Environment and Ecology Research 9(4): 159-165, 2021
DOI: 10.13189/eer.2021.090403 http://www.hrpub.org

Methylene Blue Active Substances (MBAS) and Linear Alkylbenzene Sulphonates (LAS) in Urban and Suburban Atmospheric Aerosol

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Received February 18, 2021; Revised April 12, 2021; Accepted June 5, 2021

Cite This Paper in the following Citation Styles

(a): *[1] Nurul Bahiyah Abd Wahid, Helmiah Abdul Razak, Intan Idura Mohamad Isa, Mohd Talib Latif, Noorlin Mohamad, Thunwadee Srithawirat, Doreena Dominick, Suzita Ramli, Nor Zila Abd Hamid, Tengku Noor Arbaee Tg Azha , "Methylene Blue Active Substances (MBAS) and Linear Alkylbenzene Sulphonates (LAS) in Urban and Suburban Atmospheric Aerosol," Environment and Ecology Research, Vol. 9, No. 4, pp. 159 - 165, 2021. DOI: 10.13189/eer.2021.090403.*

(b): *Nurul Bahiyah Abd Wahid, Helmiah Abdul Razak, Intan Idura Mohamad Isa, Mohd Talib Latif, Noorlin Mohamad, Thunwadee Srithawirat, Doreena Dominick, Suzita Ramli, Nor Zila Abd Hamid, Tengku Noor Arbaee Tg Azha (2021). Methylene Blue Active Substances (MBAS) and Linear Alkylbenzene Sulphonates (LAS) in Urban and Suburban Atmospheric Aerosol. Environment and Ecology Research, 9(4), 159 - 165. DOI: 10.13189/eer.2021.090403.*

Abstract Surfactant is one of the pollutants derived from atmospheric aerosol that can adversely affect the human health and environment. This study aims to characterize the level of anionic surfactants as Methylene Blue Active Substances (MBAS) and Linear Alkylbenzene Sulphonates (LAS) extracted from atmospheric aerosol from urban (Kuala Lumpur) and suburban (Bangi) area of Malaysia. For aerosol sampling, a high volume sampler (HVAS) with a cascade impactor was used to collect atmospheric aerosol sample according to particle size (coarse mode (> 1.5 μm) and fine mode (< 1.5 μm)). The level of MBAS was determined using UV-Vis Spectrophotometer based on colorimetric method, while the concentration of LAS was determined using High-Performance Liquid Chromatography (HPLC). Results showed that the composition of MBAS and LAS for both sampling stations was dominated by fine mode particles compared to coarse mode with a significant difference ($p < 0.05$). Kuala Lumpur showed higher concentration of MBAS (81.69 ± 13.01 ng m^{-3}) compared to LAS (2.96 ± 1.22 ng m^{-3}), while Bangi recorded lower level of both MBAS and LAS (44.58 ± 10.05 ng m^{-3}, 2.48 ± 1.28 ng m^{-3}), respectively. In terms of monsoonal effect, the highest level of surfactants as MBAS and LAS in both stations was recorded during southwest monsoon. A positive correlation was detected between MBAS and LAS. However, it was not significantly correlated ($p > 0.05$). From this study, it can be concluded that MBAS

concentrations in urban and suburban atmosphere are not fully affected by commercial LAS. Majority of MBAS may be presented from other natural activities and anthropogenic sources such as motor vehicle emission, combustion of biomass, and the earth's crust. The management of surfactants' use needs to be reconsidered to enhance a better atmosphere especially in urban and suburban area in the future.

Keywords Anionic Surfactants, Monsoon, Fine Mode Particle, Coarse Mode Particle, Anthropogenic Sources

1. Introduction

In recent years, the composition of atmospheric aerosol has become one of the major issues in most developing countries due to the decrease in air quality. The atmospheric aerosol is very tiny pieces of liquid or solid suspended in the Earth's atmosphere and it is invisible, including soot, smoke and dust particles [1]. According to Sharma et al. [2], vehicle exhaust, industrial emission waste burning and construction activities have increased the amount of atmospheric aerosol.

Surface active agent (known as surfactant) is one of the pollutants derived from atmospheric aerosol that might cause various environmental problems and also affect human health [3,4]. Becagli et al. [5], found that the presence of atmospheric surfactants might adversely affect vegetation. Polar organic anthropogenic micropollutants discharged from wastewater into the marine system widely led to high nutrient concentrations. Commercial products used as detergents contribute to the possible contamination of the environment by surfactants [6].

