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# Early Monitoring of Potentially Toxic Hydrocarbon Species in Sediment and Biological Samples from Southern Guimaras, Philippines After Oil spill

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***Key words:*** oil spill, PAH, alkylated PAH, Guimaras

**Abstract**

Sediment samples collected from Taklong Island one month after the oil spill incident in Southern Guimaras, Philippines were found to contain very high level of the potentially toxic hydrocarbon species, the polycyclic aromatic hydrocarbons (PAHs) and their alkylated homologues (alk-PAHs). The potentially toxic PAHs present in sediment samples were acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(l,2,3-c,d)pyrene, naphthalene, phenanthrene, and pyrene. Among the 17 PAHs in the priority list of potential hazardous compounds, 7 of these PAHs are considered as potential human carcinogens, namely benzo(a)pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenzo(a,h)anthracene, indeno (1,2,3-c,d) pyrene. Seventeen different alk-PAHs found in high level in the sediment samples were 1-methylnaphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, 1-methylfluorene, 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene, 1-methylanthracene, 1-methylphenanthrene, 2-methylphenanthrene, 2,3-dimethyanthracene, 2-methylfluoranthene, 1-methylpyrene, 1-methylbenz(a)anthracene, 4-methylchrysene, 7,12-dimethylbenz(a)anthracene, and 7-methylbenzo(a)pyrene.

Oyster, squid and fish samples collected and analyzed were found to contain relatively low level of PAHs and some alk-PAH compounds. There are 9 PAH compounds detected in the biological samples namely; naphthalene, acenaphthylene, fluorene, dibenzothiophene, phenanthrene, fluoranthene, pyrene, benz(a)anthracene and chrysene and 6 alk-PAHs; 1-methylnaphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene, and 1-methyl-phenanthrene.

## Introduction

On August 11, 2006, Motor Tanker Solar I carrying 2 million liters of Bunker B fuel in 10 tanks sank 24 km southwest of Guimaras, Western Visayas, Philippines and spilled about 220,000 liters of bunker fuel into the sea. Over 200 kilometers of coastline (barangays Cabalagnan, Canhawan, Dolores, Guiwanon, Igdarapdap, La Paz, Lucmayan, San Antonio, San Roque and Tando of Nueva Valencia) had been affected by the worst oil spill in the country's history. The hardest hit was Taklong Island, a declared National Marine Reserve, where the UPV Marine Biological Station is located.[1)] The research team committed to conduct a chemical assessment in order to determine the extent of PAH contamination and establish the level and persistence of PAH compounds in sediment and biological samples (shellfish, squid, fish) from Southern Guimaras, Western Visayas, Philippines.

## Materials and Methods

Sediment samples and some biological samples (bivalves, squid and fish) were collected one month and six months after the oil spill incident at Taklong (Tak-1 and Tak-2) and Igan in Southern Guimaras and were analyzed quantitatively for the potentially toxic hydrocarbon species, PAHs and alk-PAHs. PAH compounds were extracted from sediment and biological samples using n-hexane following US-EPA method.[2)] The analysis was done in Kagoshima University, Faculty of

