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Surfactants in the sea-surface microlayer and sub-surface water at estuarine locations: Their concentration, distribution, enrichment, and relation to physicochemical characteristics

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ABSTRACT

Samples of sea-surface microlayer (SML) and sub-surface water (SSW) were collected from two areas-Kaohsiung City (Taiwan) and the southwest coast of Peninsular Malaysia to study the influence of SML on enrichment and distribution and to compare SML with the SSW. Anionic surfactants (MBAS) predominated in this study and were significantly higher in Kaohsiung than in Malaysia. Industrial areas in Kaohsiung were enriched with high loads of anthropogenic sources, accounted for higher surfactant amounts, and pose higher environmental disadvantages than in Malaysia, where pollutants were associated with agricultural activities.

The dissolved organic carbon (DOC), MBAS, and cationic surfactant (DBAS) concentrations in the SML correlated to the SSW, reflecting exchanges between the SML and SSW in Kaohsiung. The relationships between surfactants and the physiochemical parameters indicated that DOC and saltwater dilution might affect the distributions of MBAS and DBAS in Kaohsiung. In Malaysia, DOC might be the important factor controlling DBAS.

1. Introduction

The sea-surface microlayer (SML) represents the interface between the ocean and atmosphere, where material transfer is controlled by various physicochemical and biological processes. Its unique characteristics mean that this thin layer is enriched by a complex mixture of substances, including protein, lipids, carbohydrates, and organic surfactants (Stolle et al., 2010). Organic pollutants, such as surfactants, accumulating in the SML can have harmful effects on both natural marine biodiversity and commercial fisheries (Manodori et al., 2006; Zhang et al., 2003).

Surfactants are widely used in numerous detergents, including laundry, household, and personal cleaning products. These surfactants enter into the environment through the discharge of sewage effluents (Becagli et al., 2011; Schramm et al., 2003; Ying, 2006) and can increase the solubility of organic/inorganic matter (e.g., pollutants) in water systems, reduce water quality, and cause eutrophication, thereby endangering planktonic species (Castro et al., 2005; Comber et al., 1993; Razak et al., 2012; Wurl and Obbard, 2004; Ying, 2006). Recent studies have shown that surfactants are an important subgroup of anthropogenic pollutants in the SML, and might pose a higher threat to the biota in the SML than pollutants in the sub-surface water (SSW) (Latif et al., 2012; Razak et al., 2012; Roslan et al., 2010).

At present, many relevant studies have focused on the environmental effects of surfactants in the form of aerosol particles (Becagli et al., 2011; Hanif et al., 2009; Latif et al., 2011). Much less information is available regarding the distribution and enrichment of surfactants in the SML and SSW, particularly in coastal areas. This study aimed to use methylene blue active substances (MBAS) as markers for anionic surfactants and disulphine blue active substances (DBAS) for cationic surfactants to assess SML and SSW concentrations of surfactants in two different sampling areas: Kaohsiung harbor area in Taiwan and the Straits of

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Malacca, Malaysia. The relationship between anionic and cationic surfactants and the physicochemical parameters of the aqueous phase was also investigated.

2. Method

2.1. Sampling location

The SML and SSW samples were collected from 14 stations in the two countries (Taiwan and Malaysia). The sites differed in terms of meteorological conditions and degrees of urbanization (Fig. 1). In Taiwan, the sampling area was Kaohsiung City, a rapidly urbanizing city with many industries. Fig. 1a shows the K1–K3 sites, located in the Jhongdou Wetlands Park near the middle of the Love River; this park serves a natural water purification function. The K4 samples were collected directly from the Love River. The K5–K10 samples came from sites around Kaohsiung Harbor. These sampling sites receive a variety of discharged contaminants including industrial wastewater, municipal sewage, roadway runoff, and non-point agricultural pollutants.

In Peninsular Malaysia, the four sampling locations were located in Negeri Sembilan and Johor, in the southwest coastal area. The sampling sites were selected based on the presence of nearby activities that might contribute to the SML and SSW (Fig. 1b). The sampling sites M1 and M2 (the Port Dickson site) in Negeri Sembilan were located on the west side of Peninsular Malaysia, and were exposed to anthropogenic sources from tourism, shipping and the oil industry (Fig. 1b). In Johor, the M3 site was located in the Tanjung Piai National Park, an area of mangrove swamps. The M4 station (Pontian) was located in an area of agricultural activities, notably palm oil plantations.

2.2. Sample collection

The SML samples were collected using the glass plate technique (Harvey and Burzell, 1972) in Kaohsiung and a glass rotation drum, as suggested by Harvey (1966), in Malaysia. These two devices are the most widely used for sampling SML. The thickness of the SML collected by the glass plate method was around 40–60 μm and around 70–100 μm for the rotation drum method; these values were similar to the actual SML thickness 50 ± 10 μm reported recently (Falkowska, 1999; Zhang et al., 2003). The SML thickness obtained using these two devices indicates that dilution by the water adhering to the sampler is avoided.

