Sh.Tserenpil et al. Mong. J. Chem., 19(45), 2018, 5-11
https://doi.org/10.5564/mjc.v19i45.1083

Mongolian Journal of Chemistry
www.mongoliajol.info/index.php/MJC

High molecular weight humic-like substances in carboneous aerosol of Ulaanbaatar city

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Received: 27 September 2018; revised:19 November; accepted: 28 November 2018

ABSTRACT

Total carbon content of the atmospheric suspended particulate matters consisted of as high as 89-93% organic carbon (OC) in Ulaanbaatar aerosol without showing seasonal variation. However, limited aerosol measurements have been conducted on these OC rich aerosols particularly for high molecular weight constituents. In order to address the gap above, abundance of high molecular weight humic-like substances (HULIS) in total suspended particulates (TSP) from Ulaanbaatar atmospheric aerosol were determined for the first time. HULIS molecular structure was characterised for different seasons using carbon content and UV absorbance measurements coupled with solid phase extraction methods. Although, HULIS contributions to water soluble organic fraction of the winter and summer aerosols were similar HULIS carbon concentration was higher in winter samples (9-37 $mg \cdot L^{-1}$) than in summer (2-6 $mg \cdot L^{-1}$). Consequently quantity of aromatic moieties and degree of aromaticity varied between seasons.

Keywords: air pollution, organic carbon, HULIS, water soluble organic carbon

INTRODUCTION

Organic aerosols have a potent role in atmospheric chemistry and hygroscopic properties of the aerosol particles. The hygroscopic property is often correlated with water soluble organic fractions and has been earlier studied in organic-enriched winter aerosols from urban area of Mongolia by Jung *et al* [1]. The results suggested that the aerosols consisted of high abundances of biomass burning products and aged secondary organics [1]. One of the most often measured organic species in the atmospheric aerosols are diacids (e.g., oxalic acid) and other related compounds including ketocarboxylic acids, and these were studied as a short-term observation in Ulaanbaatar city [2]. The chemical compositions of the Ulaanbaatar aerosols can also be found in few other studies, such as Nishikawa *et al* [3]. Meanwhile, higher molecular weight humic-like substances (HULIS) often have significant contribution to total organic fraction in the aerosols from the various locations [4], not least in continental cities like Ulaanbaatar where its presence is more likely than in any other environment [4-5]. For instance, the continental sites, considered as background location, have generally higher ratios of HULIS carbon to water soluble organic carbon (WSOC) than the coastal urban sites [6].

HULIS is less soluble organic fraction due to its condensed aromatic molecular structure and higher molecular weight. Carbon content of HULIS (HULIS-C) makes up a mass fraction from 9% to 72% of WSOC in the ambient aerosols [4]. HULIS origin is strongly affected by biomass burning and secondary photochemical processes [7], and the former could be intensified due to heat and energy production and the latter through intense solar radiation. Therefore, sources tend to show a winter and summer maximum, respectively. Although, the maximum could change depending upon the site specific characterizations, by enhanced emissions from plants for instance.

Ulaanbaatar, the capital of Mongolia, faces severe air pollution with very high concentrations of atmospheric suspended particulate matters (SPM), both coarse and fine by size. The total carbon (sum of organic and elemental carbon) content have been shown to contribute a significant amount to particulate matter (PM) with diameters ≤10 μm in Ulaanbaatar aerosols both during warm and cold seasons; accounting for 33% and 47%, respectively [3]. However, the Asian continent has been inferred as a major source region of natural dust, pollution and biomass burning aerosols [8] and influences on atmospheric chemistry not only in the North Pacific region but also in the rest of the World [9]. HULIS fraction in the ambient aerosol has been investigated intensively in Europe and only recently in the Chinese cities [10], but it has so far not been measured in Ulaanbaatar. This survey aimed to determine variations of the carbon species, water soluble organic matter (WSOM) and higher molecular weight HULIS fractions in TSP from Ulaanbaatar during heating and non-heating seasons. Finally, we investigated HULIS molecular structures with focus on seasonal variations.

