

Identification of an organic coating on marine aerosol particles by TOF-SIMS

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[1] Marine aerosol particles play an important role in atmospheric processes. It has been suggested that as marine aerosol particles form, they acquire a coating of organic surfactants. This theory has been supported only by indirect evidence. Recently, we gave new morphological indication of such organic coating without however providing molecular speciation. Here we have studied the surface of marine aerosol particles by time-of-flight secondary ion mass spectrometry (TOF-SIMS), which is very suitable for surface research due to its unique combination of surface sensitivity and the detailed molecular information obtained. Spectra from the outermost surface gave high intensity for palmitic acid and lower peaks for other fatty acids. According to TOF-SIMS images, palmitic acid was distributed on small particles, similar with the marine particles. Sputtering stripped palmitic acid and revealed the inner core of the sea-salt particles. Our results show that fatty acids are important ingredients of the outermost surface layer of the studied aerosol particles. **INDEX TERMS:** 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; 4548 Oceanography: Physical: Ocean fog and aerosols; **KEYWORDS:** marine aerosol, sea salt, particles, palmitic acid, TOF-SIMS, organic surfactant

1. Introduction

[2] According to the recent estimation of the *Intergovernmental Panel on Climate Change (IPCC)* [2001], global sea-salt emission are larger than all other natural and anthropogenic emissions together, the total flux being 3,300 Tg/yr in 2000. Sea-salt aerosol may be the dominant contributor to both light scattering and cloud nuclei in those regions where wind speeds are high and/or other aerosol sources are weak [IPCC, 2001; O'Dowd *et al.*, 1997; Murphy *et al.*, 1998]. The production of sea-salt aerosol is a strong function of wind speed, which is predicted to increase due to the global climate warming. Accordingly, sea salt emissions may increase to 5,880 Tg in 2100, which might lead to a potential radiative feedback of -0.8 Wm^{-2} [IPCC, 2001]. These calculations involve many uncertainties, including the properties of sea-salt particles.

[3] One important question is the assumed organic coating on marine aerosol particles. It has been suggested that as the marine aerosol particles form, they acquire a coating of organic surfactants [Blanchard, 1964; Gill *et al.*, 1983; Middlebrook *et al.*, 1998; Ellison *et al.*, 1999]. This theory

has been supported only by indirect evidence [Blanchard, 1964; Gill *et al.*, 1983; Middlebrook *et al.*, 1998; Ellison *et al.*, 1999; Tervahattu *et al.*, 2002; Baier, 1972; Husar and Shu, 1975; MacIntyre, 1972, 1974]. It is based on the works of Langmuir [1917] and Blodgett [1935], who showed that amphiphilic molecules, including lipids, could be assembled as monomolecular layers at air/water interfaces as well as transported to a solid support. Marine aerosols play an important role in atmospheric processes [O'Dowd *et al.*, 1997; Fitzgerald, 1991]. The presence of surface film may have an impact on their chemical, physical and optical properties, which may lead to a higher albedo and global negative forcing [Facchini *et al.*, 2000; Li *et al.*, 1998; Facchini *et al.*, 1999; Charlson *et al.*, 2001].

[4] The suggested surface film on sea-salt particles may originate from marine organisms, being mainly made up of fatty acids. As cells die, the hydrophobic constituents rise toward the ocean's surface. Ellison *et al.* [1999] estimated that 200 Tg yr⁻¹ of the "biological oil slick" will be concentrated at the ocean/atmosphere interface and is available for incorporation on to the surface of marine aerosols. Osterloh [1993] showed that palmitic acid had by far the highest concentration of dissolved fatty acids in Baltic Sea water followed by myristic acid, lauric acid, and stearic acid. Palmitoleic acid and oleic acid were the most abundant

