Marine Pollution Bulletin 78 (2014) 209–212

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

# History of human activity in coastal southern Brazil from sediment

L.F. Niencheski [a,*], W.S. Moore [b], H.L. Windom [c]

[a] Instituto de Oceanografia – FURG, Rio Grande, Av Italia km 8, RS 96201-900, Brazil
[b] Department of Earth and Ocean Sciences, University of South Carolina, Columbia, SC 29208, USA
[c] Skidaway Institute of Oceanography, 10 Ocean Science Circle, Savannah, GA 31411, USA

ARTICLE INFO

*Keywords:*
Patos Lagoon estuary
Radiochemical chronology
Sediment
$^{210}$Pb
$^{137}$Cs
Trace metal

ABSTRACT

This study reports results of analysis of sediment cores collected from the Patos Lagoon estuary. This estuary receives materials from land runoff into Patos and Mirim lagoons and from exchange with the adjacent South Atlantic Ocean through a narrow inlet. Sediment from these sources is mostly natural, but additional contributions associated with source/activities related to the port of Rio Grande. The aim of this study was to estimate rates of accumulation of the sediments and to assess the significance of metal inputs from these activities relative to natural inputs. Our results indicate an average sedimentation rate of 0.3 cm/yr and that the transport of suspended solids from offshore sources into the estuary was enhanced after the deepening of the channel and construction of the breakwaters (in the early 1900). Results for metal accumulation in these sediments suggest that there have been only minor enrichments which can be attributed to anthropogenic sources.



The sediment record, as revealed in sediment cores, has been used by many groups of investigators to reconstruct the history of contaminant inputs to estuaries throughout the world (Goldberg et al., 1979; Alexander et al., 1993). The basic assumptions are that contaminant inputs equilibrate relatively rapidly with sediment particles at the sediment–water interface (most toxic metals are readily adsorbed to particles) and that the sediment column represents a continuous sequence of sediment and associated contaminant accumulation with no post depositional vertical mixing or remobilization.

Using radiochemical chronologies, it is possible, theoretically, to date sediment over a period corresponding to about five radioactive decay half-lives providing that the radio nuclide is separated from its parent after accumulation in sediments. For example, $^{210}$Pb, a naturally occurring radionuclide in the $^{238}$U decay series with a half life of 22.3 years, has been used successfully to provide a temporal framework in numerous studies related to sediment accumulation in estuarine environments (Goldberg et al., 1979; Alexander et al., 1993). $^{210}$Pb is formed in the atmosphere from the decay of $^{222}$Rn, generated by $^{226}$Ra decay in the water column and it is also formed from sedimentary $^{226}$Ra decay. $^{210}$Pb accumulates in sediment, where it is separated from its parent and subsequently decays.

The present study reports the analysis of sediment cores collected from the Patos Lagoon estuary (RS-Brazil), near the city of Rio Grande which is located on the estuary of Patos Lagoon (Fig. 1). This estuary receives materials associated with the discharges into Patos (10,360 km$^2$) and Mirim (3749 km$^2$) lagoons (located near the Brazil–Uruguay border) and from exchange with the adjacent South Atlantic Ocean through a narrow inlet at the southern end of Patos Lagoon. Sediment from these sources is mostly natural. But some additions to the natural metal levels in these sediments may originate from local source/activities around the port of Rio Grande. Thus the aim of this study was to estimate rates of accumulation of the sediments in this area and to assess the significance of metal inputs from these anthropogenic activities in the region.

Because Patos and Mirim lagoons are such large and efficient traps for sediment, any signature in sediments of anthropogenic activity originating from within their watersheds is expected to be diluted by natural sediment. Therefore changes in sedimentation rate and sediment composition that cannot be explained as natural are expected to be dominated by activities associated with the city and port of Rio Grande. Port activities include harbor maintenance (dredging), transport of minerals, fuel oil, and other raw and processed chemicals. Industries that have developed around this port include food packing, fertilizer factories, oil refineries, chemical manufacturing and shipyards.

