A CRITICAL REVIEW AND EVALUATION OF APPLYING SEMI-VOLATILE ORGANIC COMPOUNDS (SVOCs) AS A GEOCHEMICAL TRACER TO INDICATE TSUNAMI BACKWASH: The Bilateral, Deutsche Forschungsgemeinschaft (DFG) and National Research Council of Thailand (NRCT) Funded Project “Tsunami Deposits in Near-Shore- and Coastal Waters of Thailand (TUNWAT)”

Siwatt Pongpiachan¹ & Klaus Schwarzer²

¹NIDA Center for Research & Development of Disaster Prevention & Management, School of Social and Environmental Development, National Institute of Development Administration (NIDA), 118 Moo-3, Sereethai Road, Klong-Chan, Bangkapi, Bangkok 10240 Thailand
Corresponding author phone: (66) 2727-3090; mobile phone: (66) 819751456; fax: (66) 27273747; e-mail: pongpiajun@gmail.com

²Institute of Geosciences Sedimentology, Coastal and Continental Shelf Research, Christian Albrechts University Kiel, Otto Hahn Platz 1, D - 24118 Kiel, Germany

ABSTRACT

Tsunamis symbolize one of the most harmful natural disasters for low-lying coastal zones and their residents, due to both its destructive power and irregularity. The 2004 Boxing Day tsunami, which attack the Andaman Sea coast of Thailand, resulted 5,395 of deaths and inestimable casualties, interrupted economies and social well-being in numerous coastal villages and caused in extreme alterations of both onshore and offshore coastal morphology. The Great Indian Ocean tsunami also highlighted that there are many missing jigsaw puzzle pieces in scientific knowledge, starting from the generating of tsunamis offshore to the countless influences to the marine ecosystems on the continental shelf, coastal areas and on land and to the economic and social systems consequences. As with all deposits that do not have a direct physical link to their causative sources, marine tsunami deposits must be distinguished from other deposits through regional correlation, dating and criteria for recognition within the deposits themselves. This study aims to provide comprehensive reviews on using Polycyclic Aromatic Hydrocarbons (PAHs) as a chemical proxy to discriminate tsunami related
deposits from typical marine sediments. The advantages and disadvantages of this chemical tracer will be critically reviewed and further discussed.

**Keywords:** Tsunami Deposits, Marine Sediments, Polycyclic Aromatic Hydrocarbons (PAHs), Andaman Sea

### 1. INTRODUCTION

Tsunamis has been a cause of concern all over the world for their tremendous destructive power. This destruction was particularly great in Asia where tsunamis have occurred often throughout history. The 2004 Indian Ocean earthquake is generally recognized as one of the world’s largest and deadliest natural disasters in modern times, responsible for estimated US$ 10 billions of damages including the number of deaths approximately 230,000 people. Since tsunamis dominate natural catastrophe statistics in term of causing casualties and damaging constructions, a large number of studies have been performed over the last three decades to assess the alteration of geological and sedimentological features related to tsunami impact around the world (Atwater, 1987; Benson et al., 1997; Bondevik et al., 1997; Choowong et al., 2007, 2008a, 2008b, 2009; Clague and Bobrowsky, 1994; Dawson et al., 1988, 1991; Gelfenbaum and Jaffe, 2003; Pinegina and Bourgeois, 2001; Szczuciński et al., 2005, 2006, 2007). Tsunamis are recorded since historical times and numerous investigations have been done about their origin, wave distribution and energy release along coastlines, potential for coastal changes as well as on sediment deposition further inland (Bryant, 2001). Tsunamis have been compared to storms even if they are two genetically unrelated phenomena. Both are remarkably similar in their physical power and in their ability to transport sediment across the shelf and to deposit it in deeper water environments, but there is some difference between large storms with long wave periods and the effects of tsunamis in terms of hydrodynamics on the shelf (Bryant, 2001). The differences exist in (i) the capacity of eroding sediments from the sea-floor and the beach-face and to carry and to deposit this material onshore if there are suitable topographic conditions existing and (ii) in the tremendous backflow of tsunami water masses from the inundated areas carrying land-borne material offshore. While it is accepted that storm surges result in the deposition of discrete sedimentary units, tsunami waves generally result in deposition of sediment sheets over relatively wide areas and considerable distances inland (Dawson, 1999). According to a recent review by Gusiakov (2005), 688 tsunamis occurred in the tsunamigenic regions of the Indo-Pacific including Indonesia during 1901 – 2000 and at least 100 megatsunamis have occurred during the past 2000 years worldwide (Scheffers and Kelletat 2003). In historical times 5 Tsunamis hit the coast of Sumatra (1797, 1833, 1843, 1861 and 1883) and might have affected the coast of Thailand as well (Department of Mineral Resources, 2005).

Most of the knowledge about offshore, shallow marine tsunami deposits results from onshore outcrops of ancient lithified strata (Cantalamessa and Di Celma, 2005). Indicators of backrush flow in Miocene sediments are described by le Roux and Vargas (2005). They consider sandstone injections and dikes associated with intraclasts, penetrating underlying strata, as well as debris flow including “wave-smoothed” beach material, as the most reliable evidence. Poor knowledge exists about the

*Vol. 32, No. 4, page 237 (2013)*
deposition on the upper and lower shore face induced by tsunami across-shelf backwash, which might produce sediment aprons, sand bars or large sediment waves. Only very few investigations have been made on submerged unconsolidated Holocene marine deposits (Le Roux and Vargas, 2005; Vargas et al. 2005). The successive run-up and backwash of tsunami waves can produce strong seaward currents causing additional erosion and sediment re-deposition, depending on the nature of the coastal topography and bathymetry (Bondevik et al., 1997; Shi et al., 1998; Dawson and Shaozhong, 2000). Also, large objects (boulders, coral blocks and human artifacts) may be dragged or deposited on the seafloor producing a debris field and other evidence on the seafloor. Einsele (1988), who proposed diagnostic criteria for tsunami deposits, noted that the backflow of tsunamis is commonly focused by the coastal geomorphology into channelized flows. Due to this channeling, the velocity of the backwash flow is more erosive and powerful than the run-up flow. Le Roux and Vargas (2005) show that the backrush of the 1960 tsunami, which hit the coastline of Chile with up to 14 m high waves, developed as kind of rip currents. In short cores obtained from water depth between 75 – 100 m Vargas et al. (2005) observed features and sediment material in two layers originating from areas shallower than 50 m. They relate these deposits to the tsunami backwash. By dating with radioisotopes and lateral correlation they inferred ages as between A.D.1409 – 1449 and A.D.1754 – 1789.

As tsunami backflows advance offshore from the coastline, they will undergo several changes known as flow transformation (Fisher 1983). Flow channelization seems to play an important role in lateral flow transformations leading to unusual deposits. Hyper concentrated flow conditions may therefore develop within the morphologically deepest channel zones, accompanied by intraclasts ripped up from the substrate. Very dense sediment-water mixtures, which the backrush might be, may initially behave as Bingham Fluids dominated by frictional grain interactions and shearing, so that shear carpets may develop at their base. According to Nittrouer and Wright (1994) the midshelf region is in many cases the dead end for many of the particles transported across continental shelves due to storm events. Besides the investigations of Le Roux and Vargas (2005) to our knowledge nothing is known about the fate and the area where most of the tsunami related material is deposited offshore. However, Shanmugam (2005) assumes that tsunami-related deposits should be volumetrically important in coastal, shallow-water and deep-water environments.

For a long time it was neglected that on wave dominated coastal and shelf areas the impact of tsunami waves on shore-face deposits can be preserved in modern sediments. However recent investigations based on modern high resolution remote sensing mapping techniques for marine areas revealed that even in highly dynamic areas and even if the perturbed shore face is in a disequilibrium state, a preservation potential of sediment distribution patterns and shore face geomorphology exist for decades (Schwarzer et al., 2003; Murray & Thieler, 2004; Ferrini & Flood, 2005; Diesing et al. 2006). Conceivably, on the deeper parts of the lower shore face and inner shelf the elevated water level may induce deposition (similar to the classic "Bruun Rule" response) if there is sufficient accommodation space. Thus, the initial morphological response of the shore face to the tsunami is hypothesized to have a pattern of sediment deposition on the lower shore face and inner shelf, erosion on the upper shore face and beach face, and deposition landward of the beach.

Vol. 32, No. 4, page 238 (2013)
1.1 General background of Tsunami Deposits in Near-Shore- and Coastal Waters of Thailand (TUNWAT) Project

In the months following the tsunami disaster, consultations between the National Research Council of Thailand (NRCT) and the German Research Foundation (DFG) resulted in a general agreement for a bilateral cooperation, which was focused on tsunami-related research. Backed by discussions during a joint NRCT-DFG workshop in Bangkok in July 2006, German and Thai scientists agreed to propose research projects, which specifically address scientific issues dealing with tsunami triggering, tsunami wave development and interaction with the sea-bottom and the impacts, alterations and risks to gain a better understanding of tsunamis, their origin, propagation, physical-, social- and economic impacts, resulting destructions and long-term effects and, thus, to improve risk management in the Andaman Sea Region (see Fig.1-3).

Figure 1. Inundation and tsunami flow of the Banda Ache Plain shown in the SPOT2 image. The image was taken about 4 h after the earthquake. (Includes material from CNES2005, Distribution Spot Image S.A., France, all rights reserved). Taken from Umitsu, M. et al., 2006. Own comment: Rip current eddies can be observed along the whole coastline.

