

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SLOVENIA

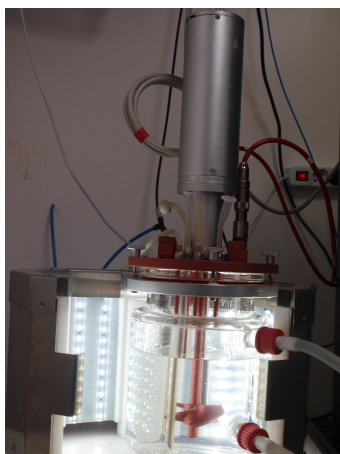
May 1st, 2016 to April 30th, 2017

New scientific results

- The research performed on mercury cycling in the marine ecosystems was related to the optimization of the method for direct determination of MeHg in seawater with the detection limit in the range of 3.94–15.9 fM. The hydride generation volatilization coupled with cryogenic trapping, separation by gas chromatography and detection by cold vapor atomic fluorescence spectrometer after pyrolysis was used. Method performance was compared with the reference ethylation method and results from a previous study. Sample repeatability represents the biggest single contribution to the expanded standard uncertainty in hydride generation, together with recovery in ethylation method.
- Further dissolved gaseous mercury (DGM) was studied in surface and deep waters of the Mediterranean Sea over the last 15 years during several oceanographic cruises on board the Italian research vessels *Urania* and *Minerva Uno*, covering the Western and Eastern Mediterranean Basins as well as Adriatic Sea as its northernmost part. DGM represents a considerable portion of THg (on average 20%) in Mediterranean waters. DGM was the highest in the northern Adriatic, the most polluted part of the Mediterranean Sea as a consequence of Hg mining in Idrija and heavy industry in northern Italy, and near the Gulf of Lion. Generally, average DGM concentration was higher in the West and East Mediterranean Deep Waters (WMDW and EMDW) and Levantine Intermediate Water (LIW) than in overlaying Modified Atlantic Water (MAW); however, it was the highest in N Adriatic Surface waters (NAdSW) and consequently in outflowing Adriatic Deep Waters (AdDW). In deep water profiles the portion of DGM typically increased at depths with oxygen minimum and then towards the bottom, especially in areas with strong tectonic activity (Alboran Sea, Strait of Sicily, Tyrrhenian Sea), indicating its bacterial and/or geotectonic origin.
- Despite the distance from large anthropogenic emission sources, toxic mercury is transported via the atmosphere and oceans to the Southern Ocean. Seawater samples were collected at selected stations and were analysed for total mercury (HgT) (8 stations), dissolved gaseous mercury (DGM) (62 stations) and methylmercury (12 stations) during winter (Weddell Sea), spring (Weddell Sea) and summer (Amundsen and Ross Seas) in the Southern Ocean. The HgT distribution in water columns was found to not vary significantly with depth. In the Weddell Sea the average column concentration was higher in spring (2.6 ± 1.3 pM, 2 stations) than in winter (2.0 ± 1.0 pM, 6 stations). We hypothesize that the seasonal HgT increase is due to atmospheric deposition of particulate Hg(II) formed during atmospheric mercury depletion events (AMDEs), as well as the addition of inorganic mercury species from melting sea ice and snow. Furthermore, HgT concentrations found in this study were significantly higher than previously measured in the Southern Ocean, which was hypothesized to be due to seasonal variations in atmospheric deposition. The average water column DGM concentration in the Weddell Sea was 454 ± 254 fM in winter and 384 ± 239 fM in spring. The lowest average DGM concentration was found in summer in the Amundsen and Ross Seas (299 ± 137 fM). The highest observed concentration in winter was hypothesized to be caused by the larger sea ice coverage, which is known to reduce the evasion of Hg(0) from the sea surface. The average monomethylmercury (MMHg) concentration in the Weddell Sea was 60 ± 30 fM in winter (6 stations) and 95 ± 85 fM in spring (2 stations), showing no significant seasonal difference. In the Amundsen and Ross Seas the summer average concentration of MeHg

(MMHg and dimethylmercury; DMHg) was 135 ± 189 fM (4 stations). The highest MeHg concentration was found in modified circumpolar deep water, which is known to have high primary production.

