-, four- and five-ring structures of nitrated PAHs have been found in the extracts of diesel engine exhaust particles [8]. The most abundant nitro-PAHs formed in diesel exhaust are: 1-nitropyrene, 2-nitrofluorene and 3-nitrofluoranthene [2, 9]. It was shown that the main portion of direct-acting mutagenicity of Diesel and air particulates is associated with nitro-PAHs [7].

The concentration of 1-nitropyrene is much lower in gasoline exhaust than in diesel exhaust, when the concentration of isomers of dinitropyrenes is on the same level. In connection with health effects, nitrated PAHs, especially 2-nitrofluorene and 1-nitropyrene, are treated as “markers” of exposure to diesel exhaust [2, 8, 9].

The presence of nitro-PAHs in the air has been investigated in numerous studies [2, 3, 21–23, 26, 29]. Based on these results, it can be stated that the concentration of nitro-PAHs in the air is very low, but such tendency could be due to the analytical problems in determination of nitro-PAHs concentrations.

Several methods for determining nitro-PAHs have been elaborated and described [2, 3, 7, 22, 29]. Most of them are based on the conversion of nitrocompounds into their

Table 1. Physical and chemical properties of selected PAHs nitro derivatives

Compound name	Structural formula	CAS Registry number	Molecular mass	Melting point [°C]	Boiling point [°C]	Solubility in organic solvents
1-nitronaphthalene		86-57-7	173.17	56	304	methanol, carbon disulfide, pyridine, cycloheksane, chloroform, ether, benzene, methylene chloride
9-nitroanthracene		602-60-8	223.23	141	–	methanol, methylene chloride
2-nitrofluorene		607-57-8	211.22	156–158	326	methanol, benzene
1-nitropyrene		5522-43-0	247.26	153–155	472	methylene chloride, methanol, benzene
6-nitrochrysene		7496-02-8	273.3	220	–	methanol, methylene chloride
3-nitrofluoranthene		892-21-7	247.26	157–159	–	methanol, benzene, methylene chloride
1,3-dinitropyrene		75321-20-9	292.25	–	–	methylene chloride, methanol, benzene
1,6-dinitropyrene		42397-64-8	292.25	300	–	methylene chloride, toluene
1,8-dinitropyrene		42397-65-9	292.25	–	–	methylene chloride, benzene

amine or amide derivatives [21–25]. The method of nitro-PAHs determination in their familiar form developed by Bamford *et al.* [2] requires the use of expensive equipment.

An own method of nitro-PAHs determination in their familiar form has been elaborated in Chemical Hazard Department of IOMEH [27, 28]. This method was used to check a concentration of these compounds in the air of urban and non-urban areas in Poland. Techniques of extraction and fractionation, primarily used for mutagenicity tests, were applied and adapted for the determination of nitro-PAHs in the air; this method is generally described in materials and methods. Literature review allowed for the selection of several nitro-PAHs, which are contaminants of ambient air and are present in diesel exhaust. The physical and chemical properties of selected nitro-PAHs are shown in Table 1 [2, 8, 9, 14, 15, 18, 23, 24, 30].

Most of the listed compounds are classified as possibly carcinogenic to humans, toxic and dangerous for human health and the environment [10, 11, 15, 19, 20].

MATERIALS AND METHODS

The study was carried out in three cities: Sosnowiec (urban area), Tucznawa and Lagisza (non-urban areas), located in Upper Silesia, the most polluted region in southern Poland. For the urban area, the sampling points were placed near bus stops and crossroads, where a high degree of urbanization was combined with a high emission of air pollutants from vehicle engines. The average traffic density at sampling points was about 8000 vehicles (cars, trucks and buses) per 24 hours. In the case of non-urban area, the sampling points were situated 1, 30 and 100 m from the road in the vicinity of detached houses with gardens. At all points, the samplings were performed in daytime (from 8 AM till 2 PM).

A 50 mg sample of total suspended particulate matter (TSP) was collected on glass fiber filter (11 cm diameter) using Staplex high volume sampler. The flow-rate was 400–500 dm^3/min. The total volume of sampled air was 150–190 m^3.

