

## ANNUAL REPORT ON GEOTRACES ACTIVITIES IN CROATIA

April 1st, 2019 to March 31st, 2020

### *New GEOTRACES or GEOTRACES relevant scientific results*

The Croatian GEOTRACES activities were mainly related to: 1) application of improved electrochemical methods (in combination with ICPMS) for trace metals speciation and determination (mostly Zn, Cd, Pb, Cu, Fe, Ni, Co and its interaction with organic matter and sulfur species) in natural waters, including monitoring of the coastal and open waters of the Adriatic Sea; 2) mercury speciation and determination by CV- AAS in natural waters, including monitoring of the coastal and open waters of the Adriatic Sea; 3) development of new methods for ex- and in-situ determination of natural and anthropogenic radionuclides in the seawater (focus is on  $^{89,90}\text{Sr}$  and  $^{210}\text{Pb}$ ); 4) update work on the automated system for voltammetric determination of trace metals in natural waters (e.g. seawater) named "Voltammetric AutoAnalyser (VoltAA)"; 5) development of electroanalytical method for determination and characterization of polysulfides in anoxic seawater conditions; 6) characterization of atmospheric precipitation (rain, aerosols - PM<sub>2.5</sub>) regarding presence of major cations and anions, organic matter, sulfur species and trace metals; 7) measurements of activity concentration of  $^7\text{Be}$  and  $^{210}\text{Pb}$  in atmospheric precipitation (rain, aerosols - PM<sub>2.5</sub>) in order to monitor dynamics of particle transport, meteorological information, origin of air mass transfer and seasonal variation of aerosol deposition; 8) geochemical research in different environmental systems; 9) study of trace elements as indicators of environmental changes in marine lakes; 10) work on software for treatment and analysis of UV-Vis spectra (ASFit - UV/Vis CDOM spectra analysis) and fluorescence; 11) work on update of New "butterfly"-type water samplers (4.5 L and 12 L) - rope or rosette mounting.

### *New projects and/or funding*

Current projects supported by the Croatian Ministry of Science, Education and Sport and Croatian Science Foundation (CSF)

- 2015-2019 CSF projekt: „New methodological approach to biogeochemical studies of trace metal speciation in coastal aquatic ecosystems“ (MEBTRACE) (PI: D. Omanovic)
- 2018-2020: MedPAN project: NaTEF – Nautical Tourism Ecological Footprint in MPAs (PI: Dario Omanović)
- 2018-2020: Chinese/Croatian project: The speciation of trace metals in seawater at phase boundaries - implementation of advanced methodologies (PI: Dario Omanović)
- 2019-2022: MARine lake (Rogoznica) as a model for EcoSystem functioning in a changing environment (PI. I. Ciglencečki-Jušić)
- 2018-2022: Geochemistry and Records of Redox Indicators in Different Environmental Conditions: Towards a better understanding of redox conditions in the past (PI: E. Bura-Nakić)
- 2020-2024, CSF project: Marine (micro)plastic litter and pollutant metals interaction: a possible pathway from marine environment to human (METALPATH) (PI Vlado Cuculić)

### ***Other activities conducted***

- ***Voltammetric AutoAnalyser – VoltAA*** an automated system for determination of trace metals in natural waters

An automated system for voltammetric determination of trace metals in natural waters (e.g. seawater) named "Voltammetric AutoAnalyser (VoltAA)", was updated. It integrates a new home-made autosampler (84 positions) with two built-in heavy-duty peristaltic pumps for dosing and dispensing of the sample in the cell. One or more automatic burette systems (e.g. CAVRO, Tecan) for sample pre-treatment and addition of stock solutions during analysis were used (Fig 1.). The automated system allows classical determination of trace metal concentrations by standard addition method or complexometric titrations for the determination of trace metal speciation (e.g. Fe, Cu).



*Figure 1. Voltammetric system for automatic determination of trace metals in natural waters*

The presented system is assembled to work with the Metrohm-AUTOLAB systems, however it could work with any other instruments/programs. Anodic stripping (ASV) and adsorptive cathodic stripping (AdCSV) voltammetry (or potentiometry) are basically used as voltammetric techniques, however other methods could be easily combined. The supporting software for automation (VoltAA) integrates creation of the measurement project procedure, manual control of autosampler, automatic data treatment and calculation of unknown trace metal concentrations. Addition of standard stock solution during analysis by standard addition method is automatically calculated based on the peaks intensities in the sample and predefined sensitivity for each analyte. A low blanks is achieved by using FEP tubes and peristaltic tube with low extractable metals (e.g. Tygoprene XL-60).

