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## Fatty acids on continental sulfate aerosol particles

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[1] Surface analyses of atmospheric aerosols from different continental sources, such as forest fires and coal and straw burning, show that organic surfactants are found on such aerosols. The predominant organic species detected by time-of-flight secondary ion mass spectrometry on the sulfate aerosols are fatty acids of different carbon chain length up to the C<sub>32</sub> acid. These observations are consistent with literature accounts of functional group analysis of bulk samples, but this is the first direct evidence of fatty acid films on the surface of sulfate aerosols. Surface analysis leads to the conclusion that fatty acid films on continental aerosols may be more common than has been previously suggested.

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### 1. Introduction

[2] It has been hypothesized that organic surfactants may reside at the surface of atmospheric aerosols [Gill *et al.*, 1983; Ellison *et al.*, 1999; Finlayson-Pitts and Pitts, 2000; Rudich, 2003]. The chemical model for such aerosols describes them as having an aqueous core with a hydrophobic organic surface film [Ellison *et al.*, 1999]. Such surfactants would affect the chemical, physical and optical properties of aerosols and their impact on climate and human health. However, there is no widespread acceptance of this idea [Intergovernmental Panel on Climate Change (IPCC), 2001; Decesari *et al.*, 2003] because only a few experiments have been performed that are capable of analyzing the surface of atmospheric aerosols [Tervahattu *et al.*, 2002b; Russell *et al.*, 2002; Peterson and Tyler, 2002].

[3] In our previous work [Tervahattu *et al.*, 2002a, 2002b] we showed fatty acids on surfaces of sea-salt aerosols. Here we report the ubiquity of fatty acid populations on a variety of continental aerosols including sulfate and nitrate aerosols. Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used for this research because of its unique combination of surface sensitivity

(uppermost 3 nm layer) and the detailed molecular information obtained (ionization with little fragmentation and MS up to 2000 amu). We emphasize that we are not analyzing a bulk sample which averages the total content of the particles; rather, TOF-SIMS looks at the surfaces of single particles or clusters of several particles.

### 2. Materials and Methods

[4] We have studied eight different aerosol samples collected mainly (seven samples) at Hyytiälä, Finland (61°51N, 19°27E) [see Kulmala *et al.*, 2001], which represent a rural background air quality. One sample was collected in Imatra, a small town near the Finnish-Russian border (Figure 1). For the source identification and the chemical characterization of the samples, we have used the following data:

[5] 1. Particle mass was measured in Hyytiälä with Dekati PM<sub>10</sub> three-stage impactor with backup filter. The cutoff diameters (D<sub>50</sub>) of the impactor stages were 10, 2.5 and 1 μm. The samples used in TOF-SIMS analysis were collected at the backup stage where the filter was Gelman Teflo R2P J047, a 47 mm Teflon filter with 2 μm pore size. Duration of sample collection was 2-3 days. The particulate matter (PM) measurement and collection procedure has been described by Laakso *et al.* [2003]. One sample was collected in Imatra, a small town near the southeastern boundary of Finland by an Eberline FH 62 I-R-sampler (Eberline Instruments GmbH, Germany) equipped with a PM<sub>10</sub> head (Andersen) and glass fiber filters.

[6] 2. Backward trajectories were produced using the vertical motion model in the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT4) model (R. R. Draxler and G. D. Rolph, Air Resources Laboratory, NOAA, 2003) (available at <http://www.arl.noaa.gov/ready/hysplit4.html>).

[7] 3. For the detection of field and forest fires we used Web Fire Mapper (available at <http://maps.geog.umd.edu>)

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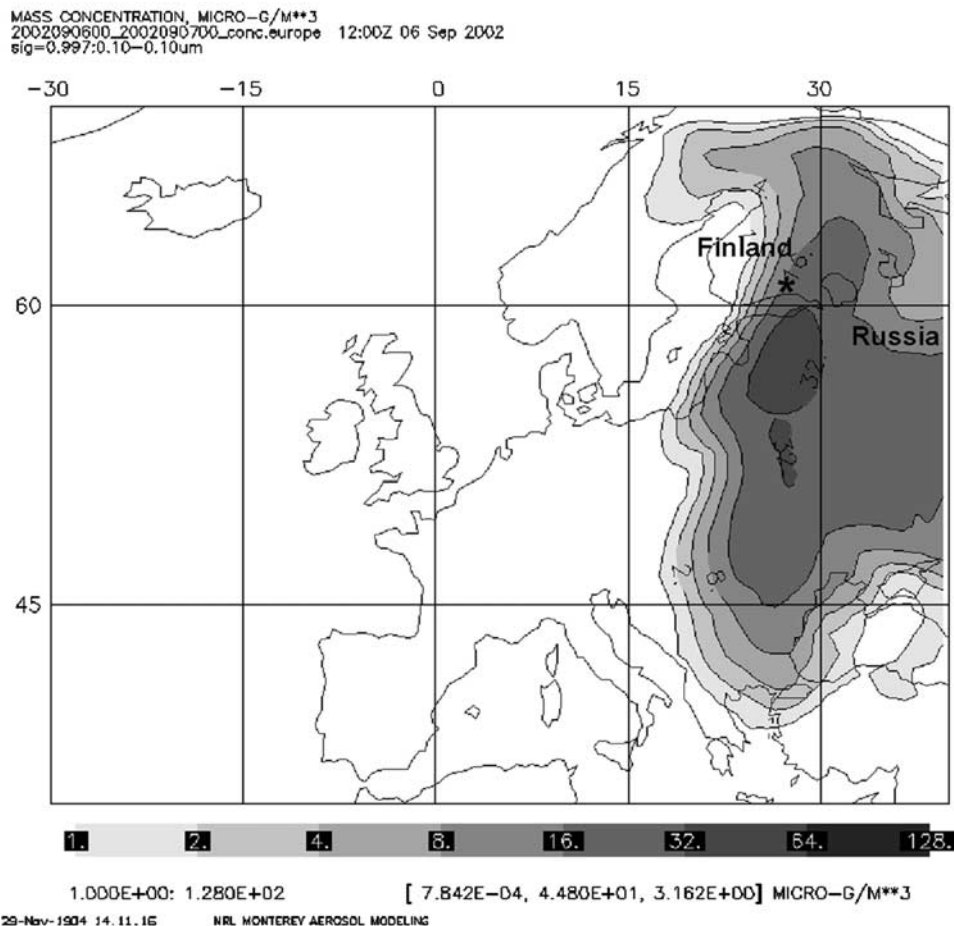
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**Figure 1.** Naval Aerosol Analysis and Prediction System model results showing surface smoke concentration ( $\mu\text{m m}^{-3}$ ) from forest fires in Russia on 6 September 2002 at 1200 UTC. The sampling site in Imatra (small town near the southeastern boundary of Finland) is marked with an asterisk. This sample was used in the analysis presented in Figure 2a. Map from [http://www.nrlmry.navy.mil/aerosol/index\\_frame.html](http://www.nrlmry.navy.mil/aerosol/index_frame.html) (Naval Research Laboratory Marine Meteorology Division, Monterey, California, USA).

