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Characterization of humic-like substances in $PM_{2.5}$ during biomass burning episodes on Weizhou Island, China

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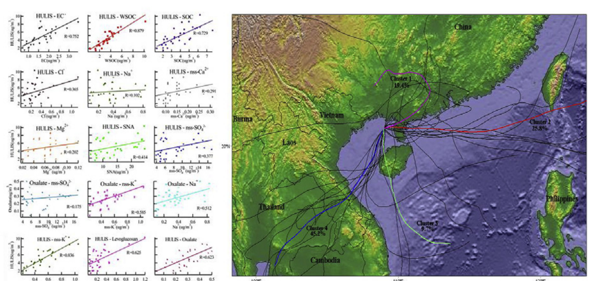
GRAPHICAL ABSTRACT



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ABSTRACT

To investigate chemical characteristics and sources of humic-like substances (HULIS) in the background region of Southwest China, daily $PM_{2.5}$ samples were collected on Weizhou Island from 14 March 2015 to 14 April 2015. Water soluble inorganic ions, organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), HULIS, oxalate, levoglucosan and mannosan were analyzed. Average concentration of $PM_{2.5}$ was $32.5 \pm 12.6\,\mu g/m^3$ with SO_4^{2-}, OC and NH_4^+ as the three most abundant components. Average concentration of HULIS was $5.00 \pm 2.21\,\mu g/m^3$ with daily values ranged from 1.46 to $10.36\mu g/m^3$. The carbon content of HULIS (HULIS-C) contributed 35.6% ± 7.2% of OC and 76.8% ± 12.9% of WSOC, indicating HULIS-C as one of the most important species in OC and WSOC in this region. The concentration of HULIS correlated well with those of non-sea salt (nss) K^+, levoglucosan, oxalate, OC, EC, WSOC, SOC and WSOC/OC, suggesting dominant source factors from both biomass burning and secondary aerosol formation. Contributions from crust and sea salt source factors to HULIS were minimal as indicated by its poor correlation with nss-Ca^{2+}, Mg^{2+} and Na^+. Research flight observations showed increasing biomass-burning indicators with increasing altitude, likely due to aerosols produced from biomass burning in Southeast Asia, which were then uplifted by deep convection to the middle troposphere and transported to this area. This hypothesis was supported by negative correlations between HULIS and sea level pressure when high-altitude air masses were transported from the Southeast Asian.

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Air mass backward trajectory analysis suggested Southeast Asian as the dominant source region for HULIS on Weizhou Island.

1. Introduction

Humic-like substances (HULIS) contain several functional groups such as hydroxyl, carbonyl, nitrate, and nitroxy organosulfate chemicals (Reemtsma et al., 2006; Altieri et al., 2009; Mazzoleni et al., 2010). They are major components of water soluble organic carbon (WSOC) (Kiss et al., 2002; Feczko et al., 2007) and can be found in atmospheric particles, fumes, clouds and precipitation. They have strong water solubility and surface activity and impact significantly on human health, natural environment, climate, and ecology (Facchini et al., 2000; Kiss et al., 2005; Lin and Yu, 2011). For example, they can influence the formation of cloud condensation nuclei and ice nuclei (Dinar et al., 2006), the hygroscopic growth of aerosols, and atmospheric chemistry processes (Gysel et al., 2004).

HULIS are released directly from biomass and residual oil combustion and can also be formed by secondary reaction (Kuang et al., 2015; Tan et al., 2016b). Low efficiency residual oil combustion releases high contents of HULIS such as from ship emission, while high efficiency combustion releases little HULIS such as from traffic vehicles. Coal combustion at low temperature could also be a source of HULIS (Tan et al., 2016b). Secondary aerosol formation processes producing HULIS including aqueous-phase oxidation and heterogeneous reactions have been demonstrated in laboratory or smog chamber studies (Hoffer et al., 2004; Holmes and Petrucci, 2006; Surratt et al., 2008). One class of HULIS, Organosulfates, has been found to be formed in sulfation processes involving heterogeneous reactions between oxidation products of biogenic volatile organic compounds and sulfate aerosols in chamber and field studies (Surratt et al., 2008; Lin et al., 2012).

