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and Environmental Sustainability - *EuNetAir*

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WGs & MC Meeting at SOFIA (BG), 16-18 December 2015

New Sensing Technologies for Indoor Air Quality Monitoring: Trends and Challenges

Action Start date: 01/07/2012 - Action End date: 30/04/2016 - Year 4: 1 July 2015 - 30 April 2016

TRACE METALS IN WATER SOLUBLE FRACTION OF MARINE AEROSOLS

Irena Ciglenečki[1], Ana Cvitešić[1], Palma Orlović-Leko[2], Sanja Frka[1], Niko Bačić[1], Nena Mikac[1]

irena@irb.hr, WG and MC 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.

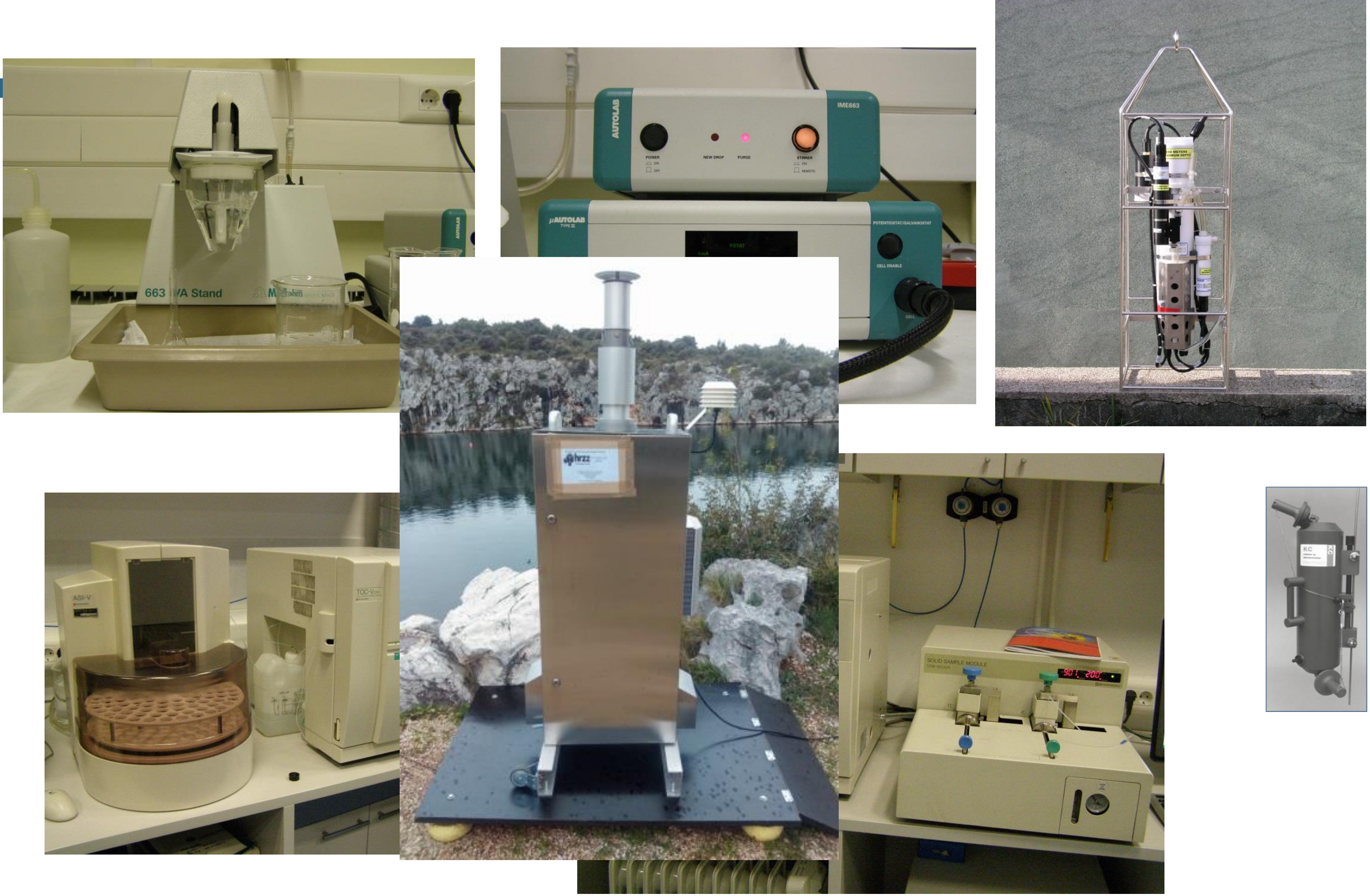
Research Facilities of the RBI group

- 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).

