DISTRIBUTION AND SOURCES OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN CORE SEDIMENT SAMPLES COLLECTED IN SOUTH CHINA SEA

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1.0 Introduction

Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes. Because of this, they have been observed to persist in the environment, to be capable of long-range transport, bioaccumulate in human and animal tissue, biomagnified in food chains, and to have potential significant impacts on human health and the environment.

Some of the chemical characteristics of POPs include low water solubility, high lipid solubility, semi-volatility, and high molecular masses. POPs released to the environment have been shown to travel vast distances from their original source. Due to their chemical properties, many POPs are semi-volatile and insoluble. These compounds are therefore unable to transport directly through the environment. The indirect routes include attachment to particulate matter, and through the food chain. The chemicals' semi-volatility allows them to travel long distances through the atmosphere before being deposited. Thus POPs can be found all over the world, including in areas where they have never been used and remote regions such as the middle of ocean. One of the most important classes of persistent organic pollutant is polycyclic aromatic hydrocarbons (PAHs) (Mahua et al.,2009; Blumer, 1976).

Polycyclic aromatic hydrocarbons (PAHs) are chemical compounds that consist of fused aromatic rings and do not contain heteroatom or carry substituent. PAHs are derives from two types of anthropogenic sources which are pyrogenic and petrogenic. The examples for pyrogenic sources are combustion of fossil fuel, biomass and so on. The combustion of fossils fuels (coal and petroleum) and biomass also produces PAHs (i.e., pyrogenic PAHs) which are released into the environment in the form of exhaust and solid residues (Zakaria et al., 2002). The petrogenic sources like crude oil, petroleum are introduced to aquatic environment through accidental oil spills, discharge from routine tanker operations, municipal and urban run off, and so on. Some PAHs are released to the environment through natural process. (Y. Liu et al., 2008)

Petrogenic PAHs are normally abundant in lower molecular weight compounds. Lower molecular weight PAHs can easily undergo weathering as compared to higher molecular weight PAHs. Weathering can alter the compositions of PAHs. Thus, PAHs composition could be used as one of the indices of weathering. Polycyclic aromatic hydrocarbons are lipophilic, meaning they mix more easily with oil than water. The larger compounds are less water-soluble and less volatile (prone to evaporate). Because of these properties, PAHs in the environment are found primarily in soil, sediment and oily substances, as opposed to in water or air. However, they are also a component of concern in particulate matter suspended in air.

Low molecular weights of PAHs are consists of two or three rings while PAHs with four to seven rings are high molecular weight. Low molecular weight can cause acute toxicity compared to height molecular weight which cause chronic toxic.

PAHs constitute a large class of compounds, a group of approximately 10000 compounds. Several of the PAHs compounds are concern as mutagenic and carcinogenic. Due to persistency and toxicity of PAHs, United State Environmental Protection Agency (US EPA) has list 16 compounds that identified as priority pollutant and seven of them are considered as animal carcinogenic by International Agency for Research on Cancer (IARC). The most dangerous of PAHs is Benzo[a]pyrene which is strongly carcinogenic.

The South China Sea is one largest sea bodies after Arctic Ocean, Atlantic Ocean, Indian Ocean and Southern Ocean. It is a part of the Pacific Ocean encompassing an area from Singapore to the Strait of Taiwan of around 3,500,000 km^2.

The South China Sea is rich in natural resources such as oil and natural gases. The sea has oil and reserves estimated at about 7.5 billion barrels, and oil production and almost 1.3 million barrels per day. It also has a strategic location and everyday many ships go through this sea. It is a very busy pathway for many ships especially tanker for carrying oil from Middle East to North East Asia. Meanwhile it is enriched with natural resources like oil.

There are many activities at this ocean like industrial activities, petroleum activities, fishing activities and so on at South China Sea. Sometimes it may occurred accidental spill, discharge from routine tanker and oil activities. Sometimes it may cause from human activities from coastlines that facing South China Sea because the coastline that facing South China Sea also busy with residential activities, industrial activities, port, transportation and tourism activities. Day after day the South China Sea became polluted by many contaminants especially oil. These scenarios cause oil pollution and this ocean may be contaminated and marine aquatic may be exposed to PAHs. Nowadays, oil pollution is global issues. Oil pollution was caused by either from sea based or land based. Human who consume the marine aquatic are danger and tendency to cancer. When PAHs are entered to human body, it will mimic the hormone and enzyme cause nerve system disorders.

2.0 Research Objectives

i. To determine the distribution of PAHs in selected core sediment of South China Sea
ii. To assess the status level of PAHs concentration in South China Sea
iii. To investigate the sources of PAHs in selected core sediment of South China Sea

3.0 Methodology

1) Sampling collection

All the equipments that used in this experiment are cleaned and wipe with methanol and keep in zip lock bag plastic. 30 core sediments samples are taken from surface at selected area by using Corer box. All samples are transferred to cooler box before we keep at -18˚C for further analysis.

