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Tuukka Petäjä
Editor of Atmospheric Chemistry and Physics

Dear Prof. Petäjä,

Please, find herewith enclosed the answers to the referees. We have fully addressed all the comments from the referees. The comments are answered one by one, starting next page.

Yours sincerely,

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# Interactive comment on “The effect of low solubility organic acids on the hygroscopicity of sodium halide aerosols” by L. Minambres et al.

**Anonymous Referee #1**

## Introduction and Materials and methods:

1. In the title, the authors denote the investigated organic acids as being of “low solubility”, but later they are describes as “insoluble” (p. 4397 l. 3). I would consider the C6, C8, and C12 fatty acids as having low, but finite solubility in water, and perhaps expect this value to decrease somewhat in salt solutions. Do the authors have any values for the specific aqueous solubilities of the fatty acids? It is my understanding that the authors consider the influence of the fatty acids on sodium halide water uptake only. A brief discussion of expected intrinsic hygroscopic properties of the acids or absence thereof, as well as the relation to water solubility, could be useful. Also, why was the C10 fatty acid not studied? And why were the fatty acids studied in the neutral form, as opposed to the carboxylate anions? One could argue (as was done by Prisle et al., 2010) that these deprotonated forms are more relevant model systems for marine organic aerosol at sea water pH > 7.

The term "insoluble" applied to the studied acids in this work has been changed to "low solubility" wherever it appears in the manuscript. Moreover, the term has been quantified, and now the water solubility of hexanoic, octanoic and lauric acid is given:

| **Compound** | **Water Solubility at 20ºC (g/l)** |
|---|---|
| Hexanoic acid (C6) | 9.9 |
| Octanoic acid (C8) | 0.68 |
| Lauric acid (C12) | 0.058 |

Ref. The Merck Index: An encyclopedia of chemicals, drugs and biologicals (11th Ed.), Merck, 1989.

These data are now included in the last paragraph of the Introduction (The revised introduction has been added at the end of these comments) and in Table 1.

Although, broadly speaking, the solubility of the studied acids in water is small when compared to other organics (e.g., dicarboxylic acids such as glutaric acid); there are significative differences among them, water solubility decreasing roughly one order of magnitude as the chain length is increased.

As to the intrinsic hygroscopic properties of fatty acids, we are unaware of any specific study about water uptake of low water soluble organic compounds, as they are assumed to be essentially hydrophobic due to their low water solubility (although hexanoic acid would expect to present some water uptake behavior). The main interest of these fatty acids lies on the effect of hydrophobic films on the hygroscopicity of water soluble compounds.

Now this point is presented more clearly in the Introduction (see the last paragraph of the revised Introduction)

Of course, our study would have been more complete if the complete sequence C6-C8-C10-C12 had been studied. However, initially we planned to study the C6-C8-C12 as potentially representative of "low" (C6), "intermediate" (C8) and "high" (C12) solubility behaviors. Thus, we did not consider that the properties of decanoic acid (C10) relevant to this study would be very different to those of lauric acid (C12): The water solubility of decanoic acid is 0.15 g/L, of the same order of magnitude of lauric acid. However, considering the obtained results, maybe decanoic acid should present some interesting and unexpected behavior.

It is true that the deprotonated forms of the acids are expected to predominate in sea water, so that primary aerosols generated from sea water are expected to include the anionic forms of fatty acids. But another possibility to form the aerosol is when organic acids in the gas phase are directly emitted to the atmosphere, presumably in their protonated form, and deposit over sea-salt aerosol. It is this second process which has been considered in our study. Moreover, additional hygroscopic studies of fatty acids as such are found in the literature, so our results can be compared.

2. A major shortcoming of the presented results is the lack of quantitative information on the investigated aerosols, specifically aerosol number size distributions and aerosol mixing states. A clearer presentation of the aerosol size

ranges measured would be most helpful (e.g. p. 4389, l. 10 onwards). I also do not see number concentrations measured with CPC presented anywhere? Furthermore, the authors could elaborate on the mixing state of the aerosols, or explain why it cannot be determined. I find that the description of whether the aerosol is internally or externally mixed is somewhat vague (e.g. p. 4398, l. 7), until the very end of the manuscript. How do the authors define internal and external, as well as homogeneous and heterogeneous mixing?

What is the variation of aerosol compositions over which the results for water u take is averaged? Is it known? This would influence the immediate usability and significance of the presented results.

## Size distribution and particle number density

A new figure has been added to the manuscript (Figure 8), showing the size distribution obtained by the APS and SEM images. Unfortunately, the aerodynamic particle spectrometer only sizes particles bigger than 0.5 µm, so smaller particle size distribution has been obtained by counting particles imaged by the SEM. The atomizer employed in our experiment generates, according to specifications, a particle number density of 2x10$^6$ particles/cm$^3$ following a lognormal distribution of sizes. This figure, however, depends on the nature and composition of the atomized solution, as the nozzle can be partially obstructed due to salt deposits, so it varied in different experiments. The generated number density of particles is later lowered by mixing with nitrogen flow and further particle loss due to wall deposition. Typical aerosol number concentration measured for dry NaCl particles is also given in Figure 8.

The distribution obtained in our experiment is compatible with a lognormal distribution of median diameter 46 nm and stardard deviation 2.0.

## Mixing state of aerosols:

As infrared spectroscopy do not give direct information on the mixing state of the aerosols, we cannot quantify this aspect, and only give estimates. SEM images reveal the morphology of the particles, but in the studied cases the organic coating is thin, so it is not possible to discriminate if the coating is covering the whole particle, or only partially. The coating system employed is expected to give dry particles with an inorganic salt core, surrounded (totally or partially) by an organic film layer. Other situations would be improbable. This assumption is in accordance with the results reported by other authors in similar experiments (see refs. in the manuscript).

We cite "internal mixing" of aerosols to refer to a largely homogenous mixture of organic and inorganic compounds in dry particles, as is the custom in the literature. We do not use the term "external mixing" in the manuscript. "Homogeneous" and "heterogeneous" terms refer to the nucleation process: in homogeneous nucleation, organic particles form from the corresponding vapor, whereas heterogeneous nucleation takes place when the organic vapor condenses over preexisting sodium halide particles, presumably forming a coating over the particle.

## Aerosol composition:

The relative proportion of organic/inorganic mass cannot be given from the infrared spectra, as NaX salts do not absorb in the infrared, and only the absorbance of the organic compound can be given. A rough estimate of the covering thickness of the organic layer is given in the 3.5 section of the manuscript: for the LA/NaCl system, an upper limit of 20 nm can be established from the SEM images, which is also a reasonable estimate for hexanoic and octanoic acids. However, the organic layer thickness can vary with the nature of the inorganic substrate (NaCl, NaBr or NaI), the size of the particles and the preexisting amount of water in the particles before the heterogeneous nucleation. This aspect has not been studied in detail.

3. Are there any implications of the purity of the inorganic chemicals used (p. 4388, l. 4)? What are the potential impurities present in the sodium halide samples? Can the authors comment on whether surface energies of organics could be sensitive to those impurities when mixed with the inorganics in the aerosol phase?

## Impurities of the chemicals

The purity of the used inorganic chemicals was ≥98% in all cases. According to the manufacturer specifications, the main impurities of NaCl are as follows:

Insoluble matter in water: 0.005%

N compounds: 0.001%

Br: 0.01%

Chlorate and nitrate: 0.003%

Fe(CN)6: 0.0001%

phosfate: 0.0005%

sulfate: 0.001%

I: 0.002%

Pb: 0.0005%

Ag: 0.00004%

The data for the rest of the inorganic salts are similar, and are available if required.

## Sensitivity of surface energy of organics to impurities:

Several studies have been carried out to address the effect of inorganic salts on surfactant adsorption at the air-solution interface (i.e., aqueous solutions) (for example, S.S. Helvaci, S. Peker, G. Özdemir, Effect of electrolytes on the surface behavior of rhamnolipids R1 and R2, 2004. Colloids and Surfaces B: Biointerfaces, 35, 225–233; D. Exerowa, N.V. Churaev, T. Kolarov, N.E. Esipova, N. Panchev, Z.M. Zorin, Foam and wetting films: electrostatic and steric stabilization, 2004. Adv. Colloid Interface Sci., 104, p. 1-24; B. Nozière, C. Baduel, J.-C. Jaffrezo, 2014. The dynamic surface tension of atmospheric aerosol surfactants reveals new aspects of cloud activation, Nature Communications, doi: 10.1038/ncomms4335). In these studies the surface activity of single chained surfactants was found to increase with added salt.