Two cores were collected in the vicinity of Rio Grande (Fig. 1) from undisturbed locations (i.e. where no dredging had taken place) and three other from areas which represent different, but important environments within the estuary. The field work was carried out in the summer of 2005. At each site, water depth is roughly 1.0 m deep and the bottom water is well mixed and remains oxic year round. Sediment cores were collected using

* Corresponding author. Tel.: +55 53 3233 6516; fax: +55 53 3233 6737.
*E-mail address:* felipeniencheski@furg.br (L.F. Niencheski).

0025-326X/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.marpolbul.2013.10.042

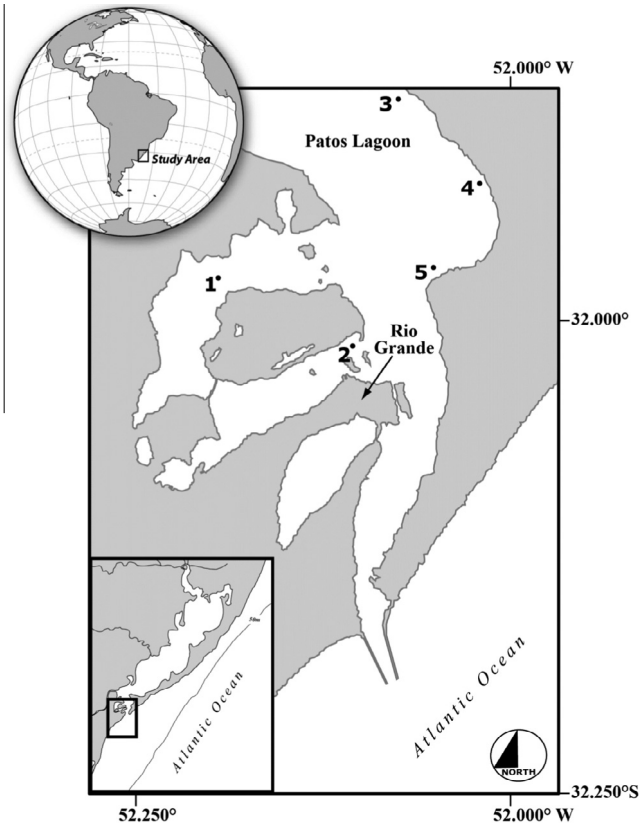


**Fig. 1.** Sampling stations at Patos Lagoon estuary: #1 and 2, geochronology and contaminants studies; #3, 4 and 5 geochronology.

pre-cleaned plastic core tubes, which penetrated about 90 cm. Subsampling was performed by extruding the sediment column in small intervals from the top of the core tube (0.5, 1.5, 2.5, 3.5, 4.5, 10.5, 20.5, 30.5, 31.5, 33.5, 35.5, 37.5, 40.5, 50.5, 60.5, 70.5 and 80.5 cm). The sediments were composed of well-rounded fine quartz sand, silt and clay with little organic detritus. The porosities of the sediments were uniform throughout the cores and ranged from about 0.3 to 0.6. The sediment sections were dried for 24 h at 80 °C, after which they were ground to a powder and stored in glass bottles at 4 °C.

