

Dynamics Analysis for Emission Sources of Polycyclic Aromatic Hydrocarbons in Tokushima Soils

Takashi Korenaga,^{*,a,b} Xiaoxing Liu,^b and Yoko Tsukiyama^a

^aFaculty of Integrated Arts and Sciences, University of Tokushima, 1-1 Minami-josanjima-cho, Tokushima 770-8502, Japan and ^bGraduate School of Engineering, University of Tokushima, 2-1 Minami-josanjima-cho, Tokushima 770-8506, Japan

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Soil samples from 30 sites in Tokushima, Japan, were analyzed to obtain contemporary normal (or typical) levels of polycyclic aromatic hydrocarbons (PAHs) in local soils. A very wide range of PAH concentration has been observed in these soils. The Σ PAH values ranged over 2 orders of magnitude, from 1 to 147 $\mu\text{g}/\text{kg}$. Fluoranthene was consistently found to be the most abundant compound. Other major constituents were pyrene, benzo[*b*]fluoranthene, and benzo[*a*]anthracene. Biomass burning and vehicular exhaust contribute PAH to soils. Higher PAH contents in rural soils principally came from biomass burning. Mobile sources (diesel- and gasoline-powered vehicles) raise PAH contents in urban soils. In addition, soil properties play some role in controlling/influencing the PAHs contents of soils.

Key words — polycyclic aromatic hydrocarbon, contemporary normal level, soil, emission source

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are compounds typically containing two to eight aromatic rings that are formed during incomplete combustion from natural and anthropogenic sources. Some are known to be mutagenic and carcinogenic. Benzo[*a*]pyrene has been listed as an endocrine

disruptor in the “environmental hormone” category. PAHs exhibit a wide range of physical-chemical properties (vapor pressure, aqueous solubility)¹⁾ that demonstrate their semivolatile and hydrophobic character and influence their environmental fate.²⁾ The anthropogenic contribution, notably vehicle emissions and the use of fuel for residential heating, industrial processes, electric power production, and waste incineration, frequently outweighs PAH input from almost all natural sources.³⁻⁶⁾ Despite the numerous sources of PAH in urban/industrial centers, they occur at relatively high concentrations in rural/remote areas. PAHs are released and dispersed whenever natural biomass is burned, resulting in a general background level of PAHs in soils and sediments. Although many PAHs are included in the “priority pollutant” listings produced by the US Environmental Protection Agency (EPA, U.S.A.) and by the European Commission, there are many uncertainties over the significance of PAHs in relation to soil quality and their transfer from the soil into the human food chain. There is very little information on contemporary normal (or typical) levels of PAHs in soils, their persistence and degradation, their behavior in soil-plant systems,⁷⁾ and their mobility from the soil surface layers.⁸⁾

Tokushima is a non-heavy industry district in Japan, because the ratio of heavy to light industries is 18 : 82.⁹⁾ Figure 1 shows that there are few of coal and petroleum industries in Tokushima, which are principal sources of PAH emission. Thus it is considered that biomass burning and vehicular exhaust contribute PAH to soils. Rice straw was chosen as the experimental biomass in this study. This paper presents information on contemporary typical PAH levels in Tokushima soils. The data in relation to factors affecting PAH contents are discussed, and PAH emissions from biomass burning and vehicle exhaust are analyzed.

MATERIALS AND METHODS

Surface soil samples (0–5 cm depth) were collected from 30 sites in Tokushima, Japan. These were selected across a range of soils along roadsides and at rice straw burning locations (Fig. 2). The transects run N–S and W–E through Tokushima. Locations where obvious anthropogenic inputs exist were not selected for sampling.

Chemicals — Special-grade reagent dichloromethane (DCM), acetonitrile, methanol, hexane, and

*To whom correspondence should be addressed: Faculty of Integrated Arts and Sciences, University of Tokushima, 1-1 Minami-josanjima-cho, Tokushima 770-8502, Japan. Tel.: +81-88-656-7263; Fax: +81-88-656-7112; E-mail: korenaga@ias.tokushima-u.ac.jp

