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A possible role of ground-based microorganisms on cloud formation in the atmosphere

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Abstract

The formation of clouds is an important process for the atmosphere, the hydrological cycle, and climate, but also a difficult one to predict because some aspects of the transformations of aerosol particles into cloud droplets are still not well understood. In this work, we show that microorganisms might affect cloud formation without leaving the Earth's surface by releasing biological surfactants (or biosurfactants) in the environment, that make their way into atmospheric aerosols and should significantly enhance their conversion into of cloud droplets.

In the first part of this work, the cloud-nucleating efficiency (or "CCN" efficiency) of standard biosurfactants was characterized by osmolality and surface tension measurements and found to be better than for any aerosol material studied so far, including inorganic salts. These results identify molecular structures that give to organic compounds exceptional CCN properties. In the second part, atmospheric aerosols sampled at different locations (temperate & tropical, forested & marine ones) were found to all have a surface tension below 30 mN/m, which can only be accounted for by the presence of biosurfactants. The results also showed that these biosurfactants were concentrated enough to significantly affect the surface tension of these aerosols and enhance their CCN efficiency.

The presence of such strong biosurfactants in aerosols would be consistent with the recent identification of organic fractions of higher CCN efficiency than ammonium sulfate in aerosols. And a role of microorganisms at the Earth's surface on clouds could also explain previously reported correlations between algae bloom and cloud cover. Our results also suggest that biosurfactants might be common in aerosols and thus of global relevance. If their impact on cloud formation is confirmed by future studies, this work would have identified a new role of microorganisms at the Earth's surface on the atmosphere, and a new component of the Earth's system and climate.

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1 Introduction

Clouds play important roles in the atmosphere, the hydrological cycle, and climate. In particular, they constitute the largest cooling contribution to climate, but also the one containing the largest uncertainties (Foster et al., 2007a) because some aspects of the nucleation of cloud droplets from atmospheric aerosols are still not well understood. A possible contribution of the biosphere in these processes has been investigated for decades. Microorganisms, for instance, were found to be efficient ice nucleating agents (see for instance Schnell and Vali, 1972; Schnell, 1976; Bauer et al., 2003; Pratt et al., 2009). Their contribution to liquid clouds, however, is unclear because airborne microorganisms seem too large and to be at too small concentrations in the atmosphere (see for instance Harrison et al., 2005) to make a significant contribution to Cloud Condensation Nuclei (CCN) (Bauer et al., 2002; Pósfai et al., 2003). A link between the biosphere and liquid clouds was presented in the CLAW hypothesis (Charlson et al., 1987): the phytoplankton in the oceans emits dimethylsulfide (DMS), which is converted into sulfate salts in the atmosphere (Shaw, 1983), one of the most efficient cloud-nucleating materials (Charlson et al., 1987). But global inventories now show that this link is rather small, since only a small fraction of DMS (~25%) produces sulfates (Nilsson et al., 2002) and over 80% of the sulfate in the atmosphere is non-biological in origin (Forster et al., 2007b). Thus, the main cloud-nucleating materials currently identified in aerosols are non-biological: inorganic salts such as sea-salt (mostly, sodium chloride) or ammonium sulfate. Some organic compounds present in aerosols, such as organic acids (Facchini et al., 1999) and "Humic-Like Substances" or "HULIS" (Taraniuk et al., 2007), display some surface-active properties, which contribute to enhance the formation of cloud droplets. But their effect is modest and, in general, none of the classes of organic compounds identified in aerosols and characterized in laboratory have shown better CCN properties than inorganic salts (McFiggans et al., 2006).

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In this work, instead of studying the role of airborne microorganisms on the nucleation of cloud droplets, we study the role of substances produced by some microorganisms and released in the environment: biosurfactants. This study will lead first to the identification of specific classes or organic molecules displaying exceptional surface-active properties. Another important advantage of these substances over airborne microorganisms is that they could make their way in aerosol particles of all sizes, including the sub-micron ones relevant for cloud droplet nucleation, and allow microorganisms to affect cloud formation without even leaving the Earth's surface. The second part of this work will thus present the first investigation of the presence and effect of biosurfactants in real aerosol samples.

