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Baseline

Distribution of surfactants along the estuarine area of Selangor River, Malaysia

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ABSTRACT

This study aims to determine the levels of methylene blue active substances (MBAS) and ethyl violet active substances (EVAS) as anionic surfactants and of disulphine blue active substances (DBAS) as cationic surfactants in the surface microlayer (SML) around an estuarine area using colorimetric methods. The results show that the concentrations of surfactants around the estuarine area were dominated by anionic surfactants (MBAS and EVAS) with average concentrations of 0.39 and 0.51 μmol L^{-1}, respectively. There were significant between-station differences in surfactant concentrations ($p < 0.05$) with higher concentrations found at the stations near the sea. The concentration of surfactants was higher during the rainy season than the dry season due to the influence of runoff water. Further investigation using total organic carbon (TOC) and total organic nitrogen (TON) shows that there is a significant correlation ($p < 0.05$) between both anionic and cationic surfactants and the TON concentration.

Estuaries constitute transition zones or ecotones where fresh water from land drainage mixes with seawater, creating some of the most biologically productive areas (Kennish, 2002). The estuary ecosystem is significantly important in terms of biogeochemical cycles due to high levels of nutrient and organic substances which inflow to the ecosystem (Turner and Millward, 2002; Martinho et al., 2008; Shan et al., 2013). The surface microlayer (SML) in estuarine areas is a specific ecosystem due the influence of river water intrusion. The SML is a layer within 50 ± 10 μm that is generally recognised by high levels of particulates and dissolved organic and inorganic compounds (Žutić et al., 1981; Zhang et al., 2006; Cunliffe et al., 2013). Several pollution sources of organic matter in the SML include plant and animal secretions, bacterial decomposition, autolysis processes, fertilizer, sewage, effluents, and erosion (Bodineau et al., 1999; Bianchi, 2001; Volkman and Tanoue, 2002; Zhang et al., 2008). Previous research shows that there are three major classes of biochemical compounds in the SML: carbohydrates, proteins and lipids (Sieburth et al., 1976; Williams et al., 1986; Calace et al., 2007).

Organic compounds with surfactant properties are an important group of organic substances in the SML due to their ability to increase the solubility of inorganic and organic substances (Li and Chen, 2002; Doong and Lei, 2003; Castro et al., 2005). The largest proportion of naturally occurring surfactants originates from phytoplankton exudates in sub-surface water (SSW); a water layer between 10 cm and 1 m from the water's surface (Pikkarainen and Lemponen, 2005; Nakajima et al., 2013). SSW comprise numerous lipids, proteins and their degradation products, glycopeptides–lipid–oligosaccharide complexes and pigments accumulating at the marine interface (Vojvodić and Ćosović, 1996; Pavlić et al., 2005; Wurl et al., 2011). Surfactants in the SML can also be generated photo-chemically from the degradation of refractory dissolved organic matter (DOM), such as humic substances (Kieber and Mopper, 1987; Kieber et al., 1990; Mopper et al., 1991). Photo-oxidation and degradation processes of humic substances containing higher aromatic and carbohydrate content by microorganisms produce smaller material organic materials dominated by aliphatic components with carboxyl functionalities (Abdulla et al., 2013). This would result in the addition of surfactants with carboxylic acid functional groups (McKnight and Aiken, 1998). In coastal areas, surfactant concentrations may be generated due to urbanisation and the contribution of waste and runoff water (Zhang et al., 2006; Stortini et al., 2009).

The amount of surfactants in the ocean's surface can determine the fate of chemicals in the SML and contribute to the amount of

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surfactants in marine aerosols through bubble-bursting processes (Cini and Loglio, 1997; Nicolotti et al., 2005; Rettori et al., 2005; Bigg, 2007; Becagli et al., 2011). Due to the importance of surfactants in the marine ecosystem, this study aimed to determine the levels of methylene blue active substances (MBAS) and ethyl violet active substances (EVAS) as anionic surfactants and disulphine blue active substances (DBAS) as cationic surfactants around an estuarine area of Kuala Selangor, Malaysia. EVAS are pH dependent anionic surfactants and reacts with a broader range of compounds compared to MBAS (Motomizu et al., 1982). The estuarine ecosystem was selected due to the concern of surfactants originating from river flow entering the marine ecosystem. The measurement of total organic carbon (TOC) and total nitrogen (TON) indicate the likelihood of natural and anthropogenic contributions to surfactant concentrations. The possible sources of surfactants in the SML from sub-surface water (SSW), soil and plant litter in the mangrove soils were also investigated.

The Selangor River is located in the northern part of Selangor, Malaysia, flowing in the south-westerly direction before discharging into the Straits of Malacca. Palm oil and rubber plantations along the riverbanks are the major land use activities within the study area. The study area also has several remaining patches of upland and swamp forests (Ali et al., 2009).

The sampling locations for the SML as well as soil and plant samples are shown in Fig. 1. Thirteen sampling stations (S1–S13) were chosen for the SML analyses in this study. Stations S1–S4 are located along the river, where most agricultural activities are generally located. Stations S5–S13 are located in the estuarine area. These areas are influenced by waste discharge from various industrial and urbanisation activities. Soil and plant samples were collected at six stations along the estuary (P1–P6).