Particulate matter samples were extracted using Soxhlet apparatus with 100 cm^3 of dichloromethane (DCM). The extract was fractionated on a glass column packed with silica gel using the following solvents: cycloheksane, dichloromethane in cycloheksane and dichloromethane (with different volume for two fractions). The separated fractions contained: first – aliphatic hydrocarbons, second – PAHs, third – mononitro-PAHs, and fourth – dinitro-PAHs [13, 16, 17]. Each eluate was evaporated to dryness. The following nine nitrated polycyclic aromatic hydrocarbons were determined: 1-nitronaphthalene, 9-nitroanthracene, 2-nitrofluorene, 1-nitropy rene, 3-nitrofluoranthene, 1,3-dinitropyrene, 1,6-dinitropyrene, and 1,8-dinitropyrene.

Gas chromatography with electron ionization mass spectrometry GC/MS (EI) analyses were carried out using Hewlett-Packard 5890 II Plus gas chromatograph interfaced with HP 5972A mass detector. The gas chromatograph was equipped with HP-5MS column. The following chromatographic conditions were set:

- oven temperature was programmed: at 50°C (2 min.); increasing temperature 10°C/min to 280°C;
- injector temperature: 290°C;
- detector temperature: 280°C;
- injection volume: 1×10^{-6} dm^3, splitless;
- carrier gas: helium.

RESULTS AND DISCUSSION

The elaborated method was selective and linear for determination of nitrated polycyclic aromatic hydrocarbons – Table 2 shows the basic parameters for this method. GC-MS chromatogram of the sample collected in Sosnowiec is shown in Figure 1. Recovery of standards of nitro-PAHs from sample was in the range of 72–79%. The results from the GC-MS analyses are shown in Table 3.

Table 2. Qualifier ions, selectivity, linearity and determination limit values for the method of nitro-PAHs determination by gas chromatography with mass spectrometry detection

Compound name	MSD Qualifier ions		Retention time [min]	Correlation factor (analytical curve)	Determination limit value [ng/m^3]
1-nitronaphthalene	115	127	15.57	0.998	0.09
2-nitrofluorene	165	211	21.17	0.999	0.09
9-nitroanthracene	223	176	21.49	0.998	0.09
3-nitrofluoranthene	247	200	25.10	0.998	0.08
1-nitropyrene	247	201	25.69	0.998	0.09
1,3-dinitropyrene	292	200	29.44	0.998	0.45
1,6-dinitropyrene	292	200	30.28	0.997	0.46
1,8-dinitropyrene	292	200	30.91	0.999	0.45

Table 3. Ranges and medians of nitro-PAHs and total PAHs concentrations in airborne particulate matter (PM) identified in analyzed samples [ng/m^3]

Compound name/ sampling location		1-nitro naphthalene	2-nitro fluorene	9-nitro anthracene	3-nitro fluoranthene	1-nitro pyrene	1,3-dinitro pyrene	Total PAHs
urban area								
1 m from road n = 6	range	0.12–0.97	4.4–21.16	0.67–5.33	0.64–4.37	< 0.09–1.81	< 0.45–0.46	75.1–158.1
	median	0.64	12.62	1.66	1.23	0.73	0.23	106.7
not-urban area								
1 m from road n = 10	range	n.d. – 1.11	0.22–0.46	n.d. – 0.31	n.d. – 0.66	n.d. – 0.10	< 0.45	7.8–16.6
	median	0.43	0.27	0.11	0.48	0.05	< 0.45	9.9
30 m from road n = 6	range	n.d. – 1.89	0.19–0.78	n.d. – 0.28	n.d. – 0.57	n.d. – 0.10	< 0.45	5.1–10.2
	median	0.59	0.38	0.22	0.51	0.06	< 0.45	8.6
100 m from road n = 8	range	n.d. – 0.71	0.18–0.54	n.d. – 0.65	n.d. – 0.66	n.d. – 0.10	< 0.45	11.4–30.6
	median	0.59	0.32	0.24	0.59	0.05	< 0.45	13.0

