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Primary and secondary marine organic aerosols over the North Atlantic Ocean during the MAP experiment

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[1] The organic chemical composition of atmospheric submicron particles in the marine boundary layer was characterized over the northeast Atlantic Ocean in summer 2006, during the season of phytoplankton blooms, in the frame of the Marine Aerosol Production (MAP) experiment. First measurements of water-insoluble organic carbon (WIOC) in marine aerosol particles by nuclear magnetic resonance (NMR) spectroscopy showed that it is structurally similar to lipids, resembling the organic fraction of sea spray formed during bubble-bursting experiments. The composition of the water-soluble organic carbon (WSOC) fraction was investigated by liquid chromatography – mass spectrometry and by 1D- and 2D-NMR spectroscopy, and showed a less hydrophilic fraction containing traces of fatty acids and rich of alkanoic acids formed by lipid degradation, and a more hydrophilic fraction, containing more functionalized species encompassing short-chain aliphatic acids and sulfate esters of hydroxyl-carboxylic acids. The more oxidized fraction of WSOC accounts for the oxidized organic aerosol components, which can form by either gas-to-particle conversion or extensive chemical aging of lipid-containing primary particles, as also suggested by the parallel measurements using online mass spectrometric techniques (presented in a companion paper), showing oxidized organic substances internally mixed with sea salt particles. These measurements are also compared with online measurements using an Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS) and Aerodyne Aerosol Mass Spectrometer (AMS). Given the large variability in the chemical composition of marine organic aerosol particles, a multitechnique approach is recommended to reduce method-dependent categorizations and oversimplifications and to improve the comparability with the results obtained in different oceanic areas.

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1. Introduction

[2] Submicron marine aerosols are an important controlling factor in the atmospheric radiative budget by dictating the number of cloud condensation nuclei (CCN) in the marine atmosphere [*O'Dowd and de Leeuw*, 2007]. The chemical nature and origin of the fine particulate matter over oceanic regions, and especially of its organic fraction, are still largely unknown, because of the insufficient spatial and temporal coverage of in situ measurements; the large variability in the emission from the ocean resulting from changing biological activity in seawater; from the complex transfer of gases and particles at the air-sea interface; and finally due to the low concentrations, typically ≤1 μg/m^3, which can be affected by the transport of aerosol particles from distant continental sources. Past studies on marine organic aerosols have focused on specific mechanisms of production, which are reviewed by the recent paper by *Rinaldi et al.* [2010], but quantitative methods for source apportionment of marine organic aerosols are still missing. Submicron particles can reside for weeks in the marine atmosphere, thus integrating the contributions from multiple secondary and primary sources of organic compounds in a complex manner. At the same time, aging of the particles in the atmosphere inevitably leads to the progressive loss of molecular markers and to their

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replacement by complex mixtures of oxidized compounds [e.g., *McFiggans et al.*, 2005; *Jimenez et al.*, 2009]. Investigating the nature of the oxidized fraction of particulate organic carbon (OC) by looking at integral chemical properties (mass fragmentation patterns, N:O:C ratio, functional group distribution, OC isotopic enrichment) of the unresolved mixtures of compounds is therefore a priority for supporting molecular tracer analysis with additional "distinguishing features" in elucidating the sources of marine organic particles [*Fuzzi et al.*, 2006]. Techniques, such as aerosol mass spectrometry (AMS), Fourier transform infrared spectroscopy (FTIR) and nuclear magnetic resonance spectroscopy (NMR) have progressively gained importance in source identification and source apportionment of airborne organic particles [e.g., *Sullivan and Prather*, 2005; *Hersey et al.*, 2009; *Dall'Osto et al.*, 2006; *Russell et al.*, 2010; *Decesari et al.*, 2007]. The inherent complexity and variability of spectral data of ambient aerosol samples can be rationalized using techniques of data clustering and factor analysis. Factor analysis in particular, allows extracting correlated variables, providing simplified patterns, which can be used to identify sources, processing or transport characteristics of atmospheric particulate organic compounds. Positive matrix factorization (PMF), for instance, is widely used for aerosol mass spectrometric data analysis in many environments [*Ulbrich et al.*, 2009], and it has also been applied to FTIR data for identification and quantification of marine phenols in airborne particles in the marine boundary layer [*Bahadur et al.*, 2010].

[3] The "Marine Aerosol Production (MAP)" project provides an integrated assessment of the sources of MBL organic aerosols in the North Atlantic using molecular marker analysis and state-of-the-art online and off-line spectroscopic techniques. The experiment was conducted at the Mace Head research station with continuous measurements of the aerosol physical properties and semi-continuous measurements of the aerosol chemical properties throughout 2006 [*Rinaldi et al.*, 2010]. Between June and July of the same year, a ship campaign was conducted during which sophisticated physical and chemical aerosol measurements were made in the marine boundary layer off the west coast of Ireland. During the cruise, online aerosol chemical measurements were performed using state-of-the-art mass spectrometric techniques (AMS, Aerodyne "Aerosol Mass Spectrometry," and ATOFMS, "Aerosol Time-Of-Flight Mass Spectrometry"), while time-integrated filter samples were collected for off-line chemical analysis with analytical techniques showing a high recovery for the polar organic fraction of the aerosol and including liquid-chromatography-mass-spectrometry (LC/MS) and nuclear magnetic resonance spectroscopy (NMR). In a companion paper (M. Dall'Osto et al., Open ocean aerosol measurements during the MAP experiment, submitted to *Journal of Geophysical Research*, 2011) the results of the online mass spectrometric techniques are discussed thoroughly, while here we focus on the off-line methods and we also provide a synthesis of the main findings of the campaign. In parallel with ambient aerosol measurements, laboratory experiments were conducted onboard the research ship for simulating the production of sea spray aerosol, and the results, reported in detail by *Facchini et al.* [2008a], are quoted in this study with the aim of comparing the composition of ambient marine aerosols with that of marine primary organic aerosol (POA) representative for the northeastern North Atlantic region.

2. Experimental Setup

2.1. Ship Campaign

[4] Aerosol measurements were carried out on board the research ship Celtic Explorer (CE) from 12 to 20 June 2006 (1st leg) and from 25 June to 5 July 2006 (2nd leg) [*Rinaldi et al.*, 2009]. The CE crossed oceanic regions rich of chlorophyll NW of Ireland between 14 and 18 June, and N of Ireland between 29 June and 3 July. In the same days, an increase of DOC and POC in seawater was also observed (auxiliary material Figure S1).[1] Other, more distant blooms were identified by MODIS (http://oceancolor.gsfc.nasa.gov/) in the north oceanic basins (Denmark Strait, Greenland and Norwegian seas) or, at lower latitudes (45°–55° N), around midway between Europe and Canada [*Rinaldi et al.*, 2009].

[5] Winds were more sustained during the first leg of the cruise, peaking on 20th June, when the CE encountered a summer storm. During the second leg, wind intensity was variable with some days with prevalently calm conditions (auxiliary material Figure S1). The analysis of back trajectories for the periods when the aerosol samplers were operative (see following section) shows that different types of maritime air masses were encountered during the campaign (auxiliary material Figure S2). During the first days of the first leg (12 – 15 June), an almost permanent cyclonic circulation brought polar air masses from the Denmark Strait and Greenland Sea toward the Irish coast. On 15 June some trajectories had a partial southwesterly component. In the following days (auxiliary material Figure S2b), the air mass origin was quite variables and the trajectories had alternatively a northerly or a southwesterly component. Finally, more stagnant conditions were encountered during the second leg (25 June – 4 July) with most of the air masses spending 48 h over an oceanic sector enclosed between 45° and 55°N and between −20° W and the Irish coast before reaching the research ship. In this period (auxiliary material Figure S2c), the air masses were characterized by a shorter range transport compared to the first days of the first leg (auxiliary material Figure S2a). Consequently, also the potential source regions for marine biogenic particles were probably different between these periods of the campaign. Further information about of air mass types and origin can be found in the parallel paper by Dall'Osto et al. (submitted manuscript, 2011).

2.2. Aerosol Sampling and OC Analysis

[6] Sampling at Mace Head during MAP for chemical analysis is discussed in the paper by *Rinaldi et al.* [2010]. Briefly, the station is equipped with an automated sectored sampling system which provided high volume (HiVol) filter samples for organic analysis differentiating between clean and polluted air masses, where the "clean" sector was defined by: wind direction from 180° to 300°, total particle number below 700 cm^{-3}, and black carbon (BC) concentrations lower than 50 ng m^{-3}. Onboard the Celtic Explorer, the collection of aerosol samples selectively in clean air masses was

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2011JD016204.

Table 1. Sampling Times of HiVol1 and HiVol2 Filter Samples[a]

	Sample	Size Cut	TSP	TC	OC	EC	WSOC	MSA	MBAS
Leg 1	HiVol1								
	12–15/06	PM1.5	n.a.	0.24	n.a.	n.a.	0.15	0.23	n.a.
		PM1.5–10	n.a.	0.12	n.a.	n.a.	0.082	0.075	n.a.
	16–20/06	PM1.5	n.a.	0.18	n.a.	n.a.	0.10	0.11	n.a.
		PM1.5–10	n.a.	0.080	n.a.	n.a.	0.062	0.050	n.a.
	HiVol2								
	12–15/06	TSP	23.59	0.50	0.40	0.10	0.64	n.a.	1.33 (0.38)
	16–20/06	Size segregated							
		>14.11	0.19	n.a.	n.a.	n.a.	0.02	n.a.	1.67 (0.48)
		5.90–14.11	ND	n.a.	n.a.	n.a.	0.19	n.a.	0.78 (0.23)
		2.93–5.90	1.26	n.a.	n.a.	n.a.	1.60	n.a.	0.55 (0.16)
		1.90–2.93	1.12	n.a.	n.a.	n.a.	0.34	n.a.	ND
		1.02–1.90	ND	n.a.	n.a.	n.a.	0.12	n.a.	2.14 (0.62)
		<1.02	28.15	n.a.	n.a.	n.a.	0.83	n.a.	18.27 (5.27)
Leg 2	HiVol1								
	26/06–04/07	PM1.5	n.a.	0.29	n.a.	n.a.	0.20	0.16	n.a.
		PM1.5–10	n.a.	0.16	n.a.	n.a.	0.11	0.12	n.a.
	HiVol2								
	26/06–02/07	TSP	16.76	0.37	0.36	0.01	0.19	n.a.	1.84 (0.53)
	02–05/07	TSP	16.92	0.44	0.44	ND	0.21	n.a.	1.40 (0.40)

[a] Total carbon (TC), organic carbon (OC), elemental carbon (EC), water-soluble organic carbon (WSOC), methansulphonate (MSA), methylene-blue-active substances (MBAS) concentrations. All units are $\mu g\ m^{-3}$ except for MBAS that is expressed both in pmol m^{-3} and ng m^{-3} (in brackets). Abbreviations: n.a. = not analyzed; ND = not detected.

performed based on weather forecast and trajectory forecast plus active (based on CPC) though manual control. Sampling was also interrupted when the CE was oriented with the aerosol inlets downwind the funnels of the ship. Samples were collected using an 8-stage Berner impactor for the analysis of inorganic ions and of water-soluble organic carbon (WSOC) [*Rinaldi et al.*, 2009] and in parallel using two Sierra Anderson HiVol samplers equipped with slotted impactors for size-segregated sampling (hereafter referred as *HiVol1* and *HiVol2*) for detailed organic analysis (Table 1). Due to the necessity of collecting sufficient amounts of samples for the subsequent detailed chemical analyses, long (~50 h) time-integrated samplings were performed. The filter samples, provided by the two HiVol systems, were processed for organic chemical characterization according to two distinct protocols (Figure 1).

2.2.1. HiVol 1

[7] The WSOC and TC analyses were performed using a Multi N/C 2100 elemental analyzer (Analytik Jena, Germany), equipped with a furnace solids module. Water-soluble organic compounds were extracted from fine particles with ultrapure Milli-Q water by sonication for 1 h. Generally

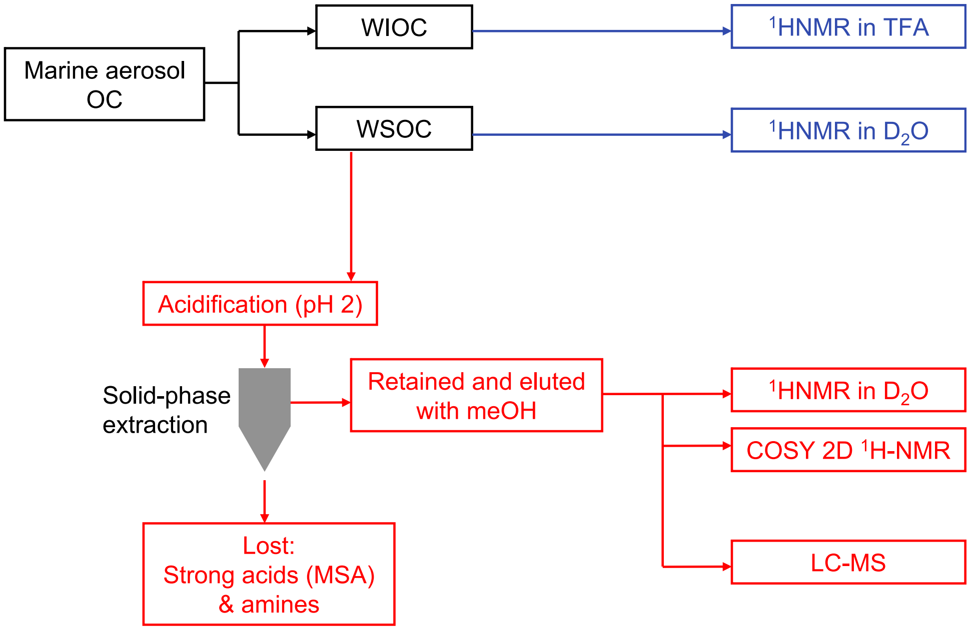

Figure 1. Scheme of the off-line analysis of aerosol organic composition. The analytical protocols adopted for HiVol1 and HiVol2 samples are indicated by blue and red lines, respectively.

