European Network on New Sensing Technologies for Air Pollution Control and Environmental Sustainability - *EuNetAir*

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Year 4: 1 July 2015 - 30 April 2016 (*Ongoing Action*)

ELECTROANALYTICAL METHODS IN MARINE AEROSOLS CHARACTERIZATION

I. Ciglenečki[1], S. Frka[1], K. Vidović[1], A. Cvitešić[1], I. Milanović[1], P. Orlović-Leko[2]

irena@irb.hr, WG member

[1]Division for Marine and Environmental Research, Rudjer Boskovic Institute, Zagreb, Croatia;

[2]University of Zagreb, Faculty of Mining, Geology and Petroleum Engineering, Zagreb, Croatia;

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Current research activities of the RBI group

- Croatian science foundation project „The Sulphur and Carbon Dynamics in the Sea- and Fresh-water Environment“(SPHERE), is studying sulphur (S) and carbon (C) dynamics between different environmental compartments (atmosphere, water, sediment, biota) of the sea- and fresh-water environment in relation to eutrophication and climate changes

- main focus - distribution between organic, inorganic, dissolved, colloidal and nanoparticulate fraction

- characterization of marine and freshwater aerosols mainly by electrochemical, chromatographic and ICPMS methods.

Research Facilities of the RBI group

- environmental electrochemistry -with 50 years experience in using electrochemical methods like polarography and voltammetry in studying the speciation and biogeochemical cycling of trace metals organic matter, sulfur species and their interaction in model solutions and in clean and polluted environmental water samples;

- use of electrochemisty in combination with other more sophisticated analytical techniques such as ICPMS, DOC/TOC, CHNS, HPLC, microscopic techniques (AFM)

- the group is very well experienced in low-level measurements of metals, sulfur species, organic matter characterization and organometal compounds (organotin).


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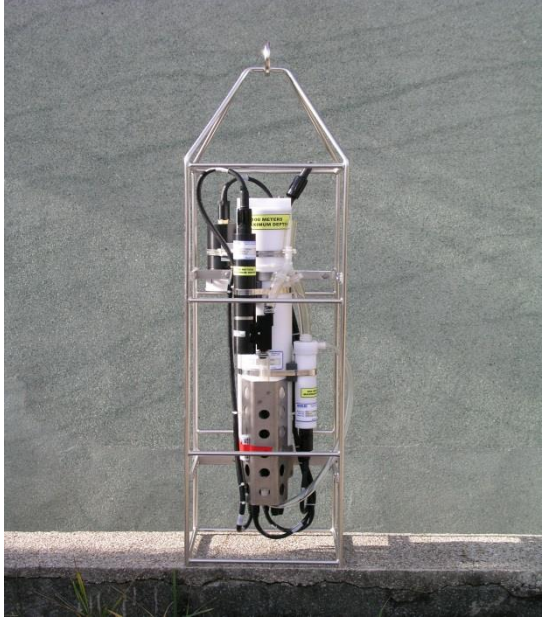


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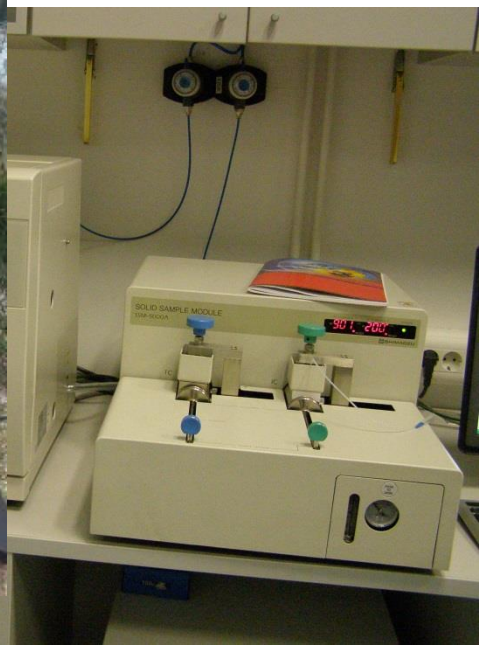
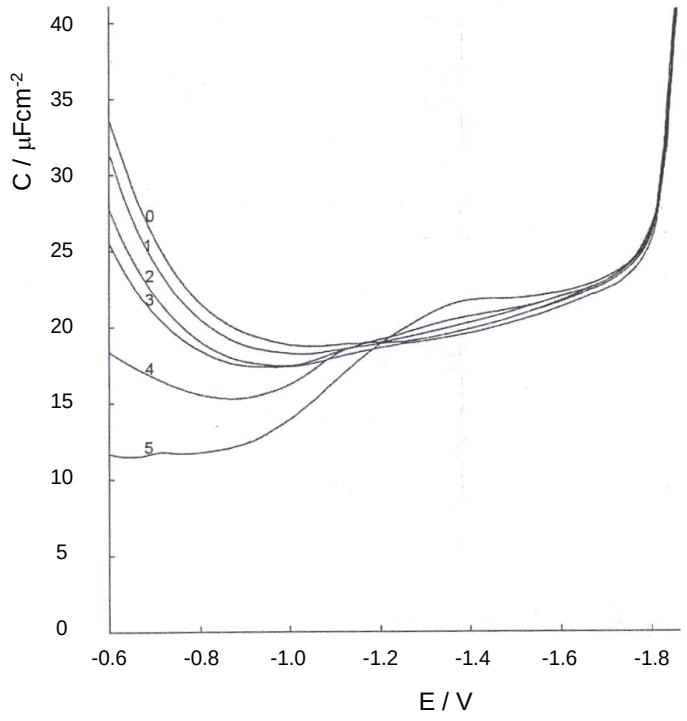
ASI-V
TOC-V


SOLID SAMPLE MODULE

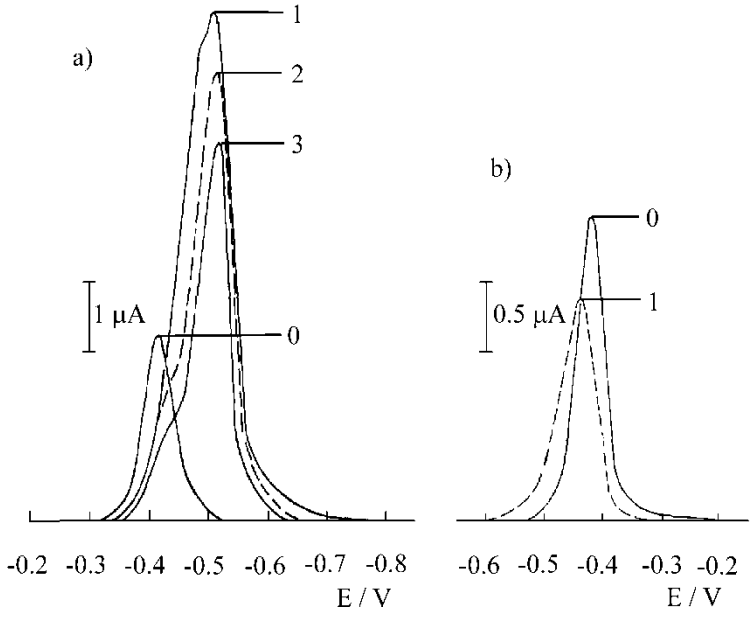
Organic matter concentrations and characteristics in bulk precipitation in Croatia

DOC –Dissolved organic carbon(sensitive high temperature catalytic oxidation (HTCO) technique)
POC - Particulate organic carbon (- " -)
SAS - electrochemical method, phase sensitive alternating current voltammetry
The surfactant activity is expressed as equivalent to a model substance in mg/l of Triton X-100.
CCu – electrochemical method,differential pulse anodic stripping voltammetry (DPASV). Direct titration of sample with increasing amount of copper ions- (CCu=copper complexing capacity)



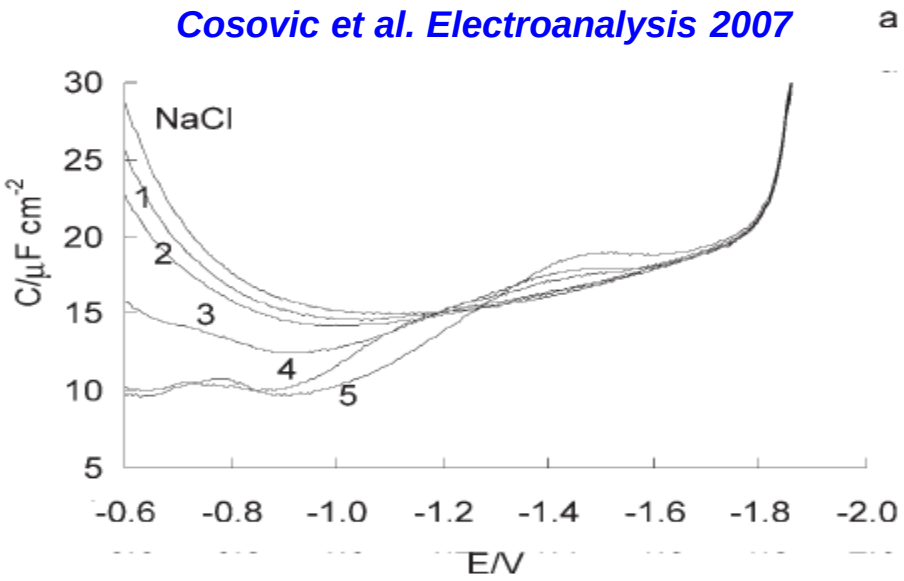
Typical capacitance vs.potential curves of rain sample collected in the Zagreb city center pH around 5, 0.135 mg/l T-X-100 in NF, 0.085 mg/l F

Additional characterization of the surface active substances in natural samples using
- electrochemical probes
(e.g.redox processes of Pb(II) ion; reduction and/or oxidation current).



