# Concentration of Surfactants Around Coastal Water: Several Possible Sources

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ABSTRACT

Surface active agents or surfactants can always be correlated to the coastal areas because of the influence of natural surfactants from sea surface microlayer. Nevertheless, the development of coastal areas from tourism industries and other developments will lead to the distribution of commercial surfactants to the coastal areas. The surfactants from sea surface microlayer will affect the atmospheric condition at the coastal zone. This study tries to determine the concentration of sea surface microlayer from different coastal environments (Port Dickson, Perhentian Island, Tinggi Island, Kuala Selangor and Selangor River). The concentration of surfactants in surface microlayer were analysed by using the colorimetric method as methylene blue active substances (MBAS) and disulphine blue active substances (DBAS). As a whole, the result showed that anionic surfactants dominated the amount of surfactants in the sea surface microlayer. Surfactants as MBAS ranged between 0.015 - 0.421 µmol/L while surfactants as DBAS was found in the range between 0.011 - 0.294 µmol/L. The high concentration of surfactans found in Port Dickson indicated that the presence of surfactants were influenced by antropogenic sources.

**Keywords:** Sea surface microlayer; surfactants; coastal areas

## Introduction

Almost 70% of the earth is covered by sea, thus indicating that the marine ecosystem is the major contributor for the production of marine aerosol. The most important step in marine aerosol production is considered to be gas-bubble collapse, mainly caused by breaker waves at the sea surface and their increase during rough sea conditions (Dobson et al. 2000). According to the model of Resch (1986), a breaking wave represents the

most powerful generator of marine aerosols due to the very high rate of gas-bubble production and collapse at the sea surface. The sea-surface microlayer (SML) can be defined as a thin film that occures between the ocean and the atmosphere, where the transfer of material is controlled by complex physicochemical processes (Zhang et al. 2003; Wurl & Obbard 2004). This interface can serve as both a sink and a source of anthropogenic compounds. Most of the identified organic matter are amino acids, fatty acids, carbohydrate and organic acid which are generated from the decomposition of macroscopic and microscopic marine organisms (Boney 1975).

Most of the water soluble organic carbon can also be released into water by healthy, actively growing phytoplankton cells in the form of extracellular products (Boney 1975; Nakatsuka et al. 2004). Phytoplankton is a community of plants adapted to suspension in the sea or in fresh water and which is liable to passive movement by wind and current (Reynolds 1984). It is found that phytoplankton exudates, which consist of proteins and their degradation products, various lipids, glycopeptides-lipid-oligosaccharide complexes and pigments are one of the largest sources of naturally organic matter and a large amount of this material is surface-active, accumulating at the marine interface (Vojvodic & Cosovic 1996). The functional groups detected are mainly carbonyl compounds and carboxylic acids (Cavalli et al. 2004; Russell et al. 2002; Sempere & Kawamura 2003; Mochida et al. 2002) which might be decomposition products of longer chain fatty acids. These compounds are known to be surface active, meaning that they are able to form a film on the aerosol which can decrease the mass transfer between the gas phase and the liquid phase (Gill et al. 1983). Moreover, aerosol particles coated with surface active agents (surfactants), have the ability to produce more cloud droplets than particles without surfactants and hence to have a significant influence on the temperature of the Earth (Gorvunov & Hamilton 1998).

The presence of surfactant organic matter from marine environments (sea surface microlayer) is well known (Blanchard 1964; Cini and Loglio 1997; Giovannelli et al. 1988; Loglio et al. 1986; Loglio et al. 1985; Nicolotti et al. 2005; Oppo et al. 1999). The sea surface microlayer (SML) represents the interface between the ocean and the atmosphere, where the transfer of material is controlled by complex physico-chemical processes. SML can be summarised as being a micro habitat made of several layers distinguished by their ecological, chemical and physical properties with a total thickness between 1 and 1000 ىm. This interface can serve as both a sink and a source of anthropogenic compounds, including chlorinated hydrocarbons, organotin compounds, petroleum hydrocarbons and heavy metals due to its unique chemical composition; in particular, its high content of lipids, fatty acids and protein (Wurl and Obbard 2004). There are several possible sources of organic matter from the sea surface microlayer including secretion by plants and animals, bacterial decomposition, autolysis processes, input by rivers and effluents and from the atmosphere.

