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ATMOSPHERIC SURFACTANTS AROUND LAKE ECOSYSTEM OF TASIK KENYIR, TERENGGANU

(Surfaktan di Atmosfera di Persekitaran Ekosistem Tasik Kenyir, Terengganu)

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Abstract

Lake ecosystem is a sources of natural organic matter characteristic by humic-like substances (HULIS) believe to have high amount of surface active agents (surfactants) which capable to influence the cloud and climate. This study determined the concentration of anionic surfactants in the atmosphere around lake ecosystems at Kenyir, Terengganu. Aerosols samples were collected by using a High Volume Air Sampler (HVAS) equipped with high volume impactor (to separate between fine and coarse mode aerosols) and glass-fibre filter paper at flow rate of 1.13 m^{3}min^{-1} for 24 hours. Several possible sources of natural surfactants in the atmosphere e.g. soils, vegetations and surface water were also collected in order to determine the possible sources and flux of anionic surfactants in the atmosphere. Anionic surfactant was analysed based on colorimetric methods by using methylene blue active substances (MBAS) and UV-visible spectrophotometer at 650 nm. Subsequently, simplified calculations were conducted in estimating the flux of anionic surfactants from various possible sources. The results indicated that the concentration of anionic surfactants in aerosols (coarse and fine mode), soil, vegetation and surface water were 59.17 ± 2.61 µmol/m^3 and 78.10 ± 9.30 µmol/m^3, 0.33 ± 0.17 µmolg^{-1}, 0.28 ± 0.08 µmolg^{-1} (dry weight) and 0.01 ± 0.004 µmolL^{-1}, respectively. The overall flux of surfactants signified that soils provide the highest amount of surfactants which is 119.39 Mmolyr^{-1} in comparison to other possible sources (vegetation = 26.88 Mmolyr^{-1}and surface water = 12.1 x 10^{-6} Mmolyr^{-1}). Results indicated that soil become a significant natural source of anionic surfactants to the atmosphere which may due to the availability of HULIS.

Keywords: anionic surfactants, lake ecosystems, flux of anionic surfactants, HULIS

Abstrak

Ekosistem tasik yang merupakan sumber bahan organik yang dicirikan sebagai sebatian seperti humik (HULIS) dipercayai mempunyai surfaktan dalam kuantiti yang tinggi dan berupaya mempengaruhi awan dan cuaca. Kajian ini dilakukan untuk menentukan kepekatan surfaktan anion di persekitaran Tasik Kenyir, Terengganu. Sampel aerosol dikutip pada kadar alir 1.13 m^{3}min^{-1} selama 24 jam menggunakan Pensampel Udara Berisipadu Tinggi *(High Volume Air Sampler, HVAS)* yang dilengkapi dengan impaktor (untuk memisahkan aerosol bersaiz halus dan kasar) dan kertas turas gentian kaca. Beberapa sumber surfaktan di udara seperti tanih, vegetasi dan air di permukaan tasik juga dikutip untuk menentukan sumber dan fluks surfaktan anion di atmosfera. Surfaktan anion dianalisis menggunakan kaedah kolorimetri dengan menggunakan sebatian aktif metilena biru *(methylene blue active substances,MBAS)* dan spektrofotometer UV-Vis pada panjang gelombang 650 nm. Seterusnya pengiraan untuk menganggar surfaktan anion daripada pelbagai sumber dilakukan. Keputusan menunjukkan bahawa kepekatan purata surfaktan anion dalam aerosol (kasar dan halus), tanih, vegetasi dan air permukaan masing-masingnya ialah 59.17 ± 2.61 µmol/m^3 dan 78.10 ± 9.30 µmol/m^3, 0.33 ± 0.17 µmolg^{-1}, 0.28 ± 0.08 µmolg^{-1} (berat kering) dan 0.01 ± 0.004 µmolL^{-1}. Fluks keseluruhan surfaktan mendapati tanih menyumbangkan nilai surfaktan anion terbesar iaitu 119.39 Mmolyr^{-1} berbanding dengan sumber-sumber lain (vegetasi = 26.88 Mmolyr^{-1} dan air permukaan = 12.1 x 10^{-6} Mmolyr^{-1}). Kesimpulan mendapati tanih adalah merupakan sumber semulajadi surfaktan anion yang utama dan ini mungkin disebabkan kehadiran HULIS.

Kata kunci: surfaktan anion , ekosistem tasik, fluks surfaktan anion, HULIS

Introduction

Surfactants (a contraction of surface active agents) have the potential in influencing the global climate. In environmental context, surfactants play an important role due to their ability to reduce surface tension, which affect the physical properties of cloud droplets and eventually lead to enhancement of cloud albedo [1]. Surfactants can be naturally derived from various possible sources. However, it is hard to differentiate significantly the contribution of each source towards load of surfactants in atmosphere. Thus, estimation of flux might be useful in predicting the contribution of possible sources. For this reason, Lake Kenyir representing the natural ecosystem was chosen where all possible biogenic sources of surfactants were available, for identifying the sources of surfactants.