2 Experimental

2.1 Biosurfactant standards

The first part of this work focused on characterizing the CCN properties of standard biosurfactants. Three different classes of biosurfactants were studied: rhamnolipids, galactolipids (mono- and di-galactosyl diacylglyceride), and a lipopeptide, (surfactin). Most biosurfactants have to be extracted from microorganisms. The known rhamnolipid sample JBR425 (Jeneil Biosurfactant Company, USA) used in our study was provided by Dr. Wang, PEER Centre, California Institute of Technology, USA (extract 1). Its composition is described in Wang et al. (2007). Another biosurfactant extract (extract 2) isolated from an environmental strain of *P. aeruginosa* was also studied (Hultberg et al., 2008). The extraction was performed as described in Zhang and Miller (1992). Monogalactosyl diacylglyceride (~95%), digalactosyl diacylglyceride (≥95%), and surfactin (≥98%) were purchased from Aldrich.

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2.2 Aerosol sampling

For the second part of the work, aerosols were sampled at Aspvreten, Sweden (forested/coastal region), 58°48′ N 17°23′ E, from April to May 2008; in the Stockholm Archipelago ~20 km at sea, Sweden ("marine" sample), 59°47′5 N 19°30′5 E, in July 2007 during an algae bloom; in Hyytiälä, Finland (temperate forest), 61°85′ N 24°28′ E, in July 2008; in the tropical forest, Brazil, 2°37′ N 60°12′ W, in May 2008. The samples were taken on Quartz fiber filters using high-volume samplers, for a duration between 48 and 150 h, corresponding to a total of 100–500 m^3 of sampled air. For the marine samples, 150 L of seawater were sampled just below the sea-surface and the aerosols were generated by jet impact on the surface of this water in a stainless steel tank. This technique has been previously shown to produce aerosols physically and chemically similar to those emitted by the sea surface (Mårtensson et al., 2003; Facchini et al., 2008). Because the analyses required large amounts of aerosol material, the size fraction sampled at these sites was PM_{10}, except in Aspvreten, where it was $PM_{2.5}$.

2.3 Sample extraction

The filters were extracted in Milli-Q water at 4°C and filtered through Millipore 0.45 μm syringe filters. An absorbent, silicone, was added and rotated (20–25 rpm) for 24 h. The amphiphilic fraction was extracted in methanol, dried, and diluted in MilliQ-water. For the surface tension measurements, 1 to 3 filters were extracted together.

2.4 Chemical analysis

In this work, chemical analyses are presented only for the identification of one of the microbial extracts (JBR425). These analyses were performed by tandem mass spectrometry (MSMS) with a Quadrupole Time-of-Flight Premier (Waters, Manchester, UK) mass spectrometer with an electrospray ion source. The microbial extract was intro-

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duced by direct infusion or following separation on an Acquity BEH C8 column fitted to an Acquity UPLC (Ultraperformance Liquid Chromatography) system (Waters, Milford, USA).

2.5 Osmolality and surface tension measurements

The CCN efficiency of substances can be quantified by their Köhler curves, which represents the water vapor pressure (or supersaturation = water vapor in excess to saturation) necessary to activate particles made of these substances into cloud droplets. These curves can be built point by point by measuring the surface tension and osmolality of solutions of these substances in water, using a method developed recently (Kiss and Hansson, 2004; Varga et al., 2007; Ekström et al., 2009). In the first part of this work, osmolality and surface tension measurements were performed to investigate the cloud-forming efficiency of different standard biosurfactants. These measurements followed the procedure described in Ekström et al. (2009), and used a KNAUER K – 7000 vapor pressure osmometer and a FTÅ 125 tensiometer.

For the second part of this work, the surface tension of real aerosol sample extracts was measured using the same tensiometer. Control tests with "blank" filters were performed to ensure that these measurements were free from artifacts due to the extraction method or to contamination during sampling. The extraction method itself did not lead to any artifacts, the surface tension obtained for blank filters being within 5% of the one of pure water (73 mN/m), which was within the experimental uncertainties (see discussion of the uncertainties in Ekström et al., 2009). Only one blank filter displayed evidence of a small contamination, possibly due to bacterial growth on the sampler, but which affected the surface tension by less than 10%. A systematic cleaning of the sampler was subsequently performed and no further contamination was observed.

