

Characterization of water-soluble organic compounds in atmospheric aerosol: A new approach

Stefano Decesari, Maria Cristina Facchini, and Sandro Fuzzi

Istituto di Scienze dell'Atmosfera e dell'Oceano, CNR, Bologna, Italy

Emilio Tagliavini

Dipartimento di Chimica "G. Ciamician," Università di Bologna, Bologna, Italy

Abstract. A new methodological approach is proposed to characterize aerosol water-soluble organic compounds (WSOC). Real aerosol and fog water samples were subjected to a procedure based on a combination of chromatographic separations, functional group investigation by proton nuclear magnetic resonance (HNMR), and total organic carbon determination. The complex mixture of aerosol/fog WSOC was separated by a chromatographic procedure into three main classes of compounds: (1) neutral/basic compounds; (2) mono- and di-carboxylic acids; (3) polyacidic compounds. Characterization by HNMR spectroscopy showed that fraction 1 is mainly composed of polyols or polyethers, fraction 2 is mainly composed of hydroxylated aliphatic acidic compounds, while fraction 3 is composed of highly unsaturated polyacidic compounds of predominantly aliphatic character, with a minor content of hydroxyl- groups. Quantitative data on the three classes of compounds were then derived from total organic carbon analysis, showing that the three separated fractions together account for 77% (in terms of C) of the total WSOC concentration of a fog water sample. Further quantitative information on the functional groups present in the three separated fractions can be obtained from HNMR spectra. This newly proposed approach to aerosol WSOC characterization provides comprehensive and synthetic information on aerosol organic composition which can be helpful for modeling purposes and is also particularly useful when aerosol chemical mass closure is pursued.

1. Introduction

There is now a general consensus in the literature that the chemical composition of atmospheric aerosol can no longer be reduced to that of inorganic salts; organic and inorganic composition must be linked in order to understand and properly describe in models the physical and chemical processes occurring in the multiphase atmospheric system (aerosols and clouds). Although several experimental results have shown that organic compounds (OC) constitute an important fraction of atmospheric aerosol [e.g., Seinfeld and Pandis, 1998], their molecular composition still remains poorly known. Identified organic compounds in aerosol typically account for 10% or less of the mass of total organic carbon measured by thermal analysis [Rogge *et al.*, 1993; Saxena and Hildemann, 1996].

Even less known is the nature and abundance of water-soluble organic compounds (WSOC) in atmo-

spheric aerosol, which contribute to the ability of aerosol particles to act as cloud condensation nuclei (CCN) [Novakov and Penner, 1993; Novakov and Corrigan, 1996]. Furthermore, WSOC, once dissolved within cloud droplets, will also influence cloud chemistry. The few data available in the literature report that WSOC account for a percentage of total aerosol carbon ranging from ~ 20 to 70% [Saxena and Hildemann, 1996, and references therein; Zappoli *et al.*, 1999; Facchini *et al.*, 1999].

Saxena and Hildemann [1996] conducted a theoretical study aimed at deriving from literature data a list of compounds that are expected to contribute to aerosol WSOC, but their hypothesis that WSOC are a mixture of polar oxygenated, multifunctional compounds (i.e., compounds with more than one of the following functional groups per molecule: COOH, C=O, CHO, COH, COC, CONO₂, CO₂⁻, CNH, CONH₂) still awaits experimental confirmation.

Traditionally, chemical analysis of aerosol OC is performed using an individual compound approach: gas chromatography coupled with mass spectrometry (GC/MS) is the most common tool for investigating the

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molecular composition of aerosol OC after single or multiple organic solvent extraction of samples [Wauters *et al.*, 1979; Mazurek *et al.*, 1987; Rogge *et al.*, 1993]. However, in these methods a substantial portion of polar oxygenated organic compounds, the more water-soluble ones, remains unanalyzed. Even if the solvent extraction is efficient in terms of recovery of total OC, the resolution of the complex mixture containing a wide range of different organic molecules is still inefficient, and the single component speciation approach normally ends up accounting for a few percent of WSOC composition.

We propose here a new approach for the characterization of aerosol WSOC, based on a combination of chromatographic separations, organic functional group analysis, and total organic carbon analysis. Functional group analysis can be performed using several spectroscopic techniques: IR spectroscopy (or Fourier transform infrared (FTIR) spectroscopy), UV spectroscopy, fluorescence, and nuclear magnetic resonance (NMR). Such techniques have been sporadically applied to the analysis of aerosol organic constituents [Allen and Palen, 1989; Gundel *et al.*, 1993; Blando *et al.*, 1998; Havers *et al.*, 1998; Suzuki *et al.*, 1998], but rarely to close the aerosol organic carbon mass balance.