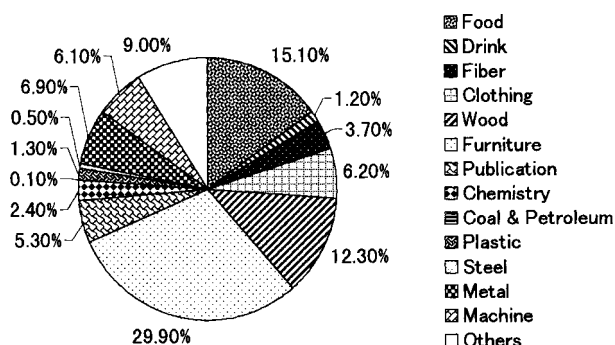


Fig. 1. Distribution of Heavy and Light Industries in Tokushima in 1993

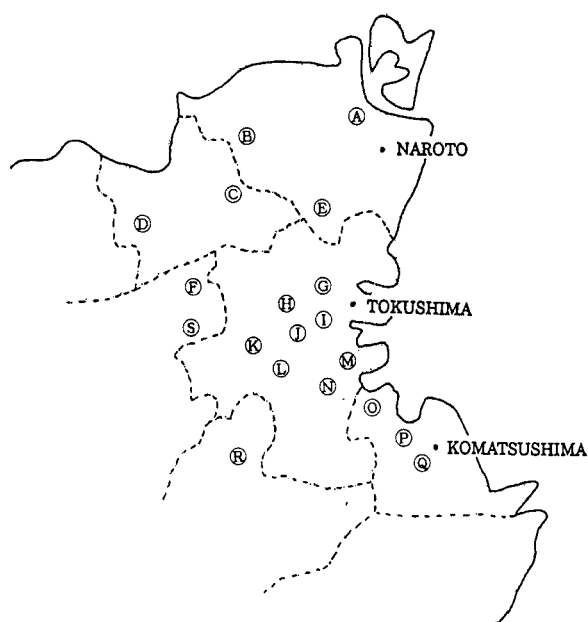


Fig. 2. Sample Location Map

ethanol were purchased from Wako Pure Chemical Industries Ltd. (Osaka, Japan). The standards of PAHs were purchased from various companies. Acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, benzo[*a*]pyrene, and dibenz[*a,h*]anthracene were purchased from Wako Pure Chemical Industries; fluoranthene, benz[*a*]anthracene, naphthacene, and perylene were purchased from Kanto Chemical (Tokyo, Japan); and chrysene was purchased from Aldrich (U.S.A.).

The standard stock solutions of 10 PAHs species (1.0 $\mu\text{g/ml}$) were prepared in ethanol and refrigerated (4°C) before use. The operative solutions were prepared by diluting the stock solution to a specified concentration with ethanol.

Sample Collection and Processing — At each site, 10 points of 0–5-cm cores were taken with a

stainless steel corer, wrapped individually in aluminum foil, transported to the laboratory in sealed vinyl bags, and stored at 4°C prior to oven drying. The soils were then disaggregated with a mortar and pestle, sieved through a 2-mm mesh, bulked, and then stored in glass jars (previously rinsed with DCM) with polypropylene lids prior to analysis.

Sample Extraction — A 20-g sample of 48-h oven-dried (at 60°C) and sieved soil was put into a Soxhlet extractor (Iwaki, Japan), which had been previously rinsed with DCM. The soil was then extracted over 20-h¹⁰⁾ with DCM 120 ml after the addition of 20 μl of phenanthridine internal standard. After extraction, the extract was removed from the Soxhlet extractor and dried in a draft chamber. For cleaning extracts, column chromatographic steps with silica gel as column packing was used. The sample was prepared by dissolving the extract in DCM, and then it was charged to the top of the column and eluted with 3 ml of hexane followed by 7 ml of a 4 : 1 (v/v) solution of DCM : hexane and 5 ml of a 4 : 1 (v/v) solution of DCM : methanol. PAHs eluted in the second eluent¹¹⁾ were collected and dried in the draft chamber. The sediment was dissolved in DCM 3 ml and refrigerated at 4°C before analysis.

Analytical Methods — Analysis of PAHs was performed with high-performance liquid chromatography (HPLC). PAHs were separated on a STR-ODS II 5- μm column (Shimadzu, Kyoto, Japan) with a mobile phase of 70 : 30 (v/v) acetonitrile/distilled deionized water, running over 45 min at a flow rate of 0.7 ml/min. The detection was by UV absorbance at 254 nm and by fluorescence operating simultaneously in series. The compounds quantified include acenaphthylene, phenanthrene, fluoranthene, pyrene, benz[*a*]anthracene, benzo[*b*]fluoranthene, perylene, benzo[*a*]pyrene, and dibenzo[*a,h*]anthracene.

The recoveries from the procedure described above were checked against spiked PAH standards. Recoveries were in the range of 30–70%, with the lower figures for the lower molecular weight PAHs. Data presented here are the means of duplicate analyses.