EXPERIMENTAL

Geography and weather in Ulaanbaatar: Ulaanbaatar city is located on the banks of the Tuul River surrounded by the mountains. Its geography, i.e., mountain river valley, provides a favorable condition to form a temperature inversion layer in the atmosphere leading to lower mixing height for pollutants and increases SPM concentrations at ground level. Heating period lasts for 6-7 months (from October through April) in Mongolia; moreover, annual coal consumption for heat and electricity cogeneration reaches ca. 5 millions tones [11] solely in Ulaanbaatar, which occupies an area of approx. 4700 km^2. Number of cloudless days averaged 257 days per year. Average annual evaporation is a large and annual precipitation equals to ~267 mm. Hence, dry soil cover easily contributes to increased amount of the ground level PM concentrations by wind transport of dust all year around. In addition, the concentration of PM increases dramatically during winter months due to the emissions from coal combustion.

Aerosol sampling: The aerosol samples were collected at two sites in Ulaanbaatar. One in an enclosure of the Central Laboratory of Environment and Metrology in Khan-Uul district (LAB), southern part of Ulaanbaatar, between January and February, 2013; and a repeated sampling was performed during winter (between 7 and 21 January) in 2014. Second sampling location was in the central Ulaanbaatar at the National Agency of Meteorology and Environmental Monitoring (NAMEM) and sampled between February and March, and from June to July in 2014. There were no natural fire events during the sampling campaign.

Atmospheric TSP was collected on a 20×25 cm filter made of glass fiber and quartz microfiber (Whatman) by using a high-volume air sampler (HI-Q, HVP3300BRL230, USA). The filters were pre-combusted at 550 ºC for 4 hours to remove organic contaminations before being used for the sample collections. The sample acquisition lasted 24 - 48 hours with an air flow rate of 650 L·min^{-1}. Field blank filters were prepared by inserting a pre-combusted filter to the sampler and left for 24 hours without pumping air. The concentration of TSP was calculated based on mass differences of pre-combusted filters before and after sampling.

Solid phase extraction of HULIS: Humic-like substances (HULIS) was isolated and concentrated from the water extracts of the TSP collected and is called HULIS as it has similar UV-sorption behavior to humic substances due to its poly-conjugated nature. Briefly, WSOM fraction was obtained by ultrasonication of filter samples with ultrapure water, and filtered through a syringe filter of 0.2 μm pore size. Then solid phase extraction (SPE) methods including relatively hydrophobic XAD-8 and polarity based DEAE [12] were employed for isolation of HULIS from other soluble constituents; and two methods were compared. The XAD-8 is a non-ionic polymer and its selectivity based on hydrophobic/hydrophilic interactions between the solutes and adsorbing solid; while, the DEAE is a weak anion exchanger with a hydrophilic matrix.

The following is a brief description of the XAD-8 method. Freshly acidified (pH 2.0) WSOM were injected onto the pre-cleaned and conditioned XAD-8 resin (Superlite XAD-8 Macroporous resin, 40 - 60 mesh size) in a glass column. After concentration of HULIS, ultrapure water was used to remove the organics not retained on the column, and inorganic materials. The organic matter adsorbed in XAD - 8 resin was then back eluted with a solution of methanol/ultrapure water in the proportion of 2/3 (40% methanol). Methanol/water elutes were evaporated and freeze-dried then dissolved in pure water for further analysis.

In the DEAE method, a resin (DEAE Sepharose, GE Healthcare, Sweden) was carefully cleaned and pre-conditioned. The WSOM fraction then passed through the DEAE column without any pre-treatment. Neutral components and hydrophobic bases were removed by ultrapure water. Retained low molecular weight organic acids (mono- and di- acids) together with anionic inorganic species were eluted with 0.04 M NaOH solution. Finally, HULIS was eluted with 1 M NaCl at flow rate of 1.0 mL·min^{-1}. This last HULIS fraction was collected for carbon quantification and subsequent analysis. The recoveries of HULIS by the extraction methods were estimated by means of total organic carbon (TOC) concentrations in the introduced WSOM to the sorbents and extracted effluents. Aldrich Humic Acid and humic acids isolated from sediment and soil were used for examining SPE method recoveries and character of isolated fractions.