These effects can be explained by the interaction of the electrostatic charges coming from the salt ions at the water surface, and the polar head groups of the surfactant molecules. Thus, addition of small amounts of salt to liquid water can influence the surface tension of organic molecules. However, the conditions in our experiment are different:

1) In aqueous droplets, the concentration of the sodium halide salt is near 0.01 kg/L (assuming that atomization from solution will not notably change the solution concentration), which will cause the main effects on surface tension, but the effects of impurities, which are present at much lower concentrations, will be presumably negligible (as far as we know, the electrostatic effect of dissolved salts will be largely independent of the nature of the salt).

2) In dry particles, surfactants adsorb on dry salt particles: in this system, the electrostatic interactions will be higher than before, but again will be dominated by the primary salt (NaCl, NaBr or NaI), and the possible impurities will add quantitatively a negligible contribution.

In conclusion, we think that the concentration of impurities is too low to affect the surface properties of the organic acids, as the main salt is always present in large concentrations, that will account for practically all surface energy changes.

4. It could be useful to clarify a bit further, which of the observed changes in spectral features are ascribed to particle size, and how, and which are due to mixing interactions (p. 4392, l. 3-24)?

3.2 section has been modified to include how the infrared spectral changes are linked to particle properties.

The changes in carbonyl absorption band wavenumber and bandwidth (collected in Table 2 of the manuscript) with respect to their bulk phase values are indicative of organic molecule/inorganic ion interactions, and can be used to address the effect of the ionic salt environment near the organic acid molecules.

This is already explained in section 3.2.

A new paragraph has been added at the end of section 3.2:

"Another notable effect in the spectra of heterogeneously nucleated particles is the sloping baseline, which is higher at higher wavenumbers, as in homogeneously nucleated particles. This effect arises because the particle size influences the scattering contribution of the infrared extinction: an increase in either the refractive index of the particle or particle size increases the scattering contribution, which manifests in a more sloping spectrum baseline."

It is rather difficult to quantify these effects, because the infrared optical constants of organic molecules are usually not known. Also the particle morphology affects the scattering signal.

**Results and discussion:**

5. In general, I think the manuscript calls for a more thorough statistical evaluation of the presented results. How significant are the variations in hygroscopic properties between pure sodium halides and the coated aerosols, and the differences in the impacts of the various organics on each salt? When statistical information is given, it is not clear exactly what quantity is given and what the value is. For example, what exactly is meant by “a change of more than 100% in some cases” (p. 4398, l. 14)? Also, in section 3.5, no experimental uncertainties for the organic-water molar ratios are given. Neither is the range of particle sizes and estimated compositions (organic/inorganic ratios) over which the spectral features are averaged. This needs to be discussed in more detail. If statistical information cannot be obtained, it should be explained why this is so.

**Statistical evaluation:**

It is true that we have not carried out an exhaustive statistical evaluation of our results. However, our main objective in this work has been to address the changes in hygroscopic properties of sodium halide aerosols coated with different organic acids, so that the emphasis has been put on qualitative differences among the studied systems, rather than on a precise characterization of all variables. We of course present results that are reproducible given the initial conditions in our experimental system.

**Significance of variations in hygroscopic properties:**

An important point is the complex variation in hygroscopic properties of the aerosols depending on the nature of the salt and the organic compound. This issue has been explained in section named: Deliquescence and Efflorescence

Curves (p. 4394-4400). In few words, deliquescence curves of pure NaCl and NaCl/HA are very similar, however the deliquescence point of NaCl/OA and NaCl/LA occurs substantially lower than in pure NaCl (from 73% to 56%). The efflorescence curves for all organic acids are very similar to pure NaCl. In the case of pure NaBr there is no significant difference between pure and covered particles neither in deliquescence nor in efflorescence modes. In spite of this behavior, is import to note that NaBr/HA particles deliquescence at higher RH than pure particles. Finally, all curves of acid-covered NaI exhibit higher deliquescence point with respect to pure salt, especially in the case of NaI/OA (from 0% to ≈70%). In efflorescence process, there are different variations depending of the organic acid.

**What exactly is meant by “a change of more than 100% in some cases”?** (p. 4398, l. 14):

This sentence has been rewritten in less ambiguous terms:

> "The band center wavenumbers shift in the -6 / +10 cm-1 range in the presence of NaX salts, but the bandwidth (FWHM) of the C=O vibration (of 20-30 cm-1 for the bulk acid) is in the 13-46 cm-1 range; this implies that the change in FWHM can amount to more than 100% with respect to the bulk phase FWHM."

**Experimental uncertainties for organic-water molar ratios**:

These molar ratios are calculated from the relative absorbances of both compounds, and the infrared measurement will introduce a negligible statistical error. In general, the error in organic/water molar ratios will depend on the errors in RH and temperature measurement, that are given in the manuscript. Also the organic/water molar ratios are dependent on the RH, the nature of the salt and acid, and the degree of covering. For this reason, in the results we present some typical molar ratios (as they can vary largely with the above conditions), but without emphasis in error analysis.

**Range of particle sizes**:

This question has been taken into account, as answered in question 2.

On the other hand, in the case of particle size, we only give an approximation and it is estimation from our values.

**Organic/inorganic ratios**:

As explained in the answer to question 2, organic/inorganic ratios cannot be quantified from infrared absorption data, so we can only give an estimate of the organic layer thickness for a given particle size.

6. When the authors discuss the various mechanisms that could explain the observed variations in inorganic hygroscopicities, it is not clear which they actually find more or less likely, or if all those mentioned are indeed considered (equally) likely (e.g. p. 4397 l. 12 and onwards).

Unfortunately, we are not able to affirm the most probable mechanism to explain the observed variations in hygroscopic processes, or to assign a certain weight to each mechanism. The proposed mechanisms are based on reasonable physical principles, that have been predicted in several molecular dynamic studies for equal or similar systems by other groups (i.e. Sun et al. 2012 or Ma et al., 2001)

7. I am not sure what the authors mean when they state that “The efflorescence process in NaX aqueous particles is not substantially affected by the presence of the acid” (p. 4399 l. 2). To me, from Fig. 6, it arguably looks like the influence of organics on the efflorescence curves is as substantial as on the deliquescence curves?

The reviewer is right, and both concepts, the deliquescence/efflorescence process and DRH/ERH, have been somewhat mixed. On the one hand, in deliquescence/efflorescence process particles take/shrink water at different RH values. In this respect, in the efflorescence curves there is substantial variation in the amount of water present in the particles at high RH for the various acids, although these contents tend to the same value at RH near crystallization. In this context, a similar efflorescence behavior is observed for all systems, so changes in the efflorescence relative humidity (ERH), hindering or enhancement of efflorescence by the organic acids cannot be reported. This is what we meant in p. 4399 l. 2. We have rewritten the sentence to express more appropriately:

> "The efflorescence process in NaX aqueous particles is not substantially qualitatively affected by the presence of the acid: neither hindrance nor enhancement of efflorescence has been observed due to any of the acids."

On the other hand, the situation in deliquescence curves is qualitatively different, due to the presence or absence of liquid water at RH near DRH for the different systems, which are atmospherically more relevant, as the particle phase may change, and so the processes that the particle may experience.

8. It is not always immediately clear whether the authors are discussing aqueous aerosol or dry crystalline aerosol, and it seems to me that sometimes arguments are transferred from one to the other with insufficient justification. This may however benefit from a clarification of the arguments. I also wonder if the authors are making any distinction between “liquid” organic acid and aqueous organic acid (e.g. p. 4399, l. 16)? Would an essentially separate organic phase on an aqueous salt aerosol have a different spectral signature than the pure solid acid, or than the organic dissolved in the aqueous phase? When the authors speculate on “dynamics” of the water uptake process, it is not always clear whether they are talking about organic-inorganic interactions on a dry crystalline surface or in the aqueous solution (e.g. p. 4399, l. 14). See also point 2) above.

**Aqueous/dry aerosol**:

In the Results and discussion section, 3.1-3.3 subsections deal only with pure or mixed substances, excluding liquid water. In the 3.4 subsection about deliquescence and efflorescence, the amount of liquid water in the particles varies with RH and is quantified in the curves of Figure 6. However, we cannot tell in all cases if the particles will form an aqueous solution, as the sodium halides do not have infrared signatures that might ease the distinction between solid and aqueous bands; in this case the technique only gives the total amount of water. Aqueous particles will form for RHs higher than the deliquescence RH, but for RH values in the immediacy of the DRH, and for the non-deliquescing NaI, supersaturated solutions or even partially aqueous particles will presumably form. However, we cannot characterize these last cases in detail. Anyway, we have tried to clarify this point in the 3.4.2 subsection of the manuscript wherever a misunderstanding may arise.