# Methodology

## Sampling Site

### Pulau Tinggi and Pulau Perhentian

Pulau Tinggi, otherwise known as Tinggi Island is a large sparsely inhabited island, which rises 2000 ft (600 m) above sea level off the east coast of Johor, Malaysia. It is located about 20 nautical miles (37 km) southeast of Mersing, on the east coast of Johor. The journey by boat to Tinggi Island takes approximately 45 minutes. The interior of the island is mostly covered with secondary lowland Dipterocarp rainforest. It has fresh waters, fruits, rattan, timber and a sheltered harbour and coral reefs which are abound with prolific marine life. It has a long coastline and white sandy beaches dotted with caves.

Pulau Perhentian (Perhentian Island) lies approximately ten nautical miles (19 km) offshore of the coast of northeastern Malaysia in the state of Terengganu, approximately 40 miles (64 km) south of the Thai border. This island is fringed by white sandy beach, and the reefs and crystalline water are host to a wide variety of coral, sea-turtles, jellyfish, small sharks and reef-fish. The islands maximum elevation is approximately 100 m and it is uniformly covered in coastal tropical jungle, with few interior foot-trails and no roads. Both islands will be chosen as a station influenced by surfactants from sea surface micro layer.

### Port Dickson

Port Dickson is a beach and holiday destination situated about 32 km from Seremban and 90 km from Kuala Lumpur. There are many beaches along Port Dickson. Leisure activities are available such as water-skiing, canoeing, snorkeling and wind surfing. Apart from that, great developments are also found nearby Port Dickson beach, hence suggesting that Port Dickson can represent antrophogenic sources.

### Kuala Selangor

Kuala Selangor is a fishing village located in Selangor River (Sungai Selangor) estuary and has a great potential for the tourism industry (Figure 1). It is known for the firefly habitat, associated with mangrove species, *Sonneratia caseoloris* that is found in the river estuary of Selangor River. This station will be selected in order to observe the input from a river namely Selangor River.

### Selangor River

Sungai Selangor is one of the major river systems in Selangor and drains into the Malacca Straits. The river is 75 km in length with a total catchments area of 1450 $km^2$. The river is 500 m wide at the mouth and about 2.5 m deep at low water but at upstream sections, the water can be over 10 m deep. The coastal zone is characterised by semi diurnal, macro-tidal regime with the mean spring tidal range of about 4.0 m. Currents can be very

strong that reach 1.3 $ms^{-1}$ during spring. This river will be chosen as a station in determining the input of river.

