



NMR spectroscopic applications to atmospheric organic aerosol analysis – Part 1: A critical review of data source and analysis, potentialities and limitations

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ABSTRACT

NMR techniques have been used for more than two decades in atmospheric aerosol research. Compared to aerosol mass spectrometric techniques, NMR applications remain limited but provide complementary information on the C–H structural properties of particulate organic compounds. Such information can be key for organic aerosol source apportionment, provided that a representative library of source-specific reference spectra is let available. In recent years, chemical shift data for a number of atmospheric organic tracers have been reported but significant gaps remain, as well as in the NMR characterization of several secondary organic aerosol systems. Although factor analysis and other multivariate techniques are gaining importance in NMR organic source apportionment, the bulk of the literature studies is based on functional group analysis. The creation of a community of research groups would be highly beneficial in setting standards, overcoming technical limitations and dealing with the complexity of the NMR spectra of atmospheric aerosol extracts.

1. Introduction

1.1. NMR spectroscopy in environmental research

Nuclear Magnetic Resonance (NMR) spectroscopy is a universal technique for organic compounds analysis and it plays a primary role in analytical chemistry applied to biogeochemistry and biology (proteomics, metabolomics). Its employ for atmospheric aerosol characterization remains instead limited with respect to other techniques, especially mass spectrometry. There are inherent limitations in NMR spectroscopy, like the poor sensitivity, especially for carbon and heteroatoms, the difficulty in achieving a second dimension with small sample loads and the challenges posed by the hyphenation with chromatographic systems. All these caveats are discussed in detail in the Part 2 of this review.

Specific challenges, however, are encountered in the NMR analysis of environmental samples i) such samples are often very complex, containing a huge number of different chemical species, each in low amount; ii) the molecular weight of those species spreads from volatile compounds containing few atoms (e.g. formaldehyde), to polymeric

macromolecules like proteins or polysaccharides, to non-repetitive high molecular weight and poorly defined entities like humic acids and related substances; iii) the polarity of components can vary from highly hydrophilic, to extremely hydrophobic, to amphiphilic; iv) environmental samples exhibit an inherent variability, therefore the developed NMR techniques must be suitable for the analysis of a sufficiently long timeline of samples aiming to achieve representativeness with respect to the varying environmental conditions; v) chromatographic fractionation further reduces the amount of sample suitable for analysis.

On the other hand, NMR investigation, targeted to both ¹H and ¹³C nuclei, usually provides a comprehensive and not biased picture of the organic composition of environmental samples, and the obtainment of absolute quantitative data is more straightforward with respect to mass spectrometry. High-resolution modern NMR spectrometers (commonly operating at 500 or 600 MHz frequency on proton) allow enough chemical shift range and resolution to target both individual compounds and the broader chemical environments of organic hydrogen and carbon atoms in the sample [1]. NMR spectroscopy involving macromolecules is usually less informative than which dealing with small molecules; nevertheless, important information regarding the presence of specific functionalities and their relative weight, of substances under

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Abbreviations

AMS (Q-AMS, HR-ToF-AMS)	Aerosol Mass Spectrometry (Quadrupole-AMS, HighResolution-Time-of-Flight-AMS)
DC07	reference Decesari et al., 2007
EUCAARI	European integrated project on Aerosol cloud Climate and Air quality interactions
FGD	Functional Group Diagram
FTICR-MS	Fourier-transform ion cyclotron resonance-mass spectrometry
HULIS	Humic-Like Substances
IEPOX	isoprene-epoxydiol
LC-MS	Liquid Chromatography-mass spectrometry
MSA	Methanesulphonate
NMR (^1H NMR, ^{13}C -NMR)	Nuclear Magnetic Resonance spectroscopy (proton-NMR, carbon-13-NMR)
OA	Organic Aerosol
OOA	Oxidized Organic Aerosol
POA	Primary organic Aerosol
SOA	Secondary Organic Aerosol
WSOC	Water Soluble Organic Carbon

investigation can be achieved. For this reason, NMR has become an essential tool for the study of environmentally occurring Humic-Like Substances (HULIS [2,3]): these include humic and fulvic acids in soil and rivers, complex macromolecules found in the atmospheric particulate or in marine organic matter. When coupled to high-resolution mass spectrometric techniques, high-field NMR spectroscopy can provide valuable information about the main chemical structures of very complex HULIS in atmospheric particulate matter [4].

The topic of NMR spectroscopy investigation of atmospheric samples has been reviewed in recent years, and excellent references can be found ([5,6]). The scope of the present review is to get an updated view of the state-of-art of the targeted topic from the viewpoints of: methodology/instrumentation; data analysis and interpretation; environmental characterization; outlook and developments.

1.2. NMR spectroscopy in atmospheric organic aerosol studies

1.2.1. Monodimensional ^1H NMR spectroscopy

The employ of NMR spectroscopy for characterization of complex atmospheric organic matrices is not new: the first 1D ^1H NMR spectrum of an extract of NIST standard for “urban particulate matter” (NIST 1648) was published twenty-five years ago [7]. The first H NMR data for fog water date back to the same year [8]. However, it was only at the beginning of the XXI century, that the first NMR studies targeting the composition of atmospheric aerosols and fog water explored the effects of environmental conditions (seasonality) and aerosol size distribution ([9,10]) while providing the first attempts to fractionate the organic mixtures into chemical classes [11]. Since then, NMR methods have been employed in a small bunch of studies focusing on cloud and fog water ([12–14]) and rainwater ([15–17]) but it is mainly aerosols the target of the bulk of the existing literature. Typically, aerosol samples collected on fiber-filters or impactor plates are extracted with ultrapure water or other solvents; then the solvent is removed by evaporation and the sample is recovered in a sub-mL quantity of deuterated solvent containing an internal standard (Fig. 1a) for analysis. The addition of a pH buffer is useful to stabilize the chemical shifts of weak acids and bases. Some studies have included a fractionation or isolation step for desalting or purification of HULIS or other chemical classes of OA. A comprehensive discussion of the specific NMR methodologies is provided in Part 2 of this review, while here we present a synthesis of the

results of 1D H NMR characterization studies performed on aerosol samples collected all over the world (see Section 3).