Surfactants can be naturally generated from various sources. Several studies indicate that some class of compound in atmosphere displayed similar characteristics as humic substances found in soil and therefore this compound is often called humic-like substances. The formation of stable humic substances was resulted from the transformation of soil organic matter comprised of plant and animal residues by microorganism and chemical process [2, 3, 4]. Humic substances are generally classified as humin, humic acid, and fulvic acid [5]. Among all, it was noted that oxidation process has the ability to generate surfactants from humic acid. Solvent extractable (lipophilic) and water soluble products are often caused by the chemical degradation (hydrolysis, oxidation, reduction) of humic acid [6]. Surfactants also can be correlated with HULIS since some characteristics (e.g ability to reduce the surface tension, water solubility etc.) were comparable [7]. Thus it can suggested that HULIS can be categorized as surfactants as it displays similar characters like surfactants.

Apart from that, various vegetation surrounded the lake environment as well can generate surfactants in atmosphere. Earth's vegetation naturally releases huge amounts of organic species into the air [8]. Certain fraction of particulate matter is present in atmosphere due to conversion of volatile organic compound. It was found that these biogenic VOC have the ability to produce condensable products as a result of rapid oxidation by radicals and ozone into less volatile oxygenated organics that have surface-active properties [9, 10]. The lake surface layer able to act as a sink that accumulate various organic substances, hence can be regarded as a source of surfactants. Besides, phytoplankton and algae that accumulate at the surface layer of water bodies can exedute certain organic compounds. Various researcher found out that these compounds comprised functional groups mainly carbonyl compounds and carboxylic acids which might be decomposition products of longer chain fatty acids [11, 12, 13, 14]. And, it was noted that these compounds are known to be surface active.

Taken all into account, lake environments proved to cater an adequate environment for the study of surfactants formation from natural sources. By estimating the flux of surfactants from various sources, it is possible for us to understand the role of surfactants which found to be able to contribute to the changes of global climate.

Experimental

Sampling location

Kenyir Lake which located in the state of Terengganu (N = $5^0$12.902', E = $102^0$38.306') is a well-known as artificial lake which surrounded by tropical forest. The lake covers 260 km² and contains 340 small islands, which were once hiltops and highlands, more than 14 waterfalls, numerous rapids and rivers. Besides, it is also home to numerous species of freshwater fishes and exotic wildlife. From studies and observations conducted by the Department of Fisheries, species such as the *big Lampam Sungai* (Barboides), *Kelah* (Malaysian Mahsee), *Toman* (Snakehead), *Kawan* (Friendly Barb), *Kalui* (Giant Gouramy) and *Kelisa* (Green Arowana) are found in waters and around dead trees. Hence, this man-made lake certainly provides a suitable environment in investigating the contribution of natural ecosystem towards the surfactants load in atmosphere.

Sampling and preparation of sample

Aerosol

High volume air sampler equipped with glass fibre filter paper with a flow rate of 1.13 $m^3 min^{-1}$ was used collect atmospheric particulate matter for 24 hours. After sampling, filter papers were divided into 4 sections. A quarter of the samples were put in a centrifuge tube containing 50ml of deionised water. Prior to analysis, the solutions were then sonicated for about 45 minutes and were filtered through 0.2um Whatman filter paper 47mm diameter in 100ml volumetric flask.

Surface water

Surface microlayer was collected at several sampling by using rotation drum as suggested elsewhere [15]. 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 vial at 4^0C prior to analysis by colorimetric methods as methylene blue active substances (MBAS) for anionic surfactants.

Soil

The surface of soil (approximately 5cm ~ representing zone A) was collected using a wooden scoop. Soil samples were placed in a sealed plastic bag and labeled before being analysed in laboratory. The samples were dried in an oven for 2 hours at 40^0C before being sieved through a 63um sieve. Next, 50mg of samples were weighed and placed in a centrifuge tube filled with 50ml of deionised water. The solutions were then sonicated for about 45minutes and were filtered through 0.2um Whatman filter paper 47mm diameter in 100ml volumetric flask.

Vegetation

Several part of vegetation (leaf, bark and stem) were collected and kept in a sealed plastic bag. Samples were dried in an oven for 2 hours at 40^0C before being meshed in a blender. Next, 50mg of grinned samples were weighed and placed in a centrifuge tube filled with 50ml of deionised water. The solutions were then sonicated for about 45 minutes and were filtered through 0.2um Whatman filter paper 47mm diameter in 100ml volumetric flask.