The main drawback in the application of all spectroscopic techniques to the characterization of complex mixtures of organic species, as in the case of atmospheric aerosol, is that they do not allow one to attribute the functional groups detected to a particular molecule or to evidence the occurrence of molecules carrying more than one functional group. For this reason, we have developed a chromatographic pre-separation procedure of WSOC into different classes, followed by NMR characterization, which has only recently been applied to the analysis of atmospheric samples [Havers *et al.*, 1998; Suzuki *et al.*, 1998]. Total organic carbon content in the individual classes of compounds separated by chromatography was also measured by a liquid Total Organic Carbon (TOC) analyser.

To implement the new approach, two different types of samples were used: (1) aerosol water extracts and (2) fog water. Fog water, in fact, contains the WSOC "naturally" extractable by condensed water upon droplet formation.

2. Experimental Result and Discussion

2.1. Fine Aerosol and Fog Water Samples

Aerosol and fog water samples were collected at the field station of S. Pietro Capofiume in the Po Valley (northern Italy). The station is located in an area characterized by intensive industrial, trading and agricultural activities, and where high levels of pollution are reported [Fuzzi *et al.*, 1996].

Fine aerosol samples ($d < 1.5 \mu\text{m}$ diameter) were collected on pre-fired 47 mm quartz-fibre filters. Filters were then cut into small pieces and extracted with 1.0 mL of high-performance liquid chromatography (HPLC) grade water by sonication.

Fog water samples were collected using an active string collector [Fuzzi *et al.*, 1997], entirely made out of stainless steel to avoid problems of artefact formation and adsorption of organic compounds on the surfaces. Fog water samples were filtered on 47 mm quartz-fibre filters within a few hours after collection and stored frozen in Pyrex glass bottles until the time of analysis.

While several aerosol and fog water samples were used to set up the procedure described below, the quantitative results presented here refer to one specific aerosol sample and one fog water sample, which underwent the entire analytical procedure. The total C, organic C, and water-soluble organic C content of the two samples measured by thermal analysis are summarized in Table 1. Total and organic C analyses of the aerosol sample were performed by evolved gas analysis [Putaud *et al.*, 1999], while the water-soluble C content of both aerosol extract and fog water were performed using a Shimadzu TOC-5000A liquid analyzer.

2.2. NMR as a Tool for the Speciation of Organic Compounds in Aerosol and Fog Water Samples

NMR is far less sensitive compared to chromatographic techniques and other spectroscopic methods. In spite of this, proton NMR spectroscopy (HNMR) is applicable to the analysis of organic aerosol components, and spectra with a good signal-to-noise ratio can be acquired for samples containing less than 1 mg

Table 1. Summary of the Carbon Content of the Two Samples Which Underwent the Complete Procedure Described in the Paper

Fine Aerosol*		Fog Water	
Mass concentration, $\mu\text{g m}^{-3}$	73		
Total carbon, $\mu\text{g C m}^{-3}$	10.4		
Organic Carbon, $\mu\text{g C m}^{-3}$	9.8		
Water-soluble organic carbon, $\mu\text{g C m}^{-3}$	5.7	dissolved organic carbon, mg C L^{-1}	230

*The aerosol was sampled with a collector provided with an inlet cutoff of $1.5 \mu\text{m}$.