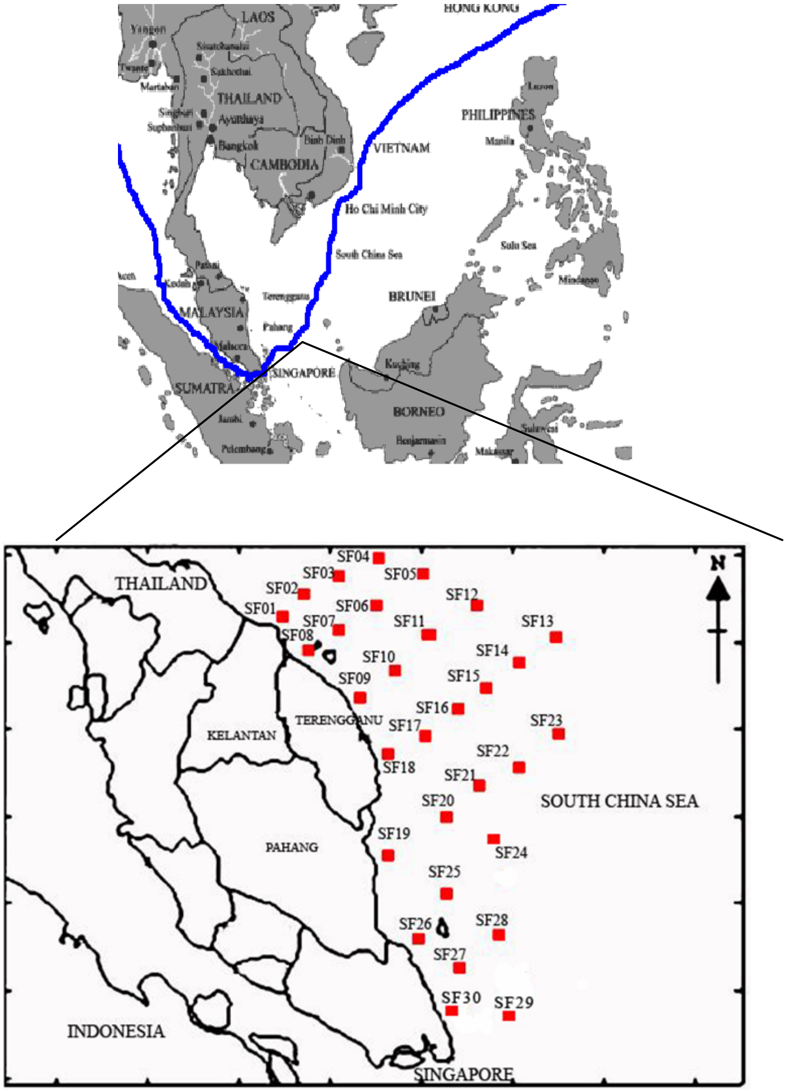

Figure 1: Map of sampling sites in South China Sea

2) Chemical Analysis

The sediment sample was dried by using sodium sulphate anhydrous until all water is removed from the sample. Transferred all dried sediment sample into cellulose thimble and extract with soxhlet extraction using 300 mL DCM for over 8 hours. Activated copper is added for overnight before filter through a glass funnel plugged with glass wool. The volume is reduced till 5ml. After that, add 50µL standard PAHs to the sample before it is put on the top of column silica chromatography (5% water deactivated silica gel). Rinsed that flask by using 20mL DCM/hexane (1:3/v,v). Eluent will rot evaporated until the volume is reduced to 5mL.

Before we transferred the mixture to column silica chromatography (activated silica gel column), dissolved it in4 mL of n-hexane. For first eluent is for hopane fraction. For second fraction is for linear alkyl benzene, we add 4mL. To get the fraction PAHs, add 16mL mixture of DCM/hexane with ratio volume over volume 1:3 to column silica chromatography. Evaporate and transferred the eluent to 1.5mL glass ampoule and dry under nitrogen gas and redissolved in 50µL-50µL of iso-octane. The sample will be injected into GCMS using SIM mode.