which is part of the MODIS Rapid Response System [Justice *et al.*, 2002] and Naval Aerosol Analysis and Prediction System (NAAPS) model (Naval Research Laboratory, Monterey, California, USA) (available at <http://www.nrlmry.navy.mil/>).

[8] 4. The ion concentration data were measured by the Finnish Meteorological Institute at the Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) stations in Ähtäri, Virolahti and Utö. Daily total suspended particle

**Table 1.** Fatty Acid Composition and Amount on the Aerosol Surfaces Studied by TOF-SIMS<sup>a</sup>

Site	Date	Fatty Acid Range	Fatty Acid Maximum	Fatty Acid Amount <sup>b</sup>	PM <sub>1</sub> , $\mu\text{g m}^{-3}$	Main Sources
1, Helsinki <sup>c</sup>	22 Feb. 1998	C14–C18	C16	2300	41 <sup>c</sup>	sea salt <sup>d</sup>
2, Hyytiälä	11 May 20011	C14–C18	C16+C18	60	1.97	sea salt
3, Hyytiälä	15 Aug. 2001	C14–C20	C16	250	6.17	sea salt
4, Hyytiälä	4 April 2003	C16–C20	C16+C18	150	4.94	sea salt and local
5, Hyytiälä	2 Dec. 2002	C16–C22	C16	250	17.0	mainly fossil fuels
6, Hyytiälä	19 March 2002	C14–C30	C16+C22	800	20.4	field fires and fossil fuels
7, Hyytiälä	14 Aug. 2002	C14–C32	C22+C16	1800	19.4	forest fire and fossil fuels
8, Hyytiälä	16 Oct. 2002	C16–C28	C22	1900	8.57	forest fire
9, Imatra <sup>c</sup>	6 Sept. 2002	C14–C30	C22	2100	NM <sup>f</sup>	forest fire

<sup>a</sup>Concentrations of submicron particulate matter (PM) and the main sources of the aerosols are given for comparison. Fatty acids were found in all samples, even in those whose PM<sub>1</sub> concentrations were low. The fatty acid component was high in the first sample and the last four samples, which were selected for their relatively high sulfate concentrations.

