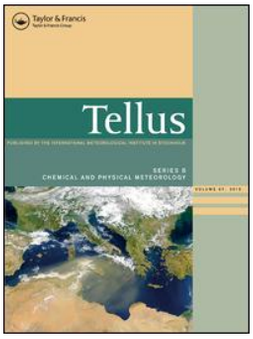

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Exploring controlling factors for sea spray aerosol production: temperature, inorganic ions and organic surfactants

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ABSTRACT

This work addresses the production of aerosol particles from bursting of air bubbles at the water-air interface. Experiments were performed in a laboratory system designed to minimize bubble interactions. Air bubbles of an equivalent spherical radius of ~3 mm were generated in both real and artificial seawater at temperatures of 0 and 19 °C respectively. Particle concentrations were measured and used to derive particle production per bursting bubble. The particle production in surface seawater from the Bay of Aarhus showed remarkably strong sensitivity to temperature, with ~40 particles per bursting bubble at 19 °C compared to ~2300 particles per bubble at 0 °C. A similar effect was observed for bubbles bursting in NaCl solutions. In contrast, the effect of temperature on particle production from artificial seawater was minimal. Further experiments including exclusion of selected inorganic components from artificial seawater point to magnesium and calcium ions as key role players on the effect of temperature. Experiments adding varying amounts of the weak surfactant succinic acid to sodium chloride solutions showed that the influence of temperature on particle production can also be modulated by organic molecules. A complex interplay between inorganic and organic constituents seems to determine the response of particle production to temperature in real seawater. Our study demonstrates that temperature can have a very large (orders of magnitude) effect on the production of particles formed from bubbles bursting at the liquid/air interface, and that chemical composition of the liquid is a controlling parameter for the magnitude of this effect.

Keywords: *sea spray aerosol, bubble bursting, temperature, single bubbles, surfactants*

1. Introduction

Sea spray aerosol (SSA) produced during wave breaking is a major contributor to the total atmospheric aerosol burden (D O'Dowd and De Leeuw, 2007). Sea spray aerosol plays an important role in the climate system by interacting with incoming light from the sun, and by acting as cloud condensation and ice nuclei (Stocker et al., 2013). Even so, the formation mechanism of sea spray aerosol, and the influence of meteorological conditions and seawater chemical composition on sea spray aerosol fluxes and properties, are poorly understood.

A central open question concerns the influence of seawater temperature on SSA production. In the past decades, some laboratory investigations have addressed this question using different types of wave breaking analogues: diffuser (Mårtensson et al., 2003; Sellegri et al., 2006; Christiansen et al., 2019), plunging jet (Sellegri et al., 2006; Zábori et al., 2012a; Salter et al., 2014; 2015; Christiansen et al., 2019), colliding parcels of water (Woolf et al., 1987; Bowyer et al., 1990), and a plunging sheet of water (Forestieri et al., 2018). These studies - all based on bubble plumes - point in different directions with respect to the dependence of particle production on seawater temperature. Another open question concerns the influence of seawater chemical composition on aerosol production. It has been reported that sea spray aerosol can be enriched in calcium (Salter et al., 2016) and Russel and Singh (Russell and Singh, 2006) explored how

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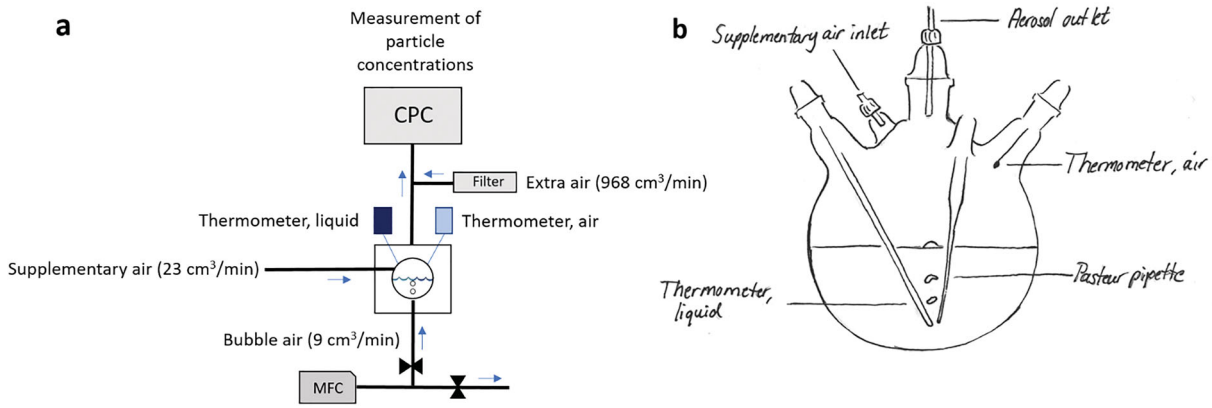

