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Chapter 23

FIELD INVESTIGATION OF PAHS IN SOILS AROUND NARA CITY IN JAPAN

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Abstract: PAHs are the general term for compounds having two or more benzene rings. These are discharged from diesel motor gas, tanker accidents, oil emissions by cars, and so on. They float in the atmosphere, and it is considered that they are absorbed in soil as a result of rain. Generally, compounds that have two and three benzene rings show only toxicity, whereas those having four or more benzene rings show toxicity, carcinogenicity and mutagenicity. Benzo(a)pylene has been shown to be an endocrine disrupter. We investigated the action of 16 PAHs specified by the U.S. EPA in soil around Nara city in Japan. Soil was collected from different locations involving traffic and vegetation. Soils from three locations around our university were collected every month, to investigate seasonal movement. PAHs were extracted from soil by soxhlet extraction with dichloromethane. They were then analyzed quantitatively by HPLC/UV. We classed PAHs by number of rings, and examined the concentration and seasonal movements. All content of 16 PAHs in soils increased in proportion to traffic volume. At the same locations of traffic volume, the gravitation at a location with plant with all content of 16 PAHs in soils was, furthermore, found to have a low concentration. There were different seasonal movements of the 2, 3-ring and 4, 5, 6-ring PAHs. 4, 5, 6-ring PAHs have a strong correlation with each other ($r>0.79$), but there were no correlations between 2, 3-ring and 4, 5, 6-ring PAHs. As a result, the traffic volumes are exposition sources of 4, 5, 6-ring PAHs in soils.

Key words: PAHs; soils; field investigation; diesel motor gas; tanker accidents; oil emissions; benzo(a)pylene; Nara City; Japan; traffic; vegetation

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental contaminants found in air, sea, river water and soil. They occur as common constituents of gasoline, coal tar and shale oil, but are most frequently formed by incomplete combustion of fossil fuels (Pothuluri and Cerniglia, 1994; Maila and Cloete, 2002). Therefore, these substances are long-lasting, poorly degradable pollutants that accumulate in the environment. Furthermore, these substances present a great affinity for organic materials in soil such as humus. Some PAHs are known to be carcinogenic and mutagenic (Laflamme and Hite, 1978; Pahlman and Pelkonen, 1987). Benzo(a)pyrene especially is known as an endocrine disrupter (Liu and Korenaga, 2001). Sixteen PAHs have been selected by the US Environmental Protection Agency (EPA) as Constant Decree priority pollutants for regulatory purposes (Hodgeson, 1990). The potential for atmospheric concentrations of PAHs to accumulate in many geographical locations of the world has been determined and reported, e.g., Massachusetts, USA (Allen et al., 1996), Athens, Greece (Viras et al., 1987), Mumbai, India (Kulkarni and Venkataraman, 2000), Lahore, Pakistan (Smith et al., 1996), and Kuala Lumpur, Malaysia (Omar et al., 2002). However, there is still very little information on the concentration of these substances in soil.

