Chemical characteristics and formation routes of humic-like substances in $PM_{2.5}$

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HUmic-Like Substances (HULIS) are a mixture of organic compounds identified in atmospheric aerosol samples. They are termed because of their similarity with terrestrial and aquatic humic and fulvic acids, especially in UV-VIS, FTIR, and NMR characteristics (Havers *et al.*, 1998). HULIS makes up a significant fraction (up to 72%) of the water-soluble organic carbon (WSOC) in the atmospheric aerosols (Kiss *et al.*, 2002; Graber and Rudich, 2006; Krivácsy *et al.*, 2008) and influence their water uptake properties. Study on HULIS could greatly help unearth the complex picture of emission, transformation and transport processes of organic aerosols. Little information on HULIS in ambient particulate matter has been reported yet in Korea. In this study 24-hr $PM_{2.5}$ samples were collected between December 2013 and October 2014 at an urban site in Gwangju, Korea and analyzed for organic carbon (OC), elemental carbon (EC), water-soluble OC (WSOC), HULIS, and ionic species, to investigate possible sources and formation processes of HULIS. HULIS was separated using HLB solid phase extraction method and quantified by total organic carbon analyzer. During the study period, HULIS concentration ranged from 0.19 to 5.65 μg C/m^3 with an average of 1.83±1.22 μg C/m^3, accounting for on average 45% of the WSOC (12-73%), with the higher fractions in cold season than in warm season (Figure 1). Strong correlation of WSOC with HULIS (R^2=0.91) indicates their similar chemical characteristics. On the basis of the relationships between HULIS and a variety of chemical species (EC, K^+, NO_3^-, SO_4^{2-}, and oxalate), it was postulated that HULIS observed during summer and winter were likely attributed to secondary formation and primary emissions from biomass burning (BB) and traffics. Stronger correlation of HULIS with K^+, which is a BB tracer, in winter (R^2=0.81) than in summer (R^2=0.66), suggests more significant contribution of BB emissions in winter to the observed HULIS. It is interesting to note that BB emissions may also have an influence on the HULIS in summer (Figure 2), but further study using levoglucosan that is a unique organic marker of BB emissions is required during summer. Higher correlation between HULIS and oxalate, which is mainly formed through cloud processing and/or photochemical oxidation processes, was found in the summer (R^2=0.76) than in the winter (R^2=0.63), reflecting a high fraction of secondary organic aerosol in the summer.

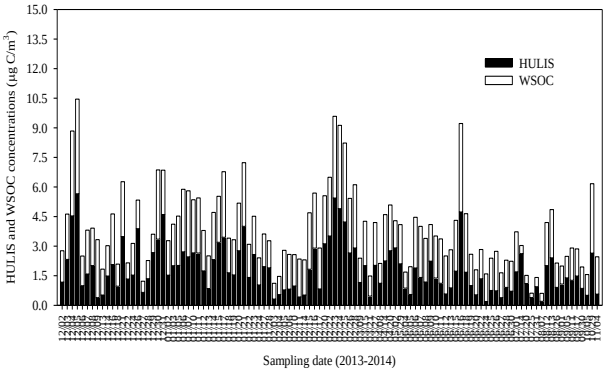

Figure 1. Temporal profiles of WSOC and HULIS concentrations over the entire study period.

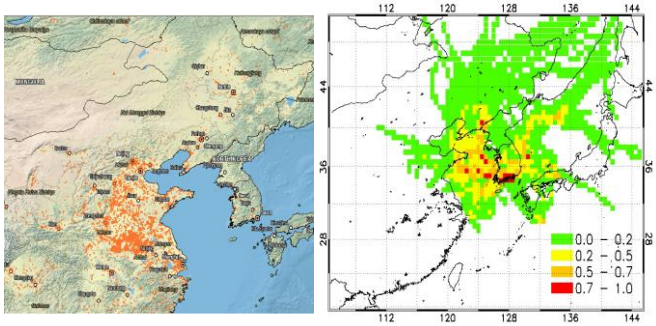

Figure 2. MODIS image (June 01 – 30, 2014) (left graph) and PSCF result for $PM_{2.5}$ (right graph).

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