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Cadmium, manganese, nickel and lead contents in surface sediments of the lower Ulla River and its estuary (northwest Spain)

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ABSTRACT

The authors determined the total contents of cadmium, manganese, nickel and lead in 16 surface sediment samples along the last 7 km of the Ulla River and in its estuary. Prior to chemical analysis, the grain-size fractions below 500, 63 and 2 µm were separated. The metal concentrations were analysed in the fraction below 63 µm, and in selected samples from the clay fraction (< 2 µm). The soil samples were digested with a HF + HNO_3 + HCl mixture and the total concentrations of Cd, Mn, Ni and Pb were analysed with the AAS method. The highest contents of metals were found in the riverine sediments, near the town of Padrón, and in the estuary. The enrichment of metals in the sediments was mainly related to the proximity of the industrial sources, and to the fine particles transported and deposited in the sediments. The Ni and Mn contents found are considered very high, at some points reaching values of up to 357 mg kg^{-1} and 2 110 mg kg^{-1}, respectively. Lead and Cd were mainly found within the range considered as natural background levels in the sediments of the Galician rias, with concentrations of 25-68 mg kg^{-1} for Pb and 0.01-0.92 mg kg^{-1} for Cd. The lower part of the Ulla River and its estuary present: l) moderate to high contamination levels of Mn and Ni; 2) moderate Pb pollution levels; and 3) no Cd contamination. The highest concentrations of metals were obtained in the river, near the wastewater discharges, and in the estuary, associated with fine particles.

Key words: Heavy metals, sediments, ria, estuary, river, Ulla, Galicia.

RESUMEN

Contenidos de cadmio, manganeso, níquel y plomo en sedimentos superficiales del río Ulla y su estuario (noroeste de España)

El contenido total de cadmio, manganeso, níquel y plomo se determinó en 16 muestras de sedimentos superficiales a lo largo de los últimos 7 km del río Ulla y en su estuario. Previamente a los análisis químicos, se realizó la separación granulométrica de los sedimentos en las fracciones inferiores a 500, 63 y 2 µm. La concentración de metales se determinó en la fracción inferior a 63 µm y, para algunas muestras, en la fracción arcilla (< 2 µm). La digestión del sedimento se realizó en una mezcla ácida de HF + HNO_3 *+ HCl y se analizó la concentración total de Cd, Mn, Ni y Pb por espectroscopia de absorción atómica. Los contenidos más altos en metales se encontraron en los sedimentos del río, en las inmediaciones de Padrón y en los del estuario. El enriquecimiento de los sedimentos en metales se ha relacionado con la proximidad a las zonas industriales y con el material fino transportado y depositado en los sedimentos. Se han encontrado contenidos muy altos de Ni y Mn con valores de 357 mg* kg^{-1} *y 2 110 mg* kg^{-1}*, respectivamente. Las concentraciones de Cd y Pb son comparables a los valores establecidos como niveles naturales en los sedimentos de las rías gallegas: 25-68 mg* kg^{-1} *para el Pb y 0.01-0.92 mg* kg^{-1} *para el Cd. El sedimento de la parte baja del río Ulla y* *su estuario presentan niveles moderados-altos de contaminación para Mn y Ni, moderados para Pb y nulos para Cd. Las mayores concentraciones de estos metales en el sedimento fueron medidas asociadas con las fracciones finas (< 63 μm): cerca de Padrón, zona de influencia fluvial y, también, aunque con valores más bajos, en la desembocadura del Ulla, zona de influencia marina.*

***Palabras clave**: Metales pesados, sedimentos, ría, estuario, río, Ulla, Galicia.*

INTRODUCTION

The Galician rias are located in the principal industrialised area of the region of Galicia (northwest Spain), which also has 40 % of its population; therefore they suffer a high risk of contamination. To study this potential pollution, the Ulla River and its estuary, while flow into the Arosa Ria, were selected. The Arosa Ria is one of the largest in Galicia, with a length of 25 km, a surface area of 200 km^2 and a depth of up to 70 m at its mouth. Along its coast, there are major urban centres, which have developed a considerable industry. The Ulla River, 131 km long and with an annual flow of 79 $m^3\ s^{-1}$, represents an extensive drainage area.

During recent years, there has been rising interest in the levels of heavy metals and their distribution, especially in sediments of the Galician rias (Guerrero Pérez, Rodríguez Puente and Jornet Sancho, 1988; Barreiro, Carballeira and Real, 1988, 1994; Carral *et al.,* 1992, 1995; Real Rodríguez, Barreiro Lozano and Carballeira Ocaña, 1993; Marcet, 1994; Belzunce-Segarra *et al.,* 1997a). The aim of the present work is to contribute to a better assessment of the metal pollution levels in the Galician coastal ecosystem. To this end, the total concentration of cadmium, manganese, nickel and lead in the surface sediments of the Ulla River and its estuary were determined.

Cadmium and Pb are scarce in igneous rocks, and their presence in the marine environment is usually related to anthropogenic inputs from the atmosphere and rivers; they are also considered good indicators of coastal environments' pollution level. In the sediments of the Galician rias, the values found for Cd and Pb range from 0.5 to 3 mg kg^{-1} and 25 108 mg kg^{-1}, respectively (Anon., 1987). Manganese is one of the most abundant elements in the igneous rocks, and has a lithogenic origin when, after the weathering of the rocks, it is incorporated into the aquatic system and precipitates as oxides/hydroxides. The main values for Mn recorded in the sediments of Galician rias vary between 93 mg kg^{-1} to 500 mg kg^{-1} (Barreiro, Carballeira and Real, 1994; Belzunce-Segarra *et al.,* 1997a). Regarding Ni, its toxic effects on humans are well known (e.g. dermatitis and respiratory tract cancers) and therefore, its study is a priority. Nickel, which is quite abundant in the Earth's crust, enters surface waters from the dissolution of rocks and soils, from biological cycles, from atmospheric fallout, and especially from industrial processes and waste disposal. At $pH > 6.7$, Ni exists predominantly as insoluble Ni hydroxides (Sunderman and Oskarsson, 1991). The values of Ni estimated in the sediments of the Galician rias range widely, from 10 to 506 mg kg^{-1} (Anon., 1987).

MATERIