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Chemometric techniques in oil classification from oil spill fingerprinting

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ABSTRACT

Extended use of GC–FID and GC–MS in oil spill fingerprinting and matching is significantly important for oil classification from the oil spill sources collected from various areas of Peninsular Malaysia and Sabah (East Malaysia). Oil spill fingerprinting from GC–FID and GC–MS coupled with chemometric techniques (discriminant analysis and principal component analysis) is used as a diagnostic tool to classify the types of oil polluting the water. Clustering and discrimination of oil spill compounds in the water from the actual site of oil spill events are divided into four groups viz. diesel, Heavy Fuel Oil (HFO), Mixture Oil containing Light Fuel Oil (MOLFO) and Waste Oil (WO) according to the similarity of their intrinsic chemical properties. Principal component analysis (PCA) demonstrates that diesel, HFO, MOLFO and WO are types of oil or oil products from complex oil mixtures with a total variance of 85.34% and are identified with various anthropogenic activities related to either intentional releasing of oil or accidental discharge of oil into the environment. Our results show that the use of chemometric techniques is significant in providing independent validation for classifying the types of spilled oil in the investigation of oil spill pollution in Malaysia. This, in consequence would result in cost and time saving in identification of the oil spill sources.

1. Introduction

Oil spill pollution in the marine environment can aggravate human health and disrupt sustainability of marine resources. The increase in urbanization has led to an increase in oil and gas exploration that causes oil and gas elated substances to be released from oil wells into the ocean water (Elijah et al., 2014). Near Malaysian coastlines, oil pollution usually results from incidents such as collision of crude oil vessels, in the course of transporting the crude oil from oil-rich nations of Africa and Middle East to Asian countries like China (Zakaria and Hedeishige, 2007). Oil spill is also generated from refinery oil plants or crude oil platforms, underwater pipelines as well as large-scale industrial-based activities. Oil spill released into the marine ecosystems can be intentional or due to accidents (Mishra and Kumar, 2015). Crude oil spillage in the marine ecological environment can endanger marine ecosystems if the substances persist in the waterways. The spillages prevent sunlight from reaching seabed marine ecological systems and may potentially be a threat to the natural environmental marine communities and aggravate human health (Zakaria and Hideishige, 2007). According to the Maritime Agency of Malaysia, there were 154 cases of petroleum spillage incidents reported from 2007 until 2015 within the Malaysia coastlines (i.e. Straits of Malacca, South China Sea and Johor Straits). Tar balls collected on the Peninsular Malaysia shorelines are known to originate from the Middle East countries based on the biomarker signatures (Zakaria et al., 2000, 2001a, 2001b).

Petroleum compound consists of a complex mixture which consists of aliphatic, polycyclic aromatic hydrocarbon and non-hydrocarbon (Bayona et al., 2015). The unambiguous identification of source from spilled oil in terms of properties and characteristics has become essentially important to assess the fate and the environmental damage caused by the spilled oil. The oil spill fingerprinting prominently used recently allows extensive diagnostic capabilities to the complex mixtures of carbon compounds in oil samples for oil spill identification and its environmental fate (Bayona et al., 2015). Moreover, oil spill fingerprinting analysis methods require very low contaminant concentrations (Guitart et al., 2012). Chemical fingerprinting (Stout and Wang, 2007) plays a main role in the investigation of pollution sources in marine environment towards to a known-source of anthropogenic activities which affect various humanitarian aspects viz. insurance, statutory compensation (company's commitment), fatality, material loss and

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other special loss (Chen et al., 2015). Assessment for oil spill restoration is time consuming and a complete system for rehabilitation (i.e. compensation, insurance and funding) of the marine water quality has been implemented in the U.S, but the system is yet to be established in many developing countries like China (Lai et al., 2015).

Deposition of various oil spills such as oil slicks and tar ball is among the major concerns in our marine ecosystems. A fundamental knowledge of how the concentration of weathered oil spill component evolves over time along beaches and coastline areas (Mulabagal et al., 2013) is of utmost importance for a better evaluation in assessing long-term effects of residues in the marine ecological systems. Oil type classification obtained via intelligent laboratory analysis allows the study of physico-chemical characteristics and background sources of the spilled oil. Gas chromatography/flame ionization detector (GC–FID) and gas chromatography mass spectrometry (GC–MS) are the advanced analytical instruments used to analyze weathered oil spill samples. This paper briefly discusses oil spill fingerprinting and data interpretation through various techniques of chemometrics in ascertaining the source of spilled oil origin. According to Satheeshkumar and Khan (2011), chemometric techniques are the most reliable techniques for a meaningful data reduction and interpretation. Likewise, the principal component analysis (PCA) and cluster analysis (CA) are the application of unbiased and precise methods, while multilinear regression offers better understanding and in-depth interpretation of oil spill fingerprinting in waters. Various applications of chemometric analyses allow reduction of the complexity of dataset amounts for better data interpretation (Kannel et al., 2007). According to Dominick et al. (2012), CA is the technique of unsupervised pattern recognition functions to group variables and observations. It provides the establishment of oil hydrocarbon signatures and evaluates oil spill source identification of pollutant variables. Results from the clustering enable data interpretation and pattern recognition of the spilled oil. To support CA, the application of DA is important as a pattern recognition methodology (Juahir et al., 2011a, 2011b; Ismail et al., 2016). PCA application provides detection correlation between oil spill variables for oil type classification and source identification in water. According to Zhou et al. (2007), large amounts of variables can be reduced by PCA into smaller set of components that can be easily interpreted. This study aims to establish the fingerprints via identification, distinguish chemical fingerprints and analyze various types of oil samples from sources recovered from Peninsular Malaysia and Sabah (East Malaysia) waters and the application of chemometric techniques for oil type classification.