1.2.2. Monodimensional ^{13}C NMR spectroscopy in solution and in the solid state

^{13}C solution NMR was occasionally applied to the analysis of atmospheric samples [18], but the sensitivity drawback makes such approach strongly challenging and restricted to the analysis of very abundant particulate samples collected in polluted areas with only limited information as the final output. However, some CP-MAS ^{13}C studies of solid PM have been pursued [19]. Although still highly challenging, this last approach is attractive because suitable – in principle – for any organic matrices without the need to bring them in solution state. The lack of a general relationship between concentration and peak intensity in ^{13}C NMR makes quantification of the spectral regions less reliable. Nevertheless, information from ^{13}C NMR is highly precious because it is complementary to that of proton NMR, targeting to carbons that are not directly linked to any hydrogen; among these carbons, carbonyls (C=O) are of outstanding importance in atmospheric chemistry. A strong limitation to MAS techniques lies in the poor resolution of the obtained spectra at medium field and slow spinning rate (<25 KHz), that prevents the identification of specific compounds. Moreover, overlap of the different spectral regions is much more severe than in standard ^1H NMR, hampering clear-cut integration. This contingency could be resolved by the employ of very high-field magnets (25 and 28 T) and very fast spinning rates (>100 KHz) in the same conditions employed for biomolecular NMR [20], but with much higher costs.

1.2.3. Bidimensional ^1H and ^{13}C NMR

In spite of much longer use in the study of humic substances, 2D-NMR correlation spectroscopy, either homo- or heteronuclear, has become an important tool in aerosol investigation from the first decade of the century [21]. In homonuclear ^1H - ^1H 2D correlation (COSY, DQF-COSY, TOCSY), the bidimensional dispersion of cross peaks, each possessing two different chemical shift labels, gives rise to improved resolution and reduction of peak overlapping; moreover, information about scalar coupling correlation is obtained. This is often missing in 1D spectra, because the high complexity of spectra rarely allows the recognition of J–J coupled multiplets. Heteronuclear ^1H - ^{13}C 2D spectroscopy (HSQC, HMBC), on the other hand, allows to gain information on carbon resonances that, as previously shown, is very difficult to obtain through direct ^{13}C NMR spectroscopy because of its low sensitivity. Exploiting 2D NMR techniques, some authors [22] identified a much larger number of individual substances in aerosol samples of diverse origins: rural, pollen, road dust, vegetable waxes, biomass burning. In parallel studies, 2D NMR spectroscopy was used in synergy with Fourier-transform ion cyclotron resonance mass spectrometry (FTICR-MS) to investigate the functional groups transformation in secondary aerosol [4].

The major challenge of 2D NMR techniques is the experimental effort required in terms of acquisition time, low sensitivity and complexity in the interpretation. Therefore, the available studies were usually dedicated to single, highly-loaded samples or to very small sample sets. Strong additional information is indubitably provided by homonuclear correlation and, even more essentially, by heteronuclear ^1H - ^{13}C correlation; therefore, the diffusion of such techniques is expected to increase with the raise of the sensitivity. Other non-correlation 2D NMR experiments, like diffusion-ordered spectroscopy (DOSY) could be very informative, providing dimensional clues, but sensitivity and low resolution on the diffusion coordinate still hamper their exploitation in the analysis of very complex atmospheric compound mixtures.

1.2.4. Other nuclei

To the best of our knowledge, in atmospheric studies nuclei different from ^1H or ^{13}C were almost not targeted, either from the monodimensional or the bidimensional approach, because of extremely low