Fig. 1. a) Schematic drawing of experimental setup. The circle represents the glass flask, and the square the temperature-controlled bath. Arrows indicate direction of airflows. b) Five-necked glass flask in which bubble generation and bursting took place.

the anion (Cl-, Br- or I-) in sodium salts affect particle production from bubble bursting, but to our knowledge, the role of the individual key inorganic ions in seawater for particle production at ocean relevant temperatures has not been investigated. With respect to organic constituents, surfactants are of particular focus because they accumulate at the air-water interface and affect sea spray flux and properties in complicated and yet unresolved ways (Paterson and Spillane, 1969; King et al., 2012; Modini et al., 2013; Chingin et al., 2018). Based on knowledge from laboratory and field work, Saliba et al. recently pointed out (Saliba et al., 2019) that it is unclear whether the dependence of the sea spray aerosol production on sea surface temperature and presence of surfactants is positive or negative.

While the oceanic wave breaking process is complex and involves bubble interactions both below and at the water-air interface, single bubble studies can provide fundamental mechanistic insight (Modini et al., 2013) and serve as an important baseline for studies addressing effects of processes such as bubble coalescence (Chingin et al., 2018).

The aim of this study is to elucidate how the total number of aerosol particles from bubble bursting at the water/air interface depends on temperature in the ocean, ranging from 0 to 19 °C. Our laboratory experiments are designed to minimize bubble interactions in the water and at the water-air interface, and we study bubble bursting and particle production from artificial salt solutions, sea salt solutions with addition of a weak model surfactant and real seawater samples

2. Method

2.1. Setup

The core of the experimental set-up used herein is a 500-mL glass, round-bottom flask (Quick-fit) modified to have five necks. In all experiments, the flask was filled with 250 ml of liquid. Air bubbles were generated by passing dry, clean air (TSI Air Filtering Supply, Model 3074B) through a 150-mm glass Pasteur pipette fixed in the round-bottom glass flask, as shown in Figure 1. The tip of the pipette was 3 cm below the water surface. The flow of air through the pipette was kept constant during all experiments (9.32 ± 0.88 cm^3/min), using a mass flow controller (Vögtlin, red-y smart series, GSC-C3SA-DD23, SN: 191067, 0.1-51 min^{-1}). A lower air flow than the lower limit of the mass flow controller was achieved by setting the mass flow controller at a flow rate of 0.3 l/min, and subsequently dividing the flow into two streams using needle valves (Swagelok) with an outlet to the laboratory. Flow rates were measured using a (Sensidyne Gilibrator 2, 0-250 cm^3/min, SN:1301010-L)) bubble flow meter.

A Condensation Particle Counter (CPC) (TSI Model 3010, sampling rate 1 l/min) was connected to the round bottom-flask as shown in Figure 1. Besides the 9 cm^3/min air flow from the bubbles, 23 cm^3/min of particle free air passed the headspace of the flask and 968 cm^3/min of particle free air was added from a side branch just before the aerosol reached the CPC.

The temperature of the liquid (Vernier, Wide Range Temperature probe) and the air in the flask (about 5 cm over the liquid surface, Vernier, Surface Temperature Probes STS-BTA) were constantly monitored. To control temperature, the glass flask was half immersed in a bath (0 °C was reached using an ice/water bath or a Julabo, Refrigerator/Heating Circulator, F-25-ED), so that the liquid in the round bottom flask was always fully immersed.

2.2. Experimental procedure

Four series of experiments were performed, each with a specific solution in the round-bottom flask: 1) NaCl aqueous solutions, 2) NaCl aqueous solution with

addition of varying amounts of succinic acid, 3) artificial seawater and 4) seawater.

In all experiments, the liquid was kept at approximately 19 °C for about 30-40 minutes before being cooled to 0 °C where it was kept stable for approximately 30-40 minutes. Hereafter the temperature was again raised to 19 °C and kept stable for about 30-40 minutes. Bubble bursting occurred continuously throughout the phases of varying temperature, and the particle concentration in the headspace was measured continuously. During each period of stable temperature, the bubble rate (k_{bubble}) (measured in bubbles/minute) was counted manually during a 60 s time interval, and a one-minute short film documenting the bubble rate, lifetime and general behavior of the bubbles was recorded (cameras: Casio, Digital Camera: EX-ZR800/Canon 750 D/Casio, EX-FH25). Prior to each experiment, the background particle concentration in the headspace (after filling with liquid, but before bubbling) was measured, and was always found to be in the range 0.02-0.06 particles per cm^3 ($\#/cm^3$). After measuring the background, the Pasteur pipette was carefully lowered into the liquid without opening the glass flask or changing the air flow through it. After each temperature cycle, the air bubbling flow, the air flow through the headspace of the flask and the total air flow out of the flask were checked. Immediately before each experiment, all equipment in contact with the liquid was thoroughly cleaned with acetone, ethanol and Milli-Q water several times. Further experimental details (e.g. air flows) can be found in the Supporting Information.

