

Mexico

Meetings

- Two oral presentations and two posters were exposed by Mexican participants on the GEOTRACES Latin American Workshop (12-15 November 2012, Pontifical Catholic University of Rio de Janeiro, Brazil).
- Six oral presentations were given in international conferences such as AOGS-AGU (WPGM) Joint Assembly (13-17 August, 2012, Resorts World Convention Centre, Singapore), Primer congreso internacional de la red de medio ambiente. Instituto Politécnico Nacional (7 – 9 de noviembre del 2012. Querétaro, México), VII International Symposium on the Sea of Cortéz (Ensenada, Baja California, 8 a 12 de abril del 2013)
- Presentación oral en la XIII Reunión Anual IMECOCAL, Estudios Oceanográficos de la Corriente de California, Ensenada, BC, México, 29-30 de noviembre del 2012.
- Presentación oral en el IV Simposio Internacional del Carbono en México, Texcoco, Estado de México, 21-24 de mayo de 2013 RCD

Cruises

R/V “ El Puma” (UNAM) was used in June 2013 in the western Gulf of California, in front of Santa Rosalía copper mining region to collect surface sediments and to study vertical profiles of dissolved oxygen in water column, because the deficit of the dissolved oxygen affects the accumulation of redox-sensitive elements such as uranium the marine sediments. The samples are necessary for geochemical studies of heavy metal pollution of the marine environment occurred as a consequence of ancient mining, as well as for the assessment of the combined impact of anthropogenic sources and water column oxygen minimum zone influence on the geochemistry of redox-sensitive trace elements with special attention to uranium and lanthanides.

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 fund. Limited financial support for the research and educational centers in the National Polytechnic Institute of Mexico system is also available.

New collaborative project “High resolution geochemical reconstructions of recent climate and oxygenation history in La Paz Bay, Gulf of California” was recently approved for next 18 months by 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

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: 2010-2013).
- “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).

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

- Multidisciplinary scientific project “Geochemical and ecotoxicological evaluation of the contamination state by heavy metals of the coastal environment of Santa Rosalía mining region (Southern Baja California)”, with the funding of \$750,000 pesos from Instituto Politécnico Nacional (P.I.- Dr. Evgueni Shumilin; duration: 2011-2012) was successfully terminated in the January of 2013.
- 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).
- Individual scientific project 20130611 “Ecology of the pelagic system of the Magdalena Bay, Baja California Sur, Mexico”, with the funding of \$48,000 pesos (P.I. –Dr. R. Cervantes Duarte; duration February 2013-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 and marine sediments, especially in contrasting environments with distinctive features such as active tectonics or environmental pollution.

The objective of this study is to characterize shale-normalized lanthanide patterns as well as trace element composition of settling particulate matter (SPM) and marine sediments of the Alfonso Basin, southwestern Gulf of California.

The SPM was collected with an automated sediment trap during 2002-2010 with a periodicity of 7-15 days near the bottom of Alfonso Basin. A recent sediment core was obtained with a box corer near the trap location. The major, trace element and lanthanide contents were determined using instrumental neutron activation analysis, aided with suitable standard reference materials. The core was dated using the Pb-210 method.

The trap material composition and sediment core analyses helped establishing fluvial supply, mostly during tropical cyclones (Sc and Fe), biogenic contribution (Ca, Ba and U), aeolian effect (Sc, Fe and As) and authigenic particle formation due to suboxic conditions of the water column or associated to organic matter (U and As). The shale-normalized patterns in SPM show an alternation between light and heavy lanthanides, as well as a typical negative Eu anomaly, which becomes positive during some events. The light/heavy (normalized La/Yb ratio) in the core, representing the time span between 1850 and 2008, showed the same alternation as the settling particles. Mostly the core has a negative Eu anomaly with rare positive Eu prominent peaks. The positive Eu anomaly in both cases is presumably related to hydrothermal activity of Gulf of California tectonics. Calcium values in the sediment core show an increase tendency after the year 1950 which seem to coincide with a superficial temperature reconstruction (NOAA ERSST v3b).

- Marine sediments from the coastal zone of Santa Rosalía are characterized by high contents of heavy metals due to ancient mining and smelting of copper ores. In order to find out the present-day levels of metals and specially due to the soon opening of the new

mining and metallurgic company of “El Boleo”, 75 surficial sediment samples were collected in September 2011. The total contents of 50 elements in the sediments were measured by a combination of ICP-AES and ICP-MS instruments after concentrated strong acid digestion and heating at 250°C. “Mobile” metals in the sediments were determined after cold acid leaching. The Principal Component Analysis with Varimax rotation was applied to the obtained dataset, which allowed distinguishing three associations of elements with high positive scores (> 0.5). The association I (Ag, Ba, Be, Bi, Cd, Co, Cu, Fe, In, Li, Mg, Mn, Mo, Ni, lanthanides, Pb, Sr, Tl, U, V, Y and Zn) presumably corresponds to the input of mineralized terrigenous material of ore deposits, naturally formed at first or modified during a smelting of ore minerals afterwards. The association II (Cs, Hf, K, Rb, Re, S, Se, Th and Corg) probably reflects the contribution of fine natural clayey material, enriched in organic matter. The association III (Al and Sc) is probably due to the supply of the terrigenous aluminosilicates. The enrichment factors (EFs) of Ag, Ba, Bi, Cd, Co, Cu, Mn, Ni, Pb, Sb, U, V and Zn in sediments, calculated using Al as a normalizing crustal element, are higher than unity. With respect to the average EFs for the marine sediments with Cu content higher than the effect range medium guideline value (ERM) of 270 mg kg⁻¹, these enriched elements showed the following sequence: Cu (115) > Zn (29) > Co (27) > Mn (23) > Cd (12.6) > U (11) > Bi (10.9) > Pb (6.7) > Sb (5.0) > Ag (4.1) > Ba (4.0) > Ni (3.2) > V(2.6). All these elements 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.