RESULTS AND DISCUSSION

Typical PAH Concentrations in Soils

The complete data set for individual PAHs, and ΣPAHs are given in Table 1. Sample location appears to be the most important factor affecting soil

Table 1. PAH Data Set for Tokushima Soil Samples ($\mu\text{g}/\text{kg}$ Dry Weight)^{a)}

Area	Site name	Site		Acy	Ph	Fla	Py	B[a]A	B[b]F	Per	B[a]P	D[a,h]A	ΣPAH	
		code	Sampling ^{b)}											
Rural	Naruto	A	1	0.3			0.4	0.3	0.2	0.3		0.2	2	
		Oasa	B	1			0.5		0.2					1
	2		11	11	3	0.5							26	
	3		5.2	0.7				0.8					7	
	Itano	C	2	5	17	3.3			0.3			1.5	27	
			3	0.8		1.8		0.5					3	
	Kamiita Takase	D	4	1.6	0.8	2.5	1.3	0.3	0.5	0.6		1.5	9	
	Yoshinari	E	2	6.4		38	6.8	0.8	2.1	2.8	0.5		1.9	59
			3	1.4		3.5	2.4	0.5	1.2	1.8	0.3		0.3	11
	Kitajima	F	2	7		2.4	3.7	0.5	0.8	0.5			0.7	16
			3	23	0.6	89	9	1.3	3.4	5.5	2.3		13	147
	Ronden	N	2	1.7		2	0.3	1.0	1.7	0.7	1.5			9
			3	1.8		3	0.5	1.0	2.3	1	2.1			12
	Nakanogo	O	2	5	0.2	11	2	0.3	0.3	0.7	0.2		2	22
			3	0.8		0.5				0.4			0.2	2
	Higaino	P	2	6.8		23	3	1	3.4	3.6	1.0		1.7	44
			3	5.3		14	4	0.8	2	1.7	0.7		0.9	29
	Tachikawa	Q	1	1.6		3.8	1.2	0.2	0.5	0.3				8
	Sanagawauchi	R	1	1.5		1.0	0.7							3
	Shimoura	S	1	1.0			0.2		0.2	0.4			1.0	3
Urban	Nakayoshino	G	2	6		3	0.8		0.5	0.2			10	
			3	4.2		16	1.3	0.6	1.7	1.6	0.5		1.7	28
	Tamiya	H	2	0.6		8	3.4	0.3	1	2	0.7		8	24
			3	3.7		22	5	0.7	2	3	1.1		4	42
	Nakajosanjima	I	2	2.4		22	5.3	0.7	1.7	3	0.8		1.3	37
			3	7		0.5	0.5							8
	Tokushima station	J	1	1.7			2.2	0.2	0.7	0.8		0.2	6	
	Kuramoto	K	1	1.8	0.3	0.5	1.4		0.3	0.5		0.6	5	
	Tsuda	L	1	12	1.5	72	4.2	1.7	6.3	7.6	2.7	5.2	113	
	Hachiman	M	1	2.7		15.5	0.2	0.3	1.1	0.5	0.2	0.7	21	

a) Blank indicates "not detected," treated as zero for averaging. b) Conditions: 1, roadside; 2, farm where rice straw is burned; 3, 5 m from burning site; 4, farm sample. Abbreviations: Acy, acenaphthylene; Ph, phenanthrene; Fla, fluoranthene; Py, pyrene; B[a]A, benz[a]anthracene; B[b]F, benzo[b]fluoranthene; Per, perylene; B[a]P, benzo[a]pyrene; D[a,h]A, dibenz[a,h]anthracene.

PAH contents. In general, samples taken along the gradient of rural-urban locations have higher contents PAHs. Table 2 presents a summary of the mean, median, and range of values reported for all the soils sampled. The typical or normal range of PAHs in Tokushima soils can be obtained from the 20 transect. These values are summarized in Table 3.

Several points are apparent from the data. First, a very wide range of PAH concentration is observed in these soils. The ΣPAH values range over 2 orders of magnitude, from 1 to 147 $\mu\text{g}/\text{kg}$. It should be stressed that these values are for "typical" soils, not those from grossly contaminated locations. Second, in general, if a soil has a high concentration of one PAH compound, others are likely to be present in

Table 2. Mean, Median, and Range Values for PAHs in Tokushima Surface Soil Samples ($\mu\text{g}/\text{kg}$ Dry Weight)

Compound	Mean	Median	Range	σ_{n-1} ^{a)}
Acenaphthylene	4.4	2.7	<1.0–23	4.7
Phenanthrene	0.7	0.6	<1.0– 1.5	0.5
Fluoranthene	16	11	<1.0–89	22
Pyrene	2.4	1.8	<1.0– 9	2
Benz[a]anthracene	0.6	0.6	<1.0– 1.7	0.4
Benzo[b]fluoranthene	1.4	1	<1.0– 6.3	1.4
Perylene	1.6	0.8	<1.0– 7.6	1.8
Benzo[a]pyrene	1.0	0.8	<1.0– 2.7	0.7
Dibenz[a,h]anthracene	2.3	1.4	<1.0–13	3
ΣPAHs	24	11	1.0–147	31

a) σ_{n-1} , standard deviation.