Within the framework of this theme, several topics have been brought forth. As there is a common focus on tsunamis and impacts, the research issues of the individual projects are interlinked by the fact

Vol. 32, No. 4, page 239 (2013)
that they are aiming at providing complementary answers to key questions about tsunamis in the study region and their potential impacts. These major questions can be described as follows; (i) Where and how can tsunamis be triggered in the Andaman Sea? (ii) How often have tsunamis struck this coast in the recent past? (iii) How does a tsunami wave propagate from offshore (deep water) via the shelf and near-shore zone onto the adjacent low-lying land areas? (iv) What are the impacts of tsunami waves to the seafloor topography, to the sediment cover and to the marine & littoral ecosystems while progressing onshore? (v) How does the land-sea loaded backflow influence the marine abiotic and biotic system? (vi) How is tsunami wave energy attenuated in the near shore zone, beachfront and hinterland and how is this attenuation influenced by the presence of natural barriers such as coastal forests? (vii) What factors determine the tsunami-related vulnerability of low-lying coastal areas, their population, communities and economies? (viii) Which kind of socio-economic, institutional and/or other factors make coastal societies or communities resilient against tsunami impacts? (ix) How can risk management, including early warning, be improved to prevent or mitigate future tsunami disasters along this coast?

Figure 2. The coastal area of Thailand when the Tsunami waves hit the shore. Far offshore the influence of the sea bottom to the tsunami waves becomes obvious when due to bottom friction by wave transformation and wave-breaking occurs (Source: http://www.crisp.nus.edu.sg/tsunami/tsunami.html).

Vol. 32, No. 4, page 240 (2013)
Figure 3. The coast of Thailand 2 hours after the tsunami hit the coast on December 26\textsuperscript{th}, 2004 at 06:25 UTC. The suspension load plume of the backrush extends approximately 20 km offshore. (Source: http://www.crisp.nus.edu.sg/tsunami/tsunami.html).

\textit{Vol. 32, No. 4, page 241 (2013)}
The questions above provide a feasible basis for addressing key issues of regional tsunami research. They also outline some spatial structure, as the planned projects may be seen as lining up along an offshore – onshore transect from the deep Andaman ocean across the shelf, near shore and beach zone into the coastal hinterland as far as a mega-tsunami can reach. While in the offshore domain natural processes dominate, towards onshore and especially on land anthropogenic influences increase and trigger the vulnerability. Consequently, the intention of the group is to establish a German – Thai tsunami research network in which project data ought to be exchanged and results ought to be generated/synthesized as to contribute to the enhancement of the region’s ability to cope with tsunami risks.

Based on this concept of interlinked and spatially adherent projects the German-Thai research group attempts to focus on the following issues:

- Analyze the possibility of tsunami-triggering by slides / slumps at the continental margin of the Andaman Sea;
- Detecting changes in seafloor topography and sediment pathways by use of remote sensing methods (satellite image investigation, mapping by multi-beam and side scan sonar techniques), sediment coring, sampling and dating by radio isotopes;
- Detection and reconstruction of previous tsunami events in order to determine the long-term history of tsunamis along this coast;
- Numerical modeling of wave propagation and run-up during the Dec. 26, 2004 tsunami. Validation of different models by comparing measured tsunami run-up characteristics with results from numerical model simulations;
- Determining the influence of coastal ecosystems, in particular coastal forests and mangroves, on the physical impacts of tsunami waves along the whole western coast of Thailand;
- Generating a scientific knowledge base and developing/validating prediction models for the tsunami attenuation performance of coastal forests;
- Assessment and evaluation of tsunami risks in flood-prone coastal areas and communities. Assisted by remote sensing techniques and field surveys, quantitative indicators are to be derived for ecologic, economic and social vulnerability as well as for local resilience;
- Comparing local and global interactions in disaster prevention and recovery in two regions strongly hit by the 2004 tsunami: Khao Lak, Thailand and Aceh, Indonesia;

The main objective of the proposed sub-projects is to complement individual research issues in such a way that a clear picture can be drawn about the destructive forces and processes of the recent tsunami and past tsunamis and to elaborate and to suggest measures how to avoid or mitigate future tsunami impacts and destructions in Thailand. Most of the deposits that are known to occur or may occur in marine environments require improvements in the criteria for recognition. Developments of such criteria are best done when there are deposits of unquestioned origin. The recognition of deposits of this tsunami gives the opportunity to extend the relatively short or non-existent historical record of tsunamis in this area. Presently most of the literature regarding marine tsunami deposits comes from ancient geologic record and cannot be tested. The December 2004 Sumatra-India earthquake and following tsunami represents an opportunity to catalogue geomarine effects from a very well recorded series of events, many of which are unknown or poorly known at present. A modern deposit of
unquestioned origin is invaluable for defining the palaeo record. This event represents the best-recorded mega-tsunami in human history and offers a unique opportunity to collect data, which have been never recorded yet. Even if offshore records offer the potential of good preservation, good spatial coverage and long-term span, data should be collected as soon as possible after this event as much of the information may be altered or destroyed over time.

Numerous field surveys have been carried out to measure the inundation, run up and deposition of marine derived sediment onshore caused by tsunamis, but no systematically detailed study exist up to now to measure geomorphological, sedimentological and geological alterations offshore beyond the upper shore face. This project aims to assess the impact of tsunami waves on changes and/or offsets of large-scale bed forms, on changes and/or offsets of shelf sediment distribution patterns and on estimating the spatial extension of erosion as well as on deposition by the backwash. The following offshore impacts are expected:

- Erosion by the onshore moving tsunami wave;
- Erosion by the channelized backwash currents;
- Transport of huge sediment plumes offshore and deposition from the shore face to the mid- or outer shelf.

Therefore the scientific questions in detail are:

- How do incoming tsunami waves influence sediments and sea bottom topography on the shelf and in near shore waters?
- How does the offshore flowing backrush influence sediments and sea bottom topography on the shelf and in near shore waters?
- Are there distinguished conduits for the sediment backflow?
- At which water-depth and at which offshore distance can a tsunami triggered alteration of the seafloor be observed?
- How will offshore tsunami deposits look like?
- How does an archive record of tsunami affected shelf deposits look like?
- How far offshore sediments are transported by the tsunami backwash?
- Was more sediment transported and deposited onshore or offshore?

To achieve the objectives of this project a multidisciplinary approach is required combining remote sensing methods, geophysical and sedimentological methods and geochemical methods.

1.2. Concept of using Semi-Volatile Organic Compounds (SVOCs) as geochemical tracers to characterize tsunami backwash deposits

Geochemical tracers have been extensively used as environmental tools to investigate the behavior and fate of target compounds in the environment (Pongpiachan et al., 2012a,b). While onshore tsunami deposits are supposed to contain organic and inorganic material of marine origin, offshore transported material should contain tracer-material originating from land, depending on landforms and
deposits, which are exposed in the areas, which were hit by the tsunami waves. For decades, both PAHs and aliphatics have been used as a “proxy” to distinguish the anthropogenic source and biogenic source. In this study we make the assumption that (i) terrestrial soils contain many anthropogenic PAHs coupling with aliphatics from terrestrial plants and (ii) marine sediments contain many of phytoplankton derived biomarkers. By analyzing these organic tracers from different points coupling with careful statistical treatments, it should be possible to investigate the impact of the tsunami to the distribution of terrestrial sediments in the recent deposits of the Andaman Sea.

Understanding the mechanisms and spatial variations of tsunami backwash sediment distribution patterns and burial within the offshore area of the Andaman Sea requires an ability to discriminate between terrigenous and marine components of organic compounds. Furthermore, the role of the shelf as a source area must be distinguished from those of basins, as sink areas and the coupling between the two should also be understood as well. A number of approaches have been used to distinguish between marine and terrigenous components in marine sediments including SVOCs such as PAHs, hopanes and cholestanes (Westerhom et al., 1992; Yunker et al., 2002, 2003; Kalaitzoglou et al., 2004). SVOCs have the advantage that they are all released into the atmosphere by imperfect combustion of organic matters and thus can be used as indicators to identify anthropogenic combustion sources (i.e. traffic emissions, industrial activities, incinerators etc) from natural combustion sources (i.e. forest fires, volcano activities, re-evaporation, etc.) by using specific binary ratios (Pongpiachan, 2013a,b,c; Pongpiachan et al., 2013c,d; Tipmanee et al., 2012; Yunker et al., 2002). Those areas which were most affected by the backrush of tsunami waters should contain more terrigenous sediments and thus as well relatively higher proportions of anthropogenic source derived organic compounds. Specific organic biomarkers such as 17 α(H) -22,29,30-Tris (Tm), 17 β(H), 21 β (H) -hopane, 17 β (H), 21 α (H) -30-northpane (Isodiatane), 17 β (H), 21 α (H) -hopane (Moretane), 17 α (H), 21 β (H) –hopane, 18 α (H), 22,29,30-Trisnorhopane (Ts), on the other hand, often yield clear evidence of sources (terrigenous and marine) even though they represent only a small proportion of the total organic material found in the sediments (Belicka et al., 2004). Furthermore, the value of CPI1 (Carbon Preference Index 1), CPI2 (Carbon Preference Index 2), CPI3 (Carbon Preference Index 3), ACL (Average Carbon Length), C_{max} (Carbon Maximum Number), Pristane and Phytane can be used as biomarkers to distinguish between terrigenous and marine derived sources of sediments (Yunker et al., 2002, 2003). By calculating SVOC concentrations against background values the spatial extension of the sediment load of the tsunami backwash can be estimated. In addition, there are other alternative analytical tools such as Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) and micro-beam synchrotron X-Ray Fluorescence (μ-SXRF) that can be used to characterize the tsunami backwash deposits (Pongpiachan et al., 2013a,b).

