Research Article

Primary and Secondary Organic Marine Aerosol and Oceanic Biological Activity: Recent Results and New Perspectives for Future Studies

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One of the most important natural aerosol systems at the global level is marine aerosol that comprises both organic and inorganic components of primary and secondary origin. The present paper reviews some new results on primary and secondary organic marine aerosol, achieved during the EU project MAP (Marine Aerosol Production), comparing them with those reported in the recent literature. Marine aerosol samples collected at the coastal site of Mace Head, Ireland, show a chemical composition trend that is influenced by the oceanic biological activity cycle, in agreement with other observations. Laboratory experiments show that sea-spray aerosol from biologically active sea water can be highly enriched in organics, and the authors highlight the need for further studies on the atmospheric fate of such primary organics. With regard to the secondary fraction of organic aerosol, the average chemical composition and molecular tracer (methanesulfonic-acid, amines) distribution could be successfully characterized by adopting a multitechnique analytical approach.

1. Introduction

The literature contains a great deal of evidence that large sectors of the marine atmosphere are influenced by continental outflows (natural or anthropogenic) and by ship exhaust emissions [1, 2]. However, the ocean is an important source of fine particles, and in background marine regions aerosol populations are dominated by natural marine particles [3, 4]. Given the ocean's extension, marine aerosol constitutes one of the most important natural aerosol systems at the global level. It contributes significantly to the Earth's radiative budget, biogeochemical cycling, with impacts on ecosystems and also on regional air quality [5]. The knowledge of particle chemical composition, as a function of size, is necessary for understanding and predicting the marine aerosol properties relevant to climate, for example, their ability to act as cloud condensation nuclei (CCN) and to influence the cloud droplet number concentration (CDNC) over background ocean regions.

In recent years, particular interest has focused on the marine aerosol organic fraction, its biogenic origin and the possible sources and mechanisms responsible for the high concentrations of organics observed in the submicron size fraction [6–8]. Figure 1 summarizes schematically the main potential formation pathways of organic aerosol in the marine boundary layer (MBL). Marine aerosol can derive both from primary or secondary processes. Primary aerosol production derives from the interaction of wind with the ocean surface and results in the mechanical production of sea spray aerosol. Traditionally, sea spray has been assumed to be composed of sea salt and water, with water reaching the equilibrium with the vapor phase after ejection. Nevertheless, the hypothesis that sea spray may become enriched in organic matter (OM) when the sea surface is characterized by high concentrations of biogenic OM, dates back to the 1960s [9]. The result of the said process is an internally mixed primary marine aerosol composed of sea
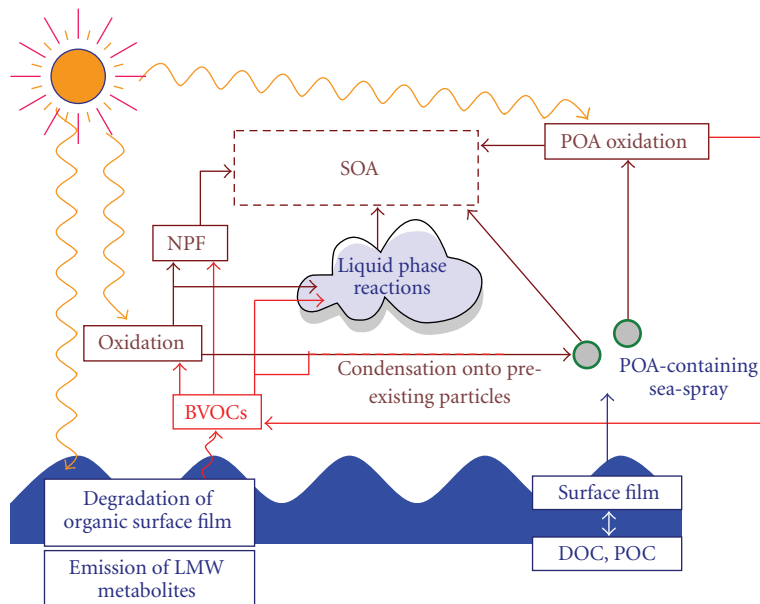
FIGURE 1: Diagram summarizing primary and secondary organic aerosol main formation routes in the marine boundary layer. DOC, POC and POA stand for Dissolved Organic Carbon, Particulate Organic Carbon and Primary Organic Aerosol, respectively

salt and organics, in which the organic fraction can be a major component [10].

