Concentrations and Adsorption Isotherms for Amphiphilic Surfactants in PM_1 Aerosols from Different Regions of Europe

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ABSTRACT. Predicting the activation of sub-micron particles into cloud droplets in the atmosphere remains a challenge. The importance of surface tension, σ (mN/m), in these processes has been evidenced by several works but information on the "surfactants" lowering σ for atmospheric particles remains scarce. In this work, PM_1 aerosols from urban, coastal and remote regions of Europe (Lyon, France, Rogoznica, Croatia, and Pallas, Finland, respectively) were investigated and found to contain amphiphilic surfactants in concentrations up to 2.8 $\mu g\ m^{-3}$ in the air and 1.3 M in the particle volume. In Pallas, correlations with the PM_1 chemical composition showed that amphiphilic surfactants were present in the entire range of particle sizes, thus confirming recent works. This implied that they were present in hundreds to thousands particles cm^{-3} and not only in a few large particles, as it has been hypothesized. Their adsorption isotherms and Critical Micelle Concentration (CMC) were also determined. The low CMC obtained ($3 \times 10^{-5} – 9 \times 10^{-3}$ M) imply that surface tension depression should be significant for all the particles containing these compounds, even at activation (Growth Factor = 10). Amphiphilic surfactants are thus likely to enhance the CCN ability of sub-micron atmospheric particles.

Introduction

Predicting the formation of cloud droplets from aerosol particles in the atmosphere is still beyond current capacities, which leads to large uncertainties in predicting important cloud properties such as their precipitation and radiative contribution to climate. For sub-micron particles, the probability to become a cloud droplet, or CCN ability, is predicted by theory[1] to be affected by its surface tension. For decades, however, the surface tension of such particles was assumed to be constant and equal to that of pure water, and the role of this parameter ignored,[2-3] mostly because the conventional instruments to investigate particle CCN properties are not sensitive to surface tension and also because information on the surfactants present in atmospheric aerosols was scarce.[4-6]

Two main classes of compounds can lower the surface tension, σ (mN/m), of aqueous particles, but employing very different mechanisms and resulting in very different efficiencies: amphiphilic surfactants and water-soluble organic compounds. Amphiphilic surfactants, which possess a hydrophilic moiety and one or more hygrophobic chains, lower σ by anchoring their hydrophilic moiety into the aqueous surface and applying a force perpendicular to it with the hygrophobic chains.[7] Water-soluble organic compounds, on the other hand, lower σ by screening off the hydrogen bonds that are responsible for the high surface tension of aqueous solutions. This later mechanism is much less effective in reducing σ than that of amphiphilic surfactants, so that much larger concentrations are necessary to achieve the same effects. This is reflected in their respective adsorption isotherms (σ vs concentration graphs): water-soluble organics such as HULIS,[8] organic acids[9] or acetaldehyde[10] display a gradual decrease of σ with increasing concentration, typically 10 mN/m per decade of concentration, resulting in σ = 40 – 60 mN/m for concentrations above 0.1 M.[8-9, 11] By contrast, those for amphiphilic surfactants display a sharp decrease, ~ 30-40 mN/m per decade of concentration, until a specific concentration called critical micelle concentration or “CMC”, beyond which σ remains constant and low, $\sigma = \sigma_{min}$, with typically σ_{min} = 25 - 45 mN/m.[11-12] The CMC is thus a key parameter for the role of surfactant on cloud droplet formation. For a particle containing initially 0.1 M of surfactant and with σ = 50 mN/m, reaching activation with a Growth Factor GF = 5 would lead to ~ 10^{-3} M of surfactant. For an amphiphilic surfactant, this concentration would likely be larger than or comparable to the

CMC (which are typically between 10^{-5} and 10^{-3} M), thus ensuring $\sigma = \sigma_{min} \leq 50$ mN/m at activation. But for a water-soluble surfactant, the same decrease in concentration would result in an increase of σ by over 20 mN/M, thus practically to the value of pure water, $\sigma_{water} = 72.8$ mN/m. Amphiphilic surfactants are therefore the most likely compounds to lower the surface tension of particles at activation.

Recent studies have started to demonstrate the role of surfactants in cloud droplet formation,[13-16] which has prompted the development of methods to investigate these compounds in atmospheric aerosols.[4-6, 17-18] These methods provide valuable information on atmospheric surfactants, in particular on their concentrations.[5, 17-18] But, without a selective extraction, they do not allow to distinguish between the different types of surfactants. Over the years we have developed analytical methods to extract and characterize specifically amphiphilic surfactants in atmospheric aerosols.[11-12, 19-20] With them, the presence of such compounds in atmospheric PM_{10}[11, 19, 21] and $PM_{2.5}$[12] aerosols was established. More recently, the selective extraction was applied to PM collected on a cascade impactor and evidenced the presence of amphiphilic surfactants throughout the entire size range, including sub-micron ones.[18] As sub-micron particles are the only ones for which surface tension effects are expected to affect the CCN ability, the concentrations and properties (adsorption isotherms) of the surfactants present in such particles in the atmosphere needed to be further characterized.

In this work, PM_1 samples were collected with a resolution of 12 or 24 h in urban, coastal and remote regions of Europe (Lyon, France; Rogoznica, Croatia; and Pallas, Finland, respectively) and analyzed with the objective to determine the presence of amphiphilic surfactants, their concentration, adsorption isotherms, CMC, and any other information (geographic and time variability…) that might be useful to predict their effects on cloud droplet activation in the real atmosphere.

