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Editorial

Chemistry of Our Oceans

I believe that our planet should have been named Water, instead of Earth. Oceans cover most of the surface of our planet! In fact, Earth's oceans hold about 1.5 x 10^{18} tons of water, which in turn contains an enormous amount of dissolved salts. As a result, a lot of chemistry is taking place in the oceans.

Oceans play a central role in the climate of our planet; provide several ecological services such as food provision, energy, transport, nutrient cycling, and biodiversity, among others. Given the importance of the ocean for humankind, and the increase pressure they are under, it is timely to improve our knowledge and prioritize ocean issues that are covered in the chemical oceanography.

The very prominent topic of the role of the oceans on the C cycle and particularly in the exchange of carbon dioxide between the ocean and the atmosphere was identified as a major research topic in the 1950s. Soon after, Keeling *et al.*[1] started the well-known time-series of carbon dioxide measurements in the atmosphere at Manua Loa, Hawaii. This study provided data to raise the flag about the steadily increasing CO_2 levels in the atmosphere from values around 310 ppm, when measurements began in 1958, to over 400 ppm today.

Since then, a number of large oceanographic programs were developed. The first chemical/biogeochemical research programs started in the late 1960s, with the Geochemical Ocean Section Study (GEOSECS). This program aimed to picture the abyssal circulation using a series of radiotracers. Results on the distribution of dissolved nutrients, radioisotopes and noble gases provided the first view of the chemical landscape of the sea. The fundamental relationships between nutrients and water masses, mixing and overturning circulation also started to be elucidated. Transient Tracers in the Ocean (TTO) evolved from GEOSECS experience. TTO used tracers introduced in the atmosphere during the nuclear bomb tests between 1958-1962 to investigate their distribution in the ocean and to gain insight in ocean mixing. Thousands of water samples were collected in the tropical and north Atlantic, with most of samples analyzed for salinity, carbon dioxide, oxygen, and nutrients, tritium and radiocarbon. Here it was observed that tracers were transported to deep water, where they started a global deep water journey. The leadership of these programs was responsibility of a single nation with limited international participation.

Later, the Joint Global Ocean Flux Study (JGOFS) also based on the foundations of GEOSECS continued the studies on carbon cycles with increasing sophistication and better time and space scale resolution. The advances obtained in these studies have been incorporated in model simulations providing valuable constraints on ocean processes.

The recognition of the importance of trace elements and their isotopes (TEIs) for several oceanographic projects were directly connected to the development of clean sampling systems along with highly sensitive analytical techniques, such ICP-MS. Only with these specially designed clean protocols and sensitive methods it was possible to generate the distribution of trace elements "oceanographically consistent". Results showed nutrient-like profiles for many trace elements, indicating coupling mechanisms of uptake of metals by plankton in surface waters and regeneration at depth along with decomposition of biological materials. The role of trace metals as micronutrients for primary production of marine ecosystems is now recognized.

By the beginning of the 2000s, there was still a limited number of trace metal distribution profiles, most of them for the North Atlantic and Pacific, whereas there was a paucity of information for the Southern Hemisphere. Information of the sources, sinks, and internal cycles of trace elements were not enough to elucidate the biogeochemical cycles of trace elements. Difficulties with adequate clean sampling, pre-treatment of samples and determination of TEIs in seawater, frequently present in the order of nmol kg^{-1} and pmol kg^{-1} were still important issues. Moreover, there was a lack of standard procedures and reference materials; even expertise to work with low level of TEIs in highly complex matrices was lacking in many countries.