Secondary organic aerosol (SOA) can form in the MBL through a number of different processes. Biogenic volatile organic compounds (BVOCs), emitted by the sea surface, or their oxidation products, can be involved in new particle formation (NPF) events via nucleation of stable clusters of 0.5–1 nm in size (such clusters can grow to larger sizes via condensation/coagulation processes). BVOCs and related oxidation products can also condense on preexisting particles and droplets, contributing to the particulate mass. SOA can also derive from the chemical transformation of primary or secondary components present in the condensed phase. Such transformations may take place at the particle surface [11, 12] or in the aqueous phase [13, 14], and may also involve a further step through the gas phase, in which semivolatile aerosol components can be oxidized to form new condensable products. The best known SOA component in marine aerosol is methanesulfonic acid (MSA), resulting from the atmospheric oxidation of dimethylsulphide (DMS) [15, 16]. Very recently, other formation processes, involving different precursors, such as biogenic isoprene [7], have been postulated. In spite of this, the observed high concentrations of oxidized OM in marine aerosol largely remain unexplained, suggesting that other formation processes and alternative SOA components should be considered.

To date, the most complete size segregated chemical characterisation of unperturbed marine aerosols is that provided by O'Dowd et al. [6] and Cavalli et al. [17], based on measurements performed at Mace Head (Ireland). They show that marine aerosol chemical composition is influenced by the oceanic yearly biological cycle and that, during periods of high biological oceanic activity (HBA), the organic fraction (mainly water insoluble) can contribute

significantly to the submicrometer aerosol mass. Their results are consistent with the evidence that cloud condensation nuclei (CCN) concentration in remote marine regions follows a seasonal trend, with maxima in spring-summer [18] and with the more recent findings of Sorooshian et al. [19], who observed increased average CCN activity during periods of higher chlorophyll-*a* levels, probably as a result of aerosol size distribution and composition changes over the North Pacific Ocean.

During the EU Project MAP (Marine Aerosol Production; http://macehead.nuigalway.ie/map/) coastal and open ocean aerosol measurements, together with field-lab experiments, were carried out to achieve a better understanding of marine organic aerosol sources, chemical properties and effects on the climate system and on atmospheric chemistry. In the present paper, some of the main MAP results are discussed, and compared with parallel results recently published in the literature. In particular, the observed aerosol chemical composition seasonal trend and a WSOC chemical composition representative of the HBA period, never published before, are presented.

2. Experimental Approach

In the MAP framework, marine aerosol samples were collected at Mace Head Atmospheric Research Station. Located on the west coast of Ireland, the station is unique in Europe, offering westerly exposure to the North Atlantic Ocean and the opportunity to study atmospheric composition under Northern Hemispheric background conditions. The site location, at 53 degrees 20 minutes N, 9 degrees 54 minutes W, is in the path of the mid-latitude cyclones which frequently traverse the North Atlantic. The main Atlantic shipping routes are over 150 km away, while the transatlantic

air corridors are over 80 km away. The site characteristics are ideal for carrying out marine background aerosol and trace gas measurements. The sampling took place throughout 2006, while, during an intensive observation period, coinciding with peak oceanic biological activity (June-July 2006), measurements were also performed onboard the oceanographic vessel Celtic Explorer sailing off the Irish coast.

Details on the adopted clean sector aerosol sampling strategy and instrumentation can be found in previously published papers [20, 21]. Laboratory experiments for the production of artificial sea spray aerosol from highly biologically active ([chlorophyll-a] = 1.4 ± 0.8 mg m^{-3}), freshly collected, sea water were performed onboard the Celtic Explorer. Full details on the experiment, including the sea water chemical characterization, and the sample analysis are described in [22].

A complete suite of chemical characterization techniques were applied to both ambient and laboratory aerosol samples: ion chromatography (IC), for the determination of inorganic water soluble ions, amines and organic acids, and solid/liquid phase elemental analyses, for the determination of water soluble organic carbon (WSOC), water soluble organic nitrogen (WSON) and water insoluble organic carbon (WIOC). Full details on sample handling and analysis can be found in [20, 21].

The organic chemical characterization was achieved through proton nuclear magnetic resonance (^{1}HNMR) spectroscopy [21–23] and by the anion-exchange high performance liquid chromatography (HPLC-TOC) technique described by Mancinelli et al. [24]. Using HPLC-TOC, it is possible to speciate WSOC into four macroclasses: neutral-basic compounds (NB), mono-acids (MA), di-acids (DA) and poly-acids (PA, representative of humic-like substances), and to quantify each fraction in terms of organic carbon content.