1.3. Physicochemical properties, fates and environmental risks of PAHs

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. By definition as organic compounds with vapor pressure ranging from $10^{-3}$ – $10^{-7}$ Pa (see Table 1), PAHs, alkanes, cholestanes, hopanes and anthropogenic sourced chemicals like organochlorine pesticides, polychlorinated biphenyls (PCBs),
Dioxins can be termed as SVOCs (Paasivirta et al., 1999). These molecules were oriented horizontal to the surface, with each carbon having three neighboring atoms much like graphite (see Table 2-5). The structures of a variety of representative PAHs can be seen in Table 2. In order to reduce the atmospheric concentration of SVOCs, the UK’s Expert Panel on Air Quality Standard (EPAQS) has selected benzo[a]pyrene (B[a]P) as a marker for levels of ambient PAHs in recognition of its carcinogenicity and mutagenicity. An annual mean of 0.25 ng m$^{-3}$ has been set. However, this value exceeded the annual mean concentration of B[a]P measured in a number of UK cities since 1997. The long term monitoring of SVOCs in urban air, therefore, is a significant approach to investigate the annual trends and seasonal variations of targeted compounds. However, the environmental persistence and a wide range of vapor pressure of SVOCs have made this group of organic compounds globally ubiquitous and thus subject to unique atmospheric fate/behavior. The complexity of its existence in the atmospheric environment together with varieties of emission sources attributed the uncertainties in source apportionment of these specific compounds. Since SVOCs can be measured in the most remote areas like Antarctica, the worldwide concerns are also focused on the long-range atmospheric transportation (LRAT).

Epidemiological evidence suggests that human exposures to PAHs, especially B[a]P are high risk factors for carcinogenic and mutagenic effects. There are hundreds of PAH compounds in the environment, but only 16 of them are included in the priority pollutants list of US EPA (EPA, 2003). Many PAHs have also been identified as cancer-inducing chemicals for animals and/or humans (IARC, 1983). In 1775, the British surgeon, Percival Pott, was the first to consider PAHs as toxic chemicals with the high incidence of scrotal cancer in chimney sweep apprentices (IARC, 1985). Occupational exposure of workers by inhalation of PAH-both volatile and bound to respirable particulate matter- and by dermal contact with PAH-containing materials, occurs at high levels during coke production, coal gasification, and iron and steel founding. Coke oven workers have a 3- to 7-fold risk increase for developing lung cancer (IARC, 1984 and IARC, 1987). For this reason, the monitoring of PAHs in environmental media is a reasonable approach to assess the risk for adverse health effects. Since the fate of PAHs in the natural environment is mainly governed by its physiochemical properties, the study of general properties of the compounds is of great concern. In spite of a large number of publications related to the environmental fates of PAHs around the world, there are only few studies conducted in Thailand (Boonyatumanond et al, 2007; Chetwittayachan et al, 2002; Pongpiachan et al., 2009; Pongpiachan, 2013b,c; Pongpiachan et al., 2013c,d, e; Ruchirawat et al, 2002, 2005, 2007; Tipmanee et al., 2012).

In this study, the authors hypothesize that the employment of PAHs coupled with various analogies of statistical analysis assist in a better understanding of offshore terrestrial deposit distribution pattern, which can be subject to erosion by tsunami/monsoon waves and surface runoff by heavy rain in the tsunami-affected coastal areas of Andaman Sea, Thailand. Note that it is the purpose of this paper to critically review both the advantages and disadvantages of using SVOCs as an innovative proxy to separate the terrestrial deposit from the background sediment in tsunami-affected coastal areas. Neither the source apportionment, nor the analysis of spatial variation of SVOCs in sediments is the main focus of this study. In addition, the risks and possibilities of applying other geochemical tracers as an alternative extreme event proxy will be reviewed and discussed.

Vol. 32, No. 4, page 245 (2013)
2. Source characterization of SVOCs

2.1 Source characterization of PAHs

The binary ratio method for PAH source identification, involves comparing ratios between pairs of frequently found PAH compound characteristics of different sources. Stationary source combustion emissions from the use of coal, oil and wood are low in coronene (Cor) relative to B[\(a\)]P, while mobile source combustion emissions from diesel and petroleum use are high in B[g,h,i]P and Cor relative to B[\(a\)]P (Stenberg et al., 1979). The ratio of these PAHs can be used to distinguish between traffic dominated PAH profiles and other sources (Brasser, 1980; Mainwaring and Stirling, 1981). Lim et al., (1999) used two methods in evaluation of PAH traffic contribution. Both of methods were adapted from Nielsen (Nielsen, 1996). Equation 1 based on the assumption that all Cor is traffic-generated, the concentration of B[\(e\)]P which is traffic generated is given by

\[
B[e]P_{\text{traffic}} = \frac{\text{Cor concentration}}{\delta \text{Cor}}
\]

Equation 1

Crucial to this method is the assumption that all Cor is traffic generated. Although this is likely to be an oversimplification, many studies have shown a high correlation between Cor and vehicular emissions. In addition, the ratios of B[g,h,i]P/B[e]P and Cor/B[e]P can also be used as traffic indicators, since both B[g,h,i]P and Cor have been reported to correlate closely with traffic emissions. Other PAHs such as retene (Ret) is also considered as a common biomarker of coniferous wood combustion, and resin acids such as abietic acid commonly found in smoke samples.

Since PAHs contents in atmosphere are sensitive to both anthropogenic and natural emissions, a more effective marker of traffic emissions is substantially required. Another potential index to distinguish the traffic emission is the use of inorganic tracers. It is widely known that particles from road dust appear to contain Pb, Fe, Mn, Ca and sometimes Zn, (Harrison et al., 1996). This can be explained by the attrition of road surfaces, resuspension of street dirt and soil dust (i.e. source of Ca and Mn; Pierson and Brachaczek, 1993), particles from tyre wear (i.e. source of Zn; Ondov et al., 1992), brake-drum abrasion, and debris from wear and rusting. In order to investigate the contributions of traffic related pollutants, several attempts were made for source apportionment of PAHs in Birmingham air by using inorganic source markers such as Cu, Fe, Pb, Zn and Mn. Lim et al (1999) reported high loading on higher MW PAHs (B[\(a\)]A to Cor) and moderate loading on BNT and Ph and the gasoline powered vehicle marker, Pb.

Based on size distribution of various elements at a road site location in Birmingham (BROS), Fe, Cu, Mg, Sr, Mo, Ce and Ba were found to be the major components in the traffic related coarse particle (i.e. 2 – 10 µm aerodynamic diameter, Harrison et al., 2003). Whilst strong correlations of Cu (\(r^2 > 0.74\)), Mo (\(r^2 > 0.54\)), Ba (\(r^2 > 0.73\)), Pb (\(r^2 > 0.68\)), Mn (\(r^2 > 0.54\)) and Zn (\(r^2 > 0.61\)) with NO\(_x\) indicated that these elements probably originate in road site particles. Until 1997, Pb and Br had been
widely employed as indicators of road traffic emissions (Harrison et al., 1997). Lead (Pb) is added to petrol in the form of an organic tetramethyl lead, an anti-knock agent, and is emitted by the exhaust stream in inorganic particulate forms, predominantly as PbClBr and 2PbClBr*NH₄Cl. Thus, the combination of Pb with Br can be used as classical marker elements for traffic emissions. However, the worldwide decline of Pb concentrations in the atmosphere has been observed due to the introduction of unleaded gasoline into the market in 1989 (Salma, et al., 2000). As a consequence, the Br/Pb ratio for determining the automotive contribution to the atmospheric lead burden may not be possible. In this study, n-alkanes and petroleum biomarkers such as hopanes and cholestanes had been introduced into the receptor models instead of inorganic marker elements like Pb. Alternatively, hopanes and cholestanes can be used as petroleum biomarkers, because: (i) these organic compounds are found mainly in exhausted gas from petroleum combustion and thus overlap PAHs combustion profiles, (ii) these organic compounds are not formed by atmospheric chemical reactions, (iii) these organic compounds are continuously released to the atmosphere by automotive emissions, and (iv) these organic compounds are prone to degradation in the environment. Because of these unique characteristics, hopanes and cholestanes have been widely used to define both the fossil origin and geological source of petroleum residues, (Rogge et al., 1993; Simoneit, 1984).

2.1.1 PAHs in aerosols from different countries

2.1.1.1 UK
PAH monitoring campaign was performed at two sites in London by Kendall et al (2001). The first sampling site was located at Bounds Green (BG) in North London. The second sampling site was positioned at St Paul’s Cathedral (SP) in Central London. The annual means of the majority of the individual PAH compounds and ΣPAHs was higher at SP (7.24 ng m⁻³) than at BG (4.27 ng m⁻³). Both sites showed the same seasonal pattern of the lowest concentration during the summer and the highest average concentration during the autumn. B[ghi]P was the most abundant PAH at both London sites, followed by B[a]A and Chry, and these three PAHs dominated during all four seasons. The highest concentrations of these compounds were measured during the sampling week containing Bonfire Night at BG and during January at SP. Concentrations of these three compounds contributed over 50% of the ΣPAHs. In London, the winter ΣPAHs concentrations were only approximately twice the summer concentrations, possibly reflecting the small number of PAHs sources in London, with vehicles dominating PAHs production.