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3 Results and discussion

3.1 Cloud-forming efficiency of standard biosurfactants

A large variety of microorganisms are known to synthesize strong surfactants, or biosurfactants, that are present at their cell surface or released into the environment, and can reduce the surface tension of water from 73 mN/m to less than 30 mN/m (Hommel and Ratledge, 1993; Desai and Banat, 1997). The production of biosurfactants is however not common to all microorganisms, and the ability of some species rather than others to synthesize these substances and the physiological functions of these substances are still unclear. But while common biological material such as cell fragments, extracellular materials, and metabolites, all display some surface-active properties, only specific molecules are able to reduce the surface tension of water below 40 mN/m, and qualify as biosurfactants (Hommel and Ratledge, 1993; Desai and Banat, 1997). These exceptional properties are of great interest for industrial applications and some artificial surfactants have been synthesized to try to match them. But the presence of artificial surfactants in natural environments and, in particular, in the aerosol samples studied in this work is unlikely.

The first part of this work was dedicated to the investigation of the CCN efficiency of standard biosurfactants, chosen among the most common in the environment (Table 1):

- rhamnolipids, which are produced by *Pseudomonas aeruginosa* (Jarvis and Johnson, 1949), and belonging to the fluorescent pseudomonads, ubiquitous in the environment (Van der Kooij, 1979; Cho and Tedje, 2000; Bodour et al., 2003) and even in cloud and rainwater (Ahern et al., 2007),

- galactolipids (mono- and di-galactosyl diacylglyceride), which are common in freshwater and marine cyanobacteria (Merritt et al., 1991; Ikawa et al., 1994), such as those responsible for algae blooms (Shapiro, 1973), and

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– lipopeptide (surfactin), produced by *Bacillus subtilis*, also common in the environment (Bodour et al., 2003).

In particular, the rhamnolipids studied in this work were from two different bacterial extracts, and contained different mixtures of mono- and dirhamnolipids having different physico-chemical properties, as the mixtures produced by the bacteria depend on the strain and external conditions (Benincasa et al., 2004). The molecular structure of the surfactants contained in these extracts was confirmed by Electrospray Ionization High Resolution Hybrid Mass Spectrometry. For instance, Fig. 1 shows the MSMS spectra obtained from the extract of JBR425 and displaying the characteristic patterns of rhamnolipids (Mw: 504.330): the negative ion mode provided the pseudomolecular ion $[M\text{-}H]^-$ at m/z=503.33, fragment ions of the fatty acid moiety (hydrophobic chain) at m/z=169.12, and fragmentations of the rhamnose moiety (hydrophilic part) at m/z=163.07.

The cloud-forming efficiency of all these standard microbial surfactants was determined from their Köhler curves, representing the supersaturation necessary to activate particles made of these substances into cloud droplets (see examples on Fig. 2). These curves were built from the surface tension and osmolality obtained for different solutions of these substances in water, as described in the Experimental section. As microbial surfactants are always mixed with water-soluble compounds in the environment, produced by the microorganisms or present as nutrients (Hommel and Ratledge, 1993; Desai and Banat, 1997; Benincasa et al., 2004), the most realistic description of their CCN properties in aerosols was given by their mixtures with small amounts of sodium chloride or ammonium sulfate (~0.07–0.2 M). The corresponding Köhler curves, calculated for an initial ("dry") particle of diameter 60 nm, are shown on Fig. 2. All the curves for the standard surfactants displayed a critical supersaturation (maximum) lower than the curves of sodium chloride and ammonium sulfate: Sc=0.08–0.21, compared with Sc=0.25 for NaCl, and 0.34 for $(NH_4)_2SO_4$. To our knowledge it is the first time that specific organic molecules are shown to have better cloud-forming efficiencies than inorganic salts (McFiggans et al., 2006). These are important results because they

identify specific molecular structures giving to organic compounds exceptional CCN properties, and therefore indicate the type of structures that should be looked for in atmospheric aerosols. The Köhler curves also imply that aerosol particles containing these substances would nucleate into cloud droplets at lower supersaturation than inorganic salt particles or that, at similar supersaturation, they would form larger cloud droplets. These larger droplets would be more prone to precipitation, thereby affecting the optical properties of the clouds and, at large scale, their contribution to climate, as confirmed by previous studies (Ervens et al., 2005). These first results thus motivated the investigation of the presence and role of biosurfactants in aerosol samples.