hrzz
Hrvatska zaklada za znanost


663 VA Stand
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IME663
POWER
NEW DROP
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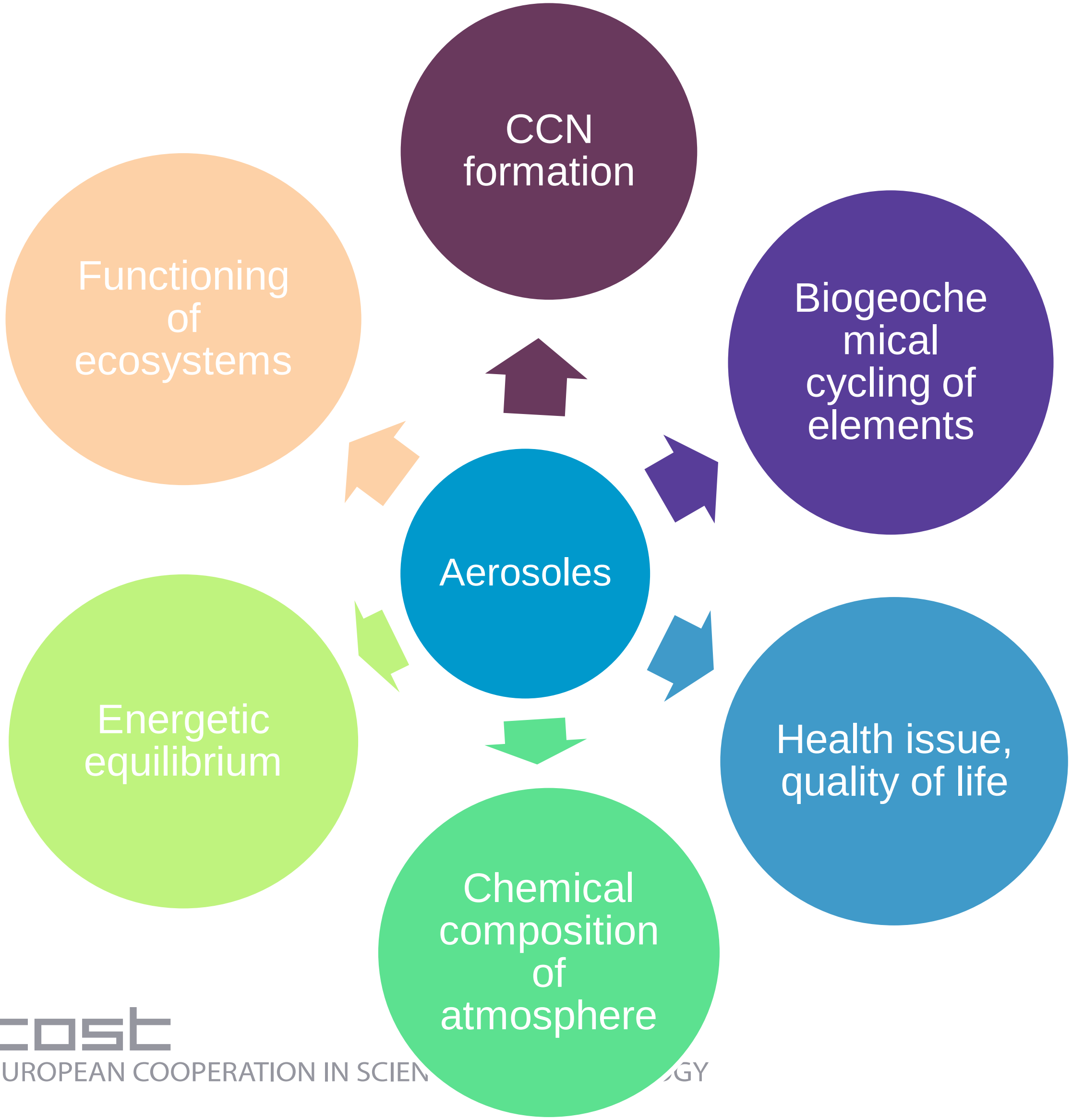
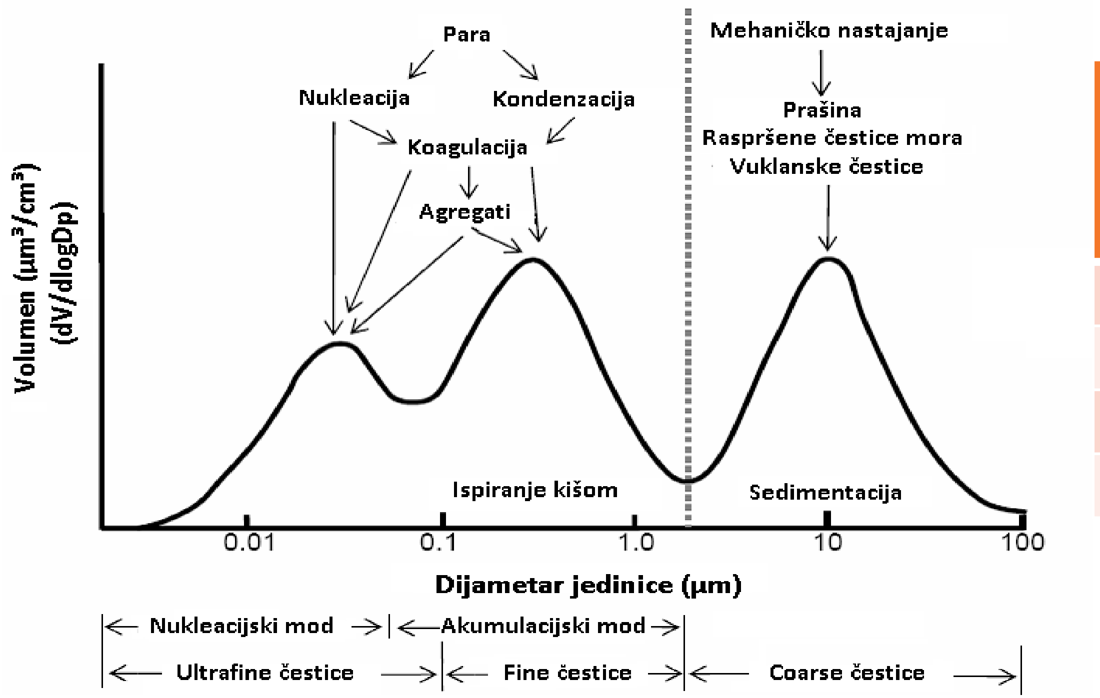
TOC-V
SOLID SAMPLE MODULE
901. 200.

Aerosols - Marine aerosols



- atmosphere as one of the Earth's major C and S reservoirs is an important component of the global C and S cycles
- delivery system to bring material and energy to and take them away of an ecosystem
- marine aerosols one of the largest aerosol system

Aerosols



Environ-ment	Particle conc. (cm^{-3})	Mass conc (μg m^{-3})
Urban	$10^5 – 10^7$	$10^1 –10^4$
Rural	$10^3 – 10^4$	$10^1 – 10^2$
Marine	10^2 - $5x10^2$	$10^1 – 10^2$
Polar	$10^0 – 10^3$	$10^{–1} – 10^1$

Distribution of aerosol particles with mechanisms of their formation and depletion

Marine aerosols

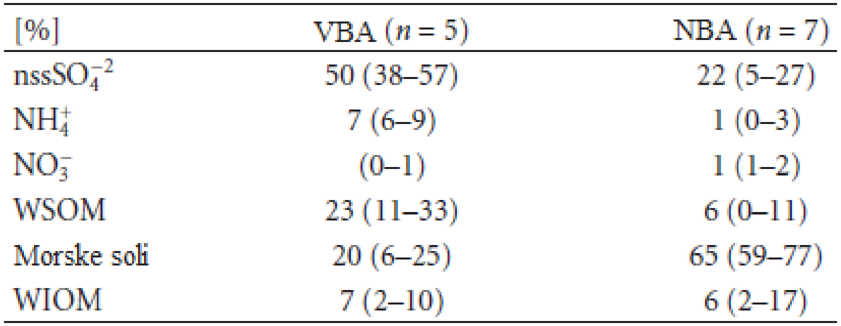
- derived from both primary and secondary processes.
- sea-salt aerosols, (global emissions of 2000–10 000 Tg yr−1, diameters less than 20 μm), - major component of primary marine aerosol mass