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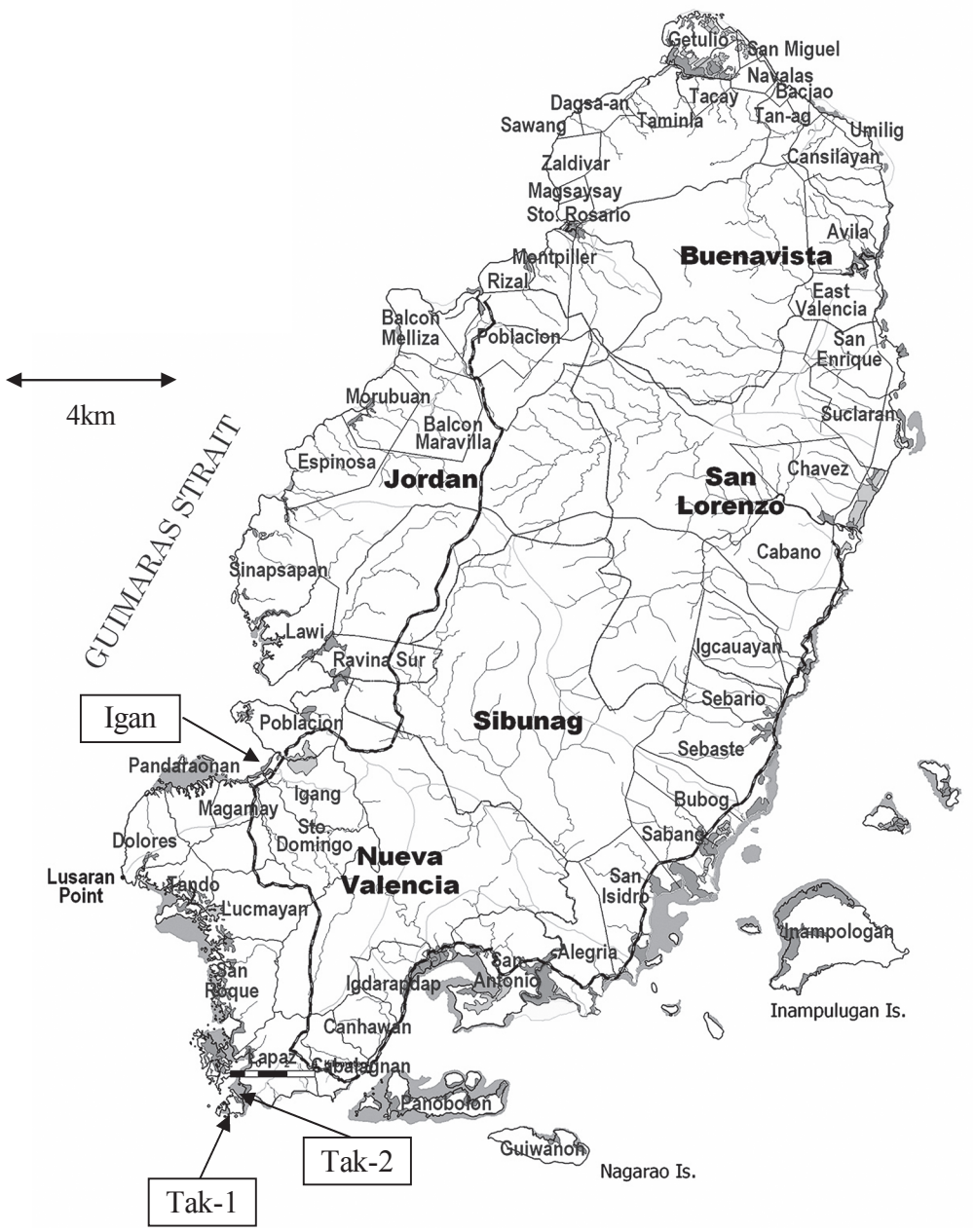


Fig.1 Sampling sites in Guimaras Island,Philippines

Fisheries, Kagoshima, Japan using Agilent GC-MS 5973 in selected ion monitor mode. PAH concentrations were shown in wet basis.

## Results

### Surface sediment

Sediment samples collected from Taklong Island one month after the oil spill incident in Southern Guimaras (Fig.1) were found to contain very high level of the potentially toxic hydrocarbon species, PAHs and their alkylated homologues. The surface sediment sample (Tak-1) taken at water level during low tide in a cove in front of UPV TINMAR (Taklong Island National Marine Reserve) in Taklong Island had total PAHs (including alk-PAHs) of 333000 ng/g and Tak-2 sample taken 3 meters upward from water level has total PAH of 135000 ng/g (Fig. 2). The total PAH levels of the surface sediment from Taklong Island was very high compared to the uncontaminated surface sediment taken from Igang, Guimaras (control) with total PAH of 0.9 ng/g and relative to the standard value for aquatic organism [3] of lowest effect concentration (4000 ng/g).

