A preliminary study of using polycyclic aromatic hydrocarbons as chemical tracers for traceability in soybean products

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ABSTRACT

Polycyclic Aromatic Hydrocarbons (PAHs) are a class of very stable organic molecules made up of only carbon and hydrogen and contain two to eight fused aromatic rings. PAHs are formed during incomplete combustion of organic materials such as fossil fuels, coke and wood. PAHs can be found in environment, the atmosphere, surface water, sediment, soil, food and in lipid tissues of both aquatic and terrestrial organisms. Natural emission sources of PAHs into the atmosphere include emissions from forest fires and volcanoes. Anthropogenic emission sources include combustion and industrial production. Incomplete combustion from motor vehicles, domestic heating and forest fires are major sources of PAHs in the atmosphere. Assuming that each region has different types of PAH emission sources, it seems rationale to hypothesize that the fingerprint of PAHs in agricultural products has its own unique locality characteristic. Since the food traceability is extremely crucial for food business, one can use PAH profile extracts from agricultural products to identify the originality. Three groups of soybean were classified according to the planting areas. In conclusion, soybean from three different countries (i.e. Thailand, Taiwan, Indonesia) can successfully be identified with the assistance of ANOVA and three-dimensional plots of binary diagnostic ratios of PAHs.

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1. Introduction

Because the food industry has been expanding internationally and customers can obtain innumerable agricultural products from all over the world, the supply-chain traceability system is one of the most crucial elements in determining the market value of fruits and vegetables. During the past few years, several techniques have been attempted for differentiating agricultural products such as nitrogen isotope analysis, polymerase chain reaction-denaturing gradient gel electrophoresis (PCR-DGGE), and ELISA (Asensio, González, García, & Martín, 2008; Kondo, 2010; Sheikha, Durand, Sarter, Okullo, & Montet, 2012; Suzuki & Nakashita, 2013). Despite various attempts to achieve a precise and comprehensive food traceability system, none of them can provide specific information about the region of cultivation. Recent studies highlight the importance of polycyclic aromatic hydrocarbons (PAHs) as alternative "chemical tracers" to identify the origins of tsunami backwash deposits in the Andaman Sea (Pongpiachan & Schwarzer, 2013; Tipmanee, Deelaman, Pongpiachan, Schwarzer, & Sompongchaiyakul, 2012). Other studies report the application of PAHs as chemical tracers to identify aerosols from industrialised areas (Giri et al., 2013), fine particulate matter emitted from light-duty gasoline vehicles (Riddle et al., 2007), particulate matter released from sugarcane burning (Hall et al., 2012) and terrigenous organic carbon in marine sediments (Yunker, Macdonald, Snowdon, & Fowler, 2011). Despite its numerous applications as a chemical proxy for source identification, none of the previous studies evaluate the possibility of PAHs as biomarkers for the traceability of agricultural products such as soybeans.

PAHs are widely acknowledged as a class of persistent organic pollutants (POPs), and several previous studies have discussed the negative impacts of PAHs on human health (Hoyer, 2001; Liao et al., 2011; Matsui, 2008; UNEP, 2013; Wickramasinghe, Karunaratne, & Sivakanesan, 2012). Both anthropogenic (e.g., traffic exhausts, industrial activities, domestic heating, burning of agricultural waste) and natural emissions (e.g., forest fires) are generally considered major sources of PAHs (Kim, Oh, & Chang, 2003; Li, Zhuang, Hsieh, Lee, & Tsao, 2001; Mu et al., 2013; Rajput, Sarin, Rengarajan, & Singh, 2011; Riva, Pedretti, Toscano, Duca, & Pizzi, 2011; Slezakova et al., 2013). Because PAHs have adverse effects on

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human health, a large number of studies have been focused on analysing PAHs in environment (Pongpiachan, 2013a, 2013b; Pongpiachan, Choochuay, Hattayanone, & Kositanont, 2013; Pongpiachan, Ho, & Cao, 2013; Pongpiachan, Tipmanee, et al., 2013; Tipmanee et al., 2012).

PAHs can be detected in roots of soybean, wheat and carrot, as well as in sunflower, soybean and virgin olive oils (Teixeira, Casal, & Oliveira, 2007; Yin, Liang, Xu, & Zhan, 2013). Because the PAH source profile (or fingerprint) is a function of combustion conditions and fuel types (i.e., the physical and chemical characteristics of both gaseous and particulate PAHs), several studies have applied a chemical mass balance (CMB) model to identify the existence of and to calculate source contributions to receptor concentrations (Chen, Teng, & Wang, 2013; Li, Lang, Yang, Peng, & Wang, 2014; Lu, Bzdusek, Christensen, & Arora, 2005). Apart from the CMB model's advantages in apportioning detected PAH concentrations to their sources, its several disadvantages and limitations include the following: (*i*) the fingerprints must be consistent over the observation period; (*ii*) all emission sources contributing significantly to detected contents must analysed, and their fingerprints must be identified; (*iii*) PAH congeners included must not chemically react to each other; and (*iv*) numbers of PAH congeners must be greater than or equal to number of emission sources. Unlike the CMB model, for which complete fingerprint information is often required, a conventional factor-analysis model such as principal component analysis (PCA) coupled with hierarchical cluster analysis (HCA) has been extensively used for source apportionment of PAHs in environmental samples because it has the advantage of not requiring information about the source profiles (Pongpiachan, 2006, 2013a, 2013b; Pongpiachan, Choochuay, et al., 2013; Pongpiachan, Ho, et al., 2013; Pongpiachan, Tipmanee, et al., 2013; Pongpiachan & Schwarzer, 2013; Tipmanee et al., 2012). Overall, the main objectives of this study are to (*i*) estimate the PAH concentrations in soybean products from Thailand, Taiwan and Indonesia, (*ii*) evaluate the possibility of PAHs as alternative chemical tracers through the use of hierarchical cluster analysis (HCA) coupled with its binary diagnostic ratios, and (*iii*) conduct a risk assessment for the dangers posed by exposure to PAHs in soybean products from Thailand, Taiwan, and Indonesia.