n.d. – not detected

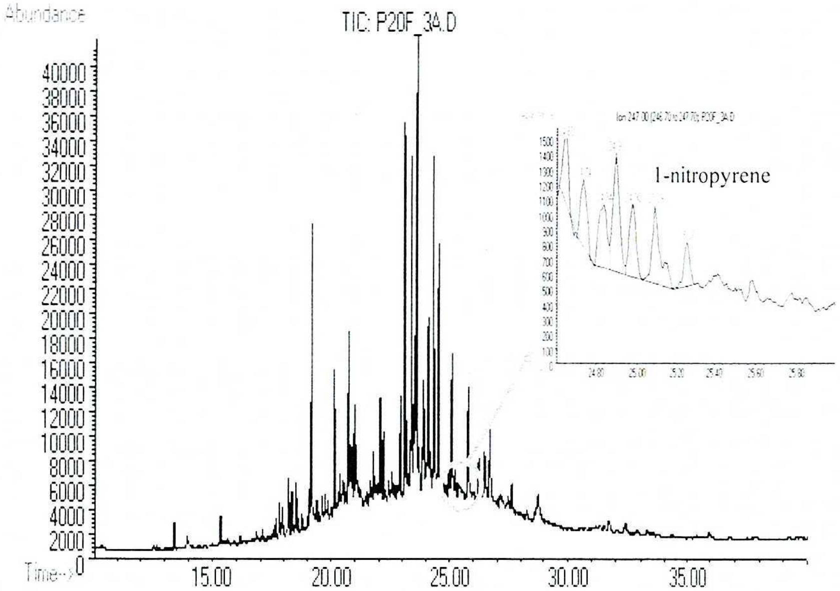


Fig. 1. GC-MS chromatogram of mononitro-PAHs fraction from airborne sample collected in urban area

Concentration of PAHs and their nitrated derivatives in urban area were about 10 times higher than concentration of these compounds in non-urban areas. The performed study showed a decrease of total PAHs concentration in a distance of 30 m from roadway. Distribution of air pollutants from "linear" emission sources, such as road traffic, depends on many different factors. Function of pollutants concentration vs. distance from road predominantly is not linear. This distribution depends mainly on wind velocity and its direction, traffic density, thermal convection and from others. In this research this function was not precisely studied, only general observations were made. Concentration of benzo(a)pyrene in urban area was between 7.21–17.69 ng/m^3 (median 9.86 ng/m^3), while in non-urban area was between 0.21–2.80 ng/m^3 (median 0.8 ng/m^3). The level of PAHs

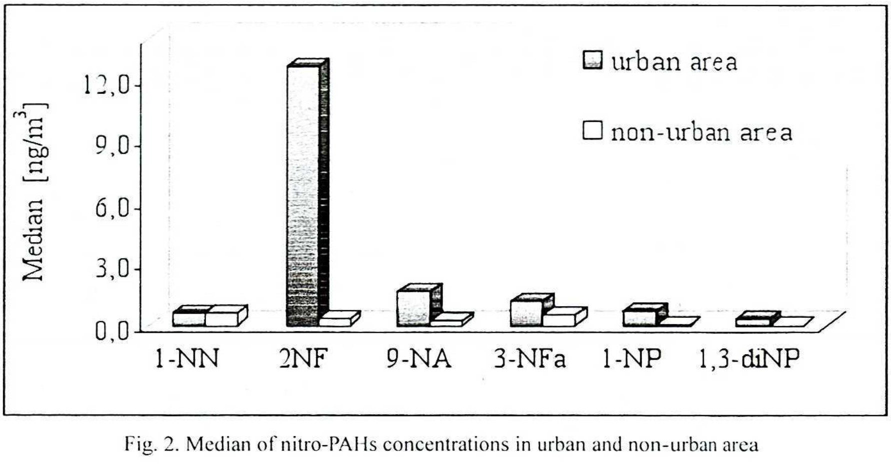


Fig. 2. Median of nitro-PAHs concentrations in urban and non-urban area

concentration is very important, because of formation more carcinogenic compounds, such as oxy- and nitro- derivatives of PAHs. This study shows presence of nitro-PAHs in urban as well as non-urban areas. The concentrations of nitro-PAHs in urban area were ten times higher than in non-urban area (with the exception of 1-nitronaphtalene).