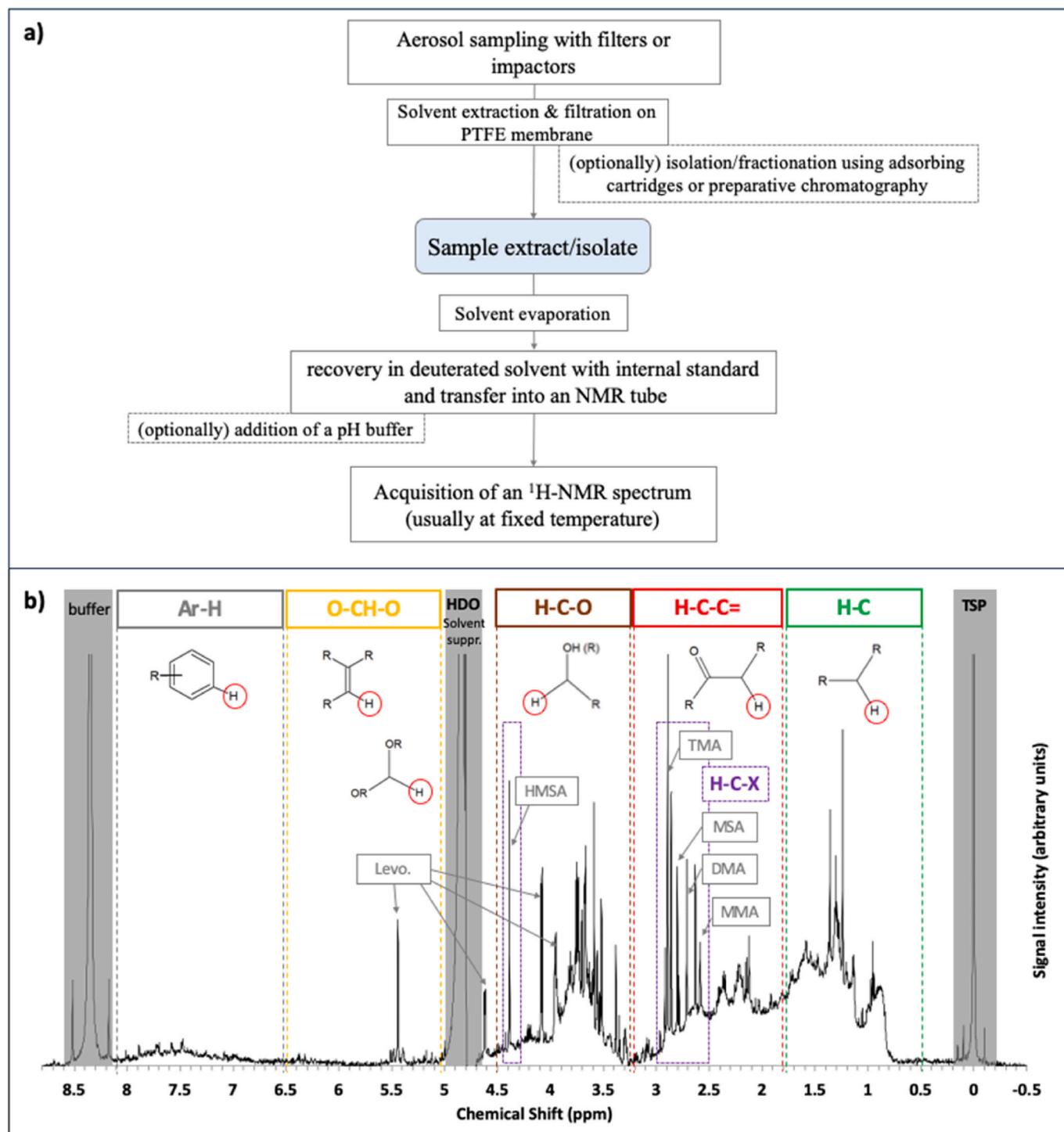


Fig. 1. a) Standard analytical protocol for NMR analysis of atmospheric aerosol samples; b) example of a 1D ^1H -NMR spectrum for an ambient aerosol sample from a polluted site (Po Valley, Italy), recorded at 600 MHz, and with indicated the range of the major functional groups and the specific resonances of a subset of individual compounds (“Levo.”: levoglucosan, “HMSA”: hydroxymethanesulfonate; “TMA”: trimethylamine; “MSA”: methanesulfonate; “DMA”: dimethylamine; “MMA”: methylamine).

sensitivity (^{15}N , ^{17}O), unfavourable spectroscopic properties (^{14}N) or limited abundance in atmospheric samples (^{31}P). This picture is however bound to change, because the outstanding importance of *N*-containing compounds in atmospheric chemistry claims for the implementation of dedicated NMR spectroscopic investigation. In respect to organic phosphorus compounds in the aerosol, at least one study exploited ^{31}P NMR spectroscopy to characterize biological material in airborne particles [23].

2. NMR chemical shift data sources

The examination of aerosol NMR spectra aiming to identify the specific resonances of individual compounds has led to the determination of low molecular weight carboxylic acids, alcohols and esters, polyols and saccharides, amines, amino acids and substituted benzenes in the ambient aerosol ([6,9,24–26] [27]). The modern software for metabolomics, including vast, interactive spectral libraries, has

enhanced the potential of ^1H NMR spectroscopy as a tool in atmospheric organic compounds analytical chemistry [28]. Such libraries, however, miss NMR data for a large range of secondary organic compounds which are common constituents of atmospheric aerosol samples but only rarely found in other environmental matrices. An exception is represented by some degradation products of aromatic compounds of atmospheric interest which have been characterized by studies of oxidation reactions in surface waters and wastewaters (e.g. Refs. [29,30]). However, a real breakthrough could be achieved only through the synthesis of authentic standards for use in calibration of liquid chromatography – mass spectrometric (LC-MS) techniques (e.g. Refs. [31–36]) and for studies of reactivity and lifetime of atmospheric compounds. Beside chemical synthesis, authentic standards can be obtained by collecting secondary organic aerosol (SOA) from reaction chambers and flow tubes and subsequently isolating specific compounds by semi-preparative chromatography [37]. At the time of writing this review, we counted around thirty research papers (see Table 1) reporting chemical shift data or spectra for chemical compounds specifically synthesized for atmospheric SOA research. The largest number is about the aqueous chemistry of carbonyls (e.g. glyoxal, methyl-glyoxal, pyruvic acid) and their reactivity toward oxidants or atmospheric bases (ammonia and amines) ([38–40]), or about the kinetics of hydrolysis of organosulfates and organonitrates ([41,42]). Many recent publications report instead chemical shift data about secondary organic compounds produced by terpene oxidation encompassing numerous key tracers such as methyl-tetrols, 2-methylglyceric acid, isoprene-epoxydiol (IEPOX) -derived compounds (e.g. Refs. [32,43,44]), along with a various range of carboxylic and oxo-carboxylic acids and their dimers formed by the oxidation of monoterpenes (α -pinene, carene, limonene) ([33,34,37,45]). Additional chemical shift data were let available for some of the above species functionalized with hydroperoxyl-, nitrate- or sulfate groups ([35,36,44,46–50]). There is then a paucity of NMR data for anthropogenic secondary organic compounds with the exception of phenolic compounds. Noticeably, no NMR data are available for tracers of alkylbenzene SOA like 2,3-dihydroxy-4-oxopentanoic acid (DHOPA) [51]. Nevertheless, the new NMR datasets originating from the analysis of authentic standards of SOA compounds have a great potential of enhancing the NMR-based molecular analysis of organic compounds in ambient aerosol samples, especially when integrated in modern metabolomic approaches.