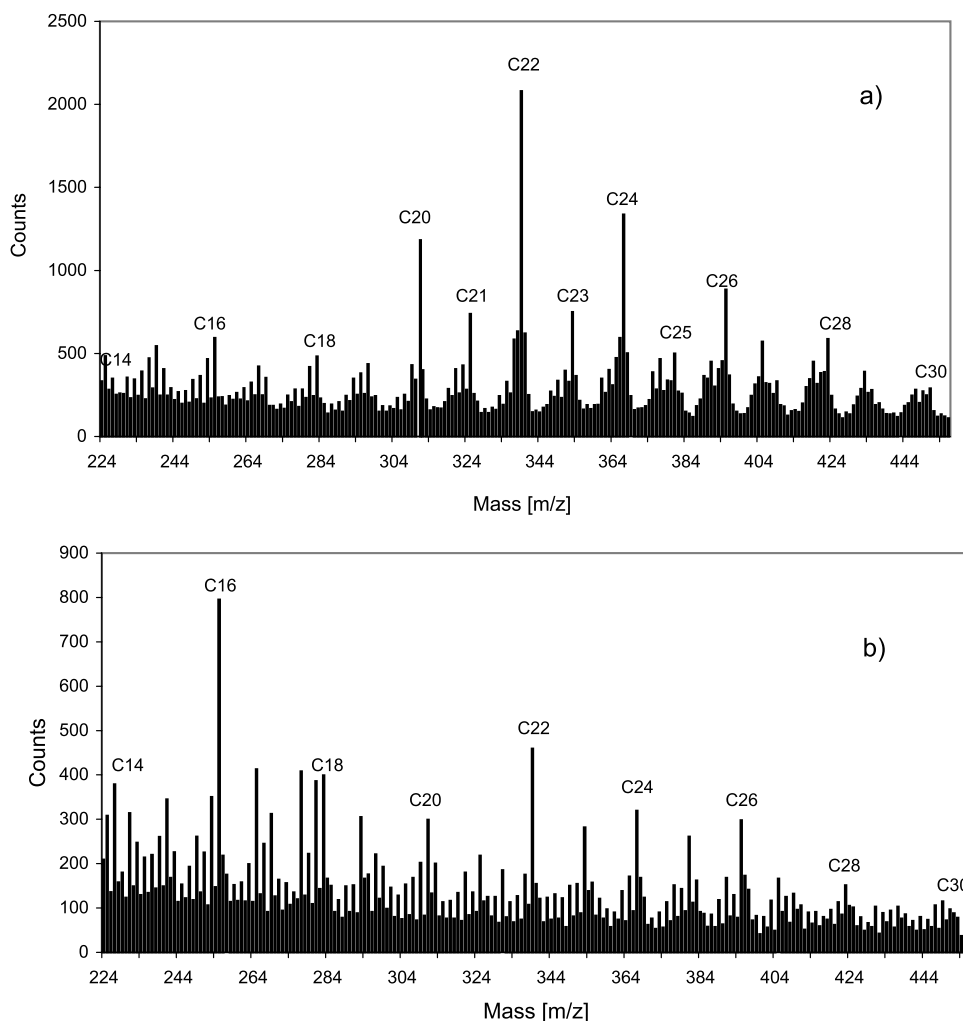
<sup>b</sup>Highest MS counts number of a single fatty acid in the sample.

<sup>c</sup>PM<sub>2.5</sub> sample is given.

<sup>d</sup>Data are published by Tervahattu *et al.* [2002a, 2002b].

<sup>e</sup>PM<sub>10</sub> sample or the identified forest/field fire impact (see Table 2).

<sup>f</sup>NM stands for not measured.

