



Review

Nuclear magnetic resonance spectroscopy for determining the functional content of organic aerosols: A review



Marie-Cecile G. Chalbot*, Ilias G. Kavouras

Department of Environmental and Occupational Health, University of Arkansas for Medical Sciences, 4301 W. Markham St., Little Rock, AR 72205-7199, USA

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ABSTRACT

The knowledge deficit of organic aerosol (OA) composition has been identified as the most important factor limiting our understanding of the atmospheric fate and implications of aerosol. The efforts to chemically characterize OA include the increasing utilization of nuclear magnetic resonance spectroscopy (NMR). Since 1998, the functional composition of different types, sizes and fractions of OA has been studied with one-dimensional, two-dimensional and solid state proton and carbon-13 NMR. This led to the use of functional group ratios to reconcile the most important sources of OA, including secondary organic aerosol and initial source apportionment using positive matrix factorization. Future research efforts may be directed towards the optimization of experimental parameters, detailed NMR experiments and analysis by pattern recognition methods to identify the chemical components, determination of the NMR fingerprints of OA sources and solid state NMR to study the content of OA as a whole.

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1. Introduction

Organic aerosol (OA) has been associated with direct and indirect climate modifications, reduced visibility, natural and anthropogenic systems destruction and severe air pollution episodes leading to premature deaths (Fowler et al., 2009; Kanakidou et al., 2005; Monks et al., 2009; Ostro et al., 2007; Park et al., 2006; Zanobetti et al., 2009). OA is a spatiotemporally variant, complex and heterogeneous mixture, whose particle size distribution and chemical content depends on emissions from various sources (anthropogenic and biogenic), atmospheric aging (physical and chemical transformations during transport) and weather conditions (Fuzzi et al., 2006; Jimenez et al., 2009; Kavouras and Stephanou, 2002a; Robinson et al., 2007; Zhang et al., 2005). It represents the most significant fraction of urban and continental background PM_{2.5} (particles with aerodynamic diameter less than 2.5 μm; fine) (Chalbot et al., 2013a; Hand et al., 2013; Koulouri et al., 2008; Schichtel et al., 2008; Yin et al., 2010), with the water soluble fraction of organic carbon (WSOC) being accountable for 30–90% of atmospheric OA (Heald et al., 2006; Yoon et al., 2007; Stone et al., 2009).

Organic compounds in the aerosol phase are directly emitted (i.e. primary particles) from the combustion of contemporary

organic material in wildfires, prescribed/agricultural fires and domestic woodburning, fossil fuel combustion and mechanically-generated processes such as wind erosion of geological dust, epicuticular waxes from terrestrial plants and traffic-induced resuspension of road dust and environmental tobacco smoke (Alfarra et al., 2007; Bond et al., 2007; Kavouras et al., 1998a; Kupiainen et al., 2005; Szidat et al., 2006). OA is also formed (i.e., secondary) from the condensation of low vapor pressure organic compounds produced from oxidation reactions of natural and anthropogenic volatile organic compounds (VOCs) with OH radicals, O₃ and NO₃ radicals (Hallquist et al., 2009; Kavouras et al., 1998b; Sakulyanontvittaya et al., 2008).

Aliphatic hydrocarbons, polycyclic aromatic hydrocarbons and their oxygenated and nitrated derivatives, aliphatic aldehydes and alcohols, free fatty acids and their salts, dicarboxylic acids, multi-functional compounds, proteins, phenols, organic nitrates, cyclic acids and humic-like macromolecules have been regularly identified in atmospheric OA (Chalbot et al., 2013b; Graber and Rudich, 2006; Goldstein and Galbally, 2007; Hung et al., 2005; Kavouras and Stephanou, 2002b; Kawamura and Yasui, 2005; Pöschl, 2005; Zhang et al., 2005). The identified organic compounds may represent approximately 20% of the OA mass (computed from OC measurements and assumed organic carbon-to-organic mass (OC-to-OM) conversion factors), leaving the largest OA fraction unaccounted for and introducing large uncertainties in assessing environmental and health impacts (Pöschl, 2005). However,

* Corresponding author.