100 mL of Milli-Q water were used for one half filter. Water extracts were filtered on quartz-fiber filters (pore size 0.45 μm) using a Büchner flask in order to remove suspended particles. After filtration, the water extract was analyzed by ion chromatography [*Cavalli et al.*, 2004] for the speciation of low-molecular weight organic acids and of inorganic ions, and by proton-Nuclear Magnetic Resonance (^{1}H-NMR) spectroscopy for WSOC functional group analysis. After the extraction with water, the filters were consequently extracted by trifluoroacetic acid (TFA), a solvent suitable for dissolving less polar substances and for hydrolyzing and solubilizing polymeric water-insoluble oxygenated compounds (such as polysaccharides and organo-silicon compounds), and proved to be effective for marine macromolecular biological material [*Kovac et al.*, 2002]. About 30 mL TFA was used for each filter and a sonication time of 30 min was chosen. The TFA solution was first separated from the filter quartz pulp using a concentrator (Eppendorf 5301) and prepared for ^{1}H-NMR analysis of water-insoluble organic carbon (WIOC).

2.2.2. HiVol 2

[8] The organic carbon (OC) and elemental carbon (EC) content of the samples was determined using the OC/EC analyzer of Sunset Laboratory Inc. and quantified straight from a small piece (1,5 cm^2) of the quartz microfiber filters. Water-soluble organic carbon (WSOC) has been measured with a Shimadzu TOC VCSH instrument. The filters were then cut into small pieces and extracted with 120–150 ml of nanopure water by the use of the accelerated solvent extraction method with a DIONEX (ASE 300) device. The oven temperature was set at 100°C. Twenty ml of the solution was used for surface activity determination with methylene blue reagent according to *Latif and Brimblecombe* [2004]. The concentration of anionic aerosol surfactants was determined as methylene blue active substances (MBAS). OASIS HLB extraction cartridges (60 mg) were used for the isolation of the water-soluble organic fraction from the extract, which was first acidified to pH 2 by the addition of HCl. The retained compounds were eluted from the column with 4 ml methanol, 2 ml are used for LC/MS analysis and the rest 2 ml was evaporated to dryness by means of a nitrogen stream and kept for NMR analysis.

2.3. Speciation of Aerosol Organic Compounds: Liquid Chromatography–Mass Spectrometry (LC/MS)

[9] LC/MS analysis of HiVol2 samples was carried out with Thermo Finnigan's TSQ Quantum, equipped with a triple quadrupole for MS^2 analysis. The HPLC conditions were: Injection loop 50 μL; column C8, 250 × 4.6 mm, 5 μm (MZ-PerfectSil 300 C8); methanol isocratic flow 500 μL/min. The analysis time was 30 min, although all compounds have been eluted by the first 8 min. Electro Spray (ES) ionization in the negative mode was used for the analysis of all samples: Spray Voltage 4.5 kV, Sheath Gas Pressure 50 psi, Aux Valve Flow 25 psi, Capillary Temperature 310°C, Source CID 0 eV, Tube Lens Offset −143 V, Lens 0 Offset 1.3 V. MS^2-CID spectra were measured with collision energies varying from 10 up to 30 eV. Additionally, with the field samples blank filters were also analyzed following the same analytical protocol to determine possible contamination during the transport, storage or laboratory. Between consecutive analyses the LC/MS system was sufficiently rinsed with methanol. Blank runs were performed to exclude memory effects between samples. For comparison purpose MS^2-CID spectra of authentic standards of linear alkylbenzene sulfonates (supplied by Lamda Detergents, Athens, Greece) and carboxylic acids (tetradecanoic acid and heptadecanoic acid puriss. supplied by Fluka, Germany) were also measured.

2.4. Speciation of Aerosol Organic Compounds: Nuclear Magnetic Resonance (NMR) Spectroscopy

[10] ^{1}H-NMR spectroscopy was exploited for functional group characterization of WSOC and WIOC. HiVol1 samples for NMR analysis of WSOC were prepared by freeze-drying an aliquot of the water-extracts in a rotary-evaporation and then re-dissolving it with 650 μL of deuterated water (D_2O). 50 μL D_2O solution containing 0.05% by weight of sodium 3-(trimethylsilyl)-2,2,3,3-d_4-propionate (TSP-d_4) were added as internal reference standard. ^{1}H-NMR spectra were acquired with a Varian Mercury 400 spectrometer in a 5mm probe. Presaturation of HDO (mono-deuterated water) was performed, nevertheless residual signals of HDO can interfere in the region between 4.5 and 6.0 ppm [*Decesari et al.*, 2007]. The TFA extract containing WIOC material was also freeze-dried by rotary-evaporation. Finally 650 μL of deuterated TFA solution (TFA-*d*) with TSP-d_4 as internal reference standard were use to re-dissolve the WIOC for ^{1}H-NMR spectroscopy.

[11] The dried water-extracts of the HiVol2 samples after the chemical workup, described in 2.2.2, were redissolved in a solution of 120 μL D_2O containing 3.22 mM trimesic acid (TMA). TMA was used as the internal standard for quantitative analysis, and it was calibrated via a sample of levoglucosan of known concentration. ^{1}H-NMR spectra were acquired on a Bruker AMX-500 spectrometer using a 5mm probe. Gradient homonuclear ^{1}H-^{1}H COSY 2D NMR spectra were acquired using a modified water suppression pulse sequence and used for further functional group analysis of the samples.

2.5. Factor Analysis of NMR Spectra

[12] The 1D ^{1}H-NMR spectra of WSOC extracted from the three HiVol1 $PM_{1.5}$ samples collected onboard the CE and the ten samples collected at Mace Head during MAP were aggregated to other eight spectra from $PM_{1.5}$ samples collected during past experiments at the same station (Table 2), and the resulting spectral data set was subjected to cluster analysis and factor analysis aiming to summarize and represent concisely the information contained in the spectra and its variability between samples. The algorithms were applied to blank-subtracted spectra and after binning to 200 or 400 points. The spectral regions containing only sparse signals ($\delta_H < 0.5$ ppm; $4.5 < \delta_H < 6.5$ ppm; and $\delta_H > 8.5$ ppm) were omitted from the data set.

[13] Cluster analysis and principle component analysis (PCA) were used to analyze the similarity between spectra and to identify main sources of variability in the shape of the spectra. To this aim, spectra were normalized for their total intensity before analysis. Hierarchical cluster analysis based on Pearson distances between samples provided a categorization scheme, which was consistent with the subjective groupings extracted from PCA score plots.

[14] Common factor analysis was performed using PMF ("Positive Matrix Factorization," EPA v3.0), NMF ("Non-

Table 2. Synopsis of the Aerosol Samples Providing NMR Data for Cluster and Factor Analysis[a]

	Sample Identification	Start Date	Stop Date	MH Sector	Na^+	$nssSO_4^{2-}$	NO_3^-	TC	WSOC	BC
Past Mace Head campaigns	MH01	05/03/02	12/03/02	marine	0.27	0.28	0.009	NA	NA	
	MH02	19/03/02	26/03/02	marine	0.14	0.15	0.016	NA	0.063	
	MH03	02/04/02	09/04/02	marine	0.31	0.35	0.076	NA	0.23	NA
	MH04	02/10/02	09/10/02	marine	0.71	0.27	0.036	NA	NA	18.3
	MH05	23/10/02	30/10/02	marine	5.7	NA	<DL	0.23	0.039	20.7
	MH06	31/05/02	06/06/02	modified marine	0.18	0.99	0.044	NA	0.29	96.0
	MH07	31/05/02	06/06/02	modified marine	0.19	0.30	0.018	0.98	0.17	70.0
	MH08	18/08/04	29/08/04	marine	0.064	0.35	0.005	0.19	0.11	26.5
MAP campaign at MH	MH09	11/01/06	18/01/06	marine	0.25	0.27	0.009	0.37	0.072	15.0
	MH10	10/02/06	20/02/06	marine	0.27	0.11	0.016	0.13	0.071	212
	MH11	12/04/06	26/04/06	marine	0.11	0.61	0.007	0.17	0.11	34.9
	MH12	03/05/06	10/05/06	continental	0.075	0.37	0.052	0.60	0.36	286
	MH13	12/06/06	19/06/06	marine	0.055	0.47	<DL	0.26	0.18	30.7
	MH14	19/06/06	28/06/06	marine	0.024	0.31	0.005	0.18	0.12	82.9
	MH15	28/06/06	05/07/06	marine	0.032	0.41	<DL	0.32	0.25	55.0
	MH16	05/07/06	12/07/06	marine	NA	NA	NA	0.35	0.25	41.9
	MH17	05/10/06	11/10/06	marine	0.16	0.17	0.008	0.071	0.051	9.7
	MH18	11/10/06	18/10/06	continental	0.062	2.2	1.4	1.57	0.68	761
Celtic Explorer samples	CE01	12/06/06	15/06/06		0.071	0.60	<DL	0.35	0.23	
	CE02	16/06/06	20/06/06		0.023	0.27	<DL	0.26	0.14	
	CE03	26/06/06	04/07/06		0.048	0.48	0.004	0.43	0.29	

[a] Concentrations are in $\mu g/m^3$ except for BC (from aethalometer) in ng/m^3. Dates are given as dd/mm/yy.

negative Matrix Factorization") and MCR ("Multivariate Curve Resolution"). Factor analysis was performed on spectra normalized to total NMR-detectable WSOC concentrations ($\mu mol\ H\ m^{-3}$). PMF [*Paatero and Tapper*, 1994] is by far the most widespread tool for AMS spectral data analysis and it is here applied exploratively to aerosol NMR spectral data. The uncertainties of the measurements were estimated for the 200- (or 400-) points binned spectra from the NMR detection limit calculated as three times the baseline noise (peak-to-peak noise in the region 6.0 – 6.5 ppm). NMF and MCR comprise the most common NMR spectral unmixing techniques in many chemometric applications [*Viant et al.*, 2009]. Two different algorithms were used for NMF, employing a projected gradient bound-constrained optimization [*Lin*, 2007], or a multiplicative update approach [*Lee and Seung*, 2001]. MCR was run according to two different approaches: the alternating least square (MCR-ALS [*Tauler*, 1995; *Jaumot et al.*, 2005]) and weighted alternating least square (MCR-WALS [*Wentzell et al.*, 2006]) methods.

3. Results

3.1. Main Carbonaceous Species and Surfactants

[15] Table 1 reports the concentrations of the main carbonaceous fractions (TC, OC, EC, WSOC) and of methanesulphonate (MSA) during the ship campaign. Concentration ranges are comparable to those found in other oceanic regions in the northern hemisphere during the season of high biological productivity [*Miyazaki et al.*, 2010]. MSA always accounted for a significant fraction of the water-soluble organic carbon, both in the submicron and in the supermicron fractions (14 ± 5% and 12 ± 2%, respectively), with a maximum (19%) during the first sampling period (12 to 15 June). The average WSOC fraction of TC was 63%, well above the water-soluble fraction of POA (ca. 10%) formed by bubble bursting experiments onboard the CE [*Facchini et al.*, 2008a]. The enrichment of WSOC in ambient aerosol particles can be explained by condensation of secondary organic aerosol (SOA) compounds, or by the progressive oxidation of POA over time scales not amenable by standard bubble bursting experiments. Aged material and gas-to-particle conversion products are therefore expected to dominate the water-soluble organic aerosol composition, while genuine, unprocessed POA are plausibly enriched in WIOC while providing only a small contribution to ambient WSOC. Indeed, the concentration of surfactants (MBAS) is poorly correlated with WSOC concentration (Table 1). Interestingly, MBAS concentrations in TSP samples was higher in the period (26 June – 2 July) most favorable for the production of primary marine aerosols on the basis of wind conditions and POC and DOC concentrations in seawater (auxiliary material Figure S1). Size-segregated determination of MBAS concentrations shows that surfactants are enriched in the PM1 fraction.

3.2. Liquid Chromatography–Mass Spectrometry

[16] LC/MS analysis of the HiVol2 filters showed that two chromatographic peaks characterized the extracts of TSP and of PM1 (i.e., back-up of the HiVol in impactor mode) samples (Figure 2).

[17] The most abundant ions in the mass spectrum of the first chromatographic peak (at Rt = 3.19 min, Figure 3a), belonging to less-retained (more hydrophilic organic compounds) were at *m*/*z* 311, 325, 265, 339, 279, and 297. We have attempted to identify the ions at *m*/*z* 297, 311, 325, and 339 by using collisional activation (CID). The MS^2 spectra of these ions imply that they belong to the linear alkylbenzene sulfonates (LAS). Previous ESI-MS studies have shown that LAS produce abundant [M-H]- ions, and upon collisional activation of these ions, yield *m*/*z* 197, 183 and 119 [*Andreu and Picó*, 2004]. We have observed the same ions in the CID-MS^2 spectra measured in our samples

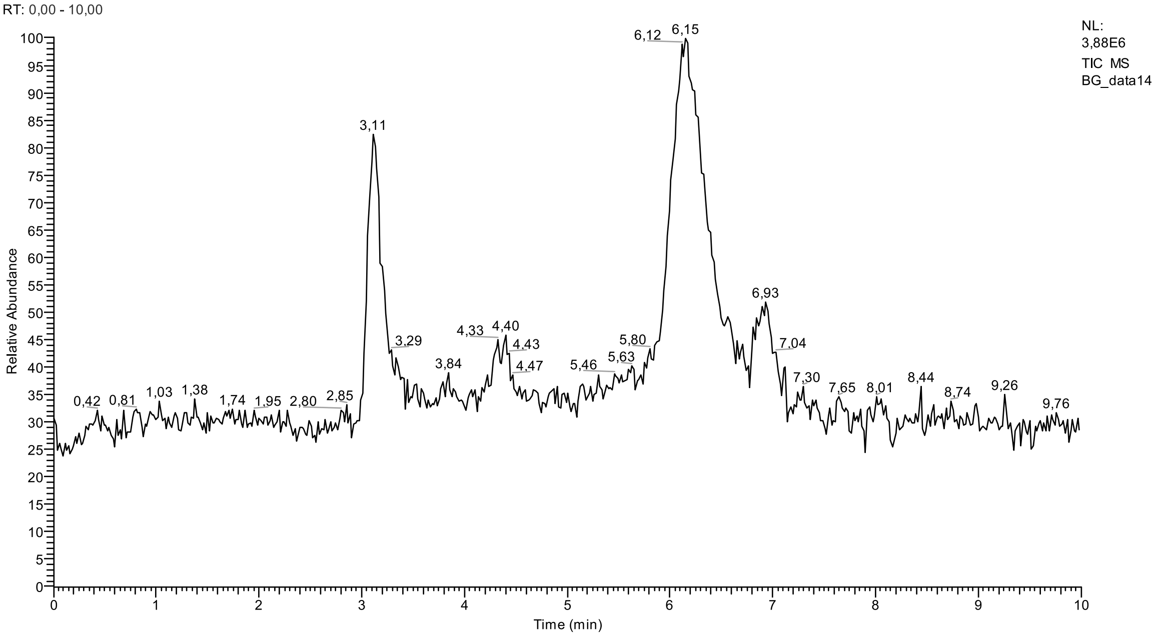

Figure 2. LC/MS chromatogram of a HiVol2 sample.

