

## ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SLOVENIA

May 1<sup>st</sup>, 2017 to April 30<sup>th</sup>, 2018

### ***New scientific results***

- Most of research was oriented to study Hg and its species cycling. An overview of the previous research on Hg abundance, distribution and speciation in environmental compartments in the Adriatic Sea revealed that Hg concentrations in seawater decreased during past decades due to the closure of industries that released Hg to the coastal environments. A decreasing gradient in Hg concentrations from the northern to the southern Adriatic indicates that the presence of legacy mercury still contributes to Hg in seawater. Concentrations of Hg in plankton and mussels follow the spatial and temporal trends observed in water, however, concentrations in fish do not follow these trends indicating the complexity of MMHg formation and accumulation in fish. In order to better understand the interaction between Hg species and the abundance and composition of microbial community in the central Adriatic Sea, more precisely in the transect from Hg contaminated coastal environment in Kaštela Bay to the Island of Vis, monthly sampling was performed over two years period in collaboration with the Institute of Oceanography and Fisheries in Split and the research vessel Bios Dva. Mercury analysis included total mercury (THg), dissolved gaseous mercury (DGM), and total methylated mercury (MeHg). Microbial structure analysis included high and low nucleic acid bacteria, nanoflagellates, picoeukaryotes, Prochlorococcus, and Synechococcus. Physico-chemical properties of seawater were also measured. The results revealed that Hg methylation in seawater is a metabolism-dependent transformation promoted by the heterotrophic activity of low nucleic acid bacteria under the absence of probable phosphorus limitation. Under these conditions, MeHg was also related to nutrients and Prochlorococcus, whose decay promotes heterotrophic activity. DGM was related with heterotrophic bacteria, autotrophic picoplankton and chlorophyll a, indicating biotic DGM production that is not metabolically dependent. MMHg biomagnification from microseston to mesozooplankton was observed through the significant increase of corresponding bioaccumulation factors. Results revealed that Hg uptake by plankton might be enhanced under phosphorous-limitation conditions.
- In an effort to study seasonal Hg transformation mechanisms and underlying processes in the coastal marine ecosystem of the Gulf of Trieste (northern Adriatic Sea), we have successfully applied the <sup>197</sup>Hg radiotracer technique in series of incubation experiments. This area is characterized by continuous Hg input from the Soča/Isonzo River as a consequence of nearly 500 years of activity at the Idrija Mine (W Slovenia). During our study, Hg methylation in the marine water column could not be detected, suggesting that sediments are the principal methylation site and the source of MeHg to the water column. Conversely, the water column showed a pronounced Hg reduction potential, mostly of photochemical origin, suggesting that the Gulf of Trieste is a source of Hg<sup>0</sup> to the atmosphere. However, the high Hg reduction potential observed in autumn was most likely related to a phytoplankton (diatom) autumn bloom, indicated by high Chl concentrations measured during that period. We hypothesize that the microbial reduction was either linked to the expression of *mer* genes or, a consequence of non-specific redox reactions. Variations in bacterioplankton community fingerprints (as determined by Denaturing Gradient Gel Electrophoresis) suggested that community structure had little influence on microbial Hg reduction potential.
- In an effort to understand the atmospheric cycling and seasonal depositional characteristics of Hg, wet deposition samples were collected for approximately 5 years at 17 selected GMOS monitoring sites located in the Northern and Southern hemispheres in the framework of the

Global Mercury Observation System (GMOS) project. These data set provides a new insight into baseline concentrations of THg concentrations in precipitation worldwide, particularly in regions such as the Southern Hemisphere and tropical areas where wet deposition as well as atmospheric Hg species were not investigated before, opening the way for future and additional simultaneous measurements across the GMOS network as well as new findings in future modeling studies.

- A Bayesian Network (BN) approach that integrates relevant biological and physical-chemical variables across spatial (two water layers) and temporal scales to identify the main contributing microbial mechanisms regulating POC accumulation in the northern Adriatic Sea was developed. Three scenario tests (diatom, nanoflagellate and dinoflagellate blooms) using the BN predicted diatom blooms to produce high chlorophyll a at the water surface while nanoflagellate blooms were predicted to occur also at lower depths (>5 m) in the water column and to produce lower chlorophyll concentrations. A sensitivity analysis using all available data identified the variables with the greatest influence on POC accumulation being the enzymes, which highlights the importance of microbial community interactions. However, the incorporation of experimental and field data changed the sensitivity of the model nodes  $\geq 25\%$  in the BN and therefore, is an important consideration when combining manipulated data sets in data limited conditions.
- We aimed at directly demonstrating the sulfur-oxidizing, chemoautotrophic nature of the symbionts and at investigating putative carbon transfer from the symbiont to the ciliate host. We performed pulse-chase incubations with  $^{14}\text{C}$ - and  $^{13}\text{C}$ -labeled bicarbonate under varying environmental conditions. A combination of tissue autoradiography and nanoscale secondary ion mass spectrometry coupled with transmission electron microscopy was used to follow the fate of the radioactive and stable isotopes of carbon, respectively. We show that symbiont cells fix substantial amounts of inorganic carbon in the presence of sulfide, but also (to a lesser degree) in the absence of sulfide by utilizing internally stored sulfur. Isotope labeling patterns point to translocation of organic carbon to the host through both release of these compounds and digestion of symbiont cells. The latter mechanism is also supported by ultracytochemical detection of acid phosphatase in lysosomes and in food vacuoles of ciliate cells. Fluorescence in situ hybridization of freshly collected ciliates revealed that the vast majority of ingested microbial cells were ectosymbionts.

