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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.

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.