

ANNUAL REPORT ON GEOTRACES ACTIVITIES IN MEXICO
JUNE 2013 – JUNE 2014

Meetings

- Oral presentations on XXth Congreso Nacional de Ciencia y Tecnología del Mar (Los Cabos, B.C.S., October 1-4, 2013), on XXIIIth Congreso Nacional de Geoquímica (October 14-17, 2013, Cuernavaca, Morelos), on The Coastal and Estuarine Federation (CERF -2013) 22 nd biennial conference “Toward Resilient Coasts and Estuaries, Science for Sustainable Solutions (November 3-7, 2013, San Diego, California, USA), and on XXth International Conference on Marine Geology (Moscow, November 18-22, 2013). Poster on the AGU 2013 Fall meeting (December 9-13, 2013, San Francisco, CA, USA).

Cruises

- *R/V Alpha Helix* (CICESE) was used in April 2014 south-west of Ensenada (North-Eastern Pacific Ocean) to install an automatic sediment trap for next year to measure the fluxes of major and trace components of the settling particulate matter and to study vertical profiles of dissolved oxygen and other characteristics of the water column.
- A small research boat “CICIMAR-XV” was used in February 2014 to study vertical profiles of salinity, temperature, dissolved oxygen, suspended particulate matter and nutrients the La Paz Bay (south-western Gulf of California) at 28 stations aiming to know the principal features of their spatial and vertical distribution during the winter season. The surface sediments at 130 stations were collected also to know their textural and chemical composition aiming to delimit the area of the influence of the depletion of water in oxygen on the accumulation of redox-sensitive elements such as molybdenum and uranium on the sea bottom.

New funding

- There is no direct funding for GEOTRACES activities in Mexico. However, GEOTRACES related projects obtain financial support from CONACyT (Mexican Council for Science and Technology) fundamental research funds. Limited financial support for the research and educational centers at the Mexican universities, research centers like CICESE and in the National Polytechnic Institute of Mexico system is also available.
- Multidisciplinary scientific project “Composition and fluxes of sedimentary material as a reflexion of the environmental changes in the La Paz Bay, Gulf of California” was approved in March 2014 with the funding of \$1,100,000 pesos from Instituto Politécnico Nacional, code 1608 (P.I.- Dr. Evgueni Shumilin; duration: 2014-2015).
- A project for strengthening of the infrastructure “Renovation and reinforcement of the oceanographic equipment for the platform of the monitoring of the fluxes of the carbon, major and trace metals in the Mexican Northwestern Pacific” was recently approved by CONACyT (grant number CN-13-563, amount requested 5,000,000 pesos and 3,398,423.33 of them will be the contribution of CONACyT and a resting amount will be funded by Instituto Politécnico Nacional of Mexico). PI: Dr. E. Choumiline (Shumilin), Department of Oceanology, Centro Interdisciplinario de Ciencias Marinas-Instituto Politécnico Nacional, La Paz, Baja California Sur, Mexico.

Ongoing projects

a) CONACyT funding:

- “Biogeochemistry of trace metals in the southern part of the Southern California Bight: a region influenced by the California Current, upwelling and anthropogenic inputs”.

Multidisciplinary project awarded to Universidad Autónoma de Baja California, Mexico with the funding of \$2,500,000 pesos (P.I.- Dr. Francisco Delgadillo-Hinojosa; duration: 2010-2014).