### ***New publications (published or in press)***

- BAJT, Oliver. Aliphatic hydrocarbons in surface sediments of the Gulf of Trieste (northern Adriatic) - sources and spatial and temporal distributions. *Journal of soils and sediments: protection, risk assessment and remediation*, ISSN 1439-0108, 2017, vol. 17, iss. 7, 1948-1960, ilustr. <http://link.springer.com/article/10.1007/s11368-016-1642-8>, doi: [10.1007/s11368-016-1642-8](https://doi.org/10.1007/s11368-016-1642-8).
- BRATKIČ, Arne, TINTA, Tinkara, KORON, Neža, RIBEIRO GUEVARA, Sergio, BEGU, Ermira, BARKAY, Tamar, HORVAT, Milena, FALNOGA, Ingrid, FAGANELI, Jadran. Mercury transformations in a coastal water column (Gulf of Trieste, northern Adriatic Sea). *Marine Chemistry*, ISSN 0304-4203. 2018, vol. , no. , 36 str., [in press], doi: [10.1016/j.marchem.2018.01.001](https://doi.org/10.1016/j.marchem.2018.01.001)
- BRATKIČ, Arne, KORON, Neža, RIBEIRO GUEVARA, Sergio, FAGANELI, Jadran, HORVAT, Milena. Seasonal variation of mercury methylation potential in pristine coastal marine sediment from the Gulf of Trieste (Northern Adriatic Sea). *Geomicrobiology journal*, ISSN 0149-0451, 2017, vol. 34, no. 7, 587-595.