(auxiliary material Figure S3). We have compared the CID-MS^2 spectra of our samples with those of authentic LAS standards. The spectra of our samples were identical, under the same collision energy, with those of the standard LAS. Semiquantitative analysis based on integration of areas of the molecular ions 297, 311, 325, and 339 corresponding to LAS C_{10}-C_{13} homologues respectively, gave some evidence of their relative amounts (integrated area/m^3 collected) in the four samples analyzed. The obtained relative amounts were strongly correlated (R^2 = 0,96) with the corresponding MBAS concentrations. LAS have been detected in coastal seawater, suspended matter and sediment [*Gonzàlez-Mazo et al.*, 1998, *Petrovic et al.*, 2002] mostly due to urban wastewater discharged into the sea. LAS are broadly used surfactants and their presence has been also confirmed in the blanks. However, even after subtraction of the blank they were still an important component of this fraction, thus their presence in the marine aerosol should not be excluded. Another series of $[M\text{-}H]^-$ ions from *m*/*z* 211 up to 309, differing with 14 amu was also observed. The CID-MS^2 spectrum of the abundant ion at *m*/*z* 253 (Figure 4a) belonging to this series contains the ions at *m*/*z* 235 $[M\text{-}H\text{-}18]^-$, 209 [M-H-44], and 97 [M-H-156]. The ion at *m*/*z* 97 is attributed to $[HSO_4]^-$ and is characteristic of sulfate esters [*Surratt et al.*, 2007]. The neutral losses of 18 and 44 amu indicate the presence of a carboxylic group [*Kerwin et al.*, 1996]. This was also checked with MS^2 fragmentation experiments using authentic fatty acid standards. The neutral losses of water, CO_2 and the presence of $[HSO_4]^-$ ion indicate the presence of sulfated hydroxyacids [*Gómez-González et al.*, 2008]. The ion at *m*/*z* 253 is tentatively attributed to a C_9 hydroxyl-carboxylic acid. However, on the base of this mass spectrum it is difficult to attribute the position of the hydroxyl group. Our results indicate the presence of the sulfate esters of hydroxyl-carboxylic acids ranging from C_6 up to C_{11}. Our observations were consistent with the recent study by *Claeys et al.* [2010] who identified sulfate esters of C_9-C_{13} hydroxyl-carboxylic acids in fine organic aerosol collected from a remote marine area with intense phytoplankton activity. *Claeys et al.* [2010] used LC/MS with ES ionization in the negative mode and, additionally, accurate mass measurements to confirm the structure of these ions. One of the most prominent signals was 253, which was also attributed to the C_9 member of the homologues.

[18] Organosulfates have been identified in secondary organic aerosols [*Surratt et al.*, 2007] in chamber experiments and in ambient aerosols [*Gao et al.*, 2006; *Inuma et al.*, 2007; *Surratt et al.*, 2008] as products of biogenically emitted VOCs (e.g., isoprene). In addition, the presence of hydroxyl-carboxylic acids is related with the photo-oxidation of unsaturated fatty acids of phytoplanktonic origin [*Cloern*, 1996; *Marchand and Rontani*, 2001; *Mochida et al.*, 2002].

[19] In the mass spectrum of the second chromatographic peak (at Rt 6.14, Figure 3b), attributable to more retained, more hydrophobic organic compounds, we have observed the presence of $[M\text{-}H]^-$ ions starting at *m*/*z* 199 up to 451, differing with 14 amu. The compounds corresponding to these masses have been identified, through their CID-MS^2 spectra (yielding the ions $[M\text{-}H\text{-}18]^-$ and $[M\text{-}H\text{-}44]^-$ [*Kerwin et al.*, 1996]), as alkanoic acids (C_{12}-C_{30}). In addition, the ions at *m*/*z* 171, 173, and 187, using the same approach have been identified as ω-oxo-C_8-carboxylic acid, a,ω-C_8-dicarboxylic acid and a,ω-C_9-dicarboxylic acid, respectively. The latter being associated with the photo-oxidation of unsaturated fatty acids can be considered as components of secondary organic aerosol [*Stephanou and Statigakis*, 1993]. The most abundant ions have been observed at *m*/*z* 211, 225, 253, and 267. We have attempted to identify these ions by using their CID-MS^2 spectra. In Figure 4b is presented the CID-MS^2 spectrum of ion at *m*/*z* 225. The spectrum contains the ions at *m*/*z* 207 ($[M\text{-}H\text{-}18]^-$), 181 ($[M\text{-}H\text{-}44]^-$), 125, 111, 97. This pattern

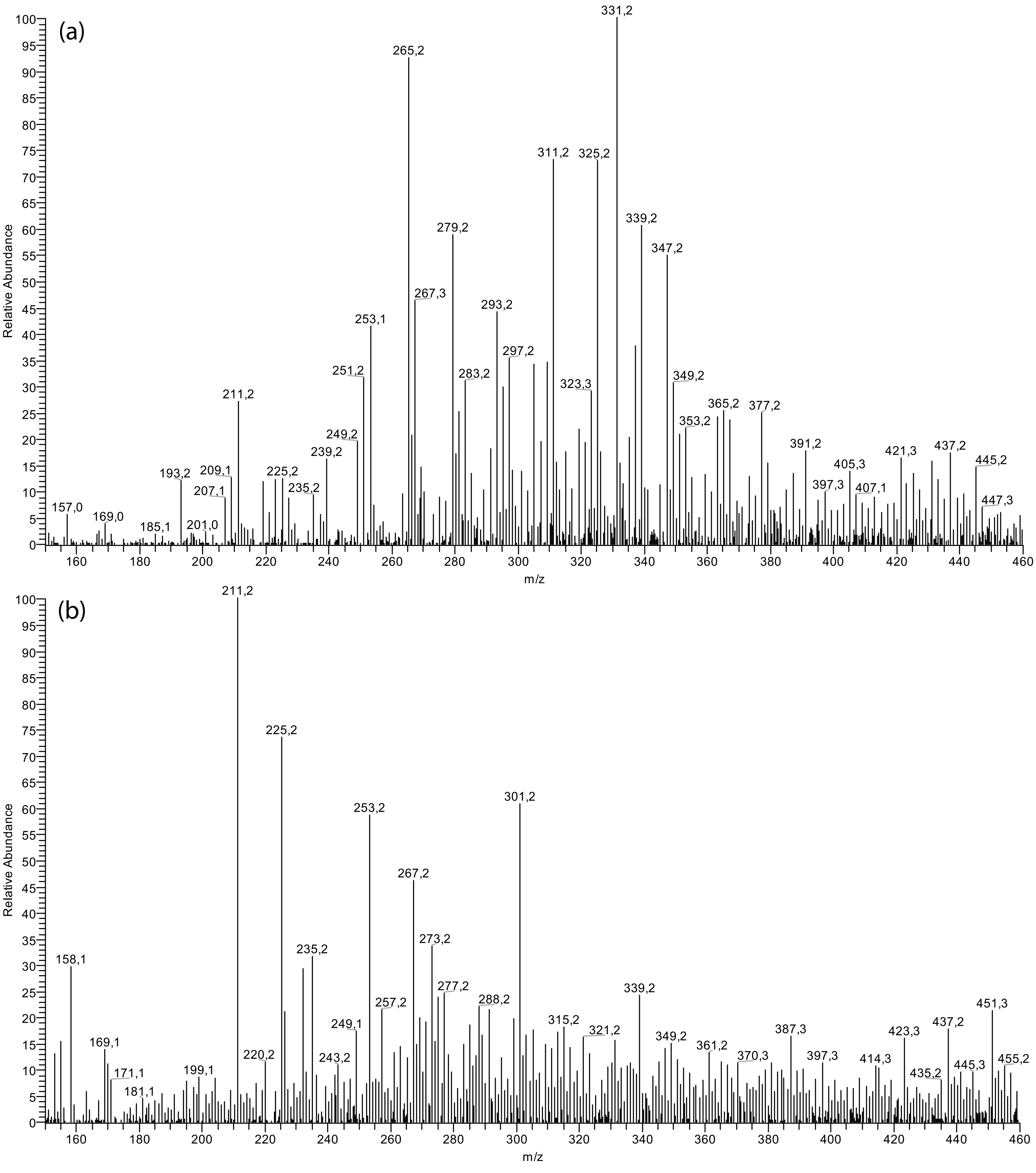

Figure 3. Full mass spectrum of the peak at (a) Rt 3.19 and (b) Rt 6.14 in the LC/MS chromatogram in Figure 2.

has been observed for unsaturated fatty acids such as myristoleic acid ($C_{14:1\omega5}$) [*Kerwin et al.*, 1996]. Thus, the series of ions from *m*/*z* 155 up to *m*/*z* 281 can be identified as monounsaturated fatty acids compounds found in the past in marine aerosols. The peak at *m*/*z* 301 corresponds to the dehydroarachidonic acid a compound related, as other polyunsaturated fatty acids (PUFA), to phytoplankton [*Cloern*, 1996].

[20] The results of the LC/ESI-MS analysis demonstrate the occurrence of unambiguous tracers of secondary organic aerosol formation, including sulfate esters of carboxylic acids and hydroxyl-carboxylic acids, together with tracers of primary organic aerosol production from sea spray, consisting of unsaturated fatty acids. Other compounds, like azelaic acid and ω-oxo-C_8-carboxylic acid, originated from the oxidation of fatty acids; however, it is not clear if such

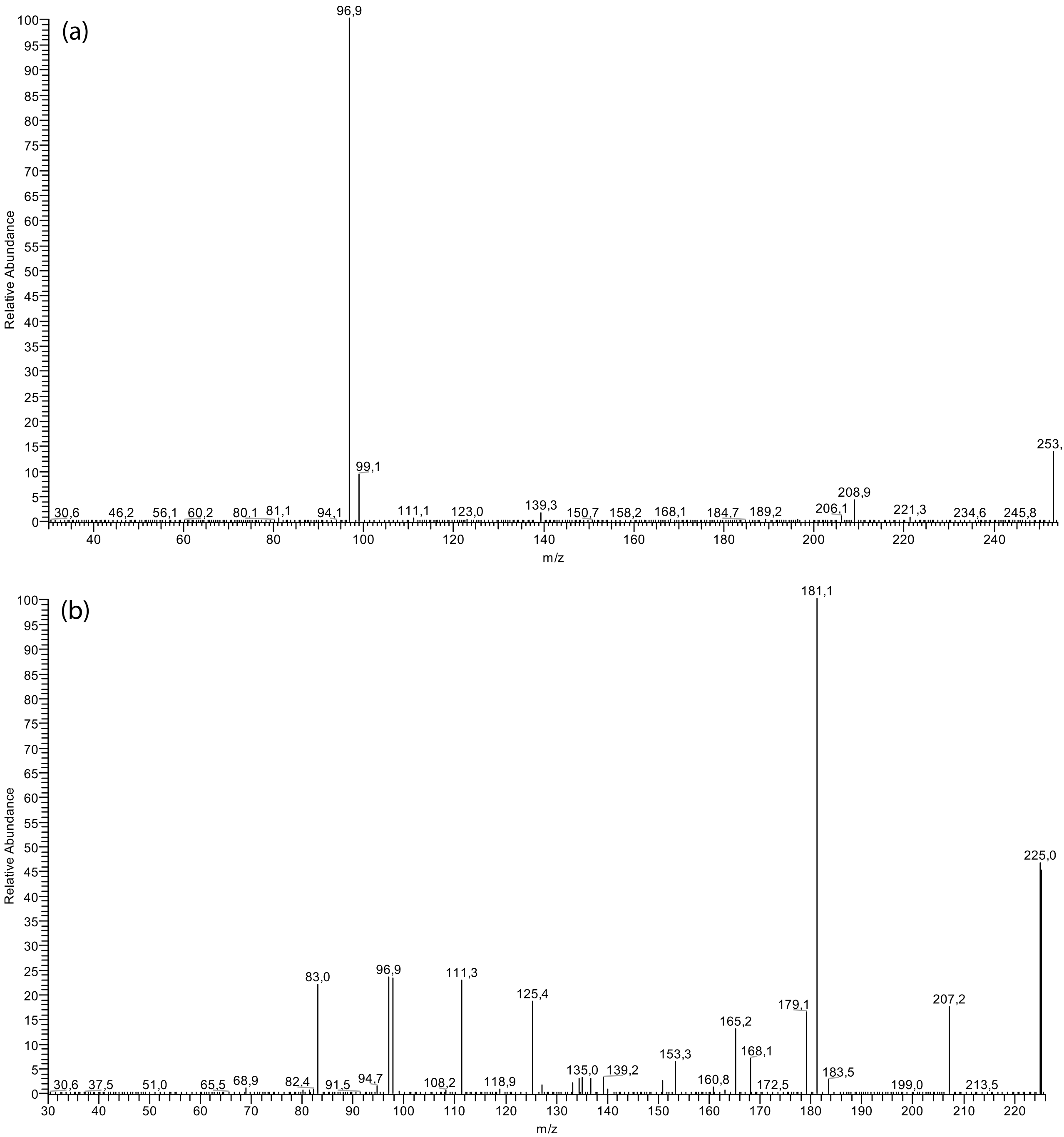

Figure 4. CID-MS^2 spectrum for the selected compound with $[M\text{-}H]^-$ (a) at *m*/*z* 253 and (b) at *m*/*z* 225.

oxidation step occurred at the sea-surface microlayer or directly at the expense of the lipids contained in the aerosol particles. In other words, azelaic acid could form from both gas-to-particle conversion and heterogeneous oxidative reactions onto primary organic aerosols. Azelaic acid and the other polar organic compounds identified by LC/ESI-MS provide precious information on the possible constituents and major routes of formation of marine oxidized organic aerosols. It should be noticed that such compounds have not been thoroughly quantified in our study. However, *Claeys et al.* [2010] reported that the organosulfates determined by them accounted for about 1% of the total of the WSOC mass. For a more inclusive and quantitative chemical characterization we have determined the functional group distributions of fine and coarse water-soluble aerosol samples by employing 1D and 2D proton NMR spectroscopy.

