

An Assessment of Anthropogenic Impact in a Nature Reserve: the Santoña Marshes (Northern Spain)

Estudio del impacto humano en una Reserva Natural: las Marismas de Santoña
(Cantabria, España)

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Abstract

The Santoña Marshes Nature Reserve is one of the most important ecosystems of the Spanish Cantabrian coast due to its ecological value as a wintering area for migratory birds. Since an increase in population and substantial changes in the use of land have been observed in this area during the last century, the aim of this work was to attempt to see if anthropogenic activities are recorded in the accumulating sediments. Two sediment cores (50 cm length) were collected for isotopic dating (²¹⁰Pb and ¹³⁷Cs) and geochemical study (heavy metals). The data indicate an increasing trend in sedimentation rates during the last century, probably related to the progressive loss of the estuarine domains and the changes in their original hydrodynamic conditions due to infilling and the construction of dykes. However, no significant anthropogenic inputs of heavy metals have been detected in recent times.

Keywords: Santoña marshes, ²¹⁰Pb and ¹³⁷Cs dating, sedimentation rates, heavy metals, anthropogenic impact

Resumen

La Reserva Natural de las Marismas de Santoña, situada en la costa cantábrica, posee un gran valor ecológico como lugar de invernada de aves migratorias. Dado el importante aumento de la presencia humana en la zona durante el último siglo, este trabajo tiene como objetivo estudiar si estas actividades antrópicas han dejado su huella en los sedimentos acumulados. Para ello se ha abordado la datación isotópica (¹³⁷Cs y ²¹⁰Pb) y el estudio geoquímico (metales pesados) de dos sondeos de 50 cm de longitud. Los resultados obtenidos señalan la existencia de un importante incremento en las tasas de sedimentación durante el último siglo, posiblemente relacionado con la pérdida progresiva de la superficie y de las dinámicas estuarinas como consecuencia de los rellenos y de la construcción de diques. Sin embargo, no se han detectado niveles significativos de contaminación en metales pesados en los sedimentos más recientes.

Palabras clave: marismas, datación con ²¹⁰Pb y ¹³⁷Cs, tasas de sedimentación, metales pesados, impacto antropogénico.

1. Introduction

The Santoña Marshes (43° 26' 29" N, 003° 27' 27" W) are one of the most important ecosystems of the northern coast of the Iberian Peninsula due to their ecological value as a wintering area or residence and nesting area for many birds on their migrations from northern Europe to the southern latitudes of Africa. However, during the last century the natural characteristics of these wetlands have been modified to some extent by anthropogenic activities such as the construction of dykes, in-filling, construction of roads, discharge of waste waters, etc. Moreover, drastic changes in the use of land have occurred in the surrounding area, transforming a quiet rural place into an important touristic centre. In 1993 the European Court of Justice condemned the Kingdom of Spain for not classifying the Santoña Marshes as Special Protection Area (SPA) and for not taking appropriate steps to avoid pollution and deterioration of habitats (EJC case n° C-355/90). As a consequence, in 1994 they were designed as a RAMSAR site and nowadays they are a part of a Nature Reserve (4000 ha.) which includes woodlands, meadows, cliffs, beaches and dunes.

This study addressed the first stage of the assessment of historical anthropogenic impact on the Santoña marshes. ^{210}Pb and ^{137}Cs dating techniques have been used to estimate local sedimentation rates and to provide an accurate chronological scale for human effects (Clifton and Hamilton 1982; Cundy *et al.*, 2003; Rubio *et al.*, 2003), and calculation of enrichment factors for heavy metals have allowed the assessment of the magnitude of the inputs of contaminants to be made (Bricker, 1993; Mil-Homens *et al.*, 2006a).