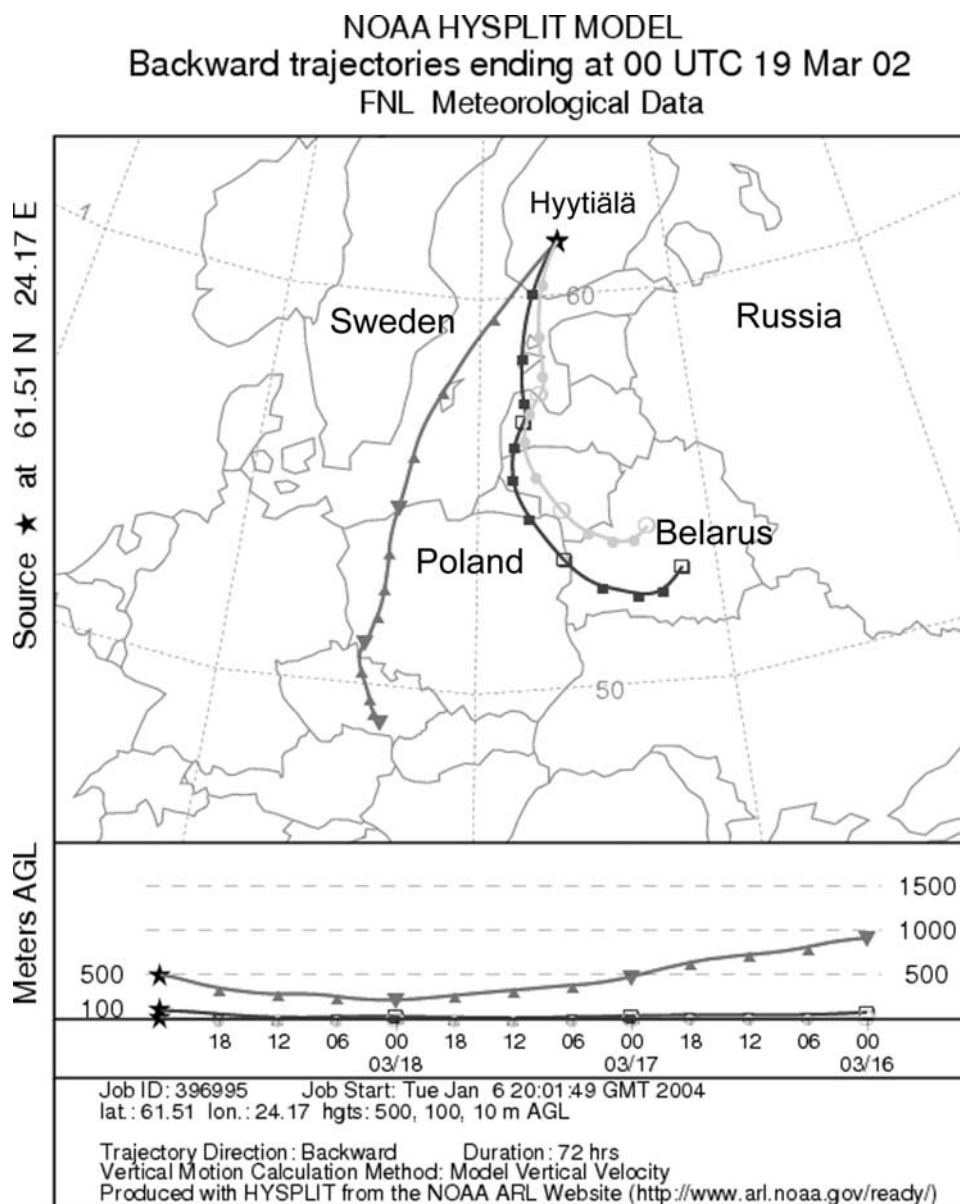


**Figure 2.** (a) Negative time-of-flight secondary ion mass spectrometry (TOF-SIMS) spectrum of the surface of aerosol particle sample collected in Imatra on the Finnish-Russian border (Figure 1) 6 September 2002 during the forest fire episode. The spectrum is dominated by *n*-alkanoic acids ranging from C<sub>14</sub> to C<sub>30</sub> with maximum at C<sub>22</sub> (339 m/z) and a strong even-to-odd carbon number predominance. The smaller peaks on the left of the *n*-alkanoic acids are monounsaturated and polyunsaturated fatty acids. (b) Negative TOF-SIMS spectrum on the surface of aerosol particle sample collected in Hyytiälä (a Finnish rural background station, see Figure 3) 19 March 2002 during the field fire episode. The *n*-alkanoic acids range from C<sub>14</sub> to C<sub>30</sub> with maxima at C<sub>16</sub> (255 m/z) and C<sub>22</sub> (339 m/z) and show lower-amplitude even-to-odd carbon number predominance as the spectrum from Imatra (Figure 2a). Several major peaks in addition to the fatty acids can be detected.

samples were collected by open-faced two-stage filter packs (NILU Products AS) into cellulose filters (Whatman 40, diameter 47 mm). Sulfate (SO<sub>4</sub><sup>2-</sup>), total nitrate (NO<sub>3</sub><sup>-</sup> + HNO<sub>3</sub>(g)), and total ammonium (NH<sub>4</sub><sup>+</sup> + NH<sub>3</sub>(g)) were analyzed by an ion chromatography (IC, Waters). The details of the sampling and IC methods have been described by Paatero *et al.* [2001]. Because ion concentrations were not measured in Hyytiälä (where the aerosol samples were collected), the data of these neighboring EMEP stations were used to calculate the ion concentrations in Hyytiälä during the sampling days (Table 2).

[9] 5. The elemental composition of individual particles was studied in our previous work and used in this paper for

the chemical characterization of aerosol particles and their source identification as described by Niemi *et al.* [2004]. Scanning electron microscope (SEM-ZEISS DSM 962) coupled with an energy dispersive X-ray microanalyzer (EDX-LINK ISIS with ZAF-4 measurement program) was used for individual particle analysis at the Electron Microscopy Unit of the Institute of Biotechnology, University of Helsinki [Kupiainen *et al.*, 2003]. For a more detailed individual particle study, a field emission SEM (FESEM-JEOL JSM-6335F) coupled with an energy dispersive X-ray microanalyzer (EDX-LINK ISIS and INCA) was used for the analyses in the laboratory of Top Analytica Ltd., Turku. Samples were prepared similarly as for conventional SEM,



**Figure 3.** Aerosols from large springtime (deliberate) field burning mixed with fossil fuel burning emissions originated from the direction of Baltic countries, northwestern Russia, Belarus, and Poland [see also Niemi *et al.*, 2004]. The studied aerosol sample was collected in Hyytiälä on 19 March 2002. This sample was used in the analysis presented in Figure 2b. Map is from NOAA (R. R. Draxler and G. D. Rolph, Air Resources Laboratory, 2003, Hybrid Single-Particle Lagrangian Integrated Trajectory model, available at <http://www.arl.noaa.gov/ready/hysplit4.html>).

with Cr as the coating material. The acceleration voltage was 15 kV.

[10] 6. The TOF-SIMS analyses were performed in the laboratory of Top Analytica Ltd., Turku, with a TRIFT II time-of-flight secondary ion mass spectrometer (Physical Electronics, Inc.). The analytical chamber was either kept at the room temperature or cooled to  $-140^{\circ}\text{C}$  to prevent evaporation of the studied compounds. Accelerating voltage of 15 kV was used for spectral measurements and 25 kV for imaging. The used dose rates were  $\sim 10^{13}$  ions  $\text{cm}^{-2}$ . Pieces of the aerosol sample filters were placed in the sample holder and analyzed with gallium ions. The filter samples were covered by the studied particles and their agglomerates

that were commonly fused together because of water condensed during the sampling. Reference analyses were performed from pure filter samples [Tervahattu *et al.*, 2002b].

### 3. Results and Discussion

#### 3.1. Composition of Fatty Acid Films

[11] Here we report fatty acids (mainly *n*-alkanoic acids with evidence for *n*-alkenoic acids) on the surfaces of all studied aerosol samples. These new results are the first clear-cut evidence that continental aerosols have such surface organic films, increasing substantially the so far

**Table 2.** Daily Average PM<sub>1</sub> Concentrations During the Sampling Days in Hyytiälä and Calculated Daily Average Concentrations of Sulfate (SO<sub>4</sub><sup>2-</sup>), Total Nitrate (NO<sub>3</sub><sup>-</sup> + HNO<sub>3</sub>), and Total Ammonium (NH<sub>4</sub><sup>+</sup> + NH<sub>3</sub>) and Their Sum (SUM)<sup>a</sup>