3.3. The 1D and 2D NMR Analysis of WSOC in CE Samples

[21] Following the distinct analytical protocols adopted for HiVol1 and HiVol2 samples (Figure 1), 1D ^{1}H-NMR spectra have been recorded for unfractionated WSOC

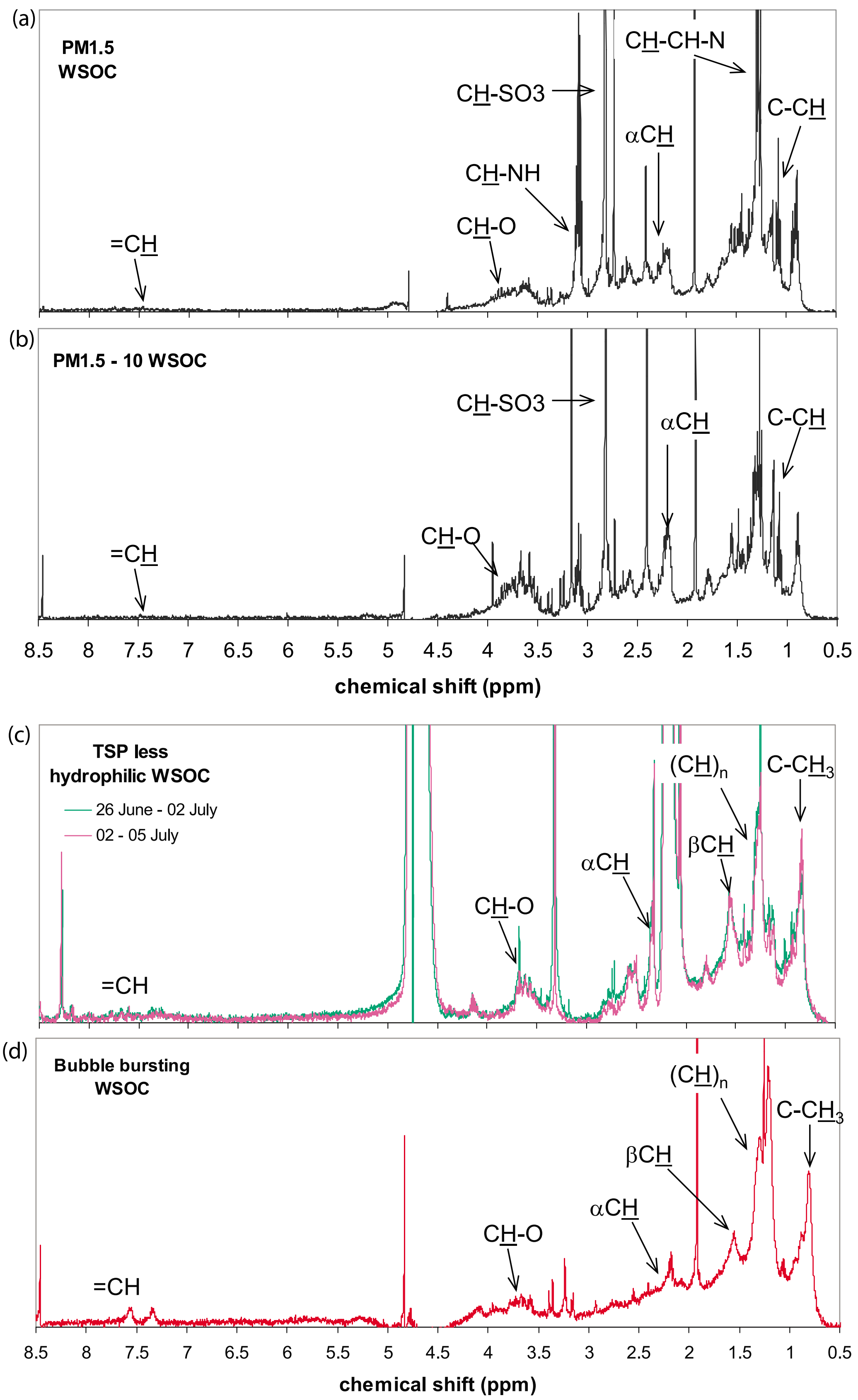
(a)
PM1.5
WSOC
CH-CH-N
CH-SO3
C-CH
αCH
CH-NH
CH-O
=CH
(b)
PM1.5 - 10 WSOC
CH-SO3
αCH
C-CH
CH-O
=CH
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
chemical shift (ppm)
(c)
TSP less
hydrophilic WSOC
26 June - 02 July
02 - 05 July
(CH)$_n$
C-CH$_3$
βCH
αCH
CH-O
=CH
(d)
Bubble bursting
WSOC
(CH)$_n$
C-CH$_3$
βCH
αCH
CH-O
=CH
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
chemical shift (ppm)

Figure 5

Table 3. NMR Functional Group Concentrations of WSOC Determined in Unfractionated Samples and in Extracts Isolated on OASIS Columns

Functional Groups	H-Ar (nmol m^{-3})	HC-O (nmol m^{-3})	HC-N (nmol m^{-3})	MSA (nmol m^{-3})	HC-C = (nmol m^{-3})	H-C (nmol m^{-3})	H-Ar (%)	HC-O (%)	HC-N (%)	MSA (%)	HC-C = (%)	H-C (%)	COOH (nmol m^{-3})
Unfractionated Samples (HiVol1 $PM_{1.5}$)													
12–15/06	0.16	0.66	2.32	6.44	4.87	7.91	1	3	10	29	22	35	ND
16–20/06	0.17	0.56	0.79	1.77	3.73	5.66	1	4	6	14	29	45	ND
26/06–4/07	0.15	1.53	1.55	3.04	6.94	10.26	1	7	7	13	30	44	ND
Unfractionated Samples (HiVol1 $PM_{1.5-10}$)													
12–15/06	ND	0.55	0.23	1.65	1.62	1.69	-	10	4	29	28	29	ND
16–20/06	ND	0.57	0.39	0.78	1.39	1.87	-	11	8	16	28	37	ND
26/06–4/07	ND	0.77	0.49	1.02	1.78	2.48	-	12	7	16	27	38	ND
Isolated WSOC Fractions (HiVol2 TSP)													
12–15/06	0.005	0.02	-	-	0.07	0.69	1	2	-	-	9	89	0.006
26/06–2/07	0.039	0.11	-	-	0.25	1.54	2	6	-	-	13	79	0.067
2–5/07	0.045	0.11	-	-	0.29	1.81	2	5	-		13	80	0.056

samples extracted from fine and coarse HiVol1 filters, while 1D and 2D ^{1}H-NMR data have been acquired for the fraction of water-soluble organic compounds isolated by OASIS HLB extraction from the extracts of bulk and size-fractionated HiVol2 filters. Such WSOC fractions isolated on the HLB cartridges correspond to the less hydrophilic compounds, i.e., those eluting with longer retention times in the LC/ESI-MS chromatograms (see previous section). These compounds do not contain lower molecular weight and more acidic species which are not retained by the cartridges. Examples of 1D spectra obtained using the two protocols and referring to the second leg of the ship campaign are reported in Figure 5, while Table 3 reports the functional group concentrations for the full sample set and resulting from the integration of the ^{1}H-NMR bands over broad intervals of chemical shifts: aromatic groups (H-Ar; 6 – 9 ppm), hydroxyl groups (HC-O; 3.2 – 4.5 ppm); amines (HC-N, with peaks at 2.7 and 3.1 ppm); MSA, showing a singlet at 2.81 ppm; aliphatics adjacent to unsaturated carbon atoms (HC-C = ; 1.9 – 3.1 ppm); purely alkylic groups (H-C; 0.7 – 1.8 ppm). The spectra of unfractionated WSOC confirm the previous findings obtained on samples collected in the clean sector at Mace Head [*Cavalli et al.*, 2004; *Facchini et al.*, 2008b], showing the occurrence of low-molecular weight organic compounds carrying heteroatoms (MSA, monomethyl- and diethyl-amines) together with complex oxygenated aliphatic compounds and virtually no aromatics. Among the oxygenated species, alcohols (C$\underline{H}$-O) were found in significant concentrations especially during the second leg of the campaign, and with larger contributions to the coarse aerosol fraction with respect to the submicron fraction (Table 3). Only traces of anomeric hydrogen atoms (δ_H 5.0–5.5 ppm) were detected, therefore sugars are not expected to contribute in large amounts to the polyols present in fine and coarse samples object of this study. Beside alcohols, the occurrence of other oxygenated compounds is confirmed by the intense resonances between 2 and 3 ppm, where the signals of most aliphatic CH groups substituted by carbonyls or carboxyls are found. The common pattern of peaks at 0.9, 1.3, 1.8, 2.2, 2.4 and 2.6 ppm can be assigned to low-molecular weight carboxylic oxoacids or diacids, on the basis of the analysis of standard compounds.

[22] The difference between the spectra of unfractionated WSOC and of the fractions isolated by HLB extraction is remarkable and the functional group distributions show a clear shift toward less polar groups following fractionation, with an evident increase of the alkyl moieties (H-C) in the isolated WSOC. MSA and low-molecular weight amines, dimethyl- and diethyl-amines [*Facchini et al.*, 2008b], were not retained by the OASIS columns, in agreement with extraction tests using standard compounds. These results confirm the outcomes of LC/MS analysis indicating that the more hydrophilic fraction of WSOC contained organic compounds in ionic form and carrying heteroatoms (N or S). The less hydrophilic water-soluble organic compounds accounted for only 8 – 10% of total NMR-detectable WSOC (Table 3), but they must recover most of the surface-active species, and indeed their ^{1}H-NMR spectra suggest the occurrence of amphiphilic aliphatic compounds carrying methylenic chains with terminal methyl group (i.e., hydrophobic tails) substituted with alcohols and carboxylic groups (polar moieties).

[23] The nature of the water-soluble aliphatic compounds isolated on the OASIS cartridges was further characterized

Figure 5. 1D NMR spectra of WSOC. (a, b, and c) Spectra of ambient aerosol samples collected during the second leg of the ship campaign. Spectra in Figure 5a (fine fraction) and Figure 5b (coarse fraction) refer to total WSOC, while the spectrum in Figure 5c was recorded for the less hydrophilic WSOC fraction obtained by HLB extraction. (d) The last spectrum was recorded for bubble bursting aerosols produced in tank experiments onboard the research vessel. The horizontal axis reports the chemical shift in ppm. Intense peaks at 2.2 ppm and at 4.8 ppm in spectrum in Figure 5c are experimental artifacts, as well as the signal disturbance and negative peaks between 4.5 and 5.2 ppm in spectra in Figures 5a, 5b and 5d. Symbols and arrows identify most prominent functionalities: = CH: aromatic groups; CH-O: alcohols and ethers; CH-NH: amines; $CH\text{-}SO_3$: MSA; αCH: aliphatic groups in alpha position to carboxyls or other unsaturated carbon atoms; CH-CH-N: aliphatic groups in α position to an amine group; C-CH: “generic” alkylic groups.

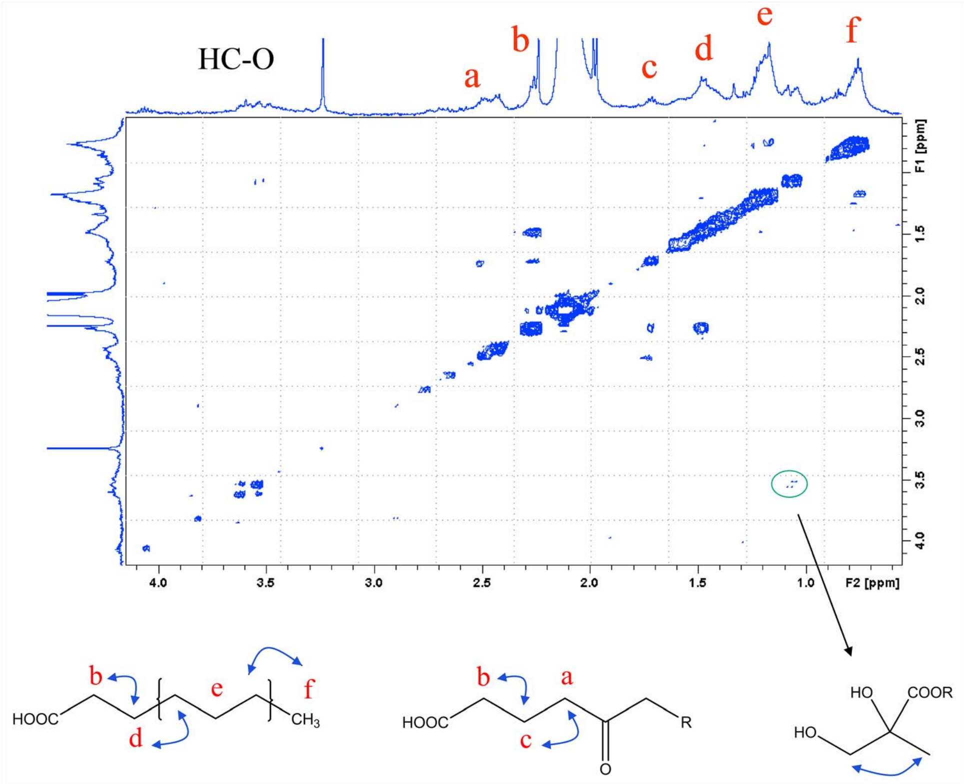

Figure 6. The 1H-1H gCOSY 2D NMR spectrum of the HiVol2 sample collected between 2 and 5 July in D2O solution. The molecular proton connectivities responsible for the main crosspeaks observed due to fatty acids, diacids, oxo-acids and hydroxy-acids are depicted.

using 2D H-NMR spectroscopy. In Figure 6 we report the ^{1}H-^{1}H gCOSY 2D NMR spectrum of the UoC sample collected between 2 and 5 July. The cross peaks resulting from proton connectivities attributed to alkanoic acids, diacids, and oxo-acids are the main contributors in the spectrum. Also visible are peaks connecting alkyl and H-C-O protons, that can be attributed to hydroxyacids, including 2-methyl,2,3-hydroxypropanoic acid, which was identified in the LC-MS spectra of the samples.