Orlovic Leko et al. JAtmosChem 2011

Cosovic et al. Electroanalysis 2007



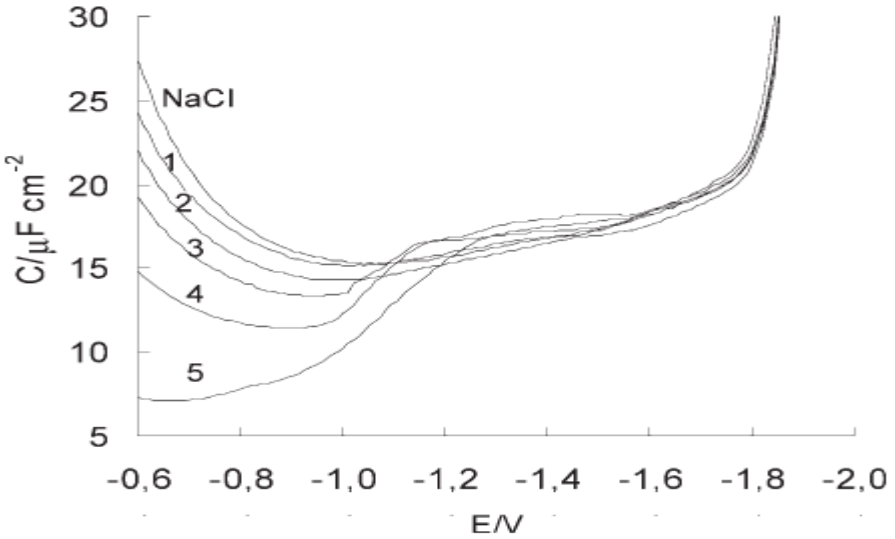
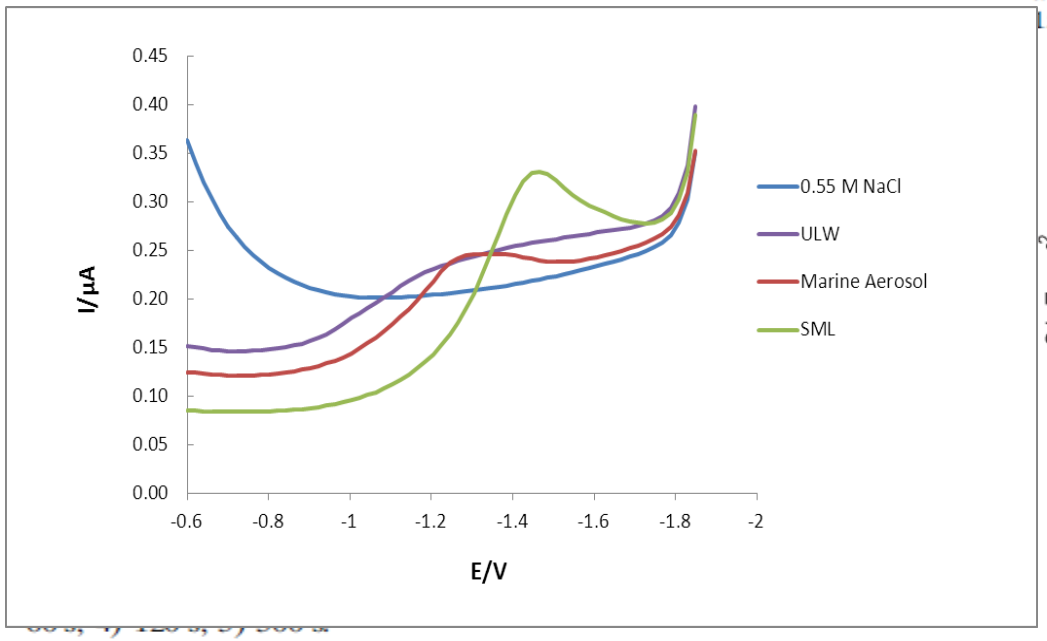
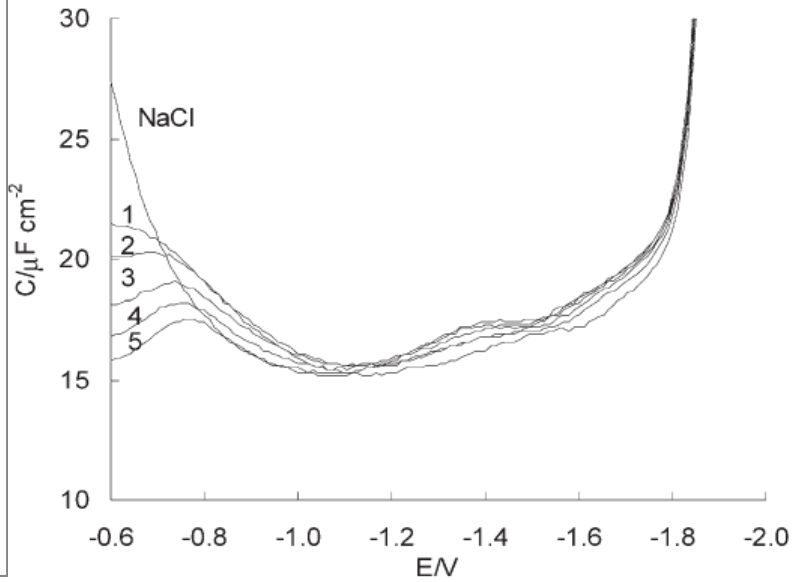


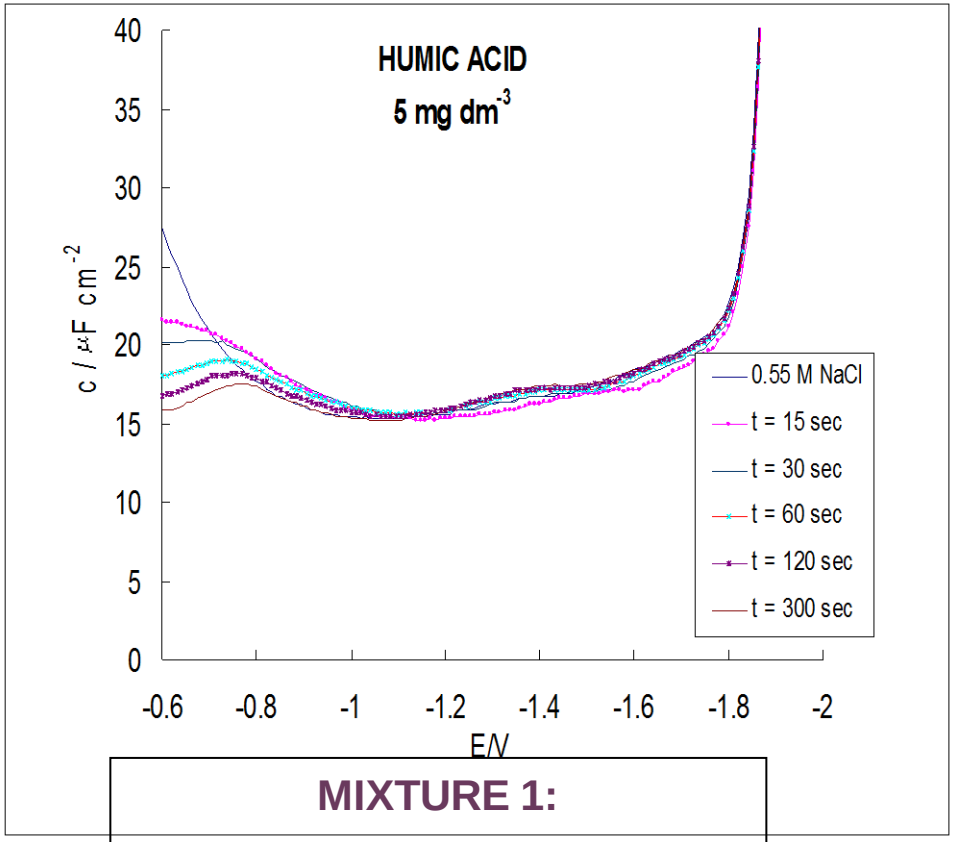
Fig. 4. AC voltammetric curves of 0.55 mol dm^{-3} NaCl and with addition of 100 mg dm^{-3} *cis*-pinonic acid. Accumulation times: 1) 15 s, 2) 30 s, 3) 60 s, 4) 120 s, 5) 300 s.

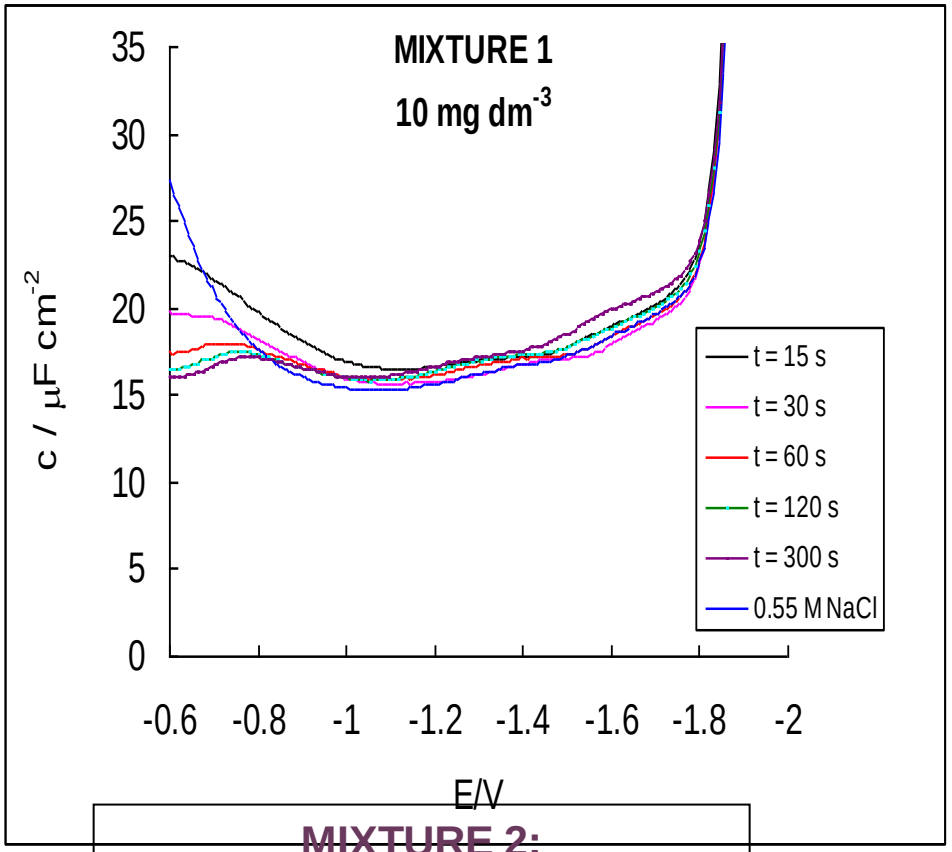




AC voltammetric curves of humic acid 5 mg/l (comercial peat) in NaCl.