2. Materials & methods

2.1. Sampling sites

2.1.1. Sampling sites of soybean products

Raw soybean (i.e., *Glycine*) samples were randomly selected from private sector planting areas in Chiang-Mai province, in northern Thailand (i.e., Thailand Soybean Products: THSP, $n = 28$), Jember province in Java island, in central Indonesia (i.e., Indonesia Soybean Products: INSP, $n = 20$) and Kaohsiung province, in southern Taiwan (i.e., Taiwan Soybean Products: TWSP, $n = 20$). It is worth mentioning that all planting areas are located in rural sites, and there were no anthropogenic emissions in the vicinity of any planting zone, which were all strategically positioned to be accessible to winds from all directions. All soybean samples were manually collected in June 2010 and stored in glass jars with dry ice.

2.1.2. Sampling sites of PM_{10}

In this study, PAHs in PM_{10} (i.e. Particulate matter concentrations refer to fine suspended particulates less than 10 microns in diameter) collected from various emission source types were successfully analysed and sampling sites were clearly described as follows:

2.1.2.1. Prince of Songkla University (PSU). This station was positioned at approximately 3 m above ground level in the Faculty of Environmental Management of Prince of Songkla University, approximately 550 m away from the main traffic road that leads to the city centre of Hat-Yai. It is crucial to stress that PSU1 and PSU2 denote the observation periods of June (28th–30th June, 2007) and October (24th–26th October, 2007), respectively. This site is considered an urban residential zone of Hat-Yai city.

2.1.2.2. Traffic intersection (TI). The observatory site was situated at the traffic intersection in front of the front gate of PSU. It is located on the eastern side and approximately 2.5 km far away from the Hat-Yai city centre. This site is considered a transportation area adjacent to a residential zone. The PM_{10} samples were monitored on 5th–7th July 2007.

2.1.2.3. Corpse incinerator (CI). This observatory site is located inside Kor-Hong temple, which is situated approximately 1.5 km north of TI. Because timbers and tires were two major fuel sources for corpse incineration, TI is regarded as an emission source of both timber and tire combustion. This monitoring station characterises the monitoring period of 19th–21st July 2007.

2.1.2.4. Charoen Phokphand factory (CPF). This observatory site was located inside the fish can manufacturing factory of Charoen Phokphand group, which is one of the largest agricultural businesses in Thailand. Because crude oil was employed for the fish can manufacture, this site can be considered an emission source of crude-oil combustion. The sampling was performed on 24th–26th July 2007.

2.1.2.5. Songkhla Lake (SL). This sampling site was positioned to the south of Songkhla Lake and approximately 13 km from the northern side of the PSU campus. This station is also located approximately 14 km from the western side of the Gulf of Thailand. Because there are few nearby anthropogenic emission sources (e.g., industrial factories, vehicles, chemical and metallurgy factories, power plants, etc.), it is reasonable to consider this station as a rural background observatory site. SL1 and SL2 represent the monitoring periods of July (27th–29th July, 2007) and October (20th–22nd October, 2007), respectively.

2.1.2.6. Rubber sheet manufacturing factory 1 (RMF1). This station was situated at Tumbol Tungwan, Hat-Yai district. As a part of the production line, the rubber sheets are dried with steam of high temperature and high pressure combined with purification with a sulphuric acid solution. Because Para rubber trees were employed as fuel for this process, this station is characterised by an emission of mixed Para rubber tree combustion, latex fragments and sulphuric acid aerosols. The PM_{10} samples were monitored from 30th July to 1st August 2007.

2.1.2.7. Rubber sheet manufacturing factory 2 (RMF2). This observatory station was located at Tumbol Tachang, Banglum district. Like RMF1, RMF2 is considered to emit a mixture of Para rubber tree combustion, latex fragments and sulphuric acid aerosols. The PM_{10} samples were monitored from 2nd–4th August 2007.

2.1.2.8. Bus terminal (BT). This station was situated to the southwest of PSU and nearly 1.4 km away from the campus. This observatory site was chosen as a fingerprint of diesel exhausts because most of the buses are diesel-fuelled. The PM_{10} sample collections were obtained from 5th–7th August 2007.

2.1.2.9. Waste incinerator (WI). This monitoring station was located at the city centre. Because the municipal waste incinerated is a heterogeneous mixture of solid wastes and burning fuels, this station can be considered a blend of solid waste combustion and diesel exhaust. The PM_{10} samples were collected from 28th–30th August, 2007.

2.1.2.10. Barbeque Festival (BF). This station was situated inside the PSU campus, on the roof of the Faculty of Natural Resources. The 40th Annual Barbecue Festival was set for Wednesday, August 15th, 2007. This station can be recognised as a release of charcoal combustion. The PM_{10} samples were monitored from 15th–18th August, 2007.

2.1.2.11. Petkasem road (PR). This observatory site was situated at the centre of Hat-Yai city. The PM_{10} samples collected from this area represent traffic emissions, with a mixture of diesel and benzene exhausts. The sampling was performed on 27th–29th August, 2007.

2.1.2.12. Kor-Hong hill (KHH). This monitoring station was positioned at the local radio station on the top of Kor-Hong Hill, with an altitude of 356 m. The PM_{10} from this sampling site was regarded as a blend of all emission sources in the urban area, and it can thus be regarded as an urban residential zone monitoring site. The sampling was conducted on 3rd–5th November, 2007.

2.1.2.13. Rice straw burning (RSB). The agricultural waste burning has been the main preparation for removing rice straw because it is fast, economical and practical for removing disease organisms. The observatory site was located at a rice field in Satingpra district, Songkhla Province and is regarded as a fingerprint of agricultural waste burning. The monitoring was performed on 16th November, 2007.