Instrumental measurements: Total carbon (TC) content was estimated as sum of organic carbon (OC) and elemental carbon (EC) those quantified using a thermal/optical analyzer (Sunset Lab carbon analyzer). The dissoluble organic carbon (DOC) content was measured at with an automated, segmented flow analyzer (Shimadzu TOC-VCPH, Japan) in the WSOM and effluents produced via two SPE methods. The data reported were the average results of three measurements. Effluents, which representing HULIS, were studied qualitatively with UV-Vis spectroscopy (UV-Vis spectrophotometer, Perkin Elmer Lambda 850) scanned from 240 to 540 nm wavelength. The specific UV absorptions at 254 nm and 280 nm (SUVA) were estimated with the following equation:

$$\mathrm{SUVA} = \mathrm{A}/(\mathrm{b} \times \mathrm{c}) \qquad \textbf{(1)}$$

Where, A is the absorbance at 254 nm or 280 nm, $L \cdot (mgC \cdot m)^{-1}$; b is the cell path length, m; c is the TOC concentration of the samples, $mg \cdot L^{-1}$

E2/E3 referred to a ratio of absorbance at 250 nm to 365 nm. The wavelength of 250 nm was selected due to a large sensitivity for natural fulvic acid, which associated with large density of aromatic structures in this compound [12].

RESULTS AND DISCUSSION

Abundances of OC and WSOC in TSP samples: Daily average concentration of total suspended particulates (TSP) ranged from 36 to 107 $\mu g \cdot m^{-3}$ in 2013 winter at the LAB sampling site, the southern part of Ulaanbaatar and the concentration was increased (98-224 $\mu g \cdot m^{-3}$) in January 2014 (Table 1). The latter being comparable with the TSP concentration of 149-244 $\mu g \cdot m^{-3}$ that was recorded at the city center (NAMEM site) during same time period. TSP remained as high as 80-223 $\mu g \cdot m^{-3}$ in July at the NAMEM; however, proportion of total carbon (TC) decreased to 4-15% compared to 12-45% of TSP for the winter samples. It can be explained by the fact that non-carbon related particulate matters increased in summer aerosols in the city. Specifically, the average TC concentration in TSP was 4.6 times higher during winter season (55 $\mu g \cdot m^{-3}$) than during summer (12 $\mu g \cdot m^{-3}$).

Average concentration of OC at the LAB site also increased from 21 to 59 $\mu g \cdot m^{-3}$ in 2013 and 2014, respectively. At another site i.e., NAMEM, the concentration was 52 $\mu g \cdot m^{-3}$ during winter and decreased to 11 $\mu g \cdot m^{-3}$ in July. However, OC contribution to the TC was predominant species and occurred nearly constant at 89-93% throughout year despite seasonal variation in TC.

Moreover, EC/OC ratio falls within a similar range during winter (0.03-0.16) and summer (0.06-0.15) regardless the concentration of TC (Figure 1). The concentrations of TC and OC were significantly correlated ($R^2 = 0.99$), which was simply because TC concentration mainly built up from OC in the atmospheric suspended particles in the Ulaanbaatar city and probably comes from same source all year around, although, carbon containing emission declines during non-heating period. Hence, TC and OC can be potentially influenced by the coal and firewood combustion that intensifies during cold seasons.