2. Materials and Methods

2.1. Study area

The Santoña Marshes Nature Reserve is located in a mesotidal estuary in the northern coast of Spain (Fig. 1). The marshes have a perimeter of 84 km and an area of 1902 ha. Around 63% of the total surface is exposed at low tide. Seawater penetrates the estuary from the northeast through the San Martín Channel, while the Asón river is the main supplier of fresh water to the system (16 m³/s). Different sorts of benthonic organisms dominate the muddy floors and the site supports a diverse flora of halophytic and freshwater communities. More than 140 species of aquatic birds have been recorded in the Reserve, with the marshes regularly housing concentrations of 20,000 individuals in winter. Unfortunately, as calcu-

lated by local authorities, around 15% of the original estuarine area has been modified by construction of dikes (total length of 14895 metres), breakwaters (eight), tide mills (four) and piers (three). In addition, there is a total population of about 60,000 inhabitants living in fifteen municipalities around the marshes, which in summer increases to more than 180,000.

2.2. Sampling and handling

Two silty sediment cores were collected in the Santoña Marshes Nature Reserve using a PVC tube of 50 cm long and 12.5 cm diameter. Both cores were taken from areas of apparent sediment accretion, and compaction during sampling was found to be negligible. Core C was retrieved in 2003 from an intertidal mudflat opposite Colindres (a fishing port with 7.000 inhabitants) where the Asón river discharges into the main channel (Fig. 1). Core S was taken in 2002 from an intertidal mudflat in the Boo area, in the northern edge of the estuary. This sampling site is located close to Santoña (a prosperous village of 14.000 inhabitants with an important fish-canning industry) and adjacent to the local road Ca-141.

Cores were sectioned into 1 cm intervals immediately after returning to the laboratory. Sediment samples for isotopic analysis were dried at 110°C for 24 hours, broken up, passed through a 2 mm sieve and kept for thirty days in closed plastic containers in order to obtain the radioactive equilibrium between ^{226}Ra and ^{222}Rn daughters (Soto *et al.*, 2006). Samples for metal analyses were dried at 60°C, sieved through 2-mm plastic mesh and ground to a powder with an agate pestle and mortar.

2.3. Radionuclide and geochemical analysis

Gamma spectrometry measurements of ^{137}Cs , ^{226}Ra and ^{210}Pb activities were made using a high purity germanium coaxial detector with an efficiency of 20%, a resolution of 1.86 keV and surrounded by shielding material to reduce background counting rate. The detector is connected to a container holding liquid nitrogen by a cold finger and it is mounted inside a 10 cm lead shielding against room and cosmic radiation background. The detector is also linked to an electronic chain, which in turn is connected to a multichannel analyser (Quindós *et al.*, 1994; Reguigui and Landsberger, 2005). The detector was calibrated using standard solutions in the same geometry as the measured samples. Corrections for self-absorption in the samples were experimentally evaluated using gamma spectra of samples prepared with similar activities but with different densities. To validate our results and to establish a