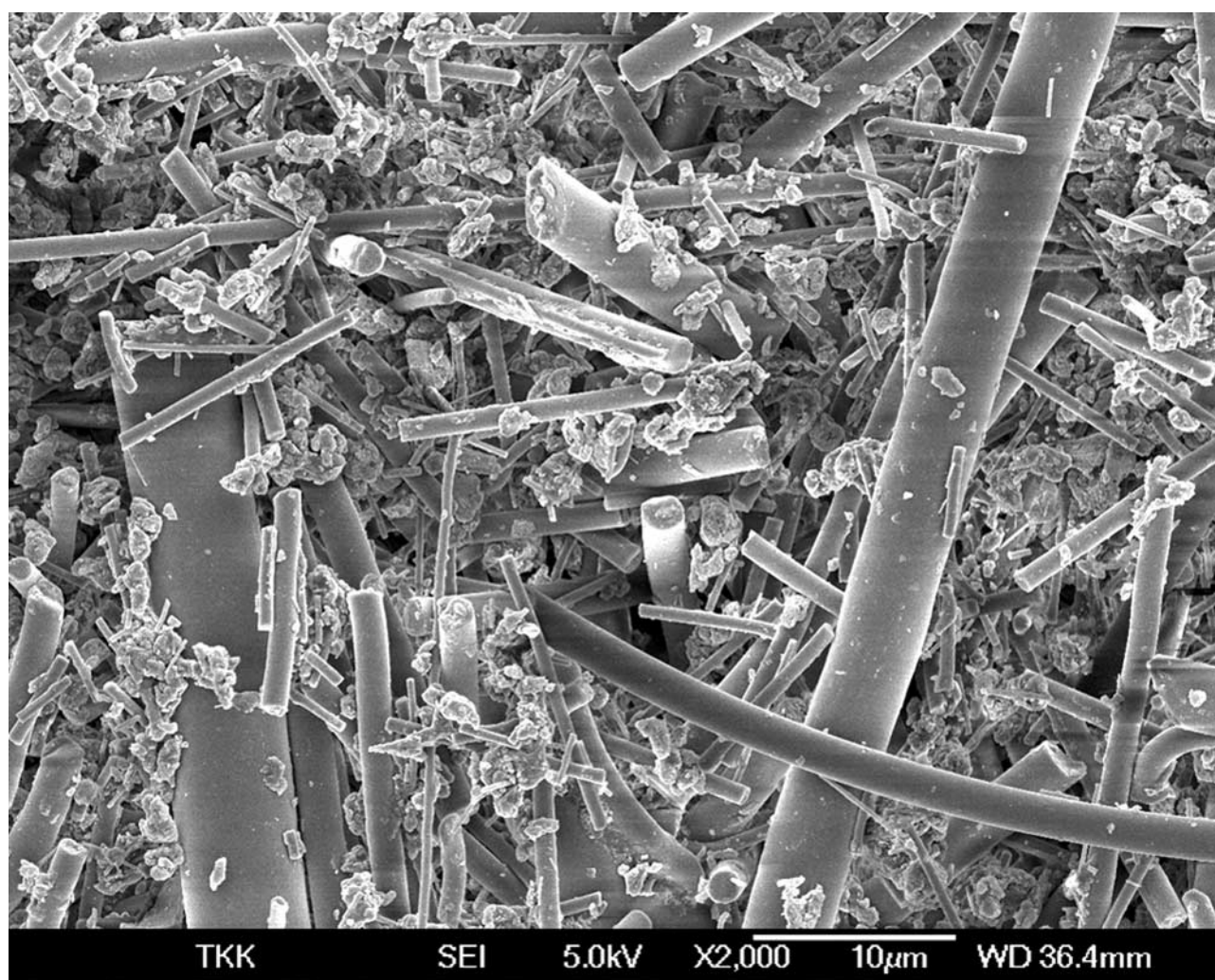


Figure 1. A scanning electron microscope micrograph of the studied sample. Single particles (diameter $\sim 1 \mu\text{m}$) and groups of particles are lying between the fibers of the filter. About half of the particles are coated by an organic layer [Tervahattu *et al.*, 2002]. Scale bar $10 \mu\text{m}$.

unsaturated acids. Marty *et al.* [1979] calculated that fatty acids (mainly C_{12-18}) are important components of the marine aerosol, in which they are enriched in relation to surface water by an enrichment factor $\sim 5-9 \times 10^4$. Fatty acids have been reported to be major constituents of marine aerosols in many other investigations [Barger and Garrett, 1976; Gagosian *et al.*, 1981; Sicre *et al.*, 1990; Stephanou, 1992a]. However, none of the mentioned investigations could show anything about the location of fatty acids in the aerosol particles.