Determination of anionic surfactant as methylene blue active substances (MBAS)

The sample solution (20 mL) was put in 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 separating funnel 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 separating funnel and 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. The limit of detection estimated as blank solution, 0.05 µM SDS, was analysed using the same method as for the aerosol extracts.

Estimation of MBAS Fluxes Produces from Various Sources

A simplify model was employed for estimating the amount of MBAS produced from various possible sources (e.g. soils, vegetation, and surface water), based on the average concentration of MBAS found in aerosols produced from key sources, and flux of particles (PF) from each source [16, 17, 18, 19, 20] (Table 1). Photo-oxidation factor (POF), the maximum value which able to generate surfactants as MBAS was estimated as four times higher from the concentration surfactants in any substances before photo-oxidation process [21]. This estimation was made by assuming that the concentration of MBAS increases about fourfold after exposure to sunlight and oxidants in the atmosphere.

Table 1**:** Particle flux of possible sources of atmospheric surfactants.

Possible sources	**Particle Flux (PF)** (Tg yr^{-1})
Soil	91
Forest/Vegetation	24
Surface water	4290

Model

Estimation of flux of MBAS based on their production from various sources (mol yr^{-1})

= MBAS x POF x PF

where

MBAS = Concentration of MBAS from various possible sources (μmol g^{-1})
POF = Photo-oxidation factor
PF = Particle flux of each source (Tg yr^{-1})

Results and Discussion

Possible sources of surfactants in lake ecosystem

The concentration of surfactants was found high in soils samples which is 0.328 ± 0.165 μmolg^{-1}, followed by vegetation (0.28 ± 0.08 μmolg^{-1}) and surface water (0.01 ± 0.004 μmolL^{-1}), respectively. The high concentration of surfactants presence in soil is corresponding with the hypothesis that surfactants might be originated from humic-like substances (HULIS) [7]. HULIS are ubiquitous may consist of vegetation-derived organic microparticles or may partially be generated from biogenic unsaturated hydrocarbons. Studies carried out by other researchers have shown that organic components in airborne dust were similar to humic substances found in soil and aqueous systems [22, 23]. Thus, it can be suggested that humic acids in soils represent one potential source of HULIS.

There is a possibility that surfactants concentration might be influenced by vegetation as the difference between sources (i.e soil and vegetation) is insignificant ($p>0.05$). Photochemical oxidation products from volatile organic precursors emitted by vegetation were also detected in the particulate matter [24]. However, spectroscopic measurement by using UV spectrometer verifies the fact that soil is the main source that contributes to the high concentration of surfactants in air (Figure 1). The UV/VIS spectra of aerosol extract exhibit featureless curves of increasing absorbance towards lower wavelength. A study on the existence of HULIS in airborne particulate matter collected in same environment which is forested and agriculturally area (Sauerland, Germany), also observe the similar pattern of spectra [25]. Thus it can be suggested that surfactants can be correlated with HULIS found in soil.

