

CONCENTRATION AND FLUX OF ATMOSPHERIC SURFACTANTS FROM COASTAL WATER

Mohd Talib Latif^{1,*}, Che Abdul Rahim Mohamad¹, Masni Mohd Ali¹,
Mohamed Rozali Othman², Nor Izanin Ramli² and Norfazrin Mohd. Hanif²

¹School of Environmental and Natural Resource Sciences,
Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi.

²School of Chemical Sciences and Food Technology,
Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 Bangi.

*e-mail: talib@pkrisc.cc.ukm.my

ABSTRACT

This study tries to determine the concentration of sea surface microlayer from different coastal environments (Port Dickson, Negeri Sembilan and Perhentian Island, Terengganu). The concentration of surfactants in both sea surface microlayer and atmospheric aerosols were analysed by using colorimetric method as methylene blue active substances (MBAS) and diethyl violet active substances (DBAS). The results indicated that the concentration of surfactants as MBAS ($0.421 \pm 0.040 \text{ } \mu\text{mol l}^{-1}$) and DBAS ($0.294 \pm 0.123 \text{ } \mu\text{mol l}^{-1}$) were still at the natural concentration level. The flux of surfactants from sea surface microlayer is expected around 2.3 Mmol yr^{-1} compared to the amount of $1300 \text{ Mmol yr}^{-1}$ surfactants in atmospheric aerosols around marine ecosystem.

Keywords: Sea surface microlayer, Surfactants, Atmospheric aerosols

INTRODUCTION

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 represents the interface between the ocean and the atmosphere, where the transfer of material is controlled by complex physico-chemical processes. The Sea Surface Microlayer (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 μm . 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.

Phytoplankton exudates, which consist of proteins and their degradation products, various lipids, glycopeptide-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 and Cosovic, 1996). Results from previous studies have shown surfactants to have been transported from the sea surface microlayer via marine aerosol to coastal regions, where hazardous effects on animals and vegetation arose (Andrews and Larson, 1993; Bussotti *et al.*, 1995; Cincinelli *et al.*, 2003; Giovannelli *et al.*, 1988).

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. Three

- Nicolotti, G., A. Rettori, E. Paoletti, and M.L. Gullino. 2005. Morphological and physiological damage by surfactant-polluted seaspray on *Pinus pinea* and *Pinus halepensis*. *Environmental Monitoring and Assessment*, 105: 175–191.
- Oppo, C., S. Bellandi, N.D. Innocenti, A.M. Stortini, G. Loglio, E. Schiavuta, and R. Cini. 1999. Surfactant components of marine organic matter as agents for biogeochemical fractionation and pollutant transport via marine aerosols. *Marine Chemistry*, 63: 235–253.
- Resch, F. 1986. Oceanic air bubbles as generator of marine aerosol Reidel, Dordercht.
- Sukhapan, J., and P. Brimblecombe. 2002. Ionic surface active compound in atmospheric aerosol. *The Scientific World Journal*, 2: 1138–1146.
- Vojvodic, V., and B. Cosovic. 1996. Fractionation of surface active substances on the XAD-8 resin: Adriatic Sea samples and phytoplankton culture media. *Marine Chemistry*, 54: 119–133.
- Wurl, O. and J.P. Obbard. 2004. A review of pollutants in the sea-surface microlayer (SML): a unique habitat for marine organisms. *Marine Pollution Bulletin*, 48: 1016–1030.

and sub-surface microlayer is estimated at only 7.0 Mmol yr⁻¹.

Comparison from other sources recorded by Latif *et al.* (2005) indicates that the concentration of surfactants from sea surface microlayer can be considered as low compare to other possible sources. Surfactants which believed generated from humic like substances (HULIS) especially generated from high molecular weight substances especially from soil is dominated as the possible sources of surfactants to the atmosphere.

CONCLUSION

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 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. Global flux of surfactants to the atmosphere as MBAS recorded based on this study is 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 as a factor to differentiate the surfactants from the ocean compare to other anthropogenic and natural sources. This factor also can contribute to the destroy of surfactants from sea surface microlayer by photo oxidation processes.