### “Liquid” or aqueous organic acid:

Regarding the distinction between the organic acid (especially hexanoic acid) in pure liquid or dissolved aqueous phase, we did not detect any infrared signal of aqueous hexanoic (or any other) acid, so their concentration must be very small or negligible (as expected from the low solubility of the acids). Certainly, one must expect that some of the infrared absorption bands of the acids change when dissolved in water (for example, the C=O strech). In order to clarify as much as possible, we have added the following sentence in the first paragraph of 3.4.1 subsection, when the deliquescence and efflorescence results are presented:

> "For all cases, no infrared absorption bands arising from aqueous dissolved acids were detected, so in all the subsequent discussion all the organic acids are assumed to be undissolved in liquid water."

### Dynamics of water exchange in HA covered particles:

When referring to the dynamics of deliquescence (p. 4399, lines 15-26), particles are assumed to be initially dry but surrounded by gas-phase molecules. For the efflorescence process discussion (p. 4399, lines 26-29 and p. 4400, lines 1-2), initially the particles are aqueous with an organic covering; then gradually RH is lowered and liquid water is lost. To avoid ambiguity, the sentences at the starting of either discussion have been rewritten:

> " In all deliquescence curves, there is a competition for surface positions between adsorbed HA and gaseous water, as indicated by the evolution of the amounts of liquid HA and water with RH (or, equivalently, the relative amount of gaseous water) in Figure 5. This can be reasoned as follows: in the deliquescence spectrum of Figure 5, the amount of liquid HA decreases as RH (and consequently the amount of gaseous water) increases, indicating that, if we start from a dry crystalline NaX particle covered with HA, gaseous water tends to displace HA molecules away from the particle surface (as manifested by the reduction in the amount of liquid HA as RH increases), to try to accommodate themselves on the NaX solid surface. "

And also:

"In efflorescence, however, the observed behavior is different: removal of liquid water from aqueous particles having an organic HA coating due to the decrease of RH is accompanied by removal of HA from the particle surface. This effect can be explained ..."

9. Another aspect that needs to be clarified in the discussion is whether the authors are describing kinetic effects on the water uptake process or thermodynamic (equilibrium) phenomena? In either case, what are the times scales involved in the measurements? How long do the aerosol condition to the various humidities? What assumptions have been made about the equilibrium state of system when making the analysis? Is the water uptake "barrier" described (e.g. p. 4403, l. 23) meant as a kinetic barrier or caused by a change in interaction energies or both? It would be beneficial to clarify, since some earlier studies have specifically addressed kinetic limitations of organic coatings. The authors do not support their hypotheses with either results of molecular dynamics simulations or quantified specific thermodynamic parameters. For example, by the lowering of the Gibbs free energy of the system mentioned on p. 4399, l. 1, are the authors relating to aerosol surface tension? And when describing how "water molecules exiting the particle will sweep away HA molecules from their surface locations" (p. 4400, l. 1), is there any simulations to support this process? The water molecules are an order of magnitude lighter in terms of molecular weight than the organics, does this have any impact on the mechanism described? In the introduction the authors reference a study showing that "the mass accommodation coefficient decreased with the degree of surface coverage of the hydrocarbon backbones" (p. 4388, l. 6). What are the rel-evant concentration ranges? How are they comparable to or applicable for the droplet surfaces in the present study?

This work has been carried out under the assumption that the aerosol system has sufficient time to equilibrate thermodynamically with both the organic acids and water, as the aerosol flow and that of the water vapor are small. However, we cannot exclude kinetic limitations in the studied systems, as organics/particle/water mixing time is limited (of the order of a few seconds). Regarding the time scales of the measurements, on the one hand, 5 minutes are needed to stabilize the system various flows previous to any measurement. On the other hand, each spectrum needs around 30 seconds to be recorded. In the case of SEM experiments, we have deposited particles in a glass slide during 30 minutes, to ensure a correct cover of particles.

**Water uptake "barrier":**

The water uptake “barrier” mentioned in the Conclusions refers to an increase in energy that the system must overcome to reach the DRH point. As long as the system is in equilibrium, it would be a thermodynamic energy, but the system can be metastable so we cannot exclude that, given enough time, the system would evolve.

**Molecular dynamics simulations**:

It is true that no molecular dynamics simulations have been carried out for this work, and it is the purpose of the authors to do so for future work, as these calculations allow to get a better microscopic view of the processes taking place. Instead, we have done our extrapolations basing on articles such as Ma et al., 2001(Molecular dynamic simulation of dicarboxylic acid coated aqueous aerosol: structure and processing of water vapor) or Sun et al. 2012 (Molecular dynamics simulations of the surface tension and structure of salt solutions and clusters). In the case of the lowering of the Gibbs energy of the system mentioned on p. 4399, l1, we related NaCl/organic acid interaction to explain the enhancement the entrance of water in the particles. And finally, we based our assumption of how “water molecules exiting the particle will sweep away HA molecules from their surface locations” (p. 4400, l. 1) on spectroscopic evidences. In other words, is important to note that the quantity of liquid hexanoic acid decrease as relative humidity increases (figure 5). Consequently, we attribute this behavior to the repulsive interactions between water and hexanoic acid, which tend to remove hexanoic acid from the particles. Nevertheless, we realize that this is only an assumption.

The mechanism described in this work is based on empirical data, for this reason it can be said that the difference in weight between water and organic acids does not have impact on the mechanism described.

Finally, Takahama and Russell (2011) have given some values of how presence of organic films affects the mass accommodation, which is defined as the fraction of molecules collinding with the surface that enter the liquid phase. They calculated that octanoic acid and tetradecanoic acids coatings with coverage of 29 $Å^2$/molecule reduced the mass accommodation coefficient from 1.0 to 0.30 and 0.0 respectively. Taking this an account, it is not strange that in our experiments DRH value diminish considerably on NaX/LA with respect to NaX/HA and NaX/OA. For this reason, we extrapolate to our experiments the behavior presented for Takahama and Russell (2011)

10. What is meant with an “activated process” (p. 4399, l. 3)?

By saying that efflorescence is not an activated process we mean that there is not an energy barrier to efflorescence, so aqueous particles loss water gradually as RH is lowered. In contrast, in the deliquescence process, there is an energy barrier that the system (solid particle + gaseous water) has to overcome to became liquid. This concept is not more clearly explained in p. 4399, line 3.

11. How is it seen that “: : :in Fig. 5 indicates that, in all deliquescence curves, there is a competition for surface positions between adsorbed HA and gaseous water” (p. 4399, l. 17)?

In the deliquescence curves of hexanoic acid (Figure 5) the existence of "a competition for surface positions between adsorbed HA and gaseous water" can be concluded because, in the deliquescence curve, the absorbance of liquid hexanoic acid (which can be monitored by the intensity of bands near 3000 and 1700 $cm^{-1}$) decreases while RH increases. This behavior can be explained by considering that, when RH is increased (so the amount of gaseous water surrounding the particle increases) gaseous molecules will displace liquid hexanoic in the surface of particles.

This aspect is now explained more clearly in the manuscript (p. 4399, line 17):

> "The evolution of the amounts of liquid HA and water with RH (or, equivalently, the relative amount of gaseous water) in Figure 5 indicates that, in all deliquescence curves, there is a competition for surface positions between adsorbed HA and gaseous water. This can be reasoned as follows: in the deliquescence spectrum, the amount of liquid HA decreases as RH (and consequently the amount of gaseous water) increases, indicating that gaseous water tends to displace HA molecules away from the particle surface, to try to accommodate themselves on the NaX solid surface."

12. When “Gaseous water tends to displace HA molecules away from the particle surface” (p. 4399, l. 18), does that specifically mean that the organic evaporates or are the molecules displaced within the surface or to the aerosol bulk? This is also unclear on p. 4394. If it indeed is the first, what are the implications of this evaporation for atmospheric processes, as well as when relating the present results to other studies of hygroscopicity, for example with HTDMA? Note that this organic evaporation is often (implicitly) assumed not to occur, when using other experimental techniques. I do realize that since water is quantified directly without an assumption of particle volume, this does not have the same implications for the present work as would otherwise be the case.

By saying that "gaseous water tends to displace HA molecules away from the particle surface", we do not mean that it is a simple evaporation process of HA from NaX particle surface, as the vapour pressure of hexanoic acid (0.267 mbar at 20ºC) is too low at the temperature of the aerosol flow, after condensation of HA on particles has taken place. The effect is related to the amount of gaseous water molecules around the particle (the RH): higher amounts of HA are removed from the particles at higher RH, as can be seen from the infrared absorption intensity of HA in Figure 5. So we conclude that there must be a competition for surface locations between adsorbed HA and gaseous water molecules. This effect must be due to a thermodynamic energy balance: an increase in the number density of gaseous water molecules will increase the Gibbs energy of the whole system (particle + vapor); at the DRH, the system minimizes its thermodynamic energy by deliquescing. The presence of an organic covering over the particle will hinder the process, creating an energy barrier to deliquescence, so gaseous water molecules will tend to displace adsorbed HA molecules to overcome the barrier.

