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Analysis of oligomers in atmospheric aerosol particles—analytical challenges

Published online: 28 March 2006
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Introduction

Ambient aerosol particles have a variety of important effects on many atmospheric processes, for example scattering and absorbing solar radiation and affecting cloud formation. Adverse health effects, for example respiratory and cardiopulmonary diseases and mortality, have also been associated with atmospheric particles. Although a major fraction (up to 50%) of ambient aerosol particles is organic material, little is known about this fraction. Despite significant efforts to elucidate the chemical nature of organic particle components in recent decades, often only 10–20% of the total organic mass can be identified on a molecular level [1, 2] although hundreds of compounds have been identified, most of them at trace levels [3].

In recent years several authors have identified high-molecular-weight organic compounds in particles collected in the ambient atmosphere or produced in laboratory experiments. These studies showed that a major part of the total organic aerosol mass (10–50%) can probably be attributed to this new class of compound and that many of these high-molecular-weight compounds pose new challenges in the chemical analysis of atmospheric aerosol particles.

Ambient samples

High-molecular-weight compounds, often named HULIS (humic-like substances), were first detected in ambient atmospheric samples with characteristics similar to those of humic and fulvic acids, especially their ultraviolet (UV) and fluorescence spectra [4, 5]. Solid-phase extraction, size-exclusion chromatography (SEC), and ion chroma-

tography have often been used to separate this class of aerosol components from lower-molecular-weight compounds [5–7] and a variety of detection methods have been used, for example UV, infrared (IR), fluorescence spectroscopy, electrospray ionization (ESI) and laser-desorption/ionization (LDI) mass spectrometry, and nuclear magnetic resonance (NMR) [5–10]. No comprehensive structural information is available for these high-molecular-weight compounds, however.

Because the chemical properties of HULIS are still largely unknown, determination of the molecular weight or concentration of these compounds is difficult to achieve with most analytical methods. Electrospray ionization mass spectrometry (ESI-MS) studies have indicated the maximum molecular weight of HULIS is approximately 500 Da [9]; this compares well with results from a comparative study of size-exclusion chromatography and LDI-MS, which measured similar values for the molecular weight of HULIS [7]. Concentration estimates using UV absorption of Suwannee river fulvic acid as surrogate standard showed that approximately 10% of the total organic carbon (OC) can be attributed to these high-molecular-weight compounds [7]. Zappoli et al. [5], using humic acid as quantification standard, showed that 10–30% of the total OC was HULIS. Limbeck et al. [11] correlated the UV absorption of HULIS with its organic carbon content (by combustion of all organic material and subsequent quantification of CO₂) and showed that use of humic acids as a calibration standard for UV detection underestimates the concentration of HULIS by a factor of approximately two. They found that 5–40% of the total OC collected at an urban site is composed of HULIS.

The sources and mechanisms of formation of this aerosol fraction are still highly speculative. Facchini et al. [12] suggested that biomass burning could be an important source of HULIS, at least in cold seasons, when wood burning for domestic heating is increased. This hypothesis was corroborated by laboratory studies showing that oxidation products from the biomass burning had optical properties and mass spectra similar to those of HULIS [13].

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This suggests that HULIS are formed in the atmosphere by heterogeneous reactions, i.e. formation of these high-molecular-weight compounds by reaction of smaller compounds in aerosol particles. Similar reactions in fog or cloud droplets, i.e. in aqueous media, are also regarded as pathways to HULIS formation [13]. Besides these atmospheric formation pathways, many high-molecular-weight compounds are emitted directly into the atmosphere; these are mainly products of degradation of biological material, for example proteins, cellulose, cell membrane components, etc. A discussion of methods for analysis of these compound classes goes beyond the scope of this article.

A very comprehensive recent review of carbonaceous aerosols in general and of high-molecular-weight compounds in particular is given by Gelencser [14].

Laboratory measurements

Only a few years ago evidence was presented first by Jang et al. and Limbeck et al. [15, 16], that small volatile organic compounds, usually not considered to partition from the gas phase into the particle phase, increase the mass of acidic particles by forming low-volatility condensation products. Several mass-spectrometric studies [17–21] showed shortly after that high-molecular-weight compounds with masses up to approximately 1000 Da are present in secondary organic aerosol (SOA) particles, i.e. particles that are formed in the atmosphere by gas-to-particle conversion. These compounds have been identified in SOA formed from a variety of volatile precursors, for example aromatic compounds or terpenes, which are regarded as the main anthropogenic and biogenic com-

pound classes contributing to SOA mass. Acid seed particles seem to increase the amount and the molecular weight of the high-molecular-weight compounds formed.

Hypotheses have been made about the structure of these high-molecular-weight compounds. Acid catalyzed acetal formation or aldol condensation reactions have been proposed on the basis of mass spectrometric evidence [15, 17, 18, 20]; this suggests most of the high-molecular-weight compounds observed in laboratory experiments are oligomers or co-oligomers. Tolocka et al. [18] performed accurate mass measurements of SOA components generated from terpenes using a Fourier-transform ion cyclotron resonance (FTICR) mass spectrometer and assigned several peaks to small oligomers of carbonyl oxidation products. In contrast with the experimental results, first model calculations showed that an oligomerization of most of these carbonyl compounds would not be favorable under atmospheric conditions [22].