Here, the acronym WSOM (water soluble organic matter) is used to indicate the estimated mass of WSOC, obtained multiplying WSOC by a conversion factor of 1.8, derived from the functional group composition of WSOC [21]. Similarly, WIOM (water insoluble organic matter) was obtained by multiplying WIOC by a conversion factor of 1.4, according to the functional group composition observed by ^{1}H NMR in sea spray organic aerosols [22].

3. Marine Aerosol Chemical Composition during the 1-Year Sampling Campaign at Mace Head

Figure 2 shows the chemical composition of the submicron aerosol samples collected during 2006 at Mace Head. Table 1 reports the percentage contribution of each of the main submicron aerosol components, in the HBA and LBA (low biological activity) periods. Marine aerosol mainly comprised a mixture of sea salt of primary origin, nssSO$_4^{-2}$, NH$_4^+$, NO$_3^-$, clearly secondary components, and soluble (WSOM) and insoluble (WIOM) organic compounds.

TABLE 1: Median, minimum and maximum (in brackets) relative contribution of the main marine aerosol components to the analyzed total mass, expressed as percentages. Median values are reported only when greater than zero. "n" indicates the number of samples.

[%]	HBA ($n = 5$)	LBA ($n = 7$)
nssSO$_4^{-2}$	50 (38–57)	22 (5–27)
NH$_4^+$	7 (6–9)	1 (0–3)
NO$_3^-$	(0–1)	1 (1–2)
WSOM	23 (11–33)	6 (0–11)
sea salt	20 (6–25)	65 (59–77)
WIOM	7 (2–10)	6 (2–17)

Parallel laboratory experiments during the same project [22] showed that nascent submicron marine organics from bubble bursting mainly comprise (94%) WIOM. Moreover, the pattern of WIOM and sea-salt content in the different size intervals observed in the laboratory experiments was similar to that measured in atmospheric marine aerosol samples collected during periods of HBA, thus pointing to a WIOM/sea-salt fingerprint associated with submicron primary marine aerosol production in biologically rich waters. The indirect consequence of this observation is that WSOM observed in HBA will derive mainly from secondary processes. A secondary formation route for WSOM is also supported by the findings of a recent experiment performed at Mace Head [25], in which downward fluxes, characteristic of chemical species forming through secondary processes, were measured for submicron aerosol nssSO$_4^{-2}$ and WSOM.

The seasonal trend of the main component concentrations in submicron size range exhibits maxima in spring and summer (HBA) and minima during winter (LBA), with the exception of sea salt (Figure 2), in good agreement with Mace Head aerosol climatology for the 2002–2004 period [26], thus suggesting a dependence of submicron aerosol chemical composition on the seasonal cycle of the North Atlantic biological activity. Similar results showing maximum concentration in spring-summer in conjunction with phytoplankton activity in surface sea water, have been reported by several investigators for MSA [27, 28] and nssSO$_4^{-2}$ [29]. The maxima observed in atmospheric concentrations for nssSO$_4^{-2}$, MSA and NH$_4^+$ can be attributed to the increase in the emission of gaseous precursors, mainly DMS [16, 30] and NH$_3$ [31], produced by the marine biota during the HBA period, and to the concurrent enhanced photochemical activity of the atmosphere [32]. In analogy, the WSOC spring-summer peak can be attributed to the increased emission of volatile organic compounds (VOCs) by the marine biota and to the concurrently enhanced photo-oxidative capacity of the atmosphere, generating low vapor pressure oxidation products which can condense on preexisting particles. Another potential path for WSOC production could be through the aging process of the insoluble primary fraction, obviously more efficient during period of high photochemical activity.

Submicron aerosol chemical composition is different during HBA with respect to the LBA period. During HBA the
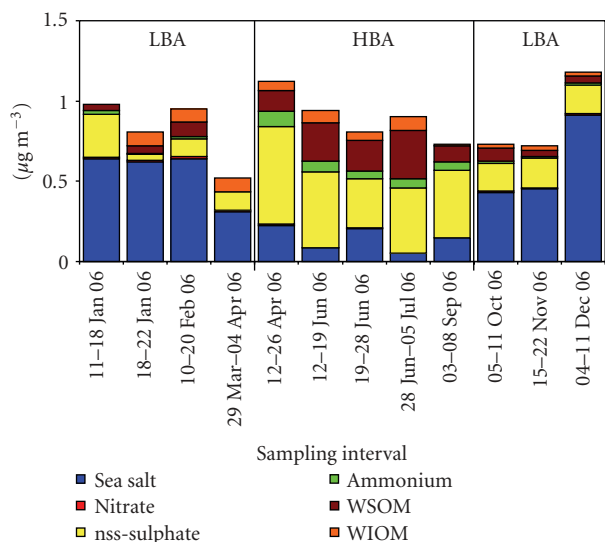
FIGURE 2: Seasonal evolution of submicron marine aerosol chemical composition observed through the twelve samples collected at Mace Head during MAP. The horizontal axis reports the nominal sampling time for each sample, that is, the time during which the filter/substrate has been exposed (the actual sampling time depended on the occurrence of the clean sector conditions during the exposition time). Samples are grouped in HBA and LBA period to evidence the differences between the two periods.