2.1.2.14. Biomass burning (BB). As part of the cultivation process, the agricultural waste must be removed to make way for replanting. This monitoring station was close to unused land and was situated in Namom district, Songkhla Province. This station can be considered as a fingerprint of agricultural waste burning. The monitoring was performed on 17th November, 2007.

2.1.2.15. Para rubber tree burning (PTB). This observatory site was situated in Namom district, Songkhla Province and can be regarded as an emission source of Para rubber tree burning. The PM_{10} samples were sampled on 18th November, 2007.

2.2. Analytical methods

2.2.1. Materials

All solvents were HPLC grade, purchased from Fisher Scientific (Pittsburg, USA). A standard mix solution of 15 native PAHs [Norwegian Standard (NS 9815: S-4008-100-T): phenanthrene (Abbreviation: Phe), anthracene (An), fluoranthene (Fluo), pyrene (Pyr), 11 H-benzo[a]fluorene (11H-B[a]F), 11H-benzo[b]fluorene (11H-B[b]F), benz[a]anthracene (B[a]A), chrysene (Chry), benzo[b]fluoranthene (B[b]F), benzo[k]fluoranthene (B[k]F), benzo[a]pyrene (B[a]P), benzo[e]pyrene (B[e]P), indeno[1,2,3-c,d]pyrene (Ind), dibenz[a,h]anthracene (D[a,h]A), and benzo[g,h,i]perylene (B[g,h,i]P)] and a mix of recovery internal standard (IS) PAHs [d$_{12}$-perylene (d$_{12}$-Per) and d$_{10}$-fluorene (d$_{10}$-Fl)] were purchased from Chiron AS (Stiklestadveine 1, N-7041 Trondheim, Norway). Standard stock solutions of deuterated and native PAHs were prepared in nonane. Working solutions were obtained by appropriate dilution in cyclohexane. Silica gel (0.040–0.063 mm) was purchased from Merck. Soxhlet thimbles were obtained from Whatman

Table 1
PAH concentrations (ng kg^{-1}) in soybeans collected from Thailand (THSP), Indonesia (INSP) and Taiwan (TWSP).

	THSP ($n = 28$)	INSP ($n = 20$)	TWSP ($n = 20$)
Phe (S)	1029 ± 896	1251 ± 460	2038 ± 822
An (S)	112 ± 115	163 ± 71	291 ± 72
Fluo (S)	62 ± 48	216 ± 26	198 ± 74
Pyr (S)	1221 ± 1123	2018 ± 649	3115 ± 1271
11H-B[a]F (N.S.)	179 ± 22	137 ± 46	211
11H-B[b]F (N.S.)	136 ± 44	63 ± 13	75
B[a]A (S)	1226 ± 1294	1881 ± 656	2745 ± 1162
Chry (N.S.)	61 ± 26	138 ± 23	N.D.
B[b]F (N.S.)	121 ± 48	116	150
B[k]F (S)	162 ± 55	166 ± 75	224 ± 42
B[e]P (S)	441 ± 498	757 ± 421	854 ± 384
B[a]P (N.S.)	65 ± 58	N.D.	N.D.
Ind (N.S.)	587	N.D.	N.D.
D[a,h]A (S)	135 ± 49	73 ± 19	123 ± 54
B[g,h,i]P (N.S.)	251	N.D.	N.D.

Note that Aver, Stdev, N.D., S and N.S. stand for average, standard deviation, not determined, significant and non-significant at a confidence level of 95%, respectively.

(Maidstone, UK). All materials used (thimbles, silica gel, glass and cotton wool) were Soxhlet extracted with DCM for 8 h and then kept dry (in desiccator) until use. All glassware was cleaned by washing with decanted water before drying at 55 °C and rinsing with DCM just before use.

2.2.2. Sampling extraction

The extraction of PAHs was performed using 250-ml Soxhlet extractors. After sample collection, soybean products were finely homogenised in a commercial juice blender (Phillips HR2067/20), followed by freeze-drying with liquid nitrogen. After freeze dry, soybean samples of approximately 500 g were placed inside the Soxhlet thimbles, spiked with a known amount of internal standard (i.e., d$_{12}$-Per and d$_{10}$-Fl), and extracted with DCM for 8 h.

2.2.3. Fractionation/cleanup and blow-down process

The fractionation/cleanup and blow-down process followed the method described by Gogou et al. (1996). After the Soxhlet extraction, the DCM solvent was concentrated to dryness by a combination of rotary evaporation and blowing under a gentle nitrogen stream. The concentrated extract was subsequently diluted in 10 ml of *n*-hexane prior to application to the top of a disposable silica gel column. The extract was then fractionated into separate compound classes by flash chromatography on silica gel as follows: The concentrate was applied to the top of a 30 × 0.7 cm diameter column containing 5 g of silica gel (activated at 150 °C for 3 h). Nitrogen pressure was used to obtain a flow of 1.4 ml min^{-1} at the bottom of the column. The following solvents were used to elute the different compound classes: (*i*) 15 ml *n*-hexane (fraction 1, aliphatic hydrocarbons and light molecular weight PAHs); (*ii*) 15 ml toluene-*n*-hexane (5.6:9.4) (fraction 2, middle and heavy molecular weight PAHs). In this study, the analyses were performed using a Varian GC = MS-MS system comprising a CP-3900 gas chromatograph (Walnut Creek, CA, USA) with a 1077 universal injector and a three-dimensional quadrupole ion trap selected ion storage mass spectrometer (Varian Saturn 2200). Based on the toxicity of the solvent and the solubility of PAHs, toluene was selected for the study. After the fractionation, the eluates were concentrated with a rotary evaporator followed by evaporation under a gentle nitrogen stream (set flow rate at 1.0 mbar). Because of the low dissipation capability of toluene, a percentage (5–25%) of acetone was added to increase the volatility. The sample was further reduced to precipitate prior to the addition of cyclohexane to a volume of exactly

100 μl in a GC/MS vial insert prior to GC/MS analysis. For more details on the GC/MS methodology, please refer to our previous publications (Pongpiachan et al., 2009, 2013a, 2013b). In addition, the QA/QC was evaluated using NIST-SRM (National Institute of Standard Technology-Standard Reference Material) 1941b. Mean recovery upon extraction of matrix-matched certified SRM ($n = 8$) was in the range of 77–119%. The precision of the analytical method, computed as the relative standard deviation of the duplicate samples, was less than 15%. In addition, t-test, ANOVA, and HCA were conducted with the statistical software SPSS (Statistical Package for the Social Sciences), version 13.