2.3. Solutions and sample collection

All artificial solutions were made using Milli-Q water (EMD Millipore, >18.2 Ω resistivity, <5 ppb TOC) as solvent. The used chemicals were NaCl (Sigma Aldrich, ≥99.5%, $MgCl_2 \cdot 6H_2O$ (Sigma Aldrich, ≥99%), Na_2SO_4 (Sigma Aldrich, ≥99.0%), Sigma Sea Salts (Sigma Aldrich), NaBr (Sigma Aldrich, ≥99.0%), $CaCl_2 \cdot 2H_2O$ (Sigma Aldrich, ≥99.5%), K_2SO_4 (Sigma Aldrich, ≥99.0%), KNO_3 (Sigma Aldrich, ≥99.0%) and Succinic acid (Sigma Aldrich, ≥99.5%).

Seawater was collected from a 36-m long bathing jetty protruding from the coast a few kilometers south of Aarhus at Ballehage beach, Denmark (position: (56°07'17''N, 10° 13'35''E) in May 2017. These samples were analyzed on the day of collection and are referred to as "near-shore samples". Seawater was also collected in the Aarhus bay from the Aarhus University research ship (AURORA) on June 9th, 2017 at depths of 0 (surface water), 0.5 and 8 m, respectively, at the same position (56°07'41.3''N, 10° 24'28.1''E) using a Sea Bird, CTD, Model 911. The samples were stored in a refrigerator at 4 °C until analysis (for 19, 20 and 21 days, respectively). These samples are referred to as "non-near-shore samples".

2.4. Data processing

For each period of stable liquid temperature an average measured particle concentration ($N_{measured,av.}$) was calculated. The first ten minutes of data in each period were excluded to ensure that the particle concentration in the headspace of the flask had stabilized. The average number of particles per bubble ($N_{bubble,av.}$) was obtained as:

$$N_{bubble,\,av.}(T) = \frac{N_{measured,\,av.}\ (\#/cm^3)}{k_{bubble}\ (bubbles/min)} * F_{CPC}\ (cm^3/min) \tag{1}$$

where F_{CPC} is the sampling flow of the CPC (1 liter min^{-1}).

We calculate the change in number of particles per bursting bubble, between cold (0 °C) and warm (19 °C) conditions as: $\Delta\#/bubble = N_{bubble,av.}(0\,°C)$ - $N_{bubble,\,av.}(19\,°C)$. Since the particle number concentration in the headspace is most stable after cooling, we use $N_{bubble,\,av.}$ (19 °C) from the period after cooling (AC) in this calculation. We speculate, that the variability observed during the first period before cooling could be due to trace amounts of impurities (inparticular surfactants) which may be depleted through the initial bubble bursting.

To estimate the lifetime of the bubbles at the liquid/air interface, the number of picture frames on the videos recorded during the experiments were counted, from the bubble's arrival on the liquid surface and until its burst. The number of frames per second, 25.00 or 29.97 depending on the camera used, determined the time resolution with which the bubble lifetime at the water/air interface could be obtained.

Given the number of bubbles counted per minute and the air flow rate through the Pasteur pipette, a measure of the bubble size can be estimated by calculating the spherical equivalent radius of the bubbles, r_{bubble}. The bubble rate (k_{bubble}) varied with liquid temperature in a way so that the bubble rate was lower at the low temperature (in av.12% comparing 19 °C to 0 °C), see Sup. Inf. (1.1) for details on each experiment. To access the variation in the volumetric air flow rate with temperature of the liquid, a series of air flow measurements were made when bubbling though a NaCl solution, 0.6 mol/l, at 19 °C and 0 °C, respectively. The change in flow was $0.4 \pm 0.01\ cm^3$/min when the solution was cooled. This factor was used to calculate the equivalent spherical bubble size in all experiments. The average (all experiments) value of r_{bubble} was 3.2 ± 0.1 mm (Sup. Inf. for individual values). At a bubble radius at or larger than 3 mm, the formation of film droplets rather than jet droplets

Table 1. Overview of experiments performed and key results: number of particles produced per bubble ($N_{bubble,\ av.}$) at 0 °C and 19 °C respectively and the difference (Δ#/bubble).

