

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN SLOVENIA

June 1st, 2015 to April 30th, 2016

New scientific results

To better understand the presence and abundance of Hg species in the remote ocean regions, waters of South Atlantic Ocean along 40°S parallel were investigated during UK-GEOTRACES cruise GA10. Total mercury (THg), methylated mercury (MeHg), and dissolved gaseous mercury (DGM) concentrations were determined. The concentrations were very low in the range of pg/L (femtomolar). All Hg species had higher concentration in western than in eastern basin. THg did not appear to be a useful geotracer. Elevated methylated Hg species were commonly associated with low-oxygen water masses and occasionally with peaks of chlorophyll a, both involved with carbon (re)cycling. The overall highest MeHg concentrations were observed in the mixed layer (500 m) and in the vicinity of the Gough Island. Conversely, DGM concentrations showed distinct layering and differed between the water masses in a nutrient-like manner. DGM was lowest at surface, indicating degassing to the atmosphere, and was highest in the Upper Circumpolar Deep Water, where the oxygen concentration was lowest. DGM increased also in Antarctic Bottom Water. At one station, dimethylmercury was determined and showed increase in region with lowest oxygen saturation. Altogether, our data indicate that the South Atlantic Ocean could be a source of Hg to the atmosphere and that its biogeochemical transformations depend primarily upon carbon cycling and are thereby additionally prone to global ocean change.

For the first time, Hg isotope composition of seawater in the Canadian Arctic Archipelago is reported. Hg was pre-concentrated from large volumes of seawater sampling using anion exchange resins onboard the research vessel immediately after collection. Elution of Hg was performed in laboratory followed by isotope composition determination by multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS). For comparison, seawater from two stations was shipped to the laboratory and processed within it. Results showed negative mass-dependent fractionation in the range from -2.85 to -1.10‰ for $\delta^{202}\text{Hg}$, as well as slightly positive mass-independent fractionation of odd Hg isotopes. Positive mass-independent fractionation of ^{200}Hg was also observed. Samples that were pre-concentrated in the laboratory showed different Hg isotope signatures and this is most probably due to the abiotic reduction of Hg in the dark by organic matter during storage and shipment after sampling. This emphasizes the need for immediate onboard pre-concentration.

We examine the large-scale distribution patterns of the nano- and microphytoplankton collected from 145 oceanic stations, at 3 m depth, the 20% light level and the depth of the subsurface chlorophyll maximum, during the Malaspina-2010 Expedition (December 2010-July 2011), which covered 15 biogeographical provinces across the Atlantic, Indian and Pacific oceans, between 35°N and 40°S. In general, the water column was stratified, the surface layers were nutrient-poor and the nano- and microplankton (hereafter phytoplankton, for simplicity, although it included also heterotrophic protists) community was dominated by dinoflagellates, other flagellates and coccolithophores, while the contribution of diatoms was only important in zones with shallow nutriclines such as the equatorial upwelling regions. The main trends of variability identified consisted of: 1) A contrast between the community composition of the upper and the lower parts of the euphotic zone, expressed respectively by positive or negative scores of the first principal component, which was positively correlated with taxa such as the dinoflagellates *Oxytoxum minutum* and *Scrippsiella* spp., and the

coccolithophores *Discosphaera tubifera* and *Syracosphaera pulchra* (HOL and HET), and negatively correlated with taxa like *Ophiaster hydroideus* (coccolithophore) and several diatoms, 2) a general abundance gradient between phytoplankton-rich regions with high abundances of dinoflagellate, coccolithophore and ciliate taxa, and phytoplankton-poor regions (second principal component), 3) differences in dominant phytoplankton and ciliate taxa among the Atlantic, the Indian and the Pacific oceans (third principal component) and 4) the occurrence of a diatom-dominated assemblage (the fourth principal component assemblage), including several pennate taxa, *Planktoniella sol*, *Hemiaulus hauckii* and *Pseudo-nitzschia* spp., in the divergence regions. Our findings indicate that consistent assemblages of co-occurring phytoplankton taxa can be identified and that their distribution is best explained by a combination in different degrees of both environmental and historical influences.

The possibility of tracing routes of dense waters toward and within the ocean abyss by the use of an extended set of observed physical and biochemical parameters was explored. To this purpose, we employ mercury, isotopic oxygen, biopolymeric carbon and its constituents, together with indicators of microbial activity and bacterial diversity found in bottom waters of the Eastern Mediterranean. In this basin, which has been considered as a miniature global ocean, two competing sources of bottom water (one in the Adriatic and one in the Aegean seas) contribute to the ventilation of the local abyss. Moreover, as the near-bottom development of exogenous bacterial communities transported by convectively-generated water masses in the abyss can provide a persistent trace of episodic events, intermittent flows like those generating abyssal waters in the Eastern Mediterranean basin may become detectable beyond the availability of concomitant measurements.

Our research performed in the Gulf of Trieste confirmed that, on an annual scale, the Gulf acts as a sink of CO₂ that is strongly controlled by the seasonal variability of the water temperature, biological processes, wind speed and riverine inputs. The results also indicated that the buffer capacity of the Gulf of Trieste is relatively high, meaning that its waters are not particularly exposed to acidification processes.

Large volumes of seawater were sampled monthly from December 2011 to October 2012 in the southeastern part of the Gulf of Trieste (northern Adriatic Sea) in order to study the seasonal changes of colloidal organic matter (COM) concentrations, its origin and composition. The lipid fraction increased up to 2-fold and the polysaccharide fraction remained nearly constant while protein fraction decreased, reflected in a higher C/N (28) molar ratio. Also, higher concentrations of humics were observed in late spring – early summer probably due to local freshwater discharges in spring. An increase of lipid fraction and nearly constant polysaccharide content in late spring - early summer, in parallel with agglomeration of high molecular weight (>200 kDa) macromolecules, indicates the possible formation of macroaggregates, which has been periodically occurred in the northern Adriatic Sea in the past.