- The changes of acetylcholinesterase activity (AChE), metallothioneins content (MTs), catalase activity (CAT) and lipid peroxidation (LPO) were assessed after 4 days exposure of mussels *Mytilus galloprovincialis* to a wide range of sublethal concentrations of chlorpyrifos (CHP, 0.03–100 µg/L), benzo(a)pyrene (B(a)P, 0.01–100 µg/L), cadmium (Cd, 0.2–200 µg/L) and copper (Cu, 0.2–100 µg/L). The activity of AChE in the gills decreased after exposure to CHP and Cu, whereas no change of activity was detected after exposure to B(a)P and Cd. Both induction and decrease of MTs content in digestive gland occurred after exposure to CHP and B(a)P, while a marked increase was evident at highest exposure concentrations of Cd. The content of MTs progressively decreased of MTs with increasing concentration of Cu. CAT activity and LPO in the gills did not change after exposure to any of the chemicals. The results demonstrate different response profile in relation to the type of chemical compound, and highlight the potential implications for evaluation of biological effect of contaminants in marine environment.
- This proof of concept study presents 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. 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 (>5m) in the water column and to produce lower chlorophyll a 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 25% in the BN and therefore, is an important consideration when combining manipulated data sets in data limited conditions. Bayesian Network (BN) is used to predict microbial mechanisms that regulate particulate organic carbon (POC) accumulation. BN predicts POC accumulation by linking biotic factors with environmental conditions using field and experimental data. Enzymatic activity was identified by BN as to have the greatest influence on POC accumulation.
- The total activity of ^{210}Po was determined by alpha-spectrometry in various samples (matrices) collected in the Gulf of Trieste (northern Adriatic Sea) where fresh water inflows, especially from the Isonzo River in the northern part, affect water quality. In seawater and tributaries, up to 80% (mean 49%) of total ^{210}Po was found in particulate form. In sediments, slightly higher levels were encountered in the Isonzo prodelta and in the central (depocenter) part of the gulf. Lower autumn ^{210}Po levels can be a consequence of biological dilution by higher mesozooplankton biomass in the autumn compared to spring. Obtained data show higher ^{210}Po levels in all matrices analyzed in the Gulf of Trieste compared to other Adriatic (central Adriatic) and western Mediterranean areas. The $^{210}\text{Po}/^{210}\text{Pb}$ ratios in water, plankton and sediments were mostly below or around 1, while this ratio was much higher at higher trophic levels (up to about 50), reflecting a preferential bioaccumulation of ^{210}Po over ^{210}Pb . Comparison of the relative importance of pelagic and benthic bioaccumulation pathways, excluding the filter feeder bivalves, suggests greater accumulation in pelagic-feeding species.



- The use of stable isotopes in carbon and CO₂ has also an applied value in other field of research for example, for detecting CO₂ leakage from proposed subsea carbon capture and storage (CCS) sites, i.e. usually depleted gas and oil reservoirs or saline formations, which lie below the seabed. CCS is regarded as one of the most important long-term measures for reducing carbon globally. In collaboration with the Institute Nazionale di Oceanografia e Geofisica Sperimentale – OGS Trieste, Italy a mesocosmos experiment was performed in order to decode how different sources (natural, anthropogenic) of CO₂ influence biological systems (phytoplankton) using stable carbon isotopes. The results indicate that differences exist on phytoplankton $\delta^{13}\text{C}_{\text{POC}}$

between natural and perturbed experiment, therefore $\delta^{13}\text{C}_{\text{POC}}$ analysis could be a valid tool for measuring CO₂ leakage impacts. Further it was found that algal metabolism does not change in presence of anthropogenic CO₂ source because discrimination values tend to be similar once the system reaches stability.