[24] By integrating the peaks attributed to alkanoic acids, i.e., terminal methyls (at 0.8 ppm), chain methylenes (at 1.3 ppm), methylenes in α and β positions (at 2.2 and 1.6 ppm, respectively), an average molecular formula can be derived. The number of carboxylic groups in the samples can be calculated from the integral of methylenes in α- position to −COOH, and is reported in Table 3, along with functional group distribution of the three HiVol2 samples. A ratio between methylenes of internal chains and in α position to carboxylic groups of ~5 was measured for the first sample collected between 12 and 15/06, while the other two samples had values of approx. 2. Taking into account that the first sample also had the smallest amount of –COOH groups, this suggests that while all samples consist of a distribution of homologous alkanoic acids and diacids, the first sample contains a higher proportion of C_8-C_9 saturated acids, while samples collected later are compatible with high D_8-D_9 carboxylic diacids contributions. These findings suggest that the less hydrophilic WSOC fraction of submicron aerosols was constituted not primarily by C_{14}-C_{20} unsaturated fatty acids (present in trace amounts) but mainly by their degradation products: C_8– C_9 carboxylic acids and C_8-C_9 diacids already identified at the molecular level by LC/MS.

[25] Our finding of oxidation products of fatty acids in the WSOC isolated by HLB extraction suggests that the less hydrophilic water-soluble organic aerosols can be accounted for by organic particles emitted with sea spray, and by the products of their chemical aging in the atmosphere. We have compared the ^{1}H-NMR spectra of WSOC from the ambient samples collected onboard the CE with those of organic particles formed in tank experiments carried out during the same cruise [*Facchini et al.*, 2008a]. The organic component of sea-spray aerosol is mainly composed of poorly soluble lipids and polysaccharides (see Section 3.6), but also contains a smaller fraction of water-soluble organic compounds, which can be interpreted as substituted aliphatic compounds, like short-chain fatty acids and hydroxyl-carboxylic acids, based on their ^{1}H-NMR spectra in D_2O solution (Figure 5d), similarly to the less hydrophilic fraction of WSOC in ambient particles (Figure 5c). A more conclusive comparison would require designed bubble bursting experiments simulating also the initial stages of atmospheric aging and also involving molecular characterization of the samples. But the results from the MAP experiments already indicate that the less hydrophilic fraction of WSOC in ambient particles is the best target to compare with when seeking the polar compounds contained in sea-spray particles, while the more hydrophilic

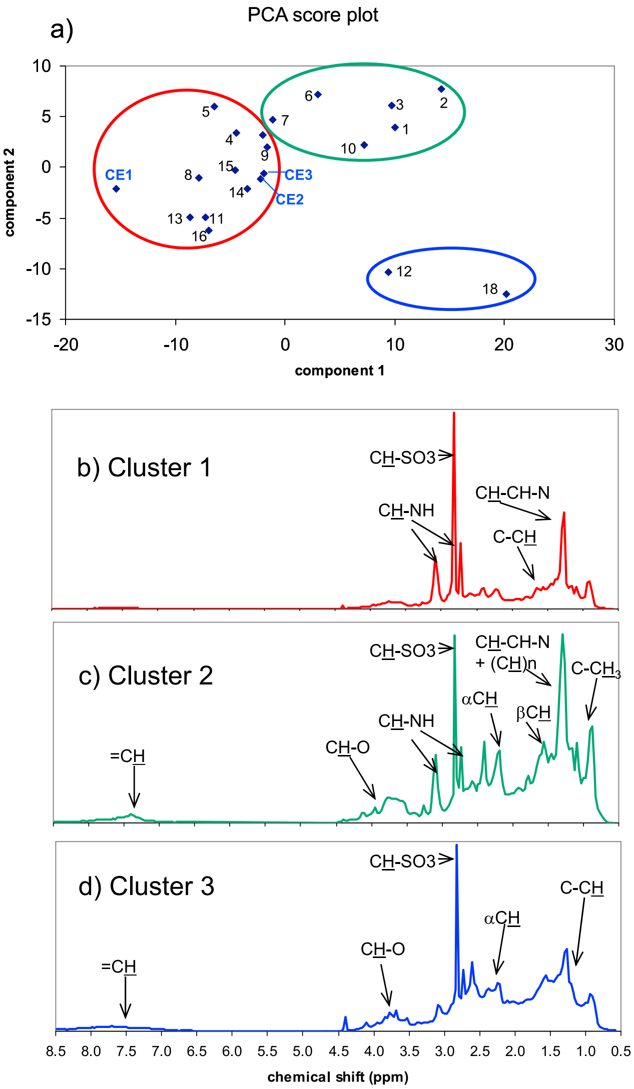

Figure 7. PCA score plot for NMR spectra of Mace Head (MH01 to MH18, Table 2) and Celtic Explorer samples (CE1, CE2, and CE3). Main groupings determined by cluster analysis are also shown together with their centroids.

fraction of ambient WSOC is clearly impacted by organic compounds which can originate from multiple secondary processes, including gas-to-particle conversion.

3.4. Factor Analysis of 1D NMR Spectra of WSOC

[26] In the previous section, we observed that only ~10% of WSOC exhibits affinities with the components of fresh primary marine particles, while the rest is believed to recover mainly secondary or extensively aged primary components. Of this larger fraction, few compounds (MSA and amines) could be identified and quantified, the rest being essentially a complex mixture of unidentified oxygenated compounds. In order to disentangle components in the unresolved mixtures, we employed statistical methods to extract spectral features on the basis of their variability between samples, and we interpreted them based on the correlation with known spectral profiles.

[27] The diversity within an aggregated set of 21 spectra of submicron aerosol samples including MAP samples and additional samples from previous experiments (Table 2) was analyzed by cluster analysis and PCA. The results are reported in Figure 7a, showing the PCA score plot as a function of the first two factors, with overlapped contours indicating the three main groupings of samples obtained by hierarchical cluster analysis. These two first PCA factors account for 85% of the variance of the spectral data set. The first factor is linked to the occurrence of aromatic NMR signals and it is also negatively correlated to the presence of MSA. The second factor is positively correlated with peaks of alkyl groups (H-C) and negatively correlated with the signals of functionalized aliphatic groups (H-C-C =). PCA clearly discriminates the spectral features of samples #12 and #18, which are the ones collected in the polluted sector at Mace Head, from the spectra of all the remaining ones, i.e., the samples collected in marine or modified marine air masses. But there is also a large spread in the NMR compositions of the maritime aerosol samples. In order to investigate such variability, we identified three main groupings of samples by hierarchical cluster analysis (the contours in Figure 7a) and we derived average spectra defined by the centroids of such clusters (Figure 7b). The split of the maritime sample set into two groupings (clusters 1 and 2 in the figure) must be considered arbitrary and there is actually a continuum between the two, but we keep this distinction with the aim of illustrating the differences in the spectra of maritime samples falling in different regions of the PCA score plot. Cluster 1 includes the most "typical" spectra of marine organic aerosol observed in the clean sector at Mace Head plus the Celtic Explorer samples, showing very little aromatic groups and intense MSA and/or amine peaks. The spectra in cluster 2 show evident signals of alkyl groups (methylenic chains and terminal methyls), traces of aromatic groups and relatively low MSA, and they characterize samples collected in Mace Head in clean or modified marine sectors (Table 2). Based on the marked similarity with the spectra of isolated less hydrophilic WSOC from the CE samples (Figure 5c), the Mace Head samples belonging to cluster 2 were probably collected when the less hydrophilic WSOC became dominant over MSA and the other marine SOA. The presence of aromatic groups, almost absent in the CE samples, may indicate some pollution contribution to the Mace Head samples of cluster 2. Interestingly, similar ^{1}H-NMR spectra have also been recorded for DOC in rain samples at an Atlantic coastal site in U.S. [*Miller et al.*, 2009] suggesting that the source of alkanoic acids characteristic of cluster 2 may be active in several sectors of the North Atlantic. Finally, the spectrum of cluster 3 centroid (polluted sector at Mace Head) shows a relatively large aromatic content and very functionalized aliphatic compounds with a strong correlation with spectral types commonly found in continental areas impacted by combustion sources [e.g., *Decesari et al.*, 2001].

[28] In our data set of 21 ^{1}H-NMR samples, when applying PCA with only three factors, communalities (i.e., the fraction of variance for a given variable accounted for by common factors) are greater than 0.60 for 96% of the variables and greater than 0.80 for 86% of the variables. This means that a large fraction of total variance is shared by the variables (chemical shifts) and justifies the use of

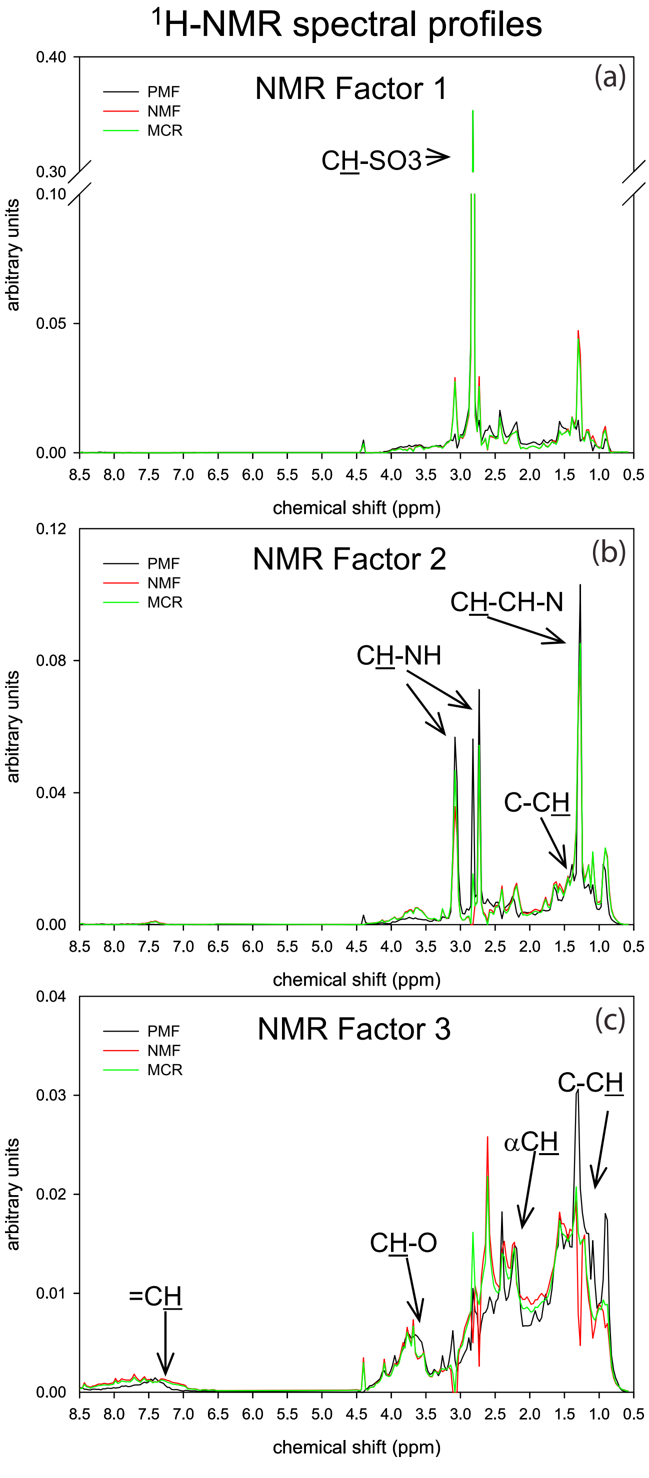

Figure 8. The 200-point NMR spectral profiles provided by three factor analysis methods: PMF, NMF and MCR (see text). Labels for functional groups as in Figure 5.

PMF, NMF and MCR techniques for common factor analysis of our NMR spectral data set.

[29] Since PCA and cluster analysis suggested that the variability in the NMR composition can be described using three spectral profiles, we discuss first the results of a 3-factor solution for MCR, NMR and PMF, followed by 5-factor solution, which is the most informative and still shows a good agreement between the different algorithms employed.

[30] The decomposition of the 1D NMR spectra from Mace Head and the Celtic Explorer into three factors using PMF, NMF and MCR provides a clear split between factors dominated by MSA, amines, and a third factor containing only resonances of the more complex, and less characterized mixtures of water-soluble organic compounds, which also provides the largest contribution to WSOC concentrations (Figures 8 and 9). The factor dominated by MSA also shows traces of hydroxyl-methane-sulphonate (HMSA) and other aliphatic compounds including low-molecular weight oxoacids and diacids (Figure 8a). The second factor recovers DMA and DEA plus unidentified aliphatic species comprising organic compounds carrying terminal methyls (peaks between 0.8 and 1.3 ppm). The profile of the third factor recovers aromatic moieties and broad aliphatic oxygenated functionalities (hydroxyl groups, aliphatic groups adjacent to carbonyls and carboxylic groups, and alkyl groups), with some differences in the outputs of the different algorithms. The contributions of the third factor are clearly affected by pollution sources, since they are largest for the samples belonging to the "polluted sector" at Mace Head and for other samples when the concentrations of BC and submicron nitrate are relatively high (Table 2), although significant contributions are also found for samples, like MH15 and MH16, apparently unaffected by pollution sources.

