

POLYCYCLIC AROMATIC HYDROCARBONS IN AGRICULTURAL SOILS OF JAPAN FROM 1959 TO 2002

Honda K¹, Ueda Y², Seike N³

¹ Department of Environmental Science for Industry, Ehime University, Japan

² Miura Institute of Environmental Science, Miura Co. Ltd., Japan

³ National Institute of Agro-Environmental Science, Japan

Abstract

21 polycyclic aromatic hydrocarbons (PAHs) were determined in agricultural soils of Japan from 1959 to 2002. The average total PAH concentrations in paddy and plowland soils were 635 ng/g (range: 52.9-5,440 ng/g), and 42.5 ng/g (range: 52.2-2,230 ng/g), respectively. The total PAH concentration was the highest in urban soils, and relatively high in soils from areas that experienced heavy snowfall and that had relatively low air temperature. In rural soils, the residue level of the PAH was the highest during the 1960s, rapidly decreased during the 1970s, while in urban soils, its level increased until the 1980s. The predominant PAHs were phenanthrene, fluoranthene, naphthalene, and pyrene, and their concentration overall and in relation to that of the total PAHs changed each year since the 1960s. As considering the characteristics of soil PAH profiles, the origin of soil PAHs changed chronologically from the burning of agricultural wastes to the combustion of fossil fuel and its secondary products since a turn in the mid-1970s.

Introduction

Polycyclic aromatic hydrocarbons are a group of environmental contaminants, and many of them are known to be mutagenic and some carcinogenic. Thus, several studies have been carried out with regard to PAHs in rural and urban soils, and soil pollution by PAHs has recently been reported^{1,2}. PAHs are formed during combustion and are released and dispersed when natural vegetation is burnt. Thus, PAHs are present at a general background level in soils and sediments. However, fossil fuel combustion and other anthropogenic processes such as waste incineration and stubble burning have greatly increased the environmental burden of these compounds in the last 100-150 years. Although many PAHs are included in the "priority pollutants" listing of the US EPA and the EU Commission, several uncertainties persist with regard to the significance of PAHs in relation to soil quality and their transfer from soil to the human food chain.

As a part of a study program on the persistent organic pollutants and related compounds in agricultural field soils in Japan: Contamination status and its future trend, 20 species of PAHs including 16 parent compounds present in the EPA priority pollutants list were selected. Methylphenanthrene compounds including 1-, 2-, 3-, 4-, and 9-methylphenanthrene were also selected to elucidate the ratio of methylphenanthrene /phenanthrene as an indicator of the PAH source. This paper aims to present information on the residue level of PAHs in paddy and plowland soils of Japan, and the temporal changes, and locational differences in this level over a period of approximately 40 years. It also discusses data in relation to factors that control the PAH concentrations observed and the profile of compounds present in samples from different locations and of different soil types.

Materials and Methods

From 1959 to 2002, samples from the plowed layers (0-15 cm) of agricultural field soils were annually collected from particular experimental sites in Japan at the same time in the year before plowing. The collected samples were individually wrapped in polyethylene bags, transported back to the laboratory, and stored at room temperature prior to air-drying them. The soils were sieved through a 9-mesh sieve, bulked, and stored in polyethylene bottles at room temperature until analysis.

A 4-g sample of air-dried sieved soil was extracted with dichloromethane for 16h in a Soxhlet apparatus. In accordance with EPA method 3630, the extract was purified using silica-gel column clean-up. The eluate was evaporated to approximately 150 μ l prior to analysis. Deuterated PAHs were used as internal standards and were added to the soil prior to extraction. After the addition of *p*-terfenyl-d₁₄ as an injection spike, all the samples were quantitated using the method of internal standardization with seven internal standards. Using a gas chromatograph-mass spectrometer, 21 PAHs were quantitatively analyzed. The method used in this study was

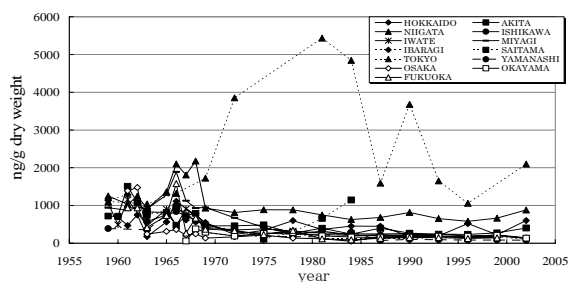


Fig.1. The concentrations of the 20 PAHs in paddy soils.