Day of Sampling	Measured PM <sub>1</sub> Concentrations, μg m <sup>-3</sup>	Calculated Ion Concentrations			
		SO <sub>4</sub> , μg m <sup>-3</sup>	NH <sub>4</sub> , μg m <sup>-3</sup>	NO <sub>3</sub> , μg m <sup>-3</sup>	SUM, μg m <sup>-3</sup>
2 Dec. 2002	17.0	1.8	0.65	2.0	4.45
14 Aug. 2002	19.4	4.5	2.0	2.0	8.5
19 March 2002	20.4	6.4	3.0	5.0	14.4
16 Oct. 2002	8.6	3.0	1.5	1.5	6.0
6 Sept. 2002	13.3	5.4	3.0	3.0	11.4

<sup>a</sup>Ion calculations are based on the data of three neighboring Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (EMEP) stations (Ähtäri, Virolahti, and Utö). The numbers show that sulfate, ammonium, and nitrate have been major compounds in all samples and made up more than half of the aerosol mass in the three last samples.

very scarce evidence of hydrophobic organic surfactants on aerosol particles [Tervahattu *et al.*, 2002b; Peterson and Tyler, 2002; Russell *et al.*, 2002]. Fatty acids showed a clear dominance in the molecular weight of organic compounds. Additionally, there were smaller mass peaks all the way out to  $m/z = 1000$ .

[12] The results of our paper are based on the nine samples, selected from hundreds to be representative (Table 1). For each sample, 2–4 randomly selected sample surface areas of 100 μm × 100 μm in size were separately analyzed by TOF-SIMS. Each scanned area contains thousands of particles. The samples were collected mainly at Hyytiälä, Finland (61°51N, 19°27E) [see Kulmala *et al.*, 2001], which represents a rural background air quality. Aerosols originating from different sources showed characteristic fatty acid compositions. Even though fatty acids have not been considered good tracers of aerosol emissions [Gogou *et al.*, 1996], different sources produce different combinations of fatty acids that can be used as fingerprints in identifying the origins of the studied fatty acids [Simoneit, 2002]. Particularly, fatty acids of microbial origin including marine plankton are composed of relatively short carbon chains while fatty acids from terrestrial plants have longer carbon chains. Three samples (Table 1) had marine origins with fatty acids on sea-salt particles ranging from C<sub>14</sub> to C<sub>18</sub> and the maximum at C<sub>16</sub> in agreement with our previous work on a single episode [Tervahattu *et al.*, 2002b] that is listed in Table 1 as sample 1.

[13] Aerosols of continental origin had fatty acids with longer carbon chains than their marine counterparts. Most typically, the sample from widespread forest fires in Russia near the Finnish border (Figure 1) represented relatively homogeneous emissions and showed major peaks ranging from C<sub>14</sub> to C<sub>30</sub> with the maximum at C<sub>22</sub> and a strong even-to-odd carbon number predominance (Figure 2a and sample 9 in Table 1). This composition indicates the involvement of the smoke from forest fires, mainly from conifer trees [Oros and Simoneit, 2001a; Simoneit, 2002]. Very similar results were obtained for the sample collected in Hyytiälä 16 October 2002, indicating that the fatty acid composition originated from forest fires. These results confirm the theoretical hypothesis of Ellison *et al.*

[1999] according to which surfactants should exist on biomass burning aerosols.

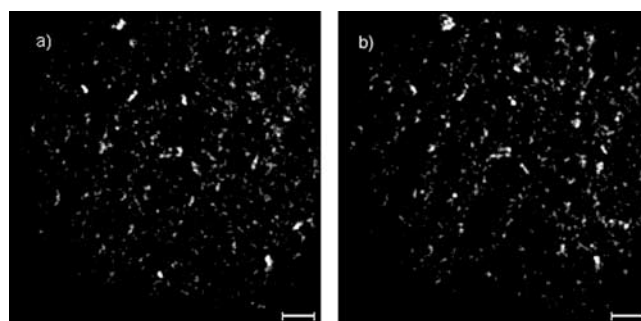
[14] The TOF-SIMS spectra of the aerosol matter sampled in Hyytiälä 19 March 2002 showed major peaks from C<sub>14</sub> to C<sub>30</sub> with two maxima at C<sub>16</sub> (highest intensity) and C<sub>22</sub> (Figure 2b and Table 1). The main fraction of the aerosol by number originated from springtime field burning but the air masses came over areas with high emissions from fossil fuel burning (Figure 3). These two aerosol sources were mixed during transport [Niemi *et al.*, 2004; see also Oros and Simoneit, 2000; Simoneit, 2002]. The fatty acids on the particles were thus consistent with the known source emissions. Because of the very low vapor pressures of the fatty acids we observe, they must have attached to the aerosols close to the aerosol source, i.e., at the fires. Several other minor peaks seen in Figure 2b may indicate products of oxidative heterogeneous reactions [Ellison *et al.*, 1999] that had been taking place during the transport of the aerosol [Eliason *et al.*, 2004].