The SML samples were collected at 13 stations along the river and estuarine areas during the rainy (October 2010) and dry seasons (March 2011) using a rotation drum during high tide. The surface collector used a smooth, rotating glass cylinder as suggested by Harvey (1966). Samples from SSW were collected from a depth around 1 m from the surface using a 1 L brown glass bottle at selected stations to represent different locations along the river and estuarine areas.

All the SML and SSW samples were kept in a brown glass bottle and were stored in an ice box. Upon arriving to the laboratory, the samples were filtered within 48 h using a glass microfiber filter paper with a 0.45 μm pore size and 47 mm diameter (Whatman GF/C) and stored in a cool room at 4 °C until further analysis.

Approximately 5 cm of the top layer of soil was taken at stations P1–P6 during low tide conditions. Soil samples were placed in a sealed plastic bag and stored in a cold room at 4 °C in the dark and labelled before being analysed. In the laboratory, the samples were dried at 100 °C in an oven for 2 h. The dried samples were sieved through a 63 μm test sieve (Retsch, Germany) and stored at room temperature. Then, 50 mg of each of the sieved samples were weighed and placed in a tube filled with 50 mL deionised water with a resistivity less than 18.2 MΩ cm prepared using an Arium 611DI deionised water system (Sartorius, Germany). The

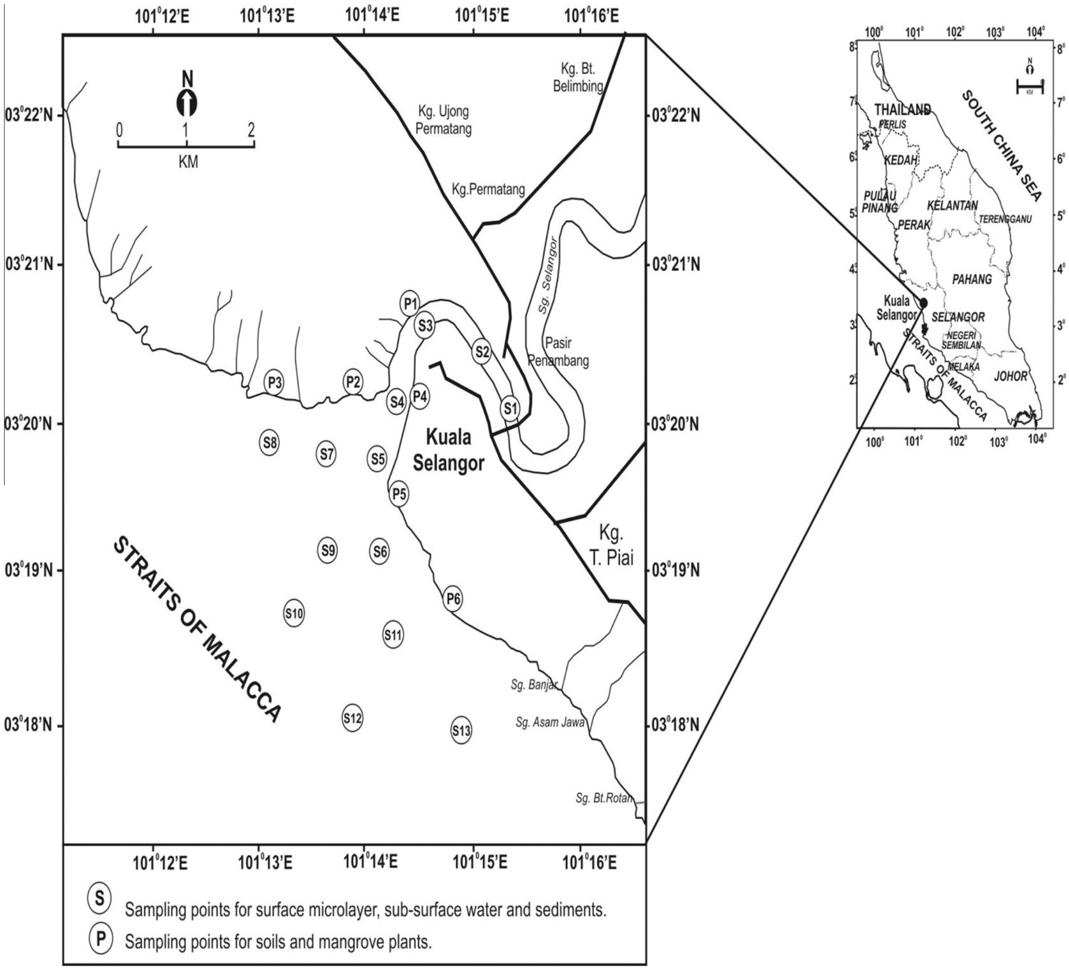

Fig. 1. Sampling locations for surface microlayer (SML), sub-surface microlayer (SSW), soils and mangrove plants.