Methylene Blue Active substances (MBAS) are one of the anionic surfactants that can be found in the atmosphere. The principal of MBAS was based on the development of a chloroform extractable ion-association complex between the anionic surfactants and anionic (methylene blue) dyes [7,8]. Ying [9], said that the use of several chemicals by motor vehicles and industries, as well as the quantity of humic-like substances led to a high amount of anionic surfactants found in atmospheric aerosol. Previous research has found that, three main sources of MBAS identified in urban and suburban atmosphere were dominated by vehicular emission, followed by soil/road dust and came from the sea spray [6,10,11].

Whereas, linear alkylbenzene sulfonate (LAS) is one of the commercial anionic surfactants used in the industry. It has been extensively used over the last 30 years [12]. The commercial products used are extremely complex mixtures containing homologous alkyl chains in the range of 10 - 13 carbon (C_{10} - C_{13} LAS) units [5,9,12]. LAS are believed to be in atmospheric aerosols as a result of chemical reactions and condensation processes through wastewater treatment plants, surface runoff and through rivers or oceans. The presence of LAS in atmospheric aerosols is in low concentrations, and may not harm humans, but it affects the growth and development of plants and can contribute significantly to climate change [5,9]. Chemically, the LAS chain contains 10 - 13 carbon units of C_{10}, C_{11}, C_{12} and C_{13}. The commercial LAS consists of 20 individual components where its global revenue is 2.2×10^6 million tons per year. Due to the adverse impacts of surfactants on the global climate change and human health, the concentration and characterization of anionic surfactants in the atmosphere need to be monitored and managed regularly.

The aim of this study is to analyze the MBAS and LAS in atmospheric aerosol based on particle sizes, sampling locations and monsoonal effect. This paper also discussed the relationship between MBAS and LAS and to see if this commercial LAS is one of the MBAS sources in the atmospheric aerosol.

2. Materials and Methods

2.1. Sampling Areas and Procedures

Kuala Lumpur (urban area) and Bangi (suburban area) were chosen as the sampling stations for this study. Kuala Lumpur is a very well-known city with many commercial activities and industries were centered here. It is located in Klang Valley which is also the centre for administration. The aerosol sampling was conducted at Station S1, which is located in front of National University of Malaysia (Kuala Lumpur Campus) (N 03º 10.088' E 101º 42.026'). The sampling was conducted at the open space which is 1.5 m above the ground level. This station is near to Jalan Tuanku Abd Rahman and a famous market known as Chow Kit Road, which is one of the areas with heavy traffic.

The second station is located in the state of Selangor, Malaysia. The sampling was conducted at Station S2, in National University of Malaysia (Bangi Campus) (N 02º 55.890' E 101º 46.662'). Bangi is a suburban area with a lot of residential areas. The development of several industries and commercial activities around this area has increased the traffic volume and number of population around Bangi. Fig. 1 shows the sampling stations.