greater part of the mass was accounted for by $nssSO_4^{-2}$ and WSOM: $nssSO_4^{-2}$ median contribution to the total analyzed mass was 50% (ranging from 38 to 57%), that of WSOM 23% (11%–33%). Conversely, in the LBA period sea salt accounts for the greater part of the analyzed submicron mass, with a median contribution of 65% (59%–77%), while the contributions of $nssSO_4^{-2}$ and WSOM are reduced to 22% (5%–27%) and 6% (0%–11%), respectively. Water insoluble organics contributed almost equally to the analyzed total submicron mass during the HBA and LBA periods.

Submicron organics were clearly dominated by WSOM during the HBA period, while the contribution of soluble and insoluble organic compounds was comparable during the LBA period. This picture of marine aerosol is different from the one reported by O'Dowd et al. [6], who observed at Mace Head a submicron aerosol chemical composition dominated by water insoluble organic species during the HBA period. Such discrepancy could be due to a different location of highly biologically productive waters with respect to the Irish coast during MAP [21], or to different meteorological conditions encountered in the sampling periods: most of the samples discussed in the present work were collected in summer, when the photochemical activity is at its maximum, while most of the 2002 samples reported in O'Dowd et al. [6] were collected during spring and autumn, when sea spray production is higher. The main difference between the two datasets, indeed, regards WIOM absolute concentration during the HBA period (~0.6 μg m^{-3} in 2002 and less than 0.1 μg m^{-3} during MAP, averagely), while WSOM one is

comparable (~0.2 μg m^{-3}), suggesting a lower influence of the primary source in MAP samples.

Sciare et al. [33] also reported marked seasonal trends for marine aerosol collected at Amsterdam Island (Southern Indian Ocean). WIOC, MSA and nMSA-WSOC (WSOC not deriving from MSA) showed concentration enhancement during the austral summer. Moreover, it was found that marine aerosol organics were mainly accounted for by WIOC, in agreement with the previous observation in the North Atlantic [6]. The investigators also pointed out the likely biogenic origin of marine aerosol organics, evidencing its main source in a very productive oceanic area located around 40°S. It must be concluded that submicron marine aerosol chemical composition can be extremely variable over the year and, probably, from year to year, depending on the predominance of the primary source with respect to secondary ones, ocean dynamic conditions, influence of different oceanic source regions and atmospheric photo-chemical activity. These studies demonstrate the importance of biogenic organic aerosols over the ocean, at high latitudes (<40°S and >40°N), during periods of high biological productivity.

In the following paragraphs, the most recent findings on primary and secondary biogenic organics in submicron marine aerosol are discussed.

4. Primary Organic Aerosol and Its Evolution in the Marine Boundary Layer

Several attempts to quantify and characterize sea spray organics have recently been carried out. Keene et al. [34] reported high enrichment factors for water soluble organics, in nascent lab-produced sea spray particles, with respect to sea water. WSOC was highly enriched in all aerosol size fractions and the greatest enrichments were associated with the smallest size fraction (about 80% of aerosol mass was organic at 0.13 μm). The authors concluded that bursting bubbles at the ocean surface produce significant numbers of subμm, hygroscopic, organic-dominated aerosols, thereby supporting the hypothesis that this pathway is a potentially important global source of climate relevant particles.

Facchini et al. [22] similarly reported a high contribution of organic matter in nascent submicron sea spray particles, up to 77 $\pm$ 5% in the 0.125–0.25 μm size range (Table 2), although their analysis discriminated between water soluble and insoluble organic carbon, finding a dominant contribution of WIOM (up to 94 $\pm$ 4% of OC in the 0.125–0.25 μm size range). Moreover, Facchini et al. [22] highlighted that sea spray organics tend to aggregate and form colloids or suspended particles, making the definition of water solubility a complex issue. Whether the difference in the results of the two experiments is attributable only to the different organic carbon measurement approach, or also to differences in the chemical properties of the sea water used for generating aerosol particles by bubble bursting (oligotrophic Sargasso Sea versus North Atlantic Ocean during algal bloom) is still an issue of debate.