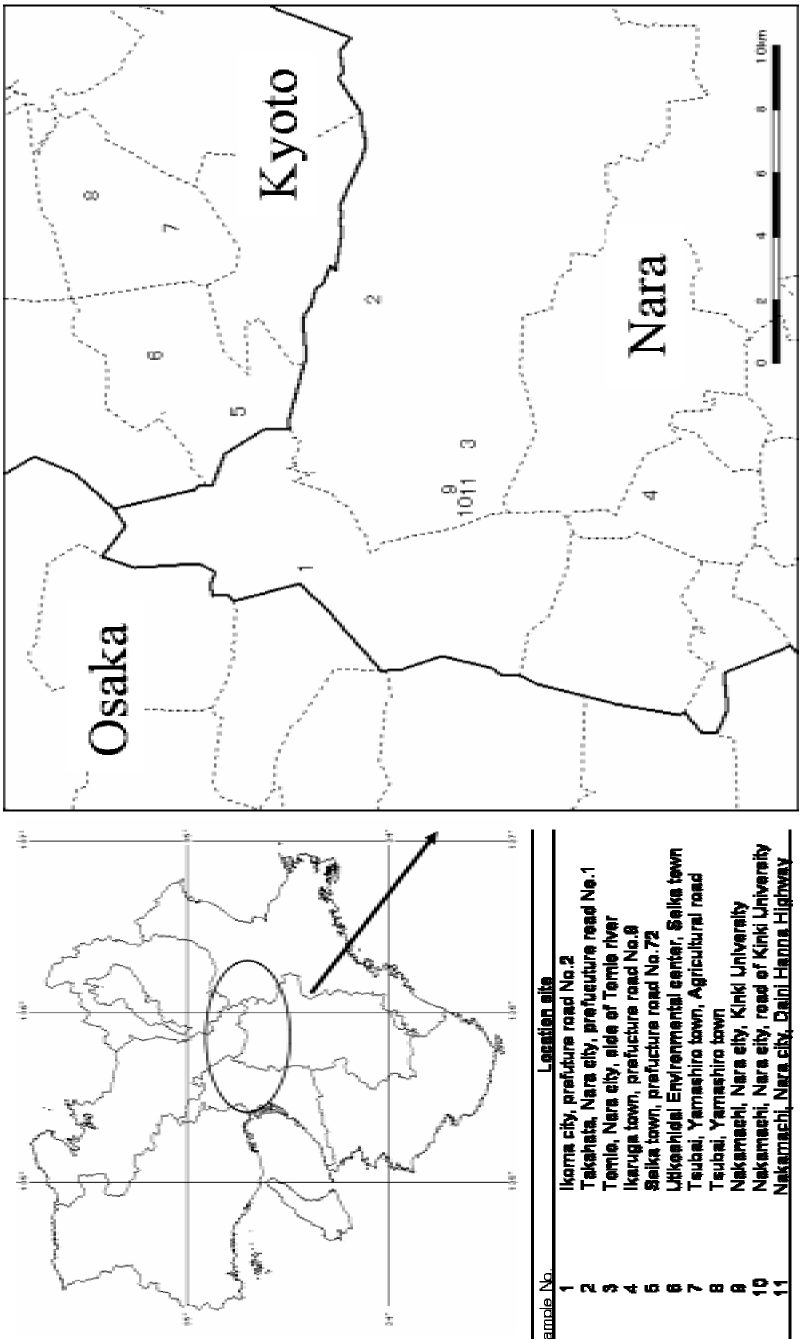
The remediation of organic pollutants uses physical and chemical techniques. The cost, however, is very expensive and the processes require significant labor. The solutions to this problem are bioremediation and phytoremediation. Bioremediation is a technique by which pollutants are biodegraded by bacteria. It has been reported that white rot fungi can extensively biodegrade PAH (Bumpus, 1989; Zheng and Obbard, 2002), because white rot fungi are capable of non-specifically oxidizing aromatic compounds through the abstraction of an electron or a hydrogen atom. (Barr and Aust, 1994; Hattaka, 1994). Phytoremediation is the process by which contaminants in the environment are removed by plants (Cunningham et al., 1996). The targets of phytoremediation are various pollutants, e.g. heavy metals, NOx, SOx, agricultural chemicals and PAHs. Enhancement of PAH degradation in soil rhizospheres has been shown in several studies (Aprill and Sims, 1990) (Qiu et al., 1994; Reilley et al., 1996) (Binet et al., 2000). Grasses are being used for microbial colonisation due to their fibrous root systems with extensive surface areas (Adam and Duncan, 2002). The studies and investigations have not provided sufficient information regarding the relationship between soil PAHs and vegetation.

In this study, we investigated the actions of 16 PAHs specified by the U.S. EPA in soil around Nara city in Japan.

2. MATERIALS AND METHODS

2.1 Soil Sampling

Soil was collected from various sites in highly trafficked and vegetated areas, as well as three sites around the university, in Figure 1.