[31] By increasing the number of factors, the goodness of the fit increases progressively without evident transitions (auxiliary material Figure S4). At the same time, we observed that different algorithms do not always perform in a consistent manner in defining new factors, and that the agreement was better for the set of spectra binned to 400 points than for that with a 200 points resolution. For the higher resolution data set the 5-factor solution still shows a considerable agreement between algorithms (Figures 10 and 11). The first two factors, dominated by MSA and amines, do not differ substantially from the correspondents in the 3-factor solutions. It is the complex, oxygenated, aromatic and aliphatic fraction, which decomposes into new groupings of organic functionalities. Factor 3 is found preferentially in moderately polluted and clean marine samples which correspond approximately to the cluster 2 from PCA and cluster analysis (Figure 7d). Its profile (Figure 10c) shows a limited content of aromatic moieties and of hydroxyl groups, with a greater proportion of alkyl moieties, containing structures attributable to methylenic chains, terminal methyls and methylenes in α and β position to carboxylic groups. The similarity between the profile of Factor 3 and the spectra of the less hydrophilic WSOC fraction isolated by HLB extraction is striking (point c in Figure 6), indicating that Factor 3 actually traces a distinct class of organic compounds which can be physically isolated using chemical extraction methods. Factor 4 contributions are clearly highest for the Mace Head samples collected in the polluted sector (Table 2), which also account for the third cluster from PCA and cluster analysis (Figure 7c), and the corresponding spectral profile (Figure 10d) shows the most prominent aromatic groups and exhibits the strongest correlation with typical spectra of WSOC in polluted environments [*Decesari et al.*, 2001]. Finally, Factor 5 traces an additional contribution to clean

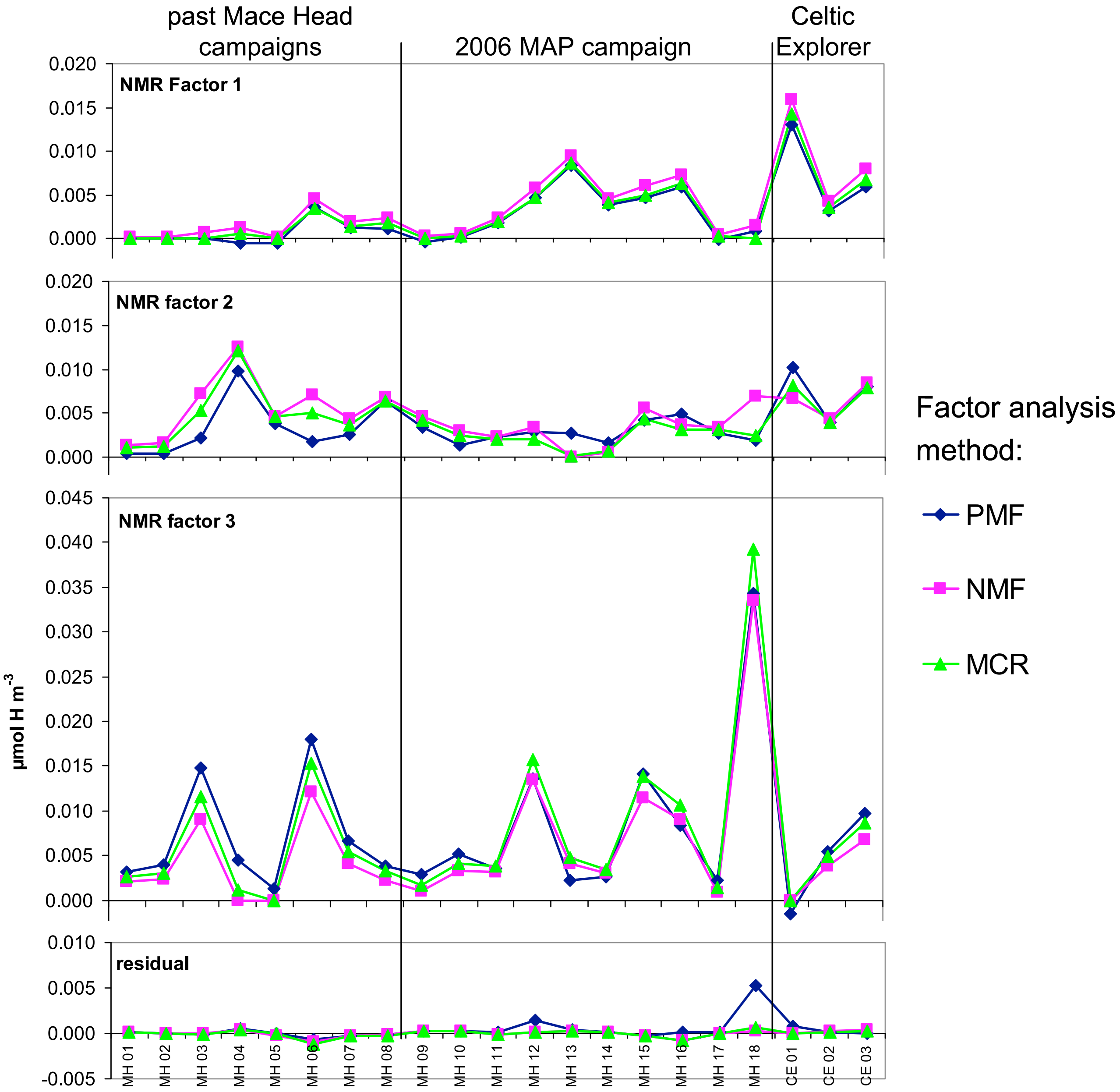

Figure 9. Contributions of NMR factors for WSOC determined by three factor analysis methods: PMF, NMF and MCR (see text). A three factor solution for 200-point binned spectra is shown. Samples are listed as in Table 2. MH: Mace Head. CE: Celtic Explorer. Samples from the polluted sector in Mace Head are samples 12 and 18.

maritime samples which did not emerge clearly from PCA and cluster analysis, and that affected prevalently the samples collected in mid-summer samples: in August 2004 and July 2006, including the last sample collected onboard the Celtic Explorer and the filter sampled in parallel at Mace Head between the end of June and the first days of July 2006 [*Rinaldi et al.*, 2009]. The profile of Factor 5 is characteristic of purely aliphatic compounds, carrying hydroxyl, and keto/carboxyl substituents (Figure 10e). There is no trace of the alkanoic acids of Factor 3, and the bands are broad and featureless, witnessing the occurrence of complex mixtures of functionalized species. The fine structure of the hydroxyl band does not match with that of polluted samples and shows no traces of levoglucosan and other anhydrosugars. We conclude that Factor 5 shows evidence of purely aliphatic, oxygenated organic compounds contributing to WSOA in clean marine air masses in the Northeast Atlantic especially in the summer season, and that cannot be reconciled with the composition of oxidized organic aerosols characteristic of polluted continental air masses.

[32] The above findings show that the variability of WSOC composition can be captured by NMR spectral fingerprints

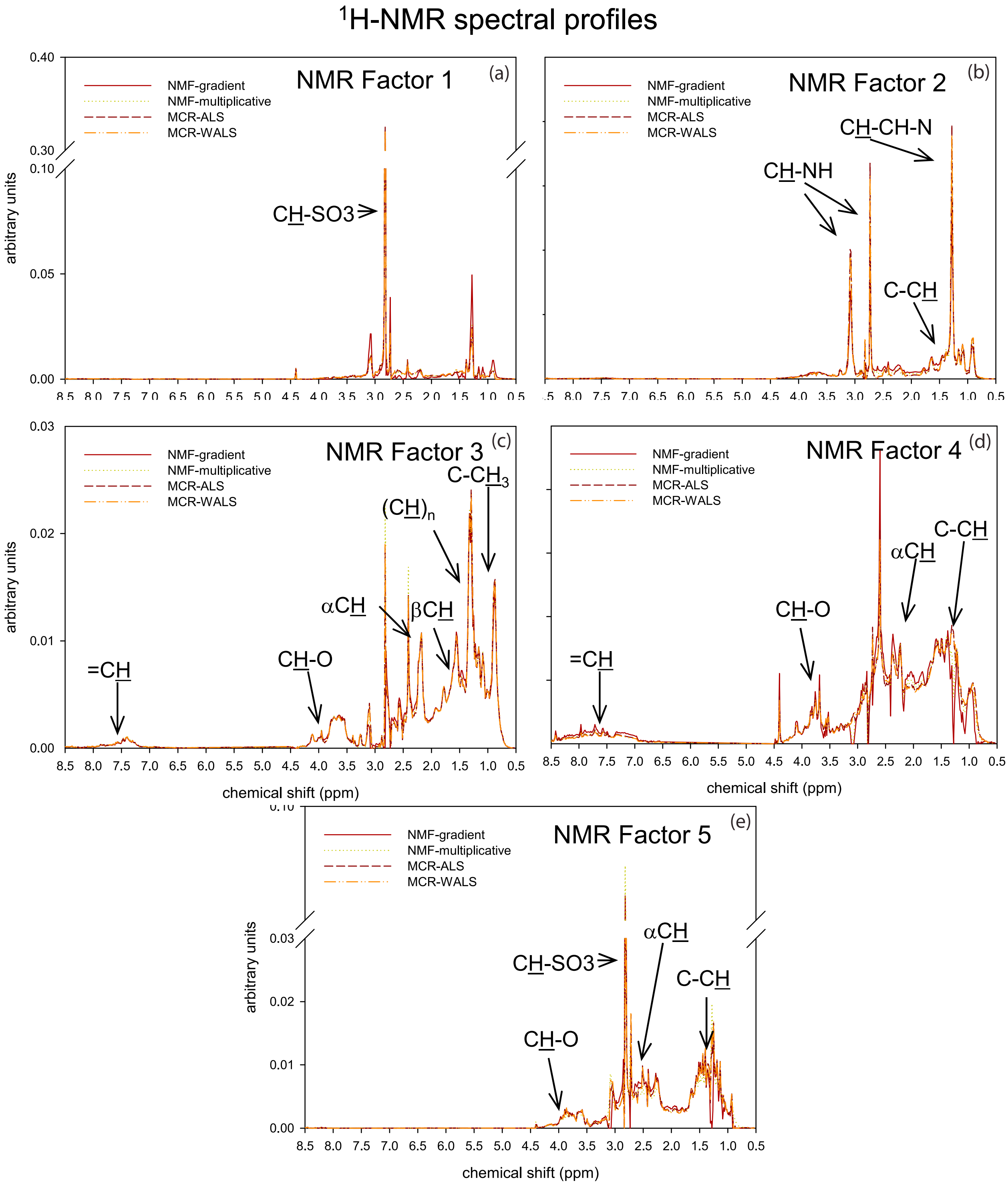

Figure 10. The 400-point NMR spectral profiles provided by four factor analysis algorithms: NMF with projected gradient optimization, NMF with a multiplicative update approach, MCR-ALS, and MCR-WALS (see text). Labels for functional groups as in Figure 5.

related to major source contributions: MSA, low-molecular-weight organic acids and amines which can be contributed by gas-to-particle conversion sources, less hydrophilic compounds rich of aliphatic chains including aged lipid material, and aromatic oxygenated compounds derived by combustion sources. An additional class of marine WSOC can be accounted for by purely aliphatic complex oxygenated compounds rich of alcohols.

3.5. NMR Analysis of WIOC

[33] Our hypothesis that aerosol WIOC is enriched in primary marine organic material, while secondary compounds

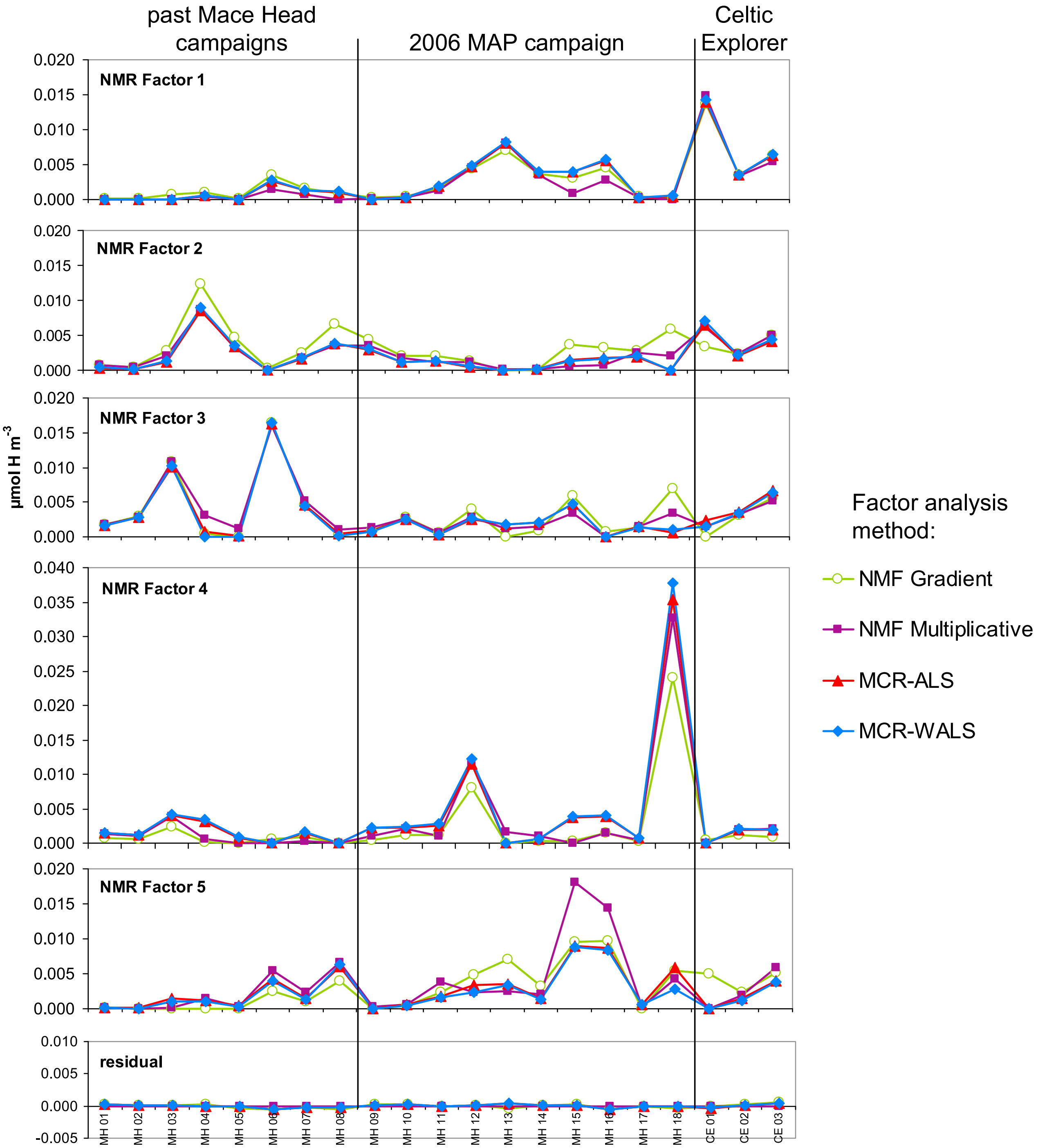

Figure 11. Contributions of NMR factors for WSOC determined by four factor analysis methods: NMF with projected gradient optimization, NMF with a multiplicative update approach, MCR-ALS, and MCR-WALS (see text). A five factor solution for 400-point binned spectra is shown. Samples are listed as in Table 2. MH: Mace Head. CE: Celtic Explorer. Samples from the polluted sector in Mace Head are MH12 and MH18.

make up the large part of WSOC is supported by the extensive chemical characterization of the water-soluble fraction of OC described in the previous section, while no data have been provided so far about water-insoluble organic compounds. The assignment of aerosol WIOC to primary organic particles is supported by laboratory bubble bursting experiments [*Facchini et al.*, 2008a] and by air-sea flux measurements of the aerosol chemical components performed at Mace Head [*Ceburnis et al.*, 2008], but awaits confirmation by chemical analysis. In this final results section, we provide a brief description of the first attempts of chemical characterization of aerosol WIOC by NMR spectroscopy.