2. Material and methods

2.1. Sample collection

Oil and oil-water samples were collected at thirty-two spilled oils at location-selected water areas of Peninsular Malaysia and Sabah (East Malaysia) (Fig. 1) based on in-situ observations by the Department of Environment, Malaysia (DOE) which were made between 2013 and 2014. Description of the samples and the sampling locations are provided in Table 1. Observational sources were not conducted in this study; only oil type identification was carried out.

Chemical fingerprinting of up to 32 samples of spilled oil at various locations were carried out in this study. Oil samples were obtained from the Department of Environment (DOE), Malaysia covering the period of 2013 until 2014. Upon arrival, the samples were registered and stored at 4 °C prior to analysis. In this study, oil spill samples were randomly collected from 32 distinctive locations (Table 1) and the samples range from C_9 to 29bbs. All the organic solvents used were of analytical grade A.

2.2. Analytical laboratory method

Two types of solvents were used in this oil spill analysis viz. dichloromethane (DCM) and hexane. For this study, specific internal reference standards commonly used in oil fingerprinting analysis were chosen, namely, terphenyl-d_{14} for PAHs, C_{30}17 β (H) for biomarker and 5α-androstane for 21β(H)-hopane and *n*-alkanes. The surrogates for this analysis consist of five mixtures of PAH compounds, namely, phenanthrene-d_{10}, perylene-d_{12}, acenapthene-d_{10}, benz(*a*)anthracene-d_{12} and o-terphenyl for *n*-alkanes. All standards and surrogates for PAHs and *n*-alkanes were purchased from AccuStandard Inc., but the internal standard and biomarker standard were purchased from Chiron.

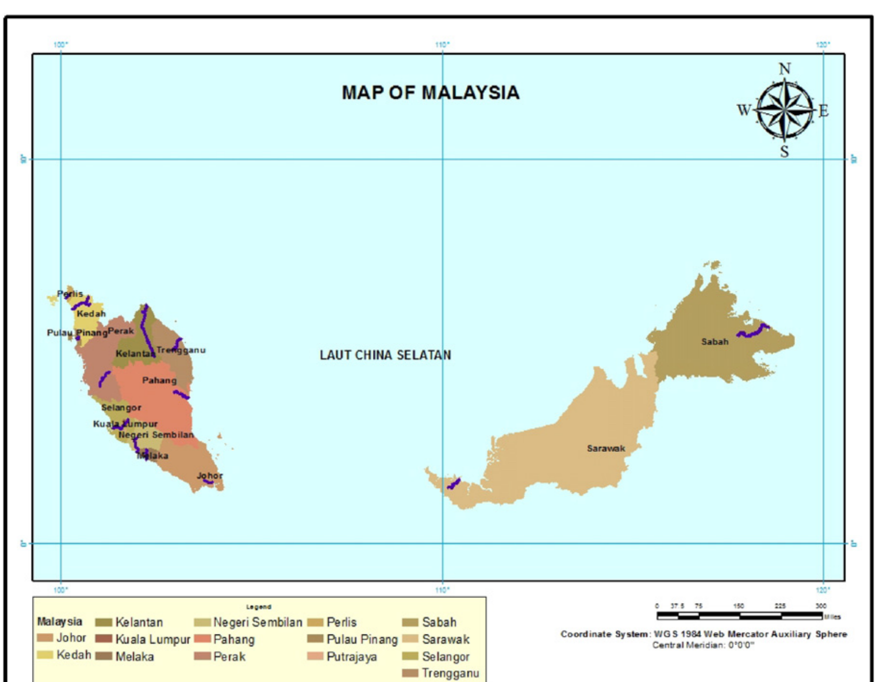

Fig. 1. Map showing the various sampling locations of oil spills in Peninsular Malaysia and Sabah (East Malaysia).