Sample No.	Location site
1	Ikoma city, prefuture road No.2
2	Takahata, Nara city, prefucuture road No.1
3	Tomio, Nara city, side of Tomio river
4	Ikaruga town, prefucture road No.9
5	Seika town, prefucture road No.72
6	Utikoshidai Environmental center, Seika town
7	Tsubai, Yamashiro town, Agricultural road
8	Tsubai, Yamashiro town
9	Nakamachi, Nara city, Kinki University
10	Nakamachi, Nara city, road of Kinki University
11	Nakamachi, Nara city, Daini Hanna Highway

Figure 1. Sampling sites around Nara City and location site.

2.2 Concentrations of 16 US EPA-identified PAHs in soils

Collected soils were sieved with a 2.0 mm nylon mesh sieve. PAHs were extracted from 5.0 g of soil by soxhlet extraction with 120 ml of dichloromethane. These extractions processes were repeated three times. Extracted solutions were condensed to 1.0 mL by an evaporator using N_2. The concentrations of 16 PAHs were determined by HPLC analysis. HPLC determination was performed using a Shimadzu Co, Ltd. LC-10AT binary pump and SPD-10A UV/VIS detector. Column and analytical parameters were as follows

Column: 25 cm × 4.6mm i.d. stainless steel analytical column packed with 5 μm Supercosil LC-PAH (Superco).

Analytical parameters: 5 min after starting analysis, linear gradient elution from 40: 60 acetonitrile/water to 100:0 acetonitrile/water 35 min after starting analysis. The temperature of the column was 23 degrees, flow rate was 1.0ml/min and detection wavelength was 254nm. Injection volume was 5.0μL.

2.3 Classed PAHs

We classed PAHs by number of rings, and examined the concentration and seasonal movements. Table 1 indicates the ring numbers of 16 PAHs.

Table 1. Ring Numbers of 16 PAHs

name	**ring numbers**
naphthalene	2
acenaphthylene	3
acenaphthene	3
fluorene	3
phananthrene	3
anthracene	3
fluoranthene	4
pyrene	4
benzo[a]anthracene	4
chrysene	4
benzo[b]fluoranthene	5
benzo[k]fluoranthene	5
benzo[a]pyrene	5
dibenz[a,h]anthracene	5
benzo[glu]perylene	6
indeno[1,2,3,-cd]pyrene	6

3. RESULTS AND DISCUSSION

3.1 Quantity of distribution of PAHs in soils of different geographical condition

Table 2 summarizes the concentrations of 16 PAHs at different vegetated and trafficked sampling sites of Nara City in Japan. Heavy traffic caused higher concentrations of total PAHs. However, sites with extensive vegetation in the same trafficked area had lower concentrations of total PAHs. When classified by the number of benzene rings, vegetation greatly influenced the number of rings. Since 2- and 3-ring PAHs have higher volatility, these did not remain in soil, while 4- to 6-ring PAHs more easily remained in soil, and were degraded by plants and bacteria.

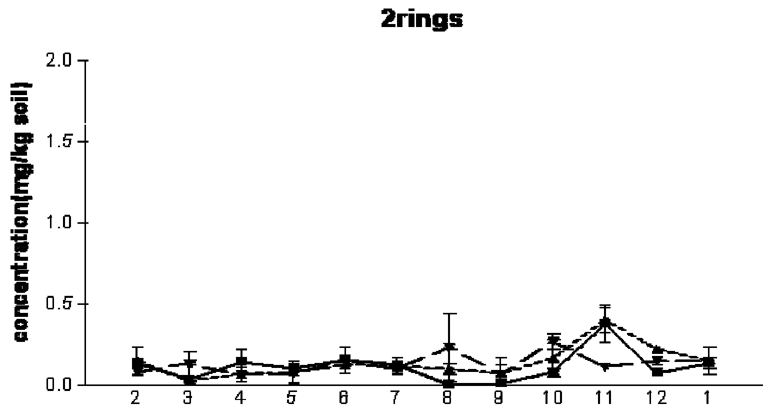
Table 2. Concentration of total and ring number of Pahs (mean ± S.D.) at different sites (Sample No. 1-8)