3. Results & discussion

Fifteen congeners of PAHs have been successfully analysed in soybean products collected at private sector planting areas in Thailand, Indonesia and Taiwan. The averages and standard deviations of individual PAH congeners measured at all sampling sites are illustrated in Table 1. The observed PAH congeners ranged from N.D. to 3115 ± 1271 ng kg^{-1} of Pyr detected in Taiwanese soybean products. To determine whether the detected alteration of PAH congeners among different soybean products is indeed due to significant emission source strengths or whether it is merely caused by coincidental effects of emissions, atmospheric transportation and chemical degradation, a statistical analysis was conducted and will be discussed below. The PAH concentrations were subjected to one-way independent ANOVA to investigate significant differences among the three soybean products. Generally, there is no evidence of any significant change in 11H-B[a]F, 11H-B[b]F, B[a]P, Ind, or B[g,h,i]P from the three data sets. For some lighter and heavier MW compounds such as Phe, An, Fluo, Pyr, B[a]A, B[k]F and B[e]P, a significant level of increase ($p < 0.05$) was observed in TWSP by using one-way independent ANOVA. It is also interesting to note that B[a]P, Ind and B[g,h,i]P were only observed in THSP, as illustrated in Table 1. Several confounding factors may be responsible for these phenomena.

First, it is well known that PAH emission factors of diesel-driven private cars are 4–5 times higher than those of gasoline vehicles, with PAHs in diesel exhaust being predominantly enriched in 4-ring PAHs (85%), whilst 5- or 6-ring PAHs were prevalent (55%) in gasoline vehicles (Perrone et al., 2014). Another study of traffic emissions of particulate matter using tunnel measurements observed comparatively high contributions of Fluo and Pyr at the entrance and exit of the tunnel (Lawrence et al., 2013). Second, numerous studies highlight the importance of biomass burning as crucial emission sources of PAHs. For instance, the particulate congeners of 5- and 6-ring congeners from paddy-residue burning are approximately 3–5 times more abundant than those from the wheat-residue burning emissions (Rajput et al., 2011). Phe and Fluo were reported as the most abundant PAH congeners from sugarcane crop burning in Brazil (José de AndradeCristale,Silva, Zocolo, Marchi, , 2010). D[a,h]A, B[k]F, and Chry was considered the most abundant isomer among other PAHs in the biomass of burning particles from household cooking in a rural region of India (Bhargava, Khanna, Bhargava, & Kumar, 2004). Third, the indicatory PAH emissions from iron and steel industries using coal as fuel (Category I), using heavy oil as fuel (Category II) and using electric arc furnaces (Category III) in Taiwan are B[a]A, B[k]F, B[g,h,i]P for Category I, B[a]P, Ac, Ace for Category II and Cor (Coronene), Pyr, B[b]C (benzo[b]chrycene) for Category III (Yang, Lai, Hsieh, Hsueh, & Chi, 2002).

The significantly high levels of Phe, An, Fluo, Pyr, and B[a]A detected in TWSP may reflect the comparatively high contributions of diesel emissions in Taiwan. The relatively high percentage of 6-ring isomers in THSP (14%) can be interpreted as a consequence

Table 2
Percentage contribution of 3-, 4-, 5-, and 6-ring aromatic groups of PAHs in soybeans collected from Thailand (THSP), Indonesia (INSP) and Taiwan (TWSP).

Ring number	THSP	INSP	TWSP
3	20%	20%	23%
4	50%	64%	63%
5	16%	16%	13%
6	14%	0%	0%

of exposure to biomass of burning aerosols in Northern provinces, which contains more D[a,h]A, Ind and B[g,h,i]P than other types of particles (See Table 2). Although certain species of PAHs can be used as indicators of particular emission sources, one should consider that other confounding factors can also affect the distribution characteristics of PAHs in soybean products. For instance, meteorological conditions (e.g., temperature, wind speed and wind direction), emitted amounts and specific site impacts are potential factors affecting the shape of the PAH fingerprint. Furthermore, no conclusion about the degree of chemical decomposition (e.g., photolysis during the atmospheric transportation) can be made because the profile is based simply on the concentration of each compound. It is therefore extremely difficult to discriminate soybean products by the concentrations of PAHs alone.

3.1. Diagnostic binary ratios of PAHs

Several attempts have been conducted to assess the influence of emission source types on environmental samples by using diagnostic binary ratios of PAHs (Pongpiachan, 2006; Pongpiachan & Schwarzer, 2013; Tipmanee et al., 2012; Yunker et al., 2002, 2011). The diagnostic binary ratios of certain PAH species can provide some evidence about the impacts of various sources of PAHs in ambient air (Bi et al., 2003; Gou et al., 2003). Phe/Pyr, Phe/B[a]A, B[k]F/B[e]P, B[a]P/B[e]P, Phe/(Phe + An), An/(An + Phe), and Fluo/(Fluo + Pyr) can be applied as characteristic diagnostic parameters to identify the emission sources (Pongpiachan, 2006; Yunker et al., 2002, 2011). For instance, the An/(An + Phe) and Fluo/(Fluo + Pyr) ratios were used as indicators for differentiating petrogenic from pyrogenic sources, with low ratios (i.e., An/(An + Phe) < 0.1 and Fluo/(Fluo + Pyr) < 0.4) indicating petrogenic, whereas higher ratios (i.e., An/(An + Phe) > 0.1 and Fluo/(Fluo + Pyr) > 0.4) can be considered as signals of pyrogenic. Similarly, B[a]P/B[e]P and Phe/(Phe + An) were employed as diagnostic ratios for characterising traffic, non-traffic, diesel vehicle, gasoline vehicle, natural gas, oil, coal, vegetation and wood combustion emissions, as illustrated in Table 3 (Brändli et al., 2008; Tobiszewski & Namieśnik, 2012; U.S. EPA, 2003; Yunker et al., 2002).