### 3.2. Location of Fatty Acids and Sulfate on Aerosol Particles

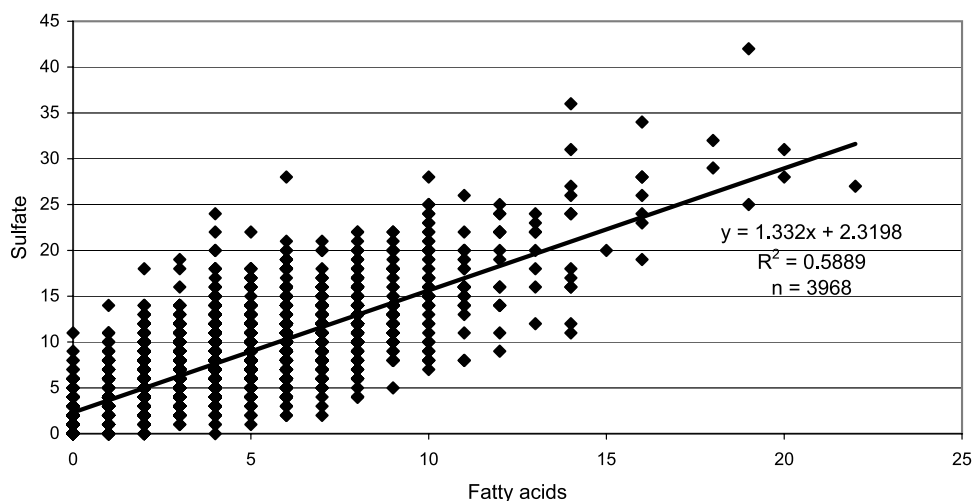
[15] In order to study on which particular particles the fatty acids were condensed we produced TOF-SIMS images separately for selected ions. The main focus was on sulfate ions (SO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub><sup>-</sup>) because sulfate concentration was high in many of the studied samples (including the samples of Figures 2a and 2b). Using the data of three neighboring EMEP stations we calculated that sulfate, ammonium and nitrate made up more than half of the submicron aerosol mass (Table 2). Our SEM/EDX studies [Niemi *et al.*, 2004] as well as the negative TOF-SIMS spectra also gave high concentrations of sulfate in the studied samples.

[16] Areas 100 μm square were scanned separately for different ions. The TOF-SIMS images showed convincingly that fatty acids (Figure 4a) were located in the same particles as the sulfurous compounds (S, SO<sub>3</sub><sup>-</sup>, HSO<sub>4</sub><sup>-</sup> in Figure 4b). The analysis depth is about 3 nm, which means that if there is a fatty acid monolayer, analyses include signals also from the uppermost layer of the inner core.

[17] The matching of the spots in Figures 4a and 4b was tested statistically. Perfect correlation between fatty acid and



**Figure 4.** TOF-SIMS images for negative ions of (a) fatty acids and (b) sulfurous compounds of exactly the same scanned area of the surface of Hyytiälä sample on 14 August 2002. Scale bar is 10 μm. Note that the bright spots indicating the location of fatty acids and sulfurous compounds are at the same places.

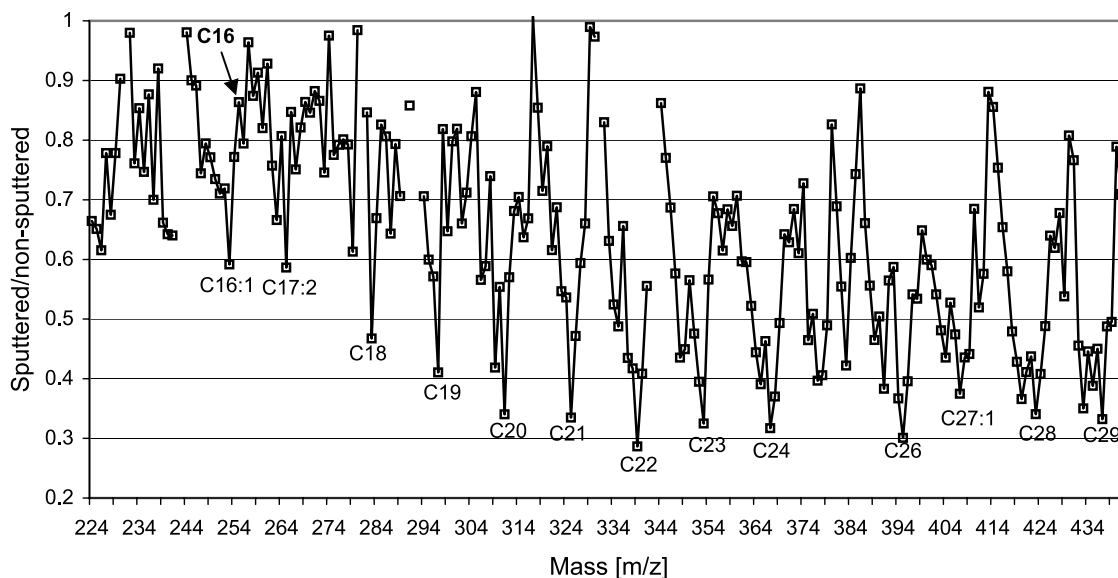


**Figure 5.** Correlation test indicating the matching of fatty acid spots with sulfurous ( $S$ ,  $SO_3^-$ , and  $HSO_4^-$ ) spots in Figure 4. The TOF-SIMS image data contain MS intensities (in arbitrary units) of fatty acids ( $x$  axis) and sulfurous ( $y$  axis) compounds at 3968 points; the size of one point is  $1.56 \mu\text{m} \times 1.56 \mu\text{m}$ .

sulfate ions should not be expected, since nitrate and other aerosols were also present, as were hitherto unidentified surface organic species with low intensities. The area of a single data point was  $1.56 \mu\text{m} \times 1.56 \mu\text{m}$ , which is much larger than that of single particles and means that the data points contain inhomogeneous material thus decreasing the correlation. The results (Figure 5) show that the correlation of the locations of fatty acids and sulfurous compounds on the scanned area is significant ( $R^2 = 0.59$ ). This is regarded as a very good correlation when the limitations of the test

are taken into account. It confirms the results that are visible in Figure 4. On the other hand, compounds like fluorine (indicative of the Teflon filter) were located at different data points than fatty acids and sulfate and did not correlate at all with them. ( $R^2$  for fatty acids/fluorine was 0.048;  $R^2$  for sulfate/fluorine 0.053.)