3.2 Presence of biosurfactants in atmospheric aerosols

For the investigation of the presence of biological surfactants in atmospheric aerosols, aerosols were sampled at the four different locations described in the Experimental section: Aspvreten, Sweden (forested/coastal), Stockholm Archipelago, Sweden, (marine with algae bloom), Hyytiälä, Finland (temperate forest), and near Manaus, Brazil (tropical forest). Their amphiphilic fraction was extracted and investigated.

LC/MSMS analyses were first applied to these aerosol extracts but the sensitivity required for the identification of microbial surfactants was not sufficient. The extraction and analysis methods are being further improved, but another approach had to be used in the present work to investigate the presence of biosurfactants in these samples. The objective of this investigation was twofold,

1. evidencing the presence of biosurfactants in these samples, and
2. showing that they are in concentration sufficient to significantly lower the surface tension of the aerosols.

the surface tension of these aerosol samples was investigated, as this would answer both questions at the same time. The surface tension of these extracts was thus

measured and compared to those of other relevant aerosol materials, such as inorganic salts (sodium chloride and ammonium sulfate), organic acids (malonic acid), and HULIS, and to those of the standard microbial surfactants studied in the first part of the work. The results are presented in Fig. 3 as a function of the concentration of these different compounds in water.

First, a comparison of the curves for the different standard compounds (curves with triangles) shows the unique signature of the microbial surfactants compared to the other standard materials:

- very low surface tension values at large concentrations, down to 30 mN/m,
- low surface tension obtained for very low concentrations of the biosurfactants, typically 3 to 5 orders of magnitude lower than the concentrations of HULIS or organic acids present in aerosols,
- a sharp transition on the curves (>20 mN/m for a factor 10 in concentration) contrasting with the gradual effects of the HULIS and organic acids on the surface tension.

As explained above, surface tension values lower than 40 mN/m such as obtained with the rhamnolipids and lipopeptide in this work, are specific to biosurfactants. The higher value obtained with digalactosyl diacylglyceride in this work is a good illustration of the intermediate surface-active properties displayed by most biological molecules, but which do not necessarily qualify them as biosurfactants. The sharp transitions on these surface tension curves corresponded to the Critical Micelle Concentration (CMC), for which the surfactant molecules in solution arrange themselves in aggregates, or micelles, exposing their hydrophilic moieties to the solvent. The importance of an amphiphilic layer on aerosol particles has been discussed, however in a different context, in Ellison et al. (1999) and Dobson et al. (2000). The values of the CMC for the compounds studied here are ~10 μM for rhamnolipids (Desai and Banat, 1997), 13 μM for digalactosyl diacylglycerol (Vishwanath et al., 1996), 24 μM for surfactin (Desai and

Banat, 1997). These CMC values imply that only a few tens of μM of biosurfactants are enough to lower the surface tension of water to about 30 mN/m. By contrast, 20 mM ($\sim$20 gL^{-1}) of HULIS would only lower the surface tension to 45 mN/m (Taraniuk et al., 2007), and 10 M of malonic acid would lower it to 50 mN/m.

Note that for concentrations larger than the CMC, all curves should all display a plateau, the maximum effect on the surface tension being reached. The curves on Fig. 3, as well as those previously reported in the literature that do not display such a plateau indicate that the measurements were limited by experimental difficulties (usually, the inability to concentrate the samples sufficiently) and that the actual minimum was not reached.

By comparison, it is clear on Fig. 3 that the curves obtained with the aerosol extracts (curves with circles) display the distinct signatures of microbial surfactants, in particular a surface tension below 30 mN/m at high concentrations. As the blanks filters showed no contamination and the presence of artificial surfactant in all these natural samples was unlikey, these very low surfance tension values can only be accounted for by microbial surfactants. These curves also display the sharp transitions characteristic of micelle-forming surfactants. These features provide strong evidences for the presence of biosurfactants in all these samples. Note, however, that the positions of these curves on the x-axis was arbitrary, the actual concentrations of surfactants in these samples being unknown. The positions chosen for these curves in Fig. 3 corresponded approximately to the total organic concentrations in the samples. The CMC for the standard biosurfactants thus suggested that the concentrations of biosurfactants in the aerosol extracts were 100 to 10 000 times lower than the total organic concentration. A possible contribution of airborne microorganisms, potentially collected together with the aerosol particles in the samples, was estimated to be negligible because airborne microorganisms represent a very small fraction of the aerosol mass in the atmosphere ($\ll$1%, Pósfai et al., 2003; Harrison et al., 2005), only some of them are surfactant producers (Ahern et al., 2007), and the quantity of biosurfactant transported by each organism would be limited.