Experimental Section

Aerosols sampling. Aerosol samples were collected on pre-baked 150 mm-Quartz filters with a DIGITEL DA80 through a PM_1 inlet with a flow of 30 m^3 h^{-1} and a frequency of 12 or 24 h. Three locations were chosen, representative of different types of environment. The first site was the campus of Université Lyon 1, France (45°47'00.3"N 4°52'02.9"E), in the middle of the Lyon-Villeurbanne agglomeration, thus an urban environment. The sampler was positioned on a top of the "Dirac" building at ~ 205 m a.s.l. The sampling took place from 1 December 2014 to 19 January 2015, resulting in 53 samples, including 8 blanks. The second site was at the Marina Frapa, Rogoznica, Croatia (43°31'47.9"N 15°57'35.1"E), on a peninsula surrounded by the Adriatic Sea, thus representative of a coastal region. The sampler was placed at close to sea level and the sampling lasted from 01 February 2015 to 20 March 2015 but resulted only in 17 samples, of which 2 were blanks, due to technical problems with the sampler. The third site was the sub-Arctic site of Sammaltunturi (67°58'23.8 N, 24°076'57.3 E) of the Pallas-Sodankylä GAW (Global Atmosphere Watch) operated by the Finnish Meteorological Institute, Finland,[22-24] a remote site. The sampler was placed at the research station at the top of the Sammaltunturi hill (565 m a.s.l) and the sampling took place from 21 April 2015 to 03 December 2015 and resulted in 255 samples, of which 23 were blanks. But only 142 of those samples were analyzed for surfactants and are presented in this work. In Lyon and Rogoznica, the samples were taken over 12 h (7:00 am/7:00 pm, thus alternating day/night) and in Pallas they were taken over 24 h (midnight- midnight). All the filters were dried for 72 h and weighted before and after sampling with a precision of ± 0.1 mg, to determine the mass of aerosol sampled.

Sample extraction and analysis. The protocols for the extraction and determination of the concentrations and adsorption isotherms for the amphiphilic surfactants have been described in detail in several publications.[12, 20] Briefly, the extraction method involves two consecutive steps, a water extraction and a SPE-based one, ensuring that only amphiphilic surfactants are collected and not water-soluble ones. For all the atmospheric aerosol samples studied until now, however, the second extraction step was found to remove all the effective surfactants from the samples (i.e. all the compounds contributing to lower σ), which was demonstrated by the σ of the first water extract increasing back to the value for pure water, σ_{water}, after the second extraction. This implies that amphiphilic surfactants are, in practice, the only effective surfactants in atmospheric aerosols, water-soluble ones having only modest (non-measurable) contributions. The concentrations in the final extracts (after the two steps) are determined separately for anionic, cationic, and non-ionic surfactants by preparing three aliquots and adding specific dyes in each of them. The absolute molar concentration of each ionic surfactant fraction is then determined by UV-visible absorbance and comparison with absolute calibration curves (i.e. independent of the identity of the surfactant). The concentrations in the initial aerosol samples were then determined from the ratio of the extract volume to the sampled aerosol volume, the latter being obtained from weighing the samples and assuming a density of 1 g cm^{-3}.

The adsorption isotherms were determined for all the surfactants extracted from the Lyon and Rogoznica samples, and for about half of those from the Pallas samples (75 out of 142) because of the large number of samples at this site and the time-consuming nature of the analysis. These isotherms were determined point by point by measuring the surface tension of the extracts and of their successive dilutions. In each case, surface tension was measured with the hanging droplet technique, using a Dataphysics OCA 15EC tensiometer.[12] On these isotherms, the CMC was determined graphically as the intersection between the sharp decrease of the curve and the plateau corresponding to σ_{min} at large concentration. Although it has been argued that surface tension measurements made on macroscopic droplets, as with the hanging droplet technique, might not be representative of σ for microscopic droplets, all the experimental works that have explored this question so far, in particular with single-particle techniques, have confirmed the good agreement between these approaches.[25-26]

PM_1 mass concentrations. For the Lyon and Rogoznica sites, the PM_1 mass concentration in air was determined for each sample by dividing the sampled mass weighed on the filters by the volume of air sampled (360 m^3). In Pallas, where the site was in clouds for a significant fraction of the time, the PM_1 volume concentration was obtained by comparing the $PM_{0.5}$ size distribution measured with a differential mobility particle sizer (DMPS) filtering out cloud droplets with the PM_1 volume measured with an Aerodynamic Particle Sizer (APS) in the absence of cloud to avoid the contributions from activated particles.[22, 27] This volume concentration was converted into a mass concentration assuming a density of 1 g cm^{-3}.