13. The discussion of salting-out effects and in particular the implications for the present results are somewhat unclear (p. 4399, l. 9-12). Salting-out (or -in) effects could be highly sensitive to aerosol mixing state, in terms of water content (organic and inorganic aqueous concentrations) and relative organic-inorganic ratios. Could the authors comment on this for the presented results?

Our comments about the salting-out effect of aqueous NaCl solutions towards organic species, specifically hexanoic acid, are based on the paper by Demou and Donaldson (Demou, E., and Donaldson, D. J. 2002). These authors comment about the influence of NaCl concentration in aqueous solution on the surface/solution partitioning of hexanoic acid. They found that, for a given solution concentration of HA on aqueous NaCl solution, an increase in salt concentration produces an increase in the surface concentration of HA. On the other hand, if HA is adsorbed on the aqueous solution from the gas phase, the surface concentration of HA decreases with an increase of NaCl concentration. However, the magnitude of these effects is rather small for hexanoic acid.

Related to these facts, these authors give two conclusions relevant for atmospheric aerosols:

a) for aerosol formed from ocean spray, including organics, there will be a significant propensity for the appearance of an organic coating, due to the salting out effect.

b) for aerosol formed by uptake of gaseous organic vapor in the atmosphere on aqueous salt droplets, the tendency to adsorb organic species will decrease with the increase of salt concentration.

In our efflorescence results, we observe that specially HA is removed as liquid water is removed due to a reduction in RH. In the manuscript, we comment that the salting out effect will contribute to this effect. However, according to the results of Demou and Donaldson, the salting out effect will produce rather a decrease in the concentration of dissolved HA in the particles, carrying them to the surface; eventually the HA will be removed from the surface together with the liquid water by the mechanism explained in the manuscript: water molecules exiting the particle will sweep away HA molecules from their surface. Anyway, due to the small magnitude expected for this effect in HA, we do not think that it will appreciably influence the results.

It is true that in our manuscript the discussion of the salting out effect is not very clear, because several effects are mentioned and somewhat mixed up, so we have rewritten it in the following way:

> "The efflorescence process in NaX aqueous particles is not substantially affected by the presence of the acid. As there is not an energy barrier to the efflorescence process (in contrast to deliquescence), water loss takes place gradually as RH is lowered. Additionally, the salting out effect of NaCl will make dissolved organic acid molecules (specially the most water soluble HA) gradually move to the surface as the concentration of the salt solution increases (Demou and Donaldson 2002), and will be eventually removed from the surface together with water. However, the magnitude of the salting out effect for HA is rather small (Demou and Donaldson 2002)."

14. The authors make no attempt to relate their results to studies of hygroscopicity using the K-value framework (Petters and Kreidenweis, 2007). As I understand, the calculated water contents using the assumptions in section 3.5 could immediately facilitate this. Again, it would be most useful to know what aerosol sizes are concerned, as well as have an estimate for the experimental uncertainties involved in the reported water contents. Furthermore, are there any biases in the measurements with respect to surface and bulk components of the aerosols? Are all molecules "counted" equally, regardless of being in the bulk or on the surface of a particle? If there are biases, how well-quantified are they?

**Kappa parameter**:

The kappa parameter is a hygroscopic parameter that relates particles dry diameter and cloud condensation nuclei activity. In our experiments, the relative humidity with the water accepted/shrunk by polydisperse particles has been compared. For the purpose of obtaining the kappa parameter, Petters and Kreidenweis (2007) related particle dry diameter with expected supersaturation – wet diameter. Unfortunately, we cannot get the activation diameter with our laboratory equipment and, for these reason, we are not able to give the kappa parameter. Taking our instrumental limitation on account, spectroscopic studies combined with deliquescence and efflorescence processes have been chosen. It is important to note that calculations done in section 3.5 are for an estimate that the thinness of organic layer increases with the number of molecules of organic compound. Unfortunately, those values are not safe enough to give a reliable kappa value.

**Bulk or surface measurements**:

Infrared absorption spectra give the molecular vibrational frequencies, which depend on the environment around the molecules. So gas-phase, surface and bulk molecules will absorb at (slightly) different frequencies. In that respect, the technique does not produce any bias, and it will equally detect bulk or surface molecules. However, the signal intensity is proportional to the molecule density number. As molecules at the surfaces (i.e., monomolecular films) are usually in much lower proportion than those in the bulk, their infrared absorption signal will be very weak or absent. Nevertheless, in the context of the present work, the estimated thickness of the organic cover (ca. 30 nm) indicates that the coating consists of several molecular layers, so infrared signals from organic species in our experiment will come mainly from bulk organic phase (liquid or solid).

15. I appreciate that it may not be entirely possible to quantify the presented results within the K-value framework, but the reasons for this should then be specifically addressed and justified, in particular considering the audience of ACP. On p. 4403, l. 7, the authors mention "growth factors", but it is not clear to me what these growth factors are and where they are presented. The authors should also keep in mind that this term is used by many for a specific quantity determined in hygroscopic measurements, which may not be the same as what is meant in the present manuscript. I would be most interested to see the presented results more quantitatively related to other hygroscopicity measurements, not necessarily for the exact same compositions. The present study would benefit from highlighting the differences between the methods, for example I see the advantage of not needing to assume either volume additivity or make specific assumptions for the particle shape(s).

The question of kappa parameter is now explained in the first part of question 14.

The sentence on p. 4403, l. 7 has been changed to avoid mentioning the growth factor, and now it reads:

> "The amount of water uptaken by these particles is also unaffected by the organic coating."

16. Do the authors have any comments on the relevance of the agglomeration induced by lauric acid in the experiments for actual sea salt aerosol? Is it more related to the laboratory production process?

The agglomeration process in our experiment is the process wherein lauric acid particles (with or without NaX) collide with another particle and adhere to form bigger particles. Agglomeration or coagulation (on wet particles) is an interparticle phenomenon and the resulting effect is that the number of concentration and size of particles change as a function of time. The description of the theory is very complicated, and in our case is a challenge because of our size distribution is polydisperse. In our case, the agglomeration process occurs more rapidly than in case of monodisperse particles due to the combination of the large absorbing surface of the big particle and the small particles rapid diffusion. Taking this in to account, we only are able to conclude with general view of the consequences of this process:

a) The total number of particles is smaller in NaX/LA than in NaX

b) The size of particles is bigger in NaX/La than in NaX

Finally, we are not totally sure if the agglomeration occurs due to the laboratory production process, nevertheless it has been observed on other works such as:

- Gadermann, M, Preston, T, Troster, C, and Signorell, R. 2008. Characterization of palmitic and lauric acid aerosols from rapid expansion of supercritical CO2 solutions Molecular Physics 106(7):945-953.
- Krueger, B. J., Grassian, V. H., Iedema, M. J., Cowin, J. P., and Laskin, A. 2003. Probing heterogeneous chemistry of individual atmospheric particles using scanning electron microscopy and energy-dispersive X-ray analysis. Anal.Chem. 75:5170-5179.
- Kwamena, N. -. A., Buajarern, J., and Reid, J. P. 2010. Equilibrium Morphology of Mixed Organic/Inorganic/Aqueous Aerosol Droplets: Investigating the Effect of Relative Humidity and Surfactants. Journal of Physical Chemistry a. 114.

Some minor corrections:

p. 4384 l. 4: performed - investigated?
p. 4387 l. 28: pressures - pressure
p. 4394 l. 20: is decreases - decreases
p. 4395 l. 14+18 (and elsewhere): more amounts - larger amounts
p. 4396 l. 1: effect in - effect on
p. 4396 l. 3: similar than in - similar to (that of)
p. 4398 l. 2: retardation on - retardation in

p. 4403 l. 9: “non-deliquescencing NaI pure particles deliquesce at: : :” - ?

All minor language corrections have been carried out in the manuscript.

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# Interactive comment on "The effect of low solubility organic acids on the hygroscopicity of sodium halide aerosols" by L. Minambres et al.

**Anonymous Referee #3**

**Major comments:**

1. The background of the paper should be described more, especially impact of organics on the marine primary aerosol (POA) properties.

This issue has been expanded in the Introduction section, with new references. (The revised introduction has been added at the end of these comments).

2. Key facts about marine aerosol in the manuscripts are based on outdated publications – I suggest expanding bibliography a bit.

This point has been taken into account, and in the new version of the Introduction more recent findings are noticed. The Introduction has been substantially expanded with new references (see the revised Introduction).

3. Authors use a heating chamber technique to coat aerosol particles with an organic film. How is this relevant to the ambient aerosol? Maybe some explanation how the fatty acids may end up on the ambient sea salts particles would be in order?

Primary marine aerosols mixed with a surfactant can be generated by wind action on the sea surface, which is covered by a low solubility organic layer. Alternatively, heterogeneous nucleation in the troposphere can take place when low vapor pressure organic vapors at low concentration condense on aerosol particles, forming a surface coating, that can be evenly or unevenly distributed over the particle.