Comparing the volumes of the aerosol extracts to those of the initial samples also answered the question of whether the biosurfactants were concentrated enough in the aerosols sampled to significantly affect their surface tension. The volumes of these extracts was larger (30–100 μL) than those of the initial samples (<10 μL, assuming a maximum aerosol loading of 100 $\mu g\,m^{-3}$) implying that these extracts were diluted compared to the initial aerosols and, therefore, that the lowest surface tension measured for these extracts were still upper limits of those of the aerosol samples. The very low surface tensions obtained for these extracts thus demonstrated that the biosurfactants were indeed in concentrations large enough to have a strong effect on the surface tension of the aerosols, or at least on some of the particles contained in these samples. These low surface tension values were comparable to those of the standard biosurfactants studied in the first part of this work, which implied that these aerosols, or at least some of the particles contained in them, should be activated into cloud droplets at lower supersaturation than particles made of other material, including inorganic salts.

4 Conclusions

The first part of this work established that specific organic molecules such as the biosurfactants rhamnolipids, galactolipids, and lipopeptides, have a higher CCN efficiency than any other material, including inorganic salts. These exceptional properties are due both to the dramatic effect of these molecules on the surface tension of water (<30 mN/m) and to the extremely small concentrations necessary to achieve them (tens of μM).These results constitute new and important information for the understanding of CCN properties and cloud droplet nucleation, as they identify for the first time specific molecular structures providing organic compounds with exceptional surface-active and CCN properties.

In the second part of the work, the surface tension of aerosol samples from very different origins were measured and all found to display exceptionally low surface-tension values, evidencing the presence of biosurfactants. These results also shown that these

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surfactant were concentrated enough to significantly lower the surface tension of these aerosols – or at least of some particles contained in them- and therefore enhance their CCN efficiency.

The presence of such powerful surfactants in atmospheric aerosols is consistent with the recent identification of organic fractions displaying better CCN efficiency than ammonium sulfate in biomass burning aerosols (Asa-awuku et al., 2008). As pointed out in introduction, the main interest of these biological substances for cloud formation is that they can make their way into aerosol particles of all sizes, as it is now well established that primary and biogenic material is also emitted in sub-micron particles, in particular from the sea surface (for instance, Mårtensson et al., 2003). Further work is currently being performed to further investigate important aspects, such as the presence of these biosurfactants in smaller aerosol size fractions (PM1 or sub-micron), more relevant for the CCN population.

The Köhler curves determined in our work suggest that the presence of biosurfactants should make the aerosols more CCN-efficient than particles that do not contain them, including inorganic salt particles. This, in turn, would affect the onset of precipitation and the optical properties of the clouds, the latter being essential for climate. The effects of such surface-active compounds on cloud formation and properties has been shown to be especially significant in low-level clouds or in air masses with small vertical updraft (Ervens et al., 2005). The surface-active properties assumed for the chemical compounds in these previous studies were however much weaker than those evidenced for biosurfactants in this work. A role of microbial surfactants on CCN numbers would also be consistent with the lack of correlation between CCN numbers and particle bulk composition, as these surfactants would be at very small concentrations in the particles and weakly correlated with their bulk composition.

If the effect of biosurfactants on the CCN properties of atmospheric aerosols is confirmed to be significant, microorganisms could affect cloud formation without even leaving the surface of the Earth (ground, oceans,...). Such processes could explain previous observations such as the correlation between cloud cover and algae bloom

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reported for the Southern Ocean (Meskhidze and Nenes, 2006).

Finally, the fact that biosurfactants were present in all the samples studied in this work suggest that they are common in aerosols, and therefore of global relevance, which is consistent with the ubiquitous presence of surfactant-producing microorganisms on Earth, even in the most hostile environments (Bodour et al., 2003; Perfumo et al., 2006; Gulati et al., 2008). Again, if the contribution of these biosurfactants to cloud formation is confirmed by future works, the present work would have identified a new link between microorganisms at the Earth's surface, atmospheric processes, the hydrological cycle, and climate. In this context, the responses of the surfactant-producing microbial populations to climate change would constitute new climate feedbacks. Such a role of microorganism on cloud formation would bring other interesting questions on the co-evolution of microorganisms and climate, such as whether this role on clouds is fortuitous or a survival strategy developed to control the availability of water.