Furthermore, Modini et al. [35] presented the results of a similar experiment in which the organic volume contribution in lab-produced sea spray particles, indirectly determined by volatility/hygroscopicity tandem measurements (HV-TDMA), was estimated to be (8 ± 6%) in the 71–77 nm size range, corresponding to a mass contribution of only 4%. Such results may be conditioned by the interpretation of HV-TDMA measurements to calculate the organic fraction, or by the use of coastal waters (potentially high in terrestrial runoff) for spray generation. However, they could also be evidence of a high system variability, stressing the necessity for further investigation.

Several papers have reported the presence of carbohydrate-like material in marine particles, attributing this to primary sea spray processes.

Bigg and Leck [36] observed the presence of complex structures behaving as lipopolysaccharides in submicron marine aerosol. Facchini et al. [22] evidenced the presence of hydroxyl groups, both in water soluble and insoluble sea spray OM, using ^{1}HNMR analyses. These hydroxyl signals were always associated in the NMR spectra to important signals due to aliphatic chains with terminal methyls, typical of lipids. Moreover, the ^{1}HNMR spectra of oceanic water closely resembled that of nascent aerosol, and were in agreement with several observations in the literature reporting the presence in oceanic waters of phytoplankton exudates with a composition dominated by lipopolysaccharides [37, 38].

Very recently Russell et al. [39] observed an ocean-derived component, in marine aerosol, dominated by carbohydrate-like material, based on multi-technique measurements of submicron marine aerosol over the North Atlantic and Arctic Oceans and on Positive Matrix Factorization data elaboration. According to these authors, the primary marine signal in submicron marine aerosol is made on average for 88% of hydroxyl groups. Although the low signal-to-noise ratio of the spectra made difficult a precise quantification of the carbohydrate-like material, ^{1}HNMR analyses exclude a contribution as high as the one observed by Russell et al. [39] for these components in the North Atlantic during periods of HBA.

Such new, often contrasting results on primary organics in marine aerosol reflect the limits of current knowledge on this topic. Furthermore, the fate of primary organics in the atmosphere is even more uncertain, and few data are available on sea spray organic oxidation routes, rates and products. Zhou et al. [40] evidenced that OM in marine aerosols plays a dual role, being an important precursor/source and a dominant sink for the OH radical, leading to the degradation of OM, and the likely production of a series of low-molecular weight (LMW) organic compounds. Therefore, primary and secondary organic components must be considered as closely correlated in marine aerosol, as the oxidation products of biogenic primary organics in marine aerosol particles can lead to the production of both oxidized aerosol components (belonging to the broad category of SOA) and of volatile LMW products, which can partition into the gas phase and influence the multiphase photochemical evolution of the marine troposphere (including SOA formation). Supporting evidence of this gliding boundary

between primary and secondary organic aerosol components were also provided by Jimenez et al. [41], who showed, in a recent chamber experiment, how aerosolized squalane, a proxy for the refractory fraction of primary marine organic aerosol, was subjected to photochemical ageing, showing mass spectral features progressively transforming into those of oxidized organic aerosols, which are ubiquitous in the atmosphere.

5. Advances in Marine SOA Chemical Characterization

New results on marine WSOC chemical composition have been obtained over past years, allowing the identification of typical marine SOA components, other than MSA and DMS oxidation products.

The presence of amines and aminoacids over the oceans has been sporadically reported since the 1980s in rain samples over the ocean [42–44]. Gibb et al. [45] reported the presence of monomethylammonium (MMA^+), dimethylammonium (DMA^+) and trimethylammonium (TMA^+) salts in aerosol particles collected in unpolluted conditions over the Arabian Sea. The authors attributed the presence of aerosol phase alkyl ammonium salts to secondary production, due to the condensation of gaseous alkyl amines emitted by the sea, in analogy with NH_4^+. More recently, this hypothesis has been strengthened by evidence that alkyl amines participate in SOA formation in many different environments through reaction with acids [46–48].