[5] Sea-to-air flux of fatty acids may be caused also by bubble scavenging [Blanchard, 1989]. Air bubbles rising to the surface can collect any material, dissolved or particulate, that is surface active and makes contact with the bubbles. When they burst, the material is skimmed off the bubbles to become highly enriched in the sea-salt drops. The enrichment factors can exceed several hundred for bubbles that have risen only a few centimeters.

[6] In our previous article [Tervahattu *et al.*, 2002], we presented results of an extraordinary aerosol episode, which occurred in Helsinki at the end of February 1998. The air masses came from the North Atlantic Ocean, as demon-

strated by air trajectories from the European Centre for Medium-Range Weather Forecasts. The particles (size mainly $\sim 1 \mu\text{m}$) did not exhibit solid shape, when examined by a scanning electron microscope (SEM, Figure 1). They were “bubbling” or “pulsating” continually, enlarging in one part and shrinking in another. Analyses by an energy dispersive X-ray microanalyzer (EDX) showed that the particles contained much carbon and together with it, mainly oxygen, sulphur and sodium. Ion chromatographic analyses revealed high concentrations of sodium, sulfate, nitrate, and ammonium, indicating the impact of polluted air during the flow over continental area. The shape fluctuations and the carbon content observed by SEM/EDX, led to the suggestion that the aerosols were enclosed by an organic membrane. Investigations with mass spectrometry using a direct insertion probe (DIP-MS) showed remarkable amounts of fragmented aliphatic hydrocarbons, which were considered to be a possible indication of a lipid membrane on the surface of the particles.

[7] In this work, the surface of atmospheric aerosol particles was studied by time-of-flight secondary ion mass spectroscopy (TOF-SIMS) in order to get molecular infor-

mation, essential for further understanding of the role of the surface layer in radiative transfer and atmospheric chemistry. TOF-SIMS is well suited for surface research, due to the unique combination of surface sensitivity and the detailed molecular information obtained [Brenda *et al.*, 1999; Hagenhoff, 2000]. The technique has been shown appropriate for aerosol particle research [Rost *et al.*, 1999; Van Ham *et al.*, 2000]. For SIMS analysis, a solid surface is bombarded by primary ions of some keV energy. The primary ion energy is transferred to the target atoms via atomic collision and a collision cascade is generated. The interaction of the collision cascade with surface molecules is soft enough to allow even large and non-volatile molecules with masses up to 10,000 amu to escape without or with little fragmentation. The emitted particles originate from the uppermost one or two monolayers.

2. Experiment

[8] We studied the same marine aerosol samples, which were used in our previous work [Tervahattu *et al.*, 2002]. Several other samples collected with the same sampler immediately before and after the studied episode as well as with different samplers at other places were studied for comparison. An Eberline FH 62 I-R-sampler (Eberline Instruments GmbH, Germany) equipped with PM₁₀ and PM_{2.5} head (Sierra-Andersen) was used for sampling. The SIMS analyses were performed with a TRIFT II Time-of-Flight Secondary Ion Mass Spectrometer (Physical Electronics, Inc.). A piece of glass-fiber filter including the aerosol sample was placed in the sample holder and analyzed with gallium-ions. Accelerating voltage of 15 kV was used for spectral measurements and 25 kV for imaging. The used dose rates were $\sim 10^{13}$ ions/cm².

[9] The samples were studied by a scanning electron microscope (Figure 1) coupled with an energy dispersive X-ray microanalyzer [Tervahattu *et al.*, 2002]. The preparations for the SEM/EDX-investigations were made by pressing the particle samples collected in aerosol filters against a thin plate of indium substrate. The analyses were performed with a HITACHI S-4300 high-resolution scanning electron microscope coupled with a LINK ISIS energy dispersive X-ray microanalyzer. The ZAF-4 program was used for quantitative analyses.

