ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SLOVENIA

April 1st, 2019 to March 31st, 2020

New scientific results

This year most of the research was oriented into the study of carbon and Hg cycles in marine ecosystems.

- The research performed on carbon cycling was related to two important questions: (i) are Mediterranean and Adriatic Seas exposed to acidification; (ii) is the Gulf of Trieste and Mediterranean Sea the source or the sink of CO_2. Although the marginal seas represent only 7% of the total ocean area, the CO_2 fluxes are intensive and important for the carbon budget, exposing them to an intense process of anthropogenic ocean acidification (OA). A decline in pH, especially in the estuarine waters, also results from eutrophication-induced acidification. The Adriatic Sea is currently a CO_2 sink with an annual flux of approximately -1.2 to -3 mol C m^{-2} yr^{-1}, which is twice as low compared to the net sink rates in the NW Mediterranean (-4 to -5 mol C m^{-2} yr^{-1}). The computed Revelle factor for the Adriatic Sea (about 10) indicates that the buffer capacity is rather high and that the waters should not be particularly exposed to acidification. Total alkalinity (TA) in the Adriatic (2.6-2.7 mM) is in the upper range of TA measured in the Mediterranean Sea. This is primarily because of riverine inputs that transport carbonates dissolved from the Alpine dolomites and karstic watersheds. The Adriatic Sea is the second sub-basin (319 Gmol yr^{-1}), following the Aegean Sea (which receives the TA contribution from the Black Sea), that contribute to the riverine TA discharges into the Mediterranean Sea. Saturation state indicate that the waters of the Adriatic are supersaturated with respect to calcite (ΩCa) and aragonite (ΩAr) throughout the year. However, saturation states are considerably lower in the bottom water layers, due to the prevalence of benthic remineralization processes in the stratification period. Significant effects on calcifying organisms and phytoplankton are expected, while the effects on microbially-driven processes are not known yet.

The influence of the riverine dissolved inorganic carbon (DIC) input was estimated. The northern Adriatic is a shallow continental shelf region strongly impacted by rivers discharges, which currently receives about 21% of total freshwater input in the Mediterranean Sea. The effects of river nutrients on the trophic state of this coastal marine ecosystem has been largely analysed, but the river transport of DIC is still not constrained, to date. Land-borne DIC contributes to the increase of the total alkalinity of the coastal waters, buffering the acidification due to the absorption of CO_2 from the atmosphere. The estimates of DIC river loads were obtained applying THINCARB software to a compilation of total alkalinity and pH data provided by Research Institutes and Regional Environmental Protection Agencies for the main rivers flowing into the northern Adriatic Sea (Po, Adige, Brenta, Piave, Livenza, Tagliamento and Isonzo), in 2010-2018.

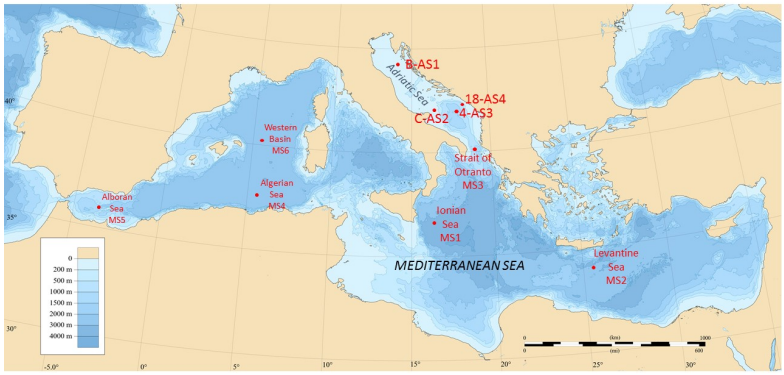
The overall river transport of DIC was 213 G mol yr^{-1}, of which around 70% originates from the Po River. About 97% of the DIC in river water is present in the form of bicarbonate. The mean $\delta^{13}C_{DIC}$ was estimated to be -10‰ that is considered today as representative of the DIC riverine inputs in oceanic carbon cycle modelling. Its flux mainly depends by mineral weathering in each river drainage basin, but this process does not exclude the presence of anthropogenic disturbances that should be better analysed.