Kalberer et al. found that possibly up to 50% of the total SOA mass can be attributed to oligomers [17]. Similarly to ambient samples, accurate quantification of the oligomer mass fraction is complicated by their unknown structure and, therefore, the lack of accurate quantification standards, which are needed for most analytical methods. Although at the current state of knowledge it seems that a major fraction of organic aerosol particles can be attributed to high-molecular-weight compounds (or oligomers), the identities of the precursors forming these compounds remain unclear.

Table 1 summarizes the analytical methods currently used to analyze different properties of HULIS or oligomers in organic aerosols from ambient atmospheric samples or laboratory experiments.

Table 1 Analytical methods and investigated properties of HULIS and oligomers in organic aerosols

Investigated property	Analytical method	Sample type	Ref.
Molecular size	ESI-MS	Field, laboratory	9, 10, 18–20
	(MA)LDI-MS ^a	Field, laboratory	7, 17, 21
	SEC	Field	5, 7
	VPO ^a	Field	9
	UF ^a	Field	9
Functional groups	NMR	Field	6
	FTIR	Laboratory	15
Structure	LDI-MS	Laboratory	17
	ESI-MS	Laboratory	18–20
	IR	Laboratory	15
Concentration	UV	Field	5, 7
	OC ^a	Field	11, 12
	VTDMA ^a	Laboratory	17
	DMA ^a	Laboratory	15, 19, 20
Formation process	ESI-MS	Laboratory	13, 18–20
	LDI-MS	Laboratory	17
	OC ^a	Field, laboratory	12, 16

^aAbbreviations not explained in the text: OC: combustion methods used to determine the total organic carbon concentration, DMA: differential mobility analyzer, VTDMA: volatility tandem differential mobility analyzer, MALDI-MS: matrix assisted LDI-MS: VPO: vapor pressure osmometry: UF: ultra filtration

Analytical challenges

Chemical analysis of atmospheric particles is performed by use of either on-line techniques, in which single particles are directly analyzed from the air without time-integrating sampling, or off-line techniques, which require sampling of particles, usually on filters or by use of impactors, often for hours or days. The advantages of on-line methods are high time-resolution and less interference from gaseous compounds that potentially interact with the particles during sampling, which is often a serious issue in off-line analyses. In contrast, off-line methods often enable more versatile analysis, for example chromatographic separations. Both approaches have their advantages and should be used complementarily for identification of high-molecular-weight compounds in atmospheric particles. Among the many open questions in the analysis of high-molecular-weight compounds in atmospheric particles, two aspects are discussed below.

1 *Chemical structure of oligomers/high-molecular-weight compounds*

- There is an urgent need to show how the structures of oligomers found in laboratory-generated particles compare with those of HULIS (high-molecular-weight compounds) found in ambient samples. The small amounts of sample usually available and the complex compound mixtures complicate such analyses. Tandem MS experiments complemented with accurate mass determination would be ideal techniques to determine the structure of these compounds in both laboratory and ambient samples. First steps towards such a detailed analysis have recently been described by Tolocka et al. [18].
- Elucidation of the structures of high-molecular-weight compounds might potentially lead to new marker compounds that distinguish SOA from directly emitted organic aerosol mass and possibly even SOA from anthropogenic and biogenic sources, a source apportionment which is not yet possible but urgently needed to assess the particle burden of the atmosphere as a result of human activity. Such marker compounds must be stable in the atmosphere for several days. Mass spectrometric analyses could reveal how stable these oligomers are in an oxidizing atmosphere in the presence of OH radicals, ozone, and nitrogen oxides by observing these compounds in time-dependent laboratory experiments.

2 *Oligomer quantification*

- Accurate quantification of oligomers in aerosols is certainly a major challenge. So far only a few preliminary estimates are available in the literature, all of them obtained with methods that have severe drawbacks. Several authors used humic substances as surrogate calibration standards for quantification of UV absorption even though it is unknown whether humic substances and the high-molecular-weight

compounds (or oligomers) in aerosols are structurally similar; this is crucial for such quantification. Oligomer quantification by thermal separation, as reported by Kalberer et al. [17], is only an approximate method for separation of monomers and oligomers and more detailed studies must be performed to achieve accurate quantification by use of this method. A liquid chromatographic method for separation of HULIS from other organic aerosol components followed by quantification of the organic carbon content, recently reported by Limbeck et al. [11], is a promising approach, because the detection method does not rely on chemical properties of a calibration compound. Similarly, evaporative light-scattering detection would enable quantification which is largely independent of the chemical properties of the calibration compounds and should be explored for analysis of atmospheric samples. Both methods rely on accurate chromatographic separation of the high-molecular-weight compounds from other particle components, however.

The discovery of high-molecular-weight compounds in aerosol particles challenges in many ways the analytical techniques currently used in the atmospheric sciences and opens a wide field for new and innovative analytical developments.

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