- FAGANELI, Jadran, FALNOGA, Ingrid, HORVAT, Milena, KLUN, Katja, LIPEJ, Lovrenc, MAZEJ, Darja. Selenium and mercury interactions in apex predators from the Gulf of Trieste (Northern Adriatic Sea). *Nutrients*, ISSN 2072-6643, 2018, vol. 10, no. 3, str. 278-1-278-11, doi: [10.3390/nu10030278](https://doi.org/10.3390/nu10030278).
- GIAMMANCO, Salvatore, KRAJNC, Bor, KOTNIK, Jože, OGRINC, Nives. Temporal analysis of  $\delta^{13}\text{C}$ CO<sub>2</sub> and CO<sub>2</sub> efflux in soil gas emissions at Mt. Etna. *Annals of geophysics*, ISSN 2037-416X, 2017, vol. 60, no. 6, str. S0663-1-S0663-13, doi: [10.4401/ag-7305](https://doi.org/10.4401/ag-7305).
- KODAMATANI, Hitoshi, BALOGH, Steven J., NOLLET, Yabing H., MATSUYAMA, Akito, FAJON, Vesna, HORVAT, Milena, TOMIYASU, Takashi. An inter-laboratory comparison of different analytical methods for the determination of monomethylmercury in various soil and sediment samples: a platform for method improvement. *Chemosphere*, ISSN 0045-6535. [Print ed.], 2017, vol. 169, str. 32-39, doi: [10.1016/j.chemosphere.2016.10.129](https://doi.org/10.1016/j.chemosphere.2016.10.129).
- KOTNIK, Jože, HORVAT, Milena, BEGU, Ermira, SHLYAPNIKOV, Yaroslav, SPROVIERI, Francesca, PIRRONE, Nicola. Dissolved gaseous mercury (DGM) in the Mediterranean Sea: spatial and temporal trends. *Marine Chemistry*, ISSN 0304-4203. [Print ed.], 2017, vol. 193, str. 8-19, doi: [10.1016/j.marchem.2017.03.002](https://doi.org/10.1016/j.marchem.2017.03.002).
- MCDONALD, Karlie S., TURK, Valentina, MOZETIČ, Patricija, TINTA, Tinkara, MALFATTI, Francesca, HANNAH, David M., KRAUSE, Stefan. Integrated network models for predicting ecological thresholds: Microbial e carbon interactions in coastal marine systems. *Environmental Modelling & Software*, ISSN 1364-8152. [Print ed.], 2017, vol. 91, str. 156-167, ilustr. <https://authors.elsevier.com/a/1UZyr4sKhE9jiq>, doi: [10.1016/j.envsoft.2017.01.017](https://doi.org/10.1016/j.envsoft.2017.01.017).
- MOZETIČ, Patricija, CANGINI, Monica, FRANCÉ, Janja, BASTIANINI, Mauro, BERNARDI AUBRY, Fabrizio, BUŽANČIĆ, Mia, CABRINI, Marina, CERINO, Federica, KRAUS, Romina, MARIĆ PFANNKUCHEN, Daniela, ROTTER, Ana, et al. Phytoplankton diversity in Adriatic ports: Lessons from the port baseline survey for the management of harmful algal species. *Marine pollution bulletin*, ISSN 0025-326X, 2017, str. [v tisku]. doi: [10.1016/j.marpolbul.2017.12.029](https://doi.org/10.1016/j.marpolbul.2017.12.029).
- NERENTORP MASTROMONACO, Michelle G., GÅRDFELDT, Katarina, ASSMANN, Karen M., LANGER, Sarka, DULALI, Talasi, SHLYAPNIKOV, Yaroslav, ŽIVKOVIĆ, Igor, HORVAT, Milena. Speciation of mercury in the waters of the Weddell, Amundsen and Ross Seas (Southern Ocean). *Marine Chemistry*, ISSN 0304-4203. [Print ed.], [in press] 2017, 37 str., doi: [10.1016/j.marchem.2017.03.001](https://doi.org/10.1016/j.marchem.2017.03.001).
- PETRANICH, Elisa, COVELLI, Stefano, ACQUAVITA, Alessandro, FAGANELI, Jadran, HORVAT, Milena, CONTIN, Marco. Evaluation of mercury biogeochemical cycling at the sediment-water interface in anthropogenically modified lagoon environments. *Journal of Environmental Sciences(China)*, ISSN 1001-0742, [in press] 2017, 19 str., doi: [10.1016/j.jes.2017.11.014](https://doi.org/10.1016/j.jes.2017.11.014).
- SPROVIERI, Francesca, HORVAT, Milena, KOTNIK, Jože, et al. Five-year records of mercury wet deposition flux at GMOS sites in the Northern and Southern hemispheres. *Atmospheric chemistry and physics*, ISSN 1680-7316, 2017, vol. 17, no. 4, str. 2689-2708, doi: [10.5194/acp-17-2689-2017](https://doi.org/10.5194/acp-17-2689-2017).
- VOLLAND, Jean-Marie, SCHINTLMEISTER, Arno, ZAMBALOS, Helena, REIPERT, Siegfried, MOZETIČ, Patricija, ESPADA-HINOJOSA, Salvador, TURK, Valentina, WAGNER, Michael, BRIGHT,

Monika. NanoSIMS and tissue autoradiography reveal symbiont carbon fixation and organic carbon transfer to giant ciliate host. *The ISME journal*, ISSN 1751-7362, 2018, vol. , iss. , 14 str., [in press], doi: [10.1038/s41396-018-0069-1](https://doi.org/10.1038/s41396-018-0069-1).

- ŽIVKOVIĆ, Igor, FAJON, Vesna, TULASI, Delali, OBU, Kristina, HORVAT, Milena. Optimization and measurement uncertainty estimation of hydride generation-cryogenic trapping-gas chromatography-cold vapor atomic fluorescence spectrometry for the determination of methylmercury in seawater. *Marine Chemistry*, ISSN 0304-4203. [Print ed.], 2017, vol. 193, str. 3-7, doi: [10.1016/j.marchem.2017.03.003](https://doi.org/10.1016/j.marchem.2017.03.003).
- ŽIVKOVIĆ, Igor, FAJON, Vesna, KOTNIK, Jože, SHLYAPNIKOV, Yaroslav, OBU, Kristina, BEGU, Ermira, HORVAT, Milena, et al. Relations between mercury fractions and microbial community components in seawater under the presence and absence of probable phosphorus limitation conditions. *Journal of Environmental Sciences(China)*, ISSN 1001-0742, [in press] 2018, 18 str., doi: [10.1016/j.jes.2018.03.012](https://doi.org/10.1016/j.jes.2018.03.012).
- ŽIVKOVIĆ, Igor, KOTNIK, Jože, ŠOLIĆ, Mladen, HORVAT, Milena. The abundance, distribution and speciation of mercury in waters and sediments of the Adriatic Sea : a review = Zastupljenost, raspodjela i specijacija žive u vodama i sedimentima Jadranskog mora: pregled. *Acta Adriatica*, ISSN 0001-5113, 2017, vol. 58, no. 1, str. 165-186.
- ŽIVKOVIĆ, Igor, ŠOLIĆ, Mladen, KOTNIK, Jože, ŽIŽEK, Suzana, HORVAT, Milena. The abundance and speciation of mercury in the Adriatic plankton, bivalves and fish : a review = Zastupljenost i specijacija žive u jadranskom planktonu, školjkašima i ribi: pregled. *Acta Adriatica*, ISSN 0001-5113, 2017, vol. 58, no. 3, str. 391-420.