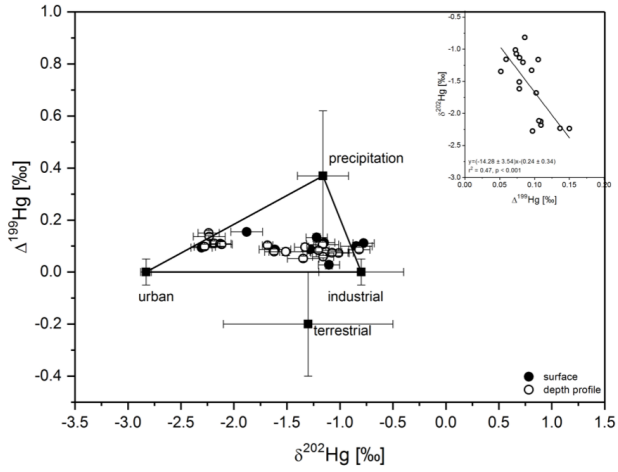
- The research on Hg was performed in deep-sea waters of Mediterranean Sea in the lower food web and lagoon environment.

The Mediterranean Region has a long lasting legacy of mercury mining activities and a high density of sub-marine volcanoes that has strongly contributed to its mercury budget. In the last forty years, field investigations that quantify mercury concentrations in marine biota have

led to a large amount of experimental data scattered in many peer-reviewed publications making it difficult for modelling applications and regional environmental assessments. The paper published in *Scientific data* reviews existing peer-reviewed literature and datasets on mercury concentration in marine flora and fauna (Animal, Plants and Chromista Kingdoms) in the Mediterranean basin. A total of 24,465 records have been retrieved from 539 sources and included in Mercury in Mediterranean Biota (M2B). Well-defined specimens account for 24,407 observations, while a few records include generic plankton and unidentified fish species. Among all considered species, we selected *Diplodus sargus*, *Sardina pilchardus*, *Thunnus thynnus* and *Xiphias gladius* to show trends of mercury concentration against WHO and EU limits. Few notes on how M2B is intended to support the implementation of the Minamata Convention on Mercury by a user-driven Knowledge Hub are finally reported.

Two research studies involved stable isotope composition of Hg to identify the fate and processes of Hg in marine sediments. The study conducted in the Mediterranean deep-sea sediments In the Mediterranean deep-sea sediments surface and down-core δ^{202}Hg values varied between -2.30 and +0.78‰, and showed consistently positive values for mass independent fractionation of odd Hg isotopes (with average values of Δ^{199}Hg = +0.10 ± 0.04‰ and Δ^{201}Hg = +0.04 ± 0.02‰) and near-zero Δ^{200}Hg values, indicating either multiple Hg sources or a combination of different Hg isotope fractionation processes occurring either before or after sediment deposition. Both mass-dependent and mass-independent fractionation processes influence the isotopic composition of Hg in the Mediterranean Sea. Positive Δ^{199}Hg values are likely the result of enhanced Hg^{2+} photoreduction in the Mediterranean water column before incorporation of Hg into the sediments, while mass-dependent fractionation decreases δ^{202}Hg values due to kinetic isotope fractionation during deposition and mobilization. An isotope-mixing model based on mass-dependent and mass-independent fractionation (δ^{202}Hg and Δ^{199}Hg) suggests at least three primary Hg sources of atmospheric deposition in the surface sediments: urban, industrial and global precipitation-derived. Overall, the results suggest that atmospheric Hg deposition to Mediterranean surface sediments is dominated by gaseous elemental mercury (58 ± 11%) rather than wet deposition.