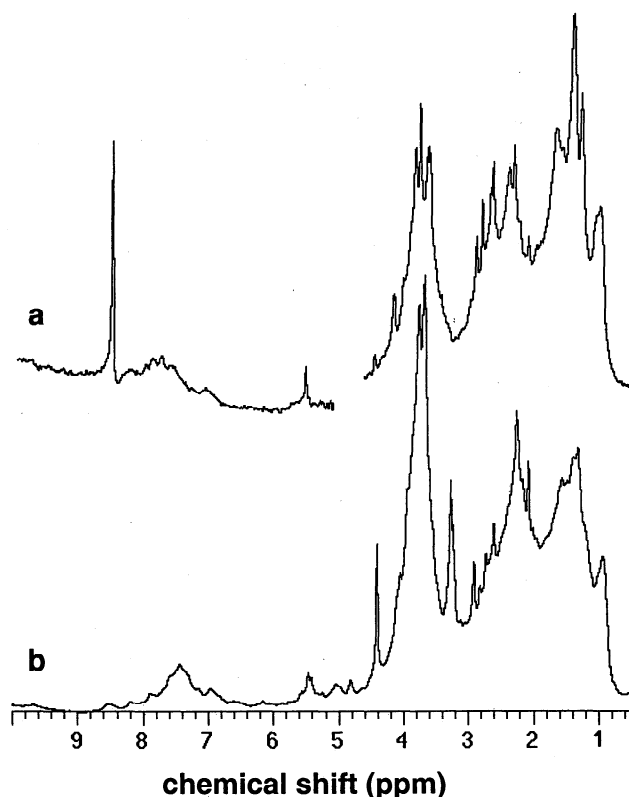


Figure 1. HNMR spectra at 300 MHz of aerosol extract (curve a) and fog water (curve b). The reported chemical shifts are referred to the internal standard TSP d_4 . About 5000 scans were collected for each spectrum. Presaturation of HDO (mono-deuterated water) was performed with transmitter radiofrequency, and a 4 s delay between scans was allowed with a 45° flip angle pulse, a 4500 Hz sweep width, and 18 K data point set. The region between 4 and 5 ppm is not shown in spectrum a because of a residual signal of HDO.

of organic carbon. NMR, as opposed to UV or fluorescence spectroscopy, is also able to identify individual compounds and is not affected by interference due to inorganic compounds, which account for the greater part of the aerosol particle mass. Another important characteristic of NMR spectroscopy is that quantita-

tive analysis is straightforward, since the integrated area of the spectra is proportional to the moles of protons present in the sample [Derome, 1987; Braun *et al.*, 1998]. The aerosol water extracts and fog water samples were first analyzed by NMR spectroscopy before chromatographic separation to obtain preliminary information on the main functional groups present. Extraction of aerosol samples for HNMR analysis was performed with D_2O containing 0.05% by weight of sodium 3-(trimethylsilyl)-2,2,3,3- d_4 -propionate (TSP d_4 , the internal reference standard). Fog samples were first freeze-dried and then redissolved in the same deuterated solution used to extract the filters. WSOC recovery after this procedure was higher than 90%.

HNMR spectra were recorded on a Varian GEMINI 300 spectrometer at 300 MHz in a 5 mm probe. Figure 1 shows the HNMR spectra of the aerosol water extract (curve a) and of the fog water sample (curve b). Some individual compounds, identified in the samples on the basis of their chemical shift, are reported in Table 2. Most of these compounds have recently been detected by HNMR spectroscopy in fog water samples collected in Japan [Suzuki *et al.*, 1998].

On the other hand, the most evident feature of both spectra of Figure 1 is that sharp signals account for a minor portion of the total integrated area of the spectra. Most of the signals remain unresolved, appearing as a continuous distribution and suggesting the occurrence of complex mixtures of structures. Nevertheless, some spectral regions or distinct peaks can be attributed to a few main categories of functional groups.

Aromatic protons appear in the spectral region between 6.7 and 8.3 ppm as a weak continuous band. The maximum is located at 7.5-7.6 ppm, suggesting that electron-attraction substituents (carbonyl-, carboxyl-, and nitro-) are more abundant than electron-donor substituents (hydroxyl-, methoxyl-, alkyl-, amino-). No aldehydic protons were observed (9-10 ppm). A relatively intense continuous spectrum of aliphatic protons appears between 0.7 and 4.2 ppm. Aliphatic protons are particularly abundant in the following regions: 0.7-1.0 ppm (methyl groups), 1.2-1.8 ppm (chain methy-

Table 2. Individual Compounds Detected by HNMR Analysis in the Aerosol Extracts and in Fog Water Samples

Compound*	Chemical Shift, ppm
Lactic acid	1.50
Acetate	1.91
Succinate	2.38
Methanesulphonate	2.80
Methanol	3.35
Polyethylene glycol	3.66
Hydroxymethanesulphonate	4.41
Formate	8.47

*Identification was confirmed by comparison with standards.

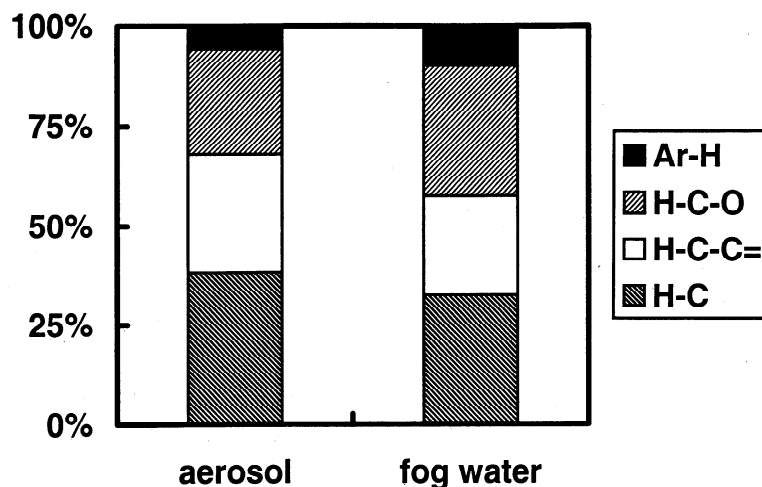


Figure 2. Normalized abundance in the aerosol water extract and fog sample of nonexchangeable protons in the four categories described in the text.