3. NMR spectroscopy for organic aerosol source apportionment

The attractiveness of NMR spectroscopy stands in its ability to provide compositional information on complex matrices based on both molecular speciation and functional group analysis. The potential of NMR as a tool for atmospheric aerosol characterization and source apportionment has been highlighted by a number of studies, most of which targeting the water-soluble organic carbon (WSOC) fraction of ambient organic aerosol (OA). Many studies made use of NMR spectral

Table 1
Data sources for ^1H NMR chemical shift data of SOA compounds.

Precursor	SOA products	References
Isoprene	Methyl-tetrols, isoprene epoxydiols (IEPOX), methylthreonic, methylthreonic and methylglyceric acids, others	[31,32,41,43,44,47,50,106–108]
Monoterpenes and sesquiterpenes	Pinonic, pinic and pinolic acid, and their dimers, ketolimononaldehyde, β -caryophyllonic acid, others	[33–37,42,45,46,48,49,109]
LMW carbonyls	Glyoxal and methylglyoxal dimers, hydrates, and adducts with ammonia, amines and aminoacids; C2–C3 aldehydes hydrates; pyruvic acid dimers; various diols and organosulfates	[38–40,110–115]
Olefines	Diols	[113,116]

information derived from laboratory experiments targeting specific sources of particulate organic matter.

3.1. Characterization of organic aerosol sources

The simplest approach for organic aerosol NMR source apportionment consists in comparing the spectra of ambient mixtures with spectra of source-specific particulate matter. As reported by Ref. [52], particulate organics from specific sources show distinct ^1H NMR patterns in terms of occurrence or lack of the individual NMR signals as well in the distribution of the broad unresolved resonances. This phenomenological approach relies on the availability of spectral libraries representative of atmospheric aerosol sources. The actual variability of the NMR patterns for specific sources has been evaluated by several studies. This is especially critical for biomass burning for its complexity and intrinsic heterogeneity in fuel types and burning conditions ([52–54]). Cao et al. [55], for instance, provided ^1H NMR spectra for biomass burning aerosols from wheat straw and coal burning. Some of these studies report the results of burning experiments conducted in laboratory while others include field data from prescribed burnings [56]. In addition, ^1H NMR characterization of biomass burning aerosol samples exposed to photo-oxidation to simulate atmospheric ageing was carried out by Hems et al. [57], while the products of soot oxidation were characterized by Decesari et al. [58].

Since the 90s', the core research on atmospheric SOA has been carried out by means of simulation chambers and other reactor systems like flow tubes, but in spite of the very large number of laboratory experiments performed and the great progress achieved in understanding the multigeneration chemistry of SOA compounds, only a very sparse literature has provided NMR spectra of SOA. Specifically, NMR spectra (typically 1D ^1H NMR but also HSQC, HMBC, COSY and ^{13}C NMR) were obtained for SOA samples originating from the oxidation of isoprene [59], α -pinene ([59,60]), limonene ([61,62]), β -caryophyllene and toluene [63], trimethylbenzene [64], naphthalene ([59,65]) and butadiene [66]. Even if specific NMR compositions were obtained for such diverse SOA systems, the range of laboratory conditions been explored is much narrower with respect to the vast variety of reactor systems, oxidant type and concentrations, and precursors concentrations investigated by means of online techniques such as aerosol mass spectrometry (AMS). Another SOA source probed by means of NMR methodologies is represented by the aqueous-phase production of SOA starting from volatile carbonyls (radical oxidation or Maillard reactions [67–69]) and phenolic compounds [70].

In marine environments, organic aerosols are formed by seaspray depending on wind speed and wave height and as a function of the enrichment of biogenic organic carbon in the sea-surface microlayer. NMR spectral profiles for such primary marine organic particles were obtained using laboratory setups for in situ aerosolization of seawater such as the “bubble bursting chambers” ([71–73]). Finally, NMR spectral profiles for terrestrial biological aerosols were obtained from pollen extracts [74].

3.2. NMR datasets of ambient aerosol composition

Fig. 2 shows a world map with the location of the field experiments providing NMR data for ambient organic aerosols. A relatively good measurement coverage was obtained for South America, with one rural site in Brazil characterized during the dry season and the onset of the rainy season ([24,75]), and seven urban locations across Countries influenced by marine, continental and mixed air masses [5]. In North America, NMR data were obtained for rural and urban sites in south US States ([6,76–78]) and New England [79]. The largest body of information apparently originates from measurements performed in European countries and especially in Portugal ([21,80,81]), Spain [82], Ireland ([83,84]), Italy ([85,86]), Hungary [4], Czech Republic [87], the Netherlands [88] and Finland [89]. Fewer observations were carried out