#### **Organization and editing of Special issues related to marine science**

- HORVAT, Milena, KNOERY, Joel, GÅRDFELDT, Katarina, SPROVIERI, Francesca. Introduction to the special issue in the marine Environment: editorial. *Marine Chemistry*, ISSN 0304-4203. [Print ed.], 2017, vol. 193, str. 1-2, doi: [10.1016/j.marchem.2017.05.005](https://doi.org/10.1016/j.marchem.2017.05.005).
- FAGANELI, Jadran, OGRINC, Nives. Introduction to the Special issue on the 22nd International Symposium on Environmental Biogeochemistry Sponsored by the International Society for Environmental Biogeochemistry (ISEB. *Geomicrobiology journal*, ISSN 0149-0451, vol. 34, no. 7, str. 577-578, doi: [10.1080/01490451.2017.1328944](https://doi.org/10.1080/01490451.2017.1328944).
- OGRINC, Nives, FAGANELI, Jadran. Preface. *Journal of soils and sediments: protection, risk assessment and remediation*, ISSN 1439-0108, 2017, vol. 17, no. 7, str. 1831-1833, doi: [10.1007/s11368-017-1677-5](https://doi.org/10.1007/s11368-017-1677-5).

#### **Invited presentations at Universities**

- OGRINC, Nives. Carbon cycling and its isotopes in the environment: invited talk, Hokaido University, 17. November 2017, Sapporo, Japan.
- OGRINC, Nives. Carbon cycling and its isotopes in the environment: invited talk, Università di Parma, Dipartimento di Scienze Matematiche, Fisiche e Informatiche, 27 marzo, 2018, Parma.

- OGRINC, Nives. Carbonate system in different aquatic sediments: stable isotope approach : invited talk, Università di Parma, Dipartimento di Scienze Matematiche, Fisiche e Informatiche, 26 marzo, 2018, Parma.

### ***New projects and/or funding***

- In May 2017 new national project entitled (2017-2020): Stable isotopes in the study of the impact of increasing CO<sub>2</sub> levels on C and Hg cycling in coastal waters was approved. The project coordinating by JSI deals with the use of stable isotopes to better understand the origin and processes of C and Hg in relation to increasing levels of atmospheric CO<sub>2</sub> in the coastal marine ecosystem.
- Two new projects in the EU framework EURAMET/EMPIR were approved (2017-2020): SIRS -Metrology for Stable Isotope Reference Standards started in June 2017 dealing with the development of new reference material of CO<sub>2</sub> and N<sub>2</sub>O for stable isotope measurements in air and MercOx - Metrology for oxidised mercury, which is coordinated by JSI started in October 2017. MercOx is dealing with the use of new analytical approaches including stable isotopes of Hg to study transport, fate and sources of Hg in the environment and also in marine systems.
- ERA Planet programme (EU H2020; 2017-2021), where JSI participates in two sub-projects (STRAND 1 SMURBS – Smart Urban Solutions for air quality, disasters and city growth; STRAND 3 – IGosp - Integrated Global Observing Systems for Persistent Pollutants), both started in September 2017. IGosp is also related to marine environment since it is dealing with Integrating remote and in-situ observations of persistent pollutant concentrations with ancillary data regarding meteorology and the composition of the atmosphere.
- TC interregional project INT7019 “Supporting a Global Ocean Acidification Observing Network towards Increased Involvement of Developing States”, where Slovenia is taking an active part is still going on. The objective of this project is to build ocean acidification observing capacity and connect countries and regions with an interest in ocean acidification to identify the most sensitive areas and inform policy measures at domestic and inter-regional level.
- European Carbon Dioxide Capture and Storage Laboratory Infrastructure (ECCSEL) project entitled: “Stable isotopes as a tool for monitoring the influence of CO<sub>2</sub> emissions on marine microalgae”. The main objective of the project is to investigate the possibility of the use of stable carbon isotopes as effective early warning tracers of CO<sub>2</sub> migration in engineered CO<sub>2</sub> storage sites. The proposed approach was used for tracing the origin, migration and fate of natural CO<sub>2</sub> in the real-world situations at a site where natural CO<sub>2</sub> is leaking from the sea floor, such as at the Natural Laboratory of Panarea.

### ***PhD theses***

- ŽIVKOVIĆ Igor. Seasonal changes in mercury speciation and the composition of the microbial community in the seawater in the central Adriatic Sea, doctoral dissertation. The PhD was successfully defended on April 25, 2018.

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