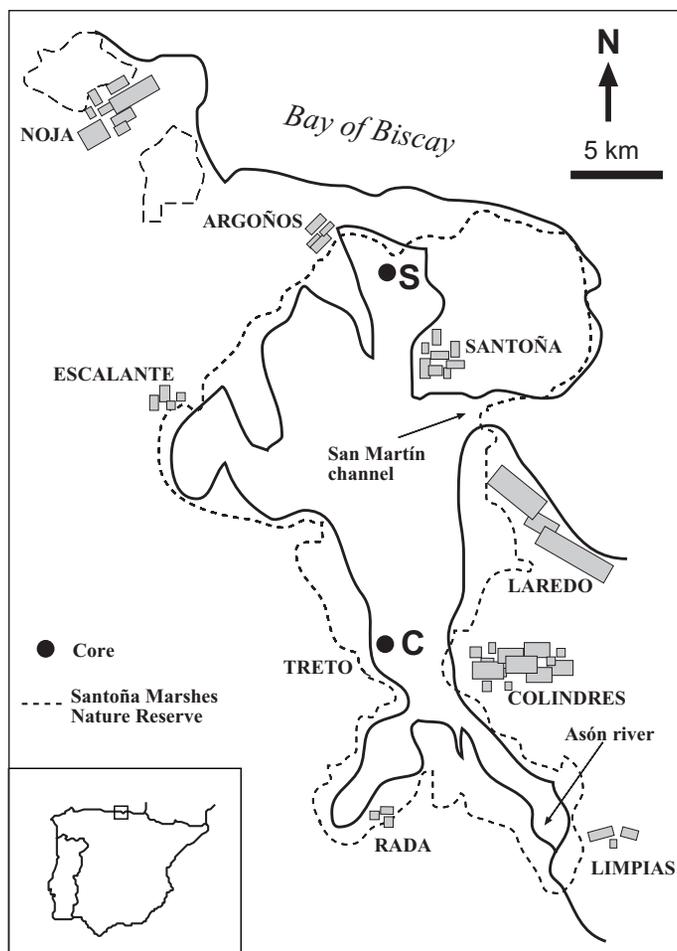


Fig. 1.- Location of sampling sites in the Santoña Marshes Nature Reserve.

Fig. 1.- Situación de los puntos de muestreo en la Reserva Natural de las Marismas de Santoña.

quality control for our measurements, our laboratory has participated in different international inter-departmental exercises of comparison of gamma spectrometry measurements of radioactivity (Quindós *et al.*, 1991).

Considering the appropriate correction for laboratory background, the activity of ^{137}Cs was determined from the 661 KeV peak, ^{210}Pb from the 46.5 KeV one, and ^{226}Ra was evaluated from the 352 and 611 KeV peaks of ^{214}Pb and ^{214}Bi , daughter products of the ^{222}Rn in equilibrium with the ^{226}Ra (Wallbrink *et al.*, 2002). The uncertainties of the obtained data are mainly due to the statistical counting error. In the conditions used, detection limits for a counting time of 24 hours were estimated to be 10 Bq Kg^{-1} for ^{210}Pb , 3 Bq Kg^{-1} for ^{226}Ra and 0.5 Bq Kg^{-1} for ^{137}Cs .

Metal concentrations in core sediments were determined by Inductively Couple Plasma–Optic Emisión Spectrometry (ICP-OES) after microwave digestion with aqua regia. Quality control was assessed by analysis of

blank reagents, duplicates and standard reference materials (GXR-1, GXR-2, GXR-4 and GXR-6). Lowest detection limits were 0.01% for Al and Fe, 0.001% for S, 0.2 mg kg^{-1} for Cd, 1 mg kg^{-1} for Mn, Zn, Cu and Ni and 2 mg kg^{-1} for Pb and Cr.

3. Results and Discussion

3.1. Isotopic geochronology

Dating of sediments has been carried out for many years using different radiometric techniques (Faure, 1986; van Wijngaarden *et al.*, 2002). Short lived-isotopes such as ^{137}Cs and ^{210}Pb have been frequently used to calculate sedimentation rates on a decadal scale time in coastal areas (Campbell, 1983; Appleby *et al.*, 1988; Andersen *et al.*, 2000). ^{137}Cs is an artificial radionuclide which was released the atmosphere as a consequence of the nuclear weapons tests which occurred from 1954 onwards. However, contents have been decreasing since 1964, except for small increases due to sporadic tests carried out by China and France or the Chernobyl accident (Edgington *et al.*, 1991; Sánchez *et al.*, 1992). In favourable conditions, these periods of maxim fallout can be registered in the sediments as marked peaks in concentrations, providing useful markers to calculate local sedimentation rates. Distribution of ^{137}Cs in cores C and S have been plotted as a function of depth in figure 2. Concentrations remain near detection limits, being distinctly lower than those found in sediments from other estuaries of the nearby area such as Nervión (Cearreta *et al.*, 2000) and Plentzia (Cearreta *et al.*, 2002). The lowest values appear in core S, and are probably related to local significant inputs of the materials used for the reclamation of adjacent areas. Moreover, the data exhibit a large scatter instead of a clear subsurface maxima, suggesting some vertical redistribution of ^{137}Cs within the sedimentary column. Therefore, on the basis of the profiles, it appears that ^{137}Cs cannot be used as a reliable chronological proxy in the studied cores.