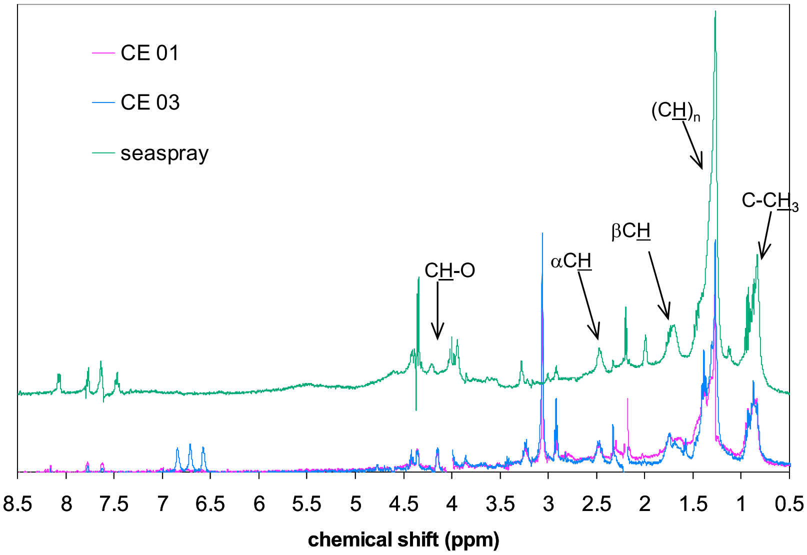

Figure 12. 1D NMR spectra of water-insoluble organic carbon (WIOC) extracted in trifluoroacetic acid (TFA) from aerosol produced in laboratory during bubble bursting experiments from seawater samples (in green) and from two ambient aerosol samples ($PM_{1.5}$ HiVol 1) corresponding to the first and third sampling periods onboard the Celtic Explorer (blue and purple lines). Labels for functional groups as in Figures 10 and 11.

[34] One D NMR characterization of the water-insoluble organic carbon (WIOC) in two $PM_{1.5}$ HiVol1 filters was performed in deuterated TFA solution and the results were compared to those obtained from the analysis of sea spray aerosols generated onboard the CE during the bubble bursting experiments (Figure 12). The aromatic region is essentially devoid of signals. Bubble bursting aerosols contain hydroxyl compounds accounted for by sugars associated with marine POC, which are missing in the ambient aerosols. On the other hand, both aerosol types contain analogous aliphatic structures attributable to methylenic chains with terminal methyls and methylenes in α and β position to carboxyl-, ester- and vinyl-groups, which can be interpreted as lipids. These findings provide therefore a proof-of-concept for quantitative chemical identification of biogenic marine organic matter in ambient water-insoluble aerosols in the North Atlantic.

4. Summary of Off-Line Chemical Analysis During MAP

[35] HiVol filter samples were collected onboard the research vessel outside the influence of ship tracks (monitored by BC measurements) and outside continental plumes. Under these conditions, molecular characterization by LC/MS provided unambiguous tracers for SOA such as oxo-carboxylic and dicarboxylic acids, the sulfate esters of hydroxyl-carboxylic acids, and tracers of biogenic marine POA such as saturated, mono- and poly unsaturated fatty acids. An overall *biogenic* source fingerprint for the identified WSOC components is indicated by the fact that ω-oxo-C_8-carboxylic acid, C_8 and C_9 a, ω- dicarboxylic acids and the sulphate esters of $C_6 - C_{11}$ hydroxyl-carboxylic acids ultimately originate from the photo-oxidation of unsaturated fatty acids. NMR analysis also indicates that the most hydrophobic fraction of the particles is structurally similar to lipids, and that the less hydrophilic fraction of WSOC consists of a distribution of homologous alkanoic acids and diacids, having an average carbon number between 8 and 9, which comprise the early generation products of fatty acid oxidation. This class of aliphatic compounds account for 4–15% of NMR-detectable WSOC during the CE cruise on the basis of the recovery of HLB extraction (Table 3), and 8–25% based on spectral factor analysis (Figure 11). The more processed oxidation products of aliphatic acids, like the sulfate esters of C_6–C_{11} hydroxyl-carboxylic acids, are found in the most polar fraction of WSOC, together with MSA and low-molecular weight amines, which are all of biogenic origin. However, NMR factor analysis assigned a small but significant (up to 15% of WSOC in the CE samples) aromatic-containing fraction of WSOC to pollution sources. A final class of compounds highlighted by NMR analysis consists in a complex mixture of purely aliphatic oxygenated organic compounds, including alcohols, remaining uncharacterized at the molecular level, and which were found in significant amounts during the second leg of the campaign, in the fine and in the coarse fraction of the aerosol (Figure 5). This NMR "OOA" may represent an additional class of marine oxidized organic particles, not apparently linked to the routes of fatty acid degradation. The actual source regions for the biogenic polar compounds identified by LC/MS and NMR analysis remain unclear. On the basis of literature studies on the kinetics of oleic acid oxidation [*Morris et al.*, 2002; *Katrib et al.*, 2005], and by considering an average ozone concentration of 40 ppb in the Atlantic boundary layer, the degradation of unsaturated fatty acids to smaller oxoacids and diacids is fast (typical time scale < ~1h) and, even when unsaturated fatty acids are mixed with much less reactive saturated lipids, their degradation can be considered complete in one or two days. It follows that a typical footprint for the less hydrophilic WSOC formation in this study can be drawn

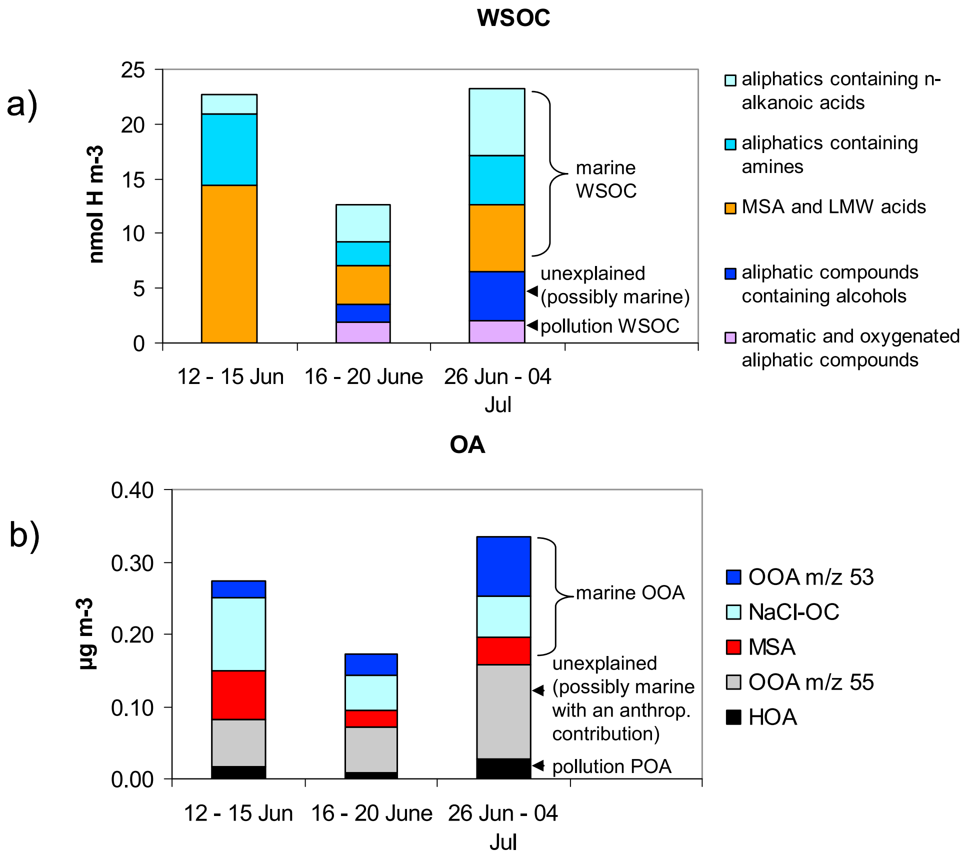

Figure 13. (a) Contribution of NMR factors (5-factor solution in Figures 10 and 11) for the $PM_{1.5}$ WSOC samples collected during the Celtic Explorer cruise. (b) Correspondent time-integrated PMF factors from AMS measurements (Dall'Osto et al., submitted manuscript, 2011).

by the 48h back trajectories in auxiliary material Figure S2. The formation of the more oxidized WSOC species can follow either fast processes (e.g., gas-to-particle conversion of amines) or slow progressive reactions in the particulate phase, which could take several days. The 120h back trajectories (auxiliary material Figure S2) are therefore more suitable to map the footprint of slowly forming SOA in the Atlantic boundary layer.

5. Comparison Between Off-Line and Online Observations

[36] In the companion paper by Dall'Osto et al. (submitted manuscript, 2011) dealing with the online mass spectrometric measurements performed onboard the CE, additional very important results about the nature of marine organic aerosol particles has been thoroughly discussed. The aerosol organic composition was found to vary according to air mass origin and, since the instruments operated in a continuous manner in pristine and polluted air, clear fingerprints for ship emissions and other anthropogenic primary sources have been highlighted on specific days of the campaign. PMF analysis provided AMS factors tracing both natural and anthropogenic components and whose contributions evolved in a complex manner through the campaign. The hydrocarbon-like organic aerosols (HOA) measured by AMS were clearly impacted by ship emissions, including the exhausts of Celtic Explorer. On the other hand, a prevalent marine source was attributed to four factors of oxygenated organic aerosols: (1) "MSA," with specific peaks such as *m*/*z* 45, 65, 79 and 96; (2) "NaCl-OC," organic matter internally mixed with NaCl (characteristic peaks at *m*/*z* 15, 27, 43, 44 and 58); (3) an oxidized organic aerosol factor "OOA m/z 53" with peaks at *m*/*z* 31, 41, 43, 44 and a unique peak at m/z 53, similar to the primary marine organic aerosol type detected by *Ovadnevaite et al.* [2011]; and (4) a second oxidized organic aerosol factor "OOA m/z 55" with peaks at *m*/*z* 27, 42, 43, 44 and a unique peak at m/z 55, found in marine air masses but also modestly enhanced during slightly polluted conditions. The characterization of OOA in clean Atlantic air masses by AMS provided further evidence that the marine organic particles observed during MAP contained highly processed/aged materials. These observations are supported by the recent study of *Ovadnevaite et al.* [2011] where HOA and OOA were measured with a high resolution time-of-flight aerosol mass spectrometer during a significant plume of marine organic matter over the North Atlantic Ocean peaking up to 4 $\mu g/m^3$ of OM and lasting over 24 h, and which was claimed to have mainly primary origin.

[37] Obviously, the very few time-integrated filter samples collected during the MAP cruise for off-line analysis cannot account for the great variability of aerosol OC composition observed by the online methods (AMS and ATOFMS). On the other hand, when averaging the AMS PMF factors over the sampling times of the HiVol1 filters (Figure 13b), we find that the off-line analyses fortuitously captured distinct AMS compositions. This is because of the different weather conditions and transport patterns observed in the different periods of the campaign (see section 2.1). Indeed, when comparing the AMS PMF factors with the factors obtained by NMR spectral analysis (Figures 10 and 11), both techniques highlighted that the sampling periods 12–15 June (CE 01) and 26 June – 4 July (CE 03) exhibit most diverse compositions. Therefore, on the basis of both online and offline aerosol chemical measurements, air mass origin had a clear impact on the organic aerosol "types" sampled onboard the research vessel. The air masses that have traveled unperturbed for up to five days north to 50°N and encountered during the first sampling period (auxiliary material Figure S2a) exhibit relatively high concentrations of MSA and of carboxylic acids internally mixed with sea salt (the AMS factor "NaCl-OC"), and that can be related to the aliphatic compounds including oxo- and di-acids shown to correlate with MSA and amines by ^{1}H-NMR analysis (NMR factors 1 and 2). Evidence of nitrogenated organic compounds were also provided by ATOFMS (Dall'Osto et al., submitted manuscript, 2011). Internally mixed particles containing sulfate, sea salt and carbonaceous material determined by the online MS methods (factors "NaCl-OC" from AMS and "Na-EC-Sul" from ATOFMS) during the first sampling period of the CE cruise indicate that well aged marine particles dominated the background aerosol composition at that time. During the second leg, corresponding to the time period of HiVol1 sample CE 03 (26 June – 4 July), there was a general increase of the concentrations of organic aerosol, favored by the more stagnant conditions (auxiliary material Figures S1 and S2c), by the slightly more polluted air masses (Dall'Osto et al., submitted manuscript, 2011), and by the accumulation of marine particles emitted from the highly productive oceanic waters, which the Celtic Explorer crossed between 30th June and 3rd of July (auxiliary material Figure S1). Contributions from both pollution and biogenic marine sources in this period are both supported by the AMS observations, showing in this period the greatest average concentrations of HOA, "OOA 55" (marine but enhanced during slightly polluted conditions), but also of the "OOA 53" (more peculiar of the marine environment) (Figure 13b). In agreement with the above reasoning, the ^{1}H-NMR analysis shows the occurrence of aromatic and oxygenated aliphatic compounds, attributable to pollution sources, together with WSOC classes of aliphatic compounds interpreted as processed marine POA (containing alkanoic acids) or postulated to be marine OA (containing alcohols) (Figure 13a). The latter showed the largest increase during the CE 3 period, and can be linked to the oxygenated organic compounds observed by AMS as "OOA 53." These alcohol-containing aliphatic compounds are found during the second leg of the campaign both in the fine mode and coarse mode of the aerosol (Figure 5) suggesting that they have not experienced long-range transport, contrary to MSA and to other classes of organics dominating the first sampling period of the campaign.

