Marine organic aerosol and biological oceanic activity

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Marine aerosol constitutes one of the most important natural aerosol systems at the global level and comprises both organic and inorganic components of primary and secondary origin. This work presents new results on organic marine aerosol properties and its link with oceanic biological productivity. Laboratory experiments have shown that sea-spray aerosol originating from highly biologically active sea water has a significant organic fraction, which increases with decreasing particle size, up to 77±5% below 0.25 µm diameter. Submicron sea-spray organic matter is mainly water-insoluble and composed of phytoplankton exudates (mainly lipo-polysaccharides). With regard to secondary organic aerosols, new components have been detected: dimethyl and diethyl amine salts turned out to be the most abundant organic species, alongside methanesulphonic acid, in fine marine particles over the North Atlantic. Clear evidence of a marine biological origin for dimethyl and diethyl amine salts has been observed, pointing to a new atmospheric organic nitrogen global source, with a seasonality connected to oceanic biological productivity and an atmospheric cycle parallel to that of the organosulphur species.

1. Introduction

The marine aerosol constitutes one of the most important natural aerosol systems globally. It contributes significantly to the Earth's radiative budget, biogeochemical cycling, impacts on ecosystems and even to regional air quality (O'Dowd & de Leeuw, 2007). Marine aerosol comprises both primary and secondary components. Primary aerosol particles are generated via wind driven bubble bursting processes at the ocean surface (sea-spray), while secondary components can be formed by gas-to-particle conversion or by chemical transformation of species present in the condensed phase. Both primary and secondary marine aerosol can contain organic compounds (O'Dowd et al., 2004), the following sections describe our most recent findings on marine organic aerosol chemical composition.

2. Methodology

Starting in 2002, the ISAC-CNR in collaboration with the University of Galway has been experimenting a specific sampling and analysis procedure for the chemical characterization of unperturbed marine aerosol at Mace Head research station (Ireland). An automated sectorized sampling system was set up to control the aerosol sampling, allowing collection only in clean marine air masses (Cavalli et al., 2004). Aerosol has been collected on multistage impactors and high volume samplers, and analyzed for the main soluble ions (ion chromatography), water soluble and insoluble organic carbon and for water soluble nitrogen (C/N elemental analyzer). The organic characterization has been achieved through a set of analytical techniques, namely ^{1}H NMR (Decesari et al., 2000), HPLC-TOC (Mancinelli et al., 2006) and surface tension measurements (Decesari et al., 2003).

In the framework of the EU project MAP (Marine Aerosol Production; http://macehead.nuigalway.ie/map/), this expertise was applied to coastal measurements at Mace Head, for the entire year of 2006, and onboard the oceanographic vessel Celtic Explorer, during a campaign off the Irish coast between June and July 2006. Moreover, during the Celtic Explorer cruise, laboratory experiments were carried out to characterize the chemical properties of sea-spray aerosol particles, generated through bubble bursting, from oceanic waters rich in organic matter, during periods of phytoplankton bloom (Facchini et al. 2008a).

3. Results

3.1 Advances in the chemical characterization of sea-spray organics

The average relative contribution of organic matter in sea-spray particles, as a function of size, resulting from the above mentioned experiments is shown in Fig. 1, together with the average mass size distribution of the sea-spray samples. Spray particles exhibit a progressive increase in the organic matter (OM) content from 3 ± 0.4% up to 77 ± 5%, with decreasing particle diameter from 8 to 0.125 μm. The OM transferred within the submicron particles generated by bubble bursting was mainly water insoluble (WIOM) (on average 94 ± 4% of total carbon), while the organic water soluble fraction (WSOM) increased its contribution (up to 33 ± 3%) of total carbon in the coarse size interval (4-8 μm).

Chemical characterization by ^{1}H NMR showed similar properties between WIOM and the seawater particulate organic carbon (POC) fraction smaller than 10 μm, demonstrating that the less hydrophilic fraction of oceanic OM is preferentially transported into the atmosphere by the bubble bursting process. In addition, the ^{1}HNMR spectral fingerprint of WIOM was similar to that of phytoplankton exudates collected from the Adriatic Sea surface (Kovac et al., 2002) with a composition dominated by lipopolysaccharides. These compounds are known from the seawater chemistry literature for their various degrees of aggregation, ranging from colloids to microgels and to large POC particles (Zhou et al., 1998) and for their surface active properties.

The pattern of WIOM and sea-salt content in the different size intervals observed within the bubble bursting experiment was similar to that measured in atmospheric marine aerosol samples collected during periods of high biological activity (HBA), pointing to a WIOM/sea-salt fingerprint associated to submicron primary marine aerosol production in biologically rich waters. For this reason most of the WIOM was attributed here to primary production and, consequently, WSOM was mainly ascribed to secondary production.