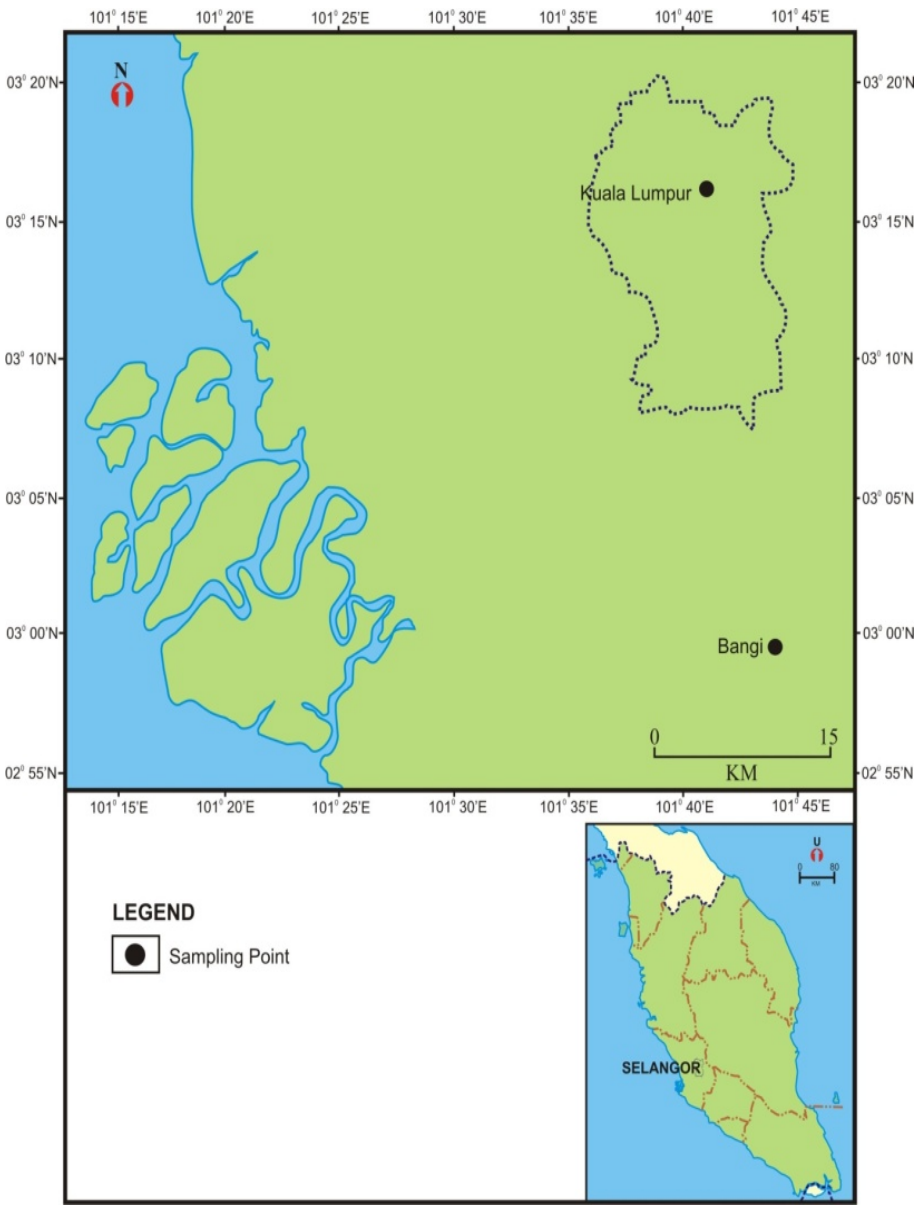

Figure 1. Sampling Locations for Atmospheric Aerosol

2.2. Sample Preparation

Two fractions of atmospheric aerosol (fine and coarse mode) were collected using a High-Volume Air Sampler, (HVAS, Model TE-5170 TSP, Tisch Environmental). A cascade impactor (Staplex) was used to separate the fine and coarse mode particles. Coarse mode particles with a diameter of more than 1.5 µm were collected on slotted filter paper (Westech Instrument). Whereas, fine mode particles with a diameter less than 1.5 µm, was collected on backup filter paper (EPM2000, Whatman). The type of the filter paper must be microfiber glass.

Before being used in sampling, all filter papers need to be wrapped using aluminum foil. The filter papers then we heated in a furnace for 5 h at 500˚C temperature. This step needs to be conducted in order to remove any organic contaminants. After that, the filter papers were put in the desiccator for at least 24 h. The four digit electronic balance was used to weigh the filter papers. During sampling, the HVAS was run for 24 h with the flow rate of 1.13 m^3 min^{-1}. After sampling, the filter papers were put back in the desiccator. After 24 h, the samples were reweighed again. Then, all the samples were kept in a fridge at 4˚C temperature until further extraction process.

2.3. MBAS Extraction and Analysis

For MBAS extraction process, 1/2 of the slotted filter papers (coarse mode particles) were used in the processes. Whereas, a 1/4 of the backup filter papers were required for fine mode samples. Before extraction, the filter papers were cut into 1 cm^2 piece. To begin the analysis, 40 mL of

ultra-pure water (18.2 MΩm resistivity) was added into the vial containing the samples. The vial was then sonicated for 45 min using ultrasonic sonicator. A vacuum filter pump was used to filter the samples through a 0.2 µm pore size filter paper (Whatman, cellulose acetate, 47 mm size). The samples were then diluted to 100 mL with ultra-pure water.

For MBAS analysis, 20 mL of extracted sample was transferred into a 40 mL glass vial equipped with a screw cap. Then, the alkaline buffer (2 mL) were added to the vial, and followed by methylene blue solution (1 mL) and chloroform (5 mL). The mixture was shaken vigorously with a vortex mixture. When the two phases liquid layer were fully separated, the bottom layer (chloroform) was transferred into a new vial which contained ultra-pure water (22 mL) and acidic methylene blue (1 mL). The vial was shaken again and then, the chloroform (bottom layer) was transferred using a Pasteur pipette into a clean quartz cell. The 10 mm quartz cell was used in this process. Then, the absorbance of the chloroform extract was determined at a wavelength of 650 nm, using a UV-Vis Spectrophotometer [11,13]. For this analysis, the MBAS calibration curve was developed using different concentration of sodium dodecyl sulfate (SDS) standard.