[18] TOF-SIMS can be used to erode the solid matter to obtain information about the distribution of molecules as a function of depth below the surface layer. The depth profiling of the sample by sputtering destroyed fatty acids



**Figure 6.** Results of sputtering of the Hyttiälä 16 October 2002 sample. The  $y$  axis indicates MS counts of the sputtered (sputtering time 4 s) sample divided by counts of nonsputtered samples. The level of fatty acids has decreased about 70%. Note that fatty acids with odd carbon chain numbers have decreased relatively as much as those with even carbon numbers. Shorter fatty acids ( $C_{16}$  and  $C_{18}$ ) show relatively higher concentrations after the sputtering. This is caused either by the fragmentation of longer unsaturated fatty acids or because the longer fatty acids are more easily broken by ion bombardment. The peaks of Teflon filter have been deleted.

rapidly but did not have great impact on the intensities of sulfate. The typical sputtering speed for organic materials with settings used by us is  $0.1\text{--}1\text{ nm s}^{-1}$ ; thus with 4 s sputtering time (in Figure 6) the depth is  $0.4\text{--}4\text{ nm}$ . This is just a small fraction of the particle (diameter of  $100\text{--}1000\text{ nm}$ ). It means that a major part of the monolayer of fatty acids will be sputtered but most of the particle is not sputtered. We plotted the ratios of sputtered and nonsputtered MS counts (Figure 6). The results showed that fatty acids have been sputtered more than other compounds indicating that they were at the surface of the aerosol samples. Odd carbon number fatty acids have been destroyed to the same extent as even carbon number species. The counts of shorter-chained fatty acids have not been decreased so much, which probably indicates the easier fragmentation of longer chains and the possible production of shorter-chained fatty acids as a result of this fragmentation.

### 3.3. Ubiquitous Existence and Atmospheric Implications of Fatty Acids

[19] Fatty acids can be considered as potentially important aerosol surfactants because they are major components of many anthropogenic and natural atmospheric emissions. As amphiphilic molecules, they can be assembled at air/water interfaces as well as transported to a solid surface. It has been suggested that as the marine aerosol particles form, they acquire a film of organic surfactants [Blanchard, 1964; Gill et al., 1983; Ellison et al., 1999]. Fatty acids have been reported to be major constituents of marine aerosols in many bulk investigations [Sicre et al., 1990; Barger and Garrett, 1976; Gagosian et al., 1981; Stephanou, 1992]. In our recent work we could show fatty acids on the surface of marine aerosols [Tervahattu et al., 2002a, 2002b].

[20] In this work, we have broadened this concept to include continental aerosols focusing on sulfate aerosols. Owing to their relatively low melting points (e.g., octadecanoic acid (stearic acid)  $69.6^\circ\text{C}$ ) and low vapor pressures (e.g., stearic acid  $6.5 \times 10^{-6}\text{ torr}$ ,  $15^\circ\text{C}$ ), fatty acids probably adsorb on to aerosol particles soon after their emissions from fuel and biomass burning. They should be found on the surfaces of aerosol particles emitted at the same time. It is therefore important to know how commonly fatty acids are coemitted from sources of sulfate aerosols and what should the ratio of fatty acids/sulfate be to enable monolayer coverage on sulfate aerosols. We calculated this ratio for ammonium sulfate particles. For particles of  $100\text{ nm}$  (aerodynamic diameter),  $\sim 10\%$  of fatty acids (by weight) is needed to cover an ammonium sulfate particle,  $3\%$  is enough for  $400\text{ nm}$  particles and  $1\%$  for  $1\text{ }\mu\text{m}$ . These ratios are similar to those that were calculated for sea salt particles by Ellison et al. [1999].

[21] Sulfate aerosols are produced by chemical reactions in the atmosphere from gaseous precursors, mainly from sulfur dioxide from anthropogenic sources (especially from burning of fossil fuel) and from dimethyl sulfide from biogenic sources, especially marine plankton [IPCC, 2001]. Substantial amounts of  $\text{SO}_2$  are emitted also from biomass burning.  $\text{SO}_2$  is oxidized to sulfate ( $\text{SO}_4^{2-}$ ) either in the gas phase by OH or by  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  after  $\text{SO}_2$  becomes dissolved in cloud droplets. The sulfate in aerosol particles is present as sulfuric acid ( $\text{H}_2\text{SO}_4$ ),

ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ), or intermediate compounds, depending on the availability of gaseous ammonia to neutralize the sulfuric acid. Sulfate is also known to condense onto larger aerosol particles in heterogeneous reactions of  $\text{SO}_2$  on mineral aerosols and in the oxidation of  $\text{SO}_2$  to sulfate in sea-salt-containing cloud droplets and deliquesced sea-salt aerosols [IPCC, 2001].