lene groups), 2.1-2.8 ppm (aliphatic protons on carbon atoms adjacent to carbonyl groups or aromatic rings), and 3.4-4.0 ppm (alcohols and ethers). The low intensity observed in the spectral region between 2.8 and 3.4 ppm suggests that aliphatic amines and sulfonates (RSO_3^-) are present only in low concentration. Strong signals in the 3.4-4.0 ppm region evidence a high concentration of hydroxy- and/or ether- functionalities, especially in the case of the fog sample (Figure 1, curve a).

The above evidence can be summarized identifying four most representative categories of functional groups in the HNMR spectra: Ar-H: aromatic protons (6.7-8.3 ppm); H-C-O: protons on carbon atoms singly bound to oxygen atoms (3.3-4.0 ppm); H-C-C=: aliphatic protons on carbon atoms adjacent to carbonyl groups or aromatic rings (2.0-2.8 ppm); and H-C: aliphatic protons (0.7-1.9 ppm).

The abundance of nonexchangeable protons in these four functional group categories can be estimated from the area of the observed HNMR bands for both aerosol extract and fog water samples (Figure 2). The figure shows that the normalized distribution of functional groups is similar in the aerosol extract and fog water samples, with fog water having a slightly higher content of H-C-O groups. It should be noticed that the mass concentration attributable to the different functionalities cannot directly be inferred from the HNMR data, since the molecular formula of the organic compounds present in the samples is not known.

In summary, this first step in the characterization of the Po Valley aerosol and fog water by HNMR leads to the conclusion that WSOC in these samples are mainly aliphatic oxygenated compounds, with a minor content of aromatics. Furthermore, among the candidate contributors to aerosol WSOC proposed by *Saxena and Hildemann* [1996], our findings exclude the

presence of significant amounts of aldehydes, esters, organic nitrates, aliphatic nitro-compounds, amines, and aminoacids.

2.3. Evaluation of a Chromatographic Procedure for WSOC Separation

While the preliminary NMR characterization of the integral aerosol and fog water samples has clearly shown the potential of this technique for defining the classes of compounds and the main functional groups present (and to exclude the presence of others), it is, however, clear that the identification of WSOC requires a further thorough examination from both a qualitative and a quantitative point of view. A chromatographic procedure was therefore developed to obtain more simplified WSOC mixtures on which further functional group HNMR analysis could be performed. Aqueous samples are usually separated by high-performance liquid chromatography (HPLC) in reverse-phase mode, but very polar compounds, such as those present in our samples, are not retained by the reverse-phase columns [*Gundel et al.*, 1993]. More suitable techniques for the fractionation of WSOC are ultrafiltration (UF), size exclusion chromatography (SEC), and ion exchange chromatography (IEC). Application of UF to the analysis of WSOC in rainwater and aqueous aerosol extracts was previously performed by *Likens et al.* [1983] and *Havers et al.* [1998], while SEC was used to detect and quantify macromolecular compounds in aerosol and fog water samples [*Zappoli et al.*, 1999; *Facchini et al.*, 1999].

In the present work, we chose to fractionate WSOC by IEC, on the basis of previous findings suggesting that carboxylic acids are the main class of organic compounds in the water-soluble fraction of atmospheric aerosol [*Gundel et al.*, 1993; *Chebbi and Carlier*, 1996]. Carboxylic acids can be separated in ionic form at alkaline pH by anion exchanger stationary phase. A

