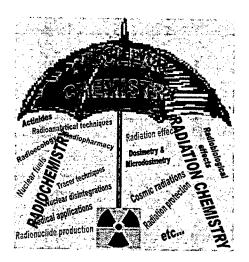
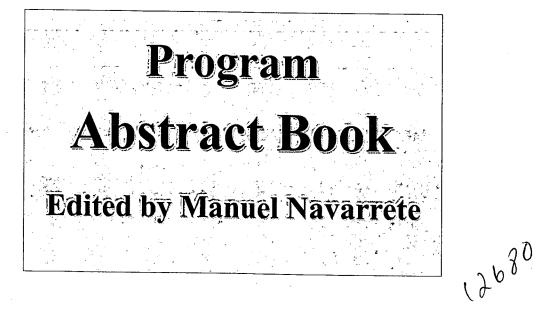


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SEASONAL VARIATION OF METAL AND TRACE ELEMENTS IN SEDIMENTS FROM SANTOS ESTUARY, BRAZIL, BY NEUTRON ACTIVATION AND ATOMIC ABSORPTION TECHNIQUES

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The Santos Estuarine system is an intricate pattern of tidal channels and small rivers originating from the adjacent Pre-Cambrian slopes. The region is comprised of two large and complex estuaries known as Santos and São Vicente. These two major estuaries share a common area in the upper portion of the region which interacts with each other. The largest harbor in Latin America is located at the Eastern outlet of the Santos Estuary. The access to the port for large ships is guaranteed by way of periodic dredging of the main shipping lane, which requires a minimum draft of 10 m. This intricate and sensitive ecosystem is highly susceptible to human impact from industrial activities, urban sewage and polluted solid waste disposal. Due to its high vulnerability CETESB (Environmental Control Agency of the São Paulo State) sporadically monitors the contamination levels of waters, sediment and marine organisms. In order to better understanding geochemical and environmental processes and their possible changes due to anthropogenic activities trace metals analyses and their distribution in marine sediments are commonly undertaken. The present study reports results concerning the distribution of some major (Fe, K and Na), trace (As, Ba, Br, Co, Cr, Cs, Hf, Hg, Rb, Sb, Sc, Ta, Tb, Th, U and Zn) and rare earth (Ce, Eu, La, Lu, Nd, Sm, Tb and Yb) elements in Santos estuarine marine sediments. Thirty bottom sediment samples (SS0501 to SS0514 and SW0501 to SW0516) were collected in this estuary, including regions of São Vicente, Santos, Cubatão and Vicente de Carvalho, by a steel van Veen sampler in two seasonal periods (summer and winter of 2005). The samples were previously dried at 50°C in a ventilated oven, passed through a 2 mm sieve and then homogenized before analysis. Samples were classified according to the anthropic impact: area 1: samples from stations 01 to 06, located at the Santos estuary extending into the upper portion of the estuarine system, near the industrial pole of Cubatão. Samples from stations 7 to 10, named area 2, located at the Santos Bay where the depuration processes tend to be more accentuated due to the circulation of chemical compounds. Area 3, from stations 11 to 14, located at the São Vicente estuary extending to the Casqueiro region, area characterized by extensive mangrove vegetation and with urban development presenting

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poor sanitary processing. Multielementar analysis was carried out by instrumental neutron activation analysis (INAA). For total mercury determination cold vapor atomic absorption technique (CV AAS) was employed. In both cases for quality control certified reference materials analyses were performed The results obtained for average organic matter for the sediment samples were: area 1, 19.05%; area 2, 18.2% and area 3, 20.0%. When the results obtained for multielemental concentrations were compared with NASC (North American Shale Composite) values it was possible to observe an enrichment for light REE (La, Ce, Eu, Nd, Sm) and U, in both periods, in the area 1. This is probably due to the influence of fertilizer plants that have been operating along the margins of some rivers producing a large volume of phosphogypsum, a by-product of the production of phosphoric acid, which are disposed of in nearby storage areas, as piles on the margins of the rivers. For areas 2 and 3 it was not possible to observe this influence. For area 1 it was also possible to verify higher concentration for most elements analyzed, especially for the heavy metals Cr, Hg and Zn. These samples are located near the Cubatão region, suffering high impact from industrial activities and harbor influence. It was verified that, the mean concentration values for the three areas are considerably different and differ for summer and winter periods for all elements analyzed. The concentration values obtained for metals As, Cr, Hg and Zn in the sediment samples were compared to Canadian Council of Minister of the Environment (CCME) oriented values Threshold Effect Level (TEL) and Probable Effect Level (PEL). For As, Cr and Zn most samples analyzed showed values above the TEL values (As - 7.24, Cr - 52.30, Zn - 124 mg kg⁻¹). As for Hg (TEL - 0.13 mg kg⁻¹, PEL - 0.696 mg kg⁻¹), sample SS0514 (located in the São Vicente estuary, area 3) presented a higher Hg level than PEL value since this point also suffers from impacts from Cubatão region. Samples SS0501 to SS0506 (area 1) presented values above TEL. These last samples are located near Cubatão region, suffering high impact from industrial activities and the harbor. The others samples were below the TEL values. Cluster analyses were applied for the chemical data.