Because Fluo/(Fluo + Pyr) and An/(An + Phe) of THSP are lower than 0.4 and 0.1, respectively, they indicate that the PAHs are derived from petrogenic sources. However, the results of other diagnostic binary ratios make this interpretation problematic. For instance, the average values of B[a]P/B[e]P of THSP (i.e., 0.71 ± 0.40) are larger than 0.6, suggesting that the samples are from traffic sources (see Table 3). In addition, the average values of Phe/(Phe + An) for all soybean products show similarities with those of natural gas, oil, coal and wood combustion emissions. By using a single binary ratio, one can obtain contradictory results, and it is thus extremely difficult to identify the agricultural source of soybean products. Notably, these binary diagnostic ratios are fairly advantageous and offer important evidence for characterising the potential sources of PAHs. However, these diagnostic ratios, as well as source profiles, should be used with great caution because physiochemical processes (e.g., photodecomposition,

Table 3
Diagnostic ratios of PAHs in soybean products from Thailand (THSP), Indonesia (INSP) and Taiwan (TWSP) in comparison with those PAHs attributed to specific sources compiled from previous studies (Brändli et al., 2008; Tobiszewski & Namieśnik, 2012; U.S. EPA, 2003; Yunker et al., 2002).

	Soybean			Source type										
	THSP	INSP	TWSP	Petrogenic	Pyrogenic	Non-traffic	Traffic	Diesel vehicle	Gasoline vehicle	Natural gas combustion	Oil combustion	Coal combustion	Vegetation combustion	Wood combustion
Phe/Pyr	0.88 ± 0.21	0.63 ± 0.12	0.66 ± 0.09											
Phe/B[a]A	0.93 ± 0.24	0.67 ± 0.15	0.76 ± 0.14											
B[k]F/B[e]P	0.67 ± 0.31	0.25 ± 0.05	0.24 ± 0.12											
B[a]P/B[e]P	0.71 ± 0.40	N.D.	N.D.			<0.6	>0.6							
Phe/(Phe + An)	0.91 ± 0.051	0.88 ± 0.043	0.88 ± 0.014					0.73 ± 0.18	0.77 ± 0.10	0.88 ± 0.13	0.89 ± 0.12	0.85 ± 0.11	N.A.	0.84 ± 0.16
An/(An + Phe)	0.093 ± 0.051	0.12 ± 0.043	0.12 ± 0.014	<0.1	>0.1									
Fluo/(Fluo + Pyr)	0.076 ± 0.046	0.11 ± 0.026	0.060 ± 0.016	<0.4	>0.4			0.40 ± 0.05	0.52 ± 0.13	0.49 ± 0.18	0.52 ± 0.20	0.57 ± 0.21	0.49 ± 0.07	0.51 ± 0.16

heterogeneous and homogeneous chemical reactions with trace gaseous species) can alter the PAH distribution pattern during their transport from the emission source to the receptor site. To minimise the above-mentioned uncertainties, the plots of three-dimensional diagnostic ratios can be used to extract potential sources of PAHs within soybean samples.

Three binary diagnostic ratios, namely, Phe/Pyr, Phe/B[a]A and B[k]F/B[e]P, have been selected as the X, Y and Z axes, respectively. The clearest features observed in Figs. 1 and 2 are as follows: (i) the 3D plot of THSP deviated substantially from those of TWSP and INSP; (ii) there are very clearly different sources of PAHs in air samples of Springwood, Texas, Seoul, Brisbane, Basque and Athens; (iii) 3D plots of THSP, INSP and TWSP were adjacent to those of Chiang-Mai, Guangzhou, and Jakarta, suggesting that long-range atmospheric transportation (LRAT) from Asian cities might be a significant source of PAHs in soybean products; (iv) the 3D plots of THSP were close to those of BB and RSB, indicating the major influence of agricultural waste burning on PAH contents in soybean products of Chiang-Mai, Thailand. This is consistent with a previous study highlighting the importance of the vast majority of hotspots as potential sources of PAHs in Chiang-Mai city during the cold period (Pongpiachan, 2013b); (v) the 3D plots of TWSP and INSP were adjacent to those of TI, BF, CI and RMF. This can be interpreted as a consequence of the mixing of air masses contaminated by traffic emissions, charcoal burning, and rubber and biomass combustions. It is obvious that various types of emission sources govern the PAH contents in TWSP and INSP, whilst the biomass burning is likely to be a single dominant source of PAHs in THSP.

