

# RELEVANCE OF PAHs EMITTED FROM AUTOMOBILES MONITORED BY PINE NEEDLES IN TOKYO, JAPAN

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## Abstract

ERI has continued to conduct research on PCDD/PCDF concentrations in ambient air by using pine needles as bio-monitors with citizen participation for 8 years (1999-2006). In addition to PCDD/PCDF, we have initiated a pilot research for the study of PAHs in ambient air using pine needles as bio-monitors as well. The study is focused on the air pollution as emitted by automobiles. The pine needles were picked as analytical samples in both roadside areas and background residential areas in 2 separate districts in Tokyo, one in central downtown of Tokyo and the other in the suburbs of Tokyo. Through this research it became clear that PAHs which had accumulated in the pine needles picked at roadside areas were higher in concentration as compared to those picked in background areas, but further research is necessary in order to find out the correlation between black and red pines as well as pine and ambient air monitored data.

## Introduction

PAH emission from automobiles has been reported in earlier research<sup>1-5</sup>. In Tokyo, automobile air pollution (Nitrogen Oxides, Particular Matter beyond 10 micro meters diameter) has improved slightly since several years ago; nevertheless, it is still serious especially in the central Tokyo area. However, with regards to PAH pollution there have been not enough research performed by Governments. Since ERI has conducted research on ambient air concentrations of PCDD/PCDFs using pine needles as bio-monitors for 8 years with citizen participation<sup>6-8</sup>, it has been found that the monitoring using pine needles is quite effective in measuring both area-wide averages and yearly averages of ambient air concentrations with a reasonable cost, and it has also been found to be a useful citizen's environmental education and participatory monitoring activity. Therefore, we have started the research on PAHs using pine needles as bio-monitors in the same way as the research on PCDD/PCDFs. The study is aimed at finding out the correlation of PAH concentration levels between the pine needles and the ambient air focusing on the comparison between roadside and background areas. Two cities were selected within greater Tokyo for the target areas of this Pilot Study; one is in central Tokyo (Toshima Ward) and the other is peripheral border of central Tokyo (Nishi-tokyo city) as shown in Figure 1.



Fig.1 Pine needles sampled area  
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## Field Sampling Procedure

### (1) Toshima Ward Sampling

As for Toshima Ward, pine needles were collected in 4 different areas (B1, B2, R1 and R2). Two of them are arterial roadside and the others are background residential area. In each one of the areas, black pine needles were picked and in other areas the red pine needles were picked. Details are shown in Table 1 and Figure 2. The pine needles, which were picked at the same labeled points were sampled at the same weight, mixed and homogenized into one sample at about 100g. Sampling period was March 2006.



Fig.2 Pine needles sampled area in Toshima Ward

Table-1 Pine Needle Sampling Points (Toshima Ward)

	Arterial Roadside Area		Background Residential Area	
	Black Pine	Roadside1 (R1)	3 points	Background (B1)
Red Pine	Roadside2 (R2)	2 points	Background (B2)	1 point

(2) Nishi-Tokyo City Sampling

As for Nishi-Tokyo City, pine needles were collected in 4 different areas as they were in the Toshima Ward. Two of them were at arterial roadsides and the others were at background residential areas. Each one of both areas are in the north of Nishi-Tokyo City and the others are in the south of Nishi-Tokyo. Details are shown in table 2 and figure 3. Pine needles that were picked at the same labeled points were sampled at the same weight, mixed, and homogenized into one sample at about 100g. Sampling period was December 2005.

Table-2 Pine Needles picked area and number of sampling points for each (Nishi-Tokyo City)

	Arterial Roadside Area		Background Residential Area	
	North Nishi-tokyo	Roadside of Hoya-Shiki ave. (Flag mark)	2points	Background (N)
South Nishi-tokyo	Roadside of Ohme ave. (Pin mark)	4points	Background (S)	8points



Fig.3 Pine needles sampled area in Nishi-tokyo city

(3) Analysis Method

Maxxam Analytics Inc. (Ontario Canada) conducted PAHs concentration and analysis with HR-MS method based on EPA Method SW846 #8270, SOP#BRL-0423 developed by Maxxam Analytics Inc.