The method we have employed to coat organic substances is essentially the same standard method used by other authors in laboratory experiments. For example:

- Abbatt, J. P. D.; Broekhuizen, K.; Pradeep Kumar, P. Cloud condensation nucleus activity of internally mixed ammonium sulfate/organic acid aerosol particles. Atmospheric Environment (2005), 39(26), 4767-4778.
- Garland, R. M.; Wise, M. E.; Beaver, M. R.; DeWitt, H. L.; Aiken, A. C.; Jimenez, J. L.; Tolbert, M. A. Impact of palmitic acid coating on the water uptake and loss of ammonium sulfate particles. Atmospheric Chemistry and Physics (2005), 5(7), 1951-1961.

- Stemmler, K.; Vlasenko, A.; Guimbaud, C.; Ammann, M. The effect of fatty acid surfactants on the uptake of nitric acid to deliquesced NaCl aerosol. Atmospheric Chemistry and Physics (2008), 8(17), 5127-5141.

- Rouviere, A.; Ammann, M. The effect of fatty acid surfactants on the uptake of ozone to aqueous halogenide particles. Atmospheric Chemistry and Physics (2010), 10(23), 11489-11500.

- Garland Eva R; Rosen Elias P; Clarke Laura I; Baer Tomas. Structure of submonolayer oleic acid coverages on inorganic aerosol particles: evidence of island formation.
- Physical chemistry chemical physics: PCCP (2008), 10(21), 3156-61.

The procedure used to coat particles gets a reproducible amount of fatty acid on particles in a fast and convenient way. Although the organic vapor is produced from the bulk substance at 60-100ºC, the organic vapor subsequently gets in contact with the $N_2$ gas flow at ambient temperature, that effectively cools the vapor by rapid heat exchange (the number density of $N_2$ molecules in the gas flow is much higher than the number density of organic vapor molecules in the tube). Eventually, gas-phase molecules heterogeneously nucleate on salt particles in the $N_2$ gas flow. We assume that these processes will be essentially the same as those taking place in the troposphere, although the precise temperatures can vary. Although the process of gas cooling can be carried out more gradually to get more reproducible conditions, it produces the same overall result: a heterogeneous coating of the inorganic particle. We think that the main differences occur when changing the organic acid and the salt. Also the temperature of the process (our measurements are carried out at ambient temperature) will influence the result.

We have included information on the formation of particles coated with an organic film in the Introduction section:

> "Primary marine aerosols mixed with a surfactant can be generated by wind action on the sea surface, which is covered by a low solubility organic layer (Donaldson and Vaida, 2006). Alternatively, heterogeneously nucleated particles can form when low vapor pressure organic vapors condense on pre-existing aerosol particles, forming a surface coating, that can be evenly or unevenly distributed."

Also, the third paragraph of the "Materials and Methods" section includes an explanation (with references) on the relevance of the laboratory technique to reproduce atmospheric aerosol properties:

> "Although in the troposphere the whole process of heterogeneous nucleation of organic vapors takes place at overall lower temperatures, in our experiment the heated organic vapor gets in contact with the nitrogen gas flow at ambient temperature, that effectively cools the vapor by rapid heat exchange (the number density of nitrogen molecules in the gas flow is much higher than the number density of organic vapor molecules in the tube). Eventually, cooled gas-phase organic molecules heterogeneously nucleate on salt particles in the nitrogen gas

flow. In that way, the way to generate heterogeneously nucleated particles can be assumed to follow the same physical process than in the atmosphere, although the temperatures can vary over a broad range."

4. More information on the overall aerosol composition should be presented – how much of NaI or NaBr in percentage is present in the marine aerosol? Is it enough to impact the bulk hygroscopicity of the aerosol, or rather more emphasis should be put on the NaCl as it is the major compound of the marine aerosol?

The information about composition of sea salt has been expanded in the first paragraph of the Introduction (see revised Introduction). Although the percentage of bromide and iodide ions in sea salt is too small to affect overall hygroscopicity of sea salt particles, which will be dominated by NaCl behaviour, these ions tend to segregate to the surface of particles, so the water uptake ability of the particle surface may be enhanced due to the presence of bromide and iodine ions. As processes taking part on the surface of particles are important (gas uptake, heterogeneous reactions), we think that it is important to examine the water uptake behavior of these minor species. These points are now more stressed in the Introduction.

## Minor comments:

P4385, L6: What other physico-chemical properties? It is important.

The properties are explained in the first paragraph of the new Introductiont:

"They also can uptake significant amounts of water, exhibiting deliquescence and efflorescence properties under atmospheric conditions (Freney et al 2009; Martin 2000; Metzger and Lelieveld 2007; Mikhailov et al 2013; Wise et al 2012), that can change the particles' phase and size, together with other interrelated physico-chemical properties: for example, water uptake increases particle size, thus favouring their sedimentation."

P4385, L11: Is this really relevant here? If yes, describe a bit more.

The role of bromine and iodine has been explained in more detail (see the revised Introduction).

P4385, L14: Vague. Describe better how can you quantify such link and how especially how the chemistry of sea water may influence size distribution of aerosol particles (important for models).

The main results of the referenced work are given, although the chemical change is related to organic matter (see the revised Introduction).

P4385, L17: Important papers are missing, expand this section by brief explanation of how much organics can be enriching the sea salt POA and what is the impact of enrichment on the properties of aerosol, link between biogenic activity and fraction of organics in the POA, statistics of the marine aerosol measured at coastal stations (e.g. (Bialek et al., 2012; Fierz-Schmidhauser et al., 2010; O'Dowd et al., 2004; O'Dowd et al., 2002; Ovadnevaite et al., 2011a; Ovadnevaite et al., 2011b; Vaishya et al., 2013)

The section has been rewritten, as can be seen in the new version of the Introduction (see the revised Introduction).

P4385, L21: Again, refer to follow-up study by (Ovadnevaite et al., 2011a)

References are given in the new version of the Introduction (see the revised Introduction).

P4385, L25: What are the implications of this statement?

The implications are explained in a rewritten sentence:

"Other models predict that certain fatty acids form pockets of micelles within the aerosol, modifying the surface tension of the particle and therefore changing the water uptake properties of atmospheric aerosols (Tabazadeh 2005), and that core-shell structures are not always the most stable (Kwamena et al 2010), again affecting the particle water uptake properties and optical properties."
(See the revised Introduction, 4th paragraph).

P4385, L29: What reaction?

The sentence is more detailed now:

"The film may act as a barrier to transport across the interface, inhibiting uptake of atmospheric gases or reactions between gas phase reactants and particle surface, such as the heterogeneous reaction $NaCl + 2NO2 \rightarrow ClNO + NaNO3$ (Finlayson-Pitts 2003, Donaldson and Vaida 2006)."
(See the revised Introduction, 5th paragraph).

P4386, L2: those are the same processes – formation and growth depends on the hygroscopic properties of aerosol

The second part of the sentence has been omitted, and now it reads:

"In particular, the surface film can affect the process of cloud condensation nuclei formation and growth (Andrews and Larson 1993; Chuang 2003)."
(See the revised Introduction, 5th paragraph).

P4386, L4: Some data for mixing state and hygroscopicity has been recently published (e.g. (Bialek et al., 2012; Dall'Osto et al., 2009) extend your bibliography in this topic.

The paragraph has been rewritten with new references included:

"Organic compounds can also change the amount of light scattered by inorganic particles (Fierz-Schmidhauser et al. 2010; Dall'Osto et al. 2010; Vaishya et al. 2013). Marine primary organic aerosol (POA) can cause large local increases in the cloud condensation nuclei concentration by 15% to more than 100% (O'Dowd et al. 2004; Ovadnevaite et al. 2011b), and the ambient mass concentration and organic mass fraction of sea-spray aerosol are related to surface ocean biological activity. Despite considerable work has been carried out in the last years, there is still much uncertainty about fundamental issues of marine primary organic aerosol (POA), such as chemical composition, mixing state, hygroscopicity, cloud droplet activation, formation, aging and removal mechanisms (Gantt and Meskhidze 2013; ICCP 2013)".
(See the revised Introduction, 5th paragraph).

P4386, L8 Sentence lacks citation (e.g. (Ovadnevaite et al., 2011a))

The paragraph has been rewritten, and new citations are included. (See the revised Introduction).

P4387, L24: What are the sources of those acids in the marine aerosol? Any newer studies?

The sources are now cited, and are backed by new references:

"Hexanoic, octanoic and dodecanoic (lauric) acids belong to the family of alkanoic acids, that make a significant proportion of the organic compounds emitted from several sources to the atmosphere, such as seed oil and meat cooking procedures or emission by plants. These three acids have been observed in the atmosphere of remote marine and continental locations (Duce et al 1983; Gill et al 1983; Schauer et al. 1999; Limbeck et al 1999; Yassaa et al. 2001; Schauer et al. 2002; Samya eta al. 2010)."
(See the revised Introduction, last paragraph).