2.1.1.2 Indonesia
The burning of biomass as a method to clear and fertilise land is practiced in Indonesia every year by farmers and forestry companies. In 1997, Indonesia had been extremely dry due to El Nino, and what is now known as the Indonesia forest fire started to get out of control in the middle part of June. Emissions from biomass burning can vary widely because the material and the burning conditions can differ greatly. In a forest fire of this duration and magnitude, the burning material and conditions can vary from time to time as well as location to location. The ΣPAHs concentration ranged from 7 ng m⁻³ to 46 ng m⁻³ (Fang et al., 1999). The highest value of B[a]P was measured in Pudu on 27-09-97 at 3 ng m⁻³ while the lowest was at the same site on 04-09-97 at 0.1 ng m⁻³. These values are comparable to those measured in Hong Kong, and the highest value matches some of the street-level monitoring

Vol. 32, No. 4, page 247 (2013)
results (Fang et al., 1996). The concentration increase in ΣPAHs from the early to late September samples was the lowest. Retene, a common biomarker of coniferous wood combustion, and resin acids such as abietic acid commonly found in smoke samples in controlled studies, were not found in any of the samples in this study. This may be due to the transformation occurring in the long distance transportation of the aerosols, although retene was found to be relatively stable in sediments and did not vary in the same way as other PAHs (Ramdahl, 1983).

2.1.1.3 Greece
The field campaign took place in a conifer forest of central, continental Greece. Measurements were taken as part of the European Commission project, “Aerosols formation from biogenic organic carbon” (AEROBIC), during the period of 20 July-12 August, 1997. PAHs and oxy-PAHs detected in the Greek aerosols present an increase of concentrations with the number of benzene rings, with a dominance of PAHs with more than 5 rings. ΣPAHs concentrations (0.1 ng m\(^{-3}\) - 18.5 ng m\(^{-3}\)) were, in general, higher compared to that reported for a Portuguese forest, 0.1 ng m\(^{-3}\) - 0.9 ng m\(^{-3}\) (Kavouras et al., 1999), and other rural area of Greece, 0.2 ng m\(^{-3}\) - 2.0 ng m\(^{-3}\) (Gogou et al., 1996). However, these levels are lower than those presented for urban aerosols of a Greek island, 21.4 ng m\(^{-3}\) - 59.0 ng m\(^{-3}\) (Gogou et al., 1996).

2.1.1.4 Hong Kong
Hong Kong, with an area of 1092 km\(^2\) and over 6.5 million in population, is surrounded by the South China Sea to the south and east, Pearl River Estuary on the west, and the landmass with complicated terrain on the north. It is also under the influence of the Asian Monsoon System. The summer monsoon brings in clean oceanic aerosols while a polluted air mass from the mainland comes with the northeasterly wind in the winter season. Thus the characteristics of Hong Kong’s aerosols are represented by outside sources superimposed on very strong local emissions. ΣPAHs concentration was in the range of 0.7 ng m\(^{-3}\) - 12.2 ng m\(^{-3}\) (Zheng et al., 2000). In general, higher PAHs concentrations were found in the winter PM\(_{2.5}\) samples. Other studies show that the changes in emission patterns (stationary and vehicular) and meteorological conditions (including less daylight hours, reduced ambient temperatures, and lower volatilization and photochemical activity) contribute to the higher PAHs levels during winter (Ramdahl et al., 1982, 1983; Freeman and Cattell, 1990, Baek et al., 1991a,b). The association of B\([g,h,i]\)P with vehicle exhaust has long been established (Baek et al., 1991a,b), and a good correlation with total PAHs was obtained in this study. This suggests that vehicular emission was the dominant source of PAHs in the PM\(_{2.5}\) cut of the aerosols in Hong Kong. The low molecular weight (LMW) PAHs such as Phe, Fluo and Pyr were enriched in the fall and winter samples. Comparing the spring and summer samples, the winter and fall samples contained more LMW PAHs. The LMW PAHs tend to be more concentrated in the vapour phase while the higher molecular weight ones are often associated with particulates. In addition, more details of PAHs in aerosols around the world are displayed in Table 6.

2.2 Source characterization of aliphatics

The enormous range of organic compounds detected in urban particles may be divided into two major source groups; primary condensates and oxidized hydrocarbons. Primary condensates (alkanes (C\(_{17}\)-
$C_{36}$, alkenes) originate directly from the incomplete combustion of fossil fuels and are sorbed onto the surface of particulate matter. Oxidized hydrocarbons (carboxylic acids, aldehydes, ketones, quinines, esters and phenols) may either be attached to the particulate as a primary condensate or may be produced during atmospheric oxidation reactions (Cautreels, 1978). Bray and Evans (1961) developed the carbon preference index (CPI) as an indicator of the extent of odd or even carbon number homologues within a sample. The CPI is expressed as a summation of the odd number homologues within a specified range of carbon numbers divided by a summation of the even number homologues within the same range. This inter-sample comparison is useful in identifying sources and establishing dominant sources of aerosol organic matter, as certain biologically produced $n$-alkanes show a pronounced predominance of odd carbon numbers (Bray and Evans, 1961). For example, organic matter of recent biogenic origin shows a preference for odd carbon numbered $n$-alkanes with CPI$_{\text{odd}}$ values of 6-9 and more. Hydrocarbons of abiological origin (e.g. fossil fuels) typically show no carbon number preference or tend towards low CPI values (i.e. CPI < 1). To reconcile sources of organic species, CPI was calculated as follows (Tarek et al., 1996):

$$CPI_1 = \frac{\sum(C_{15} - C_{31})}{\sum(C_{14} - C_{32})}$$

Equation 2

$CPI_1$ represents whole range for $n$-alkanes

$$CPI_2 = \frac{\sum(C_{15} - C_{25})}{\sum(C_{14} - C_{24})}$$

Equation 3

$CPI_2$ represents petrogenic $n$-alkanes

$$CPI_3 = \frac{\sum(C_{25} - C_{31})}{\sum(C_{26} - C_{32})}$$

Equation 4

$CPI_3$ represents biogenic $n$-alkanes

The biogenic “wax” concentration of $n$-alkanes was calculated as follows:

$$Wax - n - Alkane = \begin{bmatrix} C_n \end{bmatrix} - \frac{\left(\frac{C_{n+1} - C_{n-1}}{2}\right)}{\sum \left(\frac{C_{n+1} - C_{n-1}}{2}\right)}$$

Equation 5

Note that wax* has traditionally referred to a substance that is secreted by bees (i.e. beeswax) and used them in constructing their honeycombs. Additionally waxes may be natural or artificial. In this context, wax is natural oily substance. Chemically, a wax may be a combination of other fatty alcohols with fatty acids.

Vol. 32, No. 4, page 249 (2013)
Scalan and Smith (1970) proposed the *odd-to-even* predominance *n*-C$_{29}$ OEP ratios by using the following equation;

$$n - C_{29} OEP = \frac{(C_{27} + 6C_{29} + C_{31})}{(4C_{28} + 4C_{30})}$$

Equation 6

OEP values were plotted against carbon chain length to construct the OEP curves. The pattern of the OEP curve is determined by the source of *n*-alkanes, which indicates the potential fingerprint for source apportionment. U:R is a good indicator of petroleum residue contribution. Under the resolved peaks in a typical *n*-alkane gas chromatogram, there is an unresolved complex mixture (UCM) in the form of an envelope, which contains branched and cyclic hydrocarbons. The UCM is also termed as the “hump” and is believed to be the contribution from fossil fuel residue. U:R is the ratio of the areas of the unresolved to resolved components (peaks) and is an indicator of the contamination by anthropogenic sources (Mei, 2000).

Hopanes are widespread in both recent and ancient sediments. The origin of most hopane is the bacterial C$_{35}$ tetratetrahydroxybacteriohopane. Hopane hydrocarbons present in sediments range from C$_{35}$ and down to C$_{27}$, usually with the C$_{30}$ isomers as the predominant. Hopanoid are produced by most living organism with $\beta\beta$-configuration (17$\beta$(H),21$\beta$(H)). Increasing maturity leads to the more thermodynamically stable $\alpha\beta$-hopanes and $\beta\alpha$-hopanes, with the former being the predominant isomer. Molecular calculations have shown that the $\alpha\alpha$-isomers are less stable than the $\alpha\beta$-hopanes and $\beta\alpha$-hopanes, but more stable than $\beta\beta$-isomer (Philip et al., 1984). Most hopanoids are bio-synthesized with the 17$\beta$(H),21$\beta$(H) stereochemistry. C$_{29}$ and higher homologues of hopane are isomerized to 17$\alpha$(H),21$\beta$(H) at any early stage of diagenesis. The degree of maturation can be calculated as follows:

$$\frac{17\alpha(H),21\beta(H)}{17\beta(H),21\beta(H) + 17\alpha(H),21\beta(H)} = \frac{\alpha\beta}{\beta\beta + \alpha\beta}$$