ACSM measurements. In Pallas, the concentrations of the organic fraction and main ions, SO_4^{2-}, NO_3^-, NH_4^+, and Cl^-, in the PM_1 particles were monitored with an Aerosol Chemical Speciation Monitor (ACSM, Aerodyne)[28] with a 50-min resolution.[29]

Results and discussion

Surfactant concentrations. Amphiphilic surfactants were found in all the samples analyzed (Fig. 1) with concentration between (0.01 ± 0.003) and (2.8 ± 0.9) μg m^{-3} in the air, assuming a typical molecular weight of 500 g mol^{-1}, and between (6.8 ± 2.2) mM and (1.3 ± 0.4) M in the particle volume. The lowest concentrations were recorded in Rogoznica (median: 0.08 μg m^{-3}or 22 mM) and Pallas (median: 0.03 μg m^{-3} or 47 mM), and the largest at the urban site of Lyon (median: 0.6 μg m^{-3} or 73 mM) (Fig. 1). The concentrations obtained at the coastal site of Rogoznica, Croatia, were consistent with those of amphiphilic surfactants measured previously in $PM_{2.5}$ aerosols at the coastal site of Askö, Sweden (median: 0.1 μg m^{-3} or 38 mM),[12] in spite of the different sampling resolution (72 h). The concentrations obtained in this work were also generally consistent with those recently reported (0.07 – 0.95 μg m^{-3}) for amphiphilic surfactants in 0.038 – 1 μm size fractions of aerosols from Ljubljana, Slovenia.[18] All this supported the validity of our results and indicated that amphiphilic surfactants are present in sub-micron aerosol particles in many different regions of Europe.

As in previous works,[12, 20] the surfactants extracted from the samples were divided into three ionic types: anionic, cationic and non-ionic surfactants. In all the samples studied in this work, anionic and non-ionic surfactants largely dominated over cationic ones, the latter being detected only in a few occurrences and at very small concentrations (Fig. 1). In Lyon and Pallas, non-ionic surfactants were more abundant than anionic ones (by about a factor 2, both in μg m^{-3} and in mM). In Rogoznica the opposite trend was observed (Fig.1), as it had been also observed in the $PM_{2.5}$ from Askö, Sweden, thus confirming this trend in coastal regions. At all the sites, these ionic fractions displayed some degree of correlation with each other, in particular the anionic and non-ionic ones (r^2 = 0.8 over 15 samples in Rogoznica; r^2 = 0.62 over 43 samples in Lyon and r^2 = 0.43 over 142 samples in Pallas) (Fig. S1 of the Supplementary Information), suggesting common background sources. However, these ionic fractions also displayed important sample-to-sample variability, much larger than the uncertainties and which could not be accounted for by constant ratios between them. This suggested the existence of several sources, contributing differently to the different ionic fractions, in addition to a potential common background source.

It was important to determine if the observed sample-to-sample variability in concentration reflected an actual variability in the particles (internal mixing of different surfactants at different times on the particles) or resulted from mixing different particles containing different surfactants during the analysis (external mixing). For this, the concentrations were compared with the PM_1 volume (or mass), surface, and number concentrations. First, this comparison showed that, in average, the surfactants accounted for small fractions of the PM_1 mass (in $\mu g\ m^{-3}$): 7.3 % in Lyon, 1.5 % in Rogoznica, and 4.7 % in Pallas. Then, for the Rogoznica and Lyon samples, for which only the mass concentration of PM_1 was available (Fig. S2), comparing it with the total and ionic concentrations showed no correlation ($r^2 < 0.1$), which seemed to exclude internal mixing as the cause for the variability in surfactant concentration. However, because PM_1 number concentrations were not available at these sites, it was not possible to confirm definitely the occurrence of external mixing in these samples. In Pallas, no correlation was found between the surfactant concentrations and the PM_1 number concentrations (Fig. S2), thus excluding external mixing. But correlations were found with the PM_1 volume concentration ($r^2 = 0.52$ over 142 samples) and, more clearly, with their surface concentration ($r^2 = 0.57$) (Fig. S3), confirming internal mixing as the cause for the observed variability in surfactant concentration. The larger correlation obtained with the PM_1 surface than with the volume concentrations implied that this mixing was surface-dependent rather than bulk-dependent, which was consistent for compounds that are present exclusively at the surface of particles. The apparent correlation between surfactant concentration and PM_1 volume was likely to be indirect and result from the strong correlation between PM_1 surface and volume concentration at this site. These results thus implied that the variability in the surfactant concentrations in the Pallas samples reflected an actual variability in the surfactant mixtures present at the surface of the particles.

Interestingly, the strongest correlation with the PM_1 surface concentration was obtained with the total surfactant concentration, while correlations with each of the ionic fractions were markedly weaker ($r^2 = 0.50$ with non-ionic concentration; $r^2 = 0.39$ with anionic concentration; Fig. S3). As discussed below, the opposite was observed with particulate-phase concentrations, for which correlations with the total surfactant concentration always clearly resulted from a much stronger correlation of one of the ionic fraction. This might indicate that the surfactant mass concentrations (in $\mu g\ m^{-3}$ in air) were controlled (i.e. limited) by the aerosol surface, while the particulate-phase concentrations (in M) were controlled by the sources, determining the ratios between the different ionic fractions and other chemical components.

In Pallas, over the last 6 weeks of sampling (15 October – 24 November 2015, corresponding to 38 samples), the surfactants concentrations could also be compared with the PM_1 chemical composition in term of organic, SO_4^{2-}, NO_3^-, NH_4^+ and Cl^- fractions measured with an ACSM (Aerodyne). The average PM_1 composition over this period, including both the surfactants and the chemical composition given by ACSM, is presented in Fig. 2, where a molecular weight of 200 g mol^{-1} was assumed for the organic fraction. The surfactant concentration represented a small fraction of the total organic compounds: 5.6 % in average in the air ($\mu g\ m^{-3}$) and 2.3 % in the particulate phase (mM).