The relationships between δ^{202}Hg and Δ^{199}Hg in Mediterranean and Adriatic sediments and endmembers used for the triple-mixing model. Error bars on samples in the main panel indicate one standard deviation of the analytical uncertainty. The inset of panel shows the relationships between δ^{202}Hg and Δ^{199}Hg values in core deep-sea Mediterranean sediments.

The second study was conducted in the Canadian Arctic Archipelago (CAA). Total mercury (THg) and monomethylmercury (MMHg) concentrations as well as mercury (Hg) isotope ratios were determined in sediment cores. At most sites, THg concentrations showed a decreasing trend with depth, ranging from 5 to 61 ng/g, implicating possible increased Hg deposition and/or riverine inputs in top sediment layers. MMHg values showed large oscillations within the top 10 cm of the cores. This variability decreased at the bottom of the cores with MMHg concentrations ranging from less than12 to up to 1073 pg/g. Average concentrations of THg and MMHg in the top 10 cm were linearly correlated, whereas no correlation was observed with organic matter (loss on ignition). Mercury isotope ratios showed negative values for both δ^{202}Hg (−1.59 to −0.55‰) and Δ^{199}Hg (−0.62 to −0.01‰). δ^{202}Hg values became more negative with depth, while the opposite was observed for Δ^{199}Hg. The former is consistent with predicted historical atmospheric Hg trends as a result of increased coal burning worldwide. Hg isotope ratio measurements in CAA sediments offer additional opportunities to trace Hg processes and sources in the Arctic.

New publications (published or in press)

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Presentations at conferences

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About the European COST Project "Ocean Governance for Sustainability"

For several years now, the European Union has been increasingly interested in questions on sustainable ocean management. Above all, an impression of great conceptual fragmentation and missing connections of local, regional, national and global approaches becomes apparent. The aim of the four-year European COST project "Ocean Governance for Sustainability" is to address problems of current legislations and regulations in a transdisciplinary way in order to adapt existing strategies in research and policy. The integrative approach which brings together natural, social and human sciences, as well as, international know-how is a specific feature of the COST projects funded by the European Union.

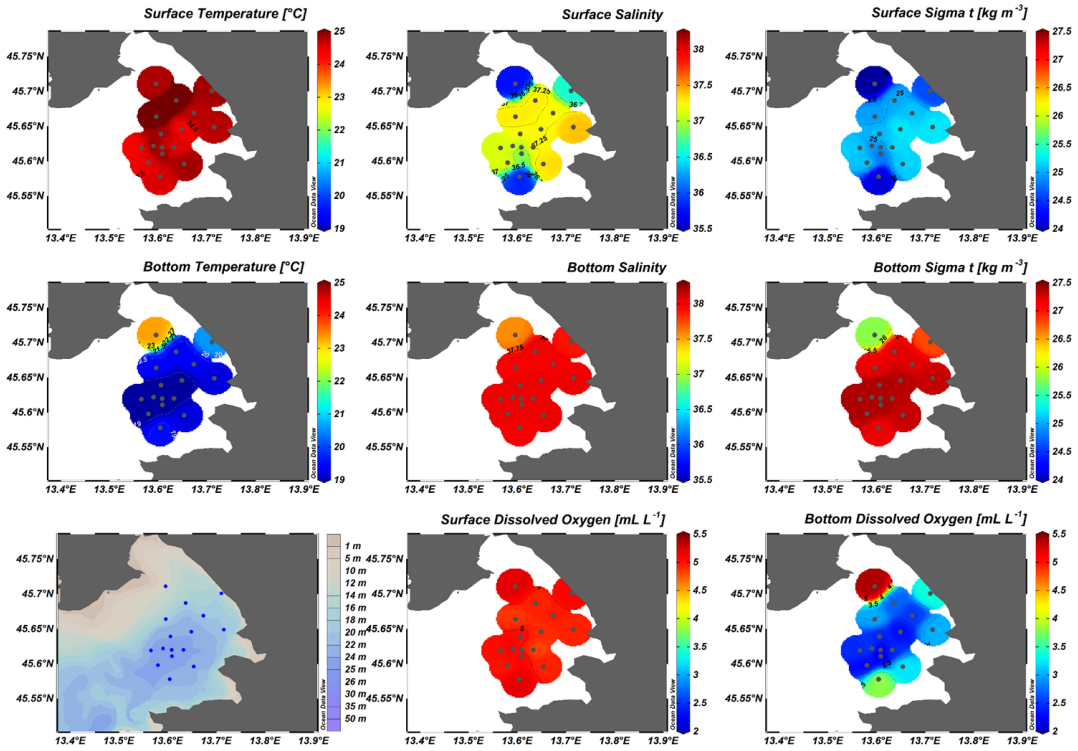
The 4th International Conference of Ocean Governance for Sustainability in Piran was organised by the National Institute of Biology, EMUNI, and Grant Holder Institution Leibniz Centre for Tropical Marine Research in cooperation with the European network funding programme "Cooperation of Science and Technology" (COST). The conference took place November 25-27 2019 and was attended by 55 participants from 29 countries.