Predominant adsorption effect of humic acid was found in the investigation mixtures





MIXTURE 1:

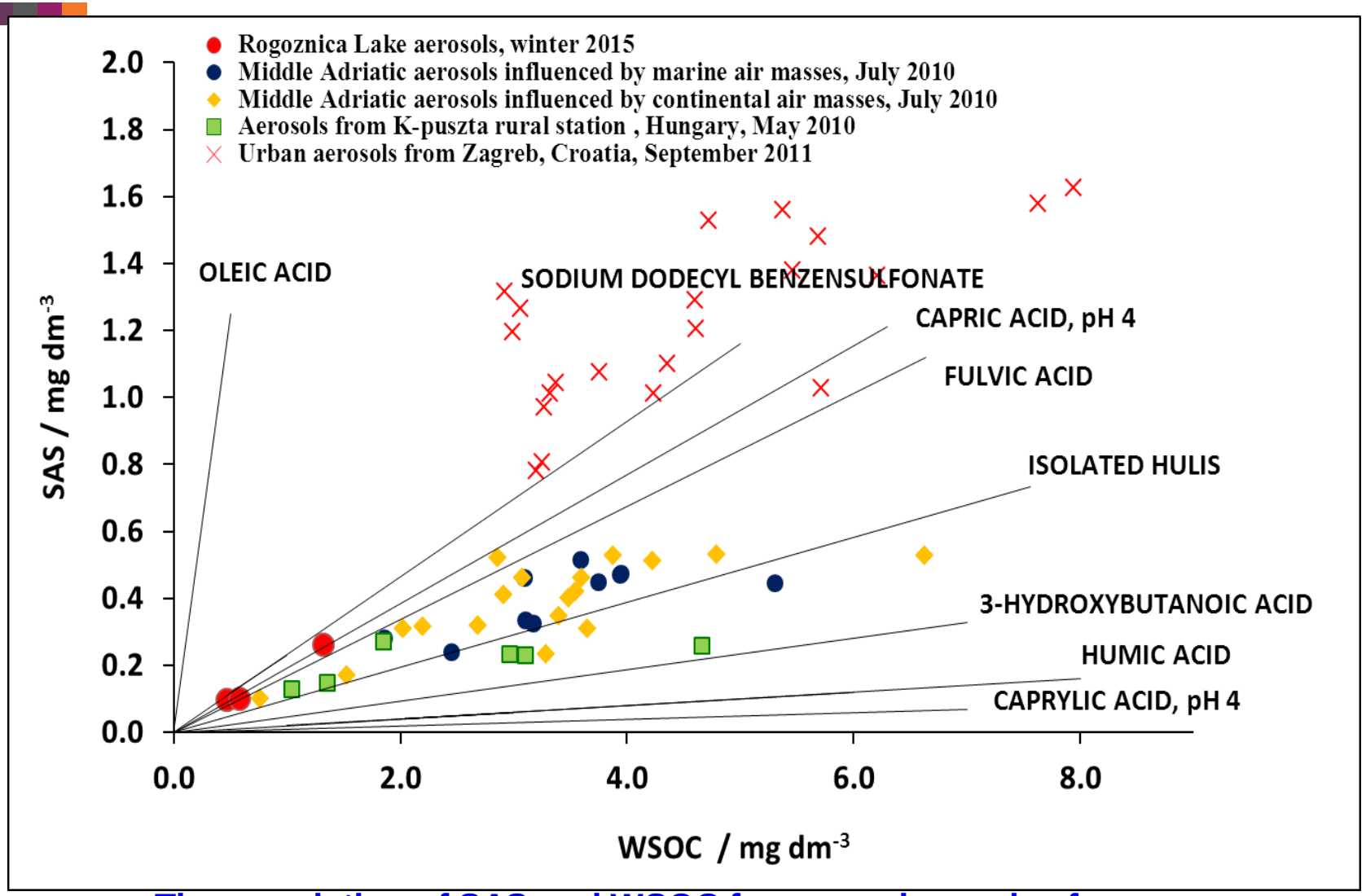
42% humic acid
17% pinonic
14% azelaic
15% 3-hydroxybutanoic acid
3% 3-hydroxybenzoic acid
9% levoglucosan

MIXTURE 2:

50% humic acid
17% azelaic
18% 3-hydroxybutanoic acid
4% 3-hydroxybenzoic acid
11% levoglucosan

Table 1. Adsorption characteristics of model surface active substances (SAS) at the mercury electrode surface in 0.55 M NaCl. Concentration of SAS is selected to produce adsorption effect at the mercury electrode equivalent to $SAS_{T\text{-}X\text{-}100}$.

SAS	C (mg dm^{-3})	DOC (mg dm^{-3})	SAS (eq. T-X-100)	SAS (eq. T-X-100/DOC)
T-X-100	0.108	0.07	0.108	1.54
NaDBS	1.00	0.62	0.13	0.21
Levoglucosan	100	44	0.03	6.8×10^{-4}
Monocarboxylic acids				
Caprylic acid (pH 4) [18, 19]	10	6.66	0.108	0.016
Capric acid (pH 4) [18, 19]	0.9	0.63	0.108	0.17
Capric acid (pH 6.5) [18, 19]	10	7	0.108	0.015
Oleic acid [16]	0.057	0.04	0.108	2.70
3-Hydroxybutanoic acid	5	2.3	0.11	0.05
3-Hydroxybenzoic acid	100	60.87	0.05	8.2×10^{-4}
cis-Pinonic acid	100	65.22	0.075	0.001
Dicarboxylic acids				
Glutaric acid [22]	4000	1820	0.108	6×10^{-5}
Azelaic acid	8.8	5.05	0.03	0.006
Polyacidic compounds				
Humic acid	5	2.5	0.095	0.04
Fulvic acid [16]	2	0.64	0.108	0.17
Polyaromatic hydrocarbon				
Naphtalene	3.0	2.8	0.115	0.041



The correlation of SAS and WSOC for aerosol samples from different locations was compared with relevant model substances.

Electrochemistry of sulfur species on the Hg electrode

- **HS^-** $HS^- + Hg \leftrightarrow HgS + H^+ + 2e^-$
  $HgS + 2e^- \leftrightarrow Hg^0 + S^{2-}$ $E_{1/2}$= -0,68V

- **S^0** $S^0 + Hg \leftrightarrow HgS_{ads}$ $E_{1/2}$= -0,68V
  $HgS_{ads} + 2e^- \leftrightarrow Hg^0 + S^{2-}$

- **S_x^{2-}** $S_x^{2-} = 1\ S^{2-} + (x-1)\ S^0$
  $S_x^{2-} + Hg \leftrightarrow HgS + (x-1)S + 2e^-$ $E_{1/2}$= -0,68V

- **SO_3^{2-}** $2SO_3^{2-} + Hg \leftrightarrow Hg(SO_3)_2^{2-} + 2e^-$ $E_{1/2}$ = -0,60V

- **$S_2O_3^{2-}$** $2S_2O_3^{2-} + Hg \leftrightarrow Hg(S_2O_3)_2^{2-} + 2e^-$ $E_{1/2}$= -0,12V

- **$M_2S\downarrow$** $M_2S + H+ + 2e- \leftrightarrow 2M^+ + HS^-$ $E_{1/2} \approx$ -1.0 V

Electrochemistry of sulfur species on the Hg electrode

thiols (MPA, GSH)

$RSH + Hg \Longleftrightarrow RSHg + H^+ + e^-$ ($(RS)_2Hg$) $E_{1/2}$= oko-0,50 V

Disulfide (GSSG, DMDS)

$RSSR + 2e^- + 2H^+ \Longleftrightarrow 2RSH$ ($(RS)_2Hg$) $E_{1/2}$= oko -0,60 V

DMS, COS

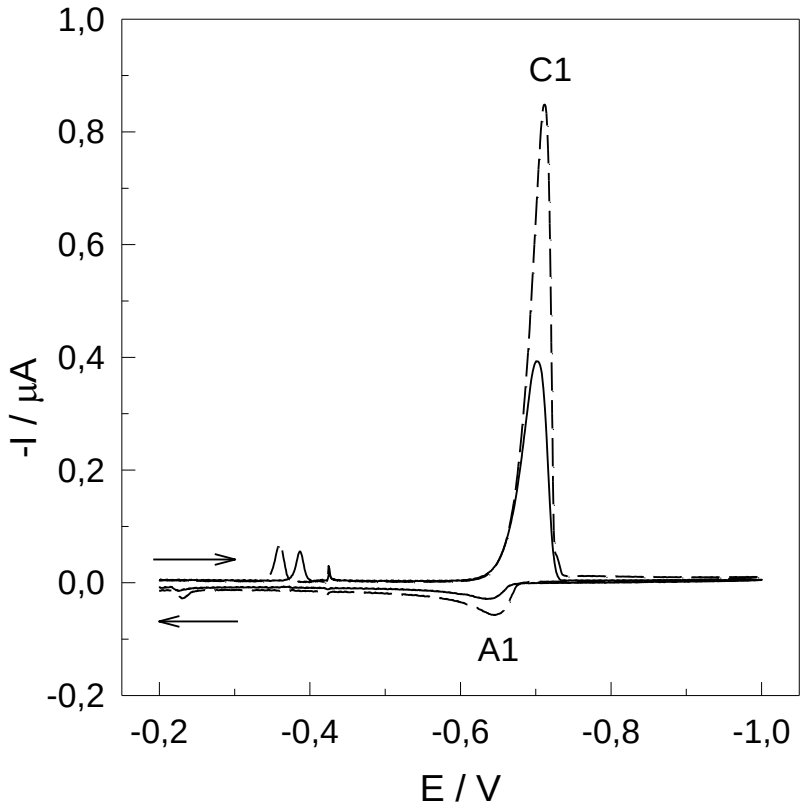
$(CH_3)_2S + Hg \Longleftrightarrow$??? $E_{1/2}$= oko -0,50 V

$Me_2As(S)CH_2CH_2OH$

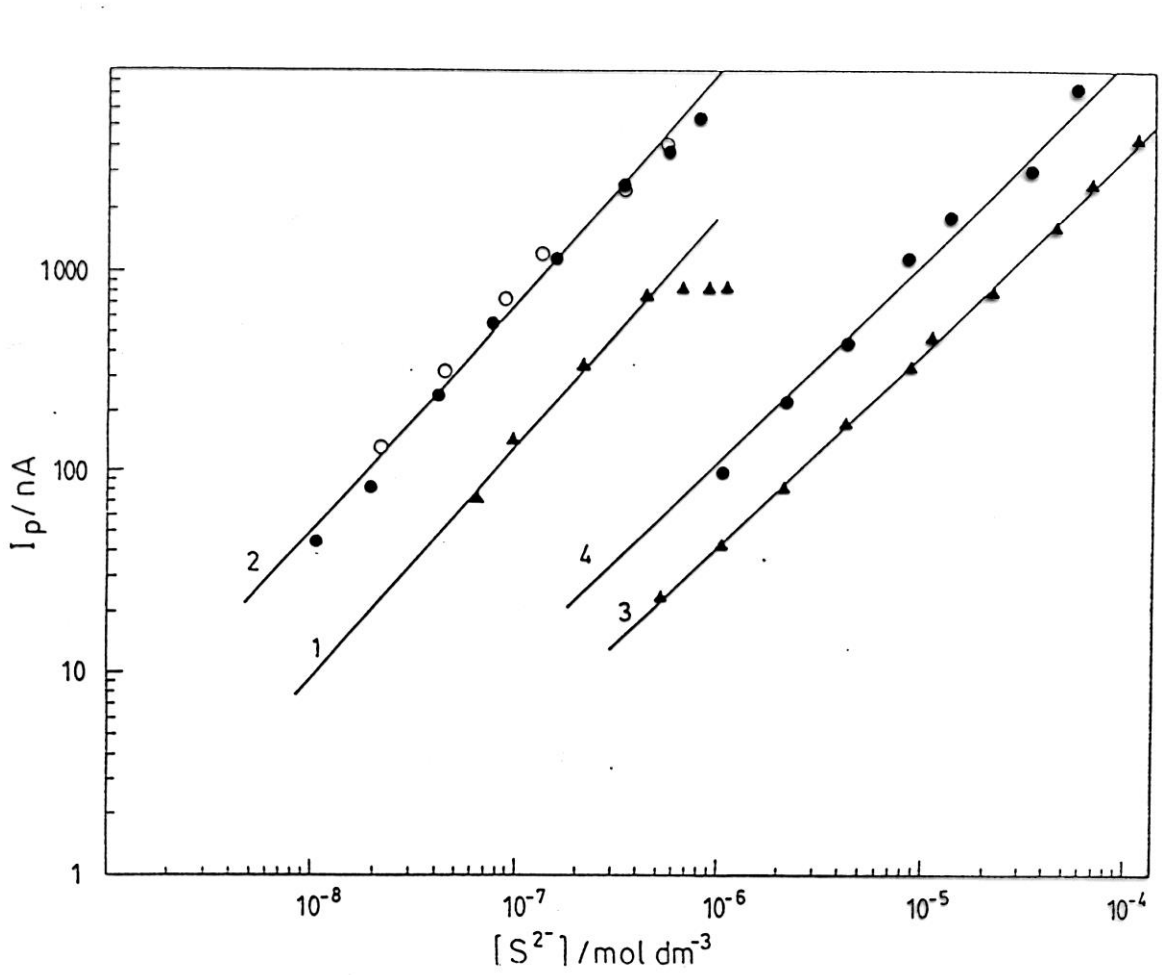
$Me_2As(S)CH_2CH_2OH + Hg \Longleftrightarrow HgS + Me_2As^{2+} + 2e^-$ $E_{1/2}$= oko -0,68 V