Potential correlations between the surfactants concentrations and the chemical fractions were explored. First, studying the concentrations in the air (in μg m^{-3}) provided mostly information on the largest particles of the population, that contributed most to the PM_1 mass. The mass concentration of the organic and NO_3^- fractions in air correlated with each other (r^2 ~ 0.65) and moderately with the PM_1 mass ($r^2 = 0.57$) (Fig. S4), while no correlation was found with the other chemical fractions. The total surfactant concentration in air correlated weakly with the organic ($r^2 = 0.46$) and NO_3^- ($r^2 = 0.31$) fractions and with the PM_1 mass ($r^2 = 0.48$) (Fig. S4), but with no other ions. This suggested that some of the surfactants were present in the large particles of the population that contributed most to the organic and NO_3^- masses in the PM_1. The absence of correlation with the SO_4^{2-} fraction suggested that these large particles did not originate from anthropogenic pollution. As above, these correlations with the surfactant concentrations in air were stronger with the total concentration than with each of the ionic fractions, probably because these total surfactant concentrations were controlled by the PM_1 surface concentration (which correlated strongly with the PM_1 mass concentration).

Then, examining the concentrations in the particulate phase (in M or mM) provided information on the smallest particles of the population, as these concentrations were obtained by dividing the gas-phase concentration by the PM_1 volume. As shown in Fig. 2 the particulate-phase composition of these small particles was dominated by NH_4^+. Strong correlations were found between NH_4^+ and Cl^- ($r^2 = 0.91$), NO_3^- ($r^2 = 0.88$), and the organic fraction ($r^2 = 0.78$) (Fig. S4), implying that these small particles mostly contained NH_4Cl, NH_4NO_3 and some organic compounds (or organo-nitrates) rather than ammonium sulfate. The total surfactant concentration also correlated strongly with NH_4^+ ($r^2 = 0.67$). But, unlike with the concentrations in air, this could be clearly attributed to the non-ionic fraction, which displayed a much stronger correlation

($r^2 = 0.82$) (Fig. 2), while the anionic surfactants had a much weaker one ($r^2 = 0.49$) (Fig. S4). As with NH_4^+, strong correlations were also found between non-ionic surfactants and Cl^- ($r^2 = 0.77$), NO_3^- ($r^2 = 0.69$), and the organic fraction ($r^2 = 0.53$) (Fig. 2). In all cases, the anionic and cationic fractions followed the same trends but with weaker correlations. These strong correlations between specific ionic surfactants and other particulate-phase components show that the particulate-phase composition of the PM_1 and relative abundance of the surfactant ionic fraction were controlled by the sources, unlike the mass concentrations in air, which were controlled by the PM_1 surface.

The strong correlations between non-ionic surfactants and the organic and inorganic composition implied that these surfactants were present together with NH_4Cl and NH_4NO_3 in the smallest particles. This, together with the evidence reported above for the presence of amphiphilic surfactant in the large particles, indicated that these compounds were present in the entire particle size range, including the smallest ones. These results were consistent with recent works reporting the presence of amphiphilic surfactants in size fractions from 38 nm to 1 μm in aerosols from Ljubljana, Slovenia[18] and confirmed that amphiphilic surfactants are present throughout the entire range of particle sizes in the atmosphere.

Number of sub-micron particles containing amphiphilic surfactants. Although the analyses in this work do not determine directly the number of particles in the aerosol populations that contain amphiphilic surfactants, this number can be estimated from the concentrations measured and the fact that the surfactants are present in all particle sizes. First, a lower limit can be calculated by assuming that all the surfactants are contained in particles made only of surfactant, with a density of 1 g cm^{-3} and a diameter of 150 nm (typical for the maximum of a PM_1 size distribution). Each pure surfactant-particle would thus contain 3.5×10^{-18} mol, so that the concentrations measured in this work would be accounted for by 20 to 430 cm^{-3} of these particles. If, as indicated by the surfactant/PM$_1$ mass ratios obtained in this work, the surfactants did not exceed 10 % of the particle mass instead of 100 %, the concentrations measured at the different sites implied that these compounds were present in 200 to 1500 particles cm^{-3} in average. These numbers are significant and in the range reported for CCN numbers.[3] These results thus clearly show that surfactants are not present only in a few, large particles in the atmosphere, as it has been hypothesized.

Isotherms and CMC. Adsorption isotherms were determined for all the surfactant samples from Lyon and Rogoznica, and about half of those from Pallas. The results are presented in Fig. 3. They all displayed a sharp decrease of the surface tension at low concentration and a minimum surface tension values between 25 and 45 mN/m, that are typical of amphiphilic surfactants. These curves are comparable to those obtained previously from amphiphilic surfactants extracted from PM$_{10}$[11, 19] and PM$_{2.5}$[12]

As explained in the Experimental Section and illustrated in Fig. 3B, the CMC was determined graphically on these isotherms, which, depending on the sample leaded to uncertainties between 30 to 50 % (× 1.5/1.5). The results are presented in Fig. S5. In Rogoznica and Pallas, the CMC were all lower than 10^{-3} M, with averages of 1.9×10^{-4} M and 2.1×10^{-4} M, respectively. In Lyon they were nearly 10 times larger, but all lower than 10^{-2} M, with an average of 2×10^{-3} M. As the CMC is mainly a characteristic of the molecular structure of the surfactant, and the environment (particle composition) affects it by less than a factor of 2,[30] the very different CMC values obtained in Lyon compared to the other sites clearly indicated the presence of very different surfactants at this site.