2.4. LAS Extraction and Analysis

HPLC is used in chemical analysis to separate, identify and measure the level of each LAS component in the samples. Each component in the sample interacts differently with an adsorption agent, resulting in different flow rates for different components and leads to the separation of components. In this research, HPLC 1220 (Agilent Technologies, USA) was used with fluorescent detectors (FLD). HPLC relies on pumps to carry fluids and sample blends through columns containing sorbents, leading to the separation of sample components. The sample mixture components are separated from each other due to different degrees of interaction with the adsorbent particles. Pressure fluid usually consists of a mixture of solvents (eg water, acetonitrile and / or methanol) referred to as the moving phase.

The preparation of 0.1M sodium perchlorate moving phase is carried out in the laboratory. 14.05 g of sodium perchloric powder (Sigma Aldrich, USA) was dissolved in 1L volatile flask using dissolved water. Then, the solution was filtered through a 0.2 µm porous cellulose filter paper. Acetonitrile (Merck, USA) is also filtered before being placed in a storage bottle of Schott Duran, USA (1L).

For sample extraction, filter paper containing the sample was cut into small parts (0.5 cm^2) in a laminar flow chamber. Next, 10 ml of methanol was placed in a glass vial containing aerosol samples. Samples were extracted in an ultrasonic irritant reservoir for 45 min at 30 ºC. Then, the sample was concentrated using a solid phase extraction (SPE) method. Samples were then filtered into 5 ml glass vials (Agilent Technologies, USA) using a nylon type syringe filter (Chromafil PP / PA) 0.2 µm porosity and 15 mm in diameter. Samples were analyzed instantly or within 48 hours after being extracted under a temperature of 4ºC.

Analysis of LAS determination was started by determining the calibration graph. In this study, the standard materials used are commercial LAS, ($C_{18}H_{29}Na0_3S$) (Sigma Aldrich, USA). Five different concentrations of concentrated solutions (10, 25, 50, 70 and 100 µg L^{-1}) were used to form a calibration graph. The extracted aerosol samples were placed in a 5 ml glass vial and analyzed to determine the LAS value. Table 1 shows the method used in this study.

Table 1. HPLC analyzing method used to analyze LAS

	Details
Column	VP- ODS (250 mm x 4.6 mm)
Mobile Phase	0.1 M sodium perchloric (35%) 65% Acetonitrile
Flow	1.0 ml/min
Temp	40ºC
FLD	RF – 10 Axl Excitation wavelength = 221nm Emission wavelength = 284 nm SPD – 10A Vp at 225 nm
Injection volume	30 µl

2.5. Statistical Analysis

Every data obtained from laboratory work was analyzed using statistical methods. In this study, XLSTAT and STATA 13 software were used for normality, *t*-test (for comparison) and Pearson correlation (for correlation analysis).

3. Result and Discussion

3.1. MBAS and LAS Concentration

A total of 12 aerosol samples from Kuala Lumpur and 12 aerosol samples from Bangi were analyzed to determine the LAS concentration for both fine and coarse modes. Then, the LAS concentration is compared to the MBAS concentration in the same sample. Table 2 shows the descriptive data of LAS concentration, MBAS and the percentage (%) of LAS concentration compared to MBAS obtained from the analysis.

Overall, the average MBAS concentration in fine mode was higher than coarse mode aerosol (p <0.05). Kuala Lumpur recorded higher MBAS concentration with 81.69 ng m^{-3} ± 13.01 (fine mode) and 28.81 ± 4.08 ng m^{-3} (coarse mode) compared to Bangi. Whereas, LAS concentration in the fine mode aerosol was higher than the LAS in the coarse mode (p <0.05). In Kuala Lumpur, the average of LAS concentration was 2.96 ± 1.22 ng m^{-3} for fine mode and 0.48 ± 0.17 ng m^{-3} for the coarse mode. For Bangi, the

LAS concentration values were 2.48 ± 1.28 ng m^{-3} and 0.38 ± 0.19 ng m^{-3} for the fine mode and coarse mode particles, respectively. Compared to MBAS, the average LAS concentration was much lower for both sampling locations and both fine and coarse modes with significant difference (p <0.05). Fig. 2 and Fig. 3 show the comparison of MBAS and LAS according to different monsoons for Kuala Lumpur and Bangi.

