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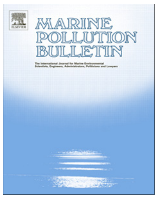

Surfactants in the sea-surface microlayer and atmospheric aerosol around the southern region of Peninsular Malaysia

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ABSTRACT

This study was conducted to determine the composition of surfactants in the sea-surface microlayer (SML) and atmospheric aerosol around the southern region of the Peninsular Malaysia. Surfactants in samples taken from the SML and atmospheric aerosol were determined using a colorimetric method, as either methylene blue active substances (MBAS) or disulphine blue active substances (DBAS). Principal component analysis with multiple linear regressions (PCA–MLR), using the anion and major element composition of the aerosol samples, was used to determine possible sources of surfactants in atmospheric aerosol. The results showed that the concentrations of surfactants in the SML and atmospheric aerosol were dominated by anionic surfactants and that surfactants in aerosol were not directly correlated ($p > 0.05$) with surfactants in the SML. Further PCA–MLR from anion and major element concentrations showed that combustion of fossil fuel and sea spray were the major contributors to surfactants in aerosol in the study area.

1. Introduction

The sea-surface microlayer (SML) is defined as a layer of the ocean's surface, tens to hundreds of μm deep, which is in direct contact with the atmosphere and where the transfer of chemical compounds is controlled by complex physicochemical processes (Liss and Duce, 2005; Guitart et al., 2007; Cunliffe et al., 2013). According to García-Flor et al. (2005), the SML is enriched by the accumulation of organic compounds such as proteins, carbohydrates, surfactants, lipids, pollutants and other organic residues. These organic compounds have the potential to change the surface properties of the ocean, for example the hydrophobicity (Olkowska et al., 2013). The SML also plays an important role in coastal and eutrophic oceanic regions due to the increased concentration of organic materials with surfactant properties in these areas. These materials have been shown to originate from both anthropogenic and natural sources (Frew et al., 1990; Brinis et al., 2004). A study by Wurl and Obbard (2004) has shown that the amount of dissolved organic matter (DOM) in the SML that has surface-active substances (i.e. surfactants) will influence the energy and mass exchange processes between sea and atmosphere, which may in turn lead to climatic changes (Sukhapan and Brimblecombe, 2002; Mazurek et al., 2008; Schwier, 2012). One proposed mechanism for climatic change is if aerosol particles gain a coating of surfactants, the particles are more likely to initiate cloud droplet formation (Sareen et al., 2012), therefore increasing cloud cover. Increased cloud cover has been shown to result in global temperature changes (Gorbunov et al., 1998; McNeill et al., 2014).

Surfactants in the SML will affect the solubility of compounds in the ocean by altering the surface tension of water (Andrews and Larson, 1993; Frew et al., 2004; Laha et al., 2009). As a consequence, the presence of surfactants will influence the distribution of pollutants dissolved in the SML. Organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), will have elevated solubility in the presence of surfactants, leading to increased concentrations in seawater and negatively affecting water quality (Cincinelli et al., 2001). Studies have shown that the accumulation of surfactants in the SML has a negative effect on aquatic species in both marine and freshwater ecosystems (Olkowska et al., 2014). As shown by previous studies, surfactants are toxic to marine and freshwater species and induce oestrogenic responses in fish

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(Comber et al., 1993; Jobling and Sumpter, 1993; Ivanković and Hrenović, 2010). Surfactants in aerosol have been found to affect human health and, at high concentrations, surfactants can disrupt the stability of the human respiratory system and lead to asthma, allergies and dry eyes (Vejrup and Wolkoff, 2002; Zimmer et al., 2002). Surfactants in SML and atmospheric aerosols as methylene blue active substances (MBAS) and disulphine blue active substances (DBAS) can be categorised as several types of organic substances based on their hydrophilic groups. MBAS represents surfactant compounds with a negative charge (anionic) group, such as carbonyl ($RCOO^-M^+$), sulfonate ($RSO_3^-M^+$) or sulphate ($ROSO_3^-M^+$). DBAS represents surfactant compounds with a positive charge (cationic) group, such as quaternary ammonium chloride ($(RN(CH_3)^{3+}Cl^-)$) (Myers, 1988; Jones-Hughes and Turner, 2005).

Environmetric methods are statistical procedures used to determine the complex relationships between a variety of environmental processes (Brown et al., 1994; Alberto et al., 2001). Principal component analysis (PCA), multiple linear regression analysis (MLR), factor analysis (FA), chemical mass balance (CMB) and a combination of these methods have been used to estimate the source apportionment of aerosol composition (Gupta et al., 2006; Srivastava et al., 2008; Mansha et al., 2012). Wahid et al. (2013) used PCA–MLR analysis to determine the source apportionment of surfactants in urban and sub-urban areas and found anthropogenic sources such as motor vehicle emissions and biomass burning, as well as the marine environment, contributed to the amount of surfactants in atmospheric aerosol. The levels of surfactants in atmospheric aerosol was also found to be influenced by the location of sampling stations and associated meteorological factors such as wind direction, temperature and rainfall.