^{210}Pb is a naturally occurring isotope which belongs to the ^{238}U radioactive chain. Sediment samples reveal deposited ^{210}Pb and another fraction of the same isotope which is produced by the decay of ^{226}Ra . The fraction that comes from ^{226}Ra is known as ^{210}Pb in equilibrium, whilst the deposited fraction is known as excess ^{210}Pb ($^{210}\text{Pb}_{\text{xs}}$). The $^{210}\text{Pb}_{\text{xs}}$ can be measured subtracting the ^{210}Pb in equilibrium from the total ^{210}Pb in each layer (El-Daoushy, 1988). Figure 3 shows the concentrations of total ^{210}Pb and ^{226}Ra versus depth in the studied cores. While ^{226}Ra shows an almost constant distribution, with average values of 22 Bq Kg^{-1} in core C and slightly higher (26 Bq Kg^{-1}) in core

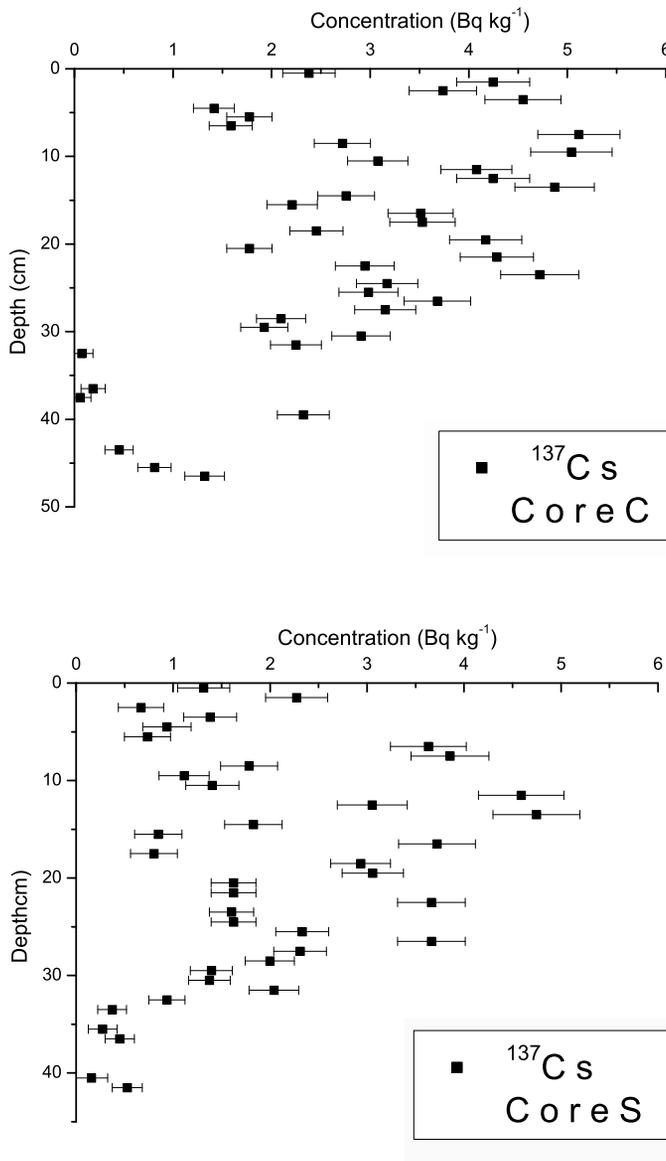


Fig. 2.- Vertical distribution of ^{137}Cs in cores C and S.
 Fig. 2.- Distribución vertical de ^{137}Cs en los sondeos C y S.

S, contents of ^{210}Pb exhibit a decreasing but fluctuating trend with depth. However, the observed activity maxima are not coincident with peaks in redox sensitive elements such as Fe, Mn and S (Figure 4), indicating little post-depositional redistribution of this radionuclide by early diagenesis. The equilibrium between ^{226}Ra and ^{210}Pb is reached below the depth of 35 cm, indicating that all the $^{210}\text{Pb}_{\text{xs}}$ has decayed (≈ 100 years).