Sequential nutrient regeneration and organic matter (OM) degradation were studied in surface coastal sediments of the Gulf of Trieste (northern Adriatic Sea). Nutrient budgets at the sediment-water interface of this sandy coastal sediment showed intensive anoxic recycling of inorganic N, but low P and Si cycling in all redox phases.

Deposition of riverine suspended solids affects operations in ports located in the proximity of river mouths. The Rižana River is the main source of riverine solids in the shallow Bay of Koper (Gulf of Trieste, northern Adriatic Sea). The mean discharge increases rapidly in relation to high precipitation, typical of spring and autumn. During such events, the runoff leads to torrential river flow with high concentration of suspended solids which are

consequently deposited in the port zone. The regression model was found to be a useful tool to estimate TSS and SOM concentrations from turbidity data in rivers and the coastal sea, thus providing an evaluation of riverine TSS and SOM input and deposition into the small bay, which in turn affects local port activities. Less than 50 % of the introduced TSS settles within the second port basin during mean river flow conditions.

The potential link between the microbial dynamics and the environmental parameters was investigated in a semi-enclosed and highly dynamic coastal system (Gulf of Trieste, northern Adriatic Sea, NE Mediterranean Sea). Our comprehensive 2-year time-series study showed that despite the shallowness of this area, there was a significant difference between the surface and the bottom bacterial community structure. The bottom bacterial community was more diverse than the surface one and influenced by sediment re-suspension. The surface seawater temperature had a profound effect on bacterial productivity, while the bacterial community structure was more affected by freshwater-borne nutrients and phytoplankton blooms. Phytoplankton blooms caused an increase of Gammaproteobacteria (Alteromonadaceae, SAR86 and Vibrionaceae) and shift in dominance from SAR11 to Rhodobacteraceae taxon at the surface. Our results propose the importance of the water mass movements as drivers of freshwater-borne nutrients and of allochthonous microbial taxa. This study emphasizes the prediction power based on association networks analyses that are fed with long-term measurements of microbial and environmental parameters. These interaction maps offer valuable insights into the response of marine ecosystem to climate- and anthropogenic-driven stressors.

Between January 30th and February 4th we collected the first turbulence observations in the Gulf of Trieste under different wind forcing and water column structure. The vertical profiles of the turbulence kinetic energy dissipation rates showed that the presence near the sea floor of different water masses, inflowing from the open sea, can prevent the complete mixing of the water column. This dumping effect is enhanced when these masses present higher suspended sediment concentrations. Coupled and uncoupled circulations in the northern Adriatic are predominantly wind-driven and show no significant mesoscale differences.

Based on the stable isotope compositions of carbon and oxygen for shells and soft tissues, invasive serpulids (*Ficopomatus enigmaticus*) in the Krka estuary (Croatia) were proven to be excellent environmental indicators of salinity and sources of particulate and dissolved nutrients, and can be therefore be used as proxies for water circulation in a permanently stratified microtidal estuary.

New publications (published or in press)

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- RUBINO, Angelo, BENSI Manuel, HAINBUCHER Dagmar, ZANCHETTIN Davide, MAPELLI Francesca, OGRINC Nives, MARCHETTO Davide, BORIN Sara, CARDIN Vanessa, FAJON Vesna, HORVAT Milena, TARICCO Carla, BALDI Franco. Biogeochemical, isotopic and bacterial distributions trace oceanic abyssal circulation. *PloS ONE*, ISSN 1932-6203, 2016, vol. 11, 0145299-1-0145299-12. doi: 10.1371/journal.pone.0145299
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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.

PhD theses

- KLUN, Katja. Composition and complexation of colloidal organic matter in coastal sea (Gulf of Trieste): doctoral dissertation. University of Ljubljana: 2016. XIII f., pp. 103 (supervisor: J. Faganeli)

Meetings

- 22nd International Symposium on Environmental Biogeochemistry (ISEB) was held in Piran, September 28 – October 2, 2015 (www.iseb22.ijs.si). The ISEB has always strived to bring together scientists from a range of disciplines with interests and this Symposium “Dynamics of Biogeochemical System: Processes and Modeling” explored issues relating to biogeochemistry in various fields including soil science, microbial ecology and marine, lacustrine and atmospheric research. The sessions have been organized around ten themes which integrate the following topics:
 - 1 The marine and coastal environment
 - 2 Surface and groundwater systems
 - 3 Soils
 - 4 Climate change
 - 5 Microbial biogeochemistry
 - 6 Nanoparticles and colloids
 - 7 Isotopes in biogeochemical processes
 - 8 Biogeochemistry of pollutants
 - 9 Archeological biogeochemistry.

The program included two Special sessions GMOS and GEOTRACES (The marine and coastal environments) and GLOBAQUA (Surface and groundwater systems). In addition, the SOIL session was devoted to the International Year of Soils (IYS), the main purpose of which is to raise global awareness of the importance of soils for food security, agriculture as well as in mitigating climate change, alleviating poverty, and sustainable development. The program included six invited speakers, 52 oral and 54 poster presentations. Prof. G. Henderson (University of Oxford, Oxford, UK) was the invited speaker in the GEOTRACES session. The symposium also continues its tradition of strong international representation, with authors of accepted abstracts from 23 countries from around the world.

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