Equation 7

The ratio of equation 1.7 usually reach one simultaneously with the disappearance of 17$\beta$(H),21$\beta$(H). Furthermore, maturation enhances the content of 17$\alpha$(H),21$\beta$(H) relative to 17$\beta$(H),21$\alpha$(H). C$_{27}$-Hopanes have no side-chain and the conversion of 17$\beta$(H) to 17$\alpha$(H) ($T_m$) reaches completion at maturity between the disappearance of 17$\beta$(H),21$\beta$(H) hopanes and 17$\alpha$(H),21$\beta$(H) hopanes, that is prior to the onset of intense hydrocarbon generation. As illustrated in Figure 1.2, 18$\alpha$(H)-Trisnorhopane ($T_s$) is not affected by maturity changes, and the ratio: $T_m/T_s$ can thus be used as a maturity indicator (Yunker et al., 2003). Recent studies have highlighted on the heterogeneous nature of hopane and sterane biomarkers in several river-dominated margins (Yunker et al., 2003 and Mudge, 2002). In the last two decades these petroleum biomarker parameters have been developed by organic geochemists to differentiate between oils, and determine their source in the aquatic environment and to trace their point sources (Zakaria et al., 2001).
For decades, pristine and phytane have been considered as biodegradable and thus these ratios might be valuable in the early stages of biodegradation (Prince et al., 1994). In particular, Burns and Teal (1979) stated that the branched alkanes extracted from marsh sediments at the West Falmouth site were completely degraded within the first seven years after the oil spill. These findings were based first on measurements of the pristine/phytane ratios. It was found that this ratio was 1.5 in the original Florida oil and that it decreased over a period of six years to 0.2. This is in contrast to another recent finding that have shown that n-alkane band in the fuel oil range (n-C_{10}-n-C_{24}) was no longer present, whereas all other compound classes such as nor-pristine, pristine and phytane are evident within the residual oil at the same sampling site (i.e. the West Falmouth site, Reddy et al., 2002). These latest results suggest that these compounds will be very useful petroleum biomarkers in understanding the distribution pattern of traffic-emitted aerosol components. In addition, steroid skeletons have been widely used as an indicator of diagenesis and the biological origin (biomarker) of organic matter (Jasper, 1993; Huang and Meinschein, 1976; Simoneit, 1984; Venkatesan et al., 2003). Steroids are also source tracers for biogenic material in complex mixtures of dissolved and particulate matter in the geosphere, especially in the marine environment (Brault and Simoneit, 1988 and Wang et al., 2004).

2.3 Cluster analysis & receptor models

2.3.1 Cluster analysis (CA)
Cluster analysis (CA), also called segmentation analysis or taxonomy analysis, seeks to identify homogeneous subgroups of cases in a population. That is, cluster analysis seeks to identify a set of groups which both minimise within-group variation and maximise between-group variation. In this study, CA was conducted using SPSS 13.0 for Windows. CA techniques may be hierarchical (i.e. the resultant classification has an increasing number of nested classes) or non-hierarchical (i.e. k-means clustering). Hierarchical clustering allows users to select a definition of distance, then select a linking method of forming clusters, then determine how many clusters best suit the data. Hierarchical clustering methods do not require pre-set knowledge of the number of groups. Two general methods of hierarchical clustering methods are available: divisive and agglomerative. The divisive technique start by assuming a single group, partitioning that group into subgroups, partitioning these subgroups further into subgroups and so on until each object forms its own subgroup. The agglomerative techniques start with each object describing a subgroup, and then combine like subgroups into more inclusive subgroups until only one group remains. In either case, the results of the application of the clustering technique are best described using a dendogram or binary tree. The objects are represented as nodes in the dendogram and the branches illustrate when the cluster method joins subgroups containing that object. The length of the branch indicates the distance between the subgroups when they are joined.

After selecting the hierarchical clustering method, it is important to select the clustering algorithm (i.e. the rules which govern between which point distances are measured to determine cluster membership). There are many methods available, the criteria used differ and hence different classifications may be obtained for the same data. Five algorithms, available within SPSS, are (i) average linkage clustering, (ii) complete linkage clustering, (iii) single linkage clustering, (iv) within
groups clustering and (v) Ward’s method. Average linkage clustering is defined as the dissimilarity between clusters and calculated using cluster average values. The most common method to calculate an average is UPGMA (Un-weighted Pair-Groups Method Average). Complete linkage clustering (Maximum or Furthest-Neighbour Method) can be described as the dissimilarity between two groups is equal to the greatest dissimilarity between a member of cluster \( i \) and a member of cluster \( j \). This method tends to produce very tight clusters of similar cases. On the other hand, single linkage clustering can be simply explained, as the dissimilarity between two clusters is the minimum dissimilarity between members of two clusters. This method has been widely employed in numerical taxonomy. Besides, it is crucial to note that within groups clustering is similar to UPGMA except clusters are fused so that within clusters variances is minimized. This tends to produce tighter clusters than the UPGMA method. Finally, Ward’s Method is assessed by calculating the total sum of squared deviations from the mean of a cluster. The criterion for fusion is that it should produce the smallest possible increase in the error sum of squares.

2.3.2 Receptor models
Receptor models can be categorized into two types, namely, Chemical Mass Balance (CMB) and multivariate models. The most widely used multivariate models are principal component analysis (PCA), positive matrix factorization (PMF), and UNMIX model. CMB predicts the contribution of different sources to measured target compound concentrations in atmosphere by means of an inverse variance weighted least-square linear regression, (Watson et al., 2001). The concept of CMB model, based on the principle of mass conservation, assumes that the total concentration of chemical species, \( C_i \), at the receptor site, is the sum of the contributions from all sources \( j \) which emit species \( i \).

\[
C_i = \sum_{j=1}^{p} \alpha_{ij} \times f_{ij} \times S_j
\]

Equation 8

where \( S_j \) is the fractional mass contribution of source \( j \) to the pollutant of target compound in the atmosphere, \( f_{ij} \) is the fraction of chemical species \( i \) in the emission from source \( j \), for \( p \) sources. \( \alpha_{ij} \) is the coefficient of fractionation used to correct uncertainties in \( f_{ij} \) between the source and the atmosphere, (Watson et al., 1990 and Engelbrecht et al., 2002).

Unlike other receptor models, which extract source compositions from the data, CMB model assumptions are based on: (i) compositions of source emissions are constant over the period of ambient and source sampling, (ii) chemical species do not react with each other, (iii) all sources with a potential for contributing to the receptor have been identified and have had their emissions characterized, (iv) the number of sources or source categories is less than or equal to the number of species, (v) the source profiles are linearly independent of each other, and (vi) the uncertainties are random, uncorrelated, and normally distributed, (CMB8 Applications and Validation Protocol for PM\(_{2.5}\) and VOCs announced by Desert Research Institute US). CMB have been widely used to assess sources of air pollutants because it: (i) theoretically yields the most likely solutions based on chemical source profiles, (ii) uses all available chemical measurements, (iii) estimates the uncertainty of the source contributions based on resolution of both the ambient concentrations and source profiles, (iv) provides greater influence to chemical species with higher resolution in both the source and receptor.
measurements than to species with lower resolution. However, the major weaknesses of the CMB are its difficulty to account for non-stable compounds and incapability to identify those sources that have similar contributions. Moreover, CMB requires chemical source profiles as fingerprints for source apportionment of environmental pollutant.

The fundamental principles of various chemical methods for receptor modeling, including chemical mass balance (CMB) and multivariate method, have been reviewed in detail (Gordon, 1988; Watson, 1994). Factor analysis offers the advantages of not requiring prior knowledge of the chemical composition and size distribution of emissions from specific sources (source profiles) but has the drawback of being mathematically indeterminate, allowing a wide range of possible solutions even when it is applied to relatively simple simulated data sets. In urban atmosphere, which is composed by many potential and diverse sources, PCA has been chosen by many workers for source apportionment. This technique has been widely applied to source apportionment of particulate pollutants, especially trace metals, and more recently, PAHs. In order to identify sources, multivariate receptor modeling can be applied to the observed target compound data. Multivariate approaches are based on the idea that the time dependence of a chemical species at the receptor site will be the same for species from the same source. Chemical species are measured in a large number of samples gathered at a single receptor site over time. Species of similar variability are grouped together in a minimum number of factors that explain the variability of data set. It is assumed that each factor is associated with a source or source type. However, the method has some limitations in that it can recognize at most only about eight individual source categories in any study, and poor discrimination of closely related source categories is commonly found. A further disadvantage of multivariate factor analysis is that large numbers of ambient air samples must be collected and analyzed (usually at least 50) and the statistically independent source tracers are required for each major source type.

In contrast to CMB model, multivariate techniques such as PCA are preferable since they require no qualitative insight of the sources of certain chemical species, and thus overcome the limitations of CMB, (Rachdawong et al., 1998 and Park et al., 2005). The aim of PCA is to identify the major sources of air pollutant emissions and to select statistically independent source tracers, (Bruno et al., 2001; Miller et al., 2002 and Gou et al., 2003). All variables are expressed in standardized form with a mean of 0 and a standard deviation of 1. The total variance therefore equals the total number of variables, and the variance of each factor expressed as a fraction of the total variance is referred to as the eigenvalue. If a factor has a low eigenvalue, then it is contributing little to the explanation of variances in the variables and may be ignored. PCA is generally used when the research purpose is data reduction (i.e. to reduce the information in many measured variables into a smaller set of components). PCA seeks a linear combination of variables such that the maximum variance is extracted from the variables. It then removes this variance and seeks a second linear combination that explains the maximum proportion of the remaining variance, and so on. This is called the principal axis method and results in orthogonal (uncorrelated) factors. Thus, the largest combination, accounting for most of the variance, becomes principal component 1 (PC1), the second largest accounts for the next largest amount of variances and becomes principal component 2 (PC2), and so on.
Over a period of about 10 years the combination of interest driven by regulations with advances in instrumental analytical analysis and the wide availability of computers resulted in the innovative field of source apportionment/receptor modeling. The first applications of a receptor model using factor analysis were done by Hopke et al. (1977) and Garrenstrom et al. (1977). The first Ph.D. thesis on multivariate air quality receptor modeling was that of Henry (1977). This work made explicit the connection between the statistical and physical models underlying multivariate receptor models for the first time. Finally, the initial development of UNMIX was fulfilled by Henry and Hidy (1979), who discovered physically significant air quality patterns in the first multivariate analysis of an air quality data set that combined pollutant gas concentrations, particulate composition, and meteorological variables.