Table 1. Elemental and organic carbon contents of TSP in Ulaanbaatar atmospheric aerosol, 2013 and 2014 (LAB and NAMEM sites)

Sampling date	**TSP, $\mu g \cdot m^{-3}$**	**OC, $\mu g \cdot m^{-3}$**	**EC, $\mu g \cdot m^{-3}$**	**OC, %TC**	**Sampling date**	**TSP, $\mu g \cdot m^{-3}$**	**OC, $\mu g \cdot m^{-3}$**	**EC, $\mu g \cdot m^{-3}$**	**OC, %TC**
LAB, 2013					NAMEM, winter 2014				
Jan 12 - 13	62.2	25.9	2.4	91.6	Feb 20 - 21	243.5	97.8	2.6	97.3
Feb 5 - 6	85.5	14.7	2.3	86.4	Feb 25 - 26	196.5	22.9	0.9	96.4
Feb 6 - 7	106.6	22.2	3.5	86.3	Feb 26 - 27	149.1	41.0	3.2	92.7
Feb 7 - 8	35.6	13.6	1.3	91.3	Feb 27 - 28	174.3	48.1	5.4	90.0
Feb 15 - 17	65.1	14.5	1.3	91.7	March 3 - 4	185.2	47.7	7.3	86.8
Feb 17 - 19	103.4	35.6	5.4	86.8	**Mean**	**189.7**	**51.5**	**3.9**	**92.7**
Feb 19 - 21	94.6	22.9	2.8	89.0	Summer, 2014				
Mean	**79.0**	**21.3**	**2.7**	**89.0**	Jun 30 - July 1	115.5	13.7	1.4	90.6
Jan 7 - 8, 2014	162.6	57.8	6.2	90.4	July 1 - 2	175.3	8.9	0.7	92.9
Jan 9 - 10	172.9	73.5	2.1	97.2	July 2 - 3	222.8	9.0	0.5	94.4
Jan 13 - 14	224.2	84.1	2.4	97.2	July 3 - 4	82.1	10.1	0.8	92.8
Jan 16 - 17	165.0	47.7	5.4	89.9	July 7 - 8	80.1	10.1	1.5	86.8
Jan 20 - 21	97.5	32.5	1.1	96.7	July 8 - 9	88.5	11.6	1.1	91.6
Mean	**164.4**	**59.1**	**3.4**	**92.7**	**Mean**	**127.4**	**10.6**	**1.0**	**91.5**

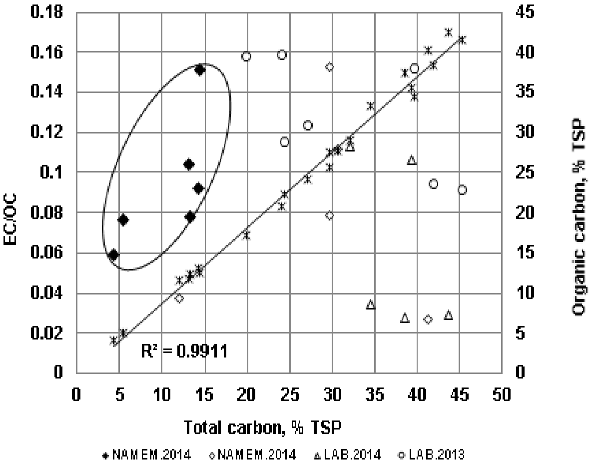

Fig. 1. Elemental carbon (EC) and organic carbon (OC) ratio of TSP samples. Filled diamond denoted summer samples; all open legends referred to winter samples. Trend line showed the correlation between TC and OC contents.