The aim of this study was to determine the concentration of surfactants in atmospheric aerosol and the SML in the southern region of Peninsular Malaysia, an area which is influenced by various anthropogenic sources. The surfactants in atmospheric aerosol have been separated into coarse (diameter size, $d > 1.5$ μm) and fine (diameter size, $d < 1.5$ μm) mode aerosols. PCA–MLR, based on the anionic and elemental compositions of atmospheric aerosol, has been used to determine the possible sources of surfactants found in atmospheric aerosol.

2. Materials and methods

2.1. Sampling sites

Ten sampling stations were chosen to collect samples of the SML, located in the Johor coastal area of Malaysia, facing the Straits of Malacca. From among the ten sampling stations, two nearby locations were also selected for aerosol sampling: Tanjung Piai (T1) and Pontian Kechil (T2). The Tanjung Piai area covers the southernmost tip of Peninsular Malaysia, facing Singapore. This area is affected by shipping, tourism and industrial activities. It is also exposed to emissions from two major ports (Tanjung Pelepas and Singapore Port) and the Tanjung Bin coal-fired power plant. Pontian Kechil is located on the West Coast of Johor, close to the small town of Pontian. The Pontian Kechil coastal area is influenced by shipping, settlements, recreational activities and small-scale fishery activities. Table 1 and Fig. 1 show the sampling locations of the SML (S1–S10) and aerosol (T1–T2).

2.2. Sampling procedures

2.2.1. Sea-surface microlayer (SML)

The SML samples were collected between December 2012 and March 2013. About 50–500 mL of the SML were collected at high tide using a glass rotation drum method (Harvey, 1966). Samples were then kept in the 500 mL glass bottles (Schott, Germany) at 4 °C prior to analysis to prevent the evaporation of the volatile components.

2.2.2. Atmospheric aerosol

The aerosol samples were collected between December 2012 and March 2013, using a high volume air sampler (HVAS) (Thermo Scientific Model GS2313-105, USA) in combination with a two-stage cascade impactor (Staplex, USA). Slotted filter papers (Westech Instrument, UK) were used to collect coarse mode aerosols ($d > 1.5$ μm) and backup filter papers (Whatman EPM 2000) were used to collect fine mode aerosols ($d < 1.5$ μm). The filter papers were wrapped in aluminium foil and pre-heated in a muffle furnace (Carbolite, England) (500 °C, 4 h) to remove any organic contaminants. The filters were then conditioned in a desiccator for at least 24 h, then weighed with an electronic balance (Shimadzu AUX220, Japan) and placed in the HVAS. After installation, the HVAS was placed in an open field near to the sea to avoid any disturbance to the flow of aerosol entering the instrument. The sampling continued for 24 h over a two day campaign at a flow rate of 1.13 $m^3\ min^{-1}$, giving a total of 18 samples. After sampling, the filter papers were wrapped with aluminium foil and conditioned in desiccators (24 h) before weighing. For quality control purposes, the blank filter papers were prepared in the same way as the filter papers for sampling without turning on the HVAS.

2.3. Sample preparation

2.3.1. Sea-surface microlayer

The SML samples were filtered using cellulose acetate filter papers (Whatman, Germany – 47 mm/0.2 μm pore size) and a vacuum filter pump (Millipore, USA). The filtration process was conducted in the clean room. 20 mL of the filtered sample were put into a 40 mL vial for surfactant analysis.

2.3.2. Aerosol sample extraction

For the determination of surfactants from the coarse mode aerosol samples, half of the filter papers were used in the extraction processes. For the fine mode samples, a quarter of the filter papers were needed. The filter papers were cut into 1 cm^2 pieces and put into a centrifuge tube. 40 mL of ultra-pure water were added to the samples before they were sonicated for 45 min, as undertaken by Roslan et al. (2010), Razak et al. (2013) and Wahid et al. (2013). The ultra-pure water had a resistivity of less than 18.2 MΩ m and was prepared using an Arium 611DI deionised water system (Sartorius, Germany). The samples were then filtered using cellulose acetate filter papers (Whatman, Germany – 47 mm/0.2 μm pore size) and a vacuum filter pump (Millipore, USA). Samples were diluted to 100 mL with ultra-pure water in a volumetric flask and then stored in glass bottles. Samples for anions and major elements were stored in polyethylene bottles. Both samples were kept in a refrigerator (<4 °C) until further analyses.

2.4. Surfactant analysis

2.4.1. Anionic surfactants as methylene blue active substances (MBAS)

The sample solution (20 mL) was put into 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), were added to vial A in that order. The vial was closed tightly and was vigorously shaken for two minutes using a vortex mixer. After shaking, the vial was left to allow phase separation and the screw-cap was loosened to release the pressure inside. Once the two phases had separated, a Pasteur pipette was used to transfer the chloroform layer into a new vial (vial B) that contained ultra-pure water (22 mL) and the acid methylene blue

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