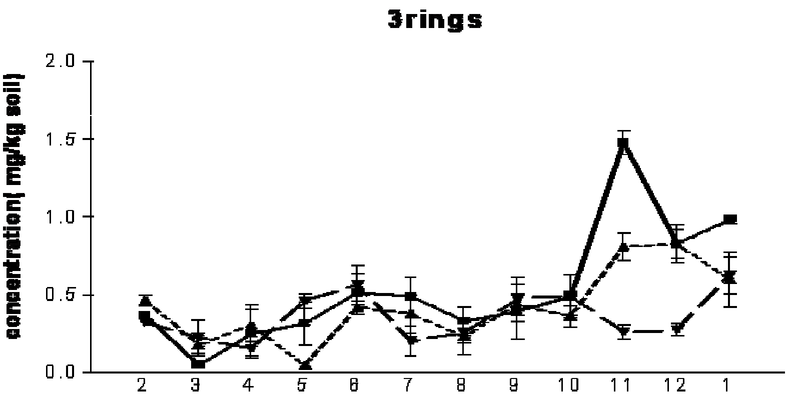
Sample No.	Traffic*	Vegetation**	Concentration (mg/kg soil)					
			Total PAHs	2-ring	3-ring	4-ring	5-ring	6-ring
1	++	-	4.25±1.18	0.29±0.07	1.06±0.29	0.53±0.17	1.21±0.27	1.16±0.39
2	++	-	3.86±1.31	0.29±0.05	1.13±0.32	0.66±0.44	0.90±0.15	0.90±0.36
3	++	+	2.59±1.53	0.38±0.22	0.82±0.69	0.50±0.29	0.54±0.30	0.35±0.25
4	+	+	0.51±0.13	0.11±0.02	0.26±0.04	0.10±0.03	0.03±0.04	0.01±0.01
5	+	+	0.37±0.12	0.03±0.01	0.07±0.02	0.08±0.01	0.15±0.05	0.05±0.01
6	-	++	0.25±0.12	0.06±0.05	0.08±0.02	0.04±0.04	0.05±0.09	0.02±0.03
7	-	ND	1.07±0.38	0.35±0.01	0.47±0.20	0.12±0.08	0.10±0.09	0.03±0.05
8	-	-	1.05±0.26	0.02±0.16	0.63±0.04	0.10±0.01	0.07±0.00	0.04±0.04

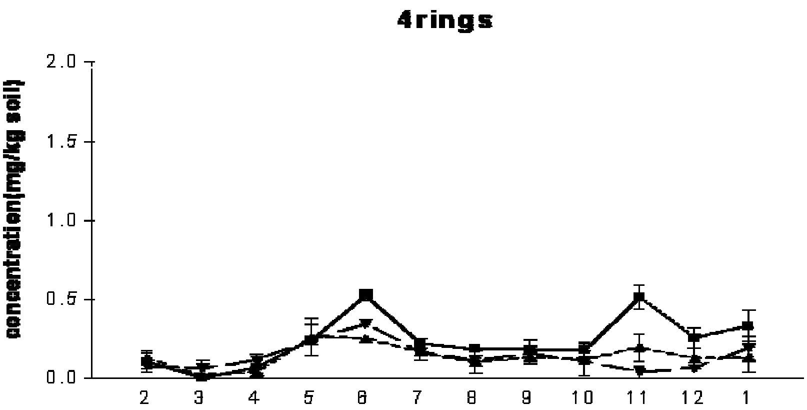
*++: >5,000 cars/day, +: 500-5,000 cars/day, -: <500 cars/day
**++: whole surface vegetation, +: 70% covered vegetation, -: less than 50% covered vegetation
ND: No vegetation