Many studies of atmospheric HULIS in China have focused on urban areas (Kuang et al., 2015; Tan et al., 2016b), and little is known about their pollution levels, sources, and physicochemical characteristic in regional background areas. The present study aims to fill this gap by selecting a remote site, Weizhou Island, in southwest China to measure HULIS and other important chemical components in $PM_{2.5}$. Field campaign was conducted during the monsoon season, corresponding to the biomass burning periods in Southeast Asia, knowing that air pollution has been rising in this region due to recent economic development and long range transport could bring pollutants to this remote site. Chemically-resolved $PM_{2.5}$ data are analyzed in detail with a focus on characterizing HULIS' pollution levels, sources and formation mechanisms.

2. Experimental

2.1. Sampling site

Weizhou Island is situated in the middle of the north bay in the Guangxi Autonomous Region, and is located in the fringe zone of South China, Southwest China, and Southeastern Asian Economic Circles. The sampling site (21°02′N, 109°06′E) is located in the southernmost of the Weizhou Island, surrounded 270° by the sea. The sampling apparatus is about 15 m above the ground. Few industrial activities exist on the island, making it an ideal place for atmospheric background study. It is, however, on the transport route of pollutants from South Asia to inland China, so the site can be used for observing the influence of the regional and long-range transport of polluted air masses.

Daily (23-h starting at 8 a.m.) samples of $PM_{2.5}$ were collected with a high volume air sampler (Graseby-Andersen, GMW High Volume Air Sampler) at a flow rate of 1.13 m^3/min. A total of 31 samples were collected from 14 March 2015 to 14 April 2015 (The sample was not collected on 16 March 2015 due to the instrumental fault). Before sampling, What-man quartz fiber filters (20.3 × 25.4 cm) were prefired at 500 °C for 4 h to remove organic species. Once sampled, the loaded filters were stored at −20 °C in a refrigerator before chemical analysis.

At the same time, gaseous pollutants and particulate matter were also monitored. The gas analyzers were installed in an air-conditioned mobile laboratory (Fig. 1). Teflon pipelines were used as sampling inlets to reduce the reactivity with monitoring species. Ozone (O_3) was measured by a Thermo 49i analyzer using the ultraviolet (UV)

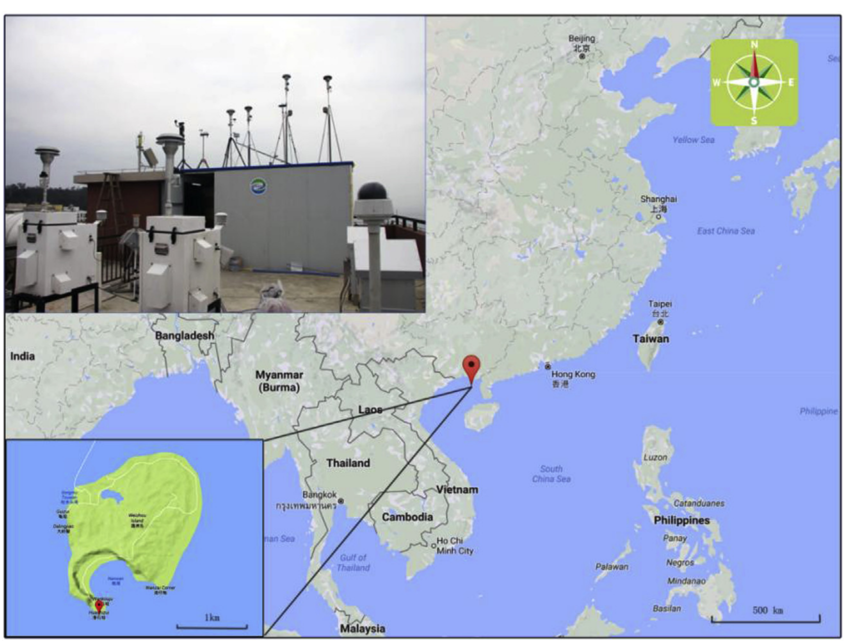

Fig. 1. The sampling location (Weizhou Island) and instruments.