Table 2. WSOC and HULIS contents in Ulaanbaatar winter and summer aerosols

Sampling site, date	WSOC, µg·m^{-3}	WSOC, % OC	HULIS-C, % WSOC
LAB, winter 2013 and 2014			
Jan 12 - 13, 2013	6.3	22.9	48.7
Feb 5 - 6	6.5	42.9	30.4
Feb 6 - 7	4.4	29.2	28.1
Feb 7 - 8	3.9	32.6	32.6
Feb 15 - 17	6.9	26.5	41.8
Feb 17 - 19	5.1	19.5	29.2
Feb 19 - 21	5.9	22.4	36.8
Jan 7 - 8, 2014	12.2	21.1	34.4
Jan 9 - 10	12.7	17.3	38.6
Jan 13 - 14	14.4	17.1	33.7
Jan 16 - 17	9.8	20.5	41.7
Jan 20 - 21	6.2	19	45.4
NAMEM, winter and summer, 2014			
Feb 20 - 21	13.7	14.1	35.7
Feb 25 - 26	5.1	15.7	41
Feb 26 - 27	9.6	23.3	33.6
Feb 27 - 28	8.2	17.1	-
March 3 - 4	8.8	18.4	35.6
June 30 - July 1	2.6	18.7	30.7
July 1 - 2	1.7	19.5	27.8
July 2 - 3	1.3	14.2	24.5
July 3 - 4	1.5	14.5	28.0
July 7 - 8	1.6	15.8	22.6
July 8 - 9	2.2	19.0	22.1

Abundances of HULIS and characterization by UV-Vis spectroscopy: Water soluble organic carbon (WSOC) constituted a significant proportion of OC content of up to 43% (Table 2). Its concentration varied from 3.9 to 14.4 µg·m^{-3} in winter (17 days observation) and 1.3-2.6 µg·m^{-3} during summer (5 days). Daily average concentration was 4.5 times higher during the heating season (8.1 µg·m^{-3}) than in the non-heating season (1.8 µg·m^{-3}). This difference was of the same magnitude as the OC distribution in aerosols between winter and summer.

HULIS is characterized by a highly poly-conjugated nature that is similar to natural humic substances (HS), despites having different formation pathways. There are different approaches to study its nature, among them solid phase extraction (SPE) is one of the common isolation methods and is followed by the instrumental analyses. Only concern regarding SPE methods is that every tested method significantly co-elute aromatic acids. However, the DEAE method extracted only a small amount of interfering compounds along with HULIS [13]. Recovery of HULIS (Table 3) extracted by the DEAE method was lower than with the XAD-8 method on the winter samples from 2013. However, absorption data revealed HULIS fraction produced by the DEAE method was more aromatic (by absorption at 250 nm) and had a high humification degree that more resembled to HS. The DEAE method also favored to humic acids isolated from different sources (soil, sediment, etc.) with recovery of 69-71% and higher absorption at 250 nm; whereas, the recovery by the XAD-8 method was only 12-27% (Table 3). Therefore, the DEAE showed higher selectivity towards UV adsorbing compounds in the aerosol water extracts obtained [13]. Further, the DEAE extraction method was selected and employed for all the samples collected in 2014. The HULIS-C concentration varied widely in the winter aerosols (9.2-37.1 mg·L^{-1}) at two sites, and it increased from 2013 to 2014 as did the OC concentration, whereas the concentration was low during summer being 2.4-5.9 mg·L^{-1} .

HULIS are important components of WSOC as reported in the previous studies [14, 15]. In our study the contribution of HULIS to WSOC was 28-49% and 22-31% during heating and non-heating seasons, respectively (Table 2).

Energy sector largely relies on fossil fuel combustion in Ulaanbaatar, with relatively trivial contribution of biomass burning i.e., firewood [16]. In the studied area other sources for HULIS could be coming from emission of terrestrial humic substances (often insignificant) and also vehicle exhaust. However, a small gap in HULIS concentrations between heating and non-heating seasons could presumably result from quantities of primary emission and secondary formation by photochemical reaction with seasonal shifts.