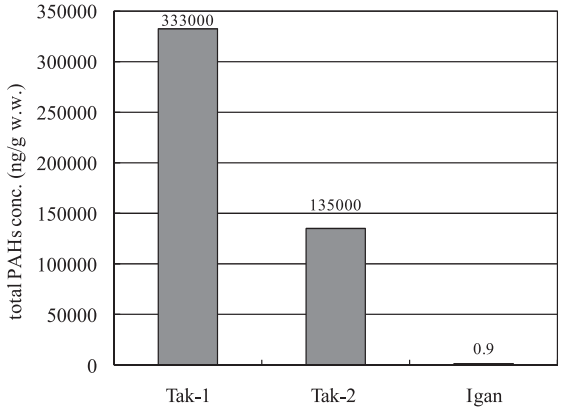


Fig. 2 Total PAH (including alk-PAHs) concentrations in surface sediments 1 month after oil spill

The potentially toxic PAHs present in sediment samples were acenaphthene, acenaphthylene, anthracene, benz(a) anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(l,2,3-c,d)pyrene, naphthalene, phenanthrene, and pyrene (Fig. 3).

Among the PAHs in the priority list of potential hazardous compounds, 7 of these PAHs, also in very high levels are considered as potential human carcinogens, namely benzo(a)

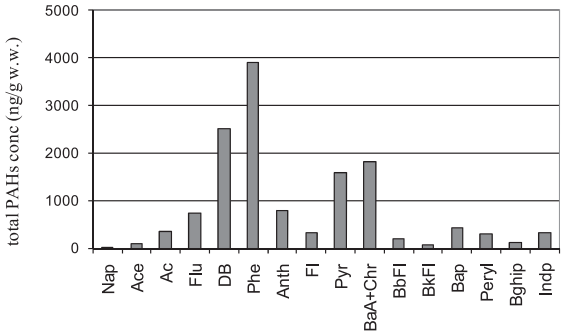


Fig. 3 PAH concentrations in sediment collected at Tak-1 1 month after oil spill
Nap: naphthalene; Ace: acenaphthylene; Ac: acenaphthene; Flu: fluorene; DB: dibenzothiophene; Phe: phenanthrene; Anth: anthracene; Fl: fluoranthene; Pyr: pyrene; BaA: benz(a) anthracene, Chr: chrysene; BbFl: benzo(b)fluoranthene; BkFl: benzo(b)fluoranthene;Bap: bonzo(a)pyrene; Pery: perylene; BghiP: benzo(g,h,i)perylene; IndP: indo(1,2,3-cd)pyrene

pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno(1,2,3-c,d) pyrene.[4, 5] Phenanthrene (3900 ng/g) and dibenzothiopene (2500 ng/g) were found to be the most abundant, followed by pyrene and benz(a)anthracene+ chrysene (1580 – 1830 ng/g) and then fluorene and anthracene (720 - 790 ng/g), while other PAHs were below 500 ng/g.

Alk-PAHs are PAH compounds attached with 1 to 3 methyl group. Seventeen different alk-PAHs also found in high level in the sediment samples (Tak-1) were 1-methylnaphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, 2,3,5-trimethylnaphthalene, 1-methylfluorene, 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene, 1-methylanthracene, 1-methylphenanthrene, 2-methylphenanthrene, 2,3-dimethylanthracene, 2-methylfluoranthene, 1-methylpyrene, 1-methylbenz(a) anthracene, 4-methylchrysene and 7,12-dimethylbenz(a)anthracene (Fig.4).

Trimethylnaphthalene (C3-Nap) and methyldibenzothiophene (C-DB) were the highest among the alkylated PAH (>5000 ng/g). It was also observed that there was higher level of alkylated naphthalene than non-alkylated naphthalene.

The sum of the alk-PAHs in sediment revealed very high levels (60,000 – 70,000 ng/g) of dimethyldibenzothiophene (3 rings), methylchrysene, +dimethylbenz(a)anthracene (4 rings), and phenanthrene+anthracene (3 rings) and relatively lower values for naphthalene (2 rings), fluoranthene+pyrene (4 rings) and fluorene (3 rings).