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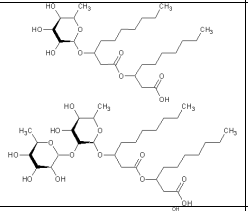
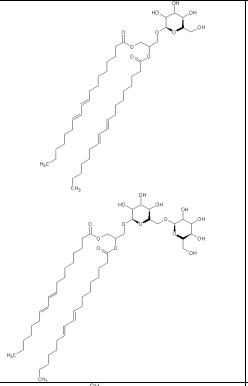
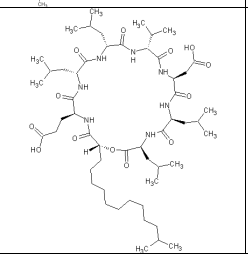
Table 1. Standard microbial substances studied in this work, and examples of microorganisms producing them and their occurrences in the environment.

Name	Chemical structure	Microorganism	Occurrence
Rhamnolopids Mono-rhamnolipid MW ~ 500 Di-rhamnolipid MW ~ 660		*Pseudomonas aeruginosa*	Freshwater, seawater, soils (HR 1993; J 1949; VK 1979; C 2000; B 2003)*
Glycolipids MonoGalactosyl DiacylGlyceride MW ~ 780 DiGalactosyl DiacylGlyceride MW ~ 940		*Synechocystis* (freshwater cyanobacteria) *Synechococcus* (marine cyanobacteria) *Aphanizomenon flos-aquae* (cyanobacteria)	Freshwater (B 2004)*, seawater (B 2004; M 1991)*
Lipopeptide Surfactin MW = 1036		*Bacillus subtilis*	Soils (B 2003)*

* HR 1993: Hommel and Ratledge, 1993; J 1949: Jarvis and Johnson, 1949; VK 1979: Van der 481 Kooij, 1979; C 2000: Cho and Tedje, 2000; B 2003: Bodour et al., 2003; B 2004: Benincasa et 482 al., 2004; M 1991: Merritt et al., 1991.

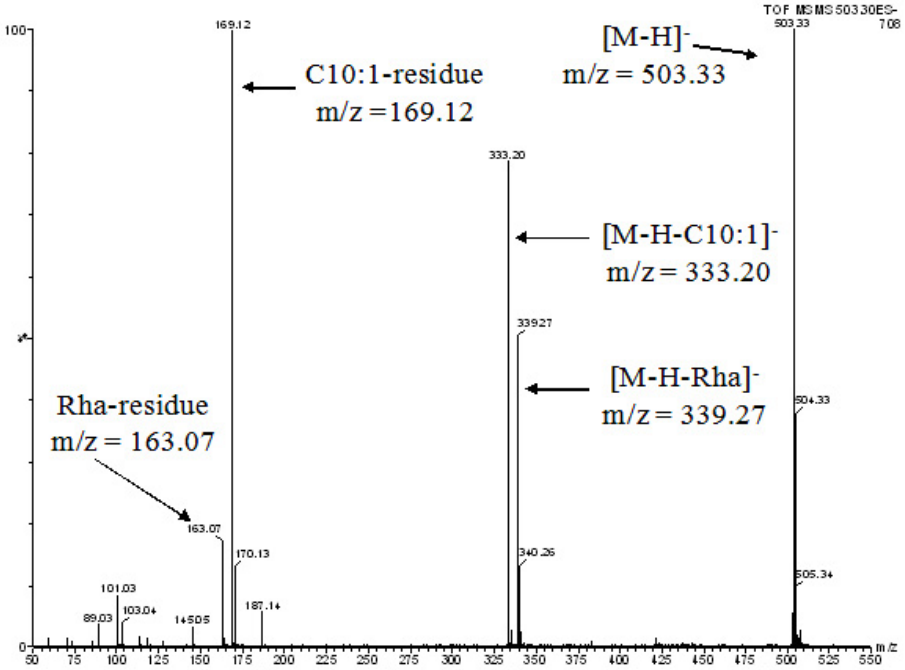


Fig. 1. SMS spectrum of the reference rhamnolipid JBR425 (Mw: 504.330) in negative ion mode: Parent ion (*m/z*=503.33), fragment ions of the rhamnose moiety, "Rha-residue" (*m/z*=163.07), and of the fatty acid moiety "C10:1-residue", (*m/z*=169.12).