REFERENCES

- Andrews, E., and S.M. Larson. 1993. Effect of surfactant layers on the size changes of aerosol-particles as a function of relative humidity. *Environmental Science & Technology*, 27: 857–865.
- Blanchard, D.C. 1964. Sea-to-air transport of surface active material. *Science*, 146:396.
- Brimblecombe, P. 1996. *Air Composition and Chemistry*. 2nd Edition ed. Cambridge University Press, Cambridge.
- Bussotti, F., P. Grossoni, and F. Pantani. 1995. The role of marine salt and surfactants in the decline of tyrrhenian coastal vegetation in Italy. *Annales Des Sciences Forestieres*, 52: 251–261.
- Cincinelli, A., S. Mandorlo, R.M. Dickhut, and L. Lepri. 2003. Particulate organic compounds in the atmosphere surrounding an industrialised area of Prato (Italy). *Atmospheric Environment*, 37: 3125–3133.
- Cincinelli, A., A.M. Stortini, M. Perugini, L. Checchini, and L. Lepri. 2001. Organic pollutants in sea-surface microlayer and aerosol in the coastal environment of Leghorn - (Tyrrhenian Sea). *Marine Chemistry*, 76: 77–98.
- Cini, R., and G. Loglio. 1997. Adsorption and pollutant transport by marine aerosol. *Marine Pollution Bulletin*, 34: 501–504.
- Cini, R., F. Prodi, G. Santachiara, F. Porcu, S. Bellandi, A.M. Stortini, C. Oppo, R. Udisti, and F. Pantani. 2002. Chemical characterization of cloud episodes at a ridge site in Tuscan Appennines, Italy. *Atmospheric Research*, 61: 311–334.
- Dobson, C.M., G.B. Ellison, A.F. Tuck, and V. Vaida. 2000. Atmospheric aerosols as prebiotic chemical reactors. *Proceedings of the National Academy of Sciences of the United States of America*, 97: 11864–11868.
- Giovannelli, G., P. Bonasoni, G. Loglio, C. Ricci, U. Tesei, and R. Cini. 1988. Evidence of anionic-surfactant enrichment in marine aerosol. *Marine Pollution Bulletin*, 19: 274–277.
- Harvey, G.W. 1966. Microlayer collection from the sea surface: A new method and initial results. *Applied Oceanography*, 11: 608–613.
- Latif, M.T., and P. Brimblecombe. 2004. Surfactants in atmospheric aerosols. *Environmental Science & Technology*, 38: 6501–6506.
- Latif, M.T., P. Brimblecombe, N.A. Ramli, J. Sentian, J. Sukhapan, and N. Sulaiman. 2005. Surfactants in South East Asian Aerosols. *Environmental Chemistry*, 2: 198–204.
- Loglio, G., U. Tesei, G. Marilli, and R. Cini. 1986. The role of surfactants in coastal sea pollution. *Marine Pollution Bulletin*, 17: 466–468.
- Loglio, G., U. Tesei, G. Mori, R. Cini, and F. Pantani. 1985. Enrichment and transport of surfactants in marine aerosol formed during particular weather conditions. *Nuovo Cimento Della Societa Italiana Di Fisica C-Geophysics and Space Physics*, 8: 704–713.
- Marcomini, A., G. Pojana, A. Giacometti, and C. Oppo. 2001. Aerosolization of an anionic surfactant (LAS) and dissolved organic carbon (DOC) under laboratory conditions. *Chemosphere*, 44: 257–262.

compared to the cationic surfactants as DBAS for both sampling stations. This results indicated that the concentration of surfactants in the sea surface microlayer more dominated by anionic surfactants compare to cationic surfactants.

The concentration of anionic surfactants can also be measured in the microgram per liter ($\mu\text{g l}^{-1}$) by assumption of the molecular weight of anionic surfactants as same as the molecular weight of sodium dodecyl sulphate ($288.38 \text{ g mol}^{-1}$). The results recorded at Port Dickson ($121 \mu\text{g l}^{-1}$) found in this study was higher than the concentration of surfactants as methylene blue active substances (MBAS) in the sea-surface microlayer (SML) found by Cincinelli *et al.* (2001) in the coastal environment of Leghorn (Tyrrhenian Sea, Italy) (ranged between 40 and $68 \mu\text{g l}^{-1}$). The sampling station around Port Dickson, which influence by tourism activities and located at the tropical area which more influenced by photo-oxidation to the humic-like substances as a source of surfactants in the natural environment (Latif *et al.*, 2005) as well as anthropogenic factors from tourism industries.

The concentration of surfactants as MBAS and DBAS in the atmospheric aerosols recorded at Perhentian Island Terengganu were $56.60 \pm 33.83 \text{ pmol m}^{-3}$ and $2.30 \pm 0.42 \text{ pmol m}^{-3}$ respectively, a little bit higher compared by the data from previous studied recorded in aerosols influenced by sea surface at Weybourne and Canary Island by Latif and Brimblecombe (2004) which indicated the concentration of MBAS were around undetected to 31.3 pmol m^{-3} and undetected for DBAS. The location of Perhentian Island at tropical areas with high influenced of humic material seems to influence the concentration of surfactants in the atmospheric aerosols.