3. Results and Discussion

[10] The TOF-SIMS spectra showed that the most intense peak from the fine-particle sample described above was the negative ion with 255 amu (Figure 2), which was considered to indicate palmitic acid. At the same time, the TOF-SIMS spectra of this sample showed peaks of -227, -241, -269, and -283 amu (Figure 2), which might be C₁₄, C₁₅, C₁₇ and C₁₈ fatty acids, as well as -281 amu might be monounsaturated C₁₈ fatty acid.

[11] Due to the high surface sensitivity of the used method, the danger of contaminations should be taken into account. Artifacts caused by fatty acid condensation onto particles might be originated from several anthropogenic sources (e.g., meat charbroiling [see Schauer *et al.*, 1999]). In order to find out possible contaminations, we analyzed by TOF-SIMS samples from different kinds of local fatty acid

sources, which might have influenced the samples during the collection, storing or preparation—including foodstuffs and chemicals containing fatty acids. No harmful contaminations could be detected.

[12] It is also important to notice that we studied by TOF-SIMS other samples stored in the same glass-fiber filter band and collected immediately before and after the studied episode (the preceding and the following day). Their particulate matter was composed of mainly local aerosol particles containing road dust and emissions from cars and energy production etc. The filter band surrounding the studied sample was similarly tested, too. None of these samples gave this peak, confirming that the observed compound was characteristic for the episode sample. We also searched for other local samples, which might have marine origin and observed low intensities of -255 amu in the sample collected in Helsinki at the end of October 2001. This aerosol mass had much smaller marine influence than the episode sample studied in this work because it came over the less saline Baltic Sea and not from the Atlantic Ocean. However, we could not detect any remarkable amounts of fatty acids on the surface of marine aerosol particles collected by the Finnish Meteorological Institute onboard during their expedition over the Atlantic Ocean in November–December 1999. We concluded that the presence of the organic film is dependant on the availability of surfactants on the sea-surface from which sea-salt particles are emitted.

[13] Because palmitic acid and stearic acid have been suggested as possible constituents of the organic surface layer of marine aerosols [Barger and Garrett, 1976; Marty *et al.*, 1979], we used pure palmitic acid (C₁₆H₃₂O₂) and stearic acid (C₁₈H₃₆O₂) on silicon substrate to investigate the ions produced from them by TOF-SIMS. It gave negative peak of 255 amu (C₁₆H₃₁O₂), indicating the presence of palmitic acid in our sample. The pure fatty acids studied in the laboratory gave additional, less intense, peaks for palmitic acid -510 (C₃₂H₆₂O₂), -253 (C₁₆H₂₉O₂), and -256 (C₁₆H₃₂O₂). We also observed positive peaks with high intensities for pure fatty acids, for palmitic acid +257 amu (C₁₆H₃₃O₂) and +239 (C₁₆H₃₁O – palmitic acid minus H₂O), which we did not find for the aerosol sample.

[14] The differences in TOF-SIMS spectra between the aerosol sample and the pure fatty acids might be due to different bond energies between the sample and substrates. On the silicon wafer, no strong bonds between the fatty acid and the substrate exist. In marine aerosol particles strong enough bonds between the suggested palmitic acid surface layer and positive ions of the inner core may exist to prevent the production of positive ions from fatty acids by the “soft” gallium-ion bombardment. This hypothesis is supported by the fact that on alkaline sea-salt particles the fatty acids are likely to be dissociated or present as salts [Gagorian *et al.*, 1982; Sicre *et al.*, 1990; Seidl, 2000]. Stephanou [1992a] observed that fatty acid salts were found in higher concentrations than fatty acids in marine aerosols, while fatty acids were more important during wind events from the island. Stephanou [1992b] also showed that while Na-salts of unsaturated fatty acids in marine aerosols undergo photo-oxidation reactions, the products are Na-salts of dicarboxylic acids. The importance of sodium in binding palmitic acid is further supported by Lynch *et al.* [2001],