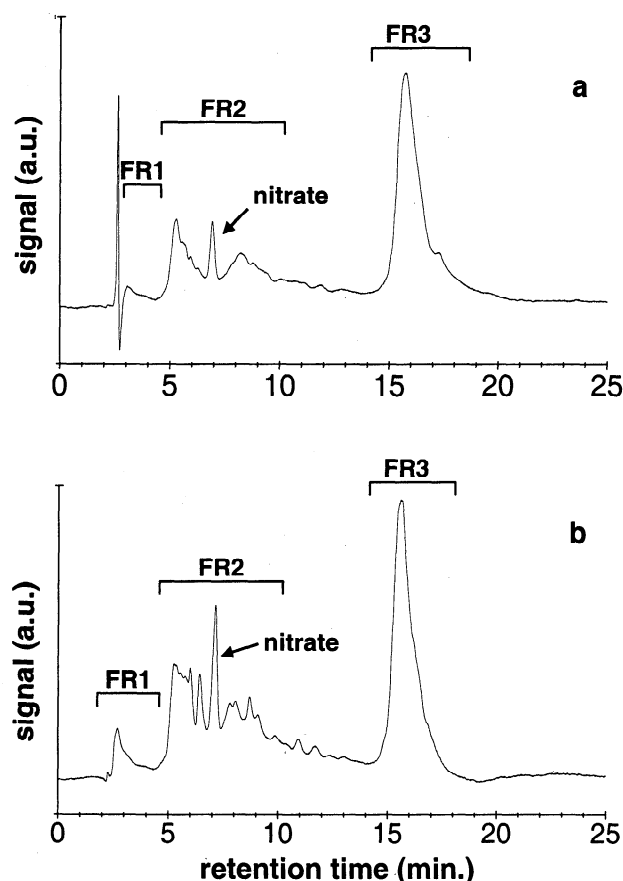


Figure 3. HPLC chromatograms of (a) aerosol extract and (b) fog water. Chromatographic separation was performed on an anion exchange DEAE-TSK gel column Toso-Haas, 7.5 mm ID x 7.5 cm length), and detected by a Varian 2550 UV detector at 254 nm. The initial mobile phase was deionized water. From 0.2 to 2 min, the solvent composition was changed linearly to NaClO_4 0.02 M, tris-hydroxymethyl-aminomethane (TRIS) 0.02 M, 10% methanol. The final solvent composition (NaClO_4 0.4 M, TRIS 0.02 M, 10% methanol) was reached after a second gradient from 10 to 15 min, and held constant for 5 min. The pH of the buffer eluent was held constant at 8.0. The change of baseline due to gradient elution was automatically subtracted. The three fractions defined in the text (FR1, FR2, FR3) are evidenced by the horizontal bars above the chromatogram. The peak due to nitrate is also evidenced.

diethylaminoethyl- (DEAE) weak anion exchanger was chosen for our purpose, and the separation was performed at pH = 8.

The chromatograms in Figure 3 refer to the aerosol water extract (Figure 3a) and the fog sample (Figure 3b) previously investigated by HNMR. Separation was carried out using a HPLC system, equipped with a DEAE-TSK gel column and UV detector (at 254 nm). A gradient elution was performed by increasing the ionic strength of the eluent buffer solution (see details in caption of Figure 3). In these conditions, anionic species (both organic and inorganic) with increasing number of

charges per molecule are sequentially eluted. Among inorganic anions which elute through the column, only nitrate significantly absorbs at 254 nm and is therefore revealed by the detector (see Figure 3). The remaining detected peaks are due to UV-absorbing organic substances.

At the beginning of the chromatogram, eluting with the void volume, a peak of neutral and/or basic compounds can be seen. Peaks with retention times between 5 and 12 min, eluted by buffer at low ionic strength, contain compounds bearing one or two charges per molecule. Mono- and di-carboxylic acids like formic, acetic, oxalic, and methansulphonic acids, usually found in condensed phase atmospheric samples, elute in this region of the chromatogram. Finally, a single broad and intense peak, eluted by buffer at high ionic strength, can be attributed to polycharged compounds (with at least three negative charges per molecule).

On the basis of the above tests, three main classes of WSOC can therefore be singled out (see Figure 3): fraction 1 (FR1, not retained by the column), neutral/basic compounds; fraction 2 (FR2), mono- and di-carboxylic acids; and fraction 3 (FR3), polyacidic organic compounds. The aerosol extract and the fog sample chromatograms are quite similar: the main differences are the larger peak of neutral and/or basic organic substances observed in the fog sample chromatogram, and the region of the chromatogram corresponding to mono- and di-carboxylic acids which appears more complex in the case of the fog sample.

2.4. Scaling up the Chromatographic Procedure and Quantitative Recovery Tests

To obtain sufficient amounts of sample for HNMR and liquid TOC analysis of the above three fractions of compounds, the HPLC procedure was scaled up using a preparative packed column filled with a DEAE-cellulose gel. Only the fog water sample was tested in this last phase of the procedure, mostly due to the availability of a larger sample, but also taking into account that the previous HNMR and HPLC tests have shown the similarity between WSOC composition and chromatographic behavior in fog water and aerosol samples.