The SSW samples were collected at a depth of 0.5 m and stored in brown glass bottles. Both the SML and SSW samples were transported to the laboratory during a single day and stored at 4 °C prior to surfactant analysis. Both samples (approximately 100 mL) were filtered through pre-cleaned 47 mm filters (Whatman GF/F with 0.7 μm effective pore size).

Several physicochemical parameters of the SML and SSW samples were characterized: water temperature, pH, salinity, and dissolved organic carbon (DOC). The environmental and hydrographic conditions at each sampling site are described in Table 1. The analysis of chemical parameters was based on the standard methods of National Institute of Environment Analysis: NIEA W217.51A and W424.52A (Taiwan EPA). The DOC was measured as total carbon by catalytic high temperature oxidation using a total organic carbon analyzer (OI Analytical, Aurora Model 1030 W) adapted from Chen et al. (2013).

2.3. Surfactant analysis

Surfactant analysis was adapted from a method described previously (Roslan et al., 2010). For anionic surfactants, the filtered sample (20 mL) was put into a 40 mL vial and then 2 mL alkaline buffer, 1 mL neutral methylene blue solution, and 5 mL chloroform were added. The vial was closed tightly with a screw-cap and Teflon liner before being vigorously shaken in a vortex mixer for 1 min. Once the two phases were separated, the chloroform layer was transferred by a Pasteur pipette into a new vial containing 22 mL Milli-Q water (Millipore, Massachusetts, USA; resistance 18 ΩM cm or greater) and 1 mL acid methylene blue solution.

Disulphine blue dye was used to determine cationic surfactants. A 20 mL volume of sample was put into a 40 mL vial with 2 mL acetate buffer and 1 mL disulphine blue solution, 5 mL chloroform was added, and the solution was shaken vigorously for 1 min using a vortex mixer.

The absorbance of the chloroform phases containing the MBAS and DBAS were measured with a ultra-violet spectrophotometer set at wavelengths of 650 and 628 nm, respectively. The concentration of MBAS was calculated from a calibration curve established with an appropriate anionic surfactant reference material such as sodium dodecyl sulfate (SDS), while the concentration of DBAS was measured using benzyl-dimethyl-tetradecyl-ammonium chloride (BDTAC) dehydrate as a reference.

2.4. Quality assurance and quality control

The repeatability and recovery of the analytical procedure was examined for each set of samples. The vials were immersed in hydrochloric acid overnight. Detergents and soaps were avoided

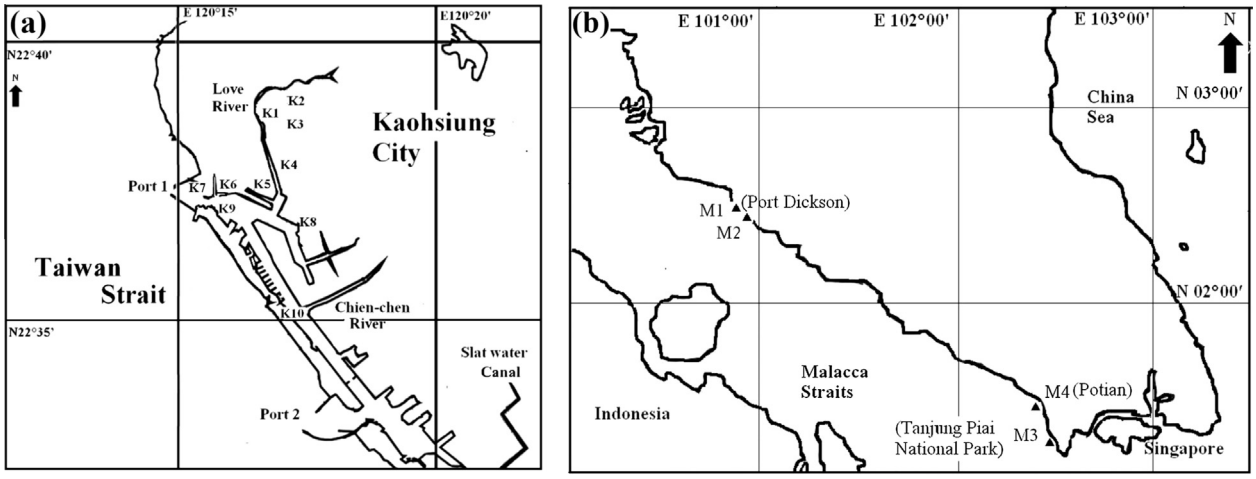

Fig. 1. The collection sites for sea-surface microlayer (SML) and sub-surface water (SSW) samples in (a) Kaohsiung City and (b) the Malaysian peninsula.