Results and Discussion

Table-3 PAHs Concentrations in Pine Needles (Unit:ng/g)

PAHs (Unit: ng/g)	Toshima city				Nishi-tokyo city			
	Roadside		Background		Background		Roadside	
	Black Pine (B1)	Red Pine (R1)	Black Pine (B2)	Red Pine (R2)	North	South	North (Hoya-Shiki Avenue)	South (Ohme Avenue)
Acenaphthene	1.8	1.1	3.1	2.8	7.1	0.55	2.6	14
Acenaphthylene	4.4	4.0	12	4.2	4.6	2.6	3.9	16
Anthracene	11	4.7	6.4	3.8	5.0	3.6	11	14
Benzo(a)anthracene	1.5	1.3	1.1	0.93	1.5	1.8	4.0	2.1
Benzo(a)pyrene	0.68	0.25	0.22	0.36	0.36	0.28	0.77	0.88
Benzo(b)fluoranthene	2.0	1.5	1.1	1.3	0.94	0.76	1.9	2.0
Benzo(g,h,i)perylene	0.97	1.5	0.48	0.93	0.63	0.65	2.3	2.0
Benzo(k)fluoranthene	1.6	1.6	1.1	0.97	0.87	0.64	1.8	1.8
Chrysene	11	9.2	7.9	7.4	7.2	4.2	7.8	6.6
Dibenzo(a,h)anthracene	0.16	<0.070	<0.060	<0.29	0.10	0.060	0.10	0.20
Fluoranthene	27	39	31	25	19	31	28	42
Fluorene	52	52	42	40	10	7.4	25	31
Indeno(1,2,3-cd)pyrene	0.76	1.2	0.29	0.26	0.32	0.31	0.80	0.84
Naphthalene	230	120	180	70	830	650	580	610
Phenanthrene	120	160	120	110	58	52	82	180
Pyrene	9.7	26	17	11	11	18	16	39
Total PAHs	470	420	420	280	960	770	770	960

Significant figures: Double digits

The analytical results of the PAHs are shown in Table 3 for both Toshima Ward and Nishi-Tokyo City. Naphthalene is remarkably high among all the 8 areas. However, Toshima Ward and Nishi-Tokyo City showed different characteristics besides Naphthalene. In the case of Toshima Ward, Phenanthrene is as high as Naphthalene, and Fluoranthene and Fluorene are relatively high compare to other compounds. As for Nishi-Tokyo City, only Naphthalene is extremely high, Phenanthrene is not as high as in Toshima Ward, and Fluoranthene and Fluorene are not high as well.

According to WHO Environmental Health Criteria<sup>9</sup>, Naphthalene and Acenaphthene are highly contained in diesel car exhaust gas, and Fluoranthene and Pyrene are high in gasoline car exhaust fumes. It has not yet quite sure which type of vehicle exhaust gas has influenced on the results of this research.

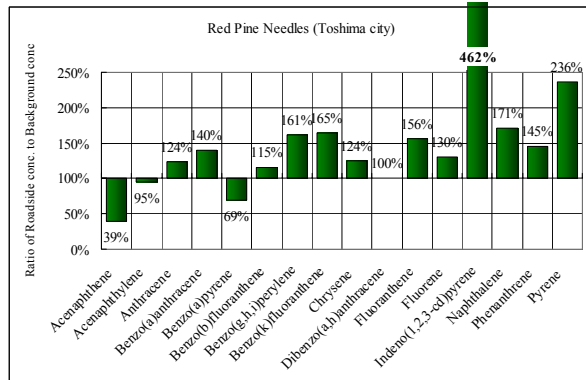
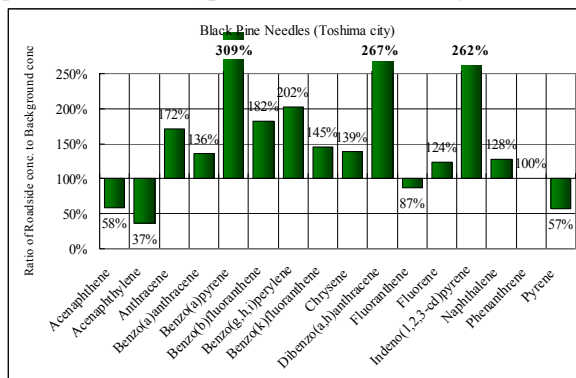


Fig.4 Ratio of Roadside concentration to Background concentration (Toshima Ward)