3.2. Hierarchical cluster analysis (HCA) of PAHs

HCA using average linkage between groups was conducted to identify the homogeneous groups of individual PAHs in the soybean samples. The results demonstrated in the dendrogram (Fig. 3) divided the 68 PAH soybean samples into five major clusters. The first cluster ($n = 11$) is composed of 82%, 9%, and 9% of TWSP, THSP, and INSP, respectively. Therefore, this cluster represents the Taiwanese soybean products. The second cluster ($n = 15$) consists of 33%, 27%, and 40% of TWSP, THSP, and INSP, respectively. This cluster can be interpreted as a mixture of soybean products from the three countries. Interestingly, THSP have been successfully
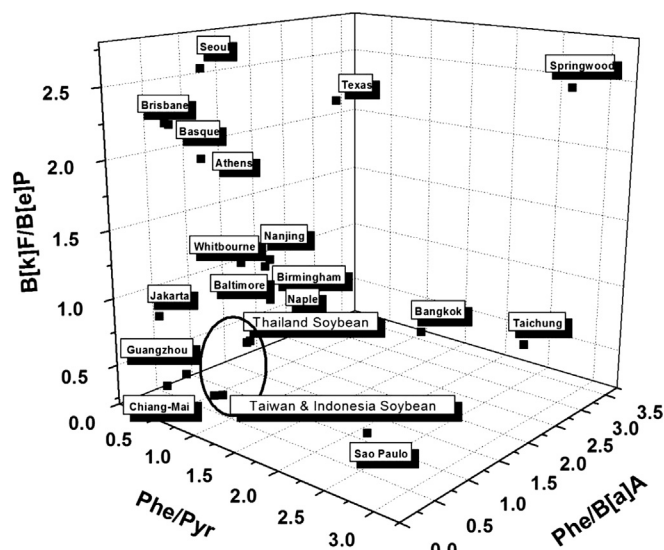

Fig. 1. Three-dimensional plots of binary diagnostic ratios of PAHs in soybean products in comparison with those of ambient aerosols around the world.
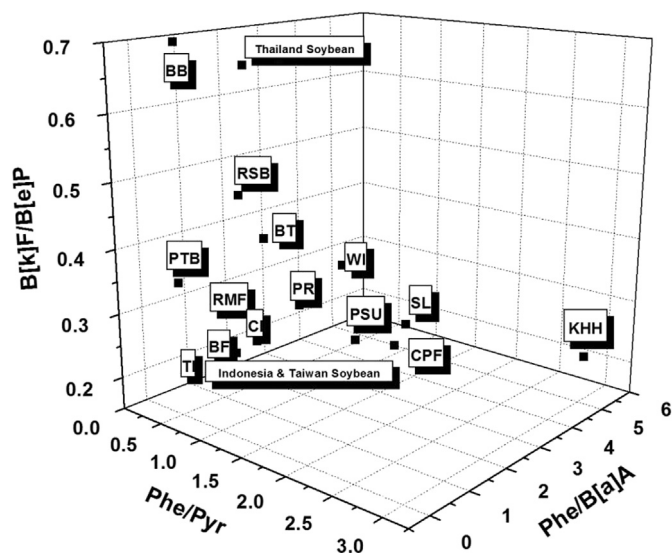
Fig. 2. Three-dimensional plots of binary diagnostic ratios of PAHs in soybean products in comparison with those of aerosols from various emission sources in Songkla province, Thailand.

grouped in the third cluster ($n = 18$), with a contribution of 94%. Consequently, it appears reasonable to assume that this cluster is representative of soybeans grown in Chiang-Mai province, Thailand. The combination of TWSP, THSP, and INSP was prominent in the fourth cluster, with contributions of 19%, 24%, and 57% respectively. The last cluster (cluster V) contains only three samples, of TWSP and THSP. Although HCA could not characterise INSP, as seen from the mixture of all samples in cluster II and IV, TWSP and THSP were obviously the dominant soybean products in cluster I and III, respectively. The fact that HCA can effectively discriminate THSP from other soybean products is consistent with the highly deviated 3D plot of PAH binary ratios of THSP from those of TWSP and INSP (See Figs. 1 and 2). This can be considered a consequence of unique PAH emission sources in Chiang-Mai province, Thailand.

Despite their promise as alternative chemical tracers to characterise soybean products, there are several limitations to using PAHs that must be emphasised. First, the concept of PAH fingerprints cannot be applied to differentiate soybean products that share similar emission source types of PAHs. In other words, there should be no PAH point sources (e.g., incinerator, industrial factory, or highway) adjacent to the soybean planting zone. Second, there should be no significant differences in the absorptivity of PAHs in soybeans growing in various geographic conditions. According to our best knowledge, there is still no report on this issue. Third, the weather conditions should play a minor role in governing PAH fingerprints. If the meteorological parameters rather than the emission source types primarily control PAH contents, soybean products grown in the same climate should have similar PAH fingerprints. Because 3D plots of PAH binary ratios reveal the similarity of TWSP and INSP (Figs. 1 and 2), it seems rationale to assume that the "latitudinal effect" plays a minor role in altering PAH profiles.