Table 3. Typical Values for PAHs in Tokushima Surface Soil Samples ($\mu\text{g}/\text{kg}$ Dry Weight)

Compound	Mean	Median	Range	σ_{n-1} ^{a)}
Acenaphthylene	4.4	1.8	<1.0– 23	5.6
Phenanthrene	0.8	0.7	<1.0– 1.5	0.5
Fluoranthene	19.5	11	<1.0– 89	28
Pyrene	2	1.3	<1.0– 9	2.2
Benz[<i>a</i>]anthracene	0.6	0.6	<1.0– 1.7	0.4
Benzo[<i>b</i>]fluoranthene	1.4	1	<1.0– 6.3	1.6
Perylene	1.7	0.8	<1.0– 7.6	2.1
Benzo[<i>a</i>]pyrene	1.2	0.9	<1.0– 2.7	1
Dibenz[<i>a,h</i>]anthracene	2.3	1.4	<1.0– 13	3.6
ΣPAHs	24	11	1.0–147	38

a) σ_{n-1} , standard deviation.

high concentration as well. This can be seen from the data in Table 1. Most PAH compounds are log normally distributed in the sample population. This can be seen by comparing the mean and median values given in Tables 2 and 3.

In Table 4, individual PAH compounds have been ranked under different ΣPAH ranges. Fluoranthene is consistently found to be the most abundant compound. Other major constituents are pyrene, benzo[*b*]fluoranthene, and benzo[*a*]anthracene. Table 4 illustrates some interesting trends. One is that acenaphthylene is the most abundant compound in soils with low ΣPAHs values, but becomes relatively less important with increasing ΣPAH values. In contrast, dibenz[*a,h*]anthracene forms a greater proportion of the total soil PAH burden in more contaminated samples; it is ranked sixth in soils with low ΣPAH values (1–10 $\mu\text{g}/\text{kg}$) but third in soils with high ΣPAH values (101–150 $\mu\text{g}/\text{kg}$).

However, it should be emphasized that these are only general trends.

Source of Soil PAHs

Edwards¹²⁾ has suggested that the typical level of endogenous ΣPAHs in soils is in the range 1–10 $\mu\text{g}/\text{kg}$, resulting from plant synthesis and natural fires. Two roadside and 11 farm samples analyzed in this study were contaminated by roughly 2–11- and 2–15- fold, respectively. Fluoranthene composed up to 61% and 64% of the ΣPAH concentration in Kitajima and Tsuda soils, respectively. Rice straw burning areas were included in this study to investigate PAH emissions from biomass burning. Seven rice straw samples with moisture contents of 0%, 5%, 10%, 15%, 20%, 25%, and 30% were burned to determine the level of PAH emission. Figure 3 shows that the highest emission of all PAHs detected during rice straw burning was of fluoranthene. Therefore the high fluoranthene content in soils is thought to be mainly due to biomass burning, and its degradation is slower in organically rich soils. Vehicular exhaust is another source to PAHs in soils. The number of diesel-engine and gasoline-engine vehicles increased by 46% and 47%, respectively, in Tokushima from 1987 to 1994. Diesel trucks are the major source of lighter PAHs, while light-weight gasoline vehicles are the dominant source of higher molecular weight. PAHs such as benzo[*a*]pyrene and dibenz[*a,h*]anthracene.¹³⁾ PAH contents in urban roadside soils were higher than in rural sample due to the greater traffic on those roads. Samples from Tsuda had the highest benzo[*a*]pyrene and dibenz[*a,h*]anthracene contents.