Exp. (#)	Date	Composition	$N_{bubble,\ av.}$ 0 °C	$N_{bubble,\ av.}$ 19 °C (AC)	Δ#/bubble
NaCl					
1a	8-3-17	NaCl, 35 g/l	1754±151	59±7	1695±151
1b	9-3-17	NaCl, 35 g/l	1542±201	35±6	1507±201
1c	10-3-17	NaCl, 35 g/l	2158±181	37±8	2121±181
1d	22-3-17	NaCl, 35 g/l	1688±110	37±6	1651±110
1e	13-12-17	NaCl, 35 g/l	2083±141	66±10	2018±141
av.	average 1a-1e	NaCl, 35 g/l	1845±237	47±13	1798±237
1f	12-4-17	NaCl, 17.50 g/l	1888±168	130±22	1758±169
1g	09-5-17	NaCl 26.25 g/l	1569±339	18±4	1551±338
NaCl and succinic acid					
2a	4-4-17	NaCl 35 g/l Succinic acid, 0.080 mol/l	7 ± 3	17 ± 4	−10 ± 5
2b	5-4-17	NaCl 35 g/l Succinic acid, 0.010 mol/l	230 ± 38	12 ± 3	218 ± 38
2c	6-4-17	NaCl 35 g/l Succinic acid, 0.004 mol/l	243 ± 36	18 ± 4	225 ± 36
Artificial sea water solutions					
3a	20-3-17	Sigma sea salt, 35 g/l	4 ± 2	7 ± 3	−3 ± 3
3b	13-12-17	Sigma sea salt, 35 g/l	5 ± 5	5 ± 6	0 ± 5
3c	12-6-18	Homemade sea salt* 35g/l	27 ± 7	9 ± 3	17 ± 8
3d	6-6-17	Homemade sea salt excluding $MgCl_2$ and $CaCl_2$, 29 g/l	1385 ± 191	27 ± 22	1357 ± 192
3e	22-6-18	Homemade sea salt excluding $MgCl_2$, 30 g/l	1463 ± 278	14 ± 4	1449 ± 257
3f	21-6-18	Homemade sea salt excluding $CaCl_2$, 34 g/l	286 ± 38	11 ± 3	275 ± 36
3g	5-7-17	Seawater, 8m, Aarhus Bay active charcoal, 26.1 PSU	80 ± 14	13 ± 4	67 ± 15
Real sea water					
4a	11-5-7_1	Ballehage, 0 m, 17 PSU	2438±322	32±6	2406±322
4b	11-5-17_2	Ballehage, 0, m 17 PSU	2472±371	30±6	2442±371
4c	16-5-17	Ballehage, 0m, 16 PSU	2346±483	40±7	2306±483
4d	24-5-17	Ballehage 0m, 16 PSU	1985±449	18±4	1967±449
4e	30-6-17	Aarhus Bay, 0m, 22.7 PSU**	2237±188	63±9	2175±189
4f	29-6-17	Aarhus Bay, 0.5m, 22.7 PSU**	3074±687	98±16	2976±687
4g	28-6-17	Aarhus Bay, 8m, 26.1 PSU	3383±278	110±12	3273±278

AC: after cooling. Uncertainties represent one standard deviation. *Cf. Sup. Inf. The date of the performance of the experiments with respect to the near-shore water is the same as the date of the collection of the sample. Salinity data for near-shore seawater comes from DMI (the Danish Institute of Meteorology)(DMI, 2017), site accessed 11/15/24 of May 2017. Salinity data for non-near-shore water was measured with a SBE 4 conductivity sensor on the Seabird CTD 911 sampling device. **The measurement of salinity of the non-near-shore water started at 1 m depth, and the values given are therefore given under the assumption that the salinity at 1 m depth is similar to the salinity at the surface.

dominates (Lewis and Schwartz, 2004; Walls et al., 2014). Analogous to Modini et al. (2013), we thus proceed on the assumption that the majority or all of the counted droplets in this work are film droplets.

3. Results and discussion

In the following sections we address temperature-dependent particle production from bubbles bursting in sodium chloride solutions (series 1 and 2), as well as more complex artificial sea salt mixtures (series 3). Finally, we present and discuss results from studies using real seawater samples (series 4). Table 1 provides an overview of the experiments and main results, and further details on all experiments can be found in the Supporting Information (Sup. Inf. 1.1).

3.1. Sodium chloride solutions

Figure 2a shows how the particle concentration in the headspace of the round bottom flask varies as a function

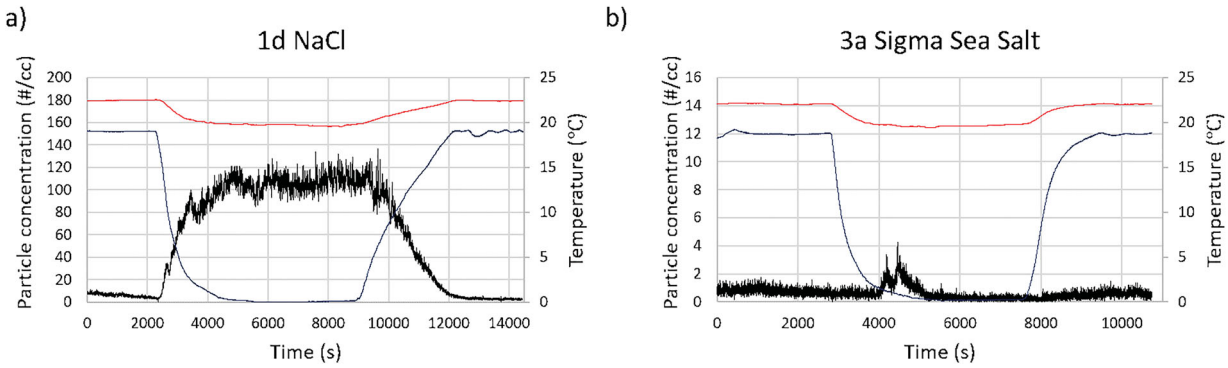

Fig. 2. Measured particle concentration (black), solution temperature (blue) and air temperature (red) in the flask headspace during bubbling experiments in: a) NaCl solution, 35 g/l, b) Sigma Sea Salt solution, 35 g/l. Notice the different scales on the y-axes showing particle concentrations.