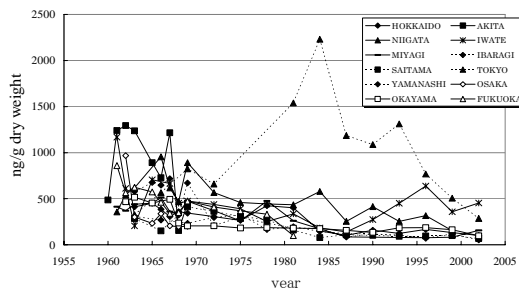


Fig.2. The concentrations of the 20PAHs in plowland soils.

validated using the standard reference sediment sample NIST SRM 1941b, and the percentages of certified value for the individual PAHs ranged from 94.1% to 121%. To allow all data to be present on a dry-matter basis, moisture content was determined by heating the air-dried soil at 105°C for 5h.

Results and Discussion

PAH concentration in soils and its temporal change

The concentrations of the 20 PAHs for each of the experimental sites obtained from paddy and plowland soils are provided in Figs 1 and 2. The concentration of the 20 PAHs spanned approximately two orders of magnitude, from 52.9 to 5,440 ng/g for paddy soils, and from 52.2 to 2,230 ng/g for plowland soils. In all the samples collected between 1959 and 2002, the mean concentrations of the 20 PAHs were 635 ng/g for paddy soils, and 425 ng/g for plowland soils.

Figs 1 and 2 also show the temporal changes in the total PAH concentration that were observed by determining the PAH concentrations at three-year intervals. The mean concentration of the 20 PAHs was the highest during the 1960s, but this value rapidly decreased during the 1970s; thereafter, it remained more or less constant from 1980 to the early 2000s. Similarly, it could be observed that the mean concentrations of most of the individual compounds have decreased since the 1960s (not shown).

Distribution of PAHs

From the results presented in Figs 1 and 2, it can be observed that the concentrations of the 20 PAHs changed temporally, but there were some locational differences in the concentration of the PAHs. In urban soil, eg., Tokyo, the soil PAH concentration increased until the 1980s, and showed approximately 10 times of that of the soils in the other locations, which indicates that a chronological PAH pollution in urban soil would apparently be different from those in rural soils. Furthermore, the soils in Niigata, Akita, and Hokkaido, which are the main rice-production areas, showed relatively high residue levels (Mann-Whitney U-test, $p < 0.05$) of the 20 PAHs compared to those in soils at the other locations. The number of pollution sources is low, and the origin of the PAHs in the soil may be mainland Asia as well as sources within the location itself, but further investigations are required to prove this hypothesis.

In addition, snowfall and/or the air temperature in the locations examined are likely to control the residue levels of the PAHs. Niigata, Akita, Iwate, Miyagi, and Hokkaido are snowy areas and the air temperature is relatively low; these factors might be responsible for the high concentration of PAHs in the soils due to slow biodegradation, leaching, and/or evaporation of these compounds. Reverse trends were observed for soils from Fukuoka, Okayama, and Osaka that have little snowfall, and the other locations that have intermediate levels of snowfall and air temperature among the locations examined had intermediate residue levels of PAHs. These observations indicate that besides the soil burden of PAHs derived from other areas and from within the location itself, differences in snowfall and air temperature might also alter the residence time of soil PAHs, and result in different residue levels among the locations examined. Additionally, it is likely that heavy snowfall results in greater deposition of PAHs from air. Furthermore, the concentrations of the 20 PAHs in the plowland soils examined were generally lower than those in the paddy soils, which might be due to a greater degradation of the plowland soil PAHs by ultraviolet irradiation compared to those in paddy soils, besides the input burden of PAHs derived from other areas and from within the plowland soil itself.