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6, 10035–10056, 2009

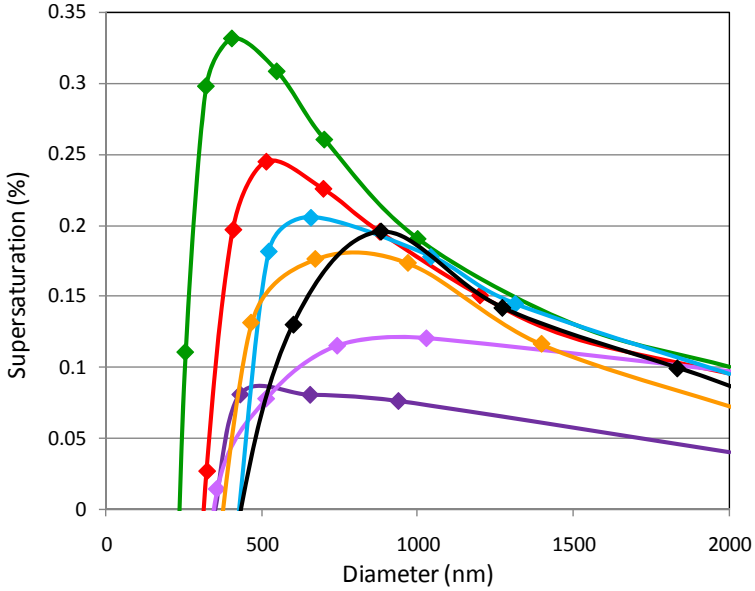

Fig. 2. Köhler curves for inorganic salts and standard microbial surfactants in aqueous solutions of sodium chloride 0.07–0.2 M (dry diameter=60 nm). Sodium chloride: red; Ammonium sulfate: green; Monogalactosyl diacylglyceride: pale blue; Digalactosyl diacylglyceride: orange; Surfactin: black; Rhamnolipid (extract 1): dark purple (this curve with ammonium sulfate instead of sodium chloride); Rhamnolipid (extract 2): pale purple.

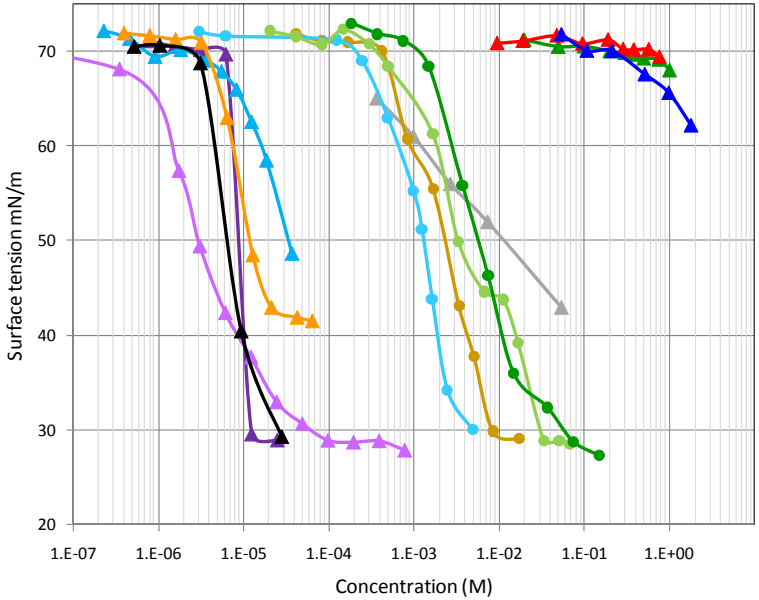

Fig. 3. Effect on the surface tension of water of different standard compounds as function of their molar concentration (curves with triangles) and comparison with the surface tension of aerosol sample extracts (curves with circles). Sodium chloride: red; Ammonium sulfate: green; Malonic acid: dark blue; HULIS: grey; Monogalactosyl diacylglyceride: pale blue; Digalactosyl diacylglyceride: orange; Surfactin: black; Rhamnolipid (extract 1): dark purple; Rhamnolipid (extract 2): pale purple. Aerosol samples from a coastal site (Aspvreten, Sweden): brown; a marine site during an algae bloom event (Sweden): clear blue; temperate forest (Hyytiälä, Finland): pale green; the Amazonian forest (Manaus, Brazil): dark green.