

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

COST Action TD1105

**WGs Meeting, Belgrade, 13 - 14 October 2015**

**organized by VINCA Institute and co-organized by Public Health Institute of Belgrade**

**hosted by Faculty of Mechanical Engineering, University of Belgrade**

Action Start date: 16/05/2012 - Action End date: 30/04/2016



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

## **CARBON SPECIES IN BLACK CRUST OF ZAGREB CATHEDRAL**

**Speaker**

**Organization**



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EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY



# Introduction

- **Atmospheric aerosol are liquid or solid particles suspended in air which exert an important influence on the global climate and air quality.**
- **Chemical composition of atmospheric aerosol are still unknown but carbonaceous components account for a large fraction of air particulate matter.**
- **Besides the influence on the climat and air quality the particulate matter can influence on the durability of stone monuments.**
- **The interaction between the atmosphere and stone monuments leads to the formation of surface black layers.**

# Introduction

- **Building and monuments act as repository of airborne organic pollutants, which accumulate at the surface in zones frequently soaked by rainwater but are not washed out.**
- **In these areas thick black crust deposits can be found, which contribute to soiling of stone surfaces.**
- **The exposure building materials act as non-selective surface, passively entrapping all deposited airborne particulate matter.**
- **Today, the SO<sub>2</sub> emission is reduced to minimum, but particulate matter represents a new danger to the damage of stone monuments..**

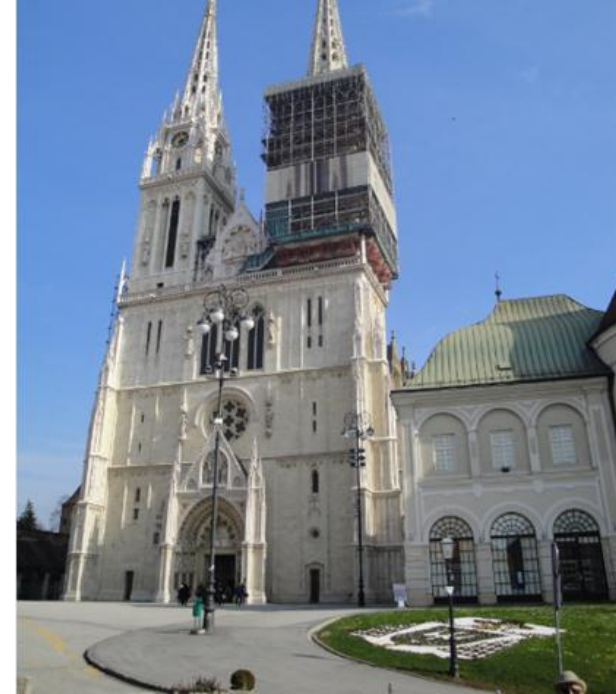
# Introduction

- **Atmosphere composition is of unquestionable importance in the study of the damage produced on building material.**
- **Carbonaceous particles in the atmosphere play an important role in the overall deterioration of materials.**
- **The carbon compounds in the alteration patinas on building materials have different origins:  $\text{CaCO}_3$  from the underlying materials, deposition of atmospheric particles containing elemental and organic, primary and secondary compounds.**

# Sampling

- The black crust, is black in colour due to the presence of carbonaceous particles, and is mainly comprised of gypsum resulting from the transformation of the calcium carbonate that constitutes the substratum and the products of atmospheric deposition.

Samples of black crust (Figure) were collected at the height of 55 m at the Zagreb Cathedral (south bell tower).



# Methodology

- **The total organic carbon (TOC) and water soluble organic carbon (WSOC) concentration were determined by using a high temperature catalytic oxidation (HTCO) technique. A TOC- 5000 system with high sensitive Pt catalyst and nondispersive infrared (NDIR) detector for CO<sub>2</sub> measurements was used.**
- **The TOC concentration was determined in powdered black crust samples.**
- **WSOC concentration was determined after filtering the solution (black crust+ MQ water) through Whatman GF/F filters.**

# Methodology

- To determine inorganic and organic sulfur species we used an Electroanalytical technique (Cathodic stripping Cyclic voltammetry)
- The electrochemical measurements were done using a  $\mu$ Autolab connected with a 663 VA Stand Metrohm mercury electrode used as the working electrode, connected with hanging mercury drop electrode (HMDE) as the working electrode. The reference electrode was an Ag/AgCl (1M KCl) electrode, and the graphite or platinum electrode served as auxiliary electrodes.





# Results

Sample No.	TOC	WSOC
1	0.6	0.1
2	0.4	0.06
3	0.8	0.14

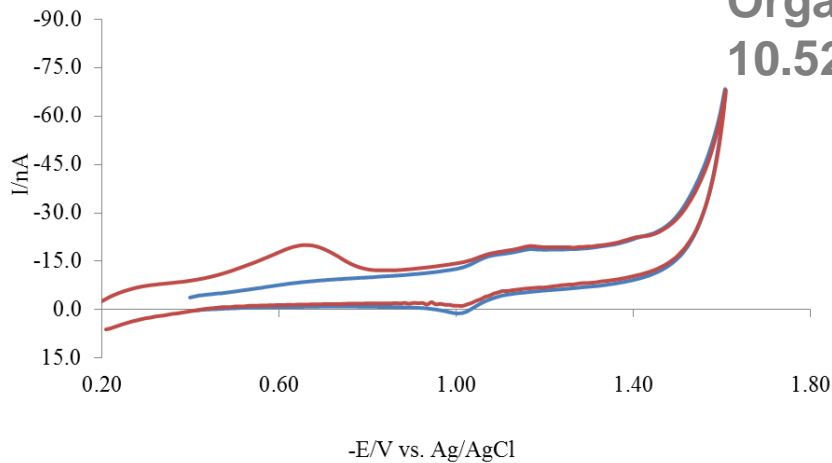
**Our data show that the content of WSOC in OC ranged from 16.5% to 21.43%**



# Results

Inorganic Sulfur:  
137 nM- 211 nM

Organic Sulfur:  
10.52 nM-51.66 nM

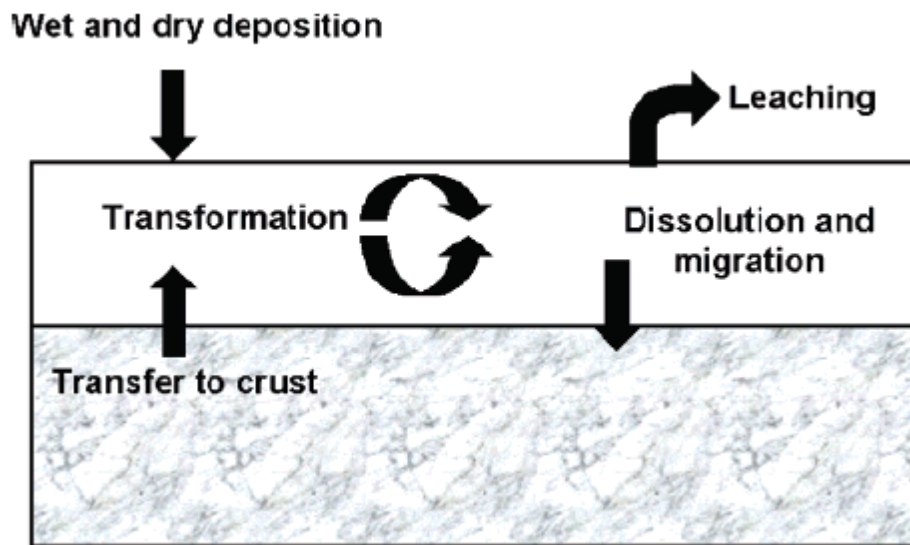


**In Figure the cyclic voltammograms obtained for different deposition potentials are present.**

**The peak which appears at around -0.6 V is a measure for presence of reduced sulfur species that deposit HgS layer at the Hg surface. Deposition at -0.2 V usually reveals HgS reduction peak from some organic and inorganic sulfur species while decrease of the same peak after the deposition at -0.4 V, indicate prevalence of organic sulfur compounds (Krznařić, Ciglencečki, Ćosović, Anal Chim Acta 431(2001) 269).**

# Future investigation

- For better understanding of formation of black crust we have intention to further investigate the WSOC fraction. WSOC fraction plays an important role in formation of black crust.



- The figure illustrates the types of fluxes and transformations of atmospheric materials on the stone surface.
- This conceptual model involves deposition and accumulation, and the formation of damage products due to material-atmosphere interaction.
- Once formed WSOC can undergo dissolution and leaching, or migrate to the underlying substrate.

# Future investigation

- **Our intention in further investigation of black crust is to characterized WSOC compounds with specific electroanalytical methods:**
- **Complexation capacity of copper ions**
- **Methods based on characterization of surface activity of different group of compounds adsorbable on the Hg electrode.**

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# CONCLUSIONS

- **Measurement of TOC is of fundamental importance for the evaluation of the atmospheric deposition contribution and establishing the pollutant sources responsible for the formation of the damage layers.**
- **In evaluating the importance of TOC and WSOC concentration, it must be remembered that the characteristics and properties of the particles are such that their effect is considerable even in the case of very low concentration**
- **The findings demonstrate that damage layers are a record of the environmental changes occurring over time, with their chemical composition reflecting that of the atmospheric combustion.**

THANK YOU FOR YOUR ATTENTION





## Acknowledgements

**This work is supported by the projects "The Sulphur and Carbon Dynamics in the Sea and Fresh-Water Environment" (IP-11-2013-1205 SPHERE) from the **Croatian Science Foundation** and the COST Action TD1105.**