Voltammetric waves of S^{2-}, S^0, S_4^{2-}

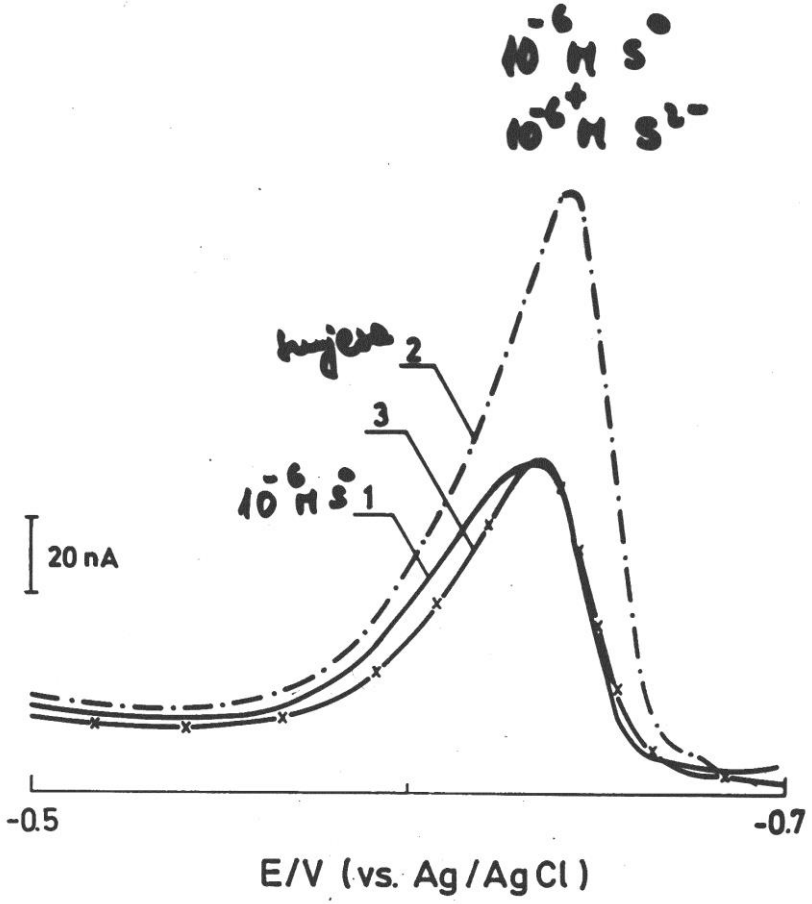
HgS + H+ + 2e- ↔ Hg(l) + HS (1)