A volume of sample corresponding to ~ 1 mg of organic carbon content was eluted through the column (1 cm ID x 10 cm length). A stepwise elution was performed at 1.0 mL min^{-1} with water, then with buffer solutions of NH_4HCO_3 0.05, and 1.0 M, at pH = 8.0. Elution of organic compounds was monitored at 254 nm, and the collected fractions (FR1, FR2, and FR3 as defined in the previous paragraph) were concentrated to dryness. Finally, the residues were dissolved in HPLC-grade H_2O for the recovery tests and in D_2O for HNMR analysis.

The purity of the separated fractions was tested by reinjection in the HPLC system described in the above paragraph, and comparing the area of the individual

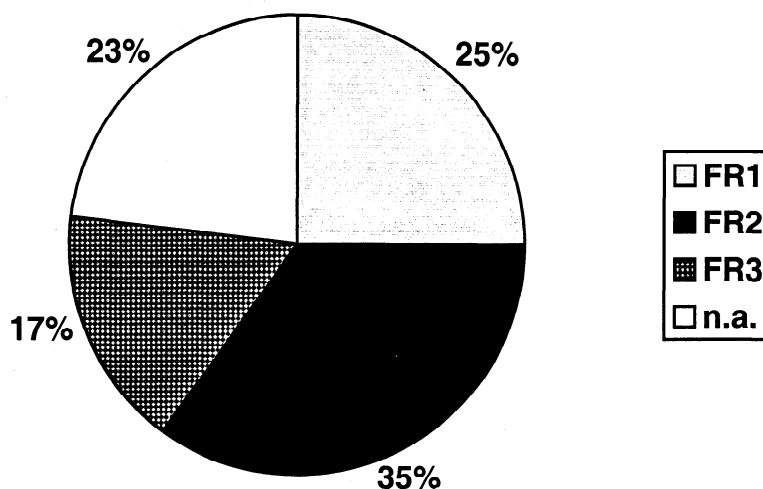


Figure 4. Relative organic carbon content of FR1, FR2, and FR3 by elemental analysis (TOC measurements) referring to the concentration of the bulk (nonfractionated) sample (see Table 1). Here n.a. is not accounted.

fractions to the total area of the chromatogram. Purity was better than 90% for the polyacidic fraction, ~ 80% for the mono- and di-carboxylic acid fraction, and ~ 50% for neutral/basic compounds. The latter fraction was further purified before HNMR analysis by a second chromatographic elution, reaching a final purity of 75%.

Total organic carbon concentration was then measured in each of the three fractions using the liquid TOC analyser. TOC measurements were performed after removing from the samples the residual inorganic carbon of the eluent by acidification.

Figure 4 shows the percent organic carbon content of the three isolated fractions. Acidic compounds (FR2 + FR3) are the dominant WSOC (52% expressed as C), while neutral/basic compounds (FR1) account for 25%. The overall recovery of WSOC, obtained by summing the carbon content of the three fractions separated by the chromatographic procedure and comparing the sum with the carbon content of the bulk sample, was 77%. The apparent loss of 23% of WSOC in the fractionation procedure is due to several concurrent reasons: compounds irreversibly adsorbed on the column, losses in the freeze-drying procedure, losses due to acidification of the samples before TOC analysis.

On the basis of the total organic carbon measurements of the three isolated fractions, it is also possible to perform a quantitative determination of organic carbon content in aerosol extracts/fog water samples by HPLC analysis. The integrated areas of the HPLC chromatogram corresponding to FR1, FR2, FR3 (see Figure 3) were calibrated in terms of concentration of C using the TOC content of the three fractions separated on the preparative column. It should be stressed that this HPLC calibration procedure is applicable to sets of samples having a chemical composition of the three fractions similar to that of our samples and that

it may not be directly applicable in the case of aerosol samples collected in different regions and conditions. In this case, a full characterization study like the one described in this paper would be necessary as a prerequisite to quantitative analysis. Once the calibration is achieved, a large number of samples can be analyzed with a fast and sensitive technique.

2.5. Functional Group Investigation of the Three Isolated Fractions

The HNMR spectra of the three isolated fractions are shown in Figure 5, curves a-c. From the spectra, the abundance in the three fractions of the four main categories of functional groups defined previously in section 2.2. can be quantified in terms of μ moles of nonexchangeable organic protons (Figure 6).

