



Role of the volatile fraction of submicron marine aerosol on its hygroscopic properties

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ABSTRACT

The hygroscopic growth factor (HGF) of 85 nm and 20 nm marine aerosol particles was measured during January 2006 for a three-week period within the frame of the EU FP6 project MAP (Marine Aerosol Production) winter campaign at the coastal site of Mace Head, using the TDMA technique. The results are compared to aerosol particles produced in a simulation tank by bubbling air through sea water sampled near the station, and through synthetic sea water (inorganic salts). This simulation is assimilated to primary production. Aitken and mode particles (20 nm) and accumulation mode particles (85 nm) both show HGF of 1.92 and 2.01 for particles generated through bubbling in natural and artificial sea water respectively. In the Aitken mode, the marine particles sampled in the atmosphere shows a monomodal HGF slightly lower than the one measured for sea salt particles artificially produced by bubble bursting in natural sea water (HGF = 1.83). This is also the case for the more hygroscopic mode of accumulation mode particles. In addition, the HGF of 85 nm particles observed in the atmosphere during clean marine sectors exhibits half of its population with a 1.4 HGF. An external mixture of the accumulation mode marine particles indicates a secondary source of this size of particles, a partial processing during transport, or an inhomogeneity of the sea water composition. A gentle 90 °C thermo-desorption results in a significant decrease of the number fraction of moderately hygroscopic (HGF = 1.4) particles in the accumulation mode to the benefit of the seasalt mode, pointing to the presence of semi-volatile compounds with pronounced hydrophobic properties. The thermo-desorption has no effect on the HGF of bubble generated aerosols, neither for synthetic or natural sea water, nor on the atmospheric Aitken mode, indicating that these hydrophobic compounds are secondarily integrated in the particulate phase. No difference between night and day samples is observed on the natural marine aerosols regarding hygroscopicity, but a more pronounced sensitivity to volatilization of the 1.4 HGF mode in the accumulation mode is observed during the day.

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1. Introduction

Because oceans represent a very large fraction of the Earth surface, a certain number of studies have focused on characterizing the aerosol size and composition in the marine environment (see O'Dowd and De Leeuw 2007 for a complete review). The chemical composition and concentration of marine aerosols depends on parameters such as wind speed and white cap

coverage (Monahan et al., 1986, Smith et al., 1993), but also on the composition of sea water (Woodcock 1948, Blanchard and Syzdek 1970). Recent findings have shown that submicron marine aerosols not only contain sea salt and sulfate, but also substantial levels of organic carbon (Cavalli et al., 2004). The contribution of the organic fraction is seasonal with maximum contributions during the spring and autumn, corresponding to the blooming periods of phytoplankton (O'Dowd et al., 2004). This finding is extremely important to better constrain the role of submicron aerosol in the marine environment, in particular considering its optical properties.

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There are still, however, a certain number of open questions in relation to the presence of organic matter onto submicron marine aerosols. In particular, we do not know how organic material is integrated into the particulate phase. Two possible processes are:

- 1) Primarily, during the mechanical process of bubble bursting: the sea surface layer is known to be enriched with organic matter and film/jet drops are likely to be enriched as well.
- 2) Secondarily, through condensation of volatile organic gases possibly released in the marine atmosphere by microorganisms and oxidized to low volatility species.

The process leading to the integration of high organic contents in the marine aerosol is important to know for prediction purposes. Are these organics already present at the sea surface or are they produced as SOA in the atmosphere? Regional scale atmospheric climate-chemistry/aerosol models fail to reproduce organic aerosol concentrations in the marine atmosphere, because of missing formation of secondary organic aerosols and deficiencies in emission data (Langmann et al., 2007). One approach to understand how organic material is integrated into submicron marine particles is to better characterize the mixing state (internal, external) of marine aerosols. Internal mixing is characterized by an homogeneous hygroscopic growth while externally mixed particle population is evidenced by the presence of multiple hygroscopic growth modes. Marine aerosols are typically found as an internal mixture in the Northern Atlantic Ocean, Southern Atlantic Ocean and Indian Ocean (Swietlicki et al., 2000; Massling et al., 2003). It has been shown recently that also the surface of the particles (Sorjamaa and Laaksonen, 2006) as well as the internal mixture structure (Sjogren et al., 2007) influence the particles activation and growth factor when they are exposed to a humid environment.