P4388, L4: Why is this important?

Now, the importance of the phenomenon is explained:

"The results indicate that formation of organic surfactant layers tend to slow NaCl deliquescence rate and to slightly lower its DRH. This may affect particle size and phase, changing the amount of scattered solar radiation and also the adsorption behavior of trace gases onto particles."
(See the revised Introduction, last paragraph).

P4388, L10-17: What is the flow through the system? Are all the splits isokinetic so that the same amount of particles goes to CPC, APS and FT-IR?

The sampling is nearly isoaxial, as the angle of the output tubes of the flow splitter relative to the input tube is very small

The aerosol flow rate through the system is 1.8 L/min. If $N_2$ is added to control RH, an extra of 5 L/min is added.

CPC inlet flow is 0.6 L/min

APS inlet flow is 1.0 L/min

So the sampling is sub-isokinetic.

These data are indicated later in the Materials and Methods section

P4389, L2: related to major comment 3. How is this way of coating relevant to the ambient measurements? The ambient processes are not taking place in such high temperatures – is it possible that the method introduces some bias in the data when compared with natural marine aerosols? It is worth to mention this in the manuscript. What about uncertainties and errors of measurements?

The main points have been addressed in the **Major comment 3**.

Error in temperature measurements: measurements were taken when temperature controller was stabilized (no difference between set and real temperature). The error of the thermocouple plus the display error is ±6.5% (0-200ºC). This information has been included in the Materials and Methods section.

P4389, L10: can you add figure showing the size distribution of generated aerosol? Comparison of treated and untreated aerosol could be of an additional value. Also, describe shortly the working principle of the FTIRS.

We have added a file with new figure showing the size distribution of NaCl and NaCl/LA particles measured by APS and SEM. In the case of the NaCl particles, we have showed two distributions, one from 0 to 0.3µm (SEM) and other from 0.5 µm to 6 µm (APS). In the case of NaCl/LA particles we showed one distribution from 0.5 µm to 6 µm (APS). The aerosol particle number concentration determined by CPC is 150000 part/cm$^3$.

In the Materials and Methods section, a new paragraph has been included to describe the working principle of the infrared spectrometer and some operating procedures:

> "Infrared extinction spectra are recorded in the 650-4000 cm$^{-1}$ range and 4 cm$^{-1}$ resolution. Infrared radiation from a colimated source (ORIEL 6580) travels lengthways the absorption cell, and the resultant radiation is directed to the infrared spectrometer (Figure 1). The incoming infrared beam is divided into two, after which both beams take slightly different path lengths, and recombine to construct an interferogram. The recombined intensity is recorded as the path length difference is changed. By applying the Fourier transform technique, the variation of the intensity with wavenumber is retrieved. The optical path is sealed and flushed by a current of dry air to reduce interference from ambient water and carbon dioxide. Background spectra are recorded after pumping out the aerosol cell. Sample spectra are averaged by collecting typically 32 scans."

P4390, L13 Use “is visible” (or similar) instead of “outstands”.

The change has been made.

P4391, L3: How it was visible in the CPC? CPC only counts particles.

The CPC only showed the presence of particles. It was assumed that these particles are formed by carboxylic acid. To be more precise, the sentence has been changed to:

> "CPC measurements confirmed the presence of particles, that were assumed to belong to the carboxylic acids"

P4391, L7: Explain the “surface effect in small particles”

In the section 3. Results and discussion (3.1. Infrared spectra of pure carboxylic acids), the effect has been explained in the following sentence:

> "Due to the interactions between surface molecules and the surrounding medium, the surface region has different structural and thus spectroscopic properties than the core of the particles (Firanescu et al 2006)"

P4391, L15: How much is slightly? Is it important for the experiment or not? Explain the indication of particle scattering and why you mention it here.

We mention the scattering phenomenon as it evidences the presence of particles in our system. We have rewritten the sentence to make this point more clear:

> "Further evidence of the presence of particles is given by the baseline increase to higher wavenumbers (Figure 2), which is indicative of particle scattering (Hinds 1998). This effect is more pronounced as T2 is increased. "

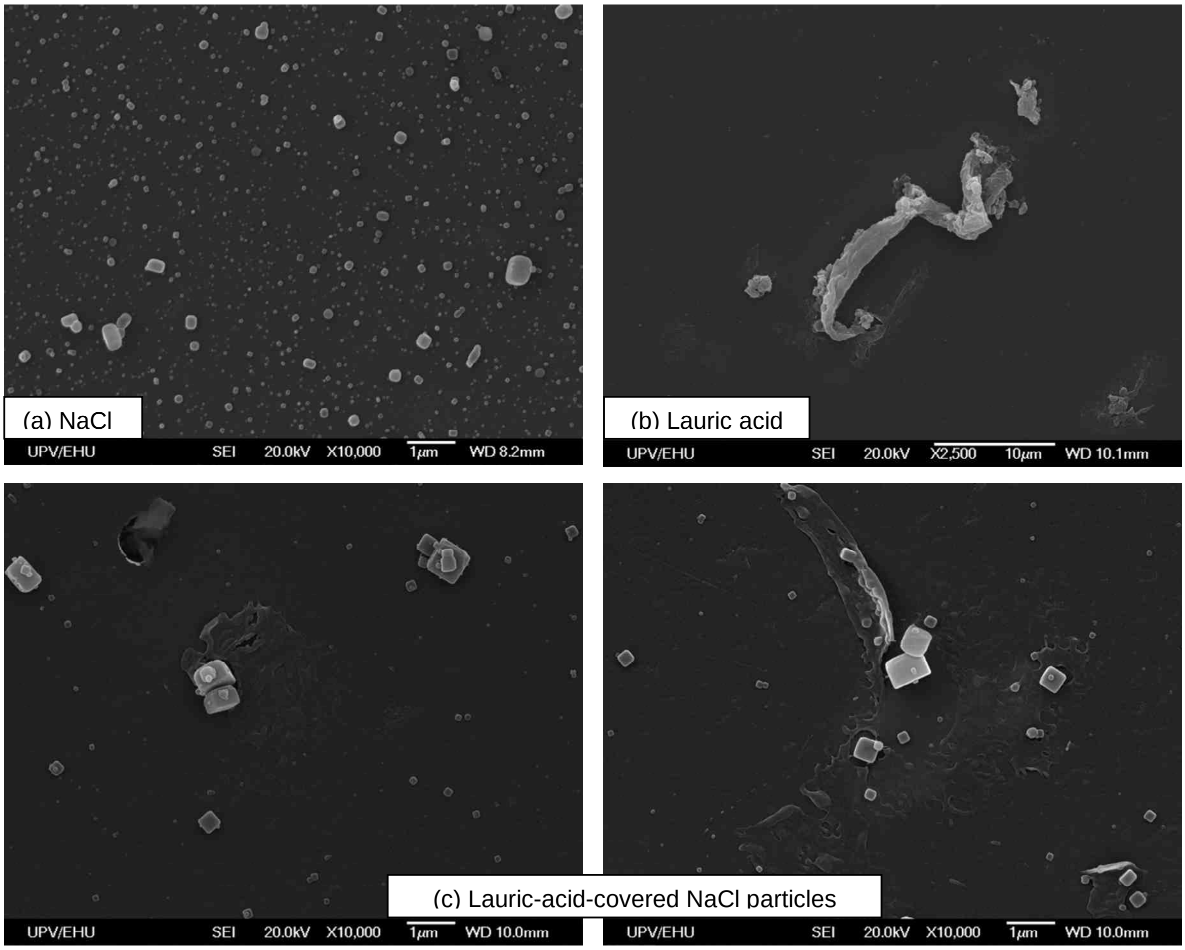
P4393, L1: According to figure 3, pure NaCl particles look much more round than those coated with acids (vide fig. 3a). This is rather strange providing that pure NaCl should have sharp cubes instead of roundish ovals. Is it possible that there was mix up of panels in this figure? One would expect that NaCl is represented on lower-left panel rather than on the upper-left. How the authors can be certain that upper-right panel shows LA instead of some organic artifact? (e.g. part of filter). EDX is not capable of distinguishing chemical compounds – only elements.

The reviewer is right, in the figure, the edges of the particles are "rounded", for this reason the particles look like not perfect cubes. We think that the main factor responsible of roundish NaCl particles is their high hygroscopicity: NaCl particles were deposited on the glass substrate but, although care was taken, particles were exposed to ambient air before being coated with the Au layer for an interval, what caused small water uptake and change of morphology. An important matter to taking account is the sputtering to the particles. The resolution of the images is dependent on the diameter of Au particles.