Table 3. Comparison of the DEAE and XAD-8 methods for HULIS investigation

Sampling date	**WSOM§**		**DEAE**		**XAD-8**	
	DOC*, mg·L^{-1}	UV$_{250\ nm}$	HULIS, % (DOC*)	UV$_{250\ nm}$	HULIS, % (DOC*)	UV$_{250\ nm}$
2013, Jan 12 - 13	32.8	2.02	48.7	1.30	50.2	0.96
Feb 5 - 6	35.0	1.58	30.4	0.86	34.9	0.67
Feb 6 - 7	37.5	1.88	28.1	0.88	34.5	0.75
Feb 7 - 8	24.3	1.31	32.6	0.73	50.0	0.66
Feb 15 - 16	44.3	2.35	41.8	1.46	41.4	1.06
Feb 17 - 18	82.0	3.33	29.2	1.81	43.9	1.72
Feb 19 - 20	58.2	2.99	36.8	1.68	45.6	1.47
HA. soil	14.0	1.26	68.8	1.12	12.4	0.27
HA. sediment	11.1	0.75	70.3	0.82	16.2	0.17
HA. Aldrich	8.6	0.91	70.5	0.80	26.8	0.31

§ Water soluble organic fraction of the TSP; * DOC refers to the total dissoluble organic content

The absorption spectra of HULIS and WSOM were plotted by normalizing the UV-Vis absorbance to the carbon concentration in the HULIS and WSOM extracts (Figure 2). The absorbance generally decreased with increasing wavelength. HULIS extracts presented relatively higher specific absorbance (with broad range up to 350 nm) than original WSOM, indicating a higher content of aromatic moieties and high molecular weight in HULIS fractions.

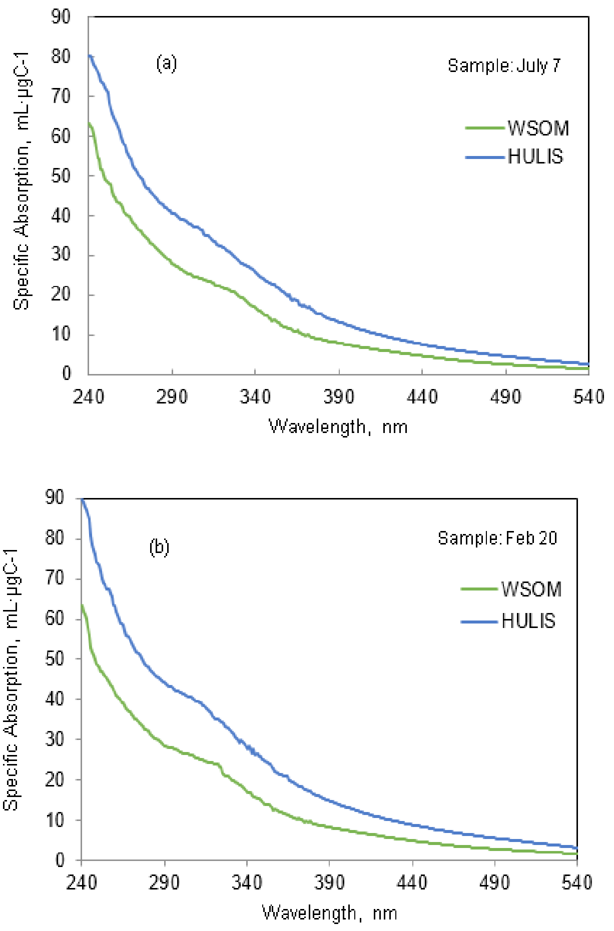

Fig. 2. Absorption spectra of WSOC and HULIS, isolated by the DEAE method (samples collected at the NAMEM site)

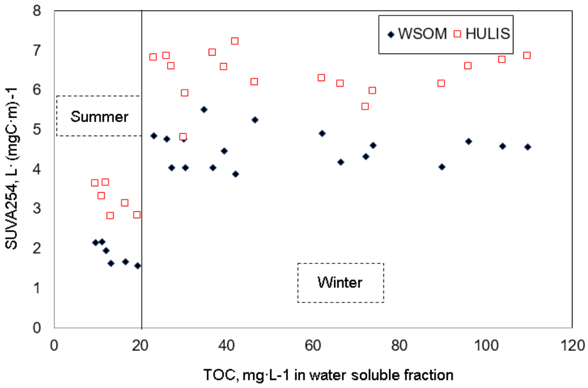

Fig. 3. Specific UV absorption at 254 nm of WSOM (filled diamond) and HULIS (open rectangle). TOC concentration referred to dissoluble organic carbon content in WSOM.