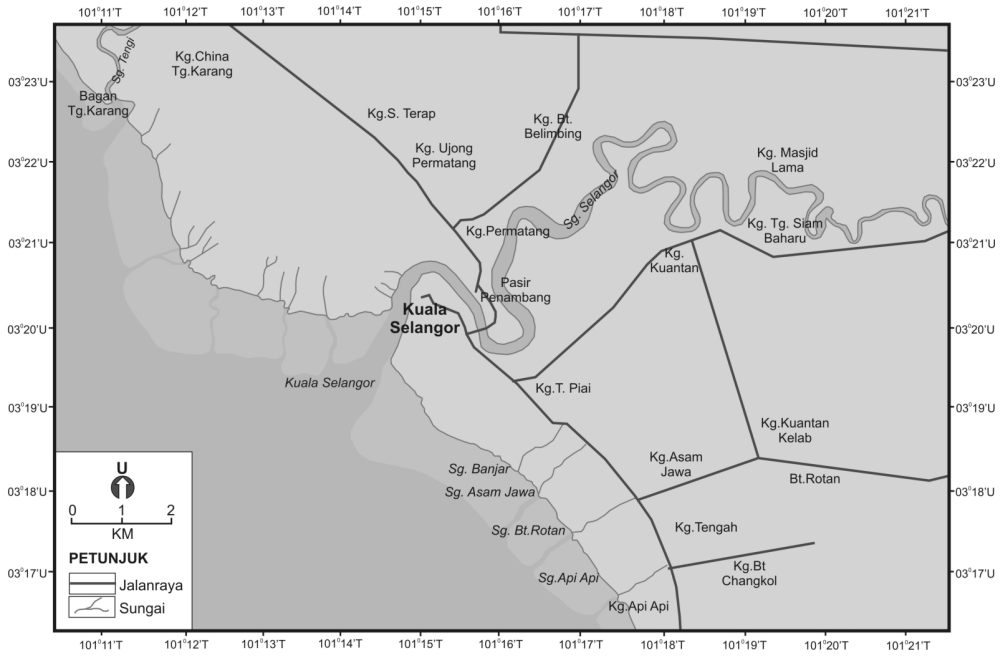


FIGURE 1: Map of Selangor River and Kuala Selangor

## Sampling and Preparation of Sample

Surface microlayer was collected at Tinggi Island, Perhentian Island, Port Dickson, Kuala Selangor and Selangor River by using a rotation drum as suggested by Harvey (1966). The surface collector uses a smooth, rotating cylinder whose surface is readily wet by water. This method results in the collection of thinner and less disturbed surface water. After sampling, samples were stored in a vial at 4°C prior to analysis by colorimetric methods as methylene blue active substances (MBAS) for anionic surfactants and as disulphine blue active substances (DBAS) for cationic surfactants.

## Determination of surfactants

### Determination of Surfactant as Methylene Blue Active Substances (MBAS)

The sample solution (20 mL) was put in a 40 mL vial (vial A) equipped with a screw cap and Teflon liner. The alkaline buffer (2 mL) and neutral methylene blue solution (1 mL), followed by chloroform (5 mL), was added to vial A in that order. The vial was closed tightly using a holed screw-cap and Teflon liner before being vigorously shaken using a vortex mixer for two minutes. After shaking, the vial was left awaiting phase separation.

The screw-cap was loosened to release the pressure inside. Once the two phases were separated, a Pasteur pipette was used to transfer the chloroform layer into the new vial (vial B) that contained ultra pure water (22 mL) and acid methylene blue solution (1 mL). Vial B was shaken using a vortex mixer for two minutes. The cap was loosened for few seconds and re-tightened. After the chloroform had completely separated from the water (after two minutes), the chloroform layer was collected after using a Pasteur pipette put into the 10 mm quartz cell. The absorbance of chloroform phase was measured by an ultra-violet spectrometer at a wavelength of 650 nm.

### Determination of Surfactant as Disulphine Blue Active Substances (DBAS)

A volume of sample solution (20 mL) was put in a 40 mL vial equipped with a screw cap. An acetate buffer (2.0 mL) and then 1 mL disulphine blue solution were added to the solution. After adding 5 mL chloroform, the solution was vigorously shaken using a vortex mixer for one minute. The cap was loosened for a few seconds to release the pressure, and then re-tightened. The vial was inverted and left until the two phases were completely separate (around two minutes). Some of the chloroform layer was removed using a Pasteur pipette. The 10 mm quartz cell and its light absorbance was measured at a wavelength of 628 nm.

## Results and Discussion

The concentration of surfactants as methylene blue active substances (MBAS) was found higher that the concentration of surfactants as disulphine blue active substaces (DBAS) in all sampling locations (Table 1). This result followed the results from previous studies (Latif and Brimblecombe 2004; Latif et al. 2005; Sukhapan and Brimblecombe 2002) which indicated that the concentration of surfactants in the sea surface microlayer was dominated by anionic surfactants compared to cationic surfactants.

TABLE 1: The Average Concentration of Surfactants in the Sea Surface Microlayer

| Station | n | MBAS , (μmol/L) | DBAS , (μmol/L) |
|---|---|---|---|
| Port Dickson | 5 | 0.421 ± 0.040(range) | 0.294 ± 0.1230(Range) |
| Pulau Tinggi | 5 | 0.022 ± 0.004 | 0.017 ± 0.0035 |
| Pulau Perhentian | 5 | 0.021 ± 0.004 | 0.016 ± 0. 004 |
| Kuala Selangor | 4 | 0.015 ± 0.008 | 0.011 ± 0.004 |
| Selangor River | 20 | 0.091 ± 0.064 | 0.016 ± 0.0075 |

By comparing the results obtained from Port Dickson (representing antropogenic sources) and Pulau Tinggi and Pulau Perhentian (representing natural sources), it was noted that the amount of surfactants in Port Dickson was found high which was 0.421 ±

0.040 µmol/L for MBAS and 0400.294 ± 0.123 µmol/L for DBAS. On the other hand, the concentration of MBAS and DBAS recorded at Pulau Perhentian and Pulau Tinggi was quite low (Table 1). This indicated that the antropogenic sources generated from the tourism industries, pollution and other development in Port Dickson might influenced the concentration of surfactants compared to Pulau Tinggi and Pulau Perhentian which are endowed with fresh waters.