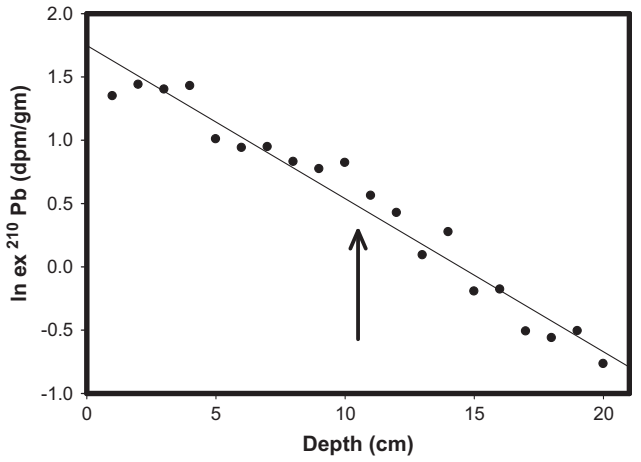


**Fig. 2.** The $^{210}$Pb depth profile of the core from Station 1. The arrow indicates the $^{137}$Cs peak for 1963.

Accumulation rates were calculated based on changes in excess $^{210}$Pb activity with depth in the sediments. Total $^{210}$Pb activity was determined directly using gamma spectroscopy to quantify the activity of its 46.5 keV gamma peak in dried, homogenized sediment (Cutshall et al., 1983). $^{226}$Ra was measured based on its 351 keV peak and subtracted from total $^{210}$Pb to yield excess $^{210}$Pb. Calculated $^{210}$Pb accumulation rates were verified using $^{137}$Cs as a complementary radiotracer. $^{137}$Cs activities were directly determined by gamma spectroscopic measurements of its 662 keV gamma peak (Alexander et al., 1991, 1999; Alexander and Windom, 1999). This tracer was primarily released to the atmosphere during nuclear tests during 1962–1963.

Sediment accumulation rates were calculated using the constant flux (also known as constant rate of supply) geochemical model when possible (Alexander et al., 1991, 2005, 2011). This model is applicable in areas where the flux of excess of $^{210}$Pb and dry-mass sedimentation rate at the seabed have remained constant over the period of interest. This assumption has been shown to be reasonable in areas where the supply of $^{210}$Pb is dominated by atmospheric sources (i.e. marine and estuarine environments).

Sediment samples were digested with nitric, perchloric and hydrofluoric acids. After digestion, samples were appropriately diluted and analyzed for Fe, Al, Cr, Zn, Mn, Cd, Cu, Ni, Pb, Ag, Sn, Sb, Ti and As by inductively coupled plasma-mass spectrometry (VG PQIII+) and/or by atomic absorption spectrophotometry. For ICPMS an internal standard of indium was added to every sample and standard prior to analysis to correct for signal stability.

The $^{210}$Pb results for Core 1 (Fig. 2) were obtained in more detail than those for the other cores. The results indicate that the rate has been relatively constant and there has been no vertical mixing within the core because the natural log of the $^{210}$Pb activity is linear with depth. The slope of this curve can then be used to calculate the sedimentation rate (Alexander et al., 1991), which yields 0.3 cm/yr. The depth of the $^{137}$Cs peak in the sediment core (indicated by the arrow in Fig. 2), which indicates the 1963 time horizon provides a confirmation of this rate. The other cores we collected in the area (Fig. 1) were also analyzed for $^{210}$Pb but in less detail, but results indicate that their average rate of accumulation is 0.34 cm/yr, the same as Core 1.

We used the 0.3 cm/yr sedimentation rate to assign times to sediment layers, which are an estimate of the time they were deposited, for Core 1 & 2, extrapolating it to deeper depth (where $^{210}$Pb activity measurements become unreliable). This then provides the temporal context in which to interpret metal levels in the sediment cores.

Metals such as cooper, zinc, and lead, accumulate naturally in estuarine sediment, primarily associated with clays transported from watersheds or from offshore. This natural metal input component of sediments is generally quantifiable based on "normalizers" or components of sediments which reflect the abundance of the natural metal-bearing phases, such as clays (Windom et al., 1989; Schropp et al., 1990). Aluminum has been found to be useful for this and in natural sediments from a given area, the metal:Al ratio is expected to remain constant as long as natural inputs are responsible for metal loadings. The dominant natural metal-bearing phase in sediments of the Patos Lagoon estuary is aluminosilicates, or clay minerals, so Al is a likely candidate for normalizing the relative abundance of the natural metal-bearing phase. In fact, Niencheski et al. (2006) have used aluminum as a proxy for the concentration of aluminosilicate (i.e. clay minerals). For natural sediments the concentration of metals covary with the concentration of aluminum, so deviations in the metal:Al ratio should indicate anthropogenic enrichments or, perhaps, changes in source.

In Fig. 3, the metal:Al ratios in Cores 1 & 2 are plotted in relation to the assigned time for the sediment layer determined from $^{210}$Pb activity. The results for Core 1 indicate significant metal