Official scientific programme comprising workshops and meetings of five working groups of the COST Action OceanGov, with a focus on jointly working on the publications with regard to five of the six core themes of this European network: Land-Sea Interaction, Area-Based Management, Seabed Resource Management, Ocean, Climate Change and Acidification, as well as, Fisheries Management. Participating researchers presented their latest results in these fields, while preparing for the final cut of their joint peer chapters to be published within the remaining months of the Action.

New projects and/or funding

- In July 2019 new national project entitled (2019-2022): *STRAP - Sources, TRAnsport and fate of persistent air Pollutants in the environment of Slovenia* was approved. The project coordinating by JSI deals with the use of stable isotopes to better understand the origin, transport and processes of C and Hg in the atmosphere including the coastal marine ecosystem.
- Department of Environmental Sciences at Jožef Stefan Institute (JSI-O2) is involved in the National Key Research & Development Program of China "*Mechanisms of red tides and hypoxia as ecological marine disasters and technologies for its early warning and emergency*

security along the sea of 'Belt and Road' countries" (2016YFE0202100). The project coordinated by IHB-CAS has started in September, 2017 and will end in July, 2020. According to the implementation plan, a part of the work was conducted in Adriatic Sea in the Gulf of Trieste. JSI-O2 is responsible for collecting and analyzing the phytoplankton and chemical analysis at two sites in the Gulf of Trieste (station F and CZ) four times a year from 2018 to 2020. The proposed dates of sampling are: September (III week) 2018, March (II week), June (II week), September (III week) and November (II week) 2019. The first report was prepared in May 2019, while the final report will be prepared in July 2020.



Surface and bottom spatial distribution of temperature, salinity, density and dissolved oxygen.

The sampling was also conducted at the Taiwan Strait at May 29-31 2019 in China. First results indicated that most of the values for total alkalinity (TA) and $\delta^{13}C_{DIC}$ are typical for marine environments, while the most negative value indicate higher degradation of organic matter (OM). It is interesting to note that higher TA are not related to lower $\delta^{13}C_{DIC}$ values indicating that there is no influence of riverine input, but rather degradation of OM. The data on POM show that higher $\delta^{13}C$ values ranging from -20.6‰ to -18.7‰ are accompanied with higher $\delta^{15}N$ values 6.5‰ and 7.1‰ indicating the contribution of marine OM from algae, while lower $\delta^{13}C$ and $\delta^{15}N$ values are typical for terrestrial input ($\delta^{13}C$ around -26‰ and $\delta^{15}N$ around 3‰). Porewater data indicate rapid degradation of OM with depth: lower $\delta^{13}C_{DIC}$ values and higher alkalinity. Further evaluation of results is in progress.

Submitted by Nives Ogrinc (nives.ogrinc@ijs.si)