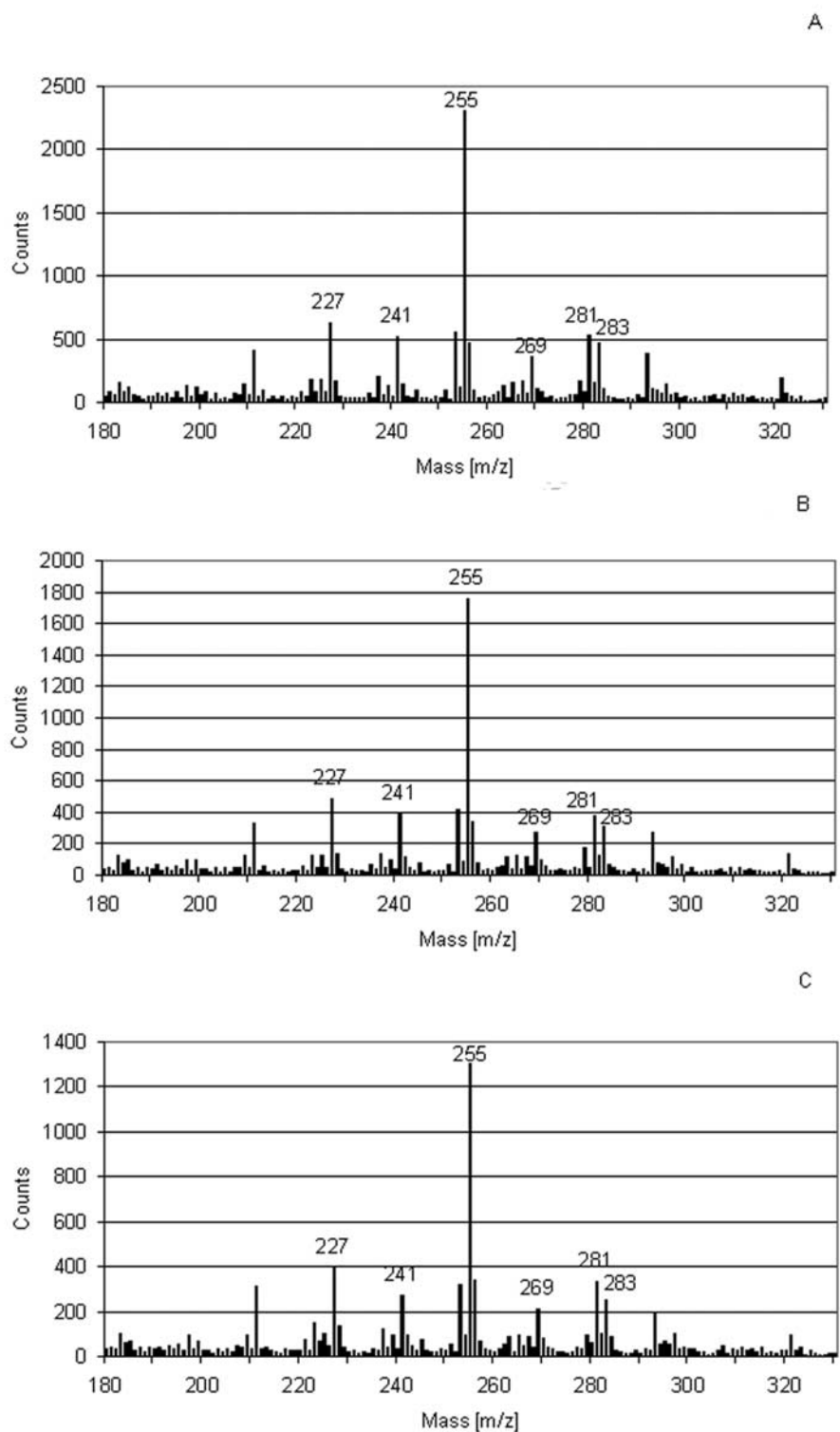


Figure 2. Negative TOF-SIMS spectra of three successive analyses (each lasting 2 min) of the same point on the surface of the glass-fibre filter. The highest intensity at 255 m/z is for palmitic acid (C16:0) and lower peaks for other fatty acids (C14:0, 227 m/z; C15:0, 241 m/z; C17:0, 269/270 m/z; C18:1, 281 m/z; C18:0, 283/284 m/z). The intensity of palmitic acid and other fatty acids clearly decreases during the bombardment.