of water temperature for bubbling of air through an aqueous NaCl solution (35 g/l). Note that the number of particles shown is measured by the CPC after dilution by a factor of 31. The number of particles produced per bubble at 19 °C is in the range 35-66 (AC). This is broadly comparable to the number of ~120 ± 30 particles produced per bubble in the study by Modini et al. (2013) (NaCl 35 g/l, volume equivalent diameter of 2.4 mm, temperatures in the range 18-22 °C, calculated from Tables 1 and 2: total number of particles produced per bubble film cap area of 60.5×10^5 m^{-2} and average surface film cap area of $2.0 \pm 0.5 \times 10^{-5}$ m^2).

From the figure, it is clear that the particle concentration (black line) is closely linked to the temperature of the saline solution (blue line). As the solution is cooled from 19 to 0 °C, the particle concentration increases significantly, from a few particles per cm^3 to around hundred particles per cm^3. When the solution is warmed up again, the particle concentration decreases to approximately the same value as before cooling. Repeatability was confirmed by performing a total of five independent experiments, following the protocol described in section 2.2 using freshly made aqueous solutions in each case. Examples of recorded videos from an experiment (exp. 1d) are available as Supporting Information (Sup. Inf. 1.9). On average, the change in number of particles produced per bubble when cooling from 19 to 0° C, is ~1800.

For the sodium chloride solutions, the bubbles burst individually at the surface both at 19 and 0 °C. The remarkable increase in particle production observed with the decrease in temperature (referred to as the "temperature effect" in the following), can thus not be due to a difference in bubble interactions, but is alone due to a difference in the bursting behavior of each individual bubble.

Experiments were also performed using concentrations of NaCl of 17.50 and 26.25 g/l, respectively. These concentrations correspond to the salinities of the seawater samples studied herein (cf. section 3.5). As for the concentration of 35 g/l, the particle production was highly sensitive to cooling for both concentrations (Table 1).

3.2. Sodium chloride and succinic acid

The presence of surfactants in a water body is known to diminish the energy available for bubble bursting and droplet production by lowering of surface tension (Long et al., 2014). A number of studies show how an increased amount of surfactants can suppress particle production (Paterson and Spillane, 1969; Modini et al., 2013). To test if the presence of surfactants influence the observed increase in particle production during cooling, experiments were performed (Exp. 2a-c) adding various amounts of a weak model surfactant (succinic acid) to sodium chloride solutions (35 g/l). As seen from Table 1 and Supporting Information, this is indeed the case; the weak surfactant dampens the influence of the temperature on particle production. Contrary to observations using sodium chloride solutions, bubble-bubble encounters and bubble-equipment encounters were significant when succinic acid was added. When the water temperature was 0 °C fewer of these interactions took place than at 19 °C (Supporting Information 1.6). Therefore, some of the change in the particle production due to a temperature change might be caused, not only by the change of the bursting process of one isolated bubble, but also from the change in the interaction pattern between the bubbles, which is a side effect of the change in temperature.

For comparison, Zabori et al. (Zábori et al., 2012b) conducted experiments using a plunging jet to create bubble plumes in solutions of pure sodium chloride. A clear tendency of decreased particle production was observed, when temperatures were raised from 0 °C to higher temperatures (10-21°C). Consistent with our results, a decrease in particle