Facchini et al. [20] highlighted the importance of alkyl-ammonium salts as submicron marine aerosol components, and reported dimethyl and diethyl-ammonium salts (DMA^+ and DEA^+) concentrations ranging, together between <0.4 and $56\ ng\ m^{-3}$ over the North Atlantic Ocean during the HBA period, turning out to be the most abundant organic species, second only to MSA, in submicron marine particles. Alkyl-ammonium salts represented on average 11% of the marine SOA and a dominant fraction (35% on average) of aerosol water soluble organic nitrogen (WSON).

The above cited paper presents considerable evidence that DMA^+ and DEA^+ are secondary aerosol components, originating from biogenic precursors emitted by the ocean. Their size distributions exhibited maxima in the accumulation mode, as is also the case of other well known secondary components ($nssSO_4^{-2}$, NH_4^+, MSA), supporting the hypothesis that a gas-to-particle conversion process is responsible for the accumulation of alkyl-ammonium salts in the fine aerosol fraction. The most likely hypothesis is that gaseous dimethylamine and diethylamine react with sulphuric acid or acidic sulphates, accumulating within aerosol particles in close analogy with ammonia. Regarding the precursor origin, a main anthropogenic source of gaseous alkyl-amines over the ocean can be excluded, because the aerosol DMA^+ and DEA^+ concentrations measured at Mace Head, were always higher in clean marine samples (roughly double) than in polluted air masses, in analogy with MSA. Like other reduced biogenic gases (DMS, CH_4) and in analogy with NH_3, DMA and DEA could be the end products

TABLE 2: Summary of the sea spray OM contribution measured in the most recent sea spray production laboratory experiments.

Sea water sampling site	Max OM mass contribution [%]	Particle diameter [nm]	Notes	Reference
Sargasso Sea (oligotrophic)	~80	130	Only WSOC measured. No filtration	Keene et al. [34]
North Atlantic Ocean (algal bloom)	77 ± 5	125–250	WSOC and WIOC measured. Filtration.	Facchini et al. [22]
Moreton Bay (Australia)	4	71–77	Coastal water	Modini et al. [35]

of microbial turnover of marine labile OM [45, 49, 50]. Furthermore, alkyl-ammonium ions in submicron aerosol particles showed the typical seasonal variation of biogenic components, with high concentrations measured in the HBA period, and much lower concentrations in the LBA period (Table 3).

Table 3 summarizes the marine aerosol alkylammonium ion concentration data so far available: two very recent papers confirm the findings of Facchini et al. [20]. Müller et al. [51] reported monomethylammonium (MA[+]), DMA[+] and DEA[+] at non-negligible concentrations in submicrometer particles at Cape Verde, during algal blooms in 2007, attributing them to secondary formation processes. Moreover, high levels of amines were observed in coincidence with high near surface Chlorophyll-*a* concentrations. Finally, Sorooshian et al. [19] also observed DEA[+] in submicron particles over the North Pacific Ocean, with concentrations rather well correlated to the chlorophyll-*a* sea surface concentration.

Besides alkylammonium salts and MSA, carboxylic and di-carboxylic acids have been identified in marine aerosol [52, 53 and references therein], found to account for less than 10% of total particulate organic carbon in remote marine environments. The above mentioned papers attribute a secondary origin to detected di-carboxylic acids, citing oxalic acid as the most abundant one. However, oxidized organics, such as C_5–C_{10} carboxylic or di-carboxylic acids, can also be produced by the oxidative degradation of primary particles generated by sea spray and rich in fatty acids [52].

Recent instrumental advances have allowed a deeper insight into organic marine aerosol chemical composition. Using liquid chromatography/negative ion electrospray ionization mass spectrometry, Claeys et al. [53] investigated marine organic aerosol chemical composition at Amsterdam Island (Southern Indian Ocean), reporting a WSOC contribution of 32 ± 12% to submicron OC. About 25% of WSOC was characterized and attributed to MSA (17%–21%), oxalate (5 ± 2%), malonate (1.8 ± 0.9%) and organosulphates (0.8 ± 1.5%). The organosulphates characterized in Claeys et al. [53] can be considered tracers for an SOA formation process that is specific to the marine environment, that is, oxidation of marine biomass. More specifically, the organosulfates correspond to sulfate esters of C_9–C_{13} hydroxyl carboxylic acids, which are attributed to oxidation of unsaturated fatty acid residues present in algal cell membranes.