3.3. Health risk assessment of PAHs

3.3.1. Toxicity equivalent concentration (TEQ) of PAHs

The toxicity equivalent concentration (TEQ) equation is extensively employed for evaluating the risk of exposure to PAHs, which can be computed as follows (Pongpiachan, Tipmanee, et al., 2013; Yang et al., 2007; Yu et al., 2008):
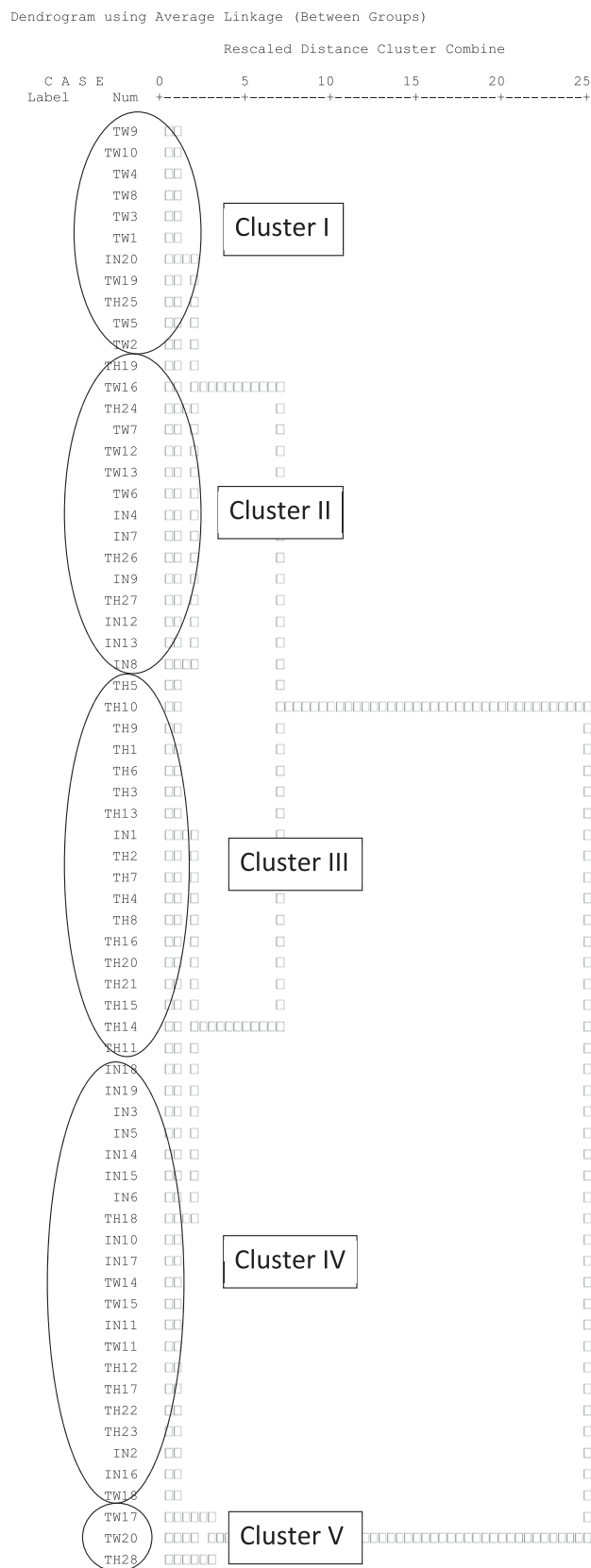

Fig. 3. Dendrogram of hierarchical cluster analysis of PAHs in soybean products collected from Thailand, Indonesia and Taiwan.

Table 4
Comparison of TEQ values of PAHs (ng kg^{-1}) in THSP, INSP, and TWSP calculated with the methods of Nisbet and Lagoy, US-EPA, and Cecinato.

	ANOVA test	THSP ($n = 28$)	INSP ($n = 20$)	TWSP ($n = 20$)
TEQ-Nisbet and Lagoy (Eq. (2))	S	416 ± 250	296 ± 94	443 ± 177
TEQ-US-EPA (Eq. (3))	S	286 ± 172	176 ± 56	265 ± 105
TEQ-Cecinato (Eq. (4))	S	410 ± 247	291 ± 93	435 ± 174

Note that S stands for significant at confidence level of 95%.

$$TEQ = \sum_i [C_i \times TEF_i] \qquad (1)$$

Here, C_i and TEF_i are abbreviations for the concentrations of individual PAH and the toxic equivalency factors, respectively. Because the toxicity of the individual PAH may vary by orders of magnitude, it is crucial to express the toxicity of PAHs in terms of the most toxic form of PAHs, B[a]P. By using TEF, the toxicity of a mixture of PAHs can be expressed in a single number: the toxic equivalency, TEQ. It is a single figure resulting from the product of the concentration and individual TEF values of each PAH, as expressed in Eq. (1). Three equations were computed for TEQ based on Nisbet and LaGoy (1992) (Eq. (2)), US EPA (1993) (Eq. (3)), and Cecinato (1997) (Eq. (4)). In these equations, the abbreviations for the PAH congeners denote their concentrations.

$$
\begin{aligned}
TEQ_{Nisbet\ and\ Lagoy} = {} & 0.001(Phe + Fluo + Pyr) + 0.01(An \\
& + B[g,h,i]P + Chry) + 0.1(B[a]A + B[b]F \\
& + B[k]F + Ind) + B[a]P + D[a,h]A
\end{aligned}
\qquad (2)
$$

$$
\begin{aligned}
TEQ_{US-EPA} = {} & 0.06(B[a]A) + 0.07(B[b]F + B[k]F) + B[a]P \\
& + 0.08(Ind) + 0.6(D[a,h]A)
\end{aligned}
\qquad (3)
$$

$$
\begin{aligned}
TEQ_{Cecinato} = {} & 0.01(Chry) + 0.1(B[a]A + B[b]F + B[k]F + Ind) \\
& + B[a]P + D[a,h]A
\end{aligned}
\qquad (4)
$$

The TEQ values computed from the three formulas described above were significantly different. The average of the TEQ$_{Nisbet\ and\ Lagoy}$ values was significantly higher than those of the TEQ$_{US-EPA}$ and TEQ$_{Cecinato}$. A comparison of TEQ values among the three different soybean sources is shown in Table 4. All three different TEQ values in INSP were significantly lower than those for the other soybean products. The most likely explanation for this might be the lack of 6-ring aromatic groups of PAHs present in INSP, as well as the relatively low concentration of D[a,h]A, which has high TEF values. The TEQ values found in THSP were the highest in the Nisbet and Lagoy model (416 ± 250 ng kg^{-1}) and in the US-EPA model (286 ± 172 ng kg^{-1}). The TEQ values in THSP were higher than those detected in other areas, possibly due to a comparatively high percentage contribution of 6-ring aromatic groups of PAHs, which are mainly generated by burning agricultural waste and other anthropogenic activities, such as traffic emissions and fossil fuel combustions from industrial sectors in Chiang-Mai province.