Finally, we discard a mix up of panels in the figure, as in lauric-acid-covered NaCl particles (panel (c) in Figure 3) the presence of lauric acid deposits can be seen on broad areas of the substrate. Besides, lauric acid tends to stick NaCl particles together, which is seen in panel (c) rather than in panel (a).
This issue has been taken into account in the manuscript. The mentioned paragraph has been modified in the section 3. Results and discussion (3.3. Morphology of pure and mixed particles) as follows:

> "SEM images of pure NaCl and LA particles, and of NaCl particles after covering them with LA, were recorded and are presented in Figure 3. This technique was not well suited to study particles that included OA or HA, due to their high vapor pressure at room temperature that difficulted their manipulation in the SEM vacuum chamber. Images of pure NaCl particles show particles of cubic form as expected but with their edges somewhat rounded, as a result of a short exposure of deposited particles to ambient air before being coated with the gold layer; as NaCl is very hygroscopic, they have uptaken a small amount of gaseous water enough to change their original morphology (see Figure 3a)."

Also, for easier visualization, the image from panel (a) in Figure 3 has been changed so that it matches the scale of the image in panel (c). The new image looks as follows:



P4394, L1: Which wavenumber represent the C=O bond?

In the section 3. Results and discussion (3.4. Deliquescence and efflorescence of heterogeneously nucleated NaX particles with HA, OA and LA [3.4.1. Infrared spectra of particles at various RHs]), we have reminded that the C=O band appears near 1700 $cm^{-1}$:

> "... we paid special attention to the C=O stretching band of the acids near 1700 $cm^{-1}$, and ..."

P4395, L6: It is worth mentioning that, in reality, water uptake by NaCl is happening before sudden deliquescence but the particles do not change their size but shape (become more “roundish” with increasing RH).

In the section 3. Results and discussion (3.4. Deliquescence and efflorescence of heterogeneously nucleated NaX particles with HA, OA and LA [3.4.2. Deliquescence and efflorescence curves]), the commentary has been included at the beginning of the paragraph:

"The deliquescence curve of NaCl/HA is very similar to that of pure NaCl particles, that deliquesce at DRH (298 K) = 75.3% (Tang and Munkelwitz 1993). No water uptake is detected until near 73% RH, where particles abruptly become liquid. However, SEM results show that particles uptake small amounts of water before sudden deliquescence, that are not enough to change their size, but modify their size slightly (becoming more "roundish" with increasing RH)."

P4395, L14: Correct “theparticles”. Particles do not uptake liquid water because liquid water is not present – only water vapour.

The typographical error has been corrected.

In the section 3. Results and discussion (3.4. Deliquescence and efflorescence of heterogeneously nucleated NaX particles with HA, OA and LA [3.4.2. Deliquescence and efflorescence curves]), the sentence has been changed to:

"In NaCl/OA, the particles uptake more amounts of liquid water vapour than in pure NaCl, whereas the opposite is observed for NaCl/LA"

P4397, L12: Again, in fig 3a NaCl particles are not cubic:

In the section 3. Results and discussion (3.4. Deliquescence and efflorescence of heterogeneously nucleated NaX particles with HA, OA and LA [3.4.2. Deliquescence and efflorescence curves]), the sentence has been corrected:

"Although the morphology of particles can sometimes influence their hygroscopic behavior, all NaX salt dry particles are expected to be cubic, as all of them have an octahedral crystal structure."

P4398, L11: Define FWHM and explain its application in the methods sections.

The meaning of FWHM has been given in the Introduction section, because its application was already given there (last paragraph of Introduction):

"Infrared spectroscopy is a well-known sensitive technique and has been applied to the study of organic/inorganic aerosol systems (Garland et al 2005; Najera and Horn 2009). It can yield aerosol composition, water content, and particle phase. Variations in the wavenumbers and widths of spectral bands (precisely their FWHM: full width at half maximum) can also reveal information about molecular interactions in mixed systems and the formation of new species."
(See the revised Introduction).

P4403, L11: The sentence is vague, please explain better how specific or use different wording.

In the section 4. Conclusion and atmospheric implications, this sentence has been rewritten as follows:

> "The general consequence is that the water uptake behavior of sodium halide particles coated with organic acids is dependent on the nature of the anion and the carboxylic acid."

P4403, L20: reword (maybe to: : : :,while the shortest one (HA) achieves the lowest.)

The sentence has been reworded following the suggestion.

Figure 1: Mark flows in the all branches of the setup.

The flows are now marked more clearly in Figure 1.

Figure 2: Expand figures so they are easier to read and explain values in the ellipses (e.g. x10).

The figure caption has been expanded and looks as follows:

> “Infrared extinction spectra of HA, OA and LA in different conditions: bottom spectra are from bulk phase acid; medium spectra corresponds to homogeneously nucleated acid particles; upper spectra are from heterogeneously nucleated acids onto NaCl particles. In all cases, the upper spectra have been increased for clarity (increasing factor: ×Number).”

Figure 3: Check the panels’ order! Maybe add EDX tables for each panel so it is certain that the particles on upper-left panels are pure NaCl?

The panel order is right. The issue has been explained previously.

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# REVISED INTRODUCTION

## 1. INTRODUCTION

Marine aerosol is one of the most abundant types of natural particulate matter in the Earth's troposphere. Sea salt particles play an active role in the Earth's radiative balance, influence mass transfer from gaseous substances and cloud-precipitation mechanisms, contribute to the formation of cloud condensation nuclei and have highly reactive surfaces that take part in heterogeneous and multiphase chemical reactions (Andreae and Rosenfeld 2008; Carslaw et al 2010; D O'Dowd and De Leeuw 2007; Finlayson-Pitts 2003; Lewis and Schwartz 2004; Quinn and Bates 2011; Rossi 2003). They also can uptake significant amounts of water, exhibiting deliquescence and efflorescence properties under atmospheric conditions (Freney et al 2009; Martin 2000; Metzger and Lelieveld 2007; Mikhailov et al 2013; Wise et al 2012), that can change the particles' phase and size, together with other interrelated physico-chemical properties: for example, water uptake increases particle size, thus favouring their sedimentation. In parallel, bigger particles increase the scattering of solar visible light, thus influencing atmospheric radiative transfer and visibility. The presence of water in atmospheric particles can also change the adsorption of trace gases and their chemical reactivity (e.g., sulfate chemistry proceeds by adsorption of gaseous $SO_2$ on aqueous particles, followed by oxidation to sulfate; this pathway is absent in crystalline particles).

Marine aerosol is generated either by the mechanical action of the ocean surface (primary sea-salt aerosol), or by gas-to-particle conversion processes (secondary aerosol) mainly in the form of nonsea-salt sulphate and organic species (O'Dowd et al 1997). Sodium chloride is the principal component of sea salt: typical sea water composition has $1.05\times10^4$ mg/L of sodium Na+ and $1.9\times10^4$ mg/L of $Cl^-$ (Lide 1994). Bromide ions are a minor component of seawater, and hence of sea salt particles, with a molar ratio of bromide to chloride of 1:650 (Lide 1994). Despite such a small contribution to the composition of sea salt particles, bromine plays a comparatively large role in tropospheric sea salt chemistry. The most important is the drop of surface-level ozone concentrations in the Artic at polar sunrise. This is due to the tendency of $Br^-$ to segregate to the salt surface in the presence of water, substantially increasing Br/Cl surface molar ratios, and to the fact that bromide ions exhibit a higher surface reactivity than chloride (Baker 2005; Ghosal et al 2008; Zangmeister et al 2001). Sea salt particles have been shown to be the source of BrO, which is involved in catalytic cycles that destroy ozone. (Finlayson-Pitts 2009; Frinak and Abbatt 2006; Hunt et al 2004; Read et al 2008; Von Glasow 2008). Although the concentrations of $I^-$ present in seawater are much smaller than those of bromine and chlorine (the molar ratio of $I^-$ to $Cl^-$ in seawater is ~1:$10^6$), there is evidence that iodine in the marine boundary layer has an influence on ozone destruction, the oxidizing capacity of the troposphere, denoxification, and particle formation (Carpenter 2003; Saiz-Lopez et al 2008). A similar role to BrO is played by IO, although its source is believed to come from marine algae (Read et al 2008). Recently advances have been made in quantifying the link between seawater chemical processes, and the production, size, and chemical composition of sea spray aerosol particles by simultaneous measurements of seawater, particle size distributions, and size-resolved single particle chemical composition in a laboratory setting reproducing the chemical complexity of sea spray aerosol, including natural seawater, breaking waves and controlled phytoplankton and heterotrophic bacteria concentrations (Ault et al 2013; Prather et al 2013) . It has been shown that the mixing state of sea aerosol is sensitive to the presence of heterotrophic bacteria, that transform dissolved organic matter.