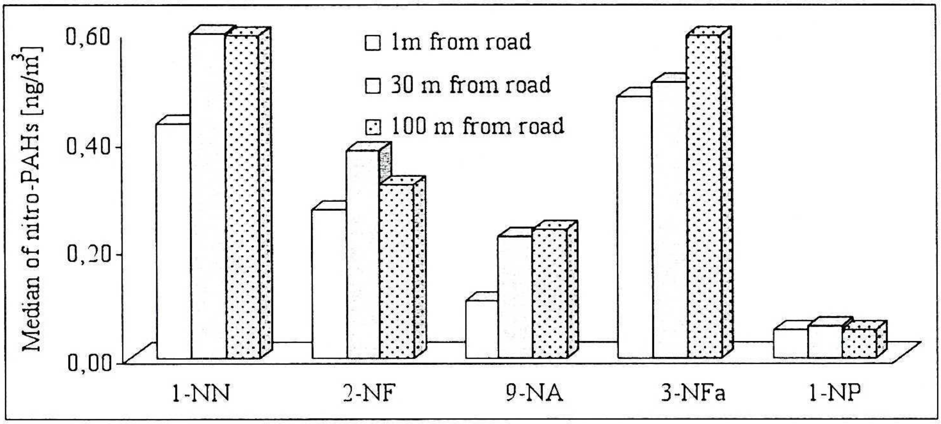


Fig. 3. Correlation between median of nitro-PAHs and distance from roadway

There was no correlation between concentration of nitro-PAHs and distance from the road (Fig. 3). 2-nitrofluoren was in the highest concentration in the air of urban area, where intensity of the traffic (especially diesel fuel powered vehicles) was high. Some studies showed 2-nitrofluorene as dominant substance in diesel exhaust, which may exceed the concentration of 1-nitropyrene by a factor of 9.8 [8, 9]. The level of exposure to 2-nitrofluorene is significant because this compound is possibly carcinogenic to humans – group 2B (according to IARC).

The concentrations of dinitropyrenes were below detection limit in almost all analyzed samples (the only exception was for the sample from urban area, where 1,3-dinitropyrene was detected at a concentration of 0.46 ng/m^3). The literature review shows that dinitropyrenes were not detected in air particulate materials [2], as well as Diesel, gasoline, ambient particulate extracts [22] and other studies [13, 26] either. Other nitro-PAHs were above the detection limit (Tab. 2). Participation of individual compounds in total mass of nitro-PAHs in urban and non-urban areas is shown in Figure 4.

CONCLUSIONS

The aim of the study was to determine the level of nitro-PAHs in the air of three towns of Upper Silesia region taking into account the intensity of traffic. Nitro-PAHs levels were investigated using the own method elaborated at IOMEH, which allows to determine traces of nitro-PAHs in their familiar form, without converting nitrocompounds into their derivatives.

Samples were collected at locations where the intensity of road transport was significant (urban area) and at locations where influence of road transport was unimportant (non-urban area). Concentration of PAHs and their nitrated derivatives were about ten times higher in urban area than in non-urban area; especially the concentration of 2-ni-

