Electrochemical study of surface active material in atmospheric aerosols

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INTRODUCTION

Monitoring chemical composition of atmospheric aerosols has attracted attention of numerous investigators. However, the knowledge on organic aerosol chemistry is less advanced compared to that on inorganic chemistry. Organic matter in atmosphere is a result of primary anthropogenic and biogenic emissions and/or of transformation processes of different precursors. Surface active substances (SAS) can form monomolecular films at the different interfaces, influencing thus the interfacial properties of atmospheric droplets. SAS influence the condensation processes and accumulation of pollutants in aerosols enhancing thus the potential of rain for washing out organic matter from the atmosphere. The atmospheric input of substances in limnological and marine ecosystems dominates on regional and global scale, having an important role in controlling the level and the dynamics of persistent organic pollutants in aquatic systems.

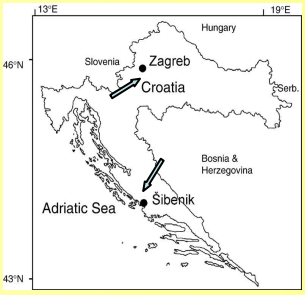
METHODOLOGY

SAS CONCENTRATION
electrochemical method, phase sensitive alternating current voltammetry (***out-of- phase* measurements**), accumulation at the potentials of -0.6 vs. Ag/AgCl (Ćosović and Vojvodić, *Mar. Chem.,* **22** (1987) 363.

ELECTROCHEMICAL PROBE
Influence of the adsorbed layers on cathodic processes of Pb $^{2+}$ and Cd $^{2+}$ ions, alternating current voltammetry, (***in-phase* measurements**)

DOC - high temperature catalytic oxidation (HTCO) technique

SAMPLING LOCATIONS

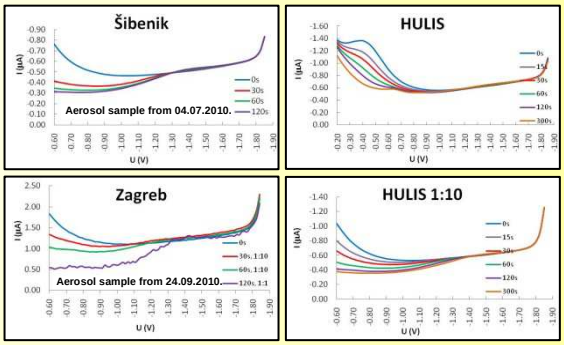


Sampling with high volume sampler (Kálmán Systems)

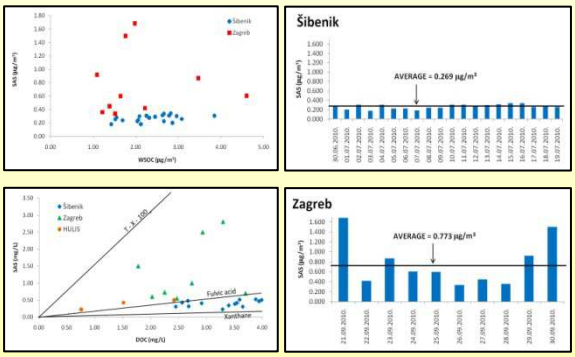
Quantitative investigation - direct determination of SAS concentration (surfactant activity) in the samples.
Surfactants activity is expressed as the equivalent amount of the selected standard Triton-X-100.

Qualitative investigation - the comparison of ac. voltammetric curves (shape, number and position of peaks) of the samples to those of selected model substances as representative for organics in investigated sample.

RESULTS



SAS concentrations in Šibenik and Zagreb

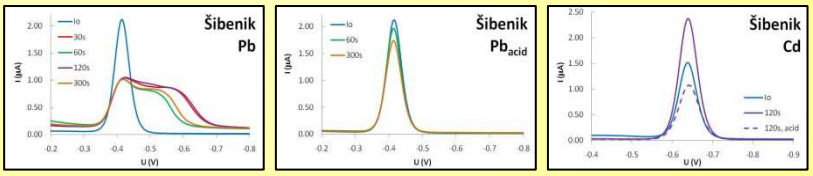


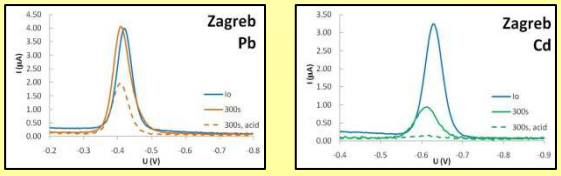
Comparison of DOC and SAS average values for different environmental compartments

Sample	DOC	SAS eq. T-X-100
Aerosol (Zagreb)	2.09 μg/m^3	0.77 μg/m^3
Aerosol (Šibenik)	2.39 μg/m^3	0.27μg/m^3
Rain (Zagreb)	2.08 mg/L	0.16 mg/L
Rain (Šibenik)	1.83 mg/L	0.12 mg/L
River Sava (Zagreb)	3.06 mg/L	0.28 mg/L
Sea water (Šibenik)	1.44 mg/L	0.16 mg/L
Surface microlayer (Šibenik)	2.79 mg/L	0.52 mg/L

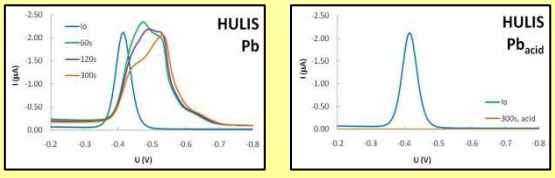
Additional test for the physico-chemical characterization of organic matter in the samples using electrochemical probe

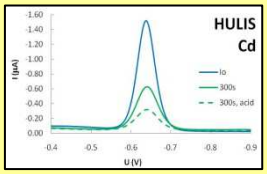
All processes depend on the composition and adsorption behaviour of SAS reflecting the structure and permeability of the adsorbed layers on the electrode surface.
For the reduction process of metal ions at the completely covered electrode surface with the adsorbed organic molecules there are three possibilities:
- **no influence**
- **inhibition of the electrode reaction**
- **accumulation of metal ions in the adsorbed layer**





Aerosol humic like substances (HULIS)





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CONCLUSION

The electrochemical techniques were introduced for the first time in measurements of SAS from atmospheric aerosols. The measurement of the electrode double layer capacity changes offers the possibility of direct investigation of adsorption characteristics of a complex mixture of naturally present organics at the electrode-electrolyte interface. Additional characterization of organic matter was performed by using electrochemical probes, namely lead and cadmium ions representing major heavy metal pollutants in environment. Adsorption characteristics of humic like substances (HULIS) isolated from aerosol samples have been investigated as well. Since HULIS has surface active properties, the electrochemical methods are very prospective for direct quantification of water soluble aerosol HULIS material.