The system thoroughly tested on thousands of samples of natural waters.

[\(https://sites.google.com/site/daromasoft/home/voltaa;](https://sites.google.com/site/daromasoft/home/voltaa;)

<https://sites.google.com/site/daromasoft/home/autosample;>

[omanovic@irb.hr](mailto:omanovic@irb.hr))

- ***ASFit - UV/Vis CDOM spectra analysis*** program for treatment and analysis of UV-Vis spectra

ASFit is currently adapted to load few file types:

1. Perkin Elmer binary or ASCII file (\*.sp or \*.asc)
2. Jasco binary or ASCII file (\*.jws or \*.txt)
3. Specord Jena binary file (\*.dat)

4. Shimadzu file (\*.spc)
5. HORIBA Aqualog spectra (\*.opj)
6. Simple two (XY) columns ASCII file (\*.txt; \*.csv)

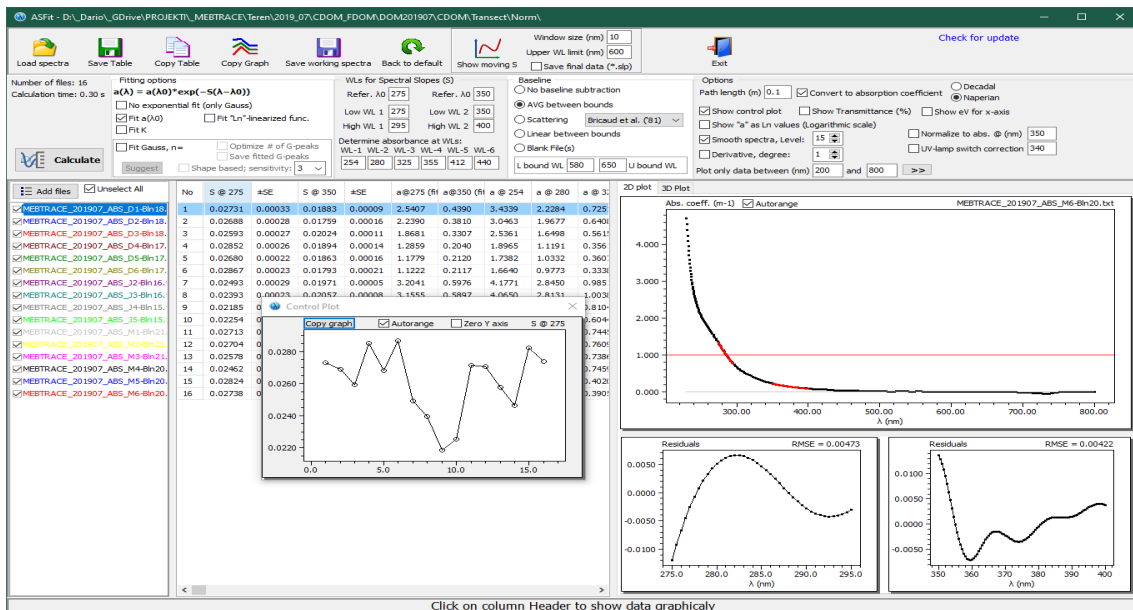


Figure 1. Screenshots of ASFit showing Spectral Slope (SS) calculation.

