

Organic Contribution on Particles Formed on Pacific Ocean: From Phytoplankton Blooms to Climate

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Abstract—These SOAP project Pacific Ocean measurements reveal that phytoplankton blooms with sunny conditions make possible secondary organic contribution to ultrafine particles size and composition, and thus on cloud formation ability, and finally on climate. This is in agreement with other biologically active region observations about the presence of secondary organics even the exact fraction is also depending on the local marine life (e.g. plankton blooms, seaweeds, corals). An organic contribution is clearly needed to add to CLAW hypothesis.

Keywords—Climate, marine aerosols, phytoplankton, secondary organics, CLAW hypothesis.

I. INTRODUCTION

MARINE biologically active regions (e.g., coasts, ice edges, frontal regions and open water areas with plankton blooms) are known to produce a range of compounds that interact with atmosphere affecting directly and indirectly particle production, composition, and wider properties of the marine atmosphere. Whilst the CLAW (Charlson, Lovelock, Andreae and Warren) hypothesis [1] supports the idea of the importance of marine biological activity on ultrafine ($d < 100\text{nm}$) particle composition and effects through secondary sulphate production via DMS, this hypothesis does not take into account the secondary organic fraction in the composition of the ultrafine particles even though the aerosols are elsewhere typically known to consist of both organic and inorganic compounds whose relative ratios strongly depend on the environmental conditions, where the emissions of various gases and particles define the overall compositions and properties of ultrafine particles.

So far, recent observations about the presence of a remarkable marine-origin secondary organic fraction in

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ultrafine particles have been identified down to nucleation mode size particles ($d < 15\text{nm}$) over Irish coastal waters of the Atlantic Ocean [2], and Arctic Ocean close to ice edges [3], and Australian sub-tropical Pacific Ocean waters [4]. In spite of the importance of a secondary fraction to the properties of radiatively active sizes in marine environments, marine produced particle composition is unknown in various other marine biologically active locations around the world.

II. METHODS

A. The Measurement Location

This Surface Ocean Particle Production (SOAP) project study about the composition of nucleation ($d < 15\text{nm}$) and the lower end of Aitken ($20\text{nm} < d < 60\text{nm}$) modes particles was focused on particle production in one such remote open ocean region on the Chatham Rise (New Zealand; latitude 41°S - 45°S , longitude 173°E - 177°W) during austral summer 2011 (1.2.2011 to 12.2.2011) and austral summer 2012 (13.2.2012-5.3.2012) expeditions on the board of New Zealander R. V. Tangaroa.

The location was in the southern Pacific Ocean over the Sub-Tropical Convergence (STC) to the east of New Zealand. The region experiences intensive austral summer phytoplankton blooms. Fig. 1 shows the measurement route with observed plankton blooms during the summer 2011 expedition.

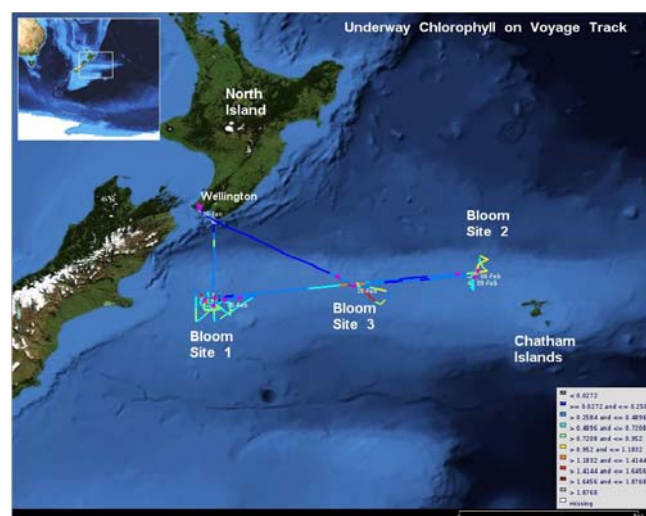


Fig. 1 The measurement route with observed plankton blooms during the summer 2011 expedition

B. The Instruments

The ultrafine particle composition was studied using the Ultra Fine Organic Tandem Differential Mobility Analyser (UFO-TDMA, Fig. 2; [5]) and the Volatility Humidity Tandem Differential Humidity Analyser (VH-TDMA; [6]) methods on board of RV Tangaroa (New Zealand). Auxiliary data were collected from the ships weather station, underway instrument suite and marine information observations, SMPS (Scanning Mobility Particle Sizer) particle size distribution measurements, total particle count CPC (Condensation Particle Counter) measurements with 5nm and 10nm cut-off sizes, and black carbon measurements. Marine biological activity was checked with MODIS (Moderate Resolution Imaging Spectroradiometer) Terra and Aqua satellite data and supported by *in situ* chlorophyll and dissolved DMS measurements. Marine air mass origin was followed with HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory; [7] and [8] trajectories.