The concentration of surfactants especially as MBAS were found quite lower compared to the concentration of MBAS recorded in the atmospheric aerosols collected from urban and semi urban areas such as Bangi Selangor ($111\text{--}287 \text{ pmol m}^{-3}$), Penang ($74\text{--}378 \text{ pmol m}^{-3}$) and Bangkok ($240\text{--}434 \text{ pmol m}^{-3}$) as mentioned by Latif and Brimblecombe (2004) which indicated that anthropogenic sources more dominated the concentration of anionic surfactants compared to the sources from sea surface microlayer. For the DBAS concentration, the results recorded from this study even though quite low compared to other studies but the different was not significant.

Once again the concentration of anionic surfactants as MBAS was found far higher than the concentration of cationic surfactants as DBAS. This results followed the results from previous studies (Latif and Brimblecombe, 2004; Latif *et al.*, 2005; Sukhapan and Brimblecombe, 2002) which indicated the concentration of anionic surfactants were dominated the concentration of surfactants in the atmospheric aerosols.

Flux of MBAS from sea surface microlayer

The flux of MBAS based on their production from sea surface microlayer (ocean) and comparison to other possible sources as recorded by Latif *et al.* (2005) is shown in Table 2. The estimation of flux of MBAS from the sea surface is estimated from the concentration of MBAS in sea water and the flux of sea water to the atmosphere. The concentration of MBAS on the sea surface and in the sub-surface microlayer is around $121 \mu\text{g l}^{-1}$. Based on this amount and the flux of sea water to the atmosphere (4290 Tg yr^{-1}) the amount of flux of MBAS from the sea surface

Table 2. Flux of MBAS from ocean to the atmosphere compare to other possible sources.

Possible sources	MBAS Flux (Mmol yr ⁻¹)
Ocean	7.0
<i>Other sources</i>	
Soil	91.0
Forest / Vegetation	3.8
Fossil Fuel	51.2
Biomass Burning	30.8

vial was turned upside-down. After the chloroform had separated out from the water, some of the chloroform layer was collected using a glass-syringe equipped with a metal needle inserted through the Teflon liner of the holed screw-cap (the vial was still in the inverted position). The absorbance of chloroform phase was measured by spectrophotometer at wavelength 650 nm. The calibration curve with a concentration range of 0 to 2 μM was constructed using sodium dodecyl sulphate, SDS (1000 μM) as the reference compound, using the same method for aerosol extract, but replacing the aerosol with SDS standard solution. The lower limit of detection was 0.05 μM SDS which was estimated as the mean of the blank sample.

Estimation of Flux of MBAS Produced from Sea Surface Microlayer

The estimation of the amount of MBAS produced from sea surface microlayer is based on the concentration of surfactants as MBAS in the sea surface microlayer ($\mu\text{mol g}^{-1}$) and the total flux of sea surface microlayer to the atmosphere (Brimblecombe, 1996). The maximum photo-oxidation factor (POF) which able to generate surfactants as MBAS especially from various sources especially from humic substances to ozone was estimated as 4 times higher from the concentration surfactants in any substances before photo-oxidation processes. This estimation was made by assuming that the concentration of

MBAS increases about fourfold after exposure to sunlight and oxidants in the atmosphere.

Model

Estimation of flux of MBAS based on their production from sea surface microlayer (mol yr^{-1})

$$= \text{MBAS} \times \text{POF} \times \text{PF}$$

where

MBAS = Concentration of MBAS from sea surface microlayer ($\mu\text{mol g}^{-1}$)

POF = Photo-oxidation factor (4)

PF = Particle flux of sea surface microlayer (4290 Tg yr^{-1})

RESULTS AND DISCUSSION

The results indicated that the concentration of as methylene blue active substances (MBAS) and disulphine blue active substances (DBAS) from sea surface microlayer collected at Port Dickson, one of the developed coastal areas was $0.421 \pm 0.040 \mu\text{mol l}^{-1}$ and the $0.294 \pm 0.123 \mu\text{mol l}^{-1}$ respectively (Table 1). On the other hand the concentration of MBAS and DBAS recorded at Perhentian Island was quite low; $0.0421 \pm 0.004 \mu\text{mol l}^{-1}$ for MBAS and $0.016 \pm 0.004 \mu\text{mol l}^{-1}$ for DBAS. Anthropogenic factors e.g. surfactants from tourism activities seem to influence the concentration of surfactants in the sea surface microlayer at Port Dickson. The concentration of anionic surfactants as MBAS was found higher