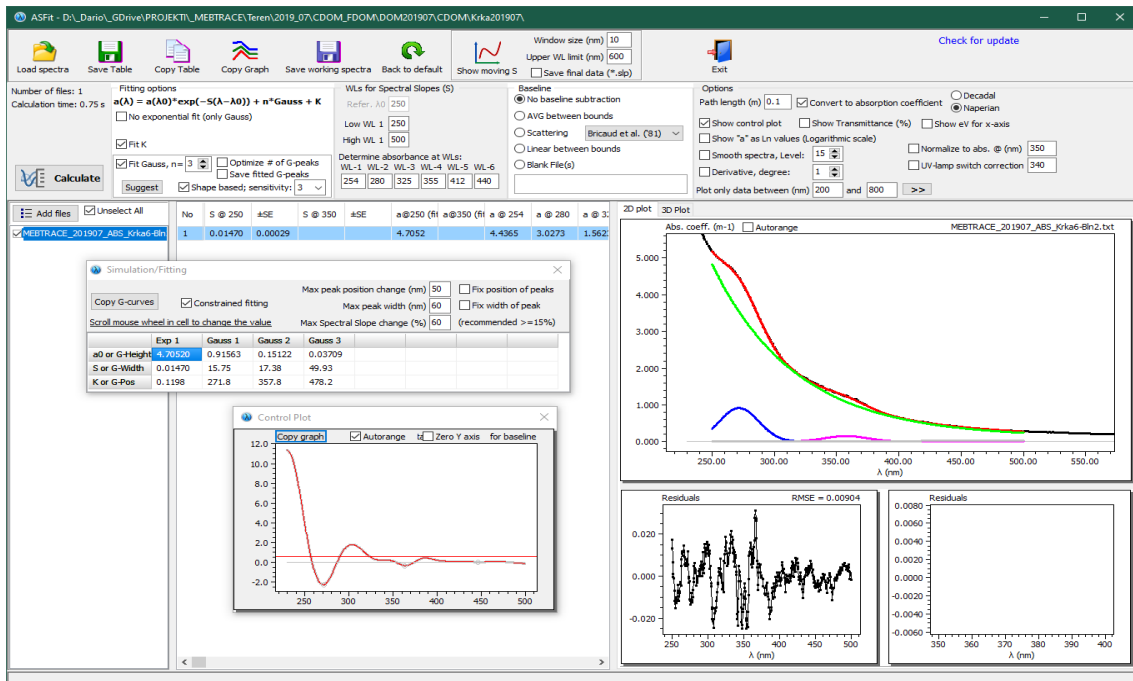


Figure 2. Screenshots of ASFit showing Gaussian decomposition of spectra.

(<https://sites.google.com/site/daromasoft/home/asfit>; [omanovic@irb.hr](mailto:omanovic@irb.hr);) )

- **TreatEEM - EEM analysis** program for treatment and analysis of fluorescence EEMs

TreatEEM is currently adapted to load few file types: 1) Aqualog (\*.opj and \*.dat);  
2) Custom \*.txt and \*.csv files

(<https://sites.google.com/site/daromasoft/home/treateem>; [omanovic@irb.hr](mailto:omanovic@irb.hr);) )