2.5.1. Neutral/basic compounds (FR1). The spectrum in Figure 5a exhibits a very low content of aromatic protons and strong signals between 3.2 and 4.0 ppm, suggesting that neutral/basic substances are mainly hydroxylated or alkoxyated aliphatic compounds (alcohols and/or ethers). The relative abundance of H-C-O protons compared to unsubstituted H-C protons (see Figure 6) is indicative of the presence of polyols (like deoxy-sugars), rather than aliphatic mono-alcohols (like *n*-alkanols). Aliphatic polyhydroxylated compounds were previously detected in aerosol samples by *Wauters et al.* [1979]. In that study, polyols were found to represent, together with carboxylic acids, the most important class of aerosol polar organic compounds. The FR1 spectrum also exhibits a strong sharp signal between 3.2 and 3.3 ppm. This may be attributed to amides, or epoxides, or to protons in α -position to two unsaturated substituents. Signals in this region are also shown in the HNMR spectra reported by *Havers et al.* [1998] and *Suzuki et al.* [1998].

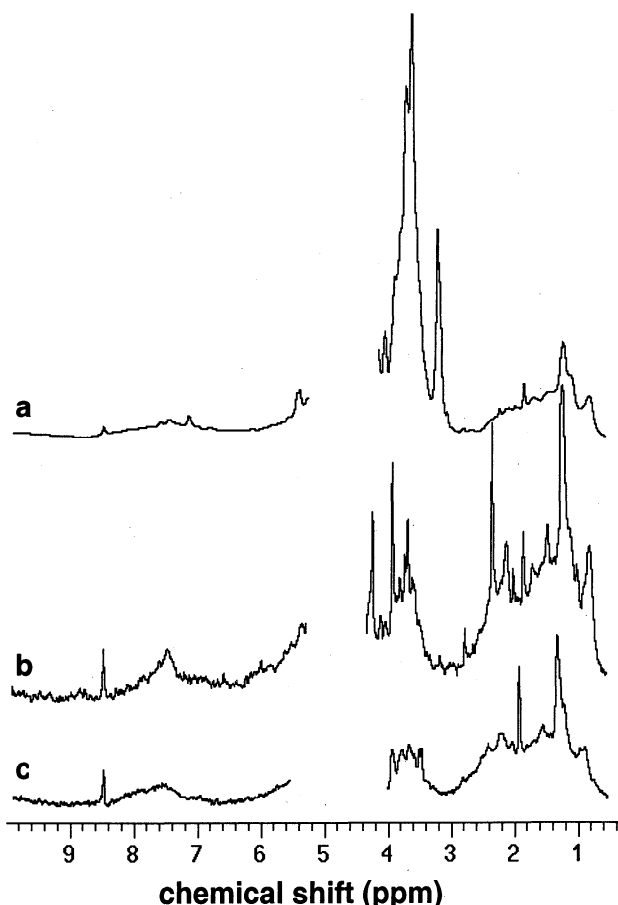


Figure 5. HNMR spectra of FR1 (curve a), FR2 (curve b), and FR3 (curve c). The region between 4 and 5 ppm is not shown because of instrumental noise due to a residual signal of HDO.

2.5.2. Mono- and di-carboxylic acids (FR2).

FR2 was found to be the most abundant in terms of concentration of nonexchangeable organic hydrogen atoms (Figure 6). The aliphatic protons evidenced in the anal-

ysis of the nonfractionated sample (section 2.2.) were for the most part detected in the spectrum of the FR2 fraction. H-C-O groups are also present, but in significantly lower amounts compared to FR1. Aromatic protons are relatively scarce, compared to aliphatic protons, but more abundant than in FR1. The overall spectrum of FR2 can be attributed to aliphatic carboxylic acids and hydroxy-carboxylic acids. In particular, the ratio between unsubstituted aliphatic protons (H-C) and aliphatic protons bearing functional groups (H-C-C=, H-C-O; see Figure 6) is indicative of the presence of highly oxidized species. Low molecular weight carboxylic and di-carboxylic acids (lactic, glycolic, oxalic, and succinic acid) have commonly been detected in aerosol and cloud water samples [Chebbi and Carlier, 1996], but the present results suggest the presence in this sample of a complex mixture of hydroxy-acids, that give rise to broad, overlapping HNMR signals. It would certainly be challenging to resolve such a mixture using conventional chromatographic techniques.