- Dimethyl sulfide (DMS) - derived sulfate was - key precursor to secondary marine aerosol mass over biologically-productive regions
- organic aerosols of marine origin follow a strong seasonal cycle, with the highest conc. in the spring/summer, lowest in the winter

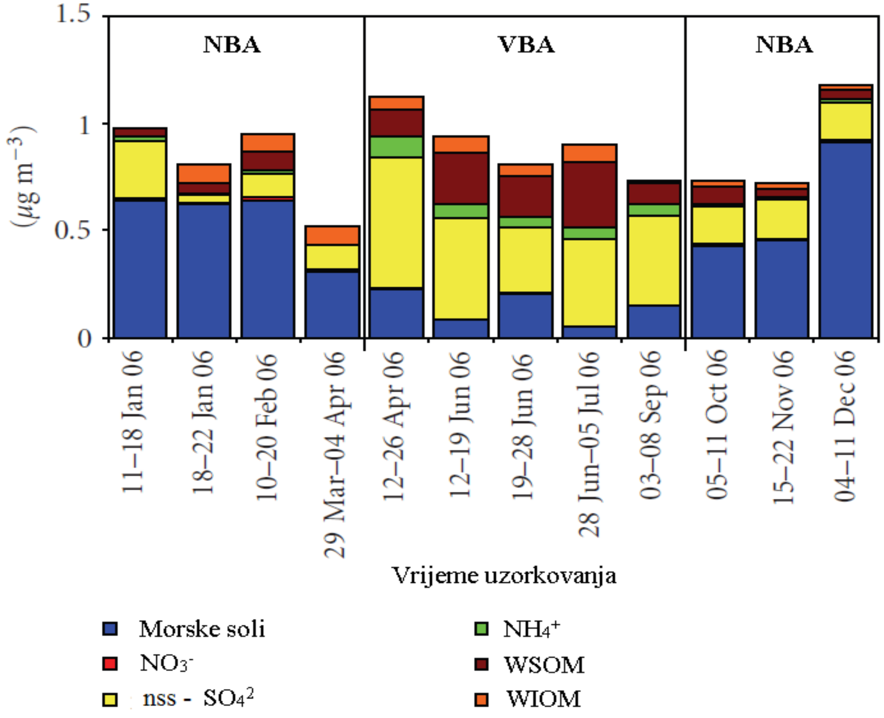
- production mechanisms for ocean-derived organic aerosol:
- (1) bubbles produced by breaking waves that scavenge surface-active organic matter and other materials (e.g., bacteria, viruses and detritus) during their ascent and inject it into the atmosphere as marine primary organic aerosols (POA) upon bursting
- (2) oxidation of phytoplankton-emitted volatile organic compounds (VOCs) such as DMS, aliphatic amines, isoprene, and monoterpenes which can form secondary organic aerosols (SOA)

Marine aerosols

- **Seasonal biochemical processes influence chemical composition of aerosols**



[%]	VBA ($n = 5$)	NBA ($n = 7$)
nssSO$_4^{-2}$	50 (38–57)	22 (5–27)
NH$_4^+$	7 (6–9)	1 (0–3)
NO$_3^-$	(0–1)	1 (1–2)
WSOM	23 (11–33)	6 (0–11)
Morske soli	20 (6–25)	65 (59–77)
WIOM	7 (2–10)	6 (2–17)



Major component of marine aerosols sampled on research station Mace Head, Ireland 2006

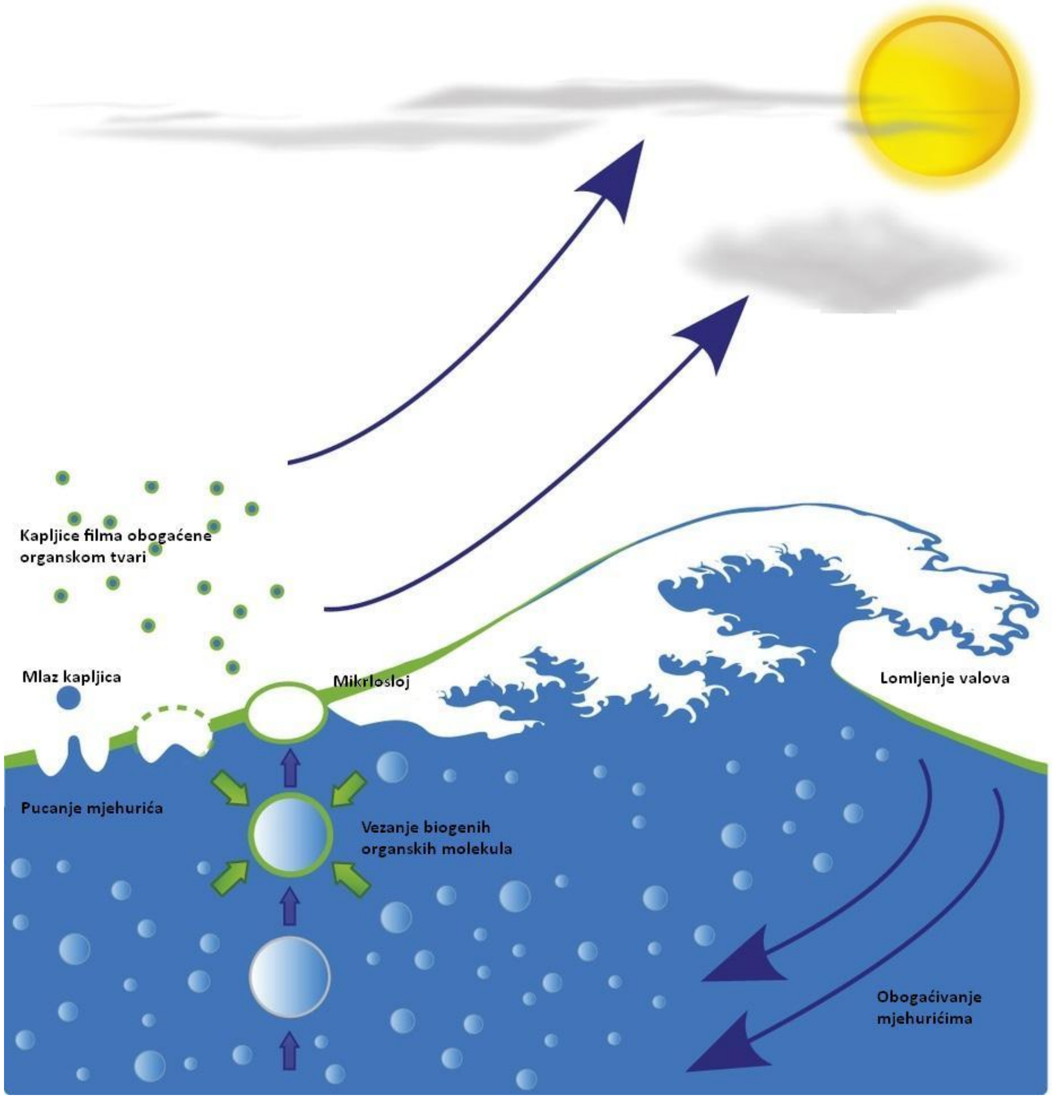
Season of high (VBA) and low (NBA) biological activities