In this work, our objective is to investigate whether the organic particulate matter is primarily or secondarily produced through the characterization of mixing state and volatility-hygroscopicity properties of the marine aerosols. For that purpose, we used a newly developed Volatility-Hygroscopicity Tandem Differential Mobility Analyser (VH-TDMA) (Villani et al., *in press*) to gently evaporate the volatile fraction on the particle surface and quantify the resulting changes in hygroscopic growth. VH-TDMAs have been successfully used in the past to link thermal and hygroscopic properties of atmospheric aerosol to their chemical properties and mixing state (Johnson et al., 2004). Ambient marine aerosol properties are compared to marine aerosol artificially produced from bubbling filtered air in a simulation tank. Measurements were performed during three weeks of the winter Marine Aerosol production (MAP) campaign.

2. Site and methods

The Mace Head Atmospheric Research Station is located on the west coast of Ireland (53° 20' N, 9° 54' W), and facing prevailing westerly-southwesterly winds which makes it an ideal location for studying marine aerosols (Jennings et al., 2003). Atmospheric measurements were performed via the community air-sampling system at a flow rate of 2 L min⁻¹. Laboratory measurements were performed inside the research station using a 5 L simulation tank filled with sea

water. Clean filtered air was bubbled through a sintered glass filter immersed in the sea water in order to simulate primary aerosol production. The procedure and set-up used for the simulated marine aerosol production in the laboratory were similar to the ones described in Sellegri et al. (2006). The bubble size distribution was previously measured and compared to the one of more realistic bubbles produced by a weir, and to natural bubble size distributions reported in the literature (Sellegri et al., 2006). Even though the bubble size distribution differed from one bubbling device to the other, it was found that the generated aerosol was very similar irrespective of the device. The resulting aerosol size distribution comprised three modes: (1) a dominant accumulation mode at 110 nm; (2) an Aitken mode at 45 nm; and (3) a third mode, at 300 nm, resulting from forced bursting of bubbles (Sellegri et al., 2006).

Atmospheric and laboratory measurements are performed with a VHTDMA (Villani et al., 2007), which is composed of two DMAs and CPCs (TSI 3010), separated by a thermo-desorbing unit (Villani et al. *in press*) and a hydration device in series. It should be noticed that, prior to initial size classification in DMA1, the aerosol is dried to a relative humidity < 10% in a diffusion drier tube. The operation procedures alternate one dry scan to control the stability of the 2 DMAs, one humid scan similar to conventional H-TDMA procedures to measure the hygroscopic growth factor (HGF) of monodispersed dry aerosol, one volatility scan similar to conventional V-TDMA procedures to measure size reduction of monodispersed dry aerosol after thermal treatment at specified temperature, and one Volatility-Humidity scan to measure the HGF of thermally treated monodispersed aerosol. The HGF after thermal treatment is calculated using the particle diameter measured after V-TDMA scan, it will be referred to as the Volatility-hygroscopic growth factor (VHGF). To optimize the temporal resolution, the volatility scan is repeated once per hour in stable conditions, whereas the system alternates only two wet scans (i.e. Humidity-scan and Volatility-Humidity-scan) every 10min. The dry scan has been tested in the laboratory as part of the instrument calibration procedures. It should be noted that the calibration of the instrument consists of independent calibration of the V-TDMA (Villani et al., 2007) and the H-TDMA (Villani et al., *submitted*) sub-systems. Laboratory studies confirmed that thermo-desorption is very efficient to remove species condensed onto the particle surface as long as the prescribed volatilisation temperature of the thermo-desorbing unit exceeds the volatilisation temperature of material condensed onto the particle surface (Johnson et al., 2004; Villani et al., *in press*). Careful checks were performed to insure that recondensation does not take place onto the particles during cooling. This was achieved with a characterization work performed by Villani et al. (2007, *in press*), by using simulations and laboratory test aerosols in the VH-TDMA. Relative humidity is monitored on the sheath and excess flows of both DMAs, and on the aerosol flow entering the first DMA. The error on the resulting HGF is calculated to be less than 4% (Villani et al., *in press*). During the campaign, (NH₄)₂SO₄ calibrations were performed on several occasions, giving a difference between measured and theoretical HGF of 2% when theoretical GF was calculated for the mean value between the experimental sheath and excess air RH. In this study, we limit our investigation to two sizes of particles selected alternatively. 20 nm-particles are the smallest to be statistically representative when selected by the first DMA. 85 nm-particles are the largest particles which could, after

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