Notwithstanding recent improvements, current knowledge on the chemical composition of marine SOA remains limited, and further research is required to address the many unresolved issues. During MAP a multi-technique approach was deployed to characterize marine WSOC. Coupling HPLC-TOC and IC, it was possible to achieve an almost-complete chemical characterization of submicron marine WSOC, on a selected subset of samples (5, from both Mace Head and Celtic Explorer sampling) representative of the HBA period (Figure 3). Marine aerosol WSOC can be divided into three chemical macroclasses based on acid-base properties: neutral-basic compounds (NB), accounting for 32 (±8) % of WSOC, mono-diacids (MDA), contributing 42 (±9) %, and polyacids (PA), accounting for 4 (±3) %. Averagely 22 (±11) % of WSOC escaped this classification, probably as a result of strong and irreversible binding with the HPLC column: this fraction is labeled "uncharacterized" in the Figure. From the HPLC-TOC macroclasses average contribution, the average contribution of each compound, identified by IC, has been subtracted, obtaining the classification of Figure 3. Only 30% of WSOC was characterized at the molecular level by IC, with MSA (11 ± 5%) and oxalic acid (3 ± 2%) being the only two MDA components identified. This leaves more than a half of the dominant class of compounds still uncharacterized, although it is likely that other LMW dicarboxylic acids, like malonic and succinic acid, not identified by IC, can account together for another 1%-2%. As for the NB compounds, 6 ± 7 and 10 ± 12% of the WSOC can be ascribed to DMA[+] and DEA[+], leaving about 15% of WSOC as uncharacterized NB compounds. In WSOC extracted from marine aerosol collected during MAP, HPLC analysis showed the occurrence of fulvic-like material (polyacids macroclass), in lower concentrations than suggested by previous studies, that is, 22% [17]. The finding indicates that primary emissions of fulvic substances from seawater did not make a major contribution to marine water-soluble aerosols during MAP. This picture of submicron marine aerosol WSOC is coherent with the hypothesis of its mainly secondary origin, even though the uncharacterized fraction escaping classification in NB, MDA and PA may be due to the contribution of primarily emitted, aggregate forming, organic matter, similar to that characterized in laboratory experiments on nascent sea spray aerosol by Facchini et al. [22].

Information on the chemical composition of the uncharacterized fractions of NB, MDA and PA has been derived

TABLE 3: Alkylammonium ions aerosol concentration range (in brackets) and median value (when available) reported in the literature for the marine environment. All concentrations are in ng m^{-3}. All data refer to submicron particles except for Müller et al. [51], whose size cut was 0.14–0.42 μm, and Gorzelska and Galloway [44], who did not report any particle size information.

| Location	MA$^+$ [ng m^{-3}]	DMA$^+$ [ng m^{-3}]	TMA$^+$ [ng m^{-3}]	EA$^+$ [ng m^{-3}]	DEA$^+$ [ng m^{-3}]	Reference
North Atlantic Jun–Sep 1988	(<dl–3.9)			(<dl–~1.4)		Gorzelska & Galloway [44]
Arabian Sea Aug-Oct 1994	<dl–6.1	1.6–4.4	0.018–0.78			Gibb et al. [45]
Arabian sea Nov-Dec 1994	2.6–4.5	3.7–17.5	0.12–0.9			Gibb et al. [45]
Mace Head Oct–Mar 2006		1 (<1–8)			(<1–12)	Facchini et al. [20]
Mace Head Apr–Sep 2006		10 (2–24)			16 (4–32)	Facchini et al. [20]
North Atlantic Jun 2006		9 (4–13)			12 (7–24)	Facchini et al. [20]
Cape Verde May 2007	0.02 (0.01–0.03)	0.21 (0.13–0.36)			0.06 (0.005–0.11)	Müller et al. [51]
Cape Verde Jun 2007	0.03 (0.01–0.12)	0.21 (0.05–0.39)			0.07 (0.06–0.14)	Müller et al. [51]
Cape Verde Dec 2007	0.15 (0.002–0.52)	0.54 (0.1–1.4)			0.29 (0.09–0.76)	Müller et al. [51]
North Pacific Jul-Aug 2007					14–35	Sorooshian et al. [19]
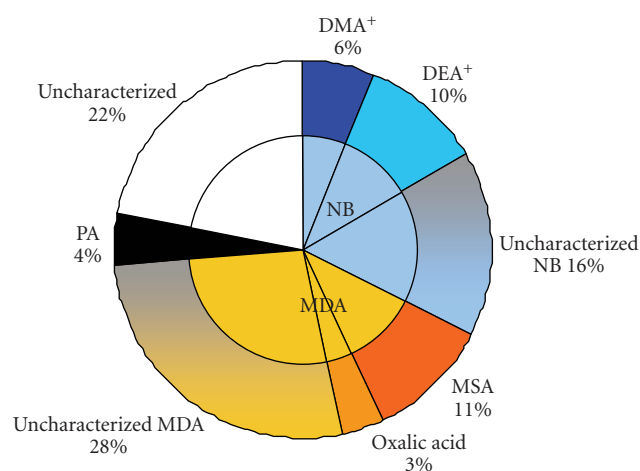
FIGURE 3: WSOC chemical composition representative of spring-summer conditions over the Atlantic Ocean, obtained by combining HPLC-TOC and IC (see text for more details). Percentages indicate the contribution of each compound or chemical macroclass in terms of carbon.