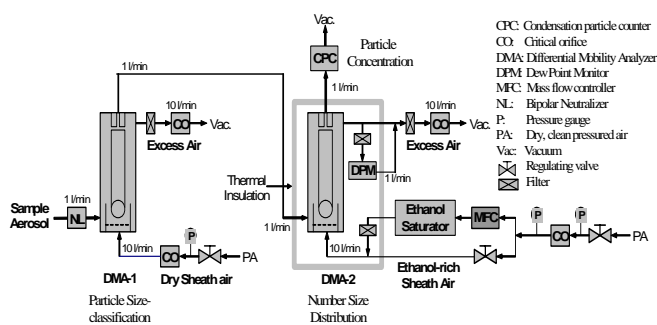


Fig. 2 A schematic picture of UFO-TDMA system

The ultrafine organic tandem differential mobility analyzer (UFO-TDMA, Fig. 2; [5], [9]) was used to determine the contribution of sulphate and organic components to nucleation mode size ($d < 15\text{nm}$) particles composition. The main principle of operation of the DMA (differential mobility analyzer; [10], [11]) is to select a narrow band of an aerosol size distribution by applying high voltage to its central rod thus selecting particles with a particular electrical mobility. This way, a monodisperse aerosol distribution is allowed to pass through the instrument. The UFO-TDMA uses ethanol vapor as the working fluid. The first DMA selects a monodisperse aerosol distribution which is brought to a selected sub-saturated ethanol vapor environment where they can grow to a new size in accordance their composition and size. The second DMA measures the final size then. The ratio between the measured size in the second DMA and the size selected in the first DMA is called organic growth factor (OGF). Depending on the chemical composition of the particles, different amounts of ethanol are consumed at a given saturation ratio by the particles. We applied the UFO-TDMA to ultrafine 10-15nm particles. The saturation ratio was $82 \pm 2\%$.

The basic analysis principle is based on the fact that inorganic particles such as sodium chloride and the ammonium sulphate do not grow (i.e. OGF is 1) in the sub-

saturated ($S = 84\%$) ethanol vapor when the particle diameter is 20nm or smaller. Ammonium bisulphate would grow in 20nm size to the OGF of 1.02–1.03 but no growth at 10nm size at 82–84% [12]. Importantly, the sulfuric acid is expected to be neutralized to ammonium sulphate in particle phase atmospheric conditions [13]. Indeed, [13] recently studied in CLOUD (Cosmics Leaving Outdoor Droplets) chamber nanoparticle formation and growth experiments that sulfuric acid was transformed to pure ammonium sulphate form since 2nm size. Furthermore, iodine compounds do not grow [12]. On the other hand, particles composed of biogenic organics (e.g. citric acid or tartaric acid; [5]) or 10 nm secondary organics [14] do grow (i.e. OGF is clearly over 1). Generally, moderately oxidized organic do grow very well [14]. It is also notable that if organic compounds are composed of non-polar compounds or if they are highly aged, they do grow less.

The organic volume fraction (OVF) was calculated based on the principle introduced in [2]. The OVF is got from the following comparison: the volume corresponding to the measured size OGF value compared with the volume corresponding to the OGF value of a very high ethanol affinity compound (i.e. ca maximum OGF). The maximum OGF of 15 nm particles was interpolated from 10nm and 20nm OGF values. Typically, freshly formed secondary organics are moderately oxidized and they have very high ethanol affinity. However, the presence of sulphate and oxidized organics make also low OGF organosulphates possible [14]. Therefore, the calculated OVF values are minimum estimates.

III. RESULTS AND DISCUSSION

Instances of particle nucleation were observed, with nucleation (10nm and 15nm) and Aitken mode sized particles (50nm) typically including a significant (i.e. up to volume fraction of 50%) secondary organic component (UFO-TDMA data) during sunny conditions (e.g., 4.2., 6.2., 9.2., and 10.2. of the summer 2011 expedition) on biologically active region with planktons whereas the ammonium sulphate fraction (VH-TDMA data supported by UFO-TDMA data) was strongly dominating during cloudy conditions (e.g. 15.2, 26.2. and 2.3 of the summer 2012 expedition). Furthermore, the comparison between *in situ* bubble burst chamber and atmospheric particles composition measurements reveal that even during windy conditions the measurements strongly support the presence of secondary compounds in the atmospherically observed ultrafine particles.

