



## Review

## Measurement of humic-like substances in aerosols: A review



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## ABSTRACT

Aerosol-phase humic-like substances (HULIS) have received increasingly attention due to their universal ambient presence, active participation in atmospheric chemistry and important environmental and health effects. In last decade, intensive field works have promoted development of quantification and analysis method, unearthed spatio-temporal variation, and proved evidence for source identification of HULIS. These important developments were summarized in this review to provide a global perspective of HULIS. The diverse operational HULIS definitions were gradually focused onto several versions. Although found globally in Europe, Asia, Australasia and North America, HULIS are far more typical in continental and near-ground aerosols. HULIS concentrations varied from  $<1 \mu\text{g}/\text{m}^3$  to  $>13 \mu\text{g}/\text{m}^3$ , with their carbon fraction making up 9%–72% of water soluble organic carbon. Dominant HULIS source was suggested as secondary processes and biomass burning, with the detailed formation pathways suggested and verified in laboratory works.

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## 1. Introduction

Humic-like substances (HULIS) are a class of compounds found ubiquitous in fogs (e.g., Krivacsy et al., 2000), clouds (e.g., Facchini et al., 2000), rainwater (e.g., Santos et al., 2010) Arctic snowpack (e.g., Voisin et al., 2012) and atmospheric aerosols (e.g., Feczko et al., 2007). They are termed so because of their similarity with terrestrial/aquatic Humic Substances (HS), especially in ultraviolet (UV) and fluorescence spectrum characteristics (Havers et al., 1998). Although they defy definition on the molecular level, some general natures could help differentiate them. Field work has observed HULIS in nearly all types of aerosols: urban and rural, continental and marine, anthropogenic-source dominated and remote areas. Generally they have a considerable atmospheric concentration, with their carbon fraction (HULIS-C) making up 9% (Feczko et al., 2007) ~72% (Kiss et al., 2002) of Water-Soluble Organic Carbon (WSOC). Despite their universality and high concentration, HULIS are of special interest because of their surface activity, light-absorbing capability and photochemical activity. They were suggested to be responsible for Cloud Condensation Nuclei (CCN) (Sun and Ariya, 2006) and ice nuclei (Wang and Knopf, 2011), to participate in atmospheric photochemistry (e.g., Chen and Valsaraj, 2007; Wentworth and Al-Abadleh, 2011), and were shown

to be strongly linked to brown carbon (Hoffer et al., 2006b), all of which having wide and sophisticated environmental and climate effect. Moreover, they were recently suggested to have significant adverse health effect (Lin and Yu, 2011). Study on HULIS could greatly help unearth the complex picture of atmospheric processes of aerosols.

Although termed “humic-like”, HULIS were found to differ from HS in a couple of characteristics. HULIS were generally more surface active, less acidic, and having much smaller Molecular Weight (MW) and lower aromaticity than HS (Graber and Rudich, 2006). Among the various proposed explanations on their dissimilarities, the different formation pathway was most supported (e.g., Limbeck et al., 2003; Jammoul et al., 2008; Ervens et al., 2011). Briefly, HULIS were suggested to form by accretion reactions of smaller molecules or by breakdown of larger molecules during combustion (esp. biomass burning), rather than by biodegradation of larger molecules as HS do. Therefore, while the term HULIS is still used, it should not be equaled to atmospheric humic substances.

In light of the not so humic-like nature, it's unnecessary to define HULIS (or its fractions) thoroughly by analogy with terrestrial/aquatic HS, which was the case in early works (mainly before 2000). HS was usually divided into Fulvic Acids (FA), Humic acids (HA) and Humin, following the procedure of aqueous alkali extraction ( $\text{pH} > 9$ ), acidic precipitation ( $\text{pH} < 2$ ) and further separation from salts. Whereas extraction with such acidic/basic solutions was not necessary for HULIS, since atmospheric water usually possesses a slightly acidic to quasi-neutral nature. As a

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result, studies on HULIS have focused on the water-soluble fraction in the last decade, while the basic-soluble fraction was of concern only in a few studies (e.g. Feczko et al., 2007).

A critical and comprehensive review emphasizing the differences between HULIS and HS was given by Graber and Rudich (2006). Intensive field works were conducted since then, promoted the development of HULIS analysis method and shed light on laboratory work of the suggested origins. This review was focused on the chemical analysis, field observation results and suggested sources of aerosol-phase water-soluble HULIS (which is the exact meaning of HULIS referred to below without notion), with less effort on summarizing its physico-chemical characteristics, such as hygroscopicity and optical characteristics. Besides, the organosulfates and nitrooxy organosulfates, a specific category of HULIS, were found to be exclusively secondary originated, and could therefore serve as ideal secondary reaction tracers. They are referred to but not the focus of this review, for research on them worth individually discussing.