- “Atmospheric fluxes of bioactive metals and their solubility in the Gulf of California: a scene towards climate change”. Multidisciplinary project awarded to Universidad Autónoma de Baja California, Mexico, with the funding of \$3,619,000 pesos (P.I. - Dr. José A. Segovia-Zavala; duration: 2012-2015).
- “High resolution geochemical reconstructions of recent climate and oxygenation history in La Paz Bay, Gulf of California” (July 2013-December 2014) UC MEXUS-CONACyT (grant number CN-13-563, amount requested 25,000 US \$). PIs: Dr. T. Lyons, Department of Earth Sciences, University California, Riverside (USA) and Dr. E. Choumilin (Shumilin), Department of Oceanology, Centro Interdisciplinario de Ciencias Marinas-Instituto Politécnico Nacional, La Paz, Baja California Sur, Mexico
- "Influence of the dinoflagellate *Lingulodinium polyedrum* (Stein) Dodge, a red tide producer, on the biogeochemistry of Cd, Pb and other trace metals (Cu, Pb, Mo) in Todos Santos Bay, Baja California" Multidisciplinary project awarded to Centro de Investigación Científica y Educación Superior de Ensenada, B.C., with funding of 2 250 000 pesos (P.I. - Dr. María Lucila del C. Lares Reyes; duration: 2011-2014).

b) Other funding from “Secretaría de Investigación y Posgrado” of the National Polytechnic Institute of Mexico (Instituto Politécnico Nacional):

- Individual scientific project 20131764 “Arsenic and other potentially toxic elements in the sediments of the La Paz Lagoon, Baja California Sur: actual levels and historical record of the natural and anthropogenic contamination”, with the funding of \$65,000 pesos from Instituto Politécnico Nacional (P.I.- Dr. E. Shumilin; duration: February 2013-January 2014) was concluded successfully in January 2014.

New results

Scientific highlights

- Biogeochemical cycles of elements in the ocean lie at the center of our understanding of the functioning of ecosystems on different scales, whether global or regional. Some major, trace elements and lanthanides are known to be useful indicators of the origin of settling particulate matter, especially in contrasting environments.

It is important to compare trace element composition of settling particulate matter (SPM) from the Alfonso Basin, southwestern Gulf of California with the elemental composition of settling particulate matter and particulate trace element fluxes of the sediment trap samples, collected in North-Eastern Pacific south-east from the Ensenada.

- Marine sediments from the coastal zone of Santa Rosalía copper mining region (Baja California Sur, Mexico) are strongly polluted with Co, Cu, Mn, U and Zn. Most of these trace metals are supplied to the marine sedimentary environment from sources related to the ore-forming mineralization in this mining district, or as the constituents of smelter slugs. Some ideas about the sources of enriched elements for the sediments can appear after the measurement of uranium isotope ratios using MC-ICPMS and range from uncovering the extent of past anoxia/euxinia registered in sedimentary rocks to tracking mineral weathering processes.

Copper mineral, smelting wastes, beach and marine sediments were analyzed for $^{238}\text{U}/^{235}\text{U}$ and $^{234}\text{U}/^{238}\text{U}$ ratios. Some of the results indicate a large variability in U isotopic composition. This suggests complex physicochemical processes that produce isotopic fractionation, mainly involving the interaction between the mineralization/industrial wastes and the marine environment, probably upon contact with

sea water. Values of $\epsilon^{235}\text{U}$ (around -20) and $\delta^{234}\text{U}$ (approx. 100 ‰) detected for the copper mineral, were not as similar to the values from most of the clearly polluted and nonpolluted samples, with the exception of two samples. One of them has a similar $\delta^{234}\text{U}$ value than the mineral mentioned above. The second one, being a marine sediment sample, displays a very negative $\delta^{234}\text{U}$ (-74‰) and peculiar $\epsilon^{235}\text{U}$ (-11.5) value.

Finally, historical data indicate that the local smelter at Santa Rosalía processed copper mineral extracted not only from the adjacent area, but also from other distant ore deposits (Sonora state, Mexico; as well as Chile). Those copper minerals might have had a distinct uranium isotopic fingerprint. This effect should not be discarded as we interpret complex systems like Santa Rosalía.