Marine aerosols

- Sea-surface microlayer SSM
  - 10-100 µm seasurface
  - Enriched with organic matter hydrocarbons, lipids, proteins,microorganisms

- POA : „bubble bursting ” mechanisms

- SOA – in the atmosphere above SSM



Mediterranean Sea

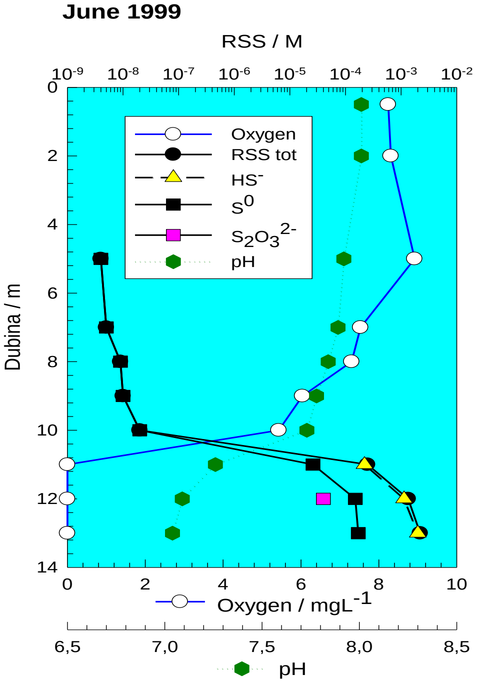
Semi-enclosed basin, senitive to climatic and environmental changes

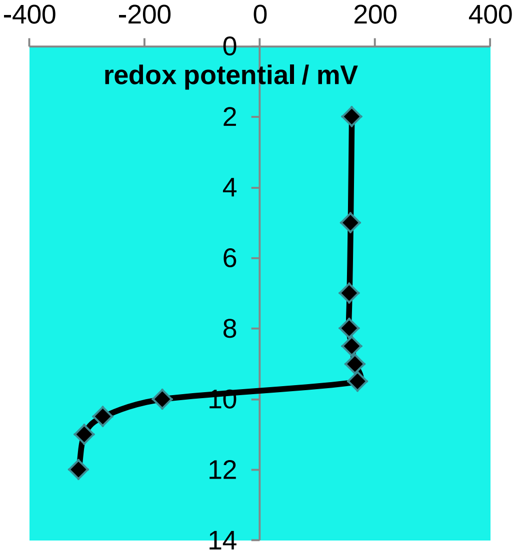
Anthropogenic pressures and Saharan dust

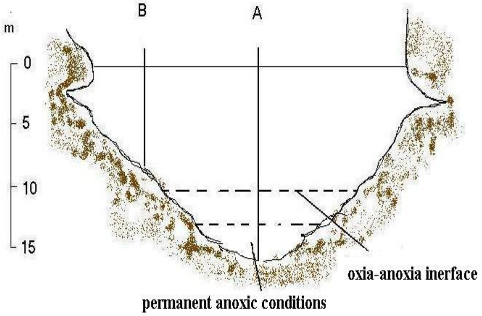
EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