## 2. Chemical analysis method of HULIS

As HULIS is an operational defined rather than a clearly defined term, whether the “HULIS” determined by different isolation procedure refers to the same part of organic fractions is in doubt. The quantification of HULIS is further complicated by lack of standard substances, although Suwannee River Fulvic Acid Standard (SRFA) and some other standard HS obtained from the International Humic Substances Society (IHSS) are usually used as temporary surrogates. Lots of efforts were devoted to establish systematical standard procedure of HULIS isolation, quantitation and chemical characterization, in which the isolation method was of fundamental importance.

### 2.1. HULIS isolation

Some consensus were reached on the chemical nature of HULIS, including high-MWs, weak polarity (thus hydrophobic), highly polyconjugated structure and polyacidic nature. Aqueous isolation methods utilizing one or more of these features are correspondingly developed, compared with each other and then applied to field observations.

An overview of the main isolation methods used is shown in Table 1. Generally, method used include acidity-based (e.g., Ion exchange chromatography (IEC)), polarity-based (e.g., Solid Phase Extraction (SPE)), and Reversed Phase Liquid Chromatography (RPLC) and molecular weight/size-based (e.g., Size Exclusion Chromatograph (SEC)) types or their combination. Among these methods, SPE was most frequently-used due to its easiness and selectivity, while several SPE versions were proposed according to the adsorbents used. Main adsorbents include C-18 (Samburova et al., 2007), HLB (Varga et al., 2001), XAD-8 (Sullivan and Weber, 2006a) and DEAE (Baduel et al., 2009; Havers et al., 1998). A method that is rather different from all others was thermal profiling techniques, which is still controversial and, as an isolation-quantification method, gives ambiguous results. Yu et al. (2004) applied a positive matrix factorization (PMF) model to resolve WSOC species into three groups, and found the group representing the fine-mode dominant, thermally recalcitrant high-MW polar fraction to be humic-like. Hoffer et al. (2006a) further defines HULIS as water-soluble refractory matter, i.e. the fraction evolved only when  $>280$  °C in oxygen atmosphere.

The comparison and evaluation of different method is needed, with respect to consistency, selectivity, recovery, and reproducibility of the fraction isolated. This kind of work is hindered by the ambiguous HULIS definition, lack of standard substances, and limited quantification method. The first comparison work was conducted by Lukacs et al. (2007), in which compounds isolated by SPE (HLB) were shown to be of larger portion than that by SPE (C18) – SAX two-step method (Feczko et al., 2007; Limbeck et al., 2005). The two-step method was again compared to SPE (DEAE) method, with SRFA as standard substance in another work (Baduel et al., 2009). These two methods were both found highly selective. SPE (DEAE) method enjoyed higher recoveries and better reproducibility, while it could limit the choice of subsequent analysis due to the presence of inorganic salts in the final isolates. The adsorbents commonly used in the one-step SPE procedures were further characterized in another comparison work (Fan et al., 2012). All the tested adsorbents (C-18, HLB, XAD-8 and DEAE) in that work were shown to have adequately high reliability, high reproducibility, and low limit of detection (LOD) to be applied to quantify aerosol-phase HULIS. Although DEAE showed higher selectivity toward UV adsorbing compounds (i.e. aromatic and conjugated systems), the potential interference of its highly ionized eluent used render it less suitable for subsequent quantification and characterization.

### 2.2. HULIS quantification

Most quantification method is followed by isolation of HULIS fraction, to avoid interference from other fraction. Gravimetry (e.g., Kiss et al., 2002; Salma et al., 2007, 2010) is the most direct measurement, while this method suffered several disadvantages. Firstly, it is complicated due to the need for dryness with nitrogen stream. Moreover, it may be inaccurate when the weight of sample is very small, due to the large uncertainty as well as possible loss in the complex pre-treatment procedure. In addition, quantification is preferred when realized simultaneously during other chemical analysis.