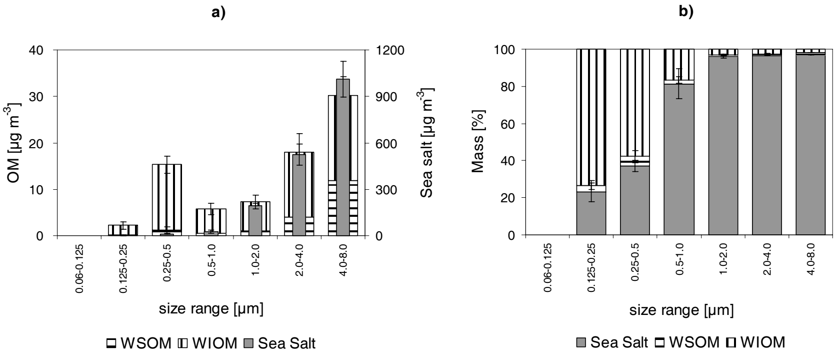

Figure 1. Average chemical composition of bubble bursting samples: (a) absolute concentration and (b) relative concentration. The bars are the standard deviation of the mean.

The above findings are also in agreement with the work of Keene et al. (2007), that shows a strong enrichment of organic matter in artificially generated sea spray particles, with an 80% contribution for 0.13 µm particles. However, the authors did not distinguish between water soluble and insoluble organics, thus providing no information on the solubility and surface active properties of primary organic matter.

3.2 A newly identified SOA component in marine aerosol

Important organic aerosol components, dimethyl and diethyl-ammonium salts (DMA^+ and DEA^+), were identified over the North Atlantic Ocean, through coastal and onboard measurements, performed at Mace Head and during the Celtic Explorer cruise, respectively (Facchini et al., 2008b). DMA^+ and DEA^+ resulted the most abundant organic species, second only to MSA, detected in submicron marine particles, together ranging between <0.4 and 56 ng m^{-3}. During HBA periods alkyl-ammonium salts represented on average 11% of the marine SOA and a dominant fraction (35% on average) of the aerosol water soluble organic nitrogen (WSON).

There is considerable evidence that DMA^+ and DEA^+ are secondary aerosol components, and that they originate from biogenic gaseous precursors emitted by the ocean. Their size distributions exhibited maxima in the accumulation mode, as is also the case for 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 DMA and DEA 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, CH4) and in analogy to NH_3, DMA and DEA could be the end products of microbial turnover of marine labile organic matter (Gibb et al., 1999; Hansell & Carlson, 2002;

Johnson et al., 2007). 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.

The importance of amine salts in marine aerosol has recently been confirmed by Sorooshian et al. (2009), measuring over the Pacific Ocean, and by Muller et al., 2009 at lower latitudes (Cape Verde).

4. Conclusion

Most recent results on sea-spray composition have shown that in conditions of intense oceanic biological productivity, submicron primary marine aerosol is mainly composed of insoluble and surfactant organic matter. Such information is currently not accounted for in most global models, determining a biased calculation of sea-spray mass and, consequently, of the direct and indirect radiative aerosol effect. Moreover, a potentially important atmospheric source of organic carbon is neglected in estimating the global carbon budget. A novel approach to developing a combined organic-inorganic submicron sea-spray source function for inclusion in large-scale models, with wind speed and surface ocean chlorophyll-a concentration as input parameters, has been presented (O'Dowd et al., 2008) and tested with satisfactory results (Vignati et al., 2009).

At present, nothing is known of the fate of primary marine organics once emitted in atmosphere. Their processing could be a source of oxygenated compounds in the condensed phase, but might also lead to the formation of volatile products possibly involved in SOA formation. Further investigations are required to address this issue.

As for secondary organics in the MBL, most marine aerosol WSOM is still uncharacterized at the molecular level. New insight on marine organic aerosol chemical composition is expected to be gained from the coupling of statistical methods (namely PMF) with traditional off-line (NMR, IR, etc.) or new on-line (AMS) aerosol analysis techniques (Decesari et al., in preparation).

Water soluble organic nitrogen measurements showed an important fraction of uncharacterised nitrogen-bearing organic compounds in marine aerosol (~60%). A fraction of the unaccounted organic nitrogen, especially during the warm season, can reasonably be attributed to products of the oxidative degradation of the same alkyl ammonium salts. Nevertheless, alternative sources of unaccounted water soluble organic nitrogen, e.g. the oxidation of insoluble primary organic material emitted by sea-spray, cannot be ruled out at present. Further work is necessary to better characterise the marine aerosol water soluble organic nitrogen, in order to define its role in the marine boundary layer chemistry and in the global nitrogen biogeochemical cycle.

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