Different approaches based on excess ^{210}Pb concentration can be applied to interpret the data. On the one hand, the CIC models are based on the assumption of constant initial activity. The constant accumulation approach (Fuller *et al.*, 1999; Ruiz Fernandez *et al.*, 2003) assumes that depositional ^{210}Pb and material incorporation into each layer have been constant during the deposi-

tion of the sediment, whereas the variable rate of sedimentation model allows changes with time (Shukla and Joshi, 1989). However, both models are only applicable when excess ^{210}Pb concentrations declines monotonically with depth. Therefore, rates ascribed in the present study were determined using the CRS (Constant Rate of Supply) model, which assumes that the net supply of $^{210}\text{Pb}_{\text{xs}}$ is constant despite variations in the mass accumulation rate. Partial inventories of unsupported ^{210}Pb in each layer were calculated in order to allow dating of the cores. The age of each sediment layer was determined by comparing the sum of partial inventories above the layer with the total inventory (Appleby and Oldfield, 1978; Joshi, 1989; Appleby, 1998), as:

$$t = (1/\lambda) \ln (A(\infty) / (A(\infty) - A(m)))$$

where t is the age of the a layer; λ is the decay constant of ^{210}Pb ; $A(m)$ is the partial inventory of the a layer, sum of the products of concentrations of ^{210}Pb , densities, and thickness of above layers; $A(\infty)$ is the total inventory of ^{210}Pb in the sediment.

The age-depth curves calculated using the CRS model reflect noticeable changes in sedimentation rates over time (Figure 5). A 4-fold increase can be observed in the first 80 years of the XX century (0.1 cm/year-0.4 cm/year). From the eighties until the present days sedimentation rates exhibit a non-steady pattern fluctuating between 0.43 and 1.00 cm/year in core S and 0.42 and 0.66 cm/year in core C. These increasing sedimentations rates are probably related to changes in patterns of water circulation as a result of in-filling works and dyking. In fact, maximum values were determined in core S, collected from the northern area near Santoña, where local authorities (Consejería de Medio Ambiente de Cantabria, 2001) have reported significant modifications of the original characteristics of the area due to the construction of a local road and artificial barriers which extend along 22% of the total perimeter. In addition, there was an accelerated expansion of the population in neighbouring villages (mainly for due to holiday visitors) is likely to have led to the increased clearing of important extensions of the land in the catchment area and to a seasonal increase in discharges of untreated domestic wastewaters to the estuarine area.

Finally, it is noteworthy that according to the ^{210}Pb -derived dating, the first occurrence of ^{137}Cs (1954) in the sediments should be observed at about 20-23 cm depth. However, in both cores this element is present in samples collected below 30 cm depth (Figure 2), confirming its downward migration. The mobility and redistribution of this artificial radionuclide in estuarine and marine sedi-