Fig. S5 also shows that, at most sites, the CMC varied by more than one order of magnitude from sample to sample, thus also indicating the presence of different surfactants at different times in the samples. As the CMC is a key parameter for the role of surfactants on cloud droplet formation, it was important to determine if this variability was actually occurring in the particles (internal mixing) or resulted from the mixing of different particles containing surfactants with different CMC during the analysis (external mixing). For this, the CMC values were compared with the PM_1 volume (or mass), surface, and number concentrations. In the Lyon samples, no correlation was found between the CMC and PM_1 mass concentration. This, together with the absence of correlation between the PM_1 mass concentration and surfactant concentration discussed above, and the significant number of samples in the series, seemed to exclude internal mixing as a cause for the concentration and CMC variability in these samples. But the absence of data on PM_1 number concentrations at this site prevented to conclude definitely that external mixing was the cause for this variability. In Rogoznica, an anti-correlation was found between the CMC and the PM_1 mass concentration ($r^2 = 0.54$) (Fig. S6), indicating that the strongest surfactants (with smallest CMC) were present in the largest particles and, more generally, that the variability in the CMC resulted from the internal mixing of surfactants at the surface of the particles. The lack of correlation between the surfactant concentration and the PM_1 mass concentration reported above, which seemed to exclude internal mixing, might thus have resulted from the limited number of samples in the series. In Pallas, weak correlations were found between the CMC and the PM_1 mass concentration ($r^2 = 0.32$) and surface concentration ($r^2 = 0.29$) (Fig. S6), but none with the number concentration ($r^2 < 0.1$). This confirmed that external mixing could be excluded and that internal mixing was responsible for the variability in surfactant concentration and CMC in these samples. But, in contrast with the Rogoznica samples, the stronger surfactants were present in the smallest particles in Pallas. All these results show that, at least at two of the sites studied, the wide variability in the surfactant concentration and CMC reflected actual variabilities at the particle level, and resulting from the mixing of different surfactants at different times at their surface.

Implications for the CCN ability of atmospheric sub-micron particles. As explained above, the CMC is a key parameter for the surfactant efficiency in droplet activation, as it determines the concentration at which the σ of a particle is minimum, thus how much this particle can take up water before σ increases. To determine if the surfactants studied in this work can maintain a σ lower than σ_{water} at activation, the ratio of surfactant concentration, C, over the CMC for each sample was thus used to calculate the σ as function of the Growth Factor, GF. For this, GF was converted into a volume change (i.e. a dilution factor on the concentration), which was then reported on the isotherm of the sample. To simplify, only three domains of σ were considered, reflecting a typical isotherm: for $C/CMC > 1$, $\sigma = \sigma_{min}$, with typically $\sigma_{min} < 45$ mN/m (cf. Fig. 3); for $1/10 < C/CMC < 1$, $\sigma_{min} < \sigma < \sigma_{water}$; for $C/CMC < 1/10$, $\sigma = \sigma_{water}$. The results are presented in Fig. 4. They show that σ for PM_1 particles is lower than σ_{water} for GF = 5 in 98 % of the samples, and in 60 % of them for GF = 10. The σ of sub-micron particles at these sites is thus very likely to be significantly depressed at activation (GF = 5 to 10). Note, however, that these calculations were based on concentrations averaged over the entire samples, thus assuming that the surfactants were uniformly present in all the particles. But if, more realistically, the surfactants are only present in a fraction of the particles, their typical concentration in the particle phase increases accordingly and the value of GF for which σ becomes lower than σ_{water} is much larger. For instance, if the surfactants are present in a fraction of the particles representing only

10 % of the total PM_1 volume concentration, the particulate-phase concentrations used in the above calculations would have to be increased by a factor 10, thus leading to $\sigma < \sigma_{water}$ for GF = 10 in the totality of the samples studied in this work. These results clearly show that the amphiphilic surfactants present in of sub-micron particles in the atmosphere are very likely to lower their σ compared to water even at activation, thus enhance their activation into cloud droplets.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge.

Figure S1: Correlations between anionic and non-ionic surfactants in PM_1 (gif file)

Figure S2: Variations of the PM_1 mass, surface and volume concentration at the different sites (gif file).

Figure S3: Correlations between the ionic fractions of surfactants and PM_1 surface concentration in Pallas, Finland (gif file).

Figure S4: Correlations between the PM_1 chemical fractions and the surfactant concentrations in Pallas, Finland (gif file).

Figure S5: Variations of the CMC obtained for the amphiphilic surfactants in the PM_1 samples at the different sites (gif file).

Figure S6: Correlations between the surfactant CMC and the PM_1 mass and surface concentrations (gif file).

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Author Contributions

V.G. performed most of the sampling and analyses, with some assistance from L.F. and from D.K.S on some samples and equipment made available by C.F. Access to the site in Rogoznica was obtained from S.F and sampling was assisted by A.C.K. Access to the site in Pallas was obtained from E.A. and H.L. Setting the sampling was assisted by L.F and A.A.F. and other data (PM_1 size distribution, ACSM measurements…) were made available by N.K., M.A. and D.B. B.N. and R.C.C supervised the joint project and scientific discussions. B.N. wrote most of the manuscript but all the authors discussed the results and contributed to the manuscript.