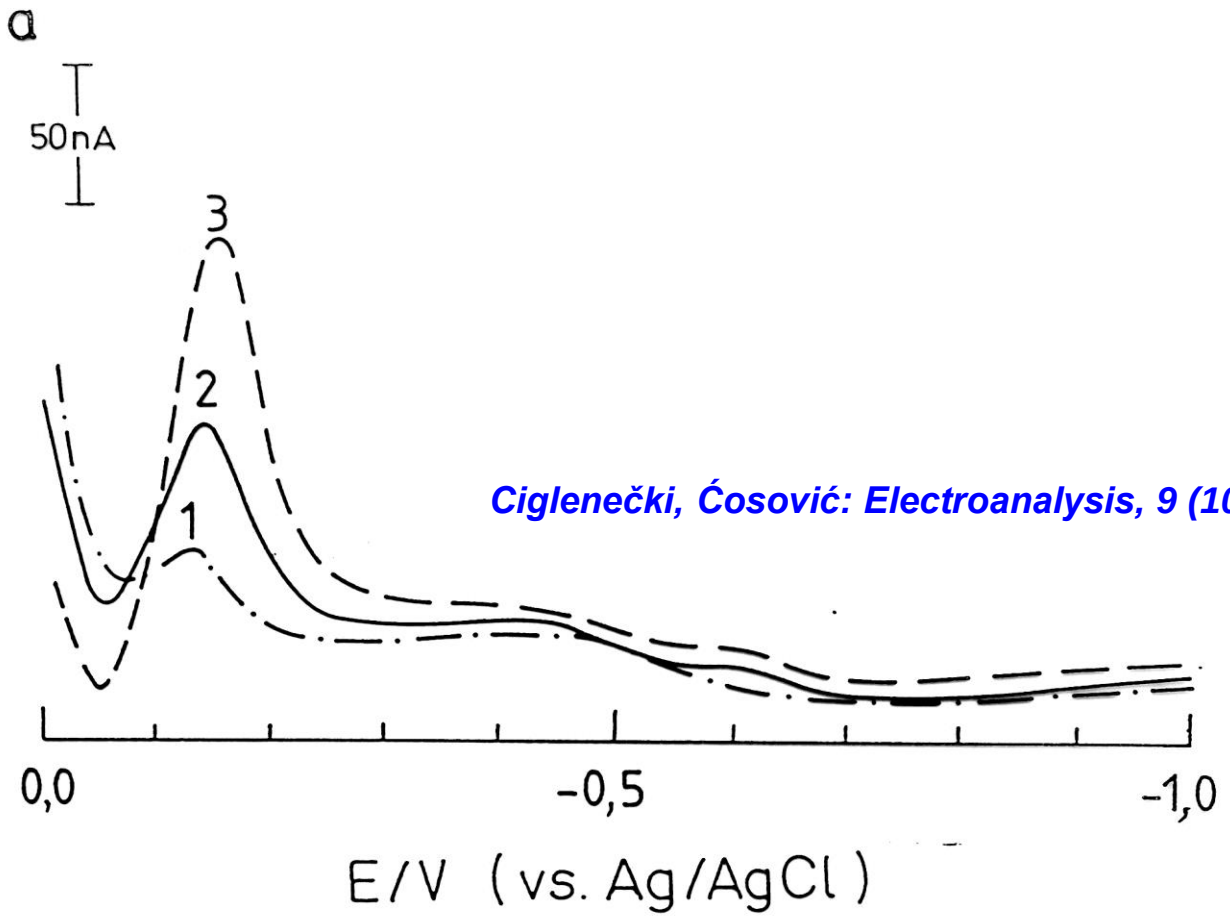
Calibration curves for sulfide



Mixtures of sulfur + sulfide

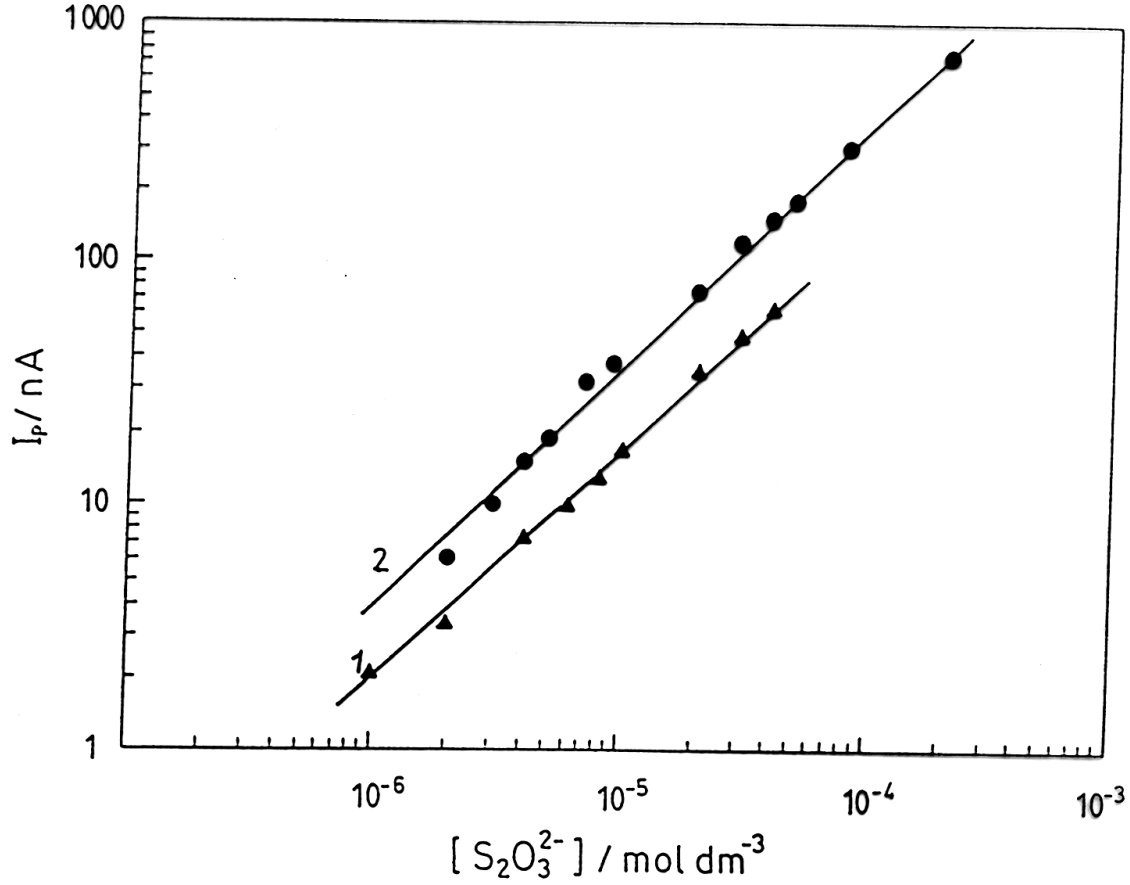


Voltammetric waves of thiosulfate

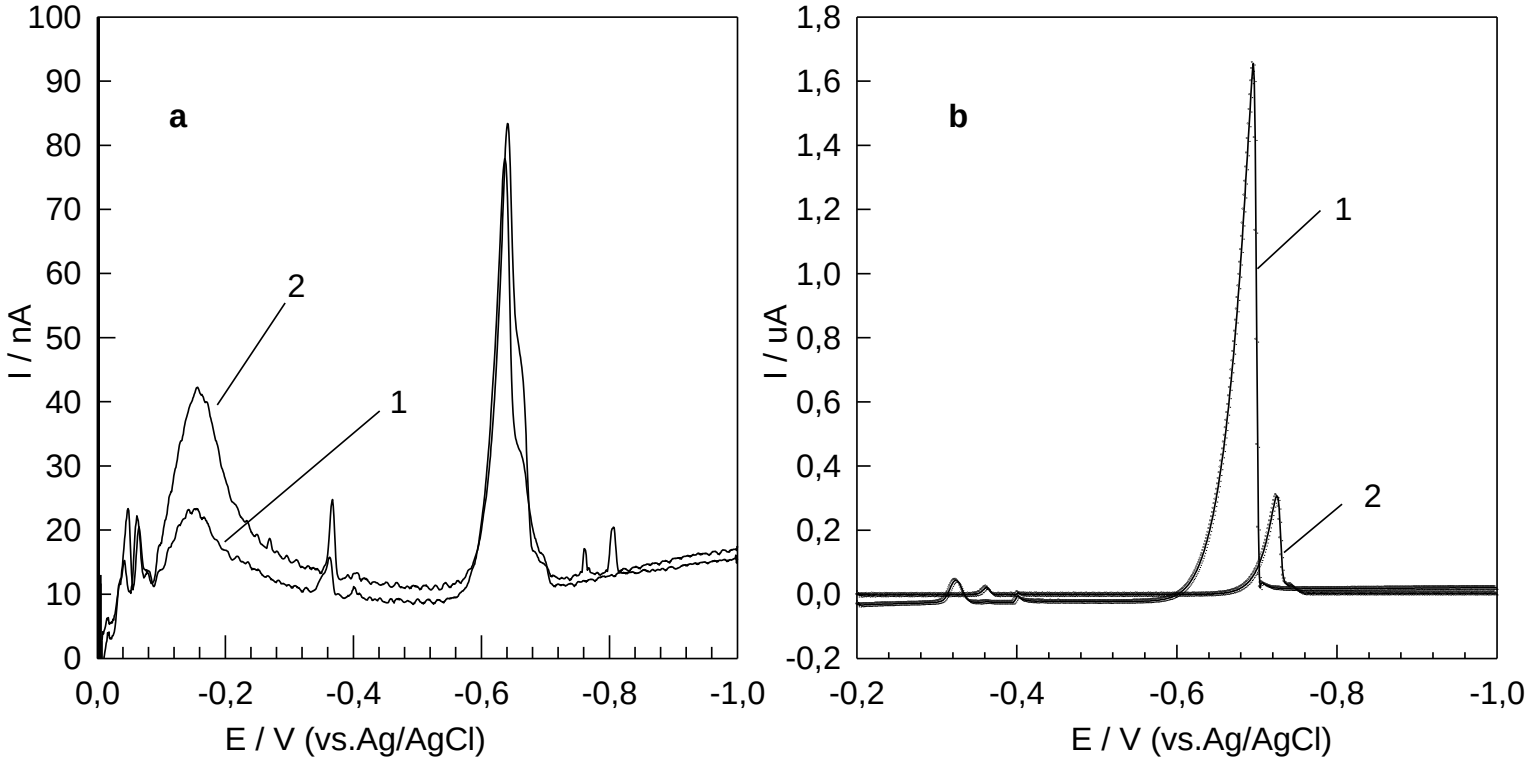


Ciglenečki, Ćosović: Electroanalysis, 9 (10) (1997) 775-781

Calibration curves for thiosulfate



Determination of thiosulfate in the mixtures with sulfide and elemental sulfur



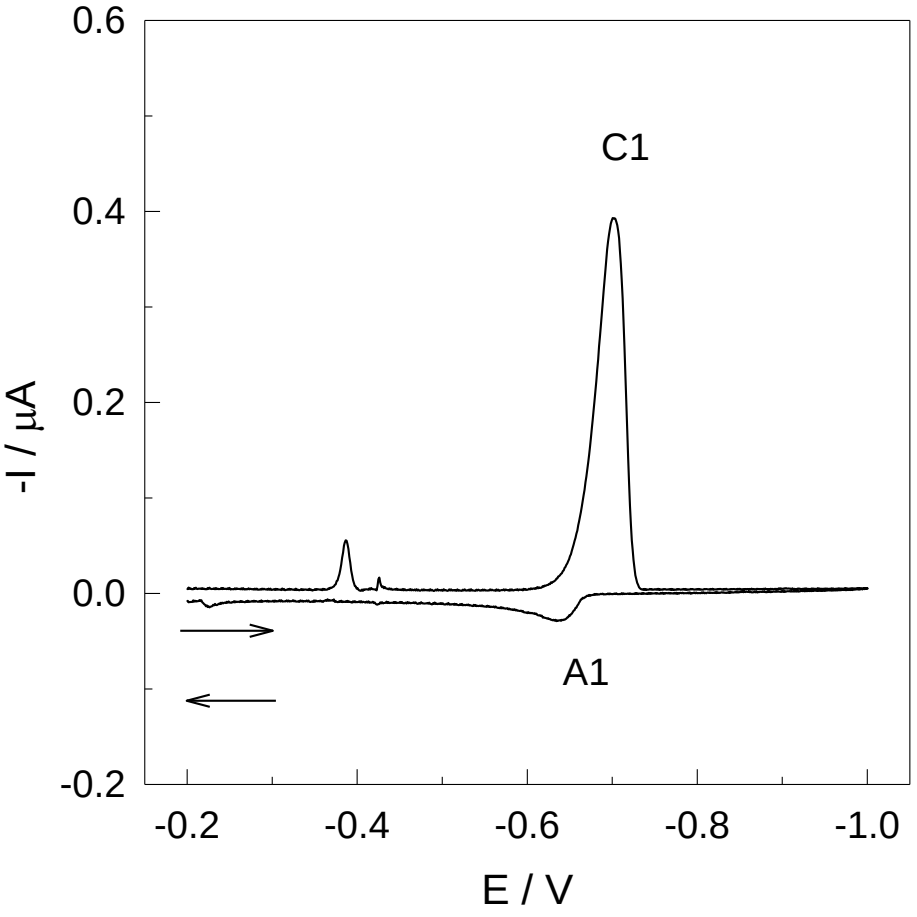
Ciglenečki, Ćosović: Electroanalysis, 9 (10) (1997) 775-781

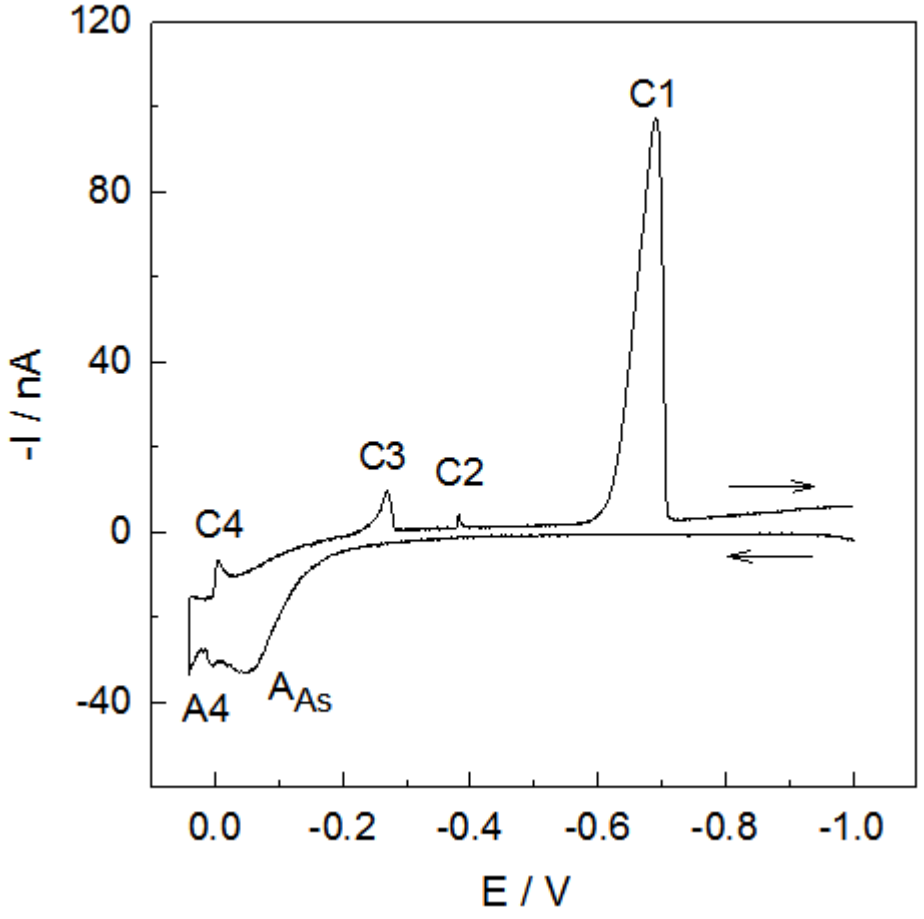
Dimethylarsinylethanol sulfide ($Me_2As(S)CH_2CH_2OH$)

- One of the possible compounds which can have important role in the stabilisation of sulfide in the oxic conditions
- Marine algae - arsenosugars (anaerobic cond.) --> **$Me_2As(O)CH_2CH_2OH$** --> **$Me_2As(S)CH_2CH_2OH$**
- Key intermediate in the biogenetic pathway from arsenosugars (major arsenic compounds in marine algae) to arsenobetaines (major arsenic compound in marine animals)

Krznarić, Ciglenečki, Ćosović, Anal Chim Acta 431(2001) 269

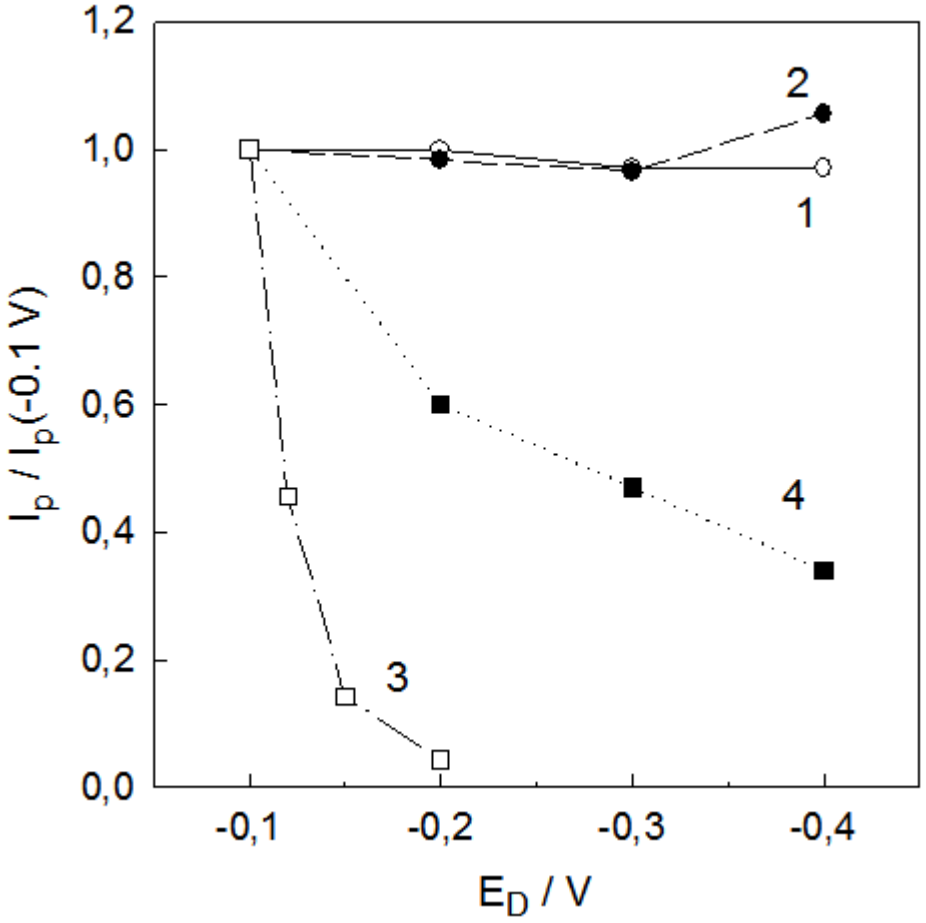
Dimethylarsinylethanol sulfide ($Me_2As(S)CH_2CH_2OH$)