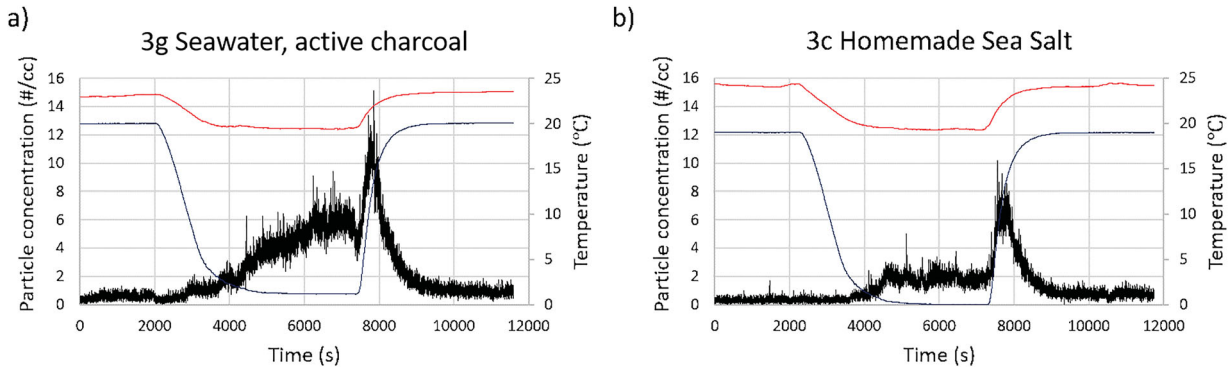

Fig. 3. Measured particle concentration (black), saline solution temperature (blue) and air temperature (red). a) Seawater sample, filtered with active charcoal, (non-near-shore) collected at 8 m depth in the bay of Aarhus (cf. section 2.3. b), Homemade sea salt, 35 g/l.

production (Dp > 10 nm) was observed when succinic acid was added to NaCl solutions.

3.3. Components of artificial sea salt mixtures

To investigate the effect of temperature on more complex mixtures, a series of experiments were performed, focusing on particle production from aqueous solutions of Sigma Sea Salt (Figure 2b) as well as a homemade sea salt mixture (Figure 3b), representing the most abundant inorganic ions in the oceans (Sup. Inf. 1.3 for composition). Such salt mixtures are often used as proxies for real seawater. To our surprise, and in sharp contrast to the experiments described above with NaCl solutions, particle production from an artificial sea salt solution only shows very little sensitivity to a change in temperature. Regarding solutions of Sigma Sea Salt, bubble-equipment contact (with the pipette or the inner glass flask surface) occurred in one case (Exp. 3 b) during all phases of the experiment, and in another (Exp. 3a) only during the last phase at 19 °C. In all cases, the particle concentrations measured were low, and we conclude that the lack of sensitivity of the particle production to a change in temperature is an effect of the chemical composition of the aqueous solution.

A main difference between NaCl and sea salt is the presence of divalent cations. To test the hypothesis that divalent cations influence particle production at different temperatures, the difference between the behavior of NaCl and artificial sea water solutions with respect to temperature was investigated further by excluding the two divalent cations Mg^{2+} and Ca^{2+} from the artificial sea salt mixture (Experiments 3d-f).

A significantly stronger response to temperature was observed, when one or both of the two salts $MgCl_2$ and $CaCl_2$ were omitted than when they were present (Table 1 and Sup. Inf. 1.1). This is a noteworthy result, and it seems reasonable to conclude that the calcium and magnesium cations play a role as inhibitors of the temperature effect.

It is interesting to compare with the recent results by Christiansen et al. (2019) investigating the effect of temperature on SSA production using a plunging jet to entrain air in artificial (Sigma sea salt) seawater. While a non-linear effect on temperature with a minimum in particle production around 10 °C was reported, we notice that at 0 °C, the particle production efficiency-expressed as the number of particles produced per volume of entrained air, is almost similar to that at 19 °C consistent with the single bubble results reported herein.

3.4. Seawater

Based on the results described above, i.e. that surfactants dampen the temperature effect and that artificial seawater solutions show minimal temperature effect, one could expect particle production from real seawater to be unaffected by temperature. Contrary to this expectation, a large effect of temperature on particle production was observed for real seawater samples, i.e. a remarkable increase in particle production was seen when the seawater was cooled. This is clearly seen in Figure 4, showing results from an experiment where two consecutive cycles of cooling and warming were performed. Figure 4 also demonstrates that within one cycle, the experimental procedure does not change the composition or concentration profile of the liquid in a way that changes the response of the bubble bursting to temperature changes.

It is gratifying to notice, cf.Table 1, that from surface seawater (AC), the number of particles produced per bubble at 19 °C is approximately 30-60, which is comparable to the values reported in the literature for real and artificial sea water and NaCl solutions (Lewis and Schwartz fig 30), respectively of around 10-40 particles for bubble sizes (radius) in the range 2-3 mm.