E-mail addresses: mchalbot@uams.edu, mc_chalbot@hotmail.fr (M.-C. G. Chalbot).

comprehensive molecular characterization of OA may not necessarily be required to describe its atmospheric fate and impact. The physical, optical and biological properties of organic compounds mixtures in the aerosol phase also depend on intermolecular interactions and the number/type of chromophores groups and may be responding in a synergistic and/or confounding mode rather than a simply additive mode (Cappa et al., 2008; Freedman et al., 2009; Kavouras and Stephanou, 2002a; Rincon et al., 2009; Tang, 1996; Zarzana et al., 2012).

Nuclear magnetic resonance (NMR) spectroscopy relies on the absorption (i.e. resonance) of radio frequency (rf) energy by nuclei. While the magnetic moment of a nucleus (e.g. ^1H) is constant, their location in a compound regulates the amount of absorbed rf energy to achieve resonance, which in turn, is related to the strength of the secondary magnetic field generated by the movement of electrons within the external magnetic field. The resonances of individual nuclei are reported in relation to a signal of a chemically non-reactive reference compound such as tetramethylsilane ($(\text{CH}_3)_4\text{Si}$). Following recent technological advances in liquid state, one-dimensional (1-D), multi-dimensional (2-D) NMR and solid state NMR, the chemical content of natural organic matter (NOM) in soil, sediments, peats and sludge of dissolved organic matter (DOM) in surface and ocean water has been extensively investigated (Preston and Blackwell, 1985; Preston, 1987; Simpson, 2001; Simpson et al., 2011, 2012; Wershaw, 1985; Xing, 2001). The results of these studies also stimulated the analysis of atmospheric organic aerosol by NMR. For instance, proton (^1H) and carbon-13 (^{13}C) analyses applied to determine the chemical structures of soil humic substances have been instrumental to the interpretation of NMR spectra from aerosol water extracts (Delort et al., 2004). Since 2000, ^1H and ^{13}C NMR experiments to characterize the functional composition of atmospheric OA have been done, including large aerosol characterization studies such as during the Aerosol Characterization Experiment in Asia (ACE-Asia) (Decesari et al., 2005), the Large-Scale Biosphere-Atmosphere Experiment in Amazonia European Studies on Trace Gases and Atmospheric Chemistry (LBA-EUSTACH; Graham et al., 2002) and Smoke Aerosols, Clouds, Rainfall, and Climate: Aerosols From Biomass Burning Perturb Global and Regional Climate (LBA-SMOCC; Decesari et al., 2006) and Marine Aerosol Production (MAP; Decesari et al., 2011). Furthermore, the content of dissolved organic matter in rainwater, cloud water and fog has been studied (Duarte and Duarte, 2011).

This review provides a synopsis of the progress and current state of the chemical characterization of OA by 1-D and 2-D ^1H and ^{13}C NMR, describes the experimental and analytical challenges and presents the potential benefits of NMR analysis on the understanding of the chemical content and impact of OA. More than 90% of studies included in this review have been published since 2000. Specific attention is paid on the ability to reconcile and quantitatively assess the sources of OA. The first part examines the analytical aspects of the NMR analysis of OA including aerosol sampling and signal processing. The second part presents the findings of NMR studies in different atmospheric environments. The interpretation of NMR spectra by source reconciliation and apportionment tools, including positive matrix factorization, is described in the third part. Lastly, current gaps and recommendations for future research are given.