Krznarić,Ciglenečki,Ćosović, Anal Chim Acta 431(2001) 269

Dimethylarsinylethanol sulfide in the mixtures with sulfide and sulfur



1,2) S^{2-} i S^0

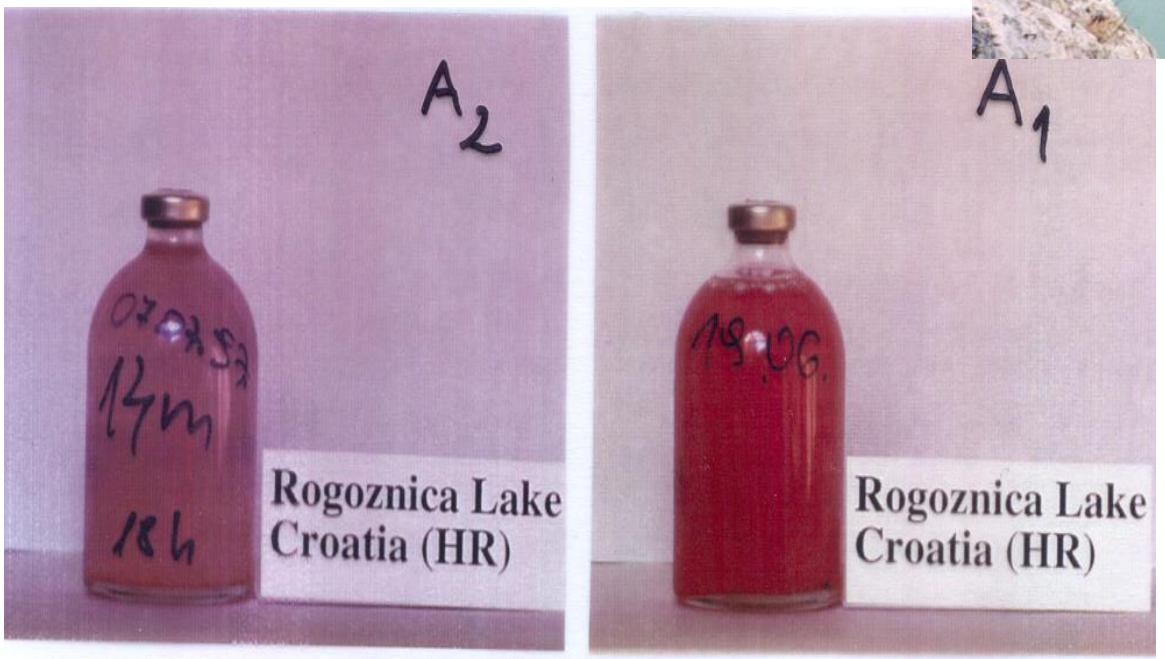
3) RMe_2AsS

4) Natural sample

Similar behavior of depositing HgS we expect for thiourea, thioacetamide,

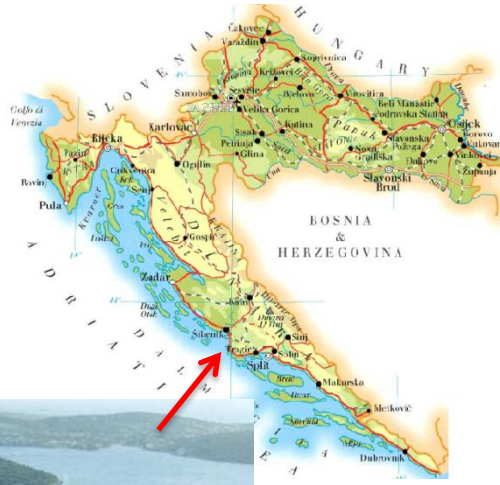
Labile metal sulfide species

Rogoznica lake- euxinic environment on the Adriatic coast



Ciglenecki et al. Cont.Shelf.Res. 2015

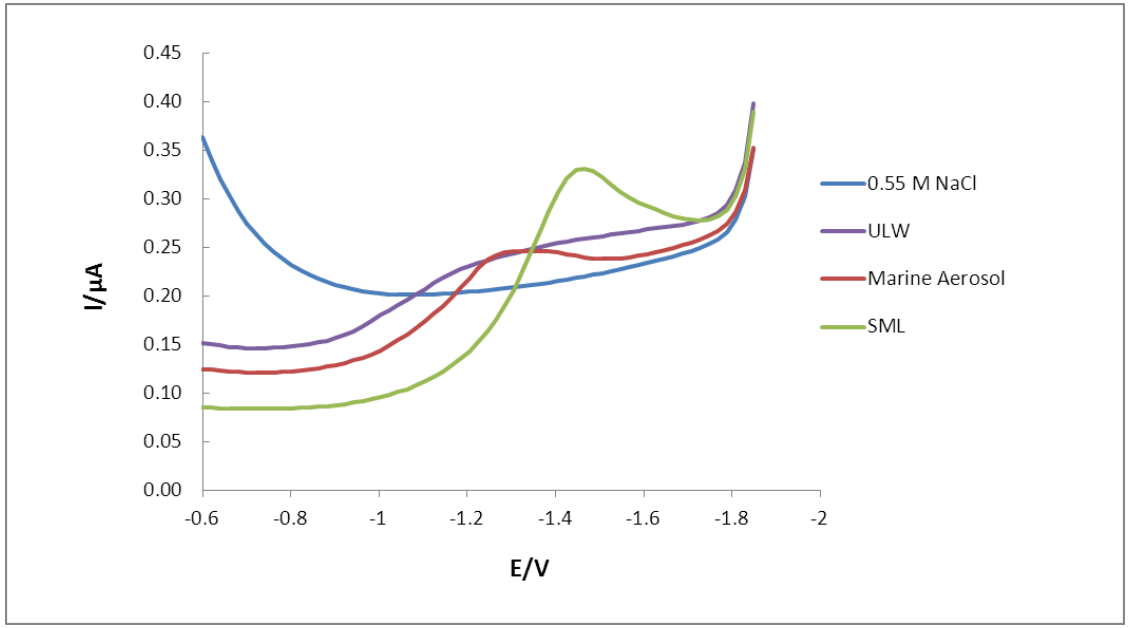
- Rogoznica Lake in central Dalmatia (43º32'N 15º58'E)
- Samples: Marine aerosol
  - Sea surface microlayer (SML)
  - Underlaying water (ULW)



Marine aerosol	
Sampler	SEQ 47/50 Low volume (2.3 m^3/h)
Period of sampling	24 h
Aerodynamic diameter of aerosol particles	2.5 µm
Filters	GF/F (47 mm)

Position of the aerosol sampler

SML (Garrett stainless steel method) and ULW sampling site

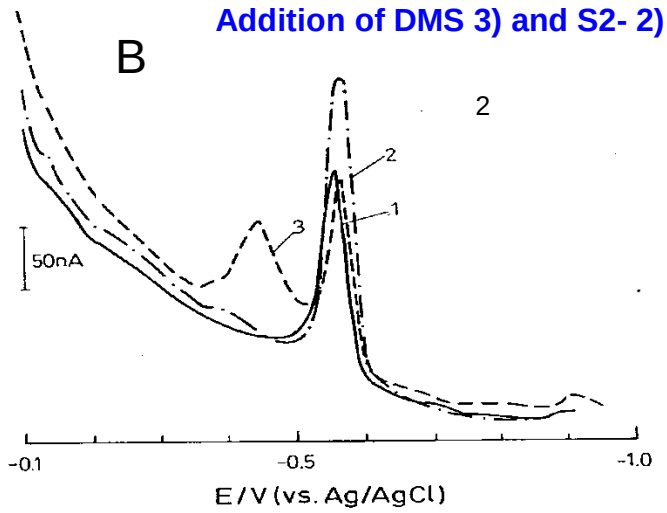


AC voltammetric curves of Aerosol, SML and ULW samples collected from the Rogoznica Lake in winter 2015.

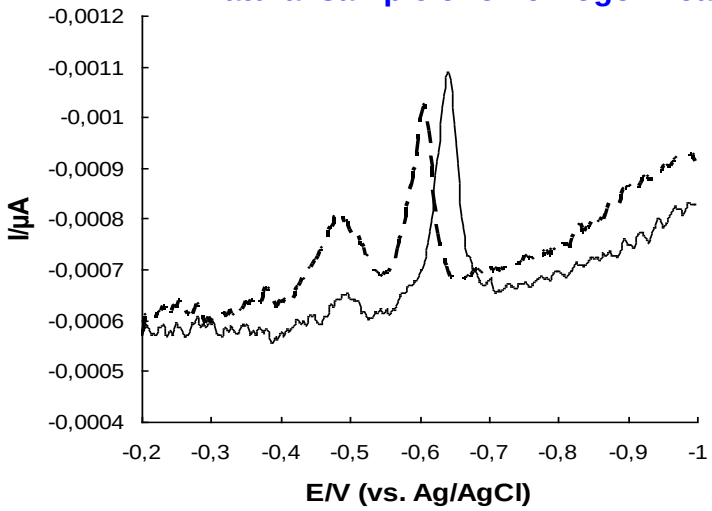
Seawater samples	WSOC (mg dm^{-3})	SAS (mg dm^{-3})
SML (1:1)	11.48	0.344
ULW (1:1)	1.52	0.141

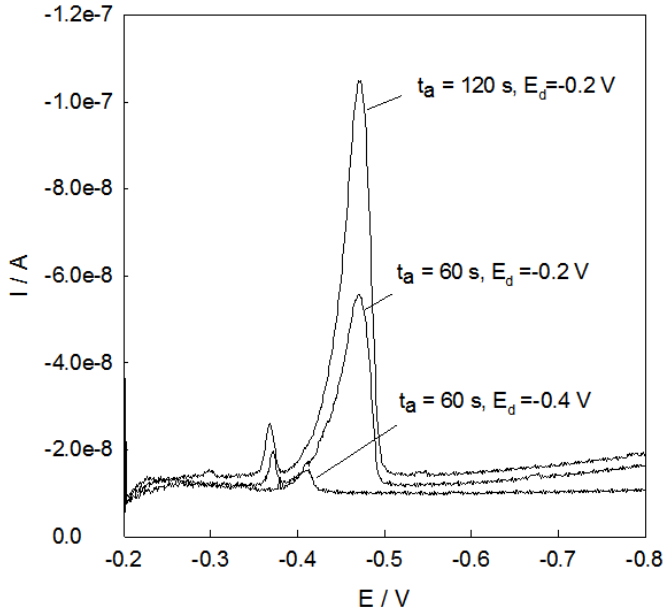
Marine Aerosol sample	WSOC (μg m^{3})	SAS (mg dm^{-3})
Aerosol sample 20.02.2015.	4	0.262