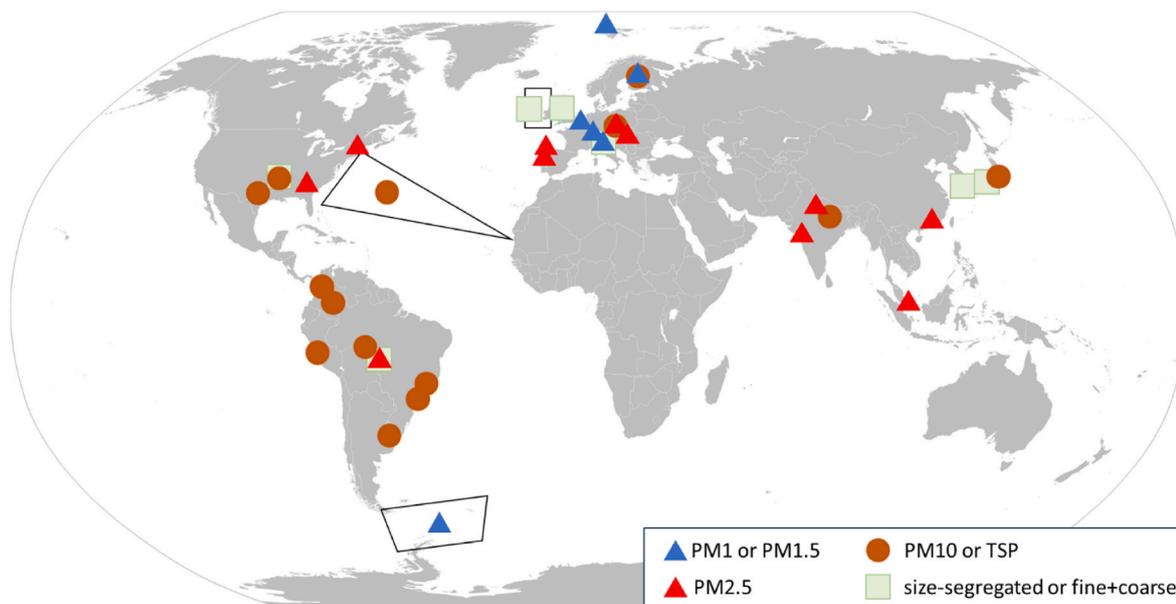


Fig. 2. Global distribution of organic aerosol NMR measurements. Explanation about data sources in the text.

in east and south-east Asia ([9,18,90,91]). All the publications from studies based in India are very recent ([92–94]) suggesting that NMR spectroscopy is gaining importance in characterizing the pollution hot-spots in the Indian subcontinent. Observations in China are still very scarce [95], and are completely missing in Oceania, Russia, central and west Asia and in the entire Africa. First NMR data from the Rwanda Atmospheric Observatory [96] are in course of analysis. At the high latitudes, submicron aerosols were characterized by ^1H NMR spectroscopy in the Southern Ocean and sub-Antarctic waters [73]. In parallel, a program for monitoring organic aerosols employing NMR methodologies has recently started in the Svalbard Islands [97]. Finally, marine aerosol data in the mid-latitudes were collected in the North Atlantic during three research cruises ([84,98]), while no data are available from other oceanic regions. Overall, the global coverage of organic aerosol observations by NMR methodologies still shows large gaps. Moreover, at most locations, data analysis is based on selected samples without characterization of the effects of air mass origin and environmental conditions. Exceptions are the studies performed in Europe by Ref. [88] and in US by Refs. [77–79].

The dependence of NMR composition on particle size was occasionally investigated by means of multi-stage impactors or dichotomous (fine and coarse) samplers (e.g. Refs. [9,75,87,99,100]). Suzuki et al. [9] identified a specific contribution of polyols in coarse particles. Polyols and saccharides (and more broadly, alkoxy H–C–O moieties) were indeed found to be enriched in the supermicron aerosol with respect to submicrometric particles in all the studies reporting size-segregated NMR compositions from all geographical locations ([84,91,100]) indicating that the contribution of biological material in 1–10 μm – sized particles must be widespread and it is well traced by ^1H NMR techniques. Saccharides and polyols are often accompanied by low MW metabolites like choline and betaine, showing characteristic singlets at 3.18 and 3.25 ppm of proton chemical shift. Such metabolites were identified in biological aerosol by Ref. [74], in coarse particles in an urban environment by Ref. [87] and in the very pristine regions of the Southern Ocean also in submicron particles [73]. The pattern of resonances of choline and betaine (possibly associated with acetyl-choline) is expected to contribute to the “H–C–X” functionalities found in coarse particles by Refs. [9,100]. We can conclude that such metabolites can be suitable – yet underexploited – tracers for biological aerosols and that could be easy and important targets for NMR-based metabolomic studies (“aerosolomics”) [26].

3.3. Functional group analysis

The functional group diagram (FGD) was introduced by Decesari et al. (2007) ([101], hereafter DC07) as a first approach to exploit the NMR functional group composition for source apportionment of aerosol WSOC. The FGD method has the advantage of its simplicity, being based on a few variables extracted from the 1D ^1H NMR spectra, namely the relative intensity of broad NMR bands tracing the abundance of the main functionalities, which are largely independent from spectral resolution (Fig. 1b). For this reason, the method was applied by several authors to 1D ^1H NMR datasets of ambient WSOC from various locations around the world ([77–80,85]). In their original study, based on a small set of samples, DC07 noticed that intensities of acyls and alkoxy groups showed an inverse correlation while H–C–X ($X \neq \text{O}$) functionalities are more important at marine locations. WSOC samples containing a relatively high amount of alkoxy groups and aromatics are characteristic of biomass burning while the samples showing a larger content of acyls are dominated by SOA sources. The study provided ranges of variability in the FGD for the three source categories. It should be noted that the “biomass burning” sector of the diagram is representative of fresh biomass burning aerosol, while aged smoke samples, becoming depleted of H–C–O alkoxy groups, exhibit a composition better fitting in the “SOA” range. Examples of ^1H NMR spectra of aged smoke, depleted of alkoxy groups, are provided by Ref. [88] (their Fig.8) and by Ref. [98].