The GEOTRACES project, officially launched in 2010, was designed in this scenario. A better description of the distribution of trace metals along all oceans, covering all latitudes was long due. Groundbreaking insights into the cycling of trace elements and linkages between micronutrients and the marine primary productivity within the ocean required a truly international, coordinated effort studying multiple trace elements and isotopes simultaneously. Overall 35 nations have been involved in diverse GEOTRACES activities, including planning meetings and cruises and in the determination of global distribution of TEIs that are either micronutrients (e.g., Zn, Fe, Mn, Co, Co, and Cu), contaminants (e.g., Pb and Hg), tracers (e.g., Al, Mn and $\delta^{15}N$) or proxies (e.g. ^{231}Pa, ^{230}Th, Nd isotopes) of a large suite of present and past processes in the oceans. The main objectives of this program[2] are: (*i*) to evaluate the global distribution and chemical speciation of selected trace elements; (*ii*) to determine sources, sinks and internal cycling of trace elements to characterize more completely the physical, chemical and biological processes regulating its distribution; (*iii*) to use proxies to understand the past environment, both in the water column and in sediments. The achievements of this relative young project on the understanding the most diverse aspects of chemical oceanography has been tremendous. A compilation of results has been published as an Intermediate Data Product (IDP2014).[3] This product consists of a digital database of trace metals and isotopes as well as hydrographic parameters, and an electronic atlas providing section plots and animated 3D scenes showing tracer distributions along all available sections in a selected basin. Key aspects of the chemistry of the ocean have been discovered and published in the scientific literature. These include observations of the dynamics of the speciation of REE (Rare Earth Elements) and Nd isotopes in the Amazon estuarine plume,[4] the nearly conservative behavior of hydrothermal dissolved Fe from the southern East Pacific Rise, resulting in a flux four times what was assumed before,[5] among so many others. There is no doubt that the chemical oceanography field has advanced dramatically during the past 20 years. We achieved progress in many fields, dealing with processes from molecular to ocean scales, and obviously exciting new contributions will come in the following decades.

The enterprise of the Brazilian scientific community to really get engaged in chemical oceanographic studies of TEIs at trace and ultra-trace levels has just started, and this journey will be long and hard. This will have to be a coordinated effort of a group of dedicated people, willing to invest time and hard work to make the transition between the current approach, where studies have primary being developed in the calm and protected coastal waters of ours bays and estuaries[6-8] to the open ocean waters. Following the action initiated at the Workshop GEOTRACES Latin America (Rio de Janeiro, 2012), where it was identified the lack of expertise in the study of trace elements and their isotopes in ocean waters in Latin American countries, the Workshop GEOTRACES Brazil was organized. This meeting, held in Santos in 2015, brought together researchers from Brazilian universities and international researchers to foster the involvement of Brazilian scientists in the studies of trace ocean chemistry. A national cooperation network in chemical oceanography for the study of TEIs in the ocean was established. It was recognized that one of the fundamental steps to engage the Brazilian community in ocean chemistry is the access to trace-metal clean sampling systems and appropriate analytical facilities. Capacity building, which already started through a series of hands-on training that included demonstrations of use of equipments in laboratory followed by field surveys, will be a key player in the preparation of the early career scientists and graduate students. The participation of researchers/students from the most diverse areas of chemistry should be stimulated. The physical chemistry, analytical, inorganic, and organic chemistry has had a pivotal role in the development of the chemical oceanography in the past. I would like to point out that every year the Scientific Committee on Oceanographic Research (SCOR) supports students and researches from everywhere to develop training aboard GEOTRACES cruises and shore-based laboratories. This effort combine to Science Without Borders Program will enable the training of a new generation interested in the study of the chemistry of the oceans.

In contrast to small-scale, coastal projects, the cost of supporting this challenge change of the focus in marine chemistry studies will be high and will require the support of the scientific community, funding and government agencies. However, the anticipated benefits will be even higher and include exciting prospect of imminent further science advances and high impact research in several fields such as climate change, biogeochemical cycles, internal processes in the oceans, fluxes across boundaries (ocean-atmosphere-continents-sediments), paleochemistry, physical chemistry, proteomics, genomics, synthesis, anthropogenic effects on the ecosystems and their services, and new interdisciplinary fields of research. These advances should benefit not only the field of chemistry, but will be central to a variety of other fields of natural sciences. The acquisition of the new Research Vessel Vital de Oliveira that just cruised to our waters was only the first step of this long and adventurous journey yet to be lived.

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