- The study of biogeochemical cycles of elements is important because they are actively involved in the functioning of coastal marine ecosystems. To determine the factors controlling the distribution of trace elements (TEs) in surface sediments of the La Paz Lagoon, their possible sources and background levels, 91 surface sediment samples were collected by free diving and a fine sediment core of 46 cm in length was extracted in the deepest portion of the lagoon. To determine total concentrations of TEs in surface sediments and in each horizon of the core, the sediments were digested with a mixture of concentrated strong acids and then the concentrations of 61 elements were measured by analytical techniques of ICP- MS and ICP- AES. The core sections were dated with the method of unsupported Pb -210 by alpha spectrometry of Po-210. The data set of total concentrations of TEs in the sediments was used to calculate the enrichment factor of the elements and the Müller's index of geo- accumulation. Total concentrations of the contaminants were also compared with the criteria for sediment quality given by Long et al. (1995) and a factor analysis was done. The results indicate the existence of natural enrichment of elements such as $\text{Se} > \text{As} > \text{Cd}$ reflecting the influence of the lithology of geological formations around the lagoon. The highest enrichments of As, Cd, P and U were found adjacent to El Mogote peninsula, which could reflect alongshore transport of phosphatic material enriched in some TEs, delivered to the Bay of La Paz by arroyos that cut the different geological formations. The Pb probably has anthropogenic origin, because its higher concentrations up to 36.8 mg kg⁻¹ were recorded near the La Paz city due to the input from petro products and local municipal effluents. The metal concentration and associations are often strongly controlled by the sulphide or organic phases which helps binds the elements together.

Sediment quality indices of the potential toxic elements give no indication of possible impairment to the biota of the lagoon by trace elements with the exception of As in 30% of the sampling stations and Cu in 20% of them.

The dated sediment core suggests a rate of sedimentation in the deepest part of the lagoon, averaging, 6.5 mm yr⁻¹ and an accumulation rate of 0.27 g cm⁻² yr⁻¹. The vertical profiles of the total concentrations of TEs in the core indicate an increase in the contribution of elements with terrigenous origin with opposite trend for the elements of biogenic origin Ba, Sr and Corg, while the contents of some elements such as Pb, Cu, Cr, among others, show the influence of sporadic events like hurricanes and/or pulses of contamination.

B.S., M.S. and Ph.D. theses related to local "GEOTRACES" problems.

- Cuauhtle-Mora D. Heavy metal levels in marine sediments and their bioaccumulation in the clam *Megapitaria squalida* in the coastal zone of the Santa Rosalía mining region, Gulf of California. M.S. Thesis, Postgraduate Program in Marine Sciences and Limnology, Universidad Nacional Autónoma de México, México, D.F. (in process).

- Salamanca-Quevedo E. (2013). Spatial distribution and temporal variability of cadmium in Bahía de Todos Santos: the region influenced by the California current and upwellings. M.S. Thesis in Coastal Oceanography. Universidad Autónoma de Baja California. Ensenada, Mexico, 89 p.
- Pérez Tribouillier H. Biogeochemistry of trace elements in the La Paz Lagoon. M.S. Thesis. Centro Interdisciplinario de Ciencias Marinas-Instituto Politécnico Nacional, La Paz, Baja California Sur, Mexico (to be concluded in June 2014).
- Reyes-Bravo M. (2014) Temporal variability of the dissolved copper in the coastal zone of the Bahía de Todos Santos, Baja California. B.S. Thesis in Oceanology. Universidad Autónoma de Baja California. Ensenada, Mexico (to be concluded in May 2014)