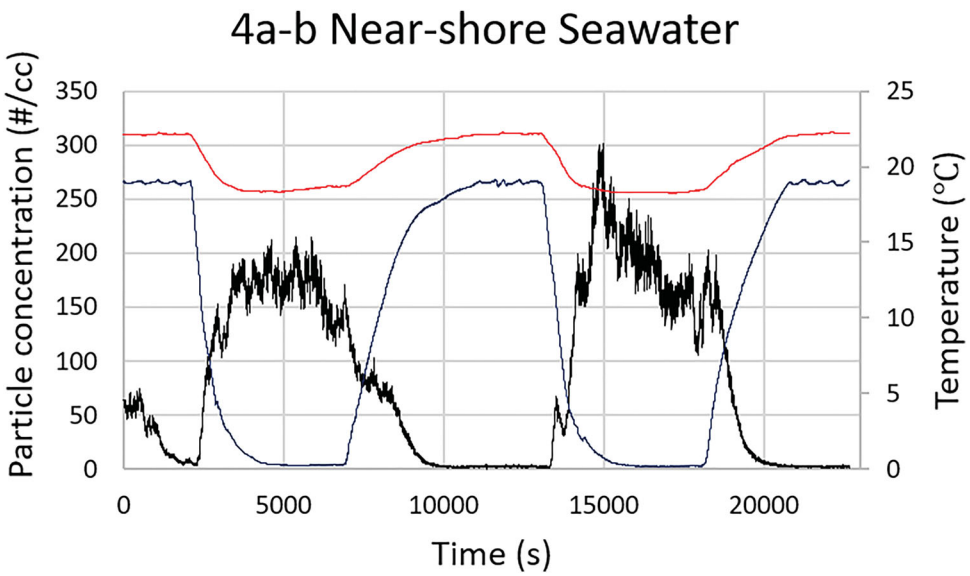

Fig. 4. Near-shore seawater from Ballehage. Measured particle concentration (black), saline solution temperature (blue) and air temperature (red).

For solutions of NaCl and for seawater a significant shortening of the bubble lifetime at the surface was observed when the water was cooled from 19 to 0 °C (on average from 0.29 to 0.11 s for NaCl, and from 0.97 to 0.22 s for seawater, average of near-shore and non-near-shore samples see appendix 1.7). The shortening of the lifetime may relate to an increase in surface tension at colder temperature compared to warmer temperature leading to a higher potential energy of the bubble at low temperature. The shorter lifetime may in turn give the liquid in the bubble cap less time to drain, thus leaving more liquid in the cap for particle formation. We also speculate that an increased brittleness of the film cap, when the liquid is cold, could increase its tendency to shatter and thereby fractionate into more pieces.

Table 1 shows the obtained number of particles produced per bursting bubble and the associated temperature effect for bubbles bursting in seawater samples. The seawater samples produce a higher (30-116%) absolute number of particles at low temperature (0 °C) than pure sodium chloride solutions at the same salinity (17 and 26 g/l, respectively). On average (near-shore and non-near-shore 0 m, AC), the particle number produced per bubble is ~40 at 19 °C and ~2300 at 0 °C.

This is remarkable, because Ca and Mg ions known to be present in seawater were found to decrease the temperature effect in the artificial seawater solutions. Likewise, surfactants of biological origin in the real seawater samples would also be expected to dampen the temperature effect. A range of organic compounds of biological origin are known for binding magnesium and calcium ions, e.g. exopolymer polysaccharides from cells form stable complexes with these ions (Chin et al., 1998; Ding et al., 2008; Verdugo and Santschi, 2010; Alpert et al., 2015). We speculate that such compounds in the seawater interact with the Mg^{2+} and Ca^{2+} cations in a way that prevents the ions from exerting their inhibiting temperature effect.

A depth profile of the chlorophyll a content of the seawater was measured (Sup. Inf. 1.5). Chlorophyll a is produced by phytoplankton and is a phytoplankton biomass indicator in a water body (Boyer et al., 2009). The highest particle productivity during cooling was measured for the sample with the highest chlorophyll a content (8 m depth) and thus presumably the highest level of phytoplankton biomass. Consistently, a number of recent studies observe correlations between increased phytoplankton and bacterial activity in seawater and particle production (Hultin et al., 2011; Alpert et al., 2015).

To further explore a potential interaction between the inorganic divalent cations (Ca^{2+} and Mg^{2+}) and organics, an experiment was performed in which seawater was filtered using activated charcoal powder; 250 ml from a seawater sample from 8 m depth was stirred with 3 spoons of activated charcoal powder for 65 min. Subsequently, the mixture was repeatedly (9 times) filtered by suction to remove the charcoal until no traces of charcoal powder could be seen on the filter. Going through the temperature cycle protocol, the behavior of this sample was indeed very similar to the sample with the homemade sea salt mixture, both with respect to the magnitude of the number concentrations and the peak in particle