Organic compounds are present in marine salt aerosol in variable proportions, that may represent a large fraction of the aerosol dry mass (Cavalli et al 2004; Gantt and Meskhidze 2013; Middlebrook et al 1998). The presence of significant concentrations of organic matter in marine aerosol was detected in earlier studies (Kleefeld et al 2002; Middlebrook et al 1998; Putaud et al 2000). Measures over the North Atlantic Ocean have revealed that the organic fraction contributes up to 63% to the submicrometre aerosol mass, of which about 45% is water-insoluble and 18% water-soluble (O'Dowd et al 2004). 37% hydrocarbon and 63% oxygenated hydrocarbon speciation was observed for the organic mass, indicating that at least 37% of the organic mass is produced via primary sea-spray (Ovadnevaite et al 2011a). It was found that predominantly organic particles contribute between 25 and 30% to general background marine number concentration, 35% for open ocean nucleation cases, and 60% for anthropogenically influenced cases (Bialek et al 2012). The organic fraction of marine aerosol can be highly enriched due to oceanic biological activity (Ault et al 2013; Gantt and Meskhidze 2013; O'Dowd et al 2002; Ovadnevaite et al 2011a; Rinaldi et al 2010). Much of the organic fraction corresponds to water insoluble fatty acids present as surface films on particles (Donaldson and Vaida 2006; Mochida et al 2002; Tervahattu et al 2002), but also as organic carbon more homogeneously mixed with cations and anions (Ault et al 2013). Moreover, fine mode marine organic aerosol can have a size distribution independent from that of sea-salt, while coarse mode aerosols are more likely to be internally mixed with sea-salt (Gantt and Meskhidze 2013).

Primary marine aerosols mixed with a surfactant can be generated by wind action on the sea surface, which is covered by a low solubility organic layer (Donaldson and Vaida 2006). Alternatively, heterogeneously nucleated particles can form when low vapor pressure organic vapors condense on pre-existing aerosol particles, forming a surface coating, that can be evenly or unevenly distributed. It has been proposed that the organic compounds arrange in a hydrophobic organic monolayer that encapsulates an aqueous particle, forming an “inverted micelle” structure (Ellison et al 1999). This model shows agreement with recent molecular dynamic simulation results (Chakraborty and Zachariah 2008). Other models predict that certain fatty acids form pockets of micelles within the aerosol, modifying the surface tension of the particle and therefore changing the water uptake properties of atmospheric aerosols (Tabazadeh 2005), and that core-shell structures are not always the most stable (Kwamena et al 2010), again affecting the particle water uptake properties and optical properties.

The presence of an organic film at the surface of a particle may affect its physical and chemical properties in a number of ways. The film may act as a barrier to transport across the interface, inhibiting uptake of atmospheric gases or reactions between gas phase reactants and particle surface, such as the heterogeneous reaction $NaCl + 2NO_2 \rightarrow ClNO + NaNO_3$ (Donaldson and Vaida 2006; Finlayson-Pitts 2003). In particular, the surface film can affect the process of cloud condensation nuclei formation and growth (Andrews and Larson 1993; Chuang 2003). Organic compounds can also change the amount of light scattered by inorganic particles (Dall'Osto et al 2010; Fierz-Schmidhauser et al 2010; Vaishya et al 2013). Marine primary organic aerosol (POA) can cause large local increases in the cloud condensation nuclei concentration by 15% to more than 100% (O'Dowd et al 2004; Ovadnevaite et al 2011b), and the ambient mass concentration and organic mass fraction of sea-spray aerosol are related to surface ocean biological activity. Despite considerable work has been carried out in the last years, there is still much uncertainty about fundamental issues of marine , such as chemical composition, mixing state, hygroscopicity, cloud droplet activation, formation, aging and removal mechanisms (Gantt and Meskhidze 2013; ICCP 2013). Several laboratory studies about the effect of organic surfactants, such as palmitic and oleic acids, on NaCl, ammonium sulfate or mineral dust aerosol particles as a function of relative humidity have been reported employing a variety of experimental techniques, such as electrodynamic balance, infrared spectroscopy, electrical mobility, optical tweezers, cavity ring-down spectroscopy or nonlinear spectroscopy (Cwiertny et al 2008; Davies et al 2013; Dennis-Smither et al 2012; Ebben et al 2013; Garland et al 2005; Hansson et al 1998; Najera and Horn 2009; Robinson et al 2013; Rossi 2003; Rubasinghege et al 2013). The general conclusions are that hygroscopic growth, deliquescence relative humidity (DRH) and efflorescence of the particles may be affected by several factors, such as coating thickness or structural arrangement of the organic film. Special effort has been carried out to study the morphology and phase partitioning of aerosol particles consisting of hydrophobic and hydrophilic phases (Ciobanu et al 2009; Kwamena et al 2010; Reid et al 2011; Veghte et al 2013). On the other hand, molecular dynamics calculations are becoming a commonplace theoretical approach in atmospheric aerosol modeling, that includes sea salt particles mixed with organic molecules (Ma et al 2011; Sun et al 2012; Sun et al 2013; Takahama and Russell 2011).

As a whole, laboratory studies on inorganic particles coated with surfactant organics have mainly focused on a few organic molecules, and most of them have been carried out with ammonium sulfate or sodium chloride. Very few studies of hygroscopic behavior have been carried out on particles containing bromide or iodide. Furthermore, sodium chloride, bromide and iodide particles exhibit very different hygroscopic properties and interact differently with water soluble dicarboxylic acids such as succinic acid (Minambres et al 2011). It has been reported that rates of gaseous iodine emissions during the heterogeneous reaction of $O_3$ with interfacial iodide are enhanced several-fold by the presence of alkanoic acids on water, such as octanoic and hexanoic acid (Hayase et al 2011). In the present work we study the hygroscopic properties of NaX (X=Cl, Br, I) sodium halide salts coated with either one of three different surfactant carboxylic acid molecules by Fourier-transform infrared extinction spectroscopy in an aerosol flow tube, aided by particle sizing methods. The examined acids, all contain one carboxylic group at the end of the molecule, are hexanoic ($CH_3(CH_2)_4COOH$), octanoic ($CH_3(CH_2)_6COOH$) and lauric acid ($CH_3(CH_2)_{10}COOH$), hereafter shortened as HA, OA and LA, respectively. These acids have water solubilities of 9.9, 0.68 and 0.058 g/L at 20ºC, respectively (see Table 1 - The Merck Index: An encyclopedia of chemicals, drugs and biologicals (11th Ed.), Merck, 1989), and have been selected as they are expected to influence the hygroscopic behaviour of sea-salt particles differently in view of their water solubilities: hexanoic acid has intermediate solubility between highly soluble and highly insoluble organic acids, whereas lauric acid, on the other end, can represent highly insoluble fatty acids, octanoic acid lying in-between. Due to their overall low water solubility, pure fatty acids are not expected to present significant intrinsic hygroscopic properties. Infrared spectroscopy is a well-known sensitive technique and has been applied to the study of organic/inorganic aerosol systems (Garland et al 2005; Najera and Horn 2009). It can yield aerosol composition, water content, and particle phase. Variations in the wavenumbers and widths of spectral bands (precisely their FWHM: full width at half maximum) can also reveal information about molecular interactions in mixed systems and the formation of new species. Infrared spectra have been combined with electron scanning microscopy (SEM) of particles, a technique that has been demonstrated to be useful to study the chemistry of isolated, individual particles of atmospheric relevance (Krueger et al 2003; Veghte et al 2013). Hexanoic, octanoic and dodecanoic (lauric) acids belong to the family of alkanoic acids, that make a significant proportion of the organic compounds emitted from several sources to the atmosphere, such as seed oil and meat cooking procedures or emission by plants. These three acids have been observed in the atmosphere of remote marine and continental locations (Duce et al 1983; Gill et al 1983; Limbeck and Puxbaum 1999; Samy et al 2010; Schauer et al 1999; Schauer et al 2002; Yassaa et al 2001).Octanoic and lauric acids exist as liquid and solid, respectively, at typical tropospheric temperatures and pressures. Hexanoic acid has higher vapor pressure than the atmospherically more abundant long chain acids, that may contribute more substantially to vapor phase processes. A few studies have been presented describing the effects of octanoic and lauric acids on the hygroscopicity of NaCl (Hämeri et al 1992; Hansson et al 1998; Wagner et al 1996). The results indicate that formation of organic surfactant layers tend to slow NaCl deliquescence rate and to slightly lower its DRH. This may affect particle size and phase, changing the amount of scattered solar radiation and also the adsorption behavior of trace gases onto particles. Molecular dynamics simulations of water vapor molecules impinging on a slab of water coated by octanoic acid film showed that the mass accommodation coefficient decreased with the degree of surface coverage of the hydrocarbon backbones (Takahama and Russell 2011).

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