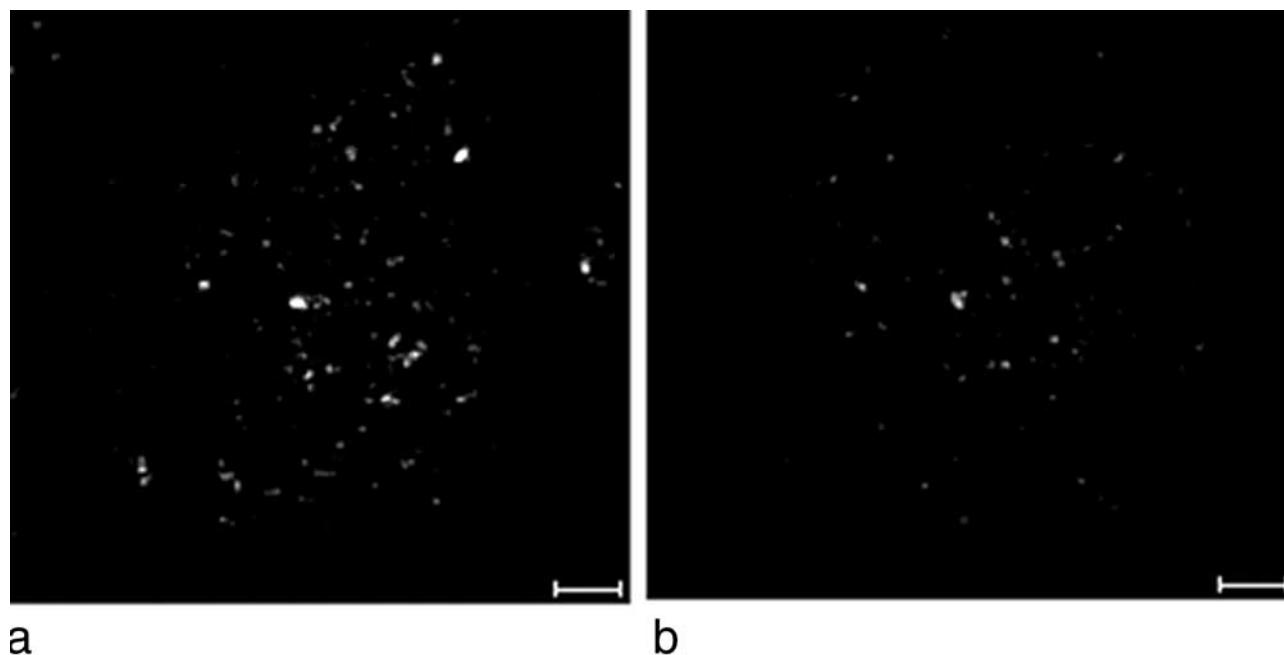


Figure 3. TOF-SIMS images for negative ion 255 m/z (palmitic acid). Two successive analyses of the same experiment as in Figure 2: (a) 0–2 min and (b) 8–10 min from the beginning. The counts number as well as the spot size and brightness decrease from Figures 3a to 3b, indicating the decrease of palmitic acid during the bombardment. The size of small single spots is $\sim 1\ \mu\text{m}$; larger spots were concluded to be similar groups of aerosol particles, which can be seen in Figure 1. The density of the spots is also similar to the density of the coated aerosol particles. Scale bar 10 μm .

who found that the leaflets of pure fatty acid (B-stearic acid) are much more weakly bound than those of sodium hydrogen dipalmitate, in which the sodium is shared among laterally adjacent carboxylate anions to create a pseudo-six-member ring, which adds to the crystal stability.

[15] Our results (Figure 2) indicate marine origin of fatty acids being in a good accordance with the analyses of *Gagosian et al.* [1981, 1982] and *Barger and Garrett* [1976]. Their bulk marine aerosol samples averaged over many particles showed relatively large concentrations of fatty acid salts with the prevalence of palmitic acid along with myristic (C_{14}) and stearic acid (C_{18}) and C_{15} and C_{17} saturated fatty acids as well as C_{16} and C_{18} monounsaturated compounds. According to *Simoneit and Mazurek* [1982], *Sicre et al.* [1990], and *Stephanou* [1992a], marine fatty acids have shorter molecules than fatty acids originated from terrigenous vascular plants ($C > 20$). However, none of the previous investigations could establish the presence of fatty acids in the surface layer of aerosol particles.