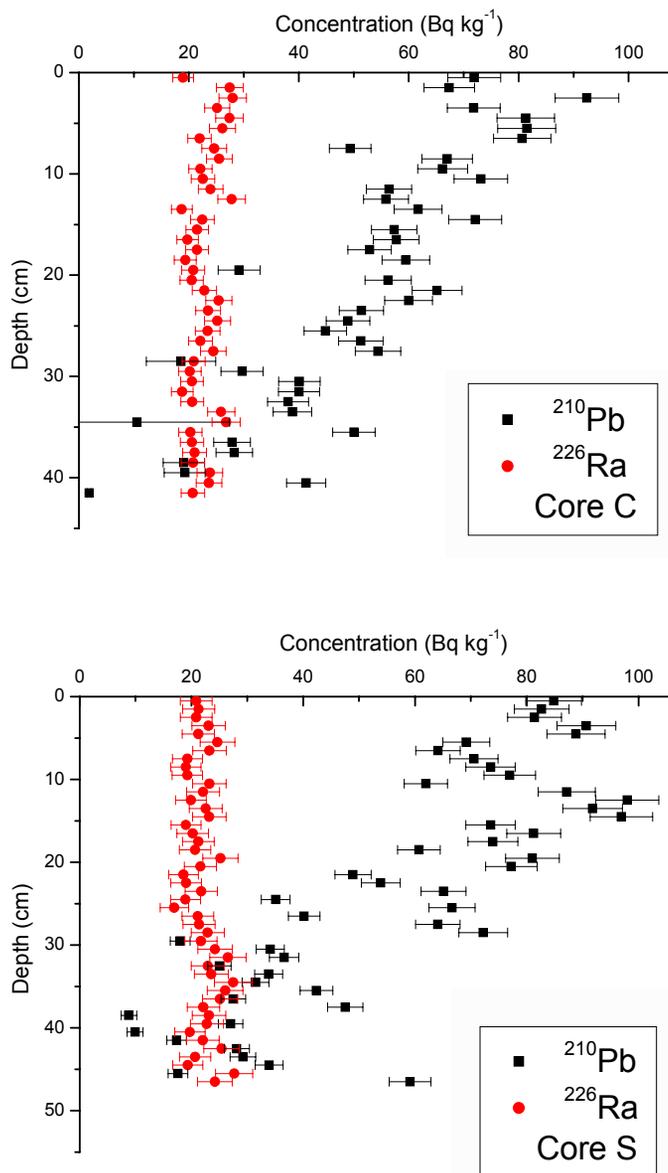


Fig. 3.- ²¹⁰Pb and ²²⁶Ra profiles in cores C and S.
 Fig. 3.- Perfiles de ²¹⁰Pb y de ²²⁶Ra en los sondeos C y S.

ment cores have been extensively documented by several workers (Ritchie and McHenry, 1990; Rosen *et al.*, 1999; Thomson *et al.*, 2002). ¹³⁷Cs is more mobile in the marine environment than ²¹⁰Pb and post-depositional diffusion often causes deeper penetration into the sediment than is predicted (Ridgway and Shimmield, 2005; Ligeró *et al.*, 2005a,b).

3.2. Metal inputs

Metal concentrations in the samples show the following ranges (mg kg⁻¹): 170-322 (Zn), 17-51 (Pb), 13-26 (Cu), 17-27 (Cr) and 17-23 (Ni) in core C and 148-338 (Zn),

33-72 (Pb), 10-23 (Cu), 20-27 (Cr) and 15-20 (Ni) in core S. When compared with other estuaries of the Spanish Cantabrian coast, maximum values are lower than those reported for the polluted sediments of Suances (García-Sepúlveda *et al.*, 1986), the Nervión estuary (Cearreta *et al.*, 2000) and the Santander Bay (Viguri *et al.*, 2007) and similar to those detected in the well preserved underdeveloped estuaries of Plentzia (Cearreta *et al.*, 2002), Urdaibai (Irabien and Velasco, 1999) and Muskiz (Alday, 2004).

As contaminants tend to concentrate in the finer fraction of sediments (Ackermann, 1980), clay-associated elements such as Al have been frequently used as a proxy for both mineralogic and granulometric variability (Trimble *et al.*, 1999; Mil-Homens *et al.*, 2006b). In samples from core C this element exhibits a reasonably close linear relationship with Zn (r=0.88), Pb (r=0.73), Cu (r=0.87), Cr (r=0.97) and Ni (r=0.80) (n=13, p<0.001 in all cases). This suggests that no significant metal contamination occurred within the sedimentary column prior to core sampling in 2003. Al and Cd show a relatively low correlation coefficient (r=0.60), which could be explained by the low contents (<1 mg kg⁻¹, near detection limits) and the low variability of the latter element. Notwithstanding this, it is worth mentioning that previous work of Canteras *et al.*, (2000) reported enhanced concentrations of Cd and Zn in surface sediments from this area.

Nevertheless, elements from core S show a different behavior. On the one hand, Cr and Ni covaried significantly with Al (r=0.92 and 0.84 respectively). When the whole dataset is applied (samples from S and C, n=25), slightly lower but significant values were obtained (r=0.83 for Cr and r=0.76 for Ni). These results seem to confirm that grain size is the main factor controlling the distribution of both metals in the sediments. In contrast, Zn, Pb and Cu did not correlate with this conservative element (r=0.18, 0.13 and 0.54 respectively). When a few samples with anomalous contents were eliminated from the dataset, better correlation coefficients with Al were obtained (r=0.81 for Zn, r=0.66 for Pb and r=0.77 for Cu). As one of the main aims of this work is to provide a better insight into anthropogenic inputs in the Santoña marshes, contents of these elements are expressed in terms of Enrichment Factor (EFs). These values were calculated by dividing the measured concentration by the background concentration predicted by the regression to Al (Skowronek *et al.*, 1994; Roach, 2005).