6. Conclusions

[38] The results of the chemical analysis of the aerosol samples collected during the Celtic Explorer campaign in early summer 2006 exemplifies the complexity of the nature of organic aerosol particles in North Atlantic boundary layer air. During the three weeks of cruising between 50° and 58°N off the Irish coast, the carbonaceous chemical composition observed by an AMS changed considerably with air mass origin. However, outside the ship tracks and the sparse continental airflows, it showed only $\leq 8\%$ of the AMS-determined organic mass accounted for by HOA and a maximum of 39% attributable to OOA with un unspecific assignment to marine or pollution sources (the "OOA 55"), which therefore must be considered as an upper limit for the anthropogenic fraction. The rest of the AMS mass was apportioned among factors pointing to more genuine marine sources. Spectral analysis of the 1D NMR data set apportions only $\leq 15\%$ of water-soluble OA to components related to pollution sources, the majority of the variability being explained by factors linked to MSA, amines and to oxygenated aliphatic compounds witnessing formation or transformation processes of organic aerosols in the marine boundary layer. In parallel, detailed molecular characterization by LC/ESI-MS and by 1D and 2D NMR spectroscopy traced the occurrence of biogenic lipids contained in sea spray particles and their progressive oxidation to short-chain functionalized aliphatic organic compounds of increasing water-solubility. In summary, the organic aerosol measurements performed during MAP depict a large pool of oxidized organic aerosol, which cannot be reconciled with the transport of aged continental polluted air. This finding is also in agreement with the conclusions of the study by *Ceburnis et al.* [2011], based on a dual carbon isotope analysis, supporting a prevalent marine origin for the particulate organic carbon in the Atlantic air masses reaching Mace Head. Finally, molecular marker analysis suggests that, in this process, the chemical aging of primary biological particles can be equally important than gas-to-particle conversion mechanisms.

[39] Given the large variability of marine aerosol chemical composition, a multitechnique approach, like that exemplified in the present study, is recommended to minimize method-dependent categorizations and oversimplifications, and to improve comparability with the results obtained in other oceanic areas. Future efforts must therefore be dedicated to extend the timeline of parallel online and off-line chemical determinations and to find robust overlaps between chemical classes defined in statistical terms or isolated through chemical methods.

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References

Andreu, V., and Y. Picó (2004), Determination of linear alkylbenzenesulfonates and their degradation products in soils by liquid chromatography-electrospray-ion trap multiple-stage mass spectrometry, *Anal. Chem.*, *76*, 2878–2885, doi:10.1021/ac035483e.

Bahadur, R., T. Uplinger, L. M. Russell, B. C. Sive, S. S. Cliff, D. B. Millet, A. Goldstein, and T. S. Bates (2010), Phenol groups in northeastern U.S. submicrometer aerosol particles produced from seawater sources, *Environ. Sci. Technol.*, *44*, 2542–2548, doi:10.1021/es9032277.

Cavalli, F., et al. (2004), Advances in characterization of size-resolved organic matter in marine aerosol over the North Atlantic, *J. Geophys. Res.*, *109*, D24215, doi:10.1029/2004JD005137.

Ceburnis, D., C. D. O'Dowd, G. S. Jennings, M. C. Facchini, L. Emblico, S. Decesari, S. Fuzzi, and J. Sakalys (2008), Marine aerosol chemistry gradients: Elucidating primary and secondary processes and fluxes, *Geophys. Res. Lett.*, *35*, L07804, doi:10.1029/2008GL033462.

Ceburnis, D., et al. (2011), Quantification of the carbonaceous matter origin in submicron marine aerosol particles by dual carbon isotope analysis, *Atmos. Chem. Phys. Discuss.*, *11*, 2749–2772, doi:10.5194/acpd-11-2749-2011.

Claeys, M., W. Wang, R. Vermeylen, I. Kourtchev, X. G. Chi, Y. Farthat, J. D. Surratt, Y. Gomez-Gonzales, J. Sciare, and W. Maenhaut (2010), Chemical characterization of marine aerosol in Amsterdam Island during the austral summer of 2006–2007, *J. Aerosol Sci.*, *41*, 13–22, doi:10.1016/j.jaerosci.2009.08.003.

Cloern, J. E. (1996), Phytoplankton bloom dynamics in coastal ecosystems: A review with some general lessons from sustained investigation of San Francisco Bay, California, *Rev. Geophys.*, *34*, 127–168, doi:10.1029/96RG00986.

Dall'Osto, M., et al. (2006), Single-particle detection efficiencies of aerosol time-of-flight mass spectrometry during the North Atlantic marine boundary layer experiment, *Environ. Sci. Technol.*, *40*, 5029–5035, doi:10.1021/es050951i.

Decesari, S., M. C. Facchini, E. Matta, F. Lettini, M. Mircea, S. Fuzzi, E. Tagliavini, and J. P. Putaud (2001), Chemical features and seasonal variation of fine aerosol water-soluble organic compounds in the Po Valley, Italy, *Atmos. Environ.*, *35*(21), 3691–3699, doi:10.1016/S1352-2310(00)00509-4.

Decesari, S., et al. (2007), Source attribution of water-soluble organic aerosol by nuclear magnetic resonance spectroscopy, *Environ. Sci. Technol.*, *41*(7), 2479–2484, doi:10.1021/es061711l.

Facchini, M. C., et al. (2008a), Primary submicron marine aerosol dominated by insoluble organic colloids and aggregates, *Geophys. Res. Lett.*, *35*(17), L17814, doi:10.1029/2008GL034210.

Facchini, M. C., et al. (2008b), Important source of marine secondary organic aerosol from biogenic amines, *Environ. Sci. Technol.*, *42*(24), 9116–9121, doi:10.1021/es8018385.

Fuzzi, S., et al. (2006), Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change, *Atmos. Chem. Phys.*, *6*, 2017–2038, doi:10.5194/acp-6-2017-2006.

Gao, S., J. D. Surratt, E. M. Knipping, E. S. Edgerton, M. Shahgholi, and J. H. Seinfeld (2006), Characterization of polar organic components in fine aerosols in the southeastern United States: Identity, origin, and evolution, *J. Geophys. Res.*, *111*, D14314, doi:10.1029/2005JD006601.

Gòmez-Gonzàlez, Y., et al. (2008), Characterization of organosulfates from the photooxidation of isoprene and unsaturated fatty acids in ambient aerosol using liquid chromatography/(-) electrospray ionization mass spectrometry, *J. Mass Spectrom.*, *43*, 371–382.

Gonzalez-Mazo, E., J. M. Forja, and A. Gomez-Parra (1998), Fate and distribution of linear alkylbenzene sulfonates in the littoral environment, *Environ. Sci. Technol.*, *32*(11), 1636–1641, doi:10.1021/es970733s.

Hersey, S. P., et al. (2009), Aerosol hygroscopicity in the marine atmosphere: A closure study using high-time-resolution, multiple-RH DASH-SP and size-resolved C-ToF-AMS data, *Atmos. Chem. Phys.*, *9*, 2543–2554, doi:10.5194/acp-9-2543-2009.

Iinuma, Y., C. Müller, O. Böge, T. Gnauk, and H. Herrmann (2007), The formation of organic sulfate esters in the limonene ozonolysis secondary organic aerosol (SOA) under acidic conditions, *Atmos. Environ.*, *41*, 5571–5583.

Jaumot, J., R. Gargallo, A. de Juan, and R. Tauler (2005), A graphical user-friendly interface for MCR-ALS: A new tool for multivariate curve resolution in MATLAB, *Chemom. Intell. Lab. Syst.*, *76*(1), 101–110, doi:10.1016/j.chemolab.2004.12.007.

Jimenez, J. L., et al. (2009), Evolution of organic aerosols in the atmosphere, *Science*, *326*, 1525–1529, doi:10.1126/science.1180353.

Katrib, Y., G. Biskos, P. R. Buseck, P. Davidovits, J. T. Jayne, M. Mochida, M. E. Wise, D. R. Worsnop, and S. T. Martin (2005), Ozonolysis of mixed oleic-acid/stearic-acid particles: Reaction kinetics and chemical morphology, *J. Phys. Chem. A*, *109*, 10,910–10,919, doi:10.1021/jp054714d.

Kerwin, J. L., A. M. Wiens, and L. H. Ericsson (1996), Identification of fatty acids by electrospray mass spectrometry and tandem mass spectrometry, *J. Mass Spectrom.*, *31*, 184–192, doi:10.1002/(SICI)1096-9888(199602)31:2<184::AID-JMS283>3.0.CO;2-2.

Kovac, N., O. Bajt, J. Faganeli, B. Sket, and B. Orel (2002), Study of macroaggregate composition using FT-IR and 1H-NMR spectroscopy, *Mar. Chem.*, *78*(4), 205–215, doi:10.1016/S0304-4203(02)00033-6.

Latif, M. T., and P. Brimblecombe (2004), Surfactants in atmospheric aerosols, *Environ. Sci. Technol.*, *38*(24), 6501–6506, doi:10.1021/es049109n.

Lee, D., and H. Seung (2001), Algorithms for non-negative matrix factorization, *Adv. Neural Inf. Process. Syst.*, *13*, 556–562.

Lin, C.-J. (2007), Projected gradient methods for non-negative matrix factorization, *Neural Comput.*, *19*, 2756–2779, doi:10.1162/neco.2007.19.10.2756.

Marchand, D., and J. F. Rontani (2001), Characterization of photo-oxidation and autoxidation products of phytoplanktonic monounsaturated fatty acids in marine particulate matter and recent sediments, *Org. Geochem.*, *32*, 287–304, doi:10.1016/S0146-6380(00)00175-3.

McFiggans, G., et al.. (2005), Simplification of the representation of the organic component of atmospheric particulates, *Faraday Discuss.*, *130*, 341–362, doi:10.1039/b419435g.

Miller, C., K. G. Gordon, R. J. Kieber, J. D. Willey, and P. J. Seaton (2009), Chemical characteristics of chromophoric dissolved organic matter in rainwater, *Atmos. Environ.*, *43*, 2497–2502, doi:10.1016/j.atmosenv.2009.01.056.

Miyazaki, Y., K. Kawamura, and M. Sawano (2010), Size distributions and chemical characterization of water-soluble organic aerosols over the western North Pacific in summer, *J. Geophys. Res.*, *115*, D23210, doi:10.1029/2010JD014439.

Mochida, M., Y. Kitamori, K. Kawamura, Y. Nojiri, and K. Suzuki (2002), Fatty acids in the marine atmosphere: Factors governing their concentrations and evaluation of organic films on sea salt particles, *J. Geophys. Res.*, *107*(D17), 4325, doi:10.1029/2001JD001278.

Morris, J. W., P. Davidovitz, J. T. Jayne, J. L. Jimenez, Q. Shi, C. E. Kolb, D. R. Worsnop, W. S. Barney, and G. Cass (2002), Kinetics of submicron oleic acid aerosols with ozone: A novel aerosol mass spectrometric technique, *Geophys. Res. Lett.*, *29*(9), 1357, doi:10.1029/2002GL014692.

O'Dowd, C. D., and G. de Leeuw (2007), Marine aerosol production: A review of the current knowledge, *Philos. Trans. R. Soc. A*, *365*(1856), 1753–1774.

Ovadnevaite, J., C. D. O'Dowd, M. Dall'Osto, D. Ceburnis, D. R. Worsnop, and H. Berresheim (2011), Detecting high contributions of primary organic matter to marine aerosol: A case study, *Geophys. Res. Lett.*, *38*, L02807, doi:10.1029/2010GL046083.

Paatero, P., and U. Tapper (1994), Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, *Environmetrics*, *5*, 111–126, doi:10.1002/env.3170050203.

Petrovic, M., et al. (2002), Occurrence and distribution of nonionic surfactants, their degradation products, and linear alkylbenzene sulfonates in coastal waters and sediments in Spain, *Environ. Toxicol. Chem.*, *21*(1), 37–46, doi:10.1897/1551-5028.

Rinaldi, M., et al. (2009), On the representativeness of coastal aerosol studies to open ocean studies: Mace Head—A case study, *Atmos. Chem. Phys.*, *9*, 9635–9646, doi:10.5194/acp-9-9635-2009.

Rinaldi, M., S. Decesari, E. Finessi, L. Giulianelli, C. Carbone, S. Fuzzi, C. D. O'Dowd, D. Ceburnis, and M. C. Facchini (2010), Primary and secondary organic marine aerosol and oceanic biological activity: Recent results and new perspectives for future studies, *Adv. Meteorol.*, *2010*, 310682, doi:10.1155/2010/310682.

Russell, L. M., L. N. Hawkins, A. A. Frossard, P. K. Quinn, and T. S. Bates (2010), Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, *Proc. Natl. Acad. Sci. U. S. A.*, *107*(15), 6652–6657, doi:10.1073/pnas.0908905107.

Stephanou, E. G., and N. Stratigakis (1993), Oxocarboxylic and alpha, omega-dicarboxylic acids—Photooxidation products of biogenic unsaturated fatty-acids present in urban aerosols, *Environ. Sci. Technol.*, *27*(7), 1403–1407, doi:10.1021/es00044a016.

Sullivan, R. C., and K. A. Prather (2005), Recent advances in our understanding of atmospheric chemistry and climate made possible by on-line aerosol analysis instrumentation, *Anal. Chem.*, *77*, 3861–3886, doi:10.1021/ac050716i.

Surratt, J. D., et al. (2007), Evidence of organosulfates in secondary organic aerosol, *Environ. Sci. Technol.*, *41*, 517–527, doi:10.1021/es062081q.

Surratt, J. D., et al. (2008), Organosulfate formation in biogenic secondary organic aerosol, *J. Phys. Chem. A*, *112*, 8345–8378.

Tauler, R. (1995), Multivariate curve resolution applied to second order data, *Chemom. Intell. Lab. Syst.*, *30*, 133–146, doi:10.1016/0169-7439(95)00047-X.

Ulbrich, I. M., M. R. Canagaratna, Q. Zhang, D. R. Worsnop, and J. L. Jimenez (2009), Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data, *Atmos. Chem. Phys.*, *9*, 2891–2918, doi:10.5194/acp-9-2891-2009.

Viant, M. R., et al. (2009), International NMR-based environmental metabolomics intercomparison exercise, *Environ. Sci. Technol.*, *43*, 219–225, doi:10.1021/es802198z.

Wentzell, P. D., T. K. Karakach, S. Roy, M. J. Martinez, C. P. Allen, and M. Werner-Washburne (2006), Multivariate curve resolution of time course microarray data, *BMC Bioinf.*, *7*, 343, doi:10.1186/1471-2105-7-343.

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