4.0 Result and Discussion

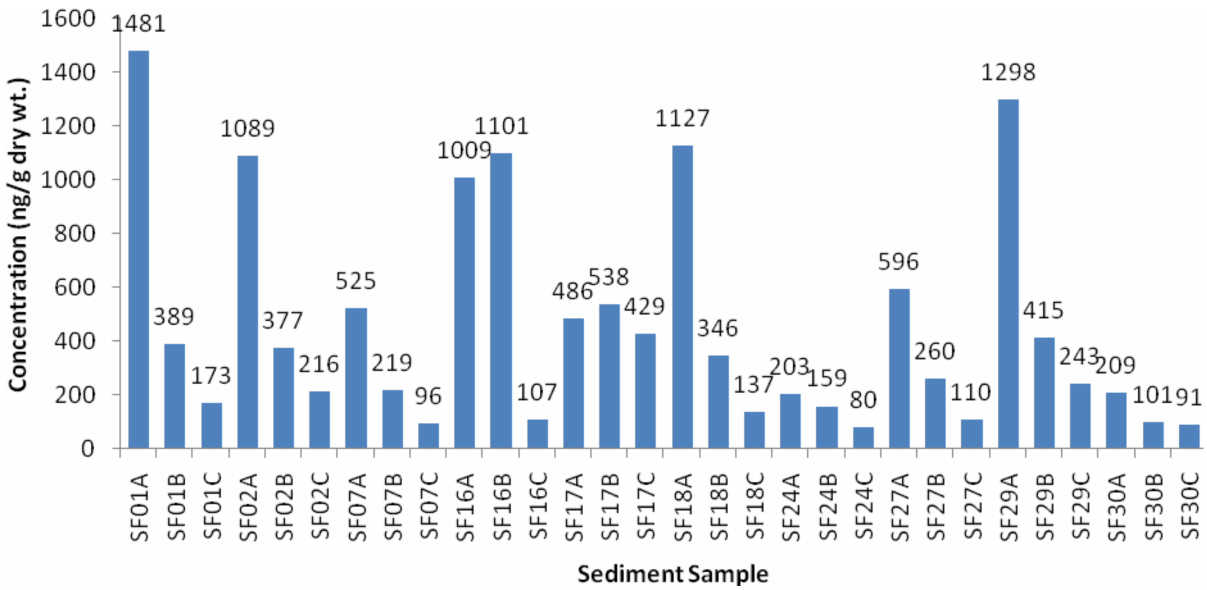

Figure 2: Total PAHs (ng/g) of sediment samples based on dry weight basis.

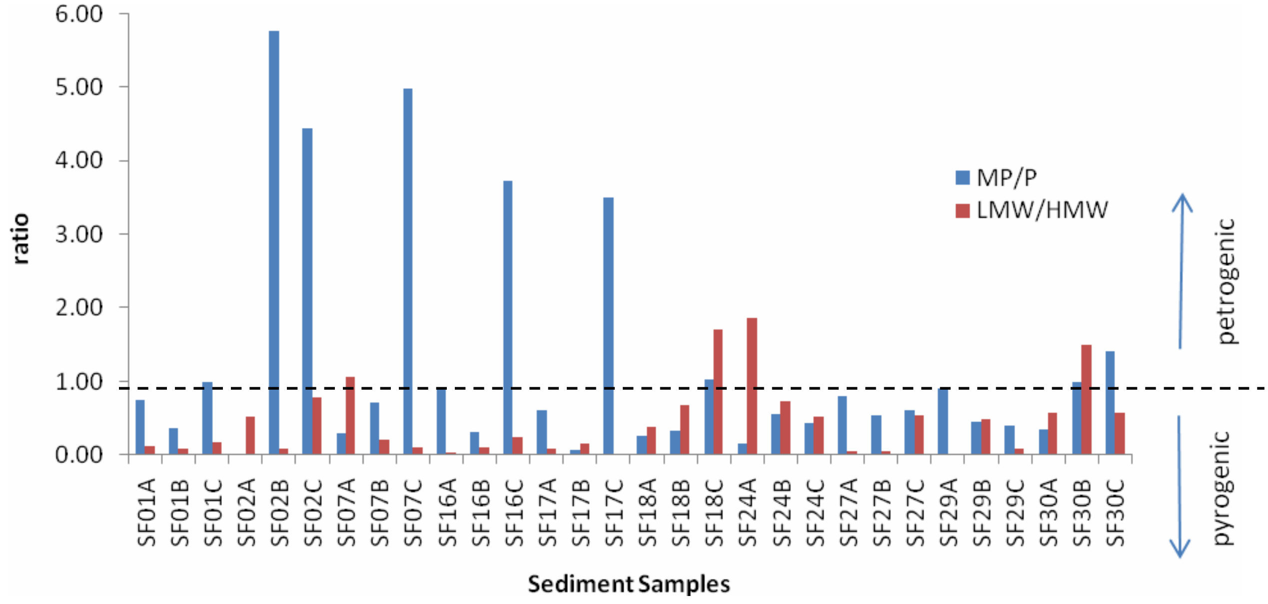

Figure 3: MP/P and L/H ratio for the sediment samples. The drifted line is the boundary for petrogenic and pyrogenic sources(i.e. ratio >1.0, the source of PAHs is petrogenic, ratio < 1.0 source of PAHs is pyrogenic).