by NMR functional group analysis (Decesari et al., in preparation), showing aliphatic moieties substituted with oxygenated groups, like carbonyls/carboxyls and, in analogy with the findings of Russell et al. [39], hydroxyl groups.

6. Conclusions

Studies performed during the past years strongly suggest that biogenic organic compounds play an important role in submicron marine aerosol chemical composition over biologically productive, high latitude, marine regions, in both hemispheres. Moreover, it has been demonstrated that marine organic aerosol chemical composition is the complex result of different primary and secondary sources.

Most recent results on sea spray composition suggest that in conditions of intense oceanic biological productivity, submicron primary marine aerosol can contain a considerable fraction of OM. Further studies are necessary to obtain deeper insight into the space/time variability of the ocean primary organics production potential worldwide. Important advances can be obtained by coupling modeling with new satellite chlorophyll, dissolved and particulate organic carbon measurement instruments, as attempted for the first time by O'Dowd et al. [54] and Vignati et al. [4]. In fact, although much information has been gathered on the DMS oxidation cycle, and several predictive tools are available to model secondary products, like MSA and nss-sulfate over the oceans, only raw empiric instruments are available to predict primary organic aerosol emissions as a function of oceanic biological productivity.

To date, little is known about sea spray organic chemical composition, lifetime and fate in the marine boundary layer. Further investigation is required to address this issue, that can also help to fill the gap between observed and modeled SOA in the MBL.

As for secondary organics in the MBL, although several classes of compounds have been identified in different marine environments as typical marine SOA components (MSA, alkylammonium salts, dicarboxylic acids), most marine aerosol WSOC remains uncharacterized at the molecular level. Closer investigation of marine aerosol

WSOC chemical composition is needed to achieve a better knowledge on SOA formation routes in the MBL. Deeper insight into marine aerosol organics chemical composition is expected from the new high time resolution aerosol measurement instrumentats, namely AMS, only seldom applied to the clean MBL so far [55–57].

Furthermore, an important fraction of marine SOA, WSON, is still mostly uncharacterized. A fraction of the unaccounted organic nitrogen, especially during the warm season, can reasonably be attributed to products of the oxidative degradation of DMA^+, DEA^+ and other minor alkylammonium ions. However, alternative sources of unaccounted water soluble organic nitrogen, for example, the oxidation of insoluble primary organic material emitted by sea spray, cannot be ruled out at present. Further studies are necessary to clarify this point.

More detailed size-resolved information on marine organic aerosols in the remote MBL are needed to define the contribution of organics to marine CCN. The atmospheric fate of primary and secondary marine organic aerosols also needs to be further evaluated, as it may significantly influence the ability of marine aerosols to act as CCN in unperturbed ocean regions.
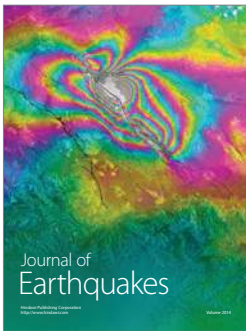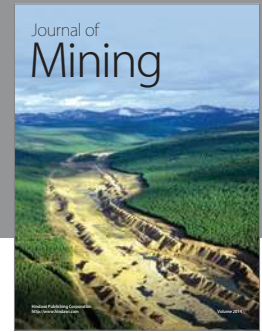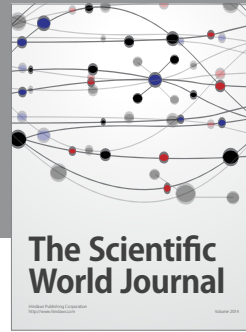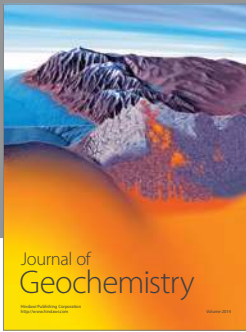
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