Calculated EFs for Zn, Pb and Cu in both cores are shown in figure 6. The values do not show any enhanced concentrations in near-surface sediments, in spite of the recent demographic expansion and subsequent increase

Fig. 4.- Concentrations of Fe, Mn and S in cores C and S.

Fig. 4.- Concentraciones de Fe, Mn y S en los sondeos C y S.

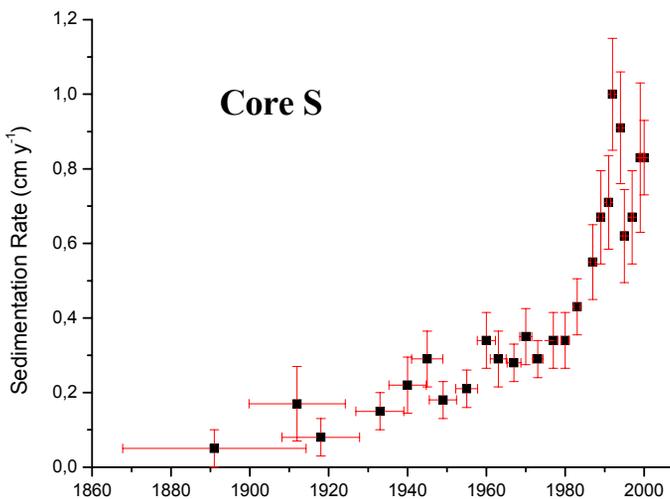
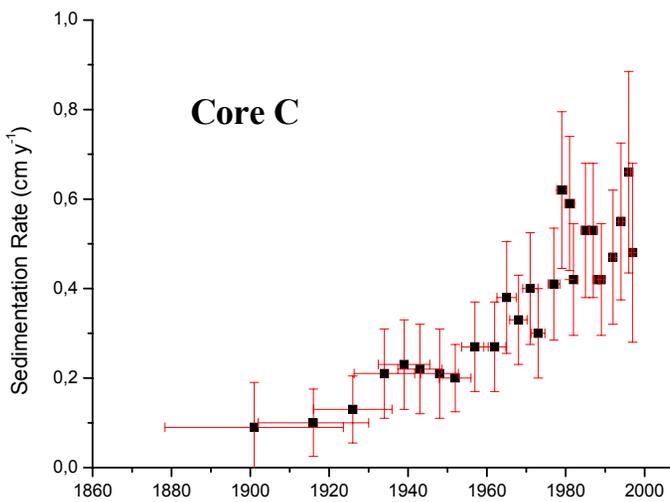
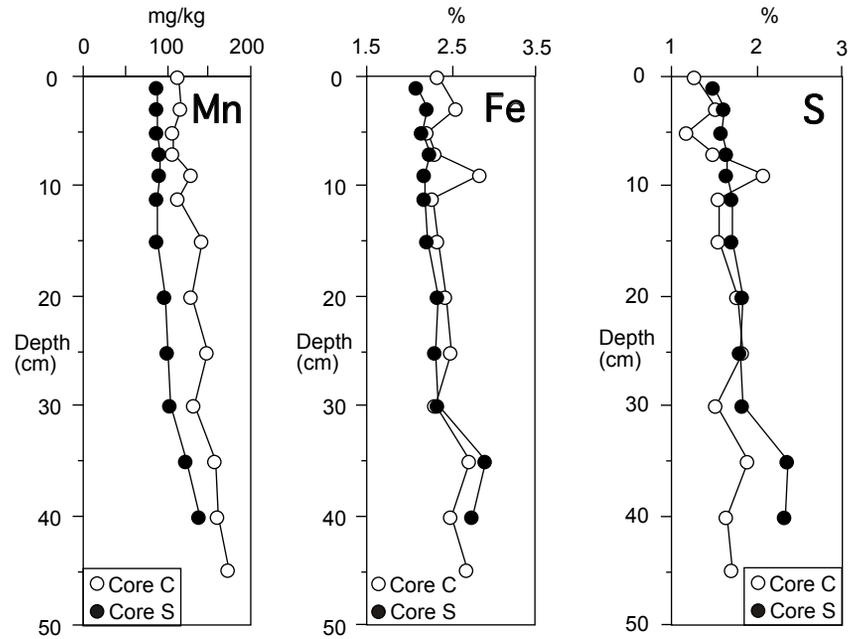