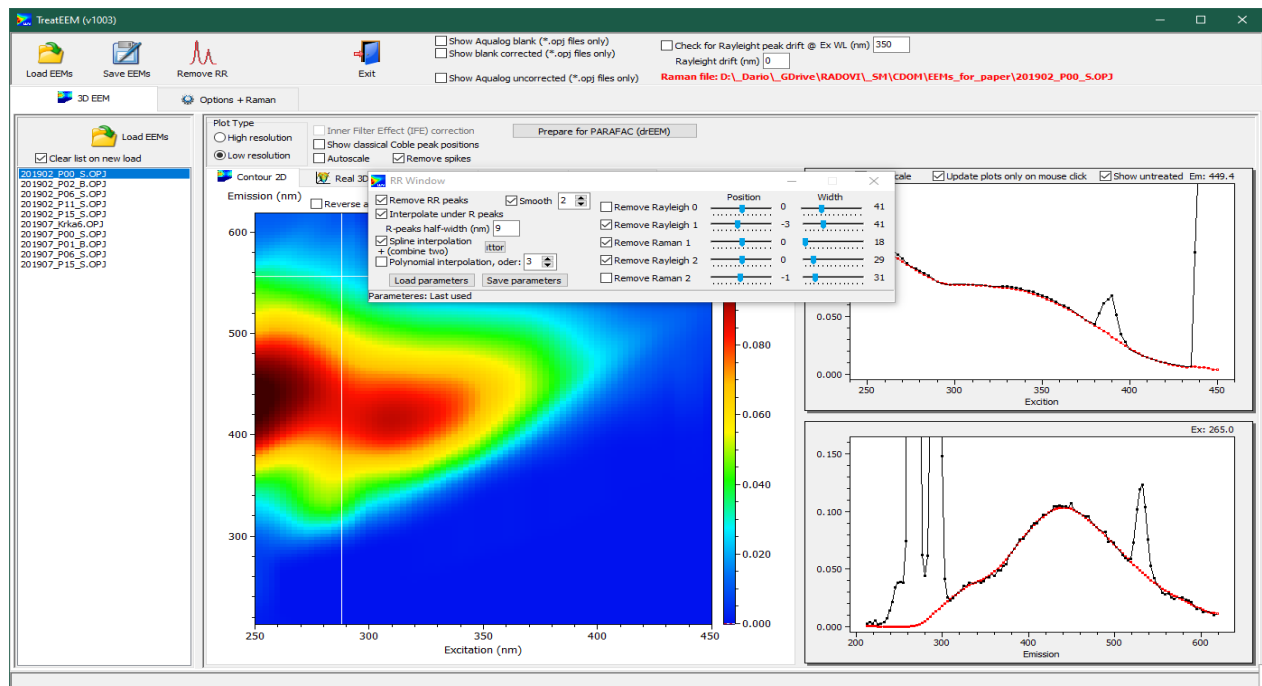


Figure 1. Screenshots of TreatEEM showing scatter peaks removal.

- **"Butterfly" Water Sampler** New "butterfly"-type water samplers (4.5 L and 12 L) - rope or rosette mounting

Closing clamps mechanism: high grade Titanium (Grade 2 or Grade 5); end-caps holders: HDPE; closing caps: HDPE + silicone seal; sampling tube: acrylic (PMMA) or polycarbonate (PC) - easy volume adaptable; silicone gaskets (no Pt); spigot: PVC or HDPE/POM-C ("Delrin"); external side closing mechanism connections: stainless steel (A4) + synthetic string + corrosion resistant springs; external screws: stainless steel (A4); external hand/rosette grips: PVC or POM-C ("Delrin"); sampler fixing mechanism on the winch rope: stainless steel (A4); easy handling - rotating knob opening mechanism - no closing cap touching (12 L)



Figure 1. Upper row: 4.5 L sampler, bottom row: 12 L sampler  
<https://sites.google.com/site/daromasoft/home/sampler>; [omanovic@irb.hr](mailto:omanovic@irb.hr)

***New GEOTRACES or GEOTRACES-relevant publications (published or in press)***

- J. Pađan, S. Marcinek, A-M. Cindrić, N. Layglon, V. Lenoble, P. Salaün, C. Garnier, D. Omanović, Improved voltammetric methodology for chromium redox speciation in estuarine waters. *Analytica Chimica Acta*, 1089 (2019) 40-47.
- D. Omanović, C. Santinelli, S. Marcinek, M. Gonnelli. ASFit - An all-inclusive tool for analysis of UV–Vis spectra of colored dissolved organic matter (CDOM), *Computers & Geosciences* 133 (2019) 104334

- Cvitešić Kušan, S. Frka, I. Ciglonečki, Electrochemical Evidence of non-Volatile Reduced Sulfur Species in Water-Soluble Fraction of Fine Marine Aerosols . Atmosphere, 10 (2019), 11; 674, 14 doi:10.3390/atmos10110674
- M. Čanković, J. Žučko, I. Dupčić Radić, I. Janeković, I. Sviličić Petrić, I. Ciglonečki, G. Collins. Microbial diversity and long-term geochemical trends in the euxinic zone of a marine, meromictic lake. Systematic and applied microbiology, 42 (2019), 126016, 13 doi:10.1016/j.syapm.2019.126016
- A.-M. Cindrić, S. Marcinek; C. Garnier, P. Salaun, N. Cukrov, B. Oursel, V. Lenoble, D. Omanović. Evaluation of Diffusive Gradients in Thin films (DGT) technique for speciation of trace metals in estuarine waters - a multimethodological approach, Science of the Total Environment, 721 (2020) 137784.
- J. Pađan, S. Marcinek, A.-M. Cindrić, N. Layglon, C. Garnier, P. Salaun, A. Cobelo-García, D. Omanović, Determination of sub-pico-molar levels of platinum in the pristine Krka River estuary (Croatia) using improved voltammetric methodology. Environmental Chemistry, 17 (2020) 77-84.
- E. Bura-Nakić, I. Sondi, N. Mikac, B. Andersen Morten. Investigating the molybdenum and uranium redox proxies in a modern shallow anoxic carbonate rich marine sediment setting of the Malo Jezero (Mljet Lakes, Adriatic Sea). Chemical Geology, 533 (2020), 119441, 43 doi:10.1016/j.chemgeo.2019.119441
- Cvitešić Kušan, A. Kroflič, I. Grgić, I. Ciglonečki, S. Frka, Chemical characterization of fine aerosols in respect to water-soluble ions at the eastern Middle Adriatic coast. Environmental science and pollution research, 27 (2020), 10249-10264 doi:10.1007/s11356-020-07617-7
- N. Cukrov, Nuša, N. Doumandji, C. Garnier, I. Tucaković, D.H. Dang, D. Omanović, N. Cukrov, Anthropogenic mercury contamination in sediments of Krka River estuary (Croatia). Environmental science and pollution research, 27 (2020), 7628-7638 , doi:10.1007/s11356-019-07475-y