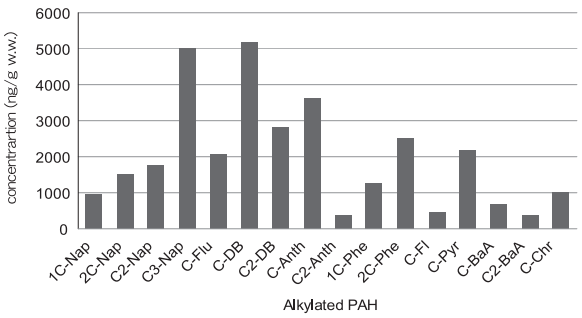


Fig. 4 Alk-PAH concentrations in sediment collected at Tak-1 1 month after oil spill.
1C-Nap: 1-methylnaphthalene, 2C-Nap: 2-methylnaphthalene, C2-Nap: 1,2-dimethylnaphthalene, C3-Nap: 2,3,5-trimethylnaphthalene, C-Flu: 1-methylfluorene, C-DB: 4-methyldibenzothiophene, C2-DB: 4,6-dimethyldibenzothiophene, C-Anth: 1-methylanthracene, C2-Anth: 2,3-dimethyanthracene, 1C-Phe: 1-methylphenanthrene, 2C-Phe: 2-methylphenanthrene, C-Fl: 2-methylfluoranthene, C-Pyr: 1-methylpyrene, C-BaA: 1-methylbenz(a)anthracene, C2-BaA: 7,12-dimethylbenz(a) anthracene, C-Chr: 4-methylchrysene

**Biological Samples**

Oyster, squid and fish samples collected around Guimaras Island (including Igan, Tak-1 and Tak-2) just after oil spill showed low level of PAHs and alkylated PAH compounds. There were 9 PAH compounds detected in the biological samples namely; naphthalene, acenaphthylene, fluorene, dibenzothiophene, phenanthrene, fluoranthene, pyrene, benz(a) anthracene and chrysene. There were more PAH compounds detected in fish and squid compared to oyster. More non-alkylated PAHs: chrysene, phenanthrene, pyrene, fluoranthene were found higher in fish and squid with fluoranthene (>6 ng/g) and chrysene (>8 ng/g) having the highest concentration in fish and squid, respectively. While non-alkylated PAH in oyster (phenanthrene, fluorene, naphthalene, acenaphthene) are all less than 4 ng/g (Fig.5)

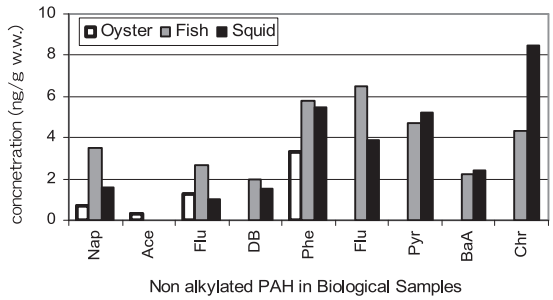


Fig 5 PAHs in Oyster, Fish and Squid just after oil spill

One month after the accidental oil spill, 6 alkylated PAHs; 1-methylnaphthalene, 2-methylnaphthalene, 1,2-dimethylnaphthalene, 4-methyldibenzothiophene, 4,6-dimethyldibenzothiophene, and 1-methylphenanthrene. methyl phenanthrene (>10 ng/g) was the predominant species of alkylated PAHs in fish and squid (Fig 6).

Six months after the accidental oil spill, shellfish samples were collected to determine the presence and persistence of PAHs. The result (Fig 7) indicated presence of PAHs and higher level of chrysene (>50 ng/g) in oyster samples collected in Luzaran and benzo(a)pyrene (>30 ng/g) in *Modiolus* sp from Taklong Island Guimaras.