The results showed that the average LAS concentration in Kuala Lumpur and Bangi during southwest monsoon was higher than other monsoon values. This is equivalent to the result obtained for MBAS where there are meteorological factors involved as southwest Moonsoon is capable of affecting aerosol concentration, particularly wind factor that carry pollutants to the study area. [10, 11]. During southwest monsoon, a lot of biomass burning was detected. According to Shaharom et al. [14], during the southwest monsoon, a larger amount of surfactants were detected compared to the northeast monsoon, which is usually associated with a heavy rain and strong winds.

Table 2. Descriptive data of LAS concentration, MBAS and percentage (%) of LAS concentration compared to MBAS obtained from the analysis

		LAS (ng m^{-3})		MBAS (ng m^{-3})		LAS compared to MBAS (%)	
		Fine mode	Coarse mode	Fine mode	Coarse mode	Fine mode	Coarse mode
KL (S1)	min	1.12	0.26	60.76	24.27	1.8	1.1
	max	4.54	0.74	100.06	37.15	4.5	2.0
	avrg	2.96	0.48	81.69	28.81	3.6	1.7
	SD	1.22	0.17	13.01	4.08		
Bangi (S2)	min	1.06	0.16	31.81	8.53	3.3	1.9
	max	4.86	0.72	59.44	15.69	8.2	4.6
	avrg	2.48	0.38	44.58	13.74	5.6	2.8
	SD	1.28	0.19	10.05	2.57		