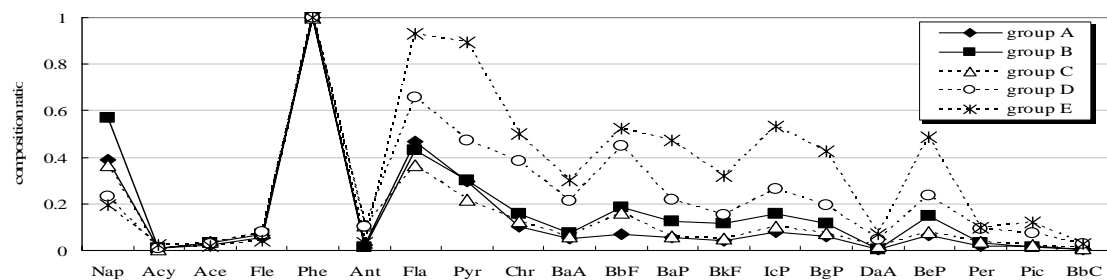


Fig.3. The PAH profile patterns(A-E) of agricultural field soils.

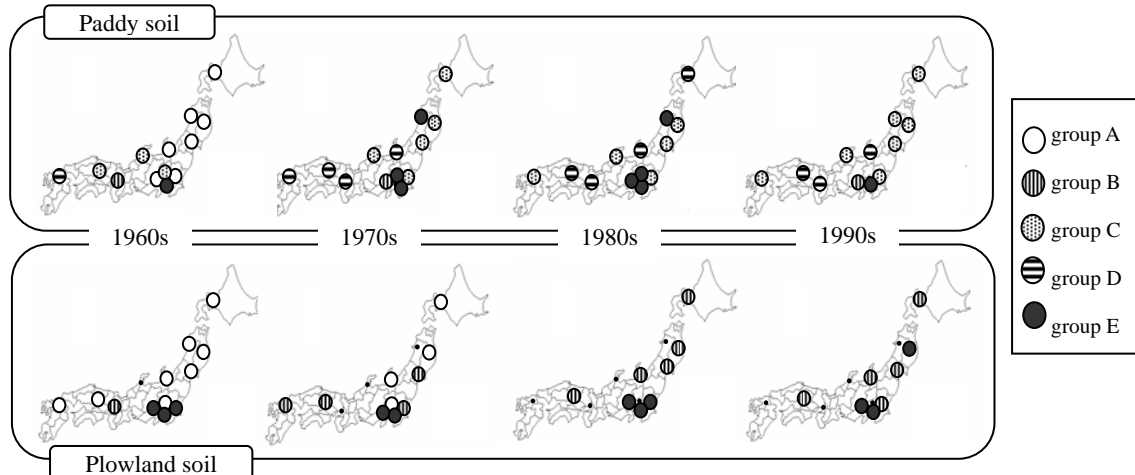


Fig.4. Temporal changes in the PAH profile patterns of agricultural field soils.

PAH profile

The predominant PAHs were phenanthrene, fluoranthene, naphtharene, and pyrene containing 3, 4, 2, and 4 rings, respectively. The percentage of phenanthrene and fluoranthene decreased gradually each year since the 1970s, implying that the temporal reduction in the concentration of these two compounds was more remarkable than that of the other compounds. This may be due to several factors besides the following: Similar to the soil PAHs in this study, those derived from the combustion of agricultural wastes such as stubble are particularly enriched with phenanthrene and fluoranthene^{3,4} because of which there is a decreased likelihood of agricultural waste burning since the 1970s. Since the mid-1970s, the use of coal and mineral oils that are rich in phenanthrene has reduced because energy sources temporally changed from fossil fuels to other sources such as atomic power and because the use of secondary products such as plastics increased throughout this period during which Japan was undergoing rapid economical development.

To elucidate the differences in the characteristics of the PAH profile among the locations examined, the similarity in the PAH profiles among the soil samples was calculated from the PAH data of individual soils by using the concentration correlation matrix and cluster analysis. The results showed that the PAH profile patterns of the individual soils could be divided into 5 groups (A-E), as shown in Fig. 3, and the profile characteristics were as follows. Group A was enriched with phenanthrene, naphtharene, and fluoranthene; group B, with phenanthrene, naphtharene, fluoranthene, and pyrene; group C, with phenanthrene, naphtharene, fluoranthene, pyrene, and benzo(b)fluoranthene; group D, with phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene, and chrysene; and group E, with phenanthrene, fluoranthene, pyrene, benzo(b)fluoranthene, indeno(1,2,3-cd)pyrene, and benzo(e)pyrene. Based on this grouping, the geographical distribution of the PAH profile groups was determined at a 10-year interval and is shown in Fig. 4.