The attribution scheme of DC07 was later improved hosting new spaces in the functional group diagram for sources of primary aerosol like pollen [100], road dust and plant waxes [52], all characterized by very high alkoxy group contents and a variable amount of aromatics. The inclusion of a specific range accounting for the functional group distribution of pollen material resulted crucial to describe the variability of the composition of PM10 in the Southern Mississippi plain [78], whereas the original three domains described by DC07 were enough to map most of the compositions of the PM1 samples collected in the Po Valley (Italy) described by Ref. [85] most probably in reason of the scarce contribution of pollen in submicron particles.

The actual range of the source-specific functional group distributions in the FGD space is controversial because several follow-up studies have reported NMR compositions falling systematically outside the boundaries indicated by DC07. Such boundaries were set based on a small sample number and may have missed important sources of variability in the composition of ambient aerosols. However, the same methodology,

when applied to an extended set of WSOC samples ($n = 157$) from eight European locations and collected during the project “European integrated project on Aerosol cloud Climate and Air quality interactions” (EUCAARI) [102], shows that the functional group composition can be relatively well mapped by the boundaries fixed by DC07 even when considering a large numerosity of samples (Fig. 3). It can be shown for instance that.

- The samples collected at an urban site in Switzerland (Zurich) were assigned to biomass burning aerosols in agreement with the presence of strong residential wood burning sources in the Swiss Plateau in wintertime.
- Several samples collected in the Po Valley in the summer show compositions at the boundary between the “SOA” and the “marine OA” sectors which can be due to the high contributions of methanesulfonate (MSA) and amines, the latter being associated also to farming/husbandry activities; therefore, the “marine OA” functional groups space can actually host also compositions for rural areas characterized by widespread agricultural sources.

- Finally, the presence of samples in the “biomass burning” sector but showing a low aromatic content can be explained by the contribution of biological material, exhibiting a functional group distribution with a very high alkoxy content [100].

In conclusion, based on the EUCAARI findings, the ranges of functionalities indicated by DC07 is confirmed even if: a) we found evidence for an extra range of compositions enriched in alkoxy groups in agreement with the source category for “pollen” and biological material proposed by Ref. [100]; and b) the observed patterns for urban aerosols were measured in areas impacted by wood burning and aged SOA, clearly differing from the samples studied by Refs. [77,94], very rich in unfunctionalized aliphatics and certainly not fitting in these ranges of functional groups distributions indicated in Fig. 3. Therefore, the FG diagram proposed by DC07 can successfully map the WSOC sources for the EUCAARI dataset, originating mostly from rural and coastal locations, but it does not fully account for sources of biological and urban aerosols. It is however challenging to explain the discrepancies with literature studies focusing on organic aerosol types whose sources