2. Analytical considerations

2.1. Sampling and processing of aerosol samples

The ability to maintain the integrity of analyzed samples (non-destructive method) by eliminating complex extraction, treatment and pre-concentration laboratory protocols (i.e. polar/non-polar

separation, acids esterification) and perform repeated/multiple tests using the same sample affords NMR spectroscopy unique benefits that may outweigh the need for relatively substantial quantities of material. In traditional ^1H NMR experiments in synthetic chemistry, a concentration of 1 mg/ml is frequently required (i.e. 500–750 μg of material in a 5 mm NMR tube). To achieve the target concentration for atmospheric samples, high volume samplers operating at flow rates of 850 L/min or higher are necessary to collect sufficient quantities of atmospheric aerosol (Decesari et al., 2007; Duarte et al., 2005; Finessi et al., 2012). High-volume Sierra-Andersen cascade impactors have also been used for the collection and analysis of size fractionated organic aerosol (Matta et al., 2003; Decesari et al., 2005). More recently, low (URG Versatile Air Pollutant Sampler) and medium volume samplers have also been used (Decesari et al., 2006; Cleveland et al., 2012).

The preparation of samples for NMR analysis involves extraction of soluble materials from the collection substrates by sonication or agitation in the solvent (i.e. H_2O), centrifuging, drying and re-dissolving in the deuterated solvent (i.e. D_2O) along with the reference compound. As a result, resonance signals of labile $-\text{OH}$ (e.g. alcohols or carboxylic acids) or $-\text{NH}$ (e.g. amines, amides, amino acids) protons may be weak. Despite the strong dependence of ^1H NMR chemical shifts on the pH of the sample, especially for compounds containing acidic and/or basic groups, the addition of buffer solutions (e.g. 0.2 M $\text{Na}_2\text{HPO}_4/0.2$ M NaH_2PO_4 , pH 7.4) was only recently introduced based on NMR analysis of biological samples (Xiao et al., 2009; Bothwell and Griffin, 2011). Attempts to characterize the organic soluble fraction (i.e. the water insoluble fraction) of aerosols included extraction with trifluoroacetic acid (TFA) re-dissolution in organic deuterated methylene chloride (CD_2Cl_2) and dimethyl-sulfoxide ($\text{DMSO}-d_6$) (Decesari et al., 2011). Alternatively, extraction using methylene chloride (CH_2Cl_2), DMSO and methanol (CH_3OH) has been done after removal of inorganic species with HF (Simpson et al., 2006). The use of organic solvents, such as deuterated methods (CD_3OD) and d_6 -DMSO, allows for the detection of exchangeable organic hydrogen atoms that are otherwise undetectable in spectra with D_2O (Duarte et al., 2008; Samburova et al., 2007; Simpson et al., 2006). The major drawback of DMSO is that it is very hygroscopic and has to be used in very dry conditions to eliminate H_2O resonance signals between $\delta^1\text{H}$ 3.0 ppm and $\delta^1\text{H}$ 4.0 ppm that may obscure protons resonance signals from heteroatom-substituted alkanes and aliphatic alcohols. In addition, the DMSO resonances signal at $\delta^1\text{H}$ 2.5 ppm could dwarf resonance signals of protons from unsaturated aliphatic compounds, as well as methyl or methylene groups in α -position of aromatic carbons.

Several studies applied intensive isolation and purification steps using flash chromatography and solid phase extraction (SPE) methods to study specific types of organic compounds. SPE separation methods have been adopted from the extraction of humic and fulvic substances in soil, lake sediments, and natural waters (Aiken, 1985; Malcolm, 1991; Malcolm and MacCarthy, 1992; Swift, 1996) are summarized elsewhere (Graber and Rudich, 2006; Zheng et al., 2013). Humic-like substances (HULIS) analyzed by NMR were isolated by alkaline extraction (0.1 M NaOH) and neutralization by 2 M HCl before separation through an ion-exchange procedure (Havers et al., 1998). Ion exchange chromatography (IEC) with a weak anion exchanger (DEAE or DEAE-cellulose) (Decesari et al., 2000, 2001; Havers et al., 1998) has been used to isolate non polar (NP)/mono-diacidic (MDA)/polyacidic (PA) fractions of aerosols and dust. XAD-8 (Sannigrahi et al., 2006), a combination of XAD-8/XAD-4 (Duarte and Duarte, 2005), or Oasis HLB SPE cartridges (Decesari et al., 2011) were used to separate the acidified hydrophilic and hydrophobic fractions of aerosols and remove inorganic paramagnetic species that might decrease the sensitivity of NMR

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