In this study, it was also observed that PAH con-

Table 4. Proportion of Individual PAH Compounds under Different ΣPAH Soil Values^{a)}

Compound	Relative ranking in different ΣPAH ranges			
	1–10 ^{b)} <i>n</i> = 14	11–30 <i>n</i> = 10	31–100 <i>n</i> = 4	101–150 <i>n</i> = 2
Acenaphthylene	1	2	3	2
Phenanthrene	9	9	9	9
Fluoranthene	2	1	1	1
Pyrene	3	3	2	4
Benz[<i>a</i>]anthracene	7	7	8	8
Benzo[<i>b</i>]fluoranthene	4	5	5	6
Perylene	5	6	4	5
Benzo[<i>a</i>]pyrene	8	8	7	7
Dibenz[<i>a,h</i>]anthracene	6	4	6	3

a) For example, acenaphthylene is the most abundant PAH compound (ranking = 1) when the ΣPAH burden of the soil is low (e.g., 1–10 $\mu\text{g}/\text{kg}$ of ΣPAH), but is ranked second in the most contaminated soils (e.g., 101–150 $\mu\text{g}/\text{kg}$ of ΣPAH). b) The typical level of endogenous ΣPAHs in soils.

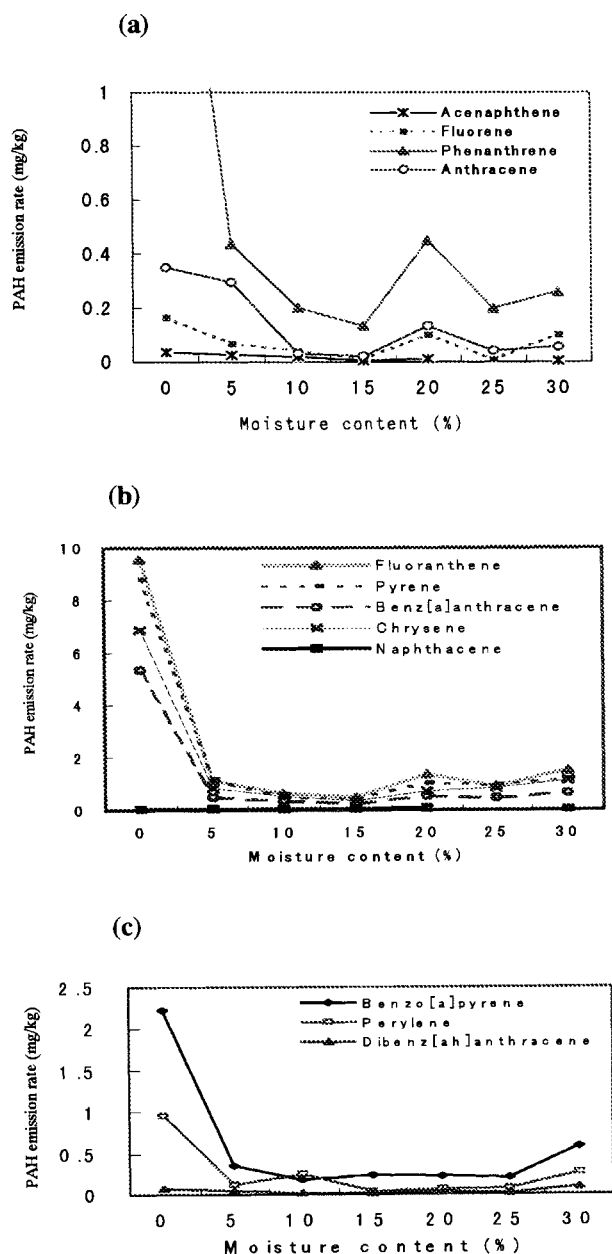


Fig. 3. Species-Specific PAHs Emission Rate When Burning Rice Straw 384 With Different Moisture
(a), (b), and (c) show light, intermediate and heavier molecular weight PAHs, respectively.

tents in rural soils where rice straw is burned were higher than the contents in samples where such burning does not occur except in Kitajima, and PAH contents in urban soils (such as Nakayoshino and Tamiya) where rice straw is burned were lower than sites where it is not burned. One possible explanation is PAH accumulation resulted from past rice straw burning because fluoranthene is the main component of Σ PAHs in those samples. This observation suggests that: 1) higher PAH contents in rural

soils principally result from biomass burning; 2) mobile sources (diesel- and gasoline-powered vehicles) raise PAH contents in urban soils; 3) soil properties play a role in controlling/influencing the PAH contents of soils; or 4) a combination of these factors occurs. In addition, one exception to the rule of "rural" low soil PAH/"urban" high soil PAH contents is where the soil has a high natural PAH level.

Overall, most of soils in Tokushima have not been seriously contaminated by PAHs based on the samples analyzed, but it is obvious that biomass burning and vehicular exhaust contribute PAHs to soils. These preliminary evaluations suggest some interesting influences due to soil properties as well as other emission sources that remain for future investigation.

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