UNMIX is a multivariate receptor modeling package that inputs observations of particulate composition and seeks to find the number, composition, and contributions of the contributing sources or source types. This model also produces estimates of the uncertainties in the source compositions. UNMIX uses a generalization of the self-modeling curve resolution method developed by Henry et al (1997). Using only ambient data, UNMIX outputs the following information: (i) number of sources, (ii) composition of each source, (iii) source contributions to each sample, (iv) uncertainties in the source compositions, and (v) apportionment of the average total mass, if total mass is included in the model. The major advantages of the UNMIX are described as follows: (i) no assumptions about the number or compositions of sources are needed, (ii) no assumptions or knowledge of errors in the data are needed, and (iii) UNMIX automatically correct source compositions for effects of chemical reactions. A major difference between UNMIX and PMF is that UNMIX does not make explicit use of errors or uncertainties in the ambient concentrations. This is not to imply that the UNMIX approach regards data uncertainty as unimportant, but rather that the UNMIX model results implicitly incorporate error in the ambient data. Assume that \( N \) air quality samples are analyzed for \( n \) species, which come from \( m \) sources. If these species are conservative, then mass balance on each species requires that

\[
C_{i,j} = \sum_{k=1}^{m} a_{jk} S_{ik} + \text{errors}
\]

Equation 9

Where \( C_{ij} \) is the concentration of the \( j^{th} \) \((j=1,\ldots,n)\) species in the \( i^{th} \) sample \((i=1,\ldots,N)\), \( a_{jk} \) is the mass fraction of species \( j \) in source \( k \) \((k=1,\ldots,m)\), and \( S_{ik} \) is the total mass of material from source \( k \) in the \( i^{th} \) sample. In the parlance of receptor modeling, the \( a_{jk} \) are the source compositions, and the \( S_{ik} \) are the source contributions. The equation above includes errors, which may be the results of analytical uncertainty and variations in the sources’ composition. The existence of errors profoundly complicates solution of the mixture problem, which is an ill-posed problem in that there are an insufficient number of constraints to define a unique solution. Several attempts to define a unique solution had been made by adding the obvious constraints of non-negativity of the source contribution and narrowing down the range of possible solutions based on physical knowledge of the sources (Henry et al., 1994, 2003 and 2005). However, the question remains under what conditions can a unique solution be found using only the data without a priori knowledge. To answer this question, the
A graphical approach had been introduced for solving the mixture problem. The main idea is to reduce the dimension of the problem by projection generalizes to any number of species and sources. Fig. 4 illustrates the single source case in which all the data points lie, except for errors, on a ray coming from origin. The direction of the ray is determined by the composition of the source. If \([p_1, p_2, p_3]\) is any point on the line, and \([a_1, a_2, a_3]\) is the source composition then \([p_1, p_2, p_3] = k[a_1, a_2, a_3]\). Since the ratio of each element relative to all others in the source composition, the mixture problem can be solved for the single source case, except that the source composition is only determined up to a multiplicative constant. In the case of two sources, as demonstrated in Fig. 5, the data are distributed in a plane through the origin. The problem is to find the vectors (or points) that represent the source composition. There are two possible choices for the source vectors namely (i) the source composition vectors of the two sources must lie in the same plane as the data and (ii) the source vectors must also be non-negative (Henry et al., 2002). This further limits the data points to lie on the plane between the two rays defined by the two source compositions. If one source is missing from some of the data points then these data points will lie along a ray defined by the composition of the single, remaining source. These data points will be distributed so that an edge is apparent (see Fig. 5) and a line drawn along that edge will give the relative source composition, just as in the single source case.

Figure 4. Plot for the one source, three species case showing the data points lying along the ray defined by the source composition (Henry et al., 1997).

However, if there are three or more sources, then the points with one source missing have two or more sources present, and it is not so simple to determine the source compositions. As illustrated in Fig. 6, all the data points are composed of three sources of three species. In this case the points with one source missing are located on the planes defined by the rays through the remaining two sources. While this can be difficult to visualize those remaining two sources in a three-dimensional plot, a projection from the origin into a plane as demonstrated in Fig. 5 enables the location of the source vectors much easier to see. In most cases of environmental data, however, data points are composed of more than three sources and many more than three species. In this case the generalization to more than three dimensions requires the concepts of a hyperplane and simplex. A hyper-plane is the...
generalization of a plane. For instance, a plane in 3-space is two dimensional, so a hyper-plane in \( n \)-space has dimension \( n-1 \). Thus, the process of reducing dimensions of the data points in UNMIX is to find the edges in the data (i.e. finding hyper-planes that define a simplex). Finally, UNMIX uses these edges to find the source points in data set.

Figure 5. Plot for the two sources, three species case showing the data points lying in the plane defined by the two source composition rays. The solid circles are edge points, which have one source missing or low. The edges defined by these points give the relative source composition for the two sources (Henry et al., 1997).

Figure 6. Plot for the three sources, three species case showing the data points (open circles) and the projection of the data points from the origin to the plane Species I = 1 (solid circles). Among the projected points, the edge points are easy to identify (Henry et al., 1997).
3. DISCUSSION & CONCLUSION

Despite of considerably large number of studies focusing on tsunami impact onshore, little is known about their geomorphologic imprints offshore. In order to gain more insights on return periods of both earthquake and tsunami hazard, it is therefore crucial to study past tsunami events by carefully investigate offshore tsunami deposits. There remain substantial difficulties, however, in discriminating between deposits triggered by tsunamis and those caused by extreme events such as hurricane/Indian Ocean monsoon (IOM) and/or other sedimentary processes. Hence, it is important to emphasize that the term of “tsunami deposit” is that it defines deposits that have created by numerous distinctive geological processes that are not necessarily specific to marine deposits formed during the tsunami 'backwash' phase (Shanmugam, 2006; Shiki and Yamazaki, 2008). Tipmanee et al (2012) attempted to use PAHs as a chemical proxy to trace the transport of land-derived materials caused by the tsunami backwash to better understand how it may have affected the distribution of sedimentary deposition throughout the seabed of Khao Lak coastal areas. The article provides interesting application of diagnostic binary ratios of PAHs from coastal sediments and marine deposits in tsunami 2004 affected coastal area of Thailand. The application of PAHs as a chemical proxy to identify tsunami backwash patterns is interesting and very challenging, however, there are several concerns and questions that need clarification as well as some of the following points for a thorough reconsideration of the proposed concept.

• As the tsunami wave approaches the shoreline its wavelength become shorter and horizontal water velocity increases. It carries large amount of marine sediments to inundated land. After reaching its maximum run-up, the backwash phenomenon is occurred and responsible for channelized and erosions in specific places. The mixture of marine sediments, beach sediments, minor part of eroded terrestrial soils and eroded older sediments from backwash channels are transported back to the sea as high density flows, part is transferred as suspension load as well as simultaneously mobilization of marine sediments. Hence, it is most likely that offshore tsunami deposits contain both terrestrial signatures and re-deposited marine sediments. In normal conditions terrestrial component may be delivered to the sea bottom as well. However, this phenomenon will take longer time than the “tsunami backwash”, which the debris flow is very fast and sediments are buried rapidly then the "terrestrial set of PAH signatures" might be hypothetically preserved.

• It is also important to emphasize that not only “tsunami wave” but also “monsoon wave” can transfer terrigenous components from land to deposit in sea bottom. Therefore, it is crucial to consider the difference in nature of "tsunami wave" and "monsoon wave". While monsoon prolongs for several hours with relatively lower magnitude of power, the tsunami wave occurred in a greater magnitude of power but shorter in backwash time (i.e. several minutes). The tsunami deposit tends to contain "suspended particle", whereas the monsoon-derived sediments typically are produced through "bed-load transport". In these particular cases, two types of hypothesis can be considered;
Hypothesis I (Difference in transportation pattern)
It is well known that different types of PAHs exist in different sizes of particles (Kukkonen and Landrum, 1996; Wang et al., 2001). Since tsunami waves are capable of transport all particle sizes of terrestrial sediments via suspended load transport, it is most likely that tsunami deposit will have a different "distribution pattern of PAHs" from those of monsoon derived sediments.

Hypothesis II (Difference in erosion time)
Tsunami backwash occurred in relatively short time scale of minutes whereas the inundation of monsoon prolonged for several hours. Differences in "time dimension" cause the fractionization of PAHs due to its differences in term of "water solubility". For instance, Phe tends to have a higher water solubility than B[a]P (Lu et al., 2008). The longer the erosion, the higher amount of Phe will dissolve into backwash water in comparison with B[a]P. As a result, the monsoon derived deposit will contain Phe more than B[a]P. However, this fractionization effect will not happen in the case of tsunami deposit. Firstly, the tsunami involved only three large waves. Once the waves had passed and receded the event was over. Therefore, both Phe and B[a]P will be washed back by tsunami wave simultaneously without providing any time for the fractionization effect. For these reasons, the fingerprint of terrestrial PAHs may hypothetically be well preserved and possibly be a better proxy than conventional terrigenous biomarker "lignin" (Tareq et al., 2004), which is highly sensitive to microdegradation procedure due to its weak chemical structure in comparison with PAHs.