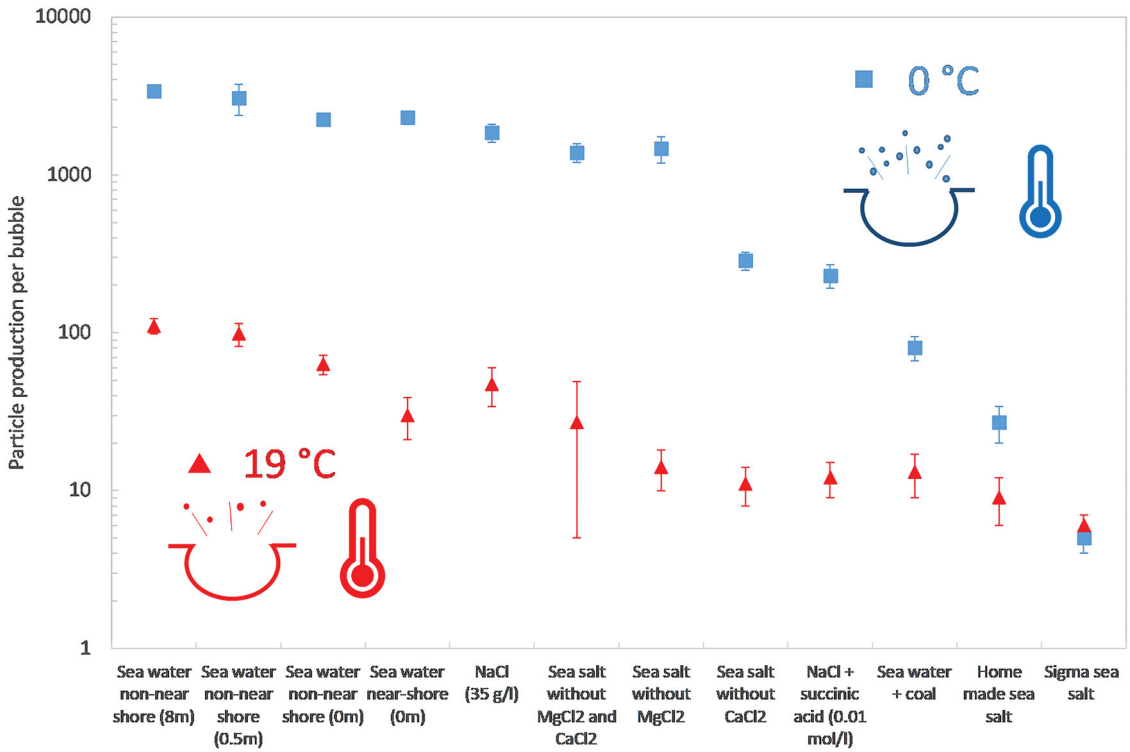

Fig. 5. Overview of experimental results. The figure illustrates the very large (orders of magnitude) change in particle production per bubble with temperature for bubbles bursting in real seawater and NaCl solutions. The figure also demonstrates the influence of a model surfactant (succinic acid) and divalent cat-ions on the temperature-dependent particle production.

concentration that was formed during the warming-up phase after cooling the water, see Figure 3. Based on this we speculate that organic and/or biological material in seawater plays an important role when it comes to the influence of the temperature of the seawater on particle production. A clarification of why calcium and magnesium ions in real seawater do not inhibit an increase in particle production when cooling the water, would be a potential key to understand a core aspect of formation mechanisms of sea spray aerosols. On a much more fundamental level, we could also understand how chemical relations between organic and inorganic species can affect particle production from bubble bursting in a crucial way.

When comparing results for seawater sampled at different depths, the non-near-shore seawater samples, which do not contain the sea surface microlayer (0.5 and 8 m depth), seem to exhibit the largest particle production at 0 °C. This may be due to a lower concentration of surfactants in these subsurface samples.

For the real seawater samples, nearly no coalescence or encounter between the bubbles or glass walls/or equipment occurred at a temperature of 0 °C. At 19 °C some of the bubbles coalesced at the surface, forming small clusters of a maximum of five bubbles, or made contact to the glass wall or equipment. Since we could not measure the particle concentration without these side effects, it is not possible to evaluate exactly how much these bubble interactions affect the measured particle concentration with respect to the seawater samples. We observed, however, that the bubbles burst individually in the beginning (Sup. Inf. 1.8)) of the experiments, and during this phase the particle concentration was clearly and measureably lower than when the water was 0 °C. We thus conclude that the main cause for the increase in particle production is temperature.

4. Discussion

Particle production from bursting bubbles is the result of a complex process influenced by molecular interactions and fluid mechanics. Russel and Singh (Russell and Singh, 2006) performed a comprehensive study of the particle production from bubbles bursting in aqueous solutions of NaI, NaBr or NaCl respectively, at constant temperature and were able to pinpoint surface forces as controlling particle production in these solutions independent of the nature of the anion. They stress, that a full mechanistic understanding of particle production from bubble bursting in ionic solution is limited by lack

of experimental and theoretical approaches to describe both molecular interactions and film rupture fluid mechanics (Russell and Singh, 2006). Figure 5 summarizes the results from this work, demonstrating for the first time a remarkable (orders of magnitude) increase in particle production per bursting bubble in NaCl and in real seawater samples, when the water is cooled from 19 to 0 °C.

While the detailed mechanism for this effect should be explored in future studies, we demonstrate herein how the effect of temperature on particle production is related to the chemical composition of the seawater, the presence of surfactants and in particular we elucidate a hitherto unexplored connection to individual inorganic ions. While in this work we have strived to minimize bubble interactions, future studies should address how bubble interactions and different bubble sizes affect particle production at different temperatures. This is particularly important in light of the current changing sea surface temperatures, melting ice in polar regions and consequent changes in biological activity.

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Supplemental data

Supplemental data for this article can be accessed here

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