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FIGURES

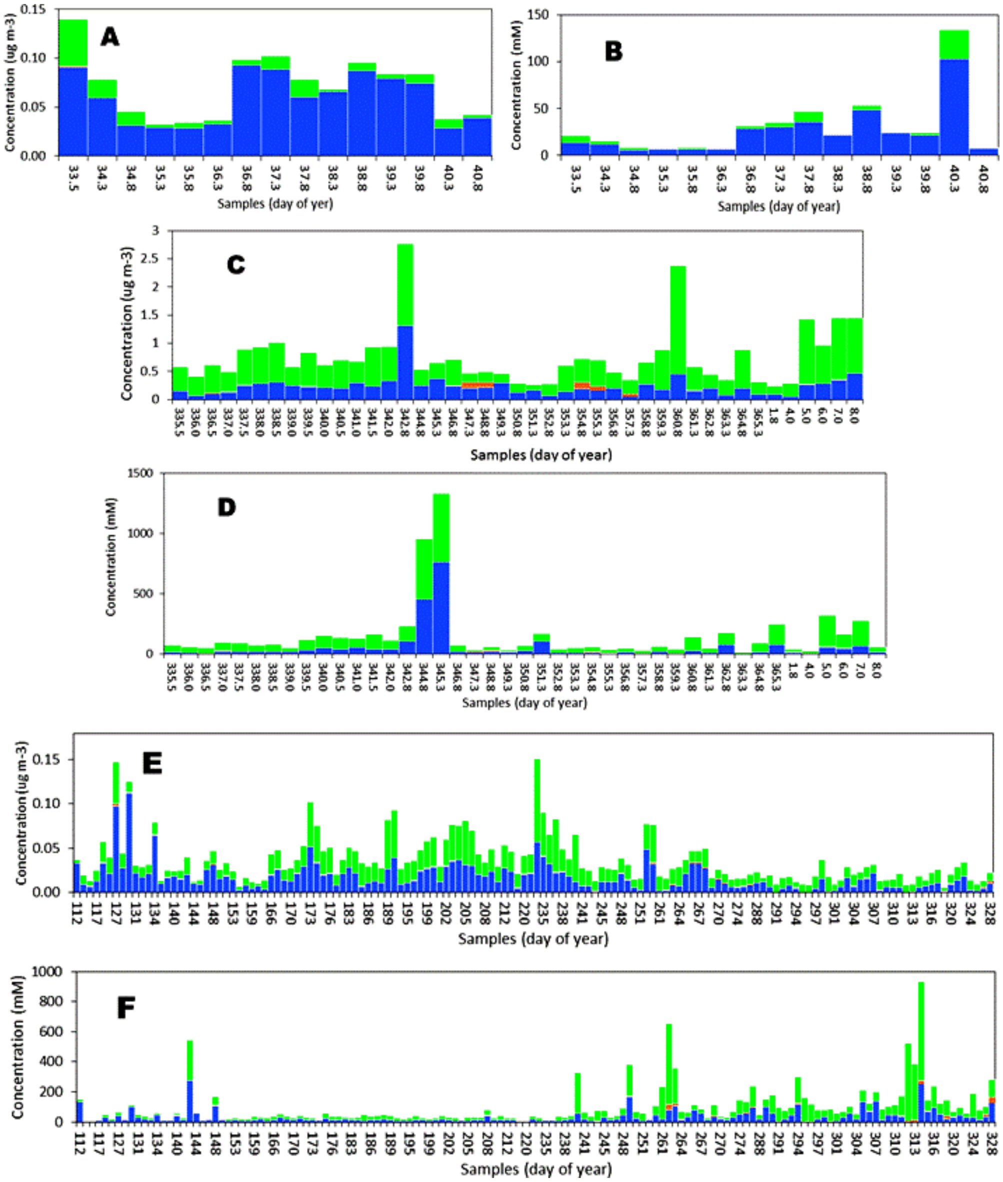

Figure 1: Concentration of amphiphilic surfactants in PM_1 Rogoznica, Croatia (A in µg m^{-3}; B in mM) and Lyon, France (C in µg m^{-3}; D in mM), and Pallas, Finland (E in µg m^{-3}, F in mM). Blue areas: anionic surfactants; red: cationic ones; green: non-ionic ones.