The spatial distributions of total and acid leachable Cd, Co, Cu, Mn, Pb and Zn contents in the surface sediments delimit the principal “hot spots”, associated with the dumped smelting wastes. About 50% of the surface sediment samples exceeded the ERM guideline value of 270 mg kg⁻¹ proposed for Cu, the principal pollutant of this specific environment.

- The study of the biogeochemical cycles of the elements is important because they regulate the functioning of marine coastal ecosystems. To determine the factors that control the distribution of potentially toxic elements (PTEs) in surface sediments of the La Paz Lagoon (south -western Gulf of California) and their possible sources, 91 sediment samples were collected by free diving. After a total digestion of oven-dried (60 oC, 24 h) sediments with a mixture of concentrated strong acids (HF+HCNO₃+HClO₄) the concentrations for over 50 elements were measured with inductively coupled plasma mass spectrometry. The enrichment factors and the Müller’s geoaccumulation index of the analyzed elements were calculated using obtained data to distinguish naturally or anthropogenically enriched PTEs.

A principal component analysis was also used to determine the possible associations between elements. The results obtained allow us to establish that there are natural inputs of elements such as Se, Ag, As, Cd and Sb into the sediments, which reflect mainly the lithology of the geological formations surrounding the lagoon. Greatest enrichments of As and Cd were found in the area adjacent to the Mogote peninsula which may reflect littoral transport of phosphatic materials rich in some trace elements, supplied to the sea by arroyos that cut through the Lomas de la Virgen geologic formation. The Pb probably has anthropogenic origin, because its higher concentrations up to 36.8 mg kg⁻¹ were recorded near the La Paz city.

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

- Cuauhlte-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).
- Félix-Bermúdez A., 2012. Biogeochemistry of Mn, Cu and Cd in the Colorado River delta. M.S. Thesis in Coastal Oceanography. Universidad Autónoma de Baja California. Ensenada, Mexico (concluded).
 - Salamanca-Quevedo E. 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 (in process).
 - 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 (in process).
 - Reyes-Bravo M. 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 (in process).

Publications

Journal articles

- Cervantes-Duarte R., López-López S., Aguirre-Bahena F., González-Rodríguez E. and S. Futema-Jiménez, 2012. Relevancia de fuentes nitrogenadas nuevas y regeneradas en la columna de agua en Bahía Magdalena (SO) Península de Baja California), México. *Revista de Biología Marina y Oceanografía*, 47 (3): 587-592.
- 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.
- 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(2): 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. **doi:** 10.1039/C2EM30866E .
- 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 (1), 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(2): 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 (3):333-337; doi: 10.1007/s00128-012-0923.

- Shumilin E., Rodríguez-Figueroa G., Sapozhnikov D., Yuri Sapozhnikov Yu. and K. Choumiline, 2012. Anthropogenic and authigenic uranium in the marine sediments of the Central Gulf of California adjacent to the Santa Rosalía mining region. *Archives of Environmental Contamination and Toxicology*, 63: 309-322; doi: 10.1007/s00244-012-9776-1.
- 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 (1), 89-96. Doi: 10.5209/rev_JIGE 2013v39.n1.41750.
- 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. Wintertime enrichment of inorganic nutrients in the Ballenas Channel, Gulf of California. *Ciencias Marinas*, 39(2): 47–64.

Other activities

- Dr. R. Cervantes Duarte from CICIMAR –IPN during 2012 passed his sabbatical year in the Laboratory of the Marine Biogeochemistry of the Instituto de Investigaciones Marinas (CSIC) in Vigo (Spain). He had participated in the project “The inputs of trace elements to the coastal zone during different oceanographic periods. The influence of phytoplankton on trace metal concentrations “ (CTM2011-28792-C02-02).
- Dr. M. L. Leal Acosta (ex-Ph.D. student of CICIMAR-IPN) has a 8-month duration stay (October 2012-June 2013) in Bermuda Institute of Ocean Studies obtaining theoretical knowledge and practical experience of doing oceanographic research, which included also the marine element biogeochemical studies with the use of the sediment traps.
- M.S. K. Choumiline, ex-student of CICIMAR-IPN) is accepted as a Ph.D. student to the Biogeochemistry Laboratory of Dr. Timothy Lyons in the Department of Earth Sciences of the University California-Riverside (California, USA).

Submitted by: Evgueni Choumiline