[16] In addition of being incorporated on the surface of marine aerosols during the bubble bursting, fatty acids might also be condensed onto existing particles through the gas-phase partitioning from ambient sources, either anthropogenic or natural. Secondary organic aerosol formation may contribute a significant proportion of fine particulate organic matter. It has been suggested that once organics have begun to condense and an organic layer has formed on the particles, even products whose gas-phase concentrations are below their saturation concentrations will partition a portion of their mass into this condensed organic phase [see *Odum et al.*, 1996]. However, little is known about the gas-particle-phase

partitioning of fatty acids. The fatty acids with 12–18 carbon atoms are most likely film-forming compounds on atmospheric particles. The shorter-chain acids are too volatile to be found in considerable quantities on the aerosol particles. Acids with more than 18 carbon atoms have too low-equilibrium spreading pressure to form films at atmospheric temperatures below 20°C [*Seidl*, 2000]. On the other hand, *Kavouras et al.* [1999] identified higher molecular weight *n*-alkanoic acids in all gas and particulate phase aerosol samples over conifer forests, with higher concentrations during the daytime (mean temperature 24–25°C) than during the nighttime (6–8°C).

[17] We ruled out the possibility of secondary fatty acid condensation on the studied episode particles for two reasons. (1) Our previous [*Tervahattu et al.*, 2002] SEM/EDX studies, as well as other chemical investigations and meteorological data, strongly supported the suggestion that the particles were covered by an organic film made up of the “biological oil slick” on the surface of the sea. To our best knowledge, there were no sources of fatty acids in the studied air masses, which might cause sufficient amount of condensation onto the aerosol particles. (2) Condensation during the storing and studying of the samples was not possible, because all other samples collected and stored in the same glass-fiber filter bands and studied at the same time, did not contain the fatty acids.

[18] The TOF-SIMS data can also be used to produce images for different ions to study, how these ions are located in the sample material. We produced images separately for $-255\ \text{amu}$ and several other ions. As can be seen in Figure 3, the negative ion 255 seems to be situated in small particles.