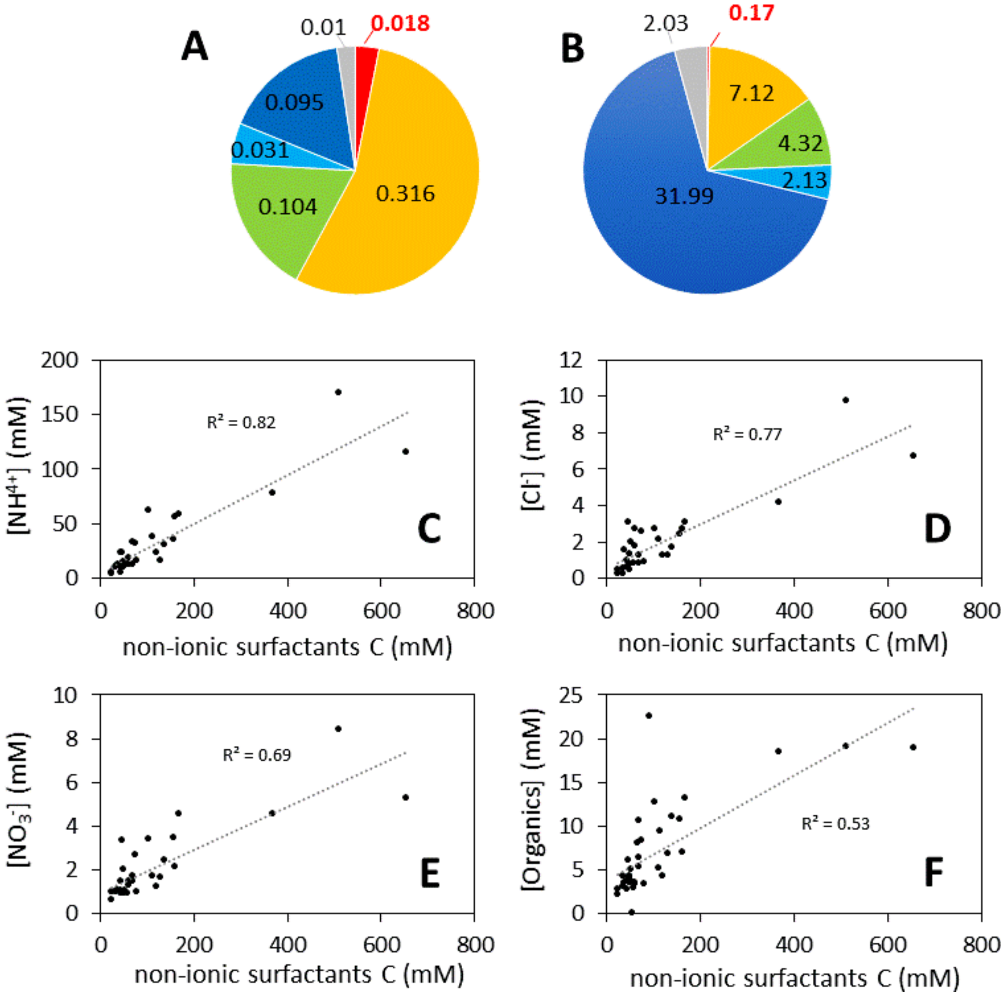

Figure 2: Average PM_1 composition measured by ACSM in Pallas, Finland, for the period 10/15-11/24/2015 (A: in µg m^{-3} in air; B: in mM in the particle volume), and correlations with the ionic fractions (C-F). For A) and B): red = surfactants; yellow: organic; dark blue = NH_4^+; clear blue = NO_3^-; green = SO_4^{2-}; grey = Cl^-.