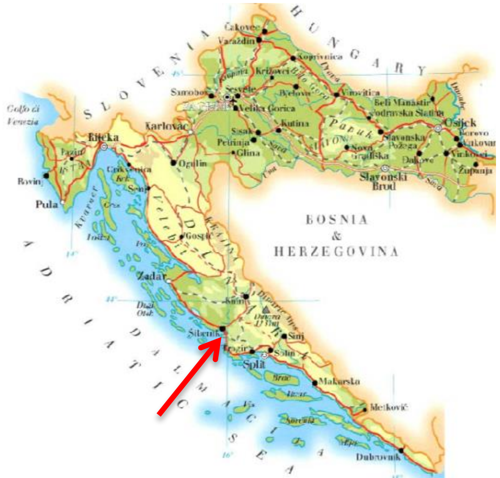
Hrvatska zaklada za znanost

Study site- Rogoznica lake – euxinic environment on the Adriatic coast

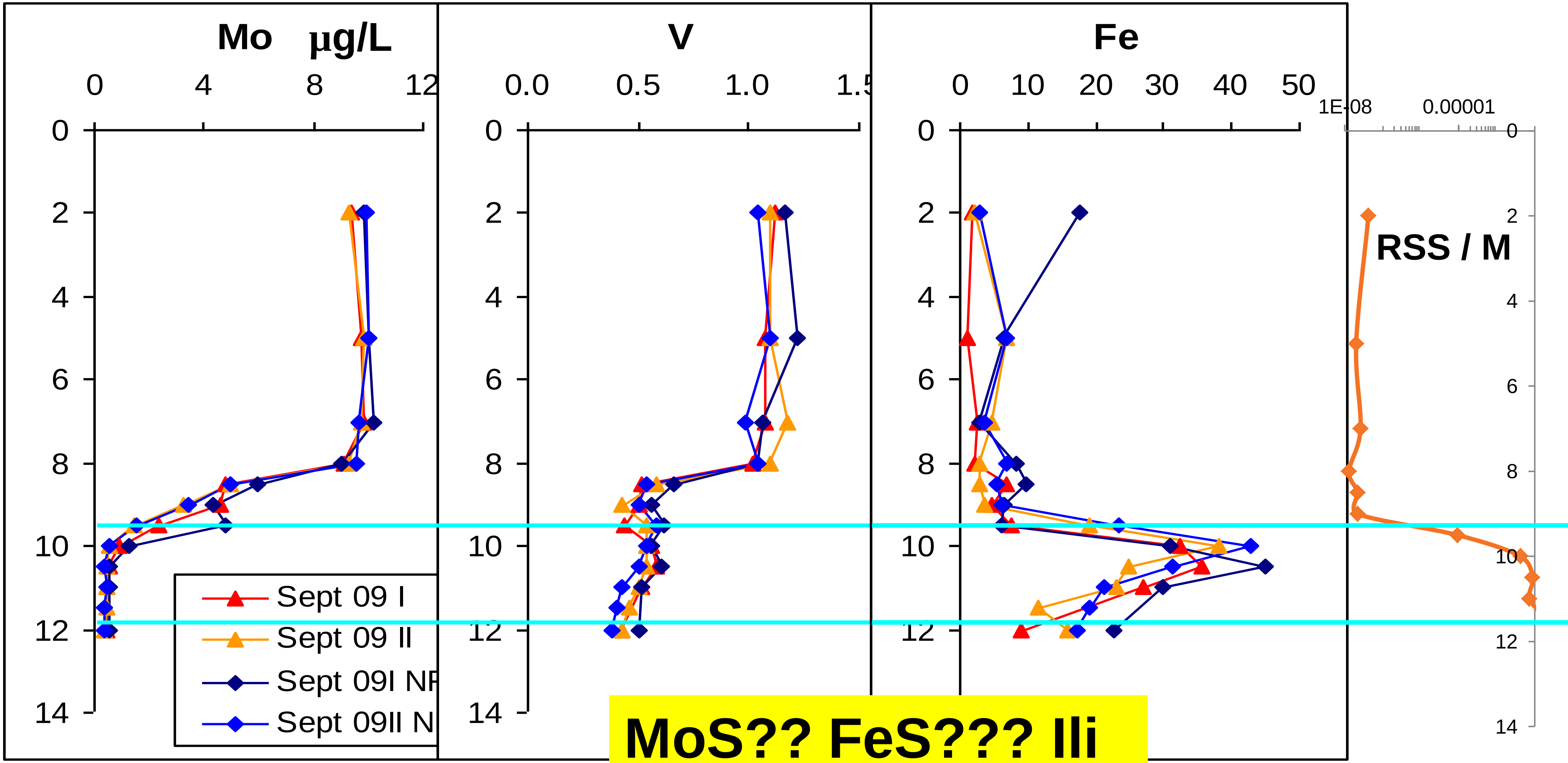








Trace metal in water column of Rogoznica



MoS?? FeS??? Ili FeMoS?

Helz, Bura-Na **4 (2011) 323**

IRB,student

STUDY SITE AND SAMPLING

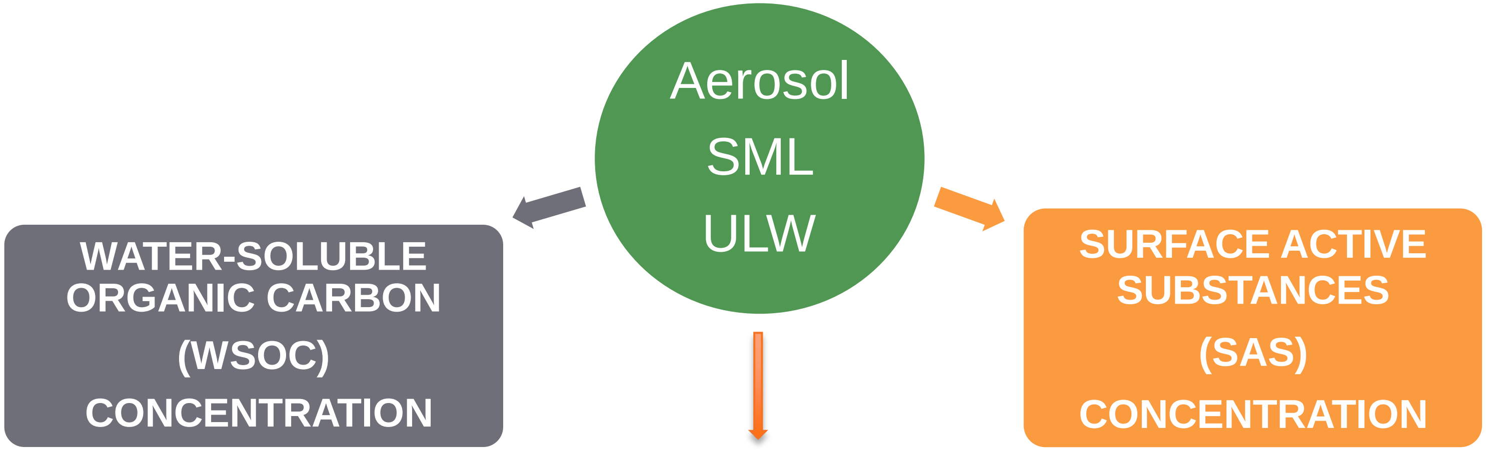
- Rogoznica Lake in central Dalmatia (43^{o}32’N 15^{o}58’E)
- Samples: ☁ Marine aerosol
  ▲ Sea surface microlayer (SML)
  ▼ Underlaying water (ULW)