Sunlight is required for nanoparticle formation from VOC (volatile organic compound) such as DMS (dimethyl sulphide) or alkenes (e.g. isoprene). Photochemically mediated oxidation of DMS results mainly in the formation of sulfur dioxide (SO_2), although lesser amounts of methanesulfonic acid (MSA) are also produced [15]. Oxidation of SO_2 leads to sulfuric acid which may undergo nucleation with other gases such as neutralizing ammonia and oxidized organics to produce thermodynamically stable clusters of nanoparticles. These may grow to larger radiatively important sizes with other VOC oxidation products and halogen (e.g. iodine)

oxides to form atmospherically important secondary aerosol. Additionally, those secondary compounds can change the properties of primary organic material and sea salt, producing

climatically relevant CCN (cloud condensation nuclei; [16], [17], [2]), Fig. 3.

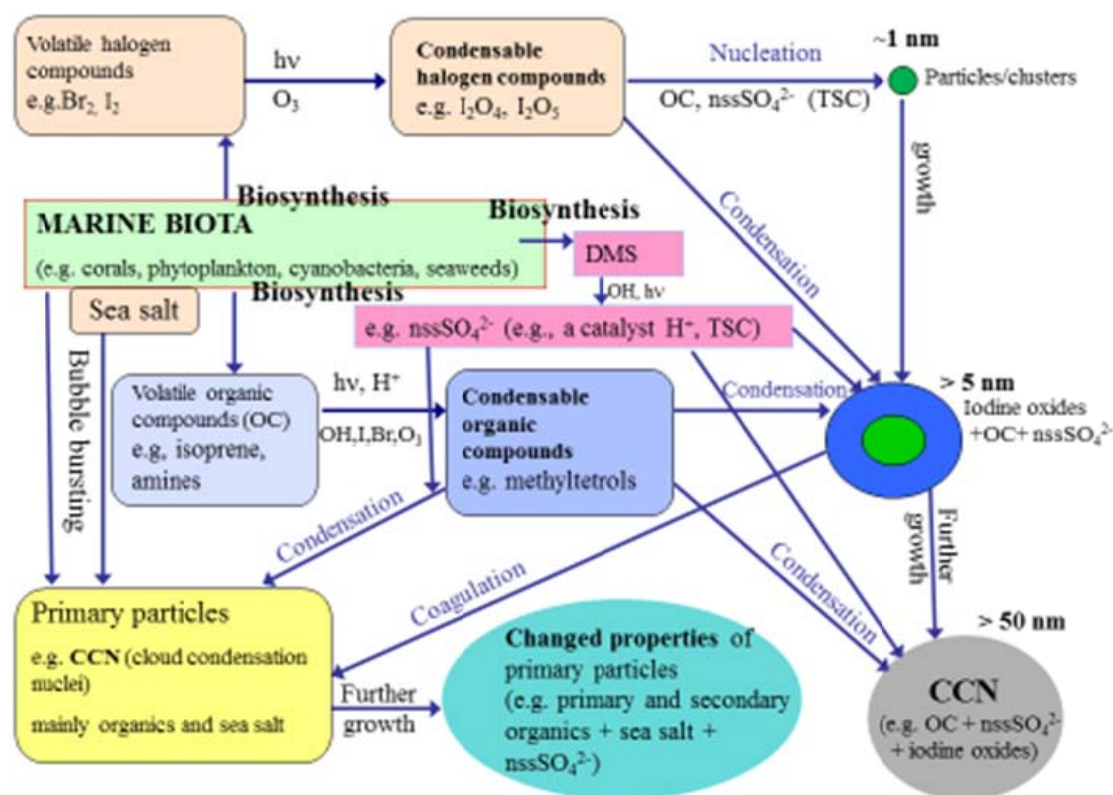


Fig. 3 A schematic of potential biogenic nucleation, Aitken and accumulation mode particle formation, growth, and composition during daylight hours at the Chatham rise open ocean environment

IV. CONCLUSION

These SOAP project Pacific Ocean measurements on remote open ocean reveal that phytoplankton blooms with sunny conditions make possible secondary organic contribution to ultrafine particles size and composition, and thus on CCN properties and cloud formation ability, and finally on climate. This is in agreement with other biologically active region observations about the presence of secondary organics even though the exact fraction is also depending on the local marine life (e.g. plankton blooms, seaweeds, corals). Importantly, the total area of marine biologically active regions is large over the world oceans. As a summary, an organic contribution is clearly needed to add to CLAW hypothesis.

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