• Fingerprinting reflects the chemical characteristics of various source emissions of the sediment samples collected at any receptor. Because a simple ratio of two or three PAHs is sensitive to both photolysis and chemical/biological degradation and may be insufficient to identify PAH emission sources at fixed monitoring sites, the best strategy to investigate the impact of backwash tsunami is the use of the entire PAH profiles. Hence, the establishment of PAHs profile of individual “end member” is therefore essentially crucial.

• It is well known that Ret can be used as indicators of "wood combustion" (Gonçalves et al., 2011). During the bonfire night episode, the highest contributions of individual PAH came from Fl, Ac, Ret, B[b+j+k]F, Ind, B[g,h,i]P, while alkane concentrations was following the decrease order of C_{29} > C_{24} > C_{27} > C_{22}. The chain-saw-distribution of alkanes was evident at the range of C_{23} to C_{31} during the bonfire night episode, suggesting a strong signal of biomass burnings (Pongpiachan, 2013a). The contribution of diesel engine to atmospheric PAHs concentrations, especially those of Fl and Phe, has been widely investigated for many years (Williams et al., 1986). It is well known that diesel fuel is relatively rich in PAHs and most of them are alkylated PAHs compared to that of the parent PAHs. Several factors like diesel-engine type and engine operating conditions reflect the ratio of MePhe/Phe in urban air. For example, the relatively high MePhe/Phe ratio was found when the combustion and exhaust temperatures were low (Barbella et al., 1989). Takada et al (1991) and Westerholm et al (1992) reported the values of MePhe/Phe ratios exhausted from diesel engine vehicle, bus and petrol engine vehicle as 5.5, 4.8 and 0.7 respectively. It is worth mentioning that the
MePhe/Phe ratio of 5.5 was the average of five types of diesel engine ranging from 1500 cc to 14000 cc running without engine load and at a constant speed of 3000 rpm. In order to enhance the reliability of using PAHs as proxy of tsunami backwash deposits, one should consider the analysis of Ret, MePhe and Phe as well as the employment of chain-saw-distribution of alkanes and CPI index. In addition, it is also important to use cholestanes and hopanes as alternative biomarkers to distinguish “typical marine sediments” from “tsunami backwash deposits”.

The representative of the “tsunami backwash” group as discussed by Tipmanee et al (2012) is not as far as approximately 25 km from the shoreline. Special signal found in this group could just be a particular dominant source, not necessary to be tsunami backwash signal. The results generated from binary ratios of PAHs, HCA coupled with PCA results obtained from Tipmanee et al (2012) were only surface sediments and there is no direct and strong evidence that the source of PAHs resulted from the tsunami in 2004. It could increase the strength if there are dated core sediment samples and showed the temporal distribution in this area. Furthermore, there are uncertainties in the estimation of source contribution by using PCA and UNMIX. Further source apportionment techniques such as a positive matrix factorisation (PMF) and a chemical mass balance (CMB) model should be conducted to increase the reliability of source contributions.

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Vol. 32, No. 4, page 266 (2013)


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Vol. 32, No. 4, page 269 (2013)


Vol. 32, No. 4, page 270 (2013)


Vol. 32, No. 4, page 271 (2013)


*Vol. 32, No. 4, page 272 (2013)*
APPENDIX. TABLES

Table 1. Physiochemical properties of PAHs

<table>
<thead>
<tr>
<th>Congeners</th>
<th>MW (g/mol)</th>
<th>MP (°C)</th>
<th>BP (°C)</th>
<th>$P_S$</th>
<th>$P_L$</th>
<th>Log $K_{ow}$</th>
<th>$H$</th>
<th>Log $K_{OA}$</th>
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<td>3.92</td>
<td>12.17</td>
<td>6.23</td>
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<td>92</td>
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<td>4.14</td>
<td>4.00</td>
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<td>6.47</td>
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<tr>
<td>Fl</td>
<td>166.2</td>
<td>116</td>
<td>295</td>
<td>0.09</td>
<td>0.72; 0.79</td>
<td>4.18</td>
<td>7.87</td>
<td>6.68</td>
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<td>Phe</td>
<td>178.2</td>
<td>101</td>
<td>339</td>
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<td>0.11; 0.06</td>
<td>4.57</td>
<td>3.24</td>
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<tr>
<td>1-MePh</td>
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<td>359</td>
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<td>An</td>
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<td>5.22</td>
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<td>187</td>
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<td>402</td>
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<td>255</td>
<td>448</td>
<td>5.70E-07</td>
<td>1.07E-04</td>
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<td>2.30E-06</td>
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<td>p-terp</td>
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<td>6.03</td>
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<td>B[α]A</td>
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<td>9.54</td>
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<td>B[α]P</td>
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<td>175</td>
<td>495</td>
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<td>10.77</td>
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<td>495</td>
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<td>Per</td>
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<tr>
<td>B[γ]F</td>
<td>252.3</td>
<td>166</td>
<td>480</td>
<td></td>
<td></td>
<td>5.80</td>
<td></td>
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<tr>
<td>B[β]F</td>
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<td>217</td>
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<td>5.20E-08</td>
<td>4.12E-06</td>
<td>6.00</td>
<td>0.58</td>
<td>11.19</td>
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<td>B[γ,h]F</td>
<td>268.4</td>
<td>277</td>
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<td>11.19</td>
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<td>D[α,h]A</td>
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<tr>
<td>Cor</td>
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<td>&gt;350</td>
<td>525</td>
<td>2.00E-10</td>
<td></td>
<td>6.75</td>
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</tbody>
</table>

Source: http://www.es.lancs.ac.uk/ecerg/kcjgroup/5.html

MP (°C) Melting Point
BP (°C) Boiling Point
$K_{ow}$ Octanol-water partition coeffic
$H$ Henry’s Law Constant
$P_S$ Vapour pressure of solid substance
$P_L$ Vapour pressure of subcooled liquid

Table 2. Chemical structures of PAHs

<table>
<thead>
<tr>
<th>Congener</th>
<th>Abbreviation</th>
<th>M.W. [g]</th>
<th>Chemical Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acenaphthylene</td>
<td>Ac</td>
<td>152</td>
<td><img src="image" alt="Chemical Structure" /></td>
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<tr>
<td>Acenaphthene</td>
<td>Ace</td>
<td>154</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Fluorene</td>
<td>Fl</td>
<td>166</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>Phe</td>
<td>178</td>
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<tr>
<td>Anthracene</td>
<td>An</td>
<td>178</td>
<td><img src="image" alt="Chemical Structure" /></td>
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<td>3-Methyl Phenanthrene</td>
<td>3-MePhe</td>
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<td><img src="image" alt="Chemical Structure" /></td>
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<tr>
<td>9-Methyl Phenanthrene</td>
<td>9-MePhe</td>
<td>192</td>
<td><img src="image" alt="Chemical Structure" /></td>
</tr>
<tr>
<td>1-Methyl Phenanthrene</td>
<td>1-MePhe</td>
<td>192</td>
<td><img src="image" alt="Chemical Structure" /></td>
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<td>Compound</td>
<td>Abbreviation</td>
<td>Page</td>
<td>Structure</td>
</tr>
<tr>
<td>----------------------------------</td>
<td>--------------</td>
<td>------</td>
<td>-----------</td>
</tr>
<tr>
<td>2-Methyl Phenanthrene</td>
<td>2-MePhe</td>
<td>192</td>
<td><img src="image_url" alt="Structure" /></td>
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<tr>
<td>1-methyl-7-isopropyl phenanthrene (Retene)</td>
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<td>234</td>
<td><img src="image_url" alt="Structure" /></td>
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<td>Fluoranthene</td>
<td>Fluo</td>
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<td>Pyrene</td>
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<td>Benz[a]anthracene</td>
<td>B[a]A</td>
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<tr>
<td>Chrysene</td>
<td>Chry</td>
<td>228</td>
<td><img src="image_url" alt="Structure" /></td>
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<tr>
<td>Triphenylene</td>
<td>Tri</td>
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</table>

*Vol. 32, No. 4, page 274 (2013)*
Table 3. Chemical structures of alkanes.

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<th>Abbreviation</th>
<th>M.W. [g]</th>
<th>Chemical Structure</th>
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<tbody>
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<td>Tetradecane</td>
<td>C\textsubscript{14}</td>
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<tr>
<td>Pentadecane</td>
<td>C\textsubscript{15}</td>
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<tr>
<td>Hexadecane</td>
<td>C\textsubscript{16}</td>
<td>226</td>
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<td>Heptadecane</td>
<td>C\textsubscript{17}</td>
<td>268</td>
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<tr>
<td>Octadecane</td>
<td>C\textsubscript{18}</td>
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<td>Nonadecane</td>
<td>C\textsubscript{19}</td>
<td>268</td>
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<td>Eicosane</td>
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<td>Henicosane</td>
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<td>Docosane</td>
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<td>Tricosane</td>
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<td>Tetracosane</td>
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<td>Pentacosane</td>
<td>C\textsubscript{25}</td>
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<td>Hexacosane</td>
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<td>Heptacosane</td>
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<td>Octacosane</td>
<td>C\textsubscript{28}</td>
<td>394</td>
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<tr>
<td>Nonacosane</td>
<td>C\textsubscript{29}</td>
<td>408</td>
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<td>Triacontane</td>
<td>C\textsubscript{30}</td>
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<tr>
<td>Hentriacontane</td>
<td>C\textsubscript{31}</td>
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<td>Dotriacontane</td>
<td>C\textsubscript{32}</td>
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<td>Pristane</td>
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<tr>
<td>Phytane</td>
<td>PC\textsubscript{20}</td>
<td>282</td>
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*Vol. 32, No. 4, page 275 (2013)*
Table 4. Chemical structures of hopanes.