☁ 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

SAMPLE ANALYSIS



Aerosol
SML
ULW

WATER-SOLUBLE ORGANIC CARBON
(WSOC)
CONCENTRATION

SURFACE ACTIVE SUBSTANCES
(SAS)
CONCENTRATION

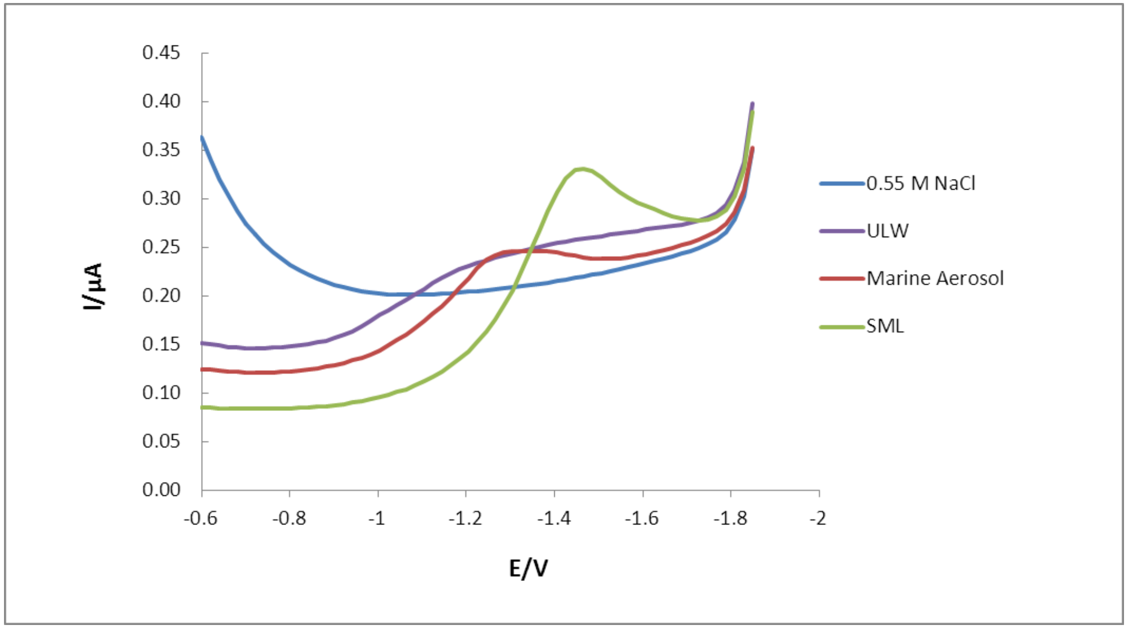
- Water-soluble aerosol fraction was extraxted from the samples in high purity deionised water (MQ) for 24 h and filtered through 0.7 µm GF/F filters.
- WSOC was determined by high temperature catalytic oxidation (HTCO) tehnique on a TOC-VCPH analyser (Shimadzu, Japan) with a non-dispersive infrared detector for CO_2.

TRACE METALS
HR-ICPMS

- Filters dissolved in conc. HNO_3

Characterization of SAS in the WSOC was preformed with an electrochemical analyser µAutolab (Metrohm, Netherland) (with a three-electrode system: hanaging mercury electrode as a working electrode; Ag/AgCl as a reference and a graphite as a auxiliary electrode).

- Phase sensitive ac. voltammetry (out-of-phase) was used for quantification of SAS.
- Surfactant activity is expressed as the equivalent amount of the selected standard T-X-100 compound.

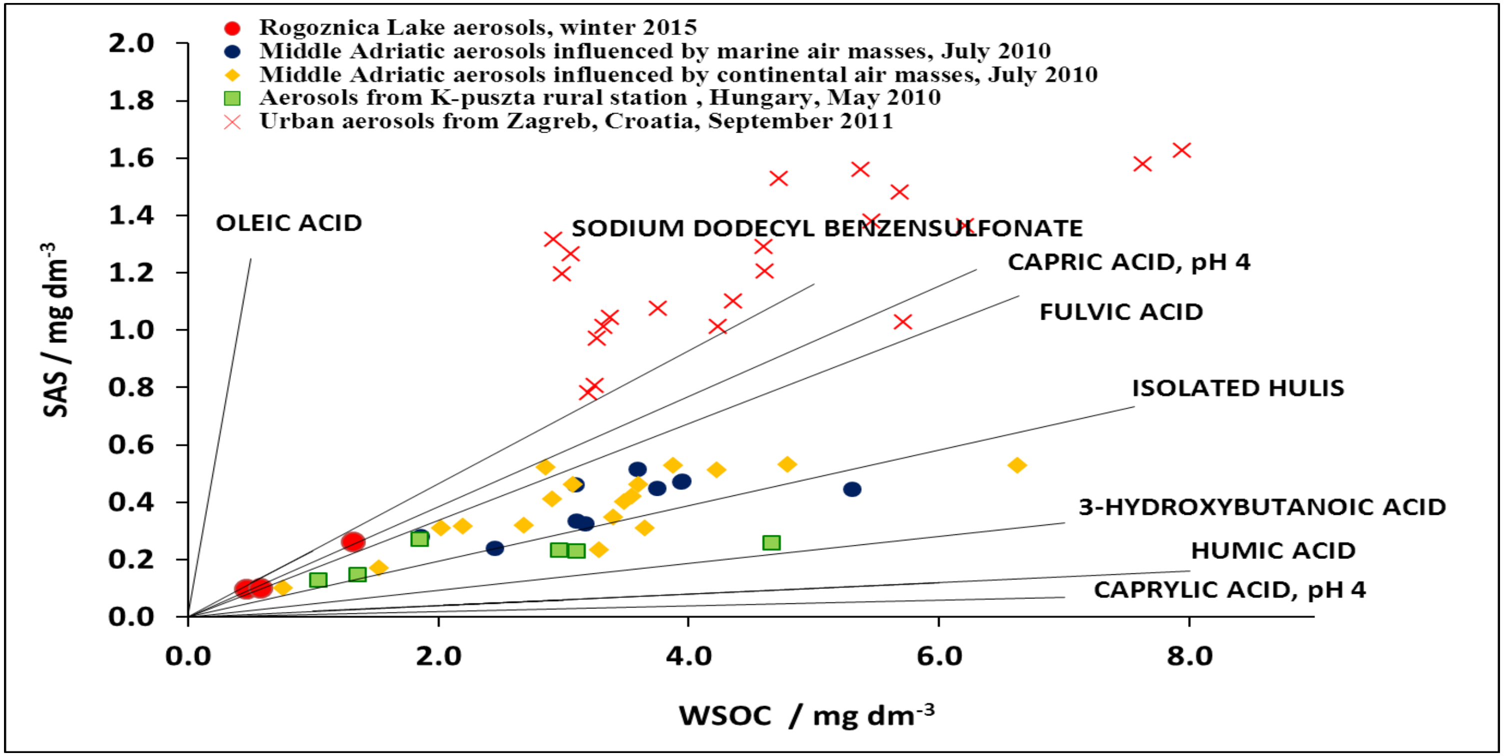


AC voltammetric curves of Aerosol, SML and ULW samples collected from the Rogoznica Lake in winter 2015.