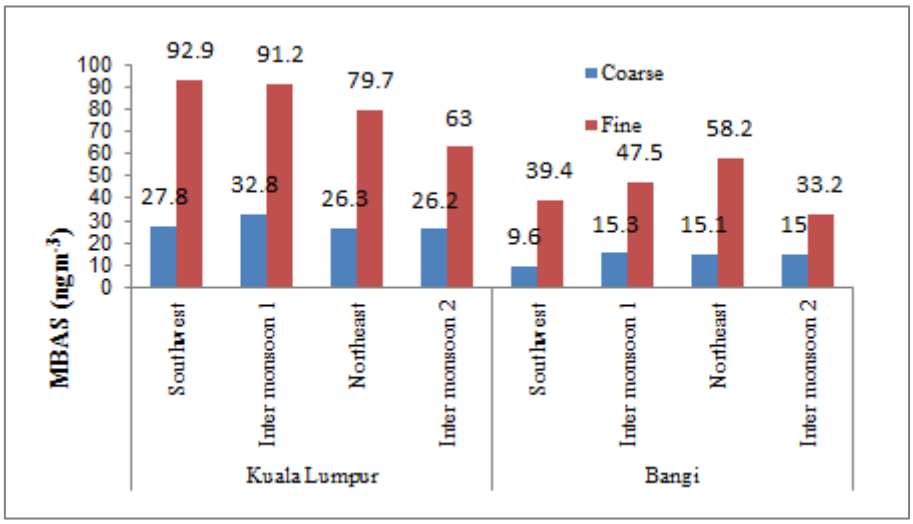

Figure 2. MBAS according to different monsoon for Kuala Lumpur and Bangi

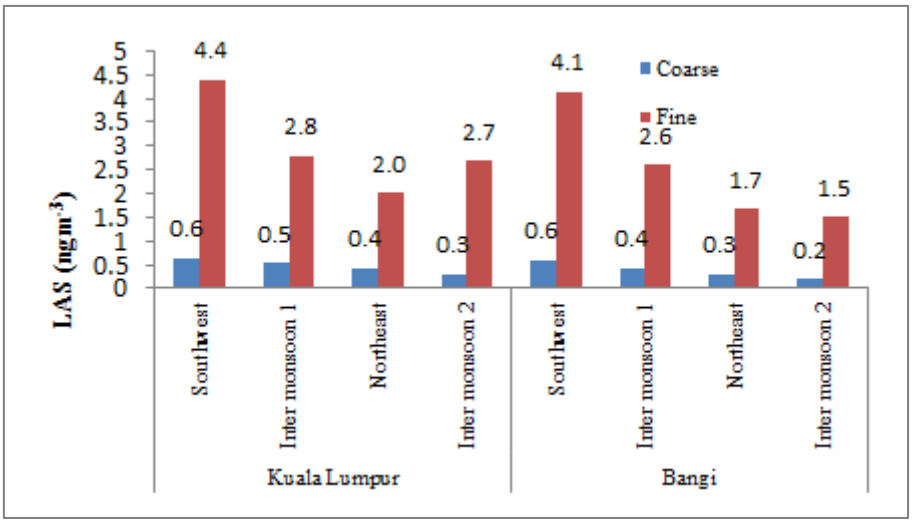

Figure 3. LAS according to different monsoon for Kuala Lumpur and Bangi

3.2. Correlation between MBAS and LAS

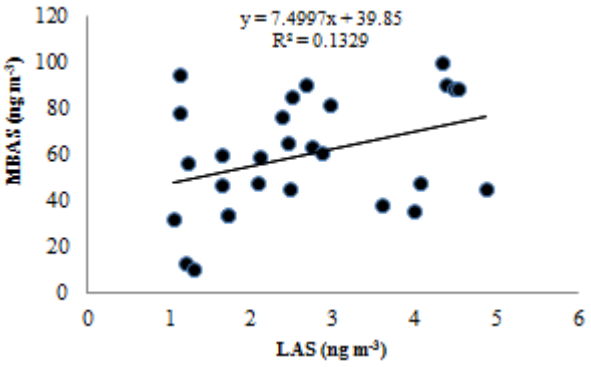

Figure 4. Correlation between LAS and MBAS in fine mode atmospheric aerosol

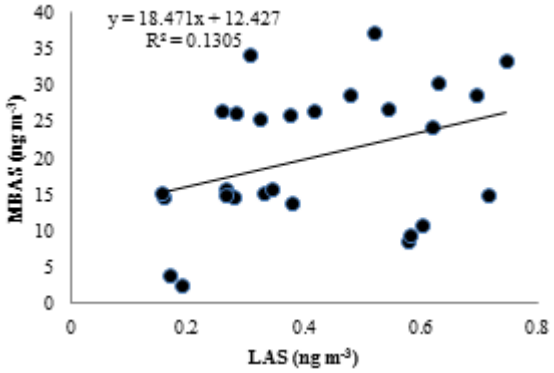

Figure 5. Correlation between LAS and MBAS in coarse mode atmospheric aerosol

Based on the data in Table 2, the LAS concentration compared to MBAS (%) has been determined. From the results obtained, it is found that all percentage of LAS concentration compared to MBAS is less than 15%. There is a positive correlation between LAS and MBAS, but it is not significant ($p > 0.05$) for both fine and coarse mode, as shown in Fig 4 and Fig 5. According to a research by Becagli et al. (2011), in a study conducted on LAS in marine ecosystem, the LAS concentration against MBAS in PM_{10} and $PM_{2.5}$ is less than 5%.

Whereas, studies by Hennes and Rapaport [15], regarding LAS in wastewater, showed that the LAS concentration against MBAS in the sample is between 10 - 50%. This indicates that MBAS in aerosol is largely absent from commercial LAS, but the influence of commercial LAS in wastewater samples on MBAS is high. This may be due to LAS molecular weight which causes LAS to be easily absorbed into the air [13]. According to Becagli et al. [5], MBAS concentration was not an appropriate measure of substitution of LAS concentration in atmospheric aerosols. It was due to other important contributions from other sources to MBAS concentration which were more significant.

According to Feczko et al. [16], the process of spreading surface active contaminants was influenced by meteorological factors which also caused differences between local influences and long-range dissemination [5,14,17].

4. Conclusion

From this study, it is concluded that fine mode aerosol showed higher MBAS and LAS concentration compared to coarse mode. Whereas, during southwest monsoon, higher concentration of both MBAS and LAS was detected compared to other monsoons. In conclusion, MBAS concentrations in atmospheric aerosols in urban and semi-urban areas are not fully affected by commercial LAS, but the majority of MBAS may be presented from other anthropogenic and natural activities such as combustion of biomass, the influence of motor vehicles and the earth's

crust. Chemical properties and meteorological factors are probably the least factor for the release of LAS content into the atmosphere in this study. Due to the negative effects of surfactants, which may influence the climate change, and affect human health, the compositions of surfactants in the atmosphere need to be regularly monitored by the authorities. The usage of commercial surfactants also needs to be reconsidered so as to increase the quality of the atmosphere in the future.

Acknowledgements

This research was carried out under University Research Grant (GPU 2018-0148-102-01) provided by Universiti Pendidikan Sultan Idris (UPSI). The authors would like to thank Mr. Tajudin for proofreading this paper.

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