Addition of DMS 3) and S2- 2)



Natural sample of oxic Rogoznica lake

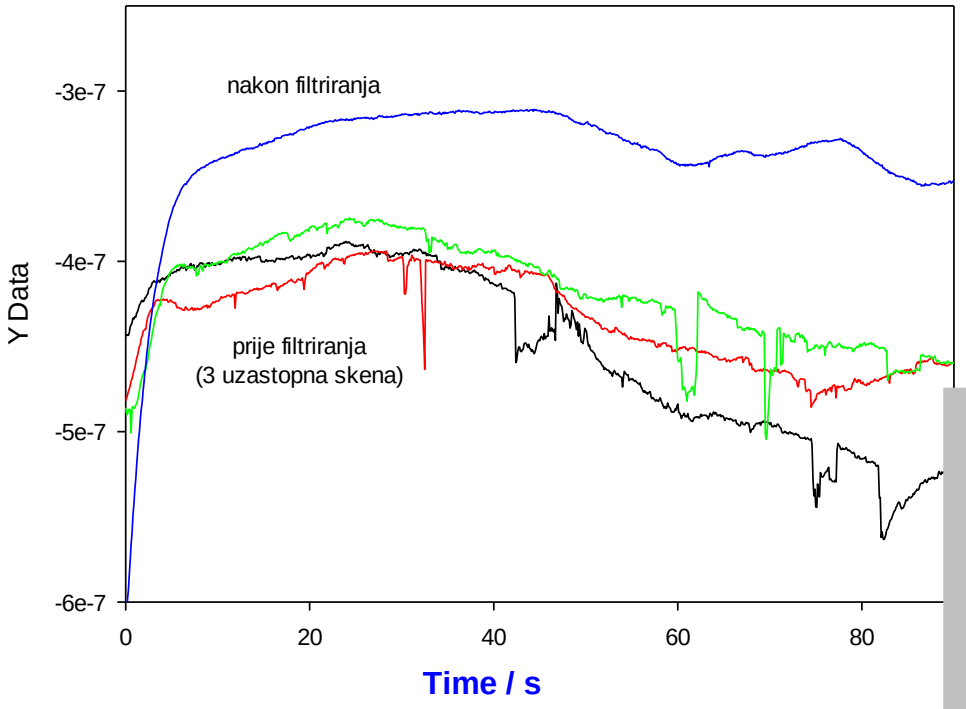


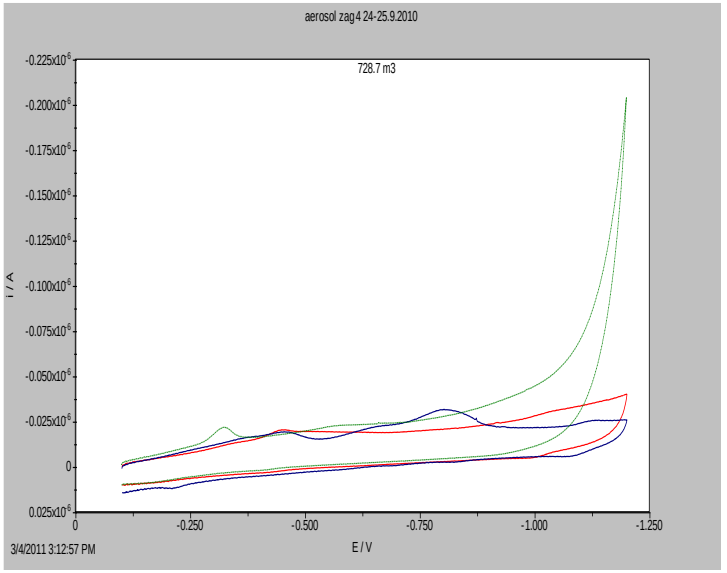


. LSV voltammograms of organosulfur species produced in aggregates of benthic diatoms after 1 month incubation in preserved anoxic conditions with 10^{-4} M sulfide.

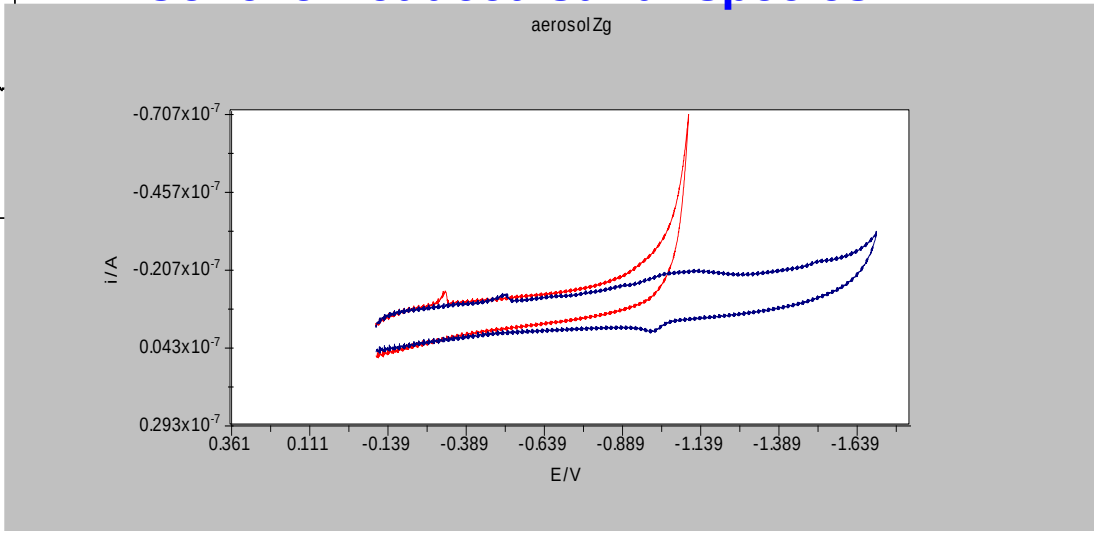
Ciglenecki et al. Mar.Chem. 2000
Bura-Nakic et al. Geochim.Cosmochim.Acta 2010