Samples collected along Selangor River until Kuala Selangor provided inconsistent concentration of both anionic and cationic surfactants (Figure 2). From observation, it was found that the Selangor River was exposed to massive pollution as the domestic activities, industrial activities and other development were carried out along the river. Thus, the surfactants might have been introduced to the river and could travel along the Selangor River, hence explaining the high concentration of surfactants in Selangor River (S6-S19).

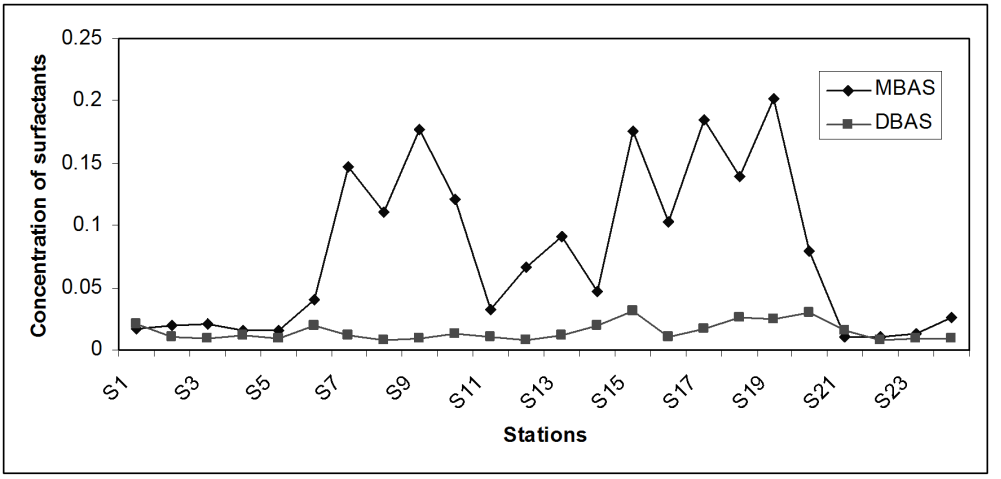


FIGURE 2: Concentration of Surfactants Along Selangor River and Kuala Selangor

In contrast with Selangor River, Kuala Selangor contained less concentration of surfactants which is 0.015 ± 0.008 µmol/L for MBAS and 0.011 ± 0.004 µmol/L for DBAS. The concentration of surfactants slowly decreased at Kuala Selangor (S20-S24) possibly due to sedimentation. Kuala Selangor estuary is the end point of several rivers before entering the Malacca Strait. According to Nedwell and Brown (1982), estuaries are very important environments of deposition and also the interface between the fresh and salt water regimes. Thus, there was a possibility that surfactants might have deposited and entered the sediments. This explained the low concentrations of surfactants in the surface layer of the water column at Kuala Selangor. Moreover, it was also noted that during the river passage through the Selangor River, the concentration of surfactants declined due to the long residence time in the water column and dilution process (Emmerton et al. 2007).

# Conclusion

Results of this study have shown that the concentration of anionic surfactants was higher compared to cationic surfactants in all sampling locations. This phenomenon indicated that the sea surface microlayer seemed to be the dominant contributor source of negatively-charge surfactants (anionic surfactants). Nevertheless, the high amount of surfactants in Port Dickson showed that the antrophogenic sources generated from tourism activities might have influenced the concentration of surfactants. This therefore suggested that antrophogenic sources might contribute to the presence of surfactants in atmosphere apart from the sea surface microlayer.

Results of this study have shown that the concentration of surfactants from sea surface microlayer was dominated by anionic surfactants recorded as methylene blue active substances (MBAS). Surfactants from sea surface microlayer, other than the product of natural sources were also found to be influenced by anthropogenic sources especially from tourism activities.

The concentration of MBAS collected around coastal areas was found quite low compared to the concentration of MBAS recorded in atmospheric aerosols influenced by anthropogenic sources. The global flux of surfactants to the atmosphere as MBAS recorded based on this study was around 7 Mmol $yr^{-1}$ far below the global flux of MBAS from soils, fossil fuel and biomass burning. Small molecular structure of surfactants from sea surface microlayer is believed to be a factor to differentiate the surfactants from the ocean compared to other anthropogenic and natural sources. This factor also can contributes to the destruction of surfactants from sea surface microlayer by photo oxidation processes.

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