3.1 Seasonal variations

Figure 2 indicates the variation of total and ring number of PAHs concentration in soils at three sites (No. 9-11) around Kinki University between February 2003 and January, 2004. Although a significant variation was not recorded overall, in November all three sites showed decreased total PAHs. More so at site no. 11 (the Daini Hanna Highway) compared to the two other sites (No. 9 and 10). At site no.11, plant residue accumulation due to fallen leaves and the apoptosis of herb plants together with atmospheric fallout and road dust, decreases the total PAH concentration in the soil. PAH levels at site No.11 return to the same levels as sites Nos 9 and 10 in January as the accumulated layer begin to be removed by physical actions such as seasonal wind and degradation action by organisms such as microbes. As for 2- and 3-ring PAHs, there is not the difference that each of the three sites of others fluctuating greatly is large after October. In contrast, for 4 or more benzene rings in PAHs, fluctuation was observed in soils between April and July, and October to December. Based on the above observations, Table 3 and Figure 3 show a correlation coefficient for content by the number of benzene rings in PAHs from February, 2003 to January, 2004. 4-, 5-, and 6-ring PAHs have strong correlations with each other ($r>0.79$), but there are no correlations between 2-, 3-ring PAHs and 4-, 5-, 6-ring PAHs. This suggests a different origin for 4-, 5-, 6-ring PAHs, i.e., their source is different from that of 2-, 3-ring PAHs. By investigation under different environments and geographical conditions, PAHs having more than 4 rings were found in sites with high traffic volume, and the content was high. It is thus thought that exhaust gases from cars are the main exposition source of PAHs having more than 4 rings. Since 2- and 3-ring PAHs have higher volatility, they are of atmospheric origin. However, we found a positive correlation of around 0.6 between 3-ring PAHs and 4-, 5-ring PAHs. From this, it was thought that microbial degradation processes stay behind through various pathways in the soil as well as one exposition source.