Table 1. Ratio of MPhe/Phe, Phe/Ant, and Fla/Pyr for paddy and plowland soils in this study.

		1960s		1970s		1980s		1990s	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range
Paddy soil	MPhe/Phe	1.1	0.58 ~ 2.1	1.0	0.52 ~ 1.6	0.91	0.51 ~ 2.0	0.86	0.44 ~ 1.9
	Phe/Ant	67	9.0 ~ 270	20	2.3 ~ 180	16	2.0 ~ 120	11	0.89 ~ 71
	Fla/Pyr	1.6	1.2 ~ 2.2	1.5	0.97 ~ 2.2	1.4	0.91 ~ 2.3	1.5	0.90 ~ 2.4
Plowland soil	MPhe/Phe	1.3	0.78 ~ 33	1.2	0.76 ~ 1.5	0.89	0.53 ~ 1.6	0.87	0.38 ~ 1.8
	Phe/Ant	82	14 ~ 410	78	20 ~ 230	56	20 ~ 210	35	6.9 ~ 110
	Fla/Pyr	1.6	1.2 ~ 4.1	1.5	1.2 ~ 1.9	1.2	0.89 ~ 1.9	1.2	0.68 ~ 1.9

From the results presented in Fig. 4, it is evident that the inter-location similarity of the PAH profiles varied chronologically, and the number of groups have been decreased since a turn in the 1970s. This implies that the sources of PAHs were complex until the late 1970s, and thereafter, they simplified over the period between the 1980s and the end of the 1990s. These observations probably agree well with the temporal changes in the economical development of Japan that are mentioned above. This involved a change from mainly agricultural production before the mid-1970s to rapid development of the mining and manufacturing industries after the mid-1970s.

The concentration ratios of PAH pairs such as methylphenanthrene /phenanthrene (MPhe/Phe), phenanthrene /anthracene (Phe/Ant), and fluoranthene /pyrene (Fla/Pyr), have often been employed as indicators of the most significant PAH source in environmental samples. Thus the ratios of MPhe/Phe, Phe/Ant, and Fla/Pyr for agricultural field soils were calculated, and the results are shown in Table 1. These ratios for paddy soils ranged from 0.44 to 2.1, 0.89 to 270, and 0.9 to 2.4, respectively, and those for plowland soils were 0.38 to 3.3, 6.9 to 410, and 0.68 to 4.1, respectively; their ratios decreased each year, and the temporal decline was remarkable for the Phe/Ant ratio but unremarkable for the Fla/Pyr ratio. These observations indicate that in recent times, pyrogenic origins of PAHs in Japanese soils, especially, urban soils, such as motor vehicle exhaust and heavy industry emissions, have been dominant. However, because soils in the 1960s were enriched with phenanthrene and fluoranthene that are known to be mainly derived from the combustion of agricultural wastes such as stubble^{3,4}, the main origin of soil PAHs might be the combustion of agricultural wastes; since the 1970s, there has been a yearly decrease in the likelihood of agricultural waste being burnt.

In summary, it is considered that the origins of soil PAHs changed chronologically from agricultural waste burning during the 1960s to the combustion of fossil fuel and its secondary products from mid-1970 to the end of the 1990s, and the residual level of PAHs also decreased each year due to the development of technologies related to combustion and exhaust gas treatment.

Acknowledgements

This work was supported in part by a Grant-in-Aid for Environmental Research from the Ministry of Environment, Japan (2005-15).

References

1. Muller S, Wilcke W, Kanchanakool N, Zech W. *Soil Sci.* 2001; 166: 672.
2. Ma L, Chu S, Cheng H, Wang X, Liu X, Xu X. *Geoderma* 2005; 129: 200.
3. Ramdahl T, Moller M. *Chemosphere* 1983; 12: 23.
4. Jenkins BM, Jones AD, Turn SQ, Williams RB. *Environ. Sci. Technol.* 1996; 30: 2462.