Aerosol, t= 90s na potencijalu od -1.9V, elektrolit 0.01 M NaCL



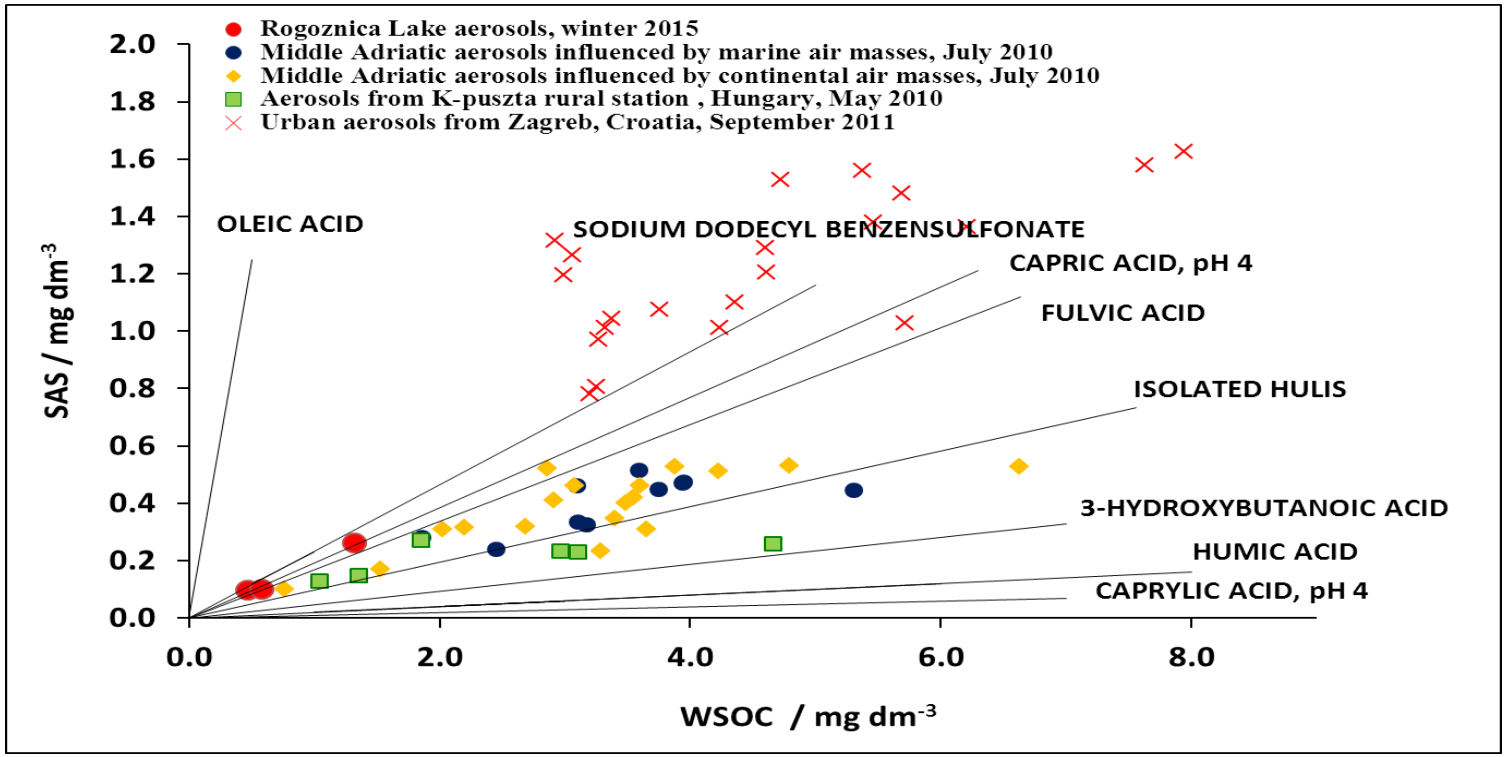


Conc. of reduced sulfur species 2-4 nM



Bura-Nakic et al. Envir.Chem.2014

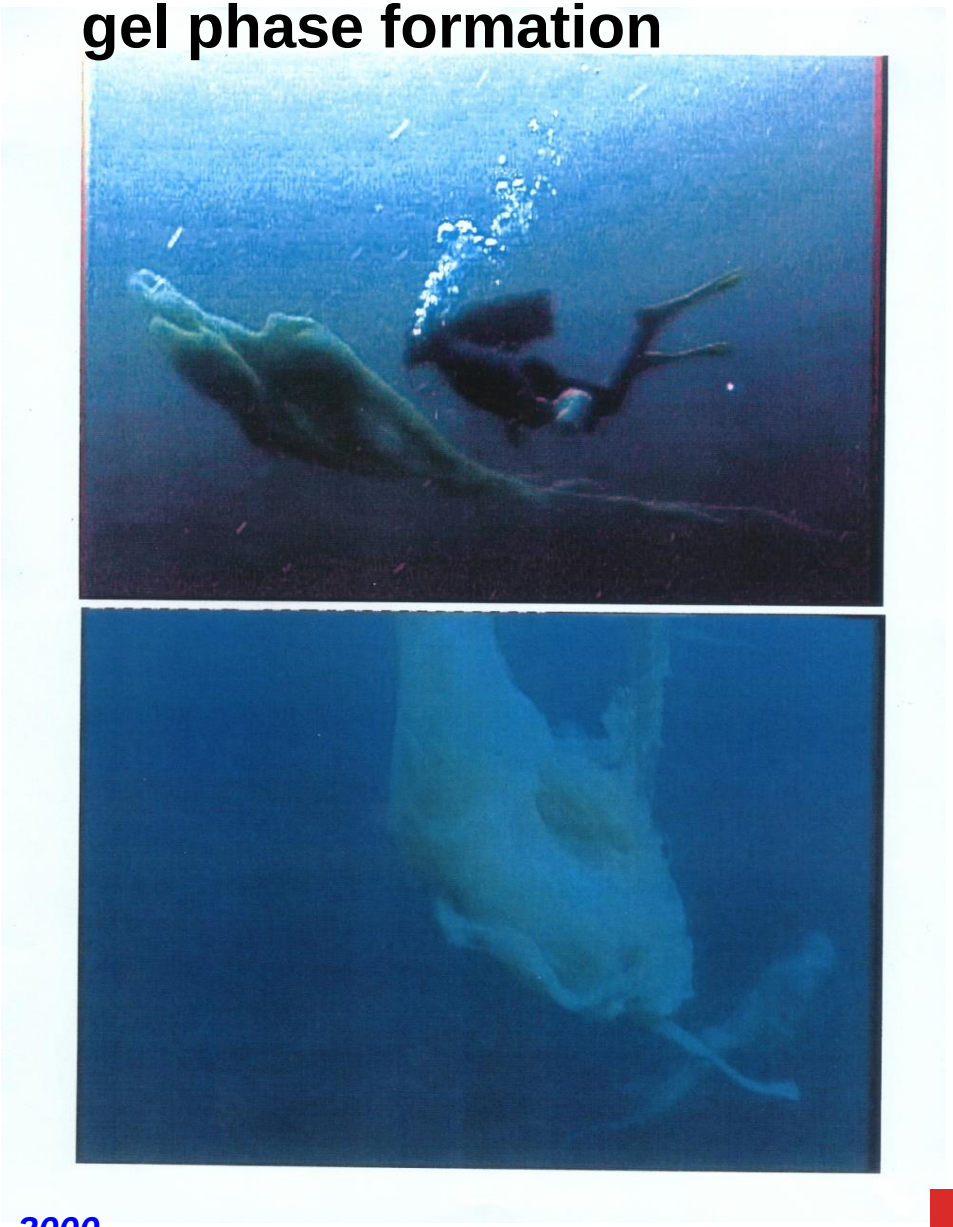
Vidovic at al. in press



The correlation of SAS and WSOC for aerosol samples from different locations was compared with relevant model substances.

The SAS/DOC ratio for Rogoznica Lake water samples shows the dominant presence of a more hydrophilic material which can be attributed to humic substances and polysaccharide type of OM.

Mucilage events in the North Adriatic Sea macroscopic gel phase formation



Ciglenecki et al. Mar.Chem. 2000

Table 1
Concentrations of organic carbon, surface active substances and reduced sulfur species in mucus aggregates and ambient water

No.	Sampling date	Station	Depth (m)	Sample	TOC (mg/l)	DOC (mg/l)	SAS eq. T-X-100 (mg/l)	Reduced sulfur species (nM)
#1.	26.08.1991	coastal (near Rovinj)	0.5	mucilage	112–279[a]	–	3.97	500
#2.	13.08.1997	coastal (near Rovinj)	0.5	mucilage	420	–	13.7	n.d.
				ambient water	50	25	2.4 (NF) 2.1 (F)	16
#3.	01.09.1997	108	20	mucilage	600	–	–	n.d.
				ambient water	–	–	–	n.d.
#4.	02.09.1997	001	bottom (30)	mucilage	140	–	2.4	200
				ambient water	–	–	0.5 (NF)	n.d.
#5.	10.06.1998	108	4	mucilage	–	–	–	81
				ambient water	–	60	3.6 (NF)	81

(F) — filtered samples.
(NF) — not filtered samples.
n.d. — not detected, i.e. below detection limit.
[a]Concentration range reported in Müller-Niklas et al. (1994).

Voltametric wave of RSS in mucilages samples

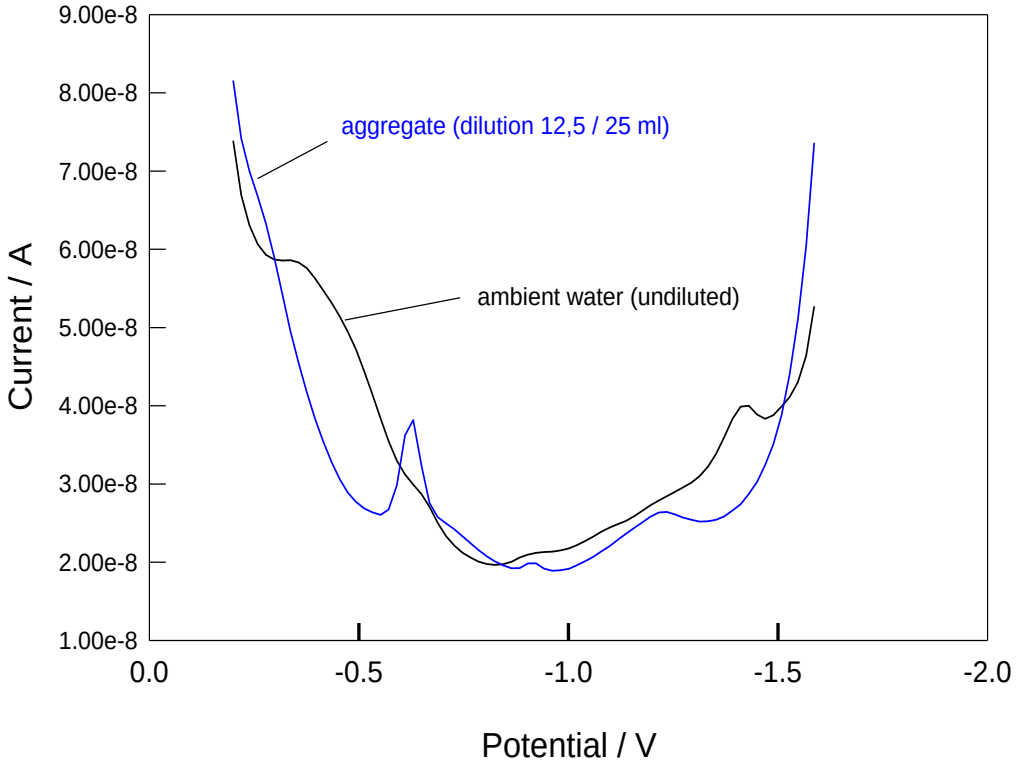


Fig 6. AC voltammograms of natural mucilage sample colected this summer in the North Adriatic Sea.

Aggregate:

(SAS)= 5mg/l

(organosulfur species)= 18 nM

Ambient water:

(SAS)= 0.34 mg/l

(organosulfur species)= 0 nM

Suggested **R&I Needs** for future research

Future prospectives

- **Additional characterization of aerosol samples by chromatographic methods**
- **Development of electrochemical methods as sensors for OM and sulfur compounds characterization and determination**
- **Improving extraction of WSOC from aerosol samples**

CONCLUSIONS

- Modern electrochemical methods has been shown very suitable for organic matter and sulfur species characterization in natural waters

- Advantages of electrochemistry: possibility of determination of different sulfur species, relative high sensitivity,direct and very fast speciation, portable and relative cheap instrumentation

- It is imortant to emphasis that measurements in fresh and not treated natural samples besides in-situ measurements are the best way of determination which leaves equlibrium state of the samples undisturbed

- Electrochemical techniques based on the measurements of adsorption effects on the Hg electrode are widely used for SAS characterization in natural waters (freshwater and seawater systems)

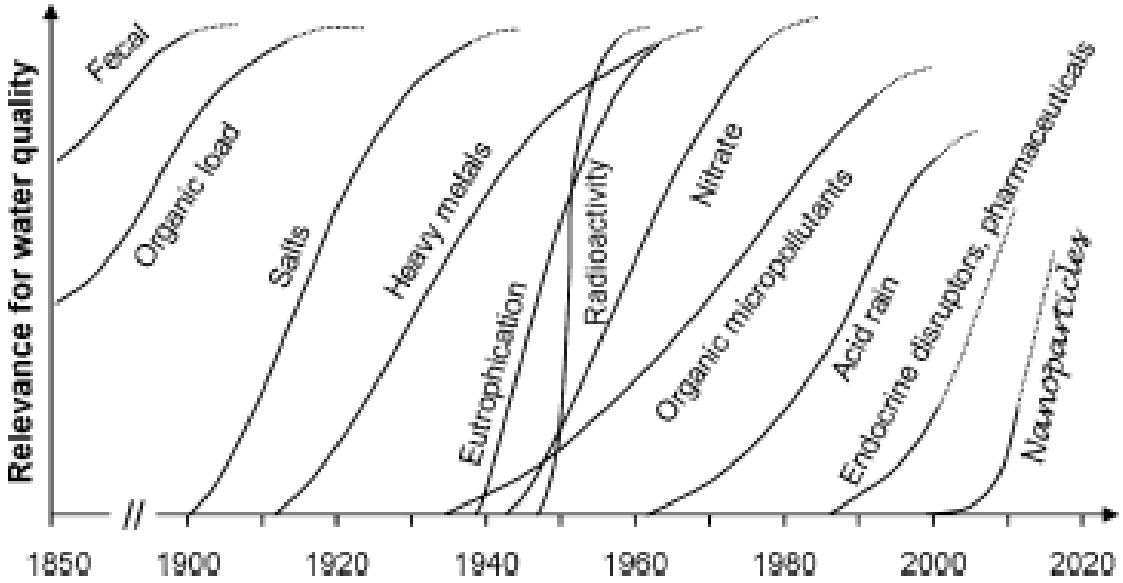
- SAS and DOC content in rain water samples are comparable to surface freshwater environment

- Electrochemical curves in river waters and bulk precipitation mainly corresponds to humic like substances –HULIS-, similar is for marine aerosols where presence of more hydrophilic material in WSOC fraction were detected, in contrast to the strongly hydrophobic SAS material found in urban aerosols

- Combination of relatively high SAS and DOC content of OM in atmospheric samples suggest concentration mechanisms of hydrophobic organic compounds in droplets and its transport to other environmental compartments

Compounds affecting aquatic environment

Fig. 3 Compounds affecting water quality during the last two centuries. (modified from [87])



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