2rings
concentration(mg/kg soil)
2.0
1.5
1.0
0.5
0.0
2 3 4 5 6 7 8 9 10 11 12 1


3rings
concentration(mg/kg soil)
2.0
1.5
1.0
0.5
0.0
2 3 4 5 6 7 8 9 10 11 12 1


4rings
concentration(mg/kg soil)
2.0
1.5
1.0
0.5
0.0
2 3 4 5 6 7 8 9 10 11 12 1

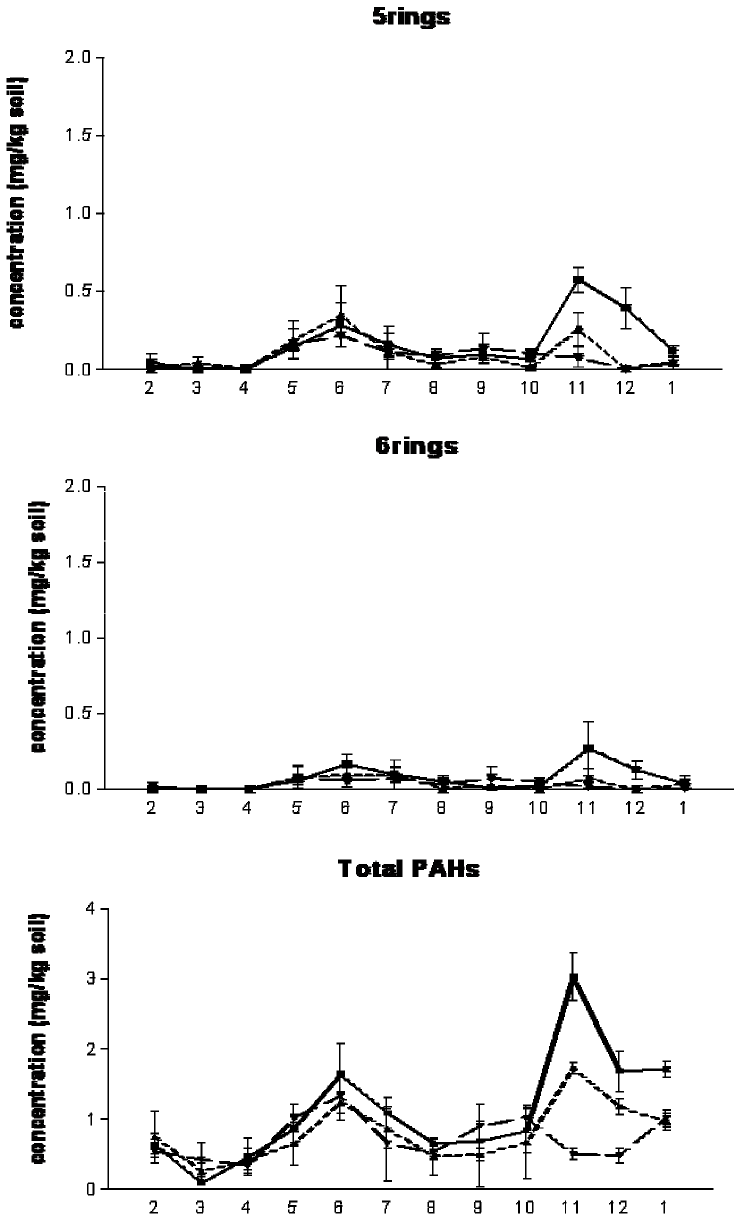


Figure 2. Variation of total and ring number of PAHs concentration in soils since Feb 2003 to Jan 2004.

■: Sample No. 9; ▲: Sample No. 10; ▼: Sample No. 11, Data represent mean±S.D.

Table 3. Correlation coefficient of different numbers of PAHs (No. 8-11)

	2-ring	**3-ring**	**4-ring**	**5-ring**	**6-ring**
2-ring	-	0.650**	0.348	0.431**	0.414
3-ring		-	0.618**	0.635**	0.592**
4-ring			-	0.796**	0.810**
5-ring				-	0.926

**: $p<0.01$

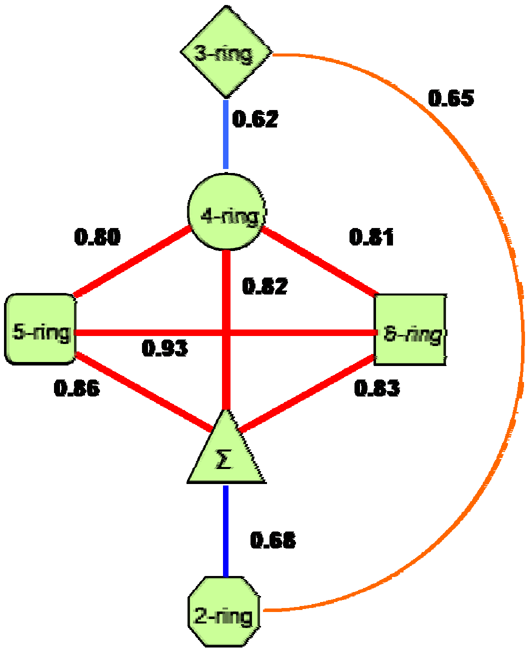


Figure 3. Correlation for content by the number of benzene rings in PAHs

4. CONCLUSION

We investigated the action of 16 PAHs specified by the U.S. EPA in soil around Nara city in Japan. We classed PAHs by number of rings, and examined their concentration and seasonal movements. The content of all 16 PAHs in the sampled soils increased in proportion to traffic volume. At the same locations of traffic volume, the gravitation at a location with plant with all content of 16 PAHs in soils was, furthermore, found to have a low concentration. There were different seasonal movements of the 2, 3-ring and 4, 5, 6-ring PAHs. 4, 5, 6-ring PAHs have a strong correlation with each other ($r>0.79$), but there were no correlations between 2, 3-ring and 4, 5, 6-

ring PAHs. As a result, the traffic volumes are exposition sources of 4, 5, 6-ring PAHs in soils.

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