### ***GEOTRACES presentations in international conferences***

- N. Mikac, N. Bačić, M. Lučić, I. Sondi, Distribution of some less studied trace elements (Ga, Ge, Nb, Te, Tl, W) and some rare earth elements (La, Y) in sediment cores from unpolluted marine and freshwater lakes in Croatia, COST ACTION TD 1407, Final meeting: Technology Critical Elements – Sources Chemistry and Toxicology, Zagreb, 2-3 April 2019. poster.
- Coha, I. Smičiklas, M. Marijana, I. Tucaković, M. Ivković, Ž. Grahek, Novel approach for strontium preconcentration from seawater RANC - 2nd International Conference on Radioanalytical and Nuclear Chemistry, 5th-10th May 2019, Budapest, Hungary (oral presentation).
- Chapoulie, S. Marcinek, D. Omanović, Application of Cu(II) ion-selective electrode (Cu-ISE) for Cu speciation in coastal waters, 9th ISE Satellite Student Regional Symposium on Electrochemistry, Zagreb, 14.06.2019. (oral presentation)
- S. Marcinek, N. Layglon, J. Pađan, A. M. Cindrić, C. Santinelli, M. Gonnelli, C. Garnier, S. Mounier and D. Omanović, Colored dissolved organic matter (CDOM) dynamics in the pristine Krka river estuary (Croatia), XV International Estuarine Biogeochemistry Symposium, Vigo, Spain, 4-5.6.2019 (oral presentation) (p.18)

- S. Marcinek, A-M. Cindrić, J. Pađan, C. Garnier, D. Omanović, Copper speciation in natural waters by CLE-AdCSV - a methodological uncertainties, GOLDSCHMIDT 2019, Barcelona, Spain, 18-23.8.2019. (oral/poster presentation)
- A-M. Cindrić, N. Cukrov, B. Oursel, G. Durrieu, C. Garnier, I. Pižeta, D. Omanović, Evaluation of Diffusive Gradients in Thin films technique for short-term and long-term assessment of trace metals at potentially polluted costal sites, 6th conference on Diffusive Gradients in Thin Films 2019, Vienna, Austria, 18.-20.9.2019. (p. 39)
- S. Marcinek, Trace metal speciation and dissolved organic matter characterization in the Krka River estuary (Croatia) using spectroscopic and spectroscopic methods, GEOTRACES summer school 2019, Cadiz, Spain, 23.-28.09.2019. (oral presentation)
- S. Marcinek, A-M. Cindrić, C. Garnier, J. Pađan, D. Omanović, Copper speciation in the Krka River estuary (Croatia), 42nd CIESM Congress, Cascais, Portugal, 7.-11.10.2019. (poster/oral presentation)
- J. Dautović, I. Ciglenečki, V. Vojvodić, N. Tepić, B. Čosović, Long-term investigations of organic matter in the northern Adriatic Sea as an indication of global changes, Rapp. Comm. int. Mer Médit., 42, 2019. (42nd CIESM Congress, Cascais, Portugal, 7.-11.10.2019. (poster/oral presentation)
- Ž. Kwokal, N. Cukrov, I. Radić Rossi, V. Cuculić, Mercury from the wreckage of a sunken ancient merchantman (Gnalić, Biograd na Moru, Croatia): a long-term danger to the marine life. (42nd CIESM Congress, Cascais, Portugal, 7.-11.10.2019. (poster/oral presentation)
- Ž. Kwokal, V. Cuculić, N. Cukrov, I. Radić Rossi, Sediment at the sinking site of the ancient ship (Gnalić, Biograd na Moru, Croatia) as a centuries-old mercury source in the marine environment. Sediment as a dynamic natural resource: from catchment to open sea, Dubrovnik 2019.
- V. Cuculić, N. Cukrov, I. Radić Rossi, Ž. Kwokal, Post medieval cargo - contemporary problem source of mercury in pristine seawater environment (Gnalić, Biograd na Moru, Croatia). EGU General Assembly 2020, Vienna, doi:10.5194/egusphere-egu2020-9204.

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