Table 1. Concentration of surfactants as methylene blue active substances in the sea surface microlayer and atmospheric aerosols

Samples	MBAS	DBAS
Atmospheric aerosols (n=5)	$56.60 \pm 33.83 \text{ pmol m}^{-3}$	$2.30 \pm 0.42 \text{ pmol m}^{-3}$
Sea surface microlayer		
Port Dickson (n=5)	$0.421 \pm 0.040 \mu\text{mol L}^{-1}$	$0.294 \pm 0.123 \mu\text{mol L}^{-1}$
Perhentian Island (n=5)	$0.021 \pm 0.004 \mu\text{mol L}^{-1}$	$0.016 \pm 0.004 \mu\text{mol L}^{-1}$

types of spray drops are produced: (1) 'jet drops' forming from the bubbles that are involved in the rotational motion of the wave scavenging the bulk seawater for some meters below the surface; (2) 'film drops', formed preferentially by the collapse of the whitecaps in front of the wave; (3) 'shearing drops' originated by strong winds ($15\text{-}20\text{ ms}^{-1}$) directly from the wave crest by the friction force of the high speed wind. This type of drop represents, for the most part, giant aerosol particles which therefore have a short life even in very strong winds (Oppo *et al.*, 1999).

According to Cini *et al.* (2002), marine aerosols can change their composition from that of sea water because of the interaction of natural surfactants with elements and organic compounds which can also be pollutants. According to several authors, who studied the marine aerosol formation process under environmental conditions, surfactants of both natural and synthetic origin partition between bulk water, surface microlayer and aerosol phases. The transfer of organic materials from marine water to the atmosphere may be responsible for the distribution of trace-level substances and may contribute to the mobilisation of micropollutants at a global level (Marcomini *et al.*, 2001). 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).

MATERIAL AND METHODS

This study tries to determine the concentration and flux of atmospheric surfactants from different coastal environments (Port Dickson, Negeri Sembilan and Perhentian Island, Terengganu).

Sea surface microlayer collection

Sea surface microlayer was collected 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.

Aerosol Sample Collection

Aerosol samples with diameter size below than 10 micrometer (PM_{10}) were collected at Perhentian Island, Terengganu, by using volumetric

flow control (VFC) of high volume sampler (HVS) equipped filter papers. The high volume sampler was calibrated before being used according to manual supplied by the manufacture. The flow rate of High Volume Sampler was recorded using special graph and pen inside the metal box.

Before being used, the Whatman QM-A glass fiber filter paper (20 x 25cm) were packed in aluminium foil and pre-fired at 500°C for 2 h in order to remove organic species, conditioned in a dessicator for 24 h, then weighted with Mettler AE240 electronic balance. After sampling, the filters were carefully packed in aluminium foils (pre-fired as the filters), conditioned in a dessicator for 24 h prior to weight and stored in a refrigerator (4°C) until analysis.

Aerosol Sample Extraction

Half of the filter paper with PM_{10} samples were cut into 1 cm^2 squares and put into a conical flask, and then 75 ml of Milli Q water was added. The mixture was sonicated for 45 minute. Then the mixed solution was filtered through a cellulose acetate filter with a porous size of $0.2\text{ }\mu\text{m}$ using a filtration apparatus linked to a vacuum pump. The filtered solution was dilute to 100 ml in volumetric flask and was kept at 4°C . Surfactant analysis was done within a few days of extraction.

Determination of surfactant as methylene blue active substances (MBAS)

A volume of 20 ml sample solution was put in 40 ml vial (vial A) equipped with screw cap. The alkaline buffer prepare by the mixture of 24 g sodium hydrogen carbonate and 27 gm sodium carbonate in 1l Milli-Q water (2 ml) and neutral methylene blue solution (0.35 g l^{-1}) (1 ml) followed by chloroform (5 ml) was added into 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 one minute. The vial was then left for phase separation. The screw-cap was loosening to release the pressure inside. Once the two phases were separated a Pasteur pipette was used to transfer all of the chloroform layer into the new vial (vial B) that contained Milli Q water (22 ml) and acid methylene blue solution ($0.35\text{ g methylene blue} + 6.5\text{ ml H}_2\text{SO}_4\text{ l}^{-1}$) (1 ml). Vial B was shaken using a vortex mixer for one minute. The cap was loosening for few seconds and re-tightened. The