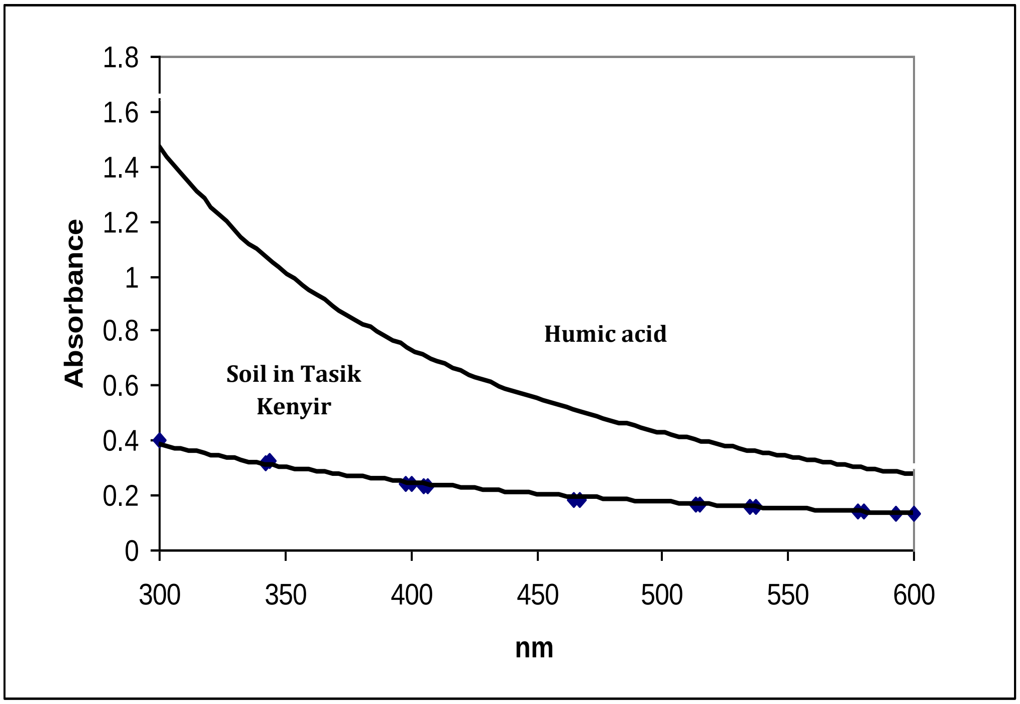

Figure 1: UV/Vis spectra

Flux of surfactants

The flux of MBAS was estimated from the average concentration of MBAS found in aerosols produced from key sources, and flux of particles (PF) from each source [18]. The overall flux of surfactants signified that soils provide the highest amount of surfactants which is 119.39 Mmolyr^{-1} in comparison to other possible sources (Table 2) (vegetation = 26.88 Mmolyr^{-1}and surface water = 0.21 Mmolyr^{-1}). This result also mirrored those from previous studies by suggest soil particles which are rich in humic substances can act as a major sources of anionic surfactants in atmospheric aerosols [17, 18, 19, 20].

Table 2: Flux of MBAS to the atmosphere based on their possible sources at Tasik Kenyir, Terengganu

Type	**Possible sources**	**MBAS Flux** (Mmol yr^{-1})
Natural resources	Soil	119.39
	Forest/Vegetation	26.88
	Ocean	0.21

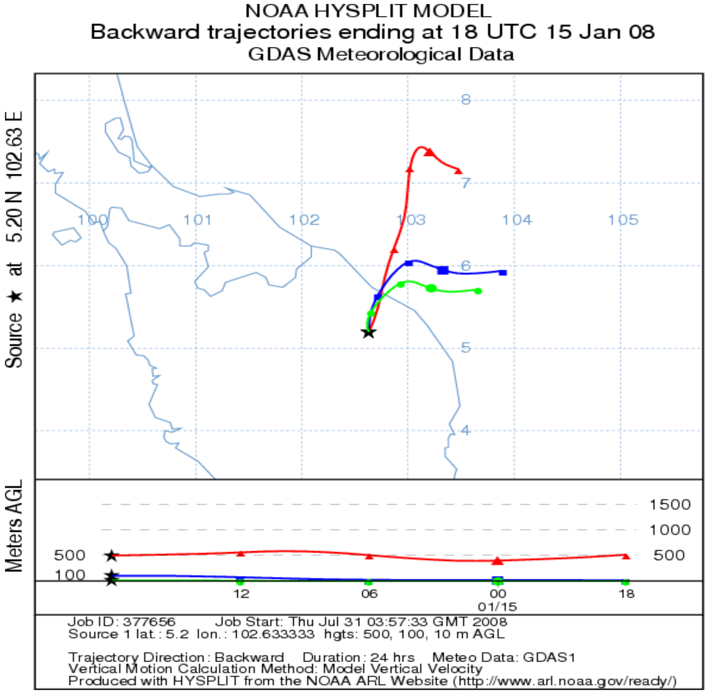

Figure 2**:** Backward trajectories

Back trajectory

The backward trajectory analysis using HYSPLIT model (***HY**brid **S**ingle- **P**article **L**agrangian **I**ntegrated **T**rajectory Model)* clearly shows that the air parcel was originated from South China Sea (Figure 2). Although the distance between sampling point and sea was considerable, it is interesting to note that sea-surface microlayer can be considered as one of the possible sources surfactants in lake ecosystem. Surfactants in sea surface microlayer generally originated from bubble bursting at the ocean surface [26]. Organic matter can be directly incorporated in marine particles when gas bubbles burst at the surface. In addition, rising gas bubbles scavenge organic material such as surfactants in the water column when they rise towards the surface. Apart from that, marine phytoplankton was also known to produce surface-active materials as part of their metabolism [27]. However, as mentioned earlier, soil remain to be the dominant source as the aerosol extracts display similar characteristic with humic acid found in soil (Figure 1). Thus, there is a possibility that, wash out and dilution processes from rain water are believed to have reduced the amount of surfactants. Hence explained the fact that the load of surfactants in lake ecosystem were not influenced by surfactants originated from sea surface microlayer.

Conclusion

Emission of surfactants as MBAS to the atmosphere can originate from various possible sources found in lake environment. Hence indicated that natural ecosystem has the potential to contribute to the amount of surfactants in atmosphere. Since surfactants and HULIS merely display similar properties, it can be suggested that surfactants might be a product generated from the oxidation of humic substances found in soil. Thus, apart from biogenic influence, that secondary mechanism also plays an important role in contributing to surfactants load in atmosphere.

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