Fig. 5.- Sedimentation rates in cores C and S (cm/year).

Fig. 5.- Tasas de sedimentación (cm/año) en los sondeos C y S.

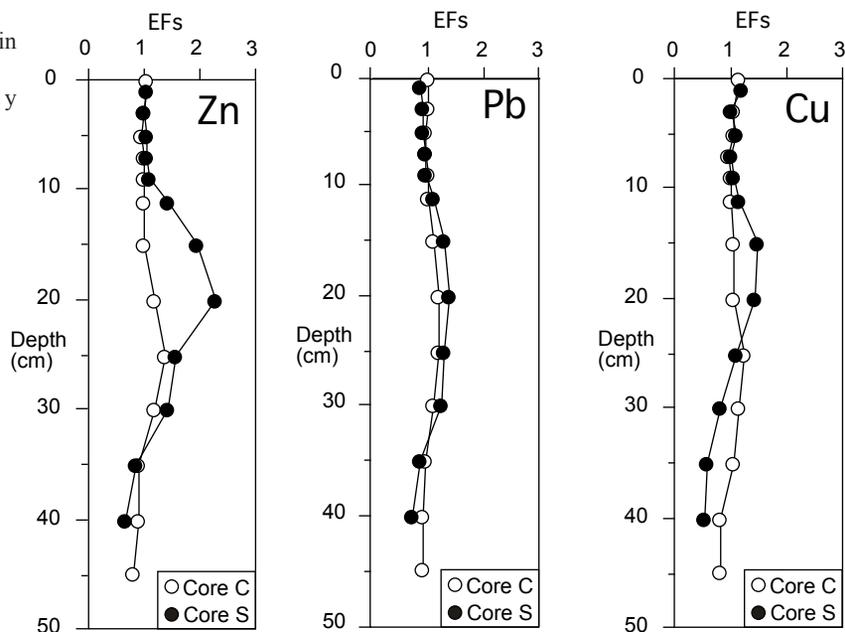
in domestic wastes discharged to the estuary. However, moderately enhanced contents of Zn (and slightly high values for Cu and Pb) were found between 10 and 25 cm depth in core S. As do the radionuclides, the vertical distribution of metals shows a poor correspondence to those of redox-sensitive elements such as Fe, Mn and S (Figure 4), thus indicating no significant element remobilization due to early-diagenesis. According to the radiometric dating, these sediments were deposited between 1960 and 1990, prior to the designation of the Santoña marshes as Nature Reserve.

4. Conclusions

The main aim of this study was to investigate the fingerprint of the anthropogenic activities in the sedimentary record of the Santoña marshes. The results show an increasing non-steady trend of sedimentation rates over time during the last century. The causes of this change may be related to the progressive loss of the natural area of the estuary, the alteration of its original hydrodynamic conditions, due to infilling and the construction of dykes, the increase in sedimentary load as a consequence of deforestation and demographic growth and the release of urban sewage to the estuary. However, despite the rapid development of the neighbouring villages and the lack of water-treatment plants, the accumulating sediments appear to be relatively free of metal pollution. However, caution is advised, as intriguing enhanced levels of Zn were found below 10 cm depth in one of the studied cores. Although no changes have been detected, the data presented in this work provide information which can be

Fig. 6.- Enrichment factors for Zn, Pb and Cu in cores C and S.

Fig. 6.- Factores de enriquecimiento en Zn, Pb y Cu en los sondeos C y S.



used as reference values for the Santoña marshes against which future geochemical changes may be compared.

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