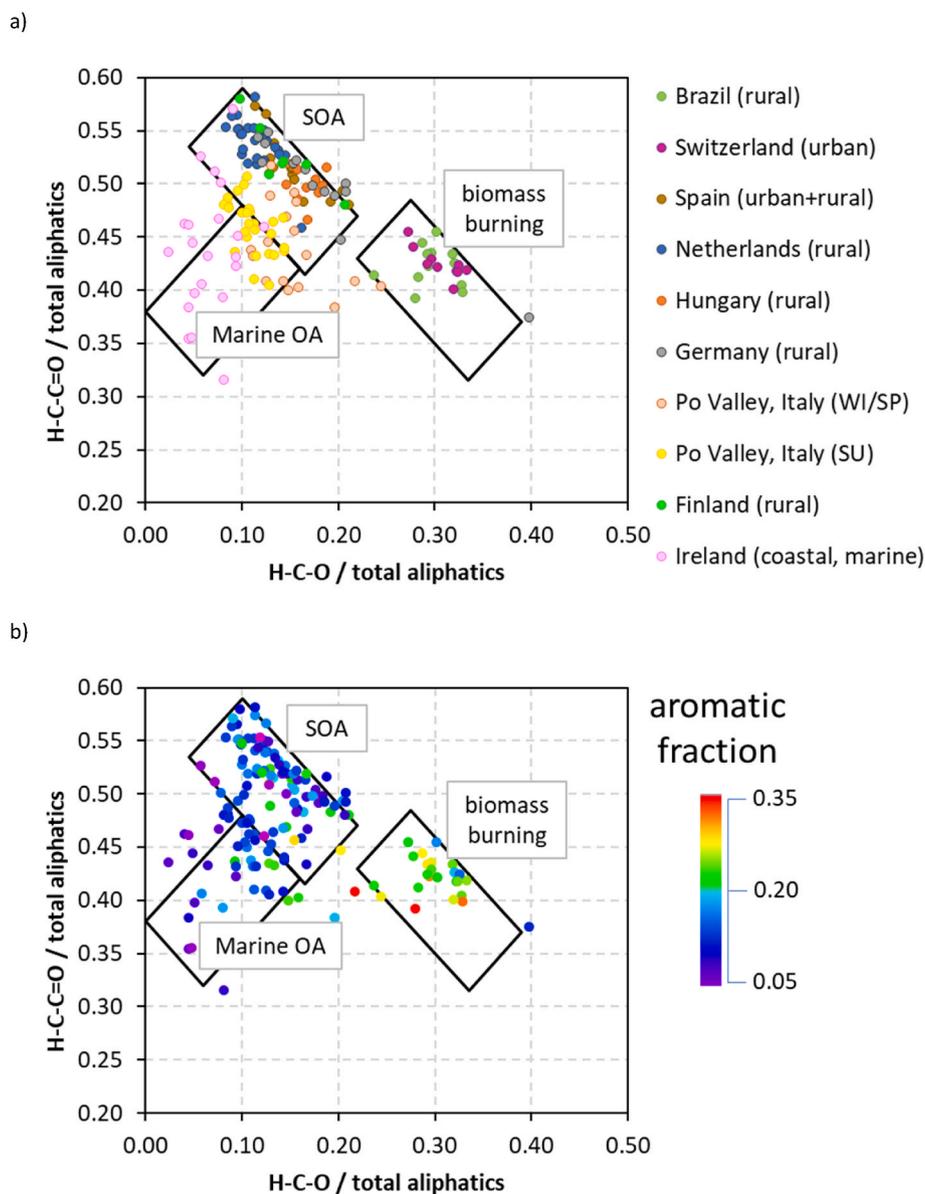


Fig. 3. Functional group distributions of the EUCAARI samples [102] analyzed by the categorization scheme of [101]. The samples are classified according to sampling location (panel a) or the fraction of aromatic carbon with respect to the total NMR-detected organic carbon in aerosol WSOC (panel b).

should be mapped onto the range of the EUCAARI samples but actually do not. For instance, functional group analysis of a large rural aerosol WSOC dataset discussed by Ref. [79] shows a poor overlap with boundaries set by DC07 for SOA, biomass burning and marine aerosol. Similarly, the functional group distributions of the samples collected in Aveiro (PT) [80] elude the DC07 classification while the datasets reported in Fig. 3 for Barcelona and Montseny (EUCAARI) fit into it. In absence of intercomparison experiments, it is difficult to assess the effect of differing protocols for sample analysis and data processing (e.g., spectral baseline processing, etc.). In conclusion, the actual span of source-specific functional group composition in the FGD remains uncertain. It is certainly larger than originally proposed by DC07 but its actual breadth is unclear because of unassessed caveats in the protocols for NMR analysis and calculation of the functional group carbon concentrations.

The employ of 1D ^1H NMR spectroscopy for functional group analysis represents a simple method for WSOC source identification and apportionment. Because of the inherent inability of ^1H NMR to detect hydrogen-depleted functional groups (like sulfates, nitrates, nitro groups, aromatic carboxylic etc.), but its superior potency in detecting H-containing functional groups, the NMR-based functional group analysis is complementary with respect to other techniques such as FTIR spectroscopy ([103,104]). Future development should therefore focus on the ability of NMR to detect specific functionalities to which the other techniques provide lower specificity, like the aromatics, and intrinsic quantitative measurements. NMR spectroscopy is unique in providing a clear split between aromatic, alkenylic, alkoxylic and aliphatic groups and this feature deserves further investigation for its use in tracing aromatic-rich organic compounds in the aerosols, as in the case of fresh and aged biomass burning particulate matter. As evidenced in the introduction, investigation of less sensitive nuclei, like ^{14}N and ^{15}N , possibly exploiting 2D techniques, represents an additional target for future research.

3.4. NMR organic source apportionment by factor analysis

Most of the recent advancements in organic aerosol NMR source apportionment are based on factor analysis techniques, in analogy with the – now well-established – approaches developed for mass spectra deconvolution methodologies in AMS applications [105]. The techniques for NMR factor analysis are discussed in the Part 2 of the present review. Briefly, a timeline of NMR spectra is decomposed into a linear combination of a few factors, each characterized by a specific spectral profile and a varying contribution to the overall OA (or WSOC) concentration. Table 2 provides a survey of organic aerosol NMR factor

analysis studies showing the most frequently found “factors” and related organic sources in the atmosphere.

The most frequently identified spectral profiles refer to methanesulfonate (MSA), low molecular weight alkyl-amines, biomass burning and the so-called humic-like substances (HULIS). Such HULIS were defined by their spectroscopic features but can comprise a broader WSOC fraction than the truly high-molecular weight humic-like substances in the aerosol [88]. The time trends of the HULIS contributions to WSOC indicates a continental origin in polluted environments. Intensive photochemistry can lead to more HULIS types, with a more or less oxidized composition, in analogy with the “oxidized organic aerosol” (OOA) factors of the AMS [86]. In more pristine continental environments, such as the boreal forest, SOA factors attributed to terpene VOC oxidation could be found [89]. Finally, when expanding the analysis from submicron aerosols to total suspended particulate matter (TSP), the contribution of pollen material in terrestrial aerosols becomes prominent and could be identified as a unique factor [78].

All the studies reported in Table 2 refer to 1D ^1H NMR datasets of WSOC. Therefore, the NMR factor analysis methods developed so far can support the interpretation of the AMS factors commonly named as “OOA”, which are largely recovered into WSOC and for which the AMS provides poor resources for identification. A limitation in most of the published NMR-based factor analysis studies is the small numerosity of samples and scarce time resolution. Nevertheless, the increasing resolution provided by a wider availability of high-magnetic field spectrometers and the consequent gain in sensitivity and acquisition times enables the analysis of a longer timeline of samples. For instance, Chalbot et al. [78] discusses a factor analysis study based on 51 TSP samples. The main limitation of the application of factor analysis to NMR datasets reflect the caveats highlighted for the AMS and in particular the need of suitable libraries of “representative” spectra for the specific sources, often provided by targeted reaction chamber experiments. In addition, factor analysis can be accurate in discriminating the contributions of primary and secondary aerosol sources which become mixed at a specific location (the receptor), but it can fail to represent chemical transformations such as ageing of organic aerosols occurring on site at the receptor level: in this case, an unconstrained number of factors tracing different ageing states is often produced. This problem is not limited to factor analysis, on the contrary it is at the heart of source apportionment of SOAs. Are there specific secondary organic compounds with sufficient stability in the atmosphere to serve as chemical tracers? And is it possible to trace SOA on the basis of its specific refractory organic constituents if the largest fraction evolves fast in composition? And to what extent source-specific SOA fractions can be traced in time at the manner of distinct components of the aerosol if