<table>
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<th>Abbreviation</th>
<th>M.W. [g]</th>
<th>Chemical Structure</th>
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</thead>
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<tr>
<td>17α(H)-22,29,30-Trisnorhopane</td>
<td>22,29,30-trisnorhopane (th)</td>
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<tr>
<td>17α(H),21β(H)-30-Norhopane</td>
<td>17,21,ab-30-norhopane (nh)</td>
<td>398</td>
<td><img src="image2" alt="Chemical Structure" /></td>
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<tr>
<td>17α(H),21β(H)-Hopane</td>
<td>17,21,ab-hopane (hop)</td>
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<tr>
<td>17α(H),21β(H)-22R-Homohopane</td>
<td>22R-17,21ab-30-homohopane (homo)</td>
<td>426</td>
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*Vol. 32, No. 4, page 276 (2013)*
Table 5. Chemical structures of cholestanes.

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<th>Abbreviation</th>
<th>M.W. [g]</th>
<th>Chemical Structure</th>
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</thead>
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<td>αββ 20R-Cholestane</td>
<td>20R-abb-cholestane</td>
<td>372</td>
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<tr>
<td></td>
<td>(abbC)</td>
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<tr>
<td>aaa 20R-Cholestane</td>
<td>20R-aaa-cholestane</td>
<td>372</td>
<td><img src="image2" alt="Chemical Structure" /></td>
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<td>(aaaC)</td>
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<td>αββ 20R 24S-Methylcholestane</td>
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<td>(MC)</td>
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<td>αββ 20R 24R-Ethylcholestane</td>
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<td>(EC)</td>
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Table 6. ΣPAH concentrations in different regions

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<th>Reference</th>
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<tr>
<td>UK (London, Bounds Green)</td>
<td>TSP</td>
<td>4.27 (0.23-27.87)</td>
<td>Kendall et al., 2001</td>
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<tr>
<td>UK (London, St Paul)</td>
<td>TSP</td>
<td>7.24 (1.04-32.04)</td>
<td>Kendall et al., 2001</td>
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<tr>
<td>Indonesia (Pudu)</td>
<td>PM$_{10}$</td>
<td>26.5 (7-46)</td>
<td>Fang et al., 1999</td>
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<tr>
<td>Greece (Rural Area)</td>
<td>TSP</td>
<td>1.1 (0.2-2.0)</td>
<td>Gogou et al., 1996</td>
</tr>
<tr>
<td>Greece (Heraklion)</td>
<td>TSP</td>
<td>17.4 (3-44.9)</td>
<td>Gogou et al., 2000</td>
</tr>
<tr>
<td>Portugal (Forest)</td>
<td>TSP</td>
<td>0.5 (0.1-0.9)</td>
<td>Kavouras et al., 1999</td>
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<tr>
<td>China (Hong Kong)</td>
<td>PM$_{2.5}$</td>
<td>9.6 (0.7-12.2)</td>
<td>Zheng et al., 2000</td>
</tr>
<tr>
<td>China (Guangzhou)</td>
<td>TSP</td>
<td>73.7 (32.5-153.7)</td>
<td>Duan et al., 2005</td>
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<tr>
<td>Canada (Urban)</td>
<td>TSP</td>
<td>2.35 (1.86-2.83)</td>
<td>Sanderson et al., 2004</td>
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<tr>
<td>Eastern Mediterranean</td>
<td>TSP</td>
<td>0.7 (0.3-1.6)</td>
<td>Tsapakis and Stephanou, 2005</td>
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<tr>
<td>Canada (Toronto)</td>
<td>P+V</td>
<td>36.5 (11.5-61.4)</td>
<td>Motelay et al., 2005</td>
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<td>Traffic, Hong Kong</td>
<td>PM$_{2.5}$</td>
<td>33.96</td>
<td>Gou et al., 2003</td>
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<tr>
<td>Industrial, Hong Kong</td>
<td>PM$_{2.5}$</td>
<td>16.72</td>
<td>Gou et al., 2003</td>
</tr>
<tr>
<td>Industrial (indoor), Shizuoka,</td>
<td>PM$_{2.5}$</td>
<td>1.6–23.7</td>
<td>Ohura et al., 2004</td>
</tr>
<tr>
<td>Japan</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Industrial (outdoor), Shizuoka,</td>
<td>PM$_{2.5}$</td>
<td>1.1–29.5</td>
<td>Ohura et al., 2004</td>
</tr>
<tr>
<td>Taiwan</td>
<td>PM$_{2.5}$</td>
<td>74.47</td>
<td>Fang et al., 2006</td>
</tr>
<tr>
<td>Pastureland (open) Taichung,</td>
<td>PM$_{2.5}$</td>
<td>284.91</td>
<td>Fang et al., 2006</td>
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<tr>
<td>Taiwan</td>
<td>PM$_{2.5}$</td>
<td>57.89</td>
<td>Li et al., 2005</td>
</tr>
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<td>Temple (semi-open)</td>
<td>PM$_{2.5}$</td>
<td>27.06</td>
<td>Li et al., 2005</td>
</tr>
<tr>
<td>Traffic Guangzhou, China</td>
<td>PM$_{2.5}$</td>
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<tr>
<td>Residential Guangzhou, China</td>
<td>PM$_{2.5}$</td>
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</tbody>
</table>

*Vol. 32, No. 4, page 278 (2013)*
### Table 7. Biological and/or environmental interpretation of \( n \)-alkanes

<table>
<thead>
<tr>
<th>Biomarker</th>
<th>Biological and/or environmental interpretation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outstanding concentrations of ( n )-15, ( n )-17 and ( n )-19 in early Paleozoic rocks</td>
<td>Marine phytoplankton of uncertain affinity, probably an alga, identified in Cambrian Devonian sediments but most prominent in Ordovician. Estonian kukersite is a typical source</td>
<td>Blokker <em>et al.</em>, 2001</td>
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<tr>
<td>( n )-C(_{27} ) with OEP(^1)</td>
<td>Waxes derived from higher plants, terrestrial input, post-Silurian age</td>
<td>Hedberg, 1968</td>
</tr>
<tr>
<td>( n )-C(_{40} )</td>
<td>Predominantly degradation products of aliphatic macromolecules such as algaenan ( marine, lacustrine), cutan and suberan (terrestrial, plant derived)</td>
<td>Allard <em>et al.</em>, 2002 Killops <em>et al.</em>, 2000</td>
</tr>
</tbody>
</table>

### Table 8. Biological and/or environmental interpretation of hopanes

<table>
<thead>
<tr>
<th>Biomarker</th>
<th>Biological and/or environmental interpretation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{30})-hopanes</td>
<td>Diverse bacterial lineages, few eukaryotic species ( e.g. some cryptogams, ferns, mosses, lichens, filamentous fungi, protests)</td>
<td>Rohmer <em>et al.</em>, 1984</td>
</tr>
<tr>
<td>Extended C(<em>{31}) to C(</em>{35}) hopanes ( homohopanes)</td>
<td>Diagnostic for bacterial, biosynthesis appears to be restricted to lineages that are not strictly anaerobic</td>
<td>Ourisson and Albrecht, 1992, Rohmer <em>et al.</em>, 1984</td>
</tr>
<tr>
<td>Extended C(<em>{32}) to C(</em>{36}) 3b-methylhopanes</td>
<td>Diagnostic for some microaerophillic proteobacteria ( certain methylotrophs, methanotrophs, acetic acid bacteria)</td>
<td>Zundel and Rohmer., 1985a, 1985b, 1985c.</td>
</tr>
<tr>
<td>28,30-dinorhopane, 25,28,30-trinorhopane</td>
<td>Often prominent in sediments from euxinic environment</td>
<td>Grantham <em>et al.</em>, 1980</td>
</tr>
</tbody>
</table>

*Vol. 32, No. 4, page 279 (2013)*
Table 9. Biological and/or environmental interpretation of cholestanes

<table>
<thead>
<tr>
<th>Biomarker</th>
<th>Biological and/or environmental interpretation</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>24-norcholestane (C_{26})</td>
<td>Possible diatom origin, high concentrations relative to 27-norcholestane indicate Cretaceous or younger crude oil</td>
<td>Holba et al., 1998a and 1998b</td>
</tr>
<tr>
<td>Cholestane</td>
<td>In aquatic sources probably almost exclusively derived from diverse eukaryotes</td>
<td>Volkman, 2003</td>
</tr>
<tr>
<td>24-n-propylcholestane</td>
<td>Pelagophyte algae, a biomarker for marine conditions with few exceptions</td>
<td>Moldowan et al., 1990</td>
</tr>
<tr>
<td>4-Methylcholestane and 4,4-dimethylcholestane</td>
<td>Diverse eukaryotic sources, high concentrations likely indicate a dinoflagellates origin</td>
<td>Summons et al., 1994</td>
</tr>
</tbody>
</table>