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 ($\mu g\ m^3$)**	**SAS ($mg\ dm^{-3}$)**
☁ Aerosol sample 20.02.2015.	4	0.262

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.

Trace metals in marine aerosols

- **Measured from glass fiber GF/F filter**
- **Elements with increased blank concentration - Li, Be, Rb, U, Al, Ti, Zn, Sr, Ba**

Element	ng/ filter	ng/m3	NWM	Atlantic
Fe	996	18,89	106	12,26
Pb	239	4,53	3,39	0,2
V	206	3,90		
Ni	64,4	1,22	2,2	
Mn	47,5	0,90	3,3	0,35
Cu	28,9	0,55	3,9	0,81
Cr	20,5	0,39		0,53
Se	20,1	0,38		
Sn	16,8	0,30		
As	5,0	0,09		
Mo	4,3	0,08		
Ag	3,8	0,07		
Cd	2,7	0,05	0,09	
Co	1,4	0,03	0,07	
Sb	1,1	0,02		
Bi	1,0	0,018		
Tl	0,9	0,017		

Fe, Mn, Cu, Cd, and Zn – essential for marine productivity

Crustal derived - Al,Fe,Mn,Co

Anthropogenic origin - Pb, Cd, Zn

Similar to trace metal composition in remote northern tropical Atlantic marine environment: case study Cape Verde islands

K. W. Fomba et al. Atmos. Chem. Phys., 13, 4801–4814, 2013

North-Western Mediterranean atmospheric aerosols (1986-2008) – seasonal patern (highest May-Nov) for crustal el. and Cu,Ni; Anthropognic- highest in atumn/winter

Heimburger et al. Sci. Total Environ. 408, 2010, 2629

Atlantic marine (AM)
Marine over Canary (MC)
Marine over Europe (ME)
Marine over North America (MNA)

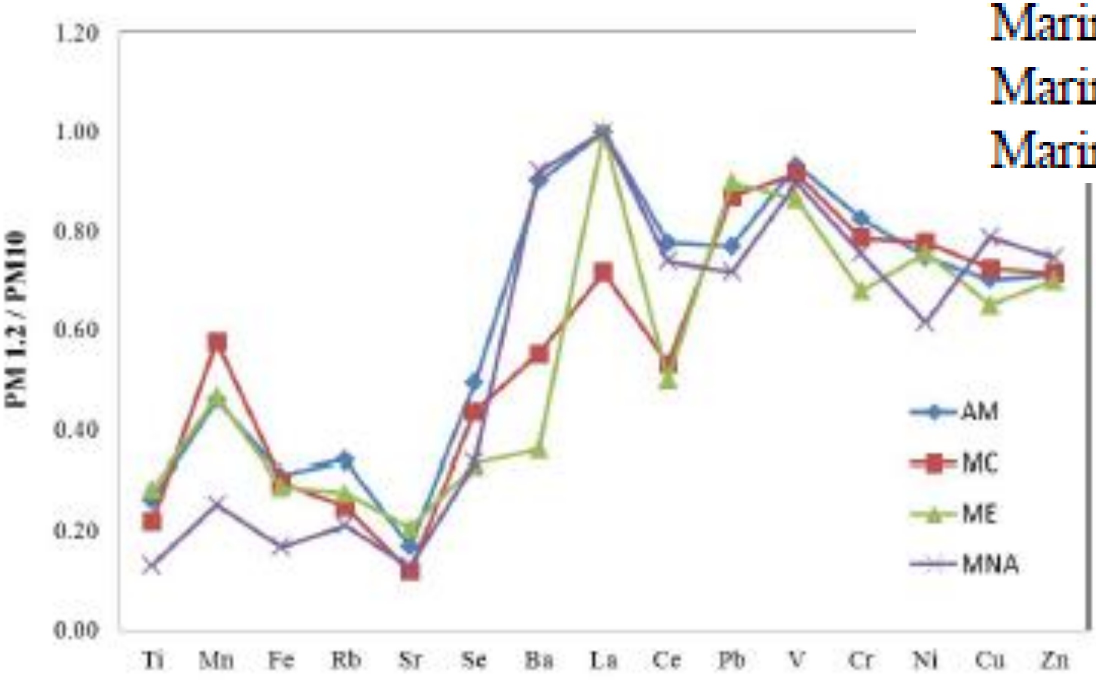


Fig. 5. Fine ($PM_{1.2}$) to coarse (PM_{10}) ratios for measured trace elements in the four major air mass footprints representative of the aerosol background at CVAO.