New publications (published or in press)

- 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. [in press] 2017, 10 str., doi: 10.1016/j.marchem.2017.03.003
- 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. [in press] 2017, 12 str., doi: 0304-4420.
- 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. [in press] 2017, 37 str., doi: 10.1016/j.marchem.2017.03.001
- Perić, Lorena, Nerlović, Vedrana, Žurga, Paula, Žilić, Luka, Ramšak, Andreja. Variations of biomarkers response in mussels *Mytilus galloprovincialis* to low, moderate and high concentrations of organic chemicals and metals. *Chemosphere*, ISSN 0045-6535. 2017, vol. 174, str. 554-562, ilustr. doi: 10.1016/j.chemosphere.2017.01.138.
- 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. 2017, vol. 91, str. 156-167, ilustr. doi: 10.1016/j.envsoft.2017.01.017.
- Bratkič, Arne, Vahčić, Mitja, Kotnik, Jože, Obu, Kristina, Begu, Ermira, Woodward, E. Malcolm S., Horvat, Milena. Mercury presence and speciation in the South Atlantic Ocean along the 40°S transect. *Global biogeochemical cycles*, ISSN 1944-9224, 2016, vol. 30, iss. 2, str. 105-119, doi: 10.1002/2015GB005275.

- Begu, Ermira, Shlyapnikov, Yaroslav, Stergaršek, Andrej, Frkal, Peter, Kotnik, Jože, Horvat, Milena. A method for semi-continuous measurement of dissolved elemental mercury in industrial and natural waters. *International journal of environmental analytical chemistry*, ISSN 0306-7319, 2016, vol. 96, no. 7, str. 609-626, doi: 10.1080/03067319.2016.1180379.
- Tsangaris, Catherine, Moschino, Vanessa, Strogyloudi, Evangelia, Coatu, Valentina, Ramšak, Andreja, Abu Alhaija, Rana, Carvalho, Susana, Feline, Serena, Kosyan, Alisa, Lazarou, Yiota, Hatzianestis, Ioannis, Oros, Andra, Tiganus, Daniela. Biochemical biomarker responses to pollution in selected sentinel organisms across the Eastern Mediterranean and Black Sea. *Environmental science and pollution research international*, ISSN 0944-1344. 2016, vol. 23, št. 2, str. 1789-1804, doi: 10.1007/s11356-015-5410-x.
- Faganeli, Jadran, Falnoga, Ingrid, Benedik, Ljudmila, Jeran, Zvonka, Klun, Katja. Accumulation of ²¹⁰Po in coastal waters (Gulf of Trieste, northern Adriatic Sea). *Journal of Environmental Radioactivity*, ISSN 0265-931X. 2016, str. 1-7, doi: 10.1016/j.jenvrad.2016.07.018.
- Hines, Mark E., Covelli, Stefano, Faganeli, Jadran, Horvat, Milena. Controls on microbial mercury transformations in contaminated sediments downstream of the Idrija mercury mine (West Slovenia) to the Gulf of Trieste (northern Adriatic). *Journal of soils and sediments*, ISSN 1439-0108, 2016, doi: 10.1007/s11368-016-1616-x.
- Estrada, Marta, Delgado, Maximino, Blasco, Dolores, Latasa, Mikel, Cabello, Ana Maria, Benitez-Barrios, Verónica, Fraile-Nuez, Eugenio, Mozetič, Patricija, Vidal, Monteserrat. Phytoplankton across Tropical and Subtropical Regions of the Atlantic, Indian and Pacific oceans. *PloS one*, ISSN 1932-6203, 2016, e0151699, iss. 31-29. doi: 10.1371/journal.pone.0151699.

New projects and/or funding

- In November the IAEA BoG approved, the TC interregional project INT7019 “Supporting a Global Ocean Acidification Observing Network towards Increased Involvement of Developing States”, where Slovenia is taking an active part. 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: “*The application of stable isotopes to monitor CO₂ at offshore CCS sites*”. The main objective of the project is to evaluate whether carbon isotope ratios can be used to identify the origin of the CO₂ (from CCS leakage or from natural processes).

PhD theses

- BEGU, Ermira. *Determination of dissolved elemental mercury in surface and industrial waters: doctoral dissertation*, Ljubljana: [E. Begu], 2016. XXIII, 109 pp.

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