2.5.3. Polyacidic compounds (FR3). The HNMR spectra of polyacids (FR3, Figure 5, curve c) and of mono- and di-acids (FR2, Figure 5, curve b) are quite similar, except that H-C-O protons are less abundant in FR3 compared to FR2 and the aromatic portion of the spectrum is relatively more pronounced in FR3. Furthermore, the abundance of nonexchangeable organic protons in FR3 is much lower than in the other two fractions (Figure 6). This observation suggests that polyacids have a more pronounced unsaturated character than the other two classes of WSOC. Model structures consisting of an aromatic core bearing substituted aliphatic chains (with -COOH, CH₂OH, -COCH₃, or -CH₃ terminal groups) properly fit the HNMR features observed in FR3. This structure is strictly analogous to that of other naturally occurring polyacidic compounds: humic substances. In addition, we also observed that a commercially available standard of humic substance

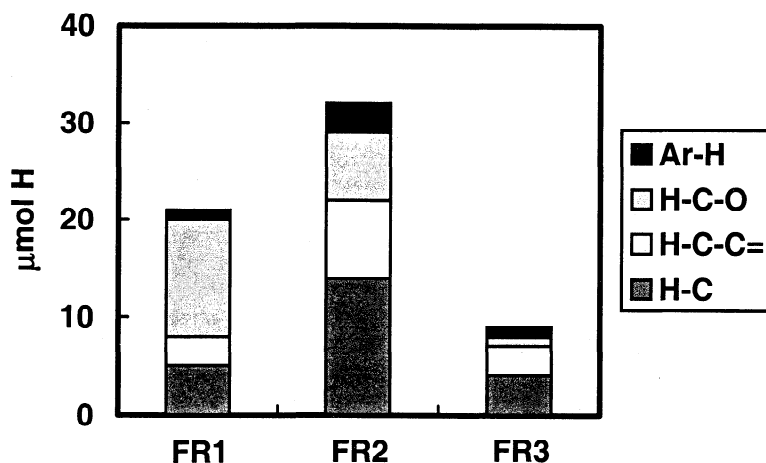


Figure 6. Abundance of identified major chemical structures and functional groups in the isolated fractions. The vertical scale reports the concentration in μ moles of nonexchangeable organic protons in the different fractions. The scale was calibrated on the basis of the known amount of internal TSP_{d4} standard. The four classes of compounds (same as in Figure 2) are defined in the text.

(Suwannee River Fulvic Acid Reference) exhibits a chromatographic behavior similar to that of FR3 on the DEAE column (similar retention time and shape of the peak). These results are consistent with previous findings concerning the presence of macromolecular humic-like organic compounds [Mukai and Ambe, 1986; Havers *et al.*, 1998; Zappoli *et al.*, 1999; Facchini *et al.*, 1999] in aerosol and fog water samples.

3. Conclusion

In this paper, we propose a new conceptual and methodological approach for the speciation of aerosol WSOC, based on a combination of ion exchange chromatography, NMR spectroscopy, and total organic carbon analysis. The complex mixture of aerosol/fog water WSOC was separated on an anion-exchange column into three main classes of compounds having different chromatographic behavior: FR1 (not retained by the column), neutral/basic compounds; FR2, mono- and di-carboxylic acids; and FR3, polyacidic organic compounds. The three fractions together accounted for 77% (in terms of C) of the total WSOC concentration of a fog water sample. Characterization of the three above classes of WSOC by HNMR spectroscopy showed that FR1 is mainly composed of polyols or polyethers, FR2 is mainly composed of hydroxylated aliphatic acidic compounds, and FR3 is composed of unsaturated polyacidic compounds of predominantly aliphatic character, with a minor content of hydroxyl- groups.

The above results are derived from a very limited number of observations and cannot directly be extrapolated to other atmospheric systems in terms of concentrations and specific classes of compounds. However, we believe that the suggested iterative investigation procedure, linking functional group analysis to chromatographic separation and using an absolute detector (the TOC analyzer) instead of many, and sometimes arbitrary, standards can constitute a powerful tool to investigate the chemical properties of aerosol WSOC, identify the main groups or classes of compounds present in the samples, and obtain a quantitative estimation of the total carbon concentration in each class of compounds.

This approach is not alternative to the classical speciation methods aimed at identifying individual compounds. On the contrary, our suggested approach can provide helpful guidance for the individual compound speciation techniques.

Finally, while our proposed approach supplies a less detailed picture compared to individual compound speciation, it certainly provides more comprehensive and useful information for modeling purposes and is particularly helpful when aerosol chemical mass closure is pursued.

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- S. Decesari, M.C. Facchini, and S. Fuzzi (corresponding author), Istituto di Scienze dell'Atmosfera e dell'Oceano, CNR, via Gobetti 101, I-40129 Bologna (Italy). (e-mail: S.Decesari@isao.bo.cnr.it; MC.Facchini@isao.bo.cnr.it; S.Fuzzi@isao.bo.cnr.it)
- E. Tagliavini, Dipartimento di Chimica "G. Ciamician," Università di Bologna, via Selmi 2, I-40126 Bologna (Italy). (e-mail: temil@ciam.unibo.it)

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