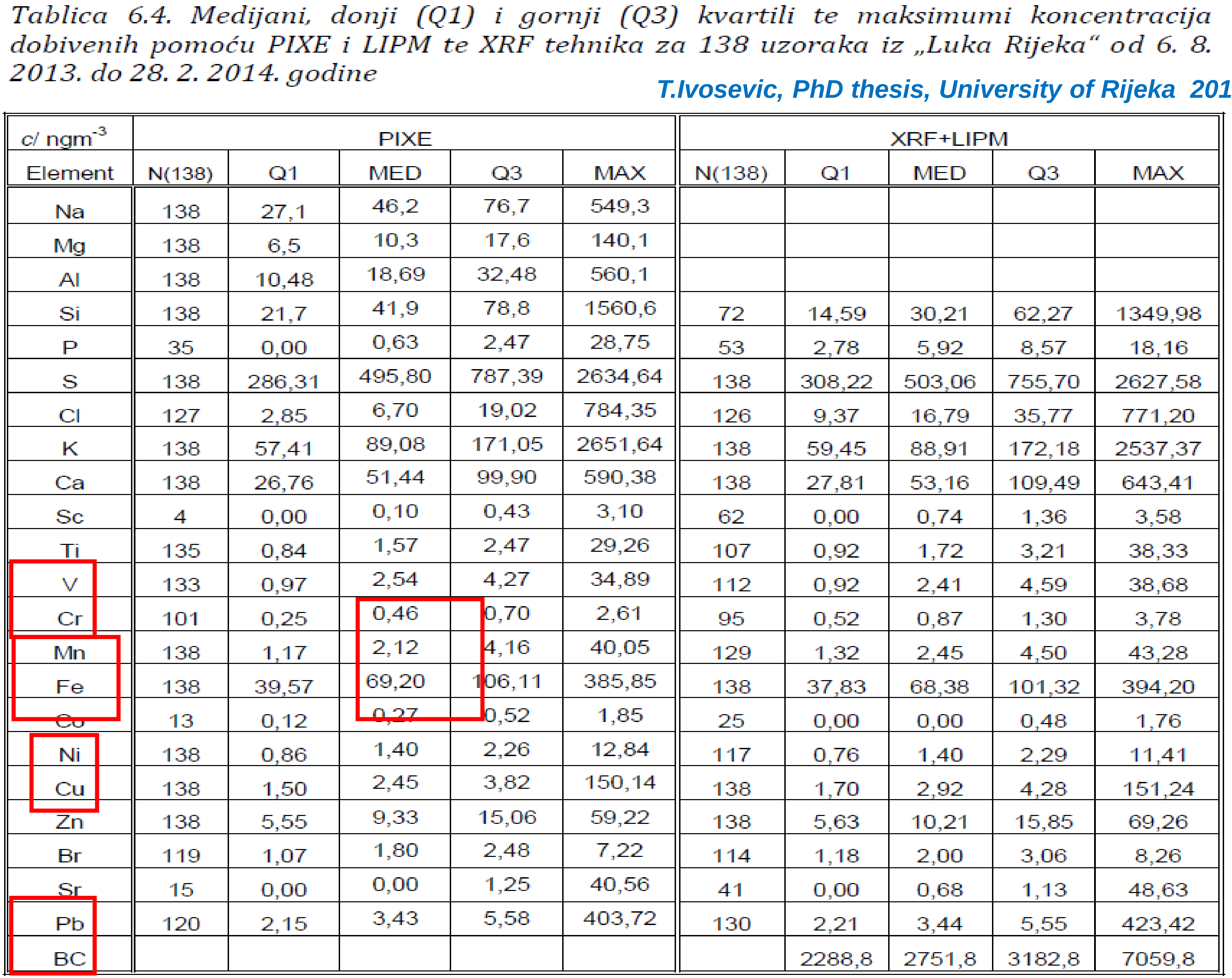
$$EF = \frac{(Z/Ti)_{Sample}}{(Z/Ti)_{Crust}}.$$

High EF anthropogenic origin
Pb, Cr, Ni, Cu, Zn

Low EF- crustal source

Fe, Mn, Co, and Rb.

Mixed sources
Ba, Ce, La, Sr, and V.



Tablica 6.4. Medijani, donji (Q1) i gornji (Q3) kvartili te maksimumi koncentracija dobivenih pomoću PIXE i LIPM te XRF tehnika za 138 uzoraka iz „Luka Rijeka“ od 6. 8. 2013. do 28. 2. 2014. godine

T.Ivosevic, PhD thesis, University of Rijeka 2014

c/ ngm^{-3}	PIXE					XRF+LIPM				
Element	N(138)	Q1	MED	Q3	MAX	N(138)	Q1	MED	Q3	MAX
Na	138	27,1	46,2	76,7	549,3					
Mg	138	6,5	10,3	17,6	140,1					
Al	138	10,48	18,69	32,48	560,1					
Si	138	21,7	41,9	78,8	1560,6	72	14,59	30,21	62,27	1349,98
P	35	0,00	0,63	2,47	28,75	53	2,78	5,92	8,57	18,16
S	138	286,31	495,80	787,39	2634,64	138	308,22	503,06	755,70	2627,58
Cl	127	2,85	6,70	19,02	784,35	126	9,37	16,79	35,77	771,20
K	138	57,41	89,08	171,05	2651,64	138	59,45	88,91	172,18	2537,37
Ca	138	26,76	51,44	99,90	590,38	138	27,81	53,16	109,49	643,41
Sc	4	0,00	0,10	0,43	3,10	62	0,00	0,74	1,36	3,58
Ti	135	0,84	1,57	2,47	29,26	107	0,92	1,72	3,21	38,33
V	133	0,97	2,54	4,27	34,89	112	0,92	2,41	4,59	38,68
Cr	101	0,25	0,46	0,70	2,61	95	0,52	0,87	1,30	3,78
Mn	138	1,17	2,12	4,16	40,05	129	1,32	2,45	4,50	43,28
Fe	138	39,57	69,20	106,11	385,85	138	37,83	68,38	101,32	394,20
Co	13	0,12	0,27	0,52	1,85	25	0,00	0,00	0,48	1,76
Ni	138	0,86	1,40	2,26	12,84	117	0,76	1,40	2,29	11,41
Cu	138	1,50	2,45	3,82	150,14	138	1,70	2,92	4,28	151,24
Zn	138	5,55	9,33	15,06	59,22	138	5,63	10,21	15,85	69,26
Br	119	1,07	1,80	2,48	7,22	114	1,18	2,00	3,06	8,26
Sr	15	0,00	0,00	1,25	40,56	41	0,00	0,68	1,13	48,63
Pb	120	2,15	3,43	5,58	403,72	130	2,21	3,44	5,55	423,42
BC							2288,8	2751,8	3182,8	7059,8

CONCLUSIONS

- our results show the presence of more hydrophilic material in WSOC fraction of marine aerosol samples in Rogoznica Lake in contrast to the strongly hydrophobic surfactant material present in urban aerosols

- **preliminary results pointed out to the dominant presence of humic like material in aerosols from coastal region and minimal influence of anthropogenic urban air masses**

- **Preliminary data on trace metals content collected on the glass fiber filters show good comparable results for Fe,Pb,V,Ni,Mn,Cu,Cr, Se, As,Mo,Ag,Cd**

- **Increased blank concentration for Li, Be, Rb, U, Al, Ti, Zn, Sr, Ba, indicate that these metals can not be measured on the glass fiber filters.**

Future research

- Parallel sampling on teflon and glass fiber samples
- Evaluation of enrichment factor pointing to source of aerosols
- Sampling of different aerosols PMs – distribution of trace metals among different particles
- Sampling for wet deposition - rain-