3.3.2. Hazard index (HI) of PAHs

The assessment of non-cancer risk can be conducted by using Eq. (5), where hazard index (HI) denotes the non-cancer risk, which can be calculated by dividing the sum of average daily dose ingestion (ADD$_i$: mg kg^{-1} body weight day^{-1}) and average daily dose dermal (ADD$_d$: mg kg^{-1} body weight day^{-1}) by the oral reference dose (RfD) (ATSDR, 2005).

$$
HI = \frac{\frac{CS \times IR \times EF \times ED \times CF}{BW \times AT_{NC}} + \frac{CS \times SA \times AF \times EF \times ED \times DAF \times CF}{BW \times AT_{NC}}}{RfD}
\qquad (5)
$$

Here, the symbols can be described as follows:

CS: Chemical Concentration (ng g^{-1})
CF: Conversion Factor of 10^{-6} kg mg^{-1}
EF: Exposure Frequency = 40 days year^{-1}
ED: Exposure Duration = 10 years
IR: Ingestion Rate = 50 mg soybean day^{-1}
BW: Body Weight = 53 kg
AT$_c$: Averaging Time for cancer risk = 25,550 days
AF: Skin Adherence Factor = 0.3 mg soybean cm^{-2}
DAF: Dermal Absorption Factor = 0.03 (unitless)
SA: Skin Surface Area (available for contact) = 4700 cm^2
HI: Hazard Index
RfD: Reference Dose (3.0 × 10^{-4} mg kg^{-1} body weight day^{-1})
AT$_{NC}$: Averaging Time for non-cancer effects = 3650 days

As illustrated in Table 5, the HI values of PAH contents in all soybean products ranged from N.D. to 1.98 × 10^{-3} with an average of 3.52 × 10^{-4} ± 1.62 × 10^{-4}, which is 865 times lower than that of world marine sediments (WMS the average value of PAHs in sediments around the world) (Pongpiachan, Tipmanee, et al., 2013). All

Table 5
Hazard index (HI) values of PAH contents in THSP, INSP, TWSP and WMS (ATSDR, 2005).

	THSP		INSP		TWSP		WMS	
	Aver[a]	Stdev[b]	Aver	Stdev	Aver	Stdev	Aver	Stdev
Phe	6.547E-04	5.698E-04	7.961E-04	2.928E-04	1.297E-03	5.231E-04	4.280E-01	1.031E+00
An	7.095E-05	7.326E-05	1.034E-04	4.496E-05	1.849E-04	4.577E-05	1.146E-01	2.846E-01
Fluo	3.963E-05	3.084E-05	1.373E-04	1.666E-05	1.261E-04	4.686E-05	5.100E-01	1.454E+00
Pyr	7.769E-04	7.144E-04	1.284E-03	4.131E-04	1.981E-03	8.085E-04	4.939E-01	1.333E+00
B[a]A	7.797E-04	8.233E-04	1.196E-03	4.171E-04	1.746E-03	7.394E-04	3.070E-01	6.946E-01
Chry	3.896E-05	1.642E-05	8.796E-05	1.451E-05	N.D.	N.D.	2.589E-01	5.344E-01
B[b]F	7.696E-05	3.027E-05	7.360E-05	N.D.	9.563E-05	0.000E+00	4.216E-01	1.216E+00
B[k]F	1.033E-04	3.503E-05	1.054E-04	4.760E-05	1.427E-04	2.674E-05	2.485E-01	3.966E-01
B[a]P	4.116E-05	3.676E-05	N.D.	N.D.	N.D.	N.D.	2.390E-01	5.053E-01
Ind	3.733E-04	N.A.	N.D.	N.D.	N.D.	N.D.	2.719E-01	5.351E-01
D[a,h]A	8.577E-05	3.124E-05	4.647E-05	1.231E-05	7.808E-05	3.408E-05	1.433E-01	5.296E-01
B[g,h,i]P	1.599E-04	N.A.	N.D.	N.D.	N.D.	N.D.	2.204E-01	4.645E-01

Note that WMS is the average of PAHs in world sediments reported by Pongpiachan, Tipmanee, et al., 2013.
[a] Average.
[b] Standard Deviation.

HI values in THSP, INSP and TWSP are significantly ($p < 0.001$) lower than those of WMS. It is interesting to note that HI can be employed as an indicator to evaluate the cumulative non-carcinogenic site risk to an individual based on reasonable maximum exposure. According to the "Role of the Baseline Risk Assessment in Superfund Remedy Selection Decisions" memorandum guided by US EPA (1993), if HI is less than one, action is not warranted unless there are adverse environmental impacts for both current and future land use. The US EPA (1993) Superfund Program uses a cancer risk level of 10^{-6} to denote the point at which risk-management decisions should be taken. Applying the same standard, the probability of adverse cancer-causing effects in consuming all soybean products is extremely low compared with those of WMS. In this study, the average HI value in all soybean products is $3.52 \times 10^{-4} \pm 1.62 \times 10^{-4}$, which is 2841 times lower than that of the US EPA (1993) baseline, underlining the circumstance that the magnitude of HI falls in the "acceptable level" range.

4. Conclusions

PAH contents in all soybean products ranged from N.D. to 3115 ± 1271 ng kg^{-1}. An exceptionally high percentage contribution of 6-ring isomers was detected in THSP. This is consistent with the three-dimensional plots of binary ratios showing the unique fingerprint of PAHs in THSP. Open burnings of agricultural wastes and other biomass materials are considered the main sources of PAHs in Chiang-Mai province and are thus responsible for the distinctive features of PAHs in THSP. Despite numerous confounding factors such as "emission source types", "meteorological conditions", "variation of LRAT", and "chemical degradations" that can alter PAH concentrations, the application of HCA can successfully distinguish THSP from other soybean samples. The TEQ values calculated from three different models indicate that soybean products from Indonesia have a comparatively lower toxicity than those from Thailand and Taiwan. Overall, the HI values highlight the result that the degree of "non-cancer risk" of all soybean products falls in the "acceptable level" range.

Acknowledgements

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