[22] Biomass burning is suggested to be the main source of aerosol in the fine mode at the global scale [Tanre et al., 2001]. Large amounts of fatty acids are released from biomass burning. Fatty acid emissions in deciduous tree smoke were measured as  $1589\text{ mg kg}^{-1}$  burned biomass which was  $56\%$  of all identified organic compounds [Oros and Simoneit, 2001b]. Large amounts of fatty acid are also emitted from burning of coniferous trees and grass [Oros and Simoneit, 2001a; Simoneit, 2002]. The ratios of sulfur dioxide and fatty acids in biomass burning emissions clearly indicate high enough fatty acid concentrations that they can cover all sulfate particles [BinAbas and Simoneit, 1996; Fang et al., 1999].

[23] Coal burning produces fatty acids ranging from  $\sim 1700\text{ mg kg}^{-1}$  burned coal for bituminous coal to  $10,000\text{ mg kg}^{-1}$  for lignite [Oros and Simoneit, 2000]. Fossil fuels are major sources for  $\text{SO}_2$  emissions [IPCC, 2001]. A substantial amount of fossil fuel-originated sulfate aerosols may have fatty acids on their surfaces [Schauer et al., 1996]. Meat cooking and deep frying of vegetables produce high amounts of fatty acids in urban air [Schauer et al., 1996, 1999, 2002a]. These emissions are  $1\text{--}2$  orders of magnitude greater than those of sulfurous compounds.

[24] Accordingly, fatty acids have ubiquitous existence and they have been found in ambient bulk aerosol samples collected in rural and urban locations [Simoneit and Mazurek, 1982; Sicre et al., 1990; Gogou et al., 1994; Zheng et al., 1997; Tzapakis et al., 2002; Billmark et al., 2003] up to concentrations of  $14.3\text{ }\mu\text{g m}^{-3}$  in the Indonesian biomass burning aerosol, in which alkanolic acids accounted  $3\text{--}4\%$  of the total loading in the aerosol [Fang et al., 1999]. Similar results were obtained in Malaysia [BinAbas and Simoneit, 1996]. Fatty acids have been observed in forest aerosols also without a forest fire [Kavouras and Stephanou, 2002]. Bulk analyses show that the  $\text{C}_{16}$  and  $\text{C}_{18}$  fatty acids (both *n*-alkanoic acids and *n*-alkenoic acids) are among the most prominent single organic compounds in the urban atmospheric fine particulate mixture [Rogge et al., 1993; Schauer et al., 2002b]. However, none of these studies provided any evidence about where the fatty acids were located in the particle.

[25] The observed hydrophobic surfactant films may have impacts on the chemical, physical and optical properties of aerosol particles. Their global importance depends on (1) how commonly particles are covered by such surfactants, (2) how extensive is the coverage of the organic film, (3) what the chemical, physical, and optical properties of the films are, and (4) how they are chemically processed.

[26] Nascent aerosol particles covered by a film of water insoluble surfactants will be hydrophobic and chemically inert. They will not react with most atmospheric species, although they are semipermeable and small molecules such as  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{SO}_2$ , and  $\text{NH}_3$  could cross the membranes at decelerated rates. Fatty acid films will decrease uptake coefficients of different gaseous substances. Properties of



semipermeable organic films should be characterized in order to be able to estimate gas molecular uptake and accommodation to aerosol particles [Kulmala and Wagner, 2001].

[27] The hygroscopic growth of aerosol particles is hindered after insoluble films are formed. The atmospheric oxidation of surfactant films leads to a more reactive, optically active hydrophilic layer as predicted by Ellison *et al.* [1999]. These transformations take several hours/days in the atmosphere. According to Bertram *et al.* [2001], OH reacts with 90% of the sites of an organic surface in less than 7 days. The aerosols of our samples were several hours to 2–3 days old and showed a strong dominance of unprocessed *n*-alkanoic acids. They were transported at relatively low temperatures and at high latitude (i.e., low-intensity solar radiation fields) that may slow down their processing. On the other hand, oxidized products are more volatile and more water soluble and therefore not expected to be abundant at the aerosol's surface.

[28] While considering the impacts of the observed surfactants on the properties of aerosols it should be taken into account that these fatty acids were mainly composed of species with longer carbon chains, especially in the case of forest fire aerosols. This is consistent with earlier observations that aerosols from terrestrial sources contained fatty acid homologs  $>C_{20}$  derived from vascular plants [Simoneit and Mazurek, 1982; Stephanou, 1992]. In the case of the Indonesian forest fire aerosol in 1997 [Fang *et al.*, 1999], the very high fatty acid concentrations ( $14.3 \mu\text{g m}^{-3}$ ) were predominantly composed of longer-chained fatty acids with  $C_{\text{max}}$  at  $C_{26}$ . Experimental studies of Oros and Simoneit [2001a, 2001b] also showed high emissions of longer-chained fatty acids from biomass burning. The carbon chain length may be important for the atmospheric implications of fatty acid films. The longer-chained fatty acids are expected to be more hydrophobic and less permeable than the shorter-chained species.

#### 4. Conclusions

[29] We conclude that numerous important continental sources may give rise to fatty acid films on sulfate aerosols; the fatty acids must deposit close to source. The analyses were selected as being representative from hundreds of aerosol samples. The common existence of fatty acid films is also supported by the known large emission sources of these molecules. Surface analyses of continental aerosols reported here are consistent with and demonstrate observationally the reality of theoretical considerations about fatty acids as aerosol surfactants [Gill *et al.*, 1983; Ellison *et al.*, 1999; Finlayson-Pitts and Pitts, 2000; Rudich, 2003]. In the light of these findings, we emphasize the need for further study of hydrophobic organic films, the conditions of their existence in the atmosphere, their physical, chemical and optical properties, and their atmospheric processing.

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