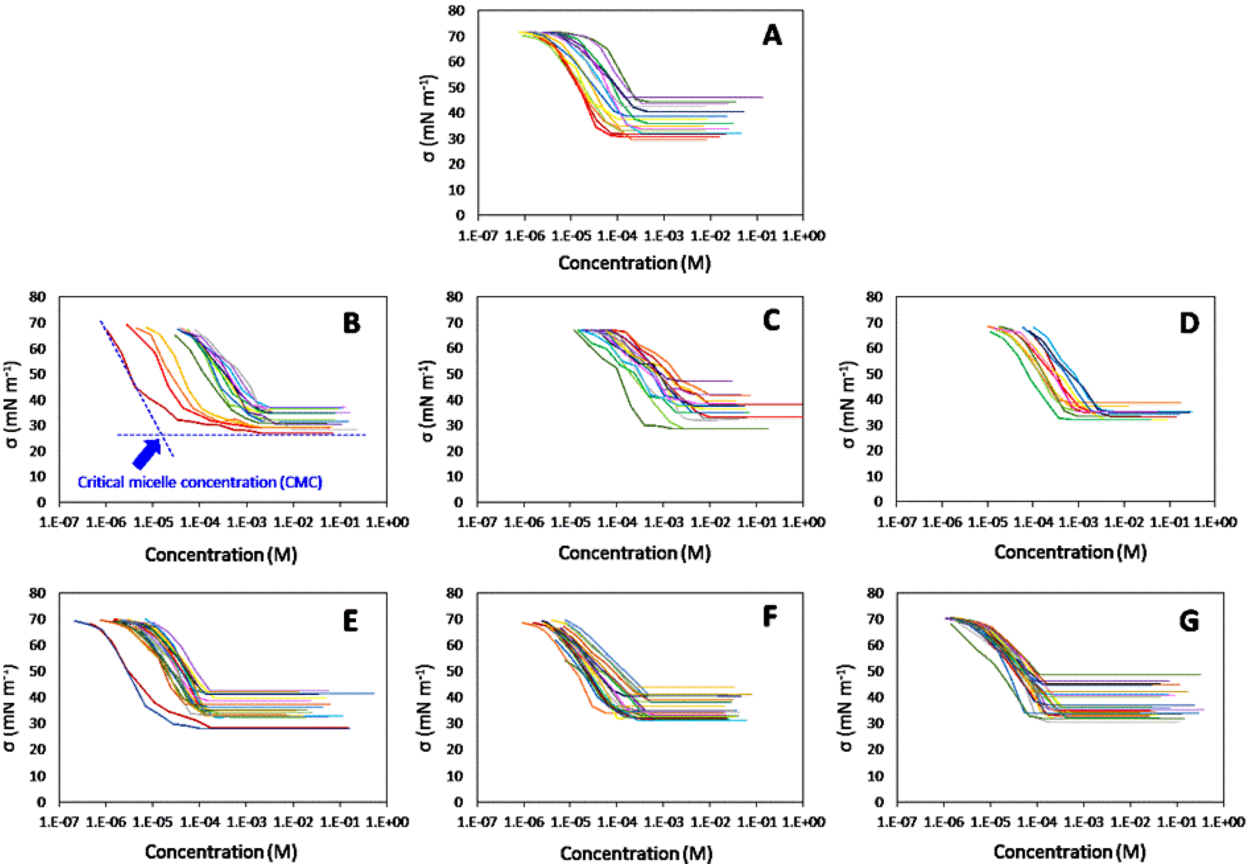

Figure 3: Adsorption isotherms for the surfactant mixtures extracted from PM1: A) Rogoznica, Croatia, 02 -09/02/2015; B-D) Lyon, France, B: 1 – 8/12/2014, C: 9 – 17/12/ 2014, D: 12 – 19/01/2015; E-G) Pallas, Finland, E: 22/04 – 30/05/2015, F: 31/05 – 31/07/2015, G: 31/07 – 14/11/2015.

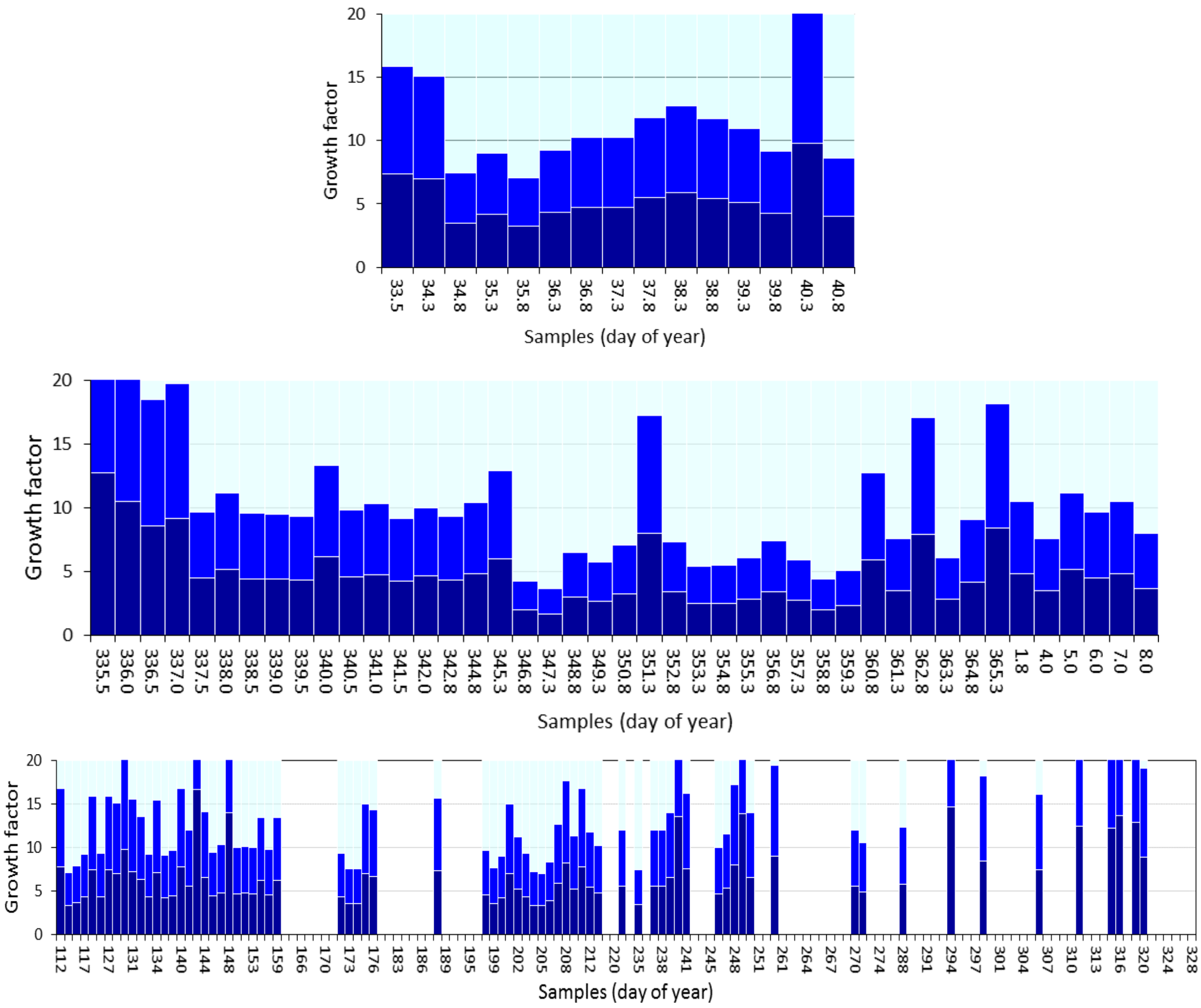

Figure 4: Surface tension domains for the PM$_1$ particles as function of the Growth Factor. Pale blue: $\sigma = \sigma_{water}$; light blue: $\sigma_{min} < \sigma < \sigma_{water}$; dark blue: $\sigma = \sigma_{min}$. Top: Rogoznica, Croatia; Middle: Lyon, France; Bottom: Pallas, Finland.