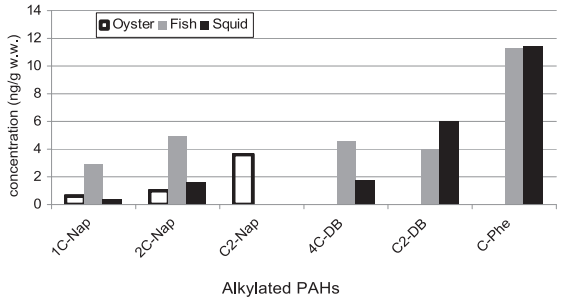


Fig.6 Alkylated PAHs in Oyster, Fish and Squid just after oil spill 1 month after oil spilll

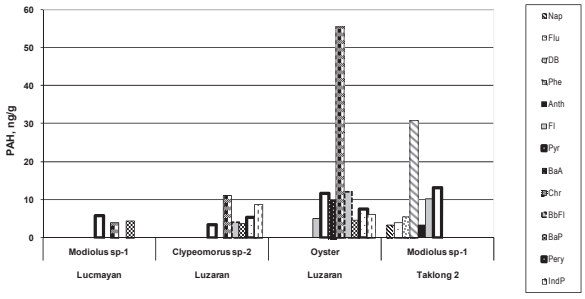


Fig 7 PAHs in Oyster, Fish and Squid 6 month after oil spill

**Discussion**

PAHs are hydrocarbon compounds with two fused or joined benzene rings. PAHs and their alkylated homologues are among the most hazardous compounds in oil spills. There are more than 100 different PAH compounds in petroleum and the health effects of the individual PAHs are not exactly alike. Fiftyfour PAHs have been identified to be hazardous and 16 to 18 PAHs are given special attention because of their toxicity, potential hazard to human.[6] Among the PAHs in the priority

list of potential hazardous compounds, 7 of these PAHs also in very high levels are considered as potential human carcinogens, namely (benzo(a)pyrene, benz(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, dibenz(a,h)anthracene, indeno (1,2,3,cd)pyrene.[4, 5)]

Petroleum naturally contains higher level of alkylated PAH homologues than the parent PAH and alkylated PAHs are more persistent and less degradable than the parent PAHs. It was also reported that most alkylated PAHs appear to be more toxic or hazardous than their parent compounds.[6)] The high level of alkylated naphthalene in the sediment and biological samples relative to the non-alkylated naphthalene is indicative of a weathered petrogenic hydrocarbon. Alkylated naphthalene was reported as the most toxic alkylated PAH compound affecting benthic aquatic invertebrates and fishes.[7)] Acute toxicity increases with increasing alkyl substitution on the aromatic nucleus, such that tetramethylnaphthalene is more toxic than the trimethylnaphthalene, the dimethylnaphthalene and monomethylnaphthalene. This is also true for other alkylated PAH compounds.

Studies revealed that alkylation of PAH compounds may lead to higher degree of bioaccumulation, persistence and toxicity but with lower degree of metabolic (oxidative) breakdown in organisms. However, metabolism of PAHs does not necessarily mean a reduction in the biological potency of the compound since the metabolites are often more hazardous.[7)]

There was significantly high level of chrysene found in oyster samples collected in Luzaran and benzo(a)pyrene in *Modiolus* sp from Taklong Island. In hydrocarbon contaminated sediments, shellfishes are reported to absorb and maintain high level of PAH in their tissues compared to fish and other aquatic organisms because shellfishes lack the metabolic pathway to breakdown polycyclic aromatic hydrocarbon in their system.[8)]

Six months after the oils pill, the seven probable carcinogenic PAHs in surface sediments dropped. Changes in the concentration of PAHs are dependent on various environmental factors and the nature of the compound. Hydrocarbons with condensed ring structures, such as PAHs with four or more rings (chrysene, pyrene, benzo(a)pyrene) have been shown to be relatively resistant to biodegradation while PAHs with only 2 or 3 rings (e.g., naphthalene (2 rings), anthracene (3 rings)) are more easily biodegraded.[9)]

In sediments, PAHs are believed to be degraded under different conditions and may be transformed into even more toxic and mutagenic compounds. Metabolic transformations of PAHs into even more hazardous compounds could also happen through microbial action in sediments through time.[6)] Animal studies show that exposure to some PAHs can cause harmful effects on the skin, body fluids, the immune system, and the lungs.[6, 10)] Individual PAH and mixture of these PAHs are also associated with human cancer.[11)]

## Acknowledgement

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