Publications

Journal articles

- Cervantes-Duarte R., Prego,R., López-López S., Aguirre-Bahena F. and N. Ospina-Alvarez, 2013. Annual patterns of nutrients and chlorophyll in a subtropical coastal lagoon under the upwelling influence (SW of Baja-California Peninsula). *Estuarine, Coastal and Shelf Science*, 120, 54-63.
- Galindo-Bect M.S., Santa-Ríos A., Hernández-Ayón J.M., Huerta-Díaz M.A, and F. Delgadillo-Hinojosa, 2013. The use of urban wastewater for the Colorado River delta restoration. *Procedia Environmental Sciences*, 18, 829 - 835.
- Hernández-Ayón J.M., Chapa-Balcorta C., Delgadillo-Hinojosa F., Camacho-Ibar V.F., Huerta-Díaz M.A., Santamaria-del-Ángel E., Galindo-Bect S. and J. A. Segovia-Zavala, 2013. Dynamics of dissolved inorganic carbon in the Midriff Islands region of the Gulf of California: Influence of water masses. *Ciencias Marinas*, 39, 65–83.
- Leal-Acosta M.L., Shumilin E., Mirlean N., Delgadillo-Hinojosa F. and I. Sánchez-Rodríguez, 2013. The impact of marine shallow-water hydrothermal venting on arsenic and mercury accumulation by seaweeds *Sargassum sinicola* in Concepcion Bay, Gulf of California. *Environmental Science: Processes & Impacts*, 15, 470-477.
- Leal Acosta M.L., Shumilin E. and N. Mirlean, 2013. Sediment geochemistry of marine shallow-water hydrothermal vents in Mapachitos, bahía Concepción, Baja California peninsula, Mexico. *Revista Mexicana de Ciencias Geológicas*, 30, 233-245.
- Prol-Ledesma R.M., Torres-Vera M.A., Rodolfo-Metalpa R., Ángeles C., Lechuga Deveze C.H., Villanueva-Estrada R. E., Shumilin E. and C.Robinson, 2012. High heat flow and ocean acidification at a nascent rift in the northern Gulf of California. *Nature Communications*, 4: 1388; doi: 10.1038/ncomms2390.
- Segovia-Zavala J.A., Delgadillo-Hinojosa F., Huerta-Díaz M.A., Muñoz-Barbosa A., Galindo-Bect S., Hernández-Ayón J.M. and E.V. Torres-Delgado, 2013. Concentration of dissolved iron in the oxygen minimum zone off San Esteban sill, Gulf of California. *Ciencias Marinas*, 39, 231–237.
- Shumilin E.N., Jiménez -Illescas A.R. and S. López-López, 2013. Anthropogenic contamination of metals in sediments of the Santa Rosalía harbor, Baja California Peninsula. *Bulletin of Environmental Contamination and Toxicology*, 90, 333-337.
- Shumilin E., Rodríguez Figueroa G., Sapozhnikov D. and N. Mirlean, 2013. Vertical profiles of cobalt and zinc in the marine sediments of the Santa Rosalía mining region, Gulf of California, Mexico. *J. Iberian Geology*, 39, 89-96.
- Torres-Delgado E.V., Delgadillo-Hinojosa F., Camacho-Ibar V.F., Huerta-Díaz M.A., Segovia-Zavala J.A., Hernández-Ayón J.M. and S. Galindo-Bect (2013). Wintertime enrichment of inorganic nutrients in the Ballenas Channel, Gulf of California. *Ciencias Marinas*, 39, 47–64

- Valdivieso-Ojeda J.A., MA Huerta-Díaz M.A. and F Delgadillo-Hinojosa (2014). High enrichment of molybdenum in hypersaline microbial mats of Guerrero Negro, Baja California Sur, Mexico. *Chemical Geology*, 363, 341–354
- Delgadillo-Hinojosa F., V Camacho-Ibar V., Huerta-Díaz M.A., V Torres-Delgado V., et al. Seasonal behavior of dissolved cadmium and Cd/PO₄ ratio in Todos Santos Bay: a retention site of upwelled waters in the Baja California peninsula, Mexico. Submitted to *Marine Chemistry*.

Extended abstracts:

- Pérez-Tribouiller H. y E.Choumiline, 2013. Evaluación de los niveles actuales de elementos traza en los sedimentos marinos de la Laguna de La Paz, B.C.S., México. In: XX Congreso Nacional de Ciencia y Tecnología del Mar, Los Cabos, B.C.S., 1-4 de octubre del 2013. 10 p. en CD con programa y resúmenes en extenso.
- Aksentov K.I., Astakhov A.S., Shumilin E.N., 2013. Fluxes of anthropogenic mercury in the bottom sediment of the Peter the Great Gulf of the Sea of Japan. Pp.192-195. In: *Geology of Seas and Oceans. Proceedings of XX International Conference on Marine Geology* (Moscow, November 18-22, 2013). Volume 4, GEOS, Moscow.

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