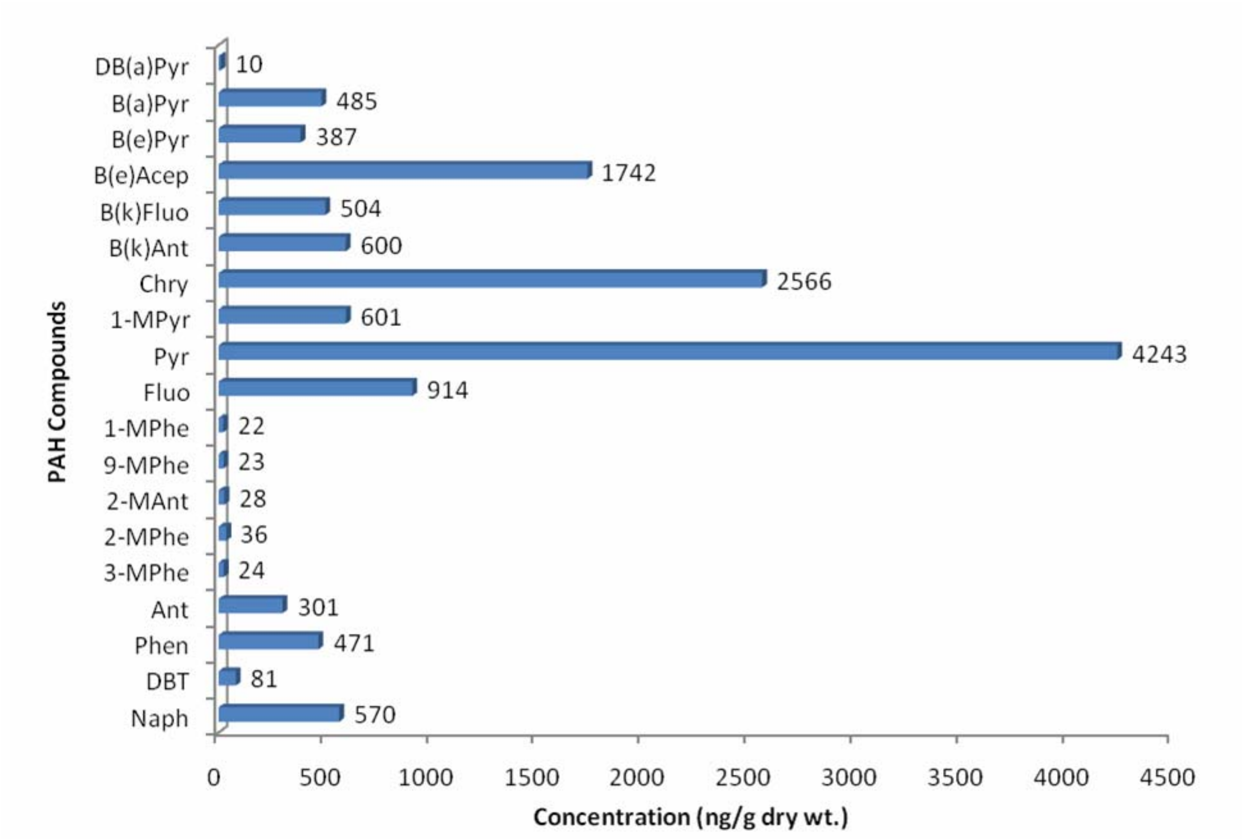

Figure 4: Total concentration of individual PAH compounds in all the marine sediments.

Figure 2 shows the total PAHs of sediment samples based on dry weight basis. The highest total PAHs is at the surface of station one (SF01A), 1481 ng/g while the lowest one is at the bottom station 24 (SF24C), 80 ng/g. The total PAHs that found at South China Sea is low to moderate concentration compared to global sedimentation records ranging from 1 to 760000 ng/g with modal concentration of 1000- 10000 ng/g (Zakaria et al, 2002).

Diagnostic ratio or environmental forensic technique is used to determine the link between anthropogenic sources and pollution. Molecular ratio consist many types included methyl alkylated compound to parent compound. Figure 3 shows the ratio of low molecular over high molecular and methylphenanthrene over phenanthrene. The ratio with over than one shows petrogenic while below than indicates pyrogenic.

5.0 Significance of Finding

This study can determine the major anthropogenic sources of PAHs which might be contributed to the pollution at South China Sea by using diagnostics ratio. Diagnostic ratio that used in this research is low molecular over high molecular and methylphenanthrene over phenanthrene ratio. Both ratios can determine the anthropogenic sources which are petrogenic or pyrogenic. The ratio with over then one shows the petrogenic sources while below indicate pyrogenic sources. The concentration level of PAHs can be determined in order to asses the status pollution in South China Sea.