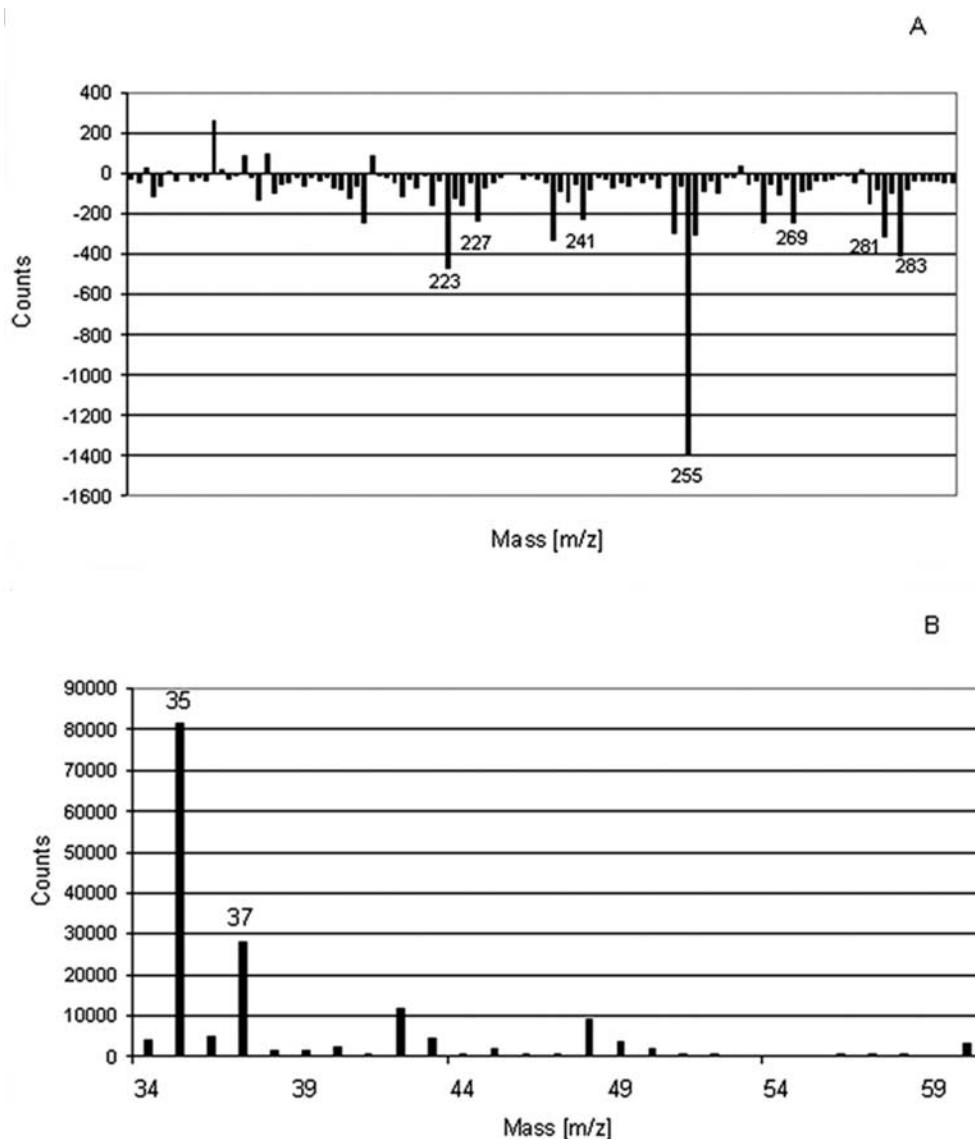


Figure 4. The effect of sputtering for TOF-SIMS peaks of chlorine and palmitic acid. The figures show the changes in the intensities during the sputtering (after sputtering minus before sputtering). The intensity of palmitic acid and other fatty acids decreased simultaneously with the increase in the intensity of chlorine.

Their density is close to the density of the particles observed by SEM at the surface of the filter (Figure 1). At the same time, the size of -255 amu spots in TOF-SIMS images is similar to the particles studied by SEM. All this supports the evidence that the observed substance is on the surface of the marine aerosol particles.

[19] For its destructive nature, SIMS can be used to erode the solid in a controlled manner to obtain information on the in-depth distribution of molecules. Accordingly, the intensity of -255 amu peak (Figure 2) and the size and the brightness of the spots (Figure 3) clearly decreased during the successive bombardments of our experiment. More distinctly, sputtering was used to strip the surface layer in the sample. In our sample, sputtering stripped palmitic acid almost totally (Figure 4a) indicating that this compound was situated on the outermost layer of the particles and not

inside them. At the same time, sputtering caused a great increase in the intensity of chlorine (Figure 4b). TOF-SIMS images and sputtering gave thus evidence about the simultaneous decrease of palmitic acid and the increase of chlorine in the particles originally giving high intensity of palmitic acid. The sputtering experiment therefore showed that these particles were sea-salt particles covered by palmitic acid and other fatty acids.

4. Conclusions

[20] Our data in this and our previous paper [Tervahattu *et al.*, 2002] directly demonstrate the hypothesis that the core of the studied aerosol particles is sea salt, which is covered by an organic layer made up of biogenic fatty acids, such as palmitic acid. The presence of lipid surface films on

marine sea-salt particles will impact significantly their chemical, physical and optical properties. In this regard, the ability of atmospheric aerosols to grow and to form cloud condensation nuclei (CCN) is a strong function of the hydrophilic properties of their surfaces. One important effect is the lowering of the particle surface tension [Facchini et al., 2000; Seidl, 2000], which promotes small particle growth at lower relative humidity in accord with the Kelvin effect, in addition to which it makes particles more CCN active [Li et al., 1998; Facchini et al., 1999]. By affecting cloud optical properties and a higher albedo, these chemical processes may cause global negative forcing thus decreasing global warming [Charlson et al., 2001]. The global impact of an organic coating depends on how commonly particles are covered by such surfactants. So far, very little is known about the occurrence of lipid surface films on marine aerosol particles.

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