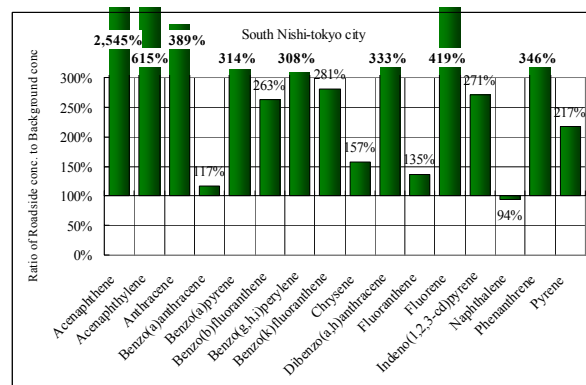
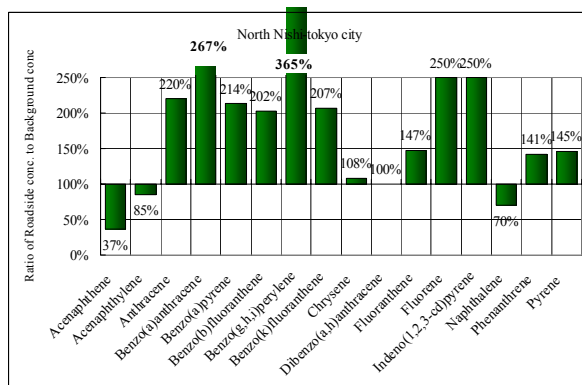


Fig.5 Ratio of Roadside concentration to Background concentration (Nishi-Tokyo City)

Fig.4 and 5 show the difference of 2 target areas indicating the ratio of roadside PAHs concentrations to background levels in each area. These are shown as a percentage of roadside concentrations to background one. Table 4 shows the data in which PAH concentration of roadside is higher than that of background. It is obvious that most of PAHs for roadside are higher than for background. The following compounds are higher in concentration at the roadside than in the background for all 4 different areas are: Anthracene, Benzo(a)anthracene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Chrysene, Fluorene and Indeno(1,2,3-cd)pyrene. These compounds are likely to be emitted from automobiles traveling on the arterial roads. On the other hand there is no compound for which the background is higher than roadside for all 8 areas.

Only for South of the Nishi-Tokyo area, Acenaphthene and Acenaphthylene roadside concentrations are higher than background. Acenaphthene levels for the roadside are more than 25 times higher than the background levels and Acenaphthylene levels for the roadside are more than 5 times higher than the background. As far as these 2 compounds are concerned, the difference between roadside (Ohme Ave.) and the background is quite obvious in the South of Nishi-Tokyo even though it is not quite certain that these compounds mainly coming from automobiles.

In this research, the differences and the correlation between black and red pine needles are also analyzed by collecting these 2 types of pine needles from almost the same areas as the Toshima Ward. The total PAH

concentration for black pine needles is higher than red ones as it was analyzed in the PCDD/PCDF fraction, but actually each of the compounds has different characteristics. Thus, it is not yet proven whether the accurate correlations between black and red pine needles, in case of PCDD/PCDF, that the black pine needle results are 2 times higher than the red pine needle samples.

Table 4 PAHs concentration for roadside is higher than for background are checked

PAHs	Toshima city		Nishi-tokyo city	
	Black Pine	Red Pine	North	South
Acenaphthene				v
Acenaphthylene				v
Anthracene	v	v	v	v
Benzo(a)anthracene	v	v	v	v
Benzo(a)pyrene	v		v	v
Benzo(b)fluoranthene	v	v	v	v
Benzo(g,h,i)perylene	v	v	v	v
Benzo(k)fluoranthene	v	v	v	v
Chrysene	v	v	v	v
Dibenzo(a,h)anthracene	v			v
Fluoranthene		v	v	v
Fluorene	v	v	v	v
Indeno(1,2,3-cd)pyrene	v	v	v	v
Naphthalene	v	v		
Phenanthrene		v	v	v
Pyrene		v	v	v
Total PAHs	v	v		v

v: Concentration for roadside is higher compared to background

This research is the first step towards citizen participatory PAH measuring using pine needles. Since there are lots of asthma patients in downtown Tokyo, it is important to continue the effective monitoring measures focusing on exhaust gas from automobiles of dense traffic areas in Tokyo, and should also be continued in same areas and be extended to other areas of Tokyo in the future, involving citizen participation.

### Acknowledgements

This project could not have been possible without the cooperation of citizens group of the “Air Pollution Measuring Activities Association in Tokyo”, which picked pine needles in Toshima Ward and the “Local Association for Stop Road Construction to Conserve Local Community in Nishi-Tokyo City” which picked pine needles in Nishi-Tokyo City. These groups are quite diligent about conservation activities against automobile air pollution in Tokyo. The authors would like to extend thanks to the HRMS Laboratory of Maxxam Analytics Inc. in Burlington, Ontario, Canada for analyzing all the pine needle samples for this Pilot Study.

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