UV–VIS detection with HS (most of the time being SRFA) as calibration standard was used for HULIS quantification since the early stage (e.g., Zappoli et al., 1999), while suggested wavelength differed among 240 nm (Samburova et al., 2005a, 2005b), 250 nm and 285 nm (Pavlovic and Hopke, 2012) or longer ( $>330$  nm), to balance between higher sensitivity and excluding interactions from other substances (Krivacsy et al., 2008). HULIS determined this way are thus considered as “HS equivalent” concentrations, which could be underestimated up to a factor of 2.5 as compared to ELSD (Emmenegger et al., 2007).

Total Organic Carbon (TOC) analysis is another common, but indirectly, method for HULIS quantification, which determines the total carbon rather than whole mass in the isolated HULIS (HULIS-C). The concentration of HULIS is subsequently estimated by multiplying HULIS-C with a conversion factor. This method is extremely suitable for field work considering its rapidity and easiness to compare with Organic Carbon (OC) and Elemental Carbon (EC) concentrations. The major uncertainty arises from the conversion factor, which ranges from 1.81 (Salma et al., 2007) to 2.5 (Polidori et al., 2008). For HULIS isolated by SPE method, the factor ranged from 1.8 to 2.3, with 1.81 (Salma et al., 2007) for urban HULIS, 1.93 (Kiss et al., 2002) for rural aerosols, 1.94 (Lin et al., 2010b) for a rural site during a harvest season, 2.04 for tropical biomass burning particles (Salma et al., 2010), and a range of 1.89–2.28 for three types of aerosol in summer and winter in Guangzhou (Song et al., 2012). These results indicated that this factor was not universal. On the other hand, Polidori et al. (2008) found a much larger HULIS/HULIS-C value of 2.25–2.54, which may be due to their unique isolation method used. Thus TOC may not be suitable for comparison of different isolation method.

Evaporative Light-Scattering Detection (ELSD) is a recently proposed quantitative detection method for HULIS (Emmenegger et al., 2007). This method is favored for its exclusively analyte concentration dependence (as proved by the good agreement among different calibration standard of SRFA, NAFA and sucrose showed), directness (i.e. no need for conversion factor), and stability (i.e. no baseline shift with mobile-phase changes in separation methods such as gradient elution). This kind of quasi-universal mass detector is especially suitable for the quantification of compounds with unknown structures just like HULIS. In addition, the ELSA itself can offer as a complementary step for some most commonly used polarity-based isolation method (e.g., SPE). The most hydrophobic low-molecular matter which was not separated during isolation (Miyazaki et al., 2009) could be evaporated by the thermodeuder part (i.e. the evaporation tube) included in ELSA before the actual detection (Emmenegger et al., 2007; Young and Dolan, 2003, 2004).

Generally, gravimetry and ELSA seemed accurate way to determine HULIS, with ELSA a better choice as discussed above. UV–VIS is more qualitative than quantitative for its large uncertainty. TOC is also a good choice, for it could offer a direct comparison with other carbonaceous components as represented by OC and EC with acceptable uncertainty.

### 2.3. Analysis method applied for HULIS chemical characteristics

As HULIS is a complex mixture, various analytical methods were applied to characterize it. In the critical review of Graber and Rudich (2006), both the spectroscopic (including UV–VIS, fluorescence, infrared (IR), proton- and  $^{13}\text{C}$ Nuclear Magnetic Resonance (NMR) spectroscopy) and non-spectroscopic (including Gas Chromatography/Mass Spectrometer (GC/MS), Capillary Electrophoresis (CE), elemental analysis, thermal profiling, SEC and ultrafiltration) method applied by then were summarized, with a particularly concern on the technique of determining MW by MS. A lot of new developments were gained since then. Despite the ever-spreading application of the well-established methods, new techniques have been introduced and provided more insights into the chemical characteristics traditionally concerned. In addition, some previously un-explored characteristics were recently investigated. Moreover, molecular-level determination of HULIS was made possible with the development of MS technique.

Traditionally major concerned HULIS characteristics included: (i) **Characteristic spectrum.** Well-characterized UV–VIS and fluorescence spectroscopy of HULIS (Graber and Rudich, 2006) were now commonly used for validation of the presence of HULIS in isolated ambient fractions (e.g. Krivacsy et al., 2008). Moreover, Raman micro-spectroscopic analysis was recently applied to size-resolved atmospheric aerosols (Ivleva et al., 2007), by which soot and HULIS as a whole could be discriminated and quantified in terms of relative abundance. (ii) **Molecular weight range and distribution.** Method mentioned in the review of Graber and Rudich (2006) to address this need included ultrafiltration, SEC and MS techniques.

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