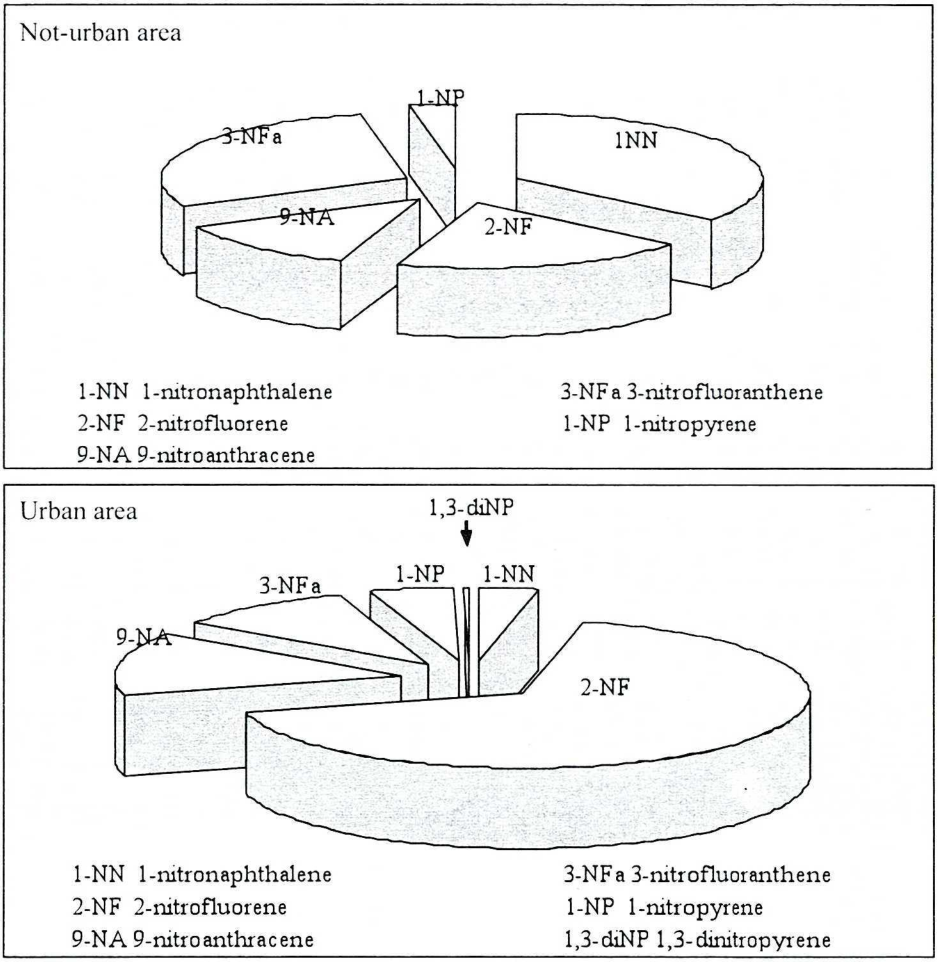


Fig. 4. Participation of individual compounds in total mass of nitro-PAHs

trofluoren was significant. High emission of nitro-PAHs compounds in urban area can be caused by diesel fuel powered buses and trucks, which are the primary source of nitro-PAHs exposure in urban area [2, 8, 9]. It can be assumed that a majority of engines in old vehicles are technically in bad condition and have been used for many years, burning a high amount of diesel fuel (about 30 dm^3 per 100 km). The performed study showed a presence of nitro-PAHs in ambient air. The exposure to mutagenic nitro- and dinitro-PAHs in ambient air causes human health hazard. For this reason the monitoring of nitro-PAHs levels in ambient air is very important. It is also necessary to take on some activities to reduce PAHs emission – the basic precursor of nitro-PAHs.

Acknowledgement

This study was supported by the Polish Ministry of Science and Higher Education (research grant 2 P05D 03629).

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Received: October 22, 2008; accepted: July 29, 2009.

ŚRODOWISKOWE NARAŻENIE NA NITRO-WWA OZNACZANE W PYLE CAŁKOWITYM W POWIETRZU GÓRNEGO ŚLĄSKA (POLSKA)

Nitrowe pochodne wielopierścieniowych węglowodorów aromatycznych (nitro-WWA) mogą powstawać podczas spalania paliwa w silnikach Diesla i w silnikach benzynowych oraz mogą powstawać podczas reakcji WWA z tlenkami azotu zachodzących w fazie gazowej. Związki te mogą być odpowiedzialne głównie za aktywność mutagenną pyłu zawieszonego w powietrzu. Stosując alternatywną do obecnych metodę oznaczania nitro-WWA w powietrzu, zbadano poziomy stężeń dla sumy WWA, nitro-WWA i dinitro-WWA w obszarze miejskim oraz pozamiejskim w trzech miastach Górnego Śląska w Polsce. Znaleziono zależność pomiędzy stężeniem WWA i nitro-WWA w obszarze miejskim i poza miejskim jak również zbadano rozprzestrzenienie się tych związków w zależności od odległości od drogi. Badania wykazały znaczący wpływ środków transportu drogowego na poziomy stężeń nitro-WWA w powietrzu.