Table 2

NMR factors and related Organic Aerosol sources most frequently identified in factor analyses studies. First column: sampling location; second column: PM size fraction; third column: factor analysis methods applied; fourth column: factors/sources identified; fifth column: other complementary techniques used to organic aerosol source apportionment in each specific studies.

Location	Sample type	Factor analysis technique	Factors identified	Ancillary measurements
Eastern North Atlantic [84]	PM1.5, WSOC	PCA, PMF, NMF, MCR	up to 5 factors: 1) MSA, 2) amines, 3) aliphatic primary marine OA, 4) anthropogenic OA, 5) marine SOA	Q-AMS
Boreal forest in Finland [89]	PM1, WSOC	PMF, NMF, MCR	three factors: 1) local unknown sources, 2) HULIS, 3) amines, 4) biogenic terpene SOA	Q-AMS
The Netherlands [88]	PM1, WSOC	PCA, PMF, NMF, MCR	up to four factors: 1) MSA, 2) HULIS, 3) aliphatic less aged SOA	HR-ToF-AMS
Po Valley, Italy [85]	PM1, WSOC	PMF, NMF, MCR	up to five factors: 1) MSA, 2) primary biomass burning, 3) secondary biomass burning, 4) background pollution (HULIS), 5) amines	HR-ToF-AMS
Po Valley, Italy [86]	PM1, WSOC	PMF, NMF, MCR	up to four factors: 1) amines, 2) cooking aerosol, 3) HULIS (less oxidized), 4) HULIS (more oxidized)	HR-ToF-AMS, ATOFMS, TAG-GC/MS
Po Valley, Italy [117]	PM1, WSOC	NMF, MCR	up to three factors: 1) Biomass Burning primary organic aerosol (POA), 2) biomass burning aqueous-SOA, 3) local SOA (with amines)	HR-TOF-AMS
Southern Mississippi Valley [78]	TSP, WSOC	PMF	three factors: 1) pollen, 2) biomass burning, 3) biomass burning + SOA	
North Atlantic [98]	TSP, WSOC	PCA	Four factors: 1) marine OA, 2) biomass burning, 3) urban, 4) mixed sources	FTICR-MS

chemical compounds from different sources react together leading to new products? These are the long-standing questions about source apportionment of atmospheric SOA for which no general answers have been found yet.

4. Conclusions

NMR techniques remain a niche in aerosol organic chemistry, but NMR spectroscopy has a great potential for the characterization of complex mixtures of particulate organic compounds, especially if in combination with other techniques (e.g., AMS, FTIR, FT-ICR, fluorescence spectroscopy). While NMR spectroscopy is inferior with respect to the other techniques in determining oxygen-containing functionalities and the oxidation state of organic matter, it provides a more clear split between aromatic and aliphatic structures together with accurate structural information on the C–H backbones of the organic compound complex mixtures in the aerosol which turns particularly useful with the aim of source attribution and source apportionment. Most of the existing aerosol NMR studies have focused on 1D ^1H NMR techniques, in virtue of their better sensitivity and suitability for the analysis of larger sets of samples. 2D techniques (both homonuclear and heteronuclear) provide a powerful tool of structural analysis but have been limited to the analysis of fewer, selected samples. Finally, the NMR determination of heteronuclei is yet to be extensively explored but sensitivity remains an issue with generally available, middle-field spectrometers.

The ^1H NMR functional group distributions of aerosol WSOC have been used for source identification in several field campaigns across the world, highlighting a potential for mapping patterns of C–H-containing functional groups onto a few major source categories such as biomass burning, pollen, SOA and marine aerosols. There remain inconsistencies between studies in setting the boundaries for such source-specific functional groups distributions which highlight the need for better data sharing and standardization of the techniques for NMR spectra acquisition and processing.

The development of multivariate statistical techniques for spectral deconvolution is expanding and it provides new opportunities for the elaboration of the spectral information from long timeline of samples, now made possible by the easier access to and better automatization of middle-field NMR spectrometers. However, the potential of NMR-based factor analysis can be fully exploited only if benchmarked on comprehensive libraries of representative source-specific NMR spectra. Currently, even if specific NMR datasets have been acquired for several biogenic and anthropogenic sources and chemical shift data for a number of atmospheric chemical tracers have been reported, large gaps remain, because the great variability in the sources requires more systematic investigation. The spreading of NMR applications in aerosol studies claims for strengthening the network of a growing NMR atmospheric community for better standardization of protocols for the acquisition and processing of the spectra, as well as for sharing chemical shift data and libraries of reference NMR spectra.

CRedit authorship contribution statement

Stefano Decesari: Conceptualization, Data curation, Project administration, Visualization, Writing – original draft, Writing – review & editing. **Marco Paglione:** Conceptualization, Data curation, Writing – review & editing, Visualization. **Andrea Mazzanti:** Conceptualization, Data curation, Methodology, Writing – review & editing. **Emilio Tagliavini:** Conceptualization, Data curation, Formal analysis, Methodology, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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