Absorption data for HULIS were tabulated in Table 4, and SUVA at 254 nm wavelength was compared between total WSOM and its high molecular organic fraction i.e., HULIS in Figure 3. The specific UV at 254 nm value, expressing the content of aromatic moieties in HS, was 4.8-7.2 L·(mgC·m)$^{-1}$ and 2.8-3.7 L·(mgC·m)$^{-1}$ for HULIS extracted from winter and summer aerosols, respectively (Figure 3 and Table 4). Likewise, SUVA280 [14] and E2/E3 [6] also provides information about degree of aromaticity and molecular weight of HS. Moreover, HULIS isolated from the winter aerosol contained more condensed aromatic groups (3.3-4.8 L·(mgC·m)$^{-1}$) than summer samples (2.1-2.6 L·(mgC·m)$^{-1}$) in terms of SUVA280 value.

HULIS in the Ulaanbaatar aerosol had less aromatic molecular structure in summer than in winter. This

Table 4. Absorbance of HULIS fraction extracted by the DEAE method

Sampling date	TOC, mg·L^{-1}	E_2/E_3	SUVA254, L·(mgC·m)$^{-1}$	SUVA280, L·(mgC·m)$^{-1}$	Sampling date	TOC, mg·L^{-1}	E_2/E_3	SUVA254, L·(mgC·m)$^{-1}$	SUVA280, L·(mgC·m)$^{-1}$
Khan Uul, 2013 - 2014 winter					NAMEM, 2014 winter				
Jan 12 - 13	17.3	5.00	4.81	3.25	Feb 20 - 21	37.1	3.93	6.59	4.45
Feb 5 - 6	11.9	4.94	6.75	4.54	Feb 25 - 26	11.2	4.26	5.58	3.77
Feb 6 - 7	11.9	4.94	6.93	4.58	Feb 26 - 27	24.2	4.02	6.30	4.10
Feb 7 - 8	9.2	4.85	6.58	4.41	March 3 - 4	23.6	4.14	6.15	3.99
Feb 15 - 17	19.8*	5.28	6.86	4.44					
Feb 17 - 19	25.2*	4.67	6.82	4.60	Summer, 2014				
Feb 19 - 21	22.7*	4.34	7.23	4.49	Jun 30-Jul 1	5.9	4.10	2.83	2.07
Jan 7- 8, 2014	30.9	4.02	6.15	4.07	July 1 - 2	3.7	4.12	2.81	2.15
Jan 9 - 10	37.1	3.80	6.60	4.57	July 2 - 3	2.4	4.24	3.63	2.61
Jan 13 - 14	37	3.66	6.86	4.81	July 3 - 4	3.1	3.44	3.31	2.49
Jan 16 - 17	30.8	3.96	5.97	4.05	July 7 - 8	2.7	3.12	3.66	2.63
Jan 20 - 21	21.2	3.83	6.21	4.37	July 8 - 9	3.7	3.23	3.13	2.37

*TOC was normalized to sampling duration of 24 hours

apparent seasonal variation could be the result of changes in emission sources or may also reflect of seasonal variations in intensity of atmospheric photoxidation process, as mentioned above. Such differences have been reported previously in a nuclear magnetic resonance study [15].

The photochemical reactions may produce more oxidized and less aromatic products, which will result in more hydrophilic and less aromatic nature of HULIS and increases the yield of the soluble matters particularly in summer aerosols.

CONCLUSION

For the first time, seasonal variations in abundance and nature of HULIS in water soluble organic matters from Ulaanbaatar ambient aerosols have been studied. Though, contribution of HULIS–C did not vary significantly between seasons (28-49% and 22-30% of WSOC for winter and summer aerosols, respectively) the molecular structures showed some differences between heating and non-heating seasons. The content and degree of aromaticity of HULIS decreased in summer aerosols, which could be due to both seasonal variation in HULIS emission sources and photochemical reactions.

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