



## Seasonal pattern of source and transport processes of natural and anthropic surfactants in coastal aerosol (Tuscany coast – Italy).

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Surface active agents have been detected in coastal aerosols for decades. Their partial hydrophilicity could affect the hygroscopicity of aerosol particles. The ecological significance of surface active substances has thus been much debated, including pre-biotic processes, global climate changes by influencing optical properties and Cloud Condensation Nuclei forming ability, and in decline of coastal vegetation exposed to sea spray. Based on results obtained using non specific analytical methods (e.g., Methylene Blue coloration – MBAS), MBAS reactive surface active agents, like surfactants used in detergents, have been singled out as one of the causing factors of some of these aerosol effects.

In order to increase the knowledge on the atmospheric concentration, source and distribution of surfactants, an aerosol sampling campaign was arranged at San Rossore (Pisa): a costal site located in the NW Mediterranean sea. The aerosols were collected at a distance of 500 meters from the sea, on the roof of a building at about 10 m above the sea level. A preliminary spot sampling campaign, at weekly resolution, was carried out in February-March 2006, using an Andersen 8-stages impactor. The main sampling campaign covered more than one year (from March 2007 to June 2008) and the sampling was accomplished at daily resolution by two sequential aerosol samplers operating in parallel way. The samplers were equipped with PM10 and PM2.5 sampling heads designed according to EN12341 European rule.

After weighting, the filter was analysed for ionic content by ion chromatography. The concentration of the anthropogenic surfactant LAS was measured in all collected samples using specific analytical techniques (LC-MS-MS) and was compared with the MBAS signal.

In the PM10 aerosol, MBAS concentration was on average 887 ng/m<sup>3</sup> MBAS, while the LAS concentration detected in the same aerosol samples represent less than 5% of the total MBAS signal. Analysis of the temporal trends in LAS and MBAS in the fine and the coarse aerosol fractions indicated different sources and transport processes.

MBAS concentrations show a clear maximum during the winter months in the fine fraction (PM 2.5) and summer maxima in the coarse (PM 10-2.5) fraction, and considering the prevailing different synoptic conditions in the different seasons, we suppose that MBAS have different dominant sources in the two seasons: in winter, MBAS likely originated from polluted continental areas, in the summer MBAS probably reflected the production of biogenic surfactants in the water mass during algal blooms or increased activity in the sea grass meadow.

Low but detectable LAS concentrations could be measured mainly in the coarse fraction of the collected coastal aerosols. The data indicate a primary source of LAS, probably originating from the sea surface microlayer in coastal regions receiving untreated waste water discharge. Then, MBAS signal was not an appropriate surrogate measurement of LAS in aerosols. MBAS and LAS can have a primary marine source, but MBAS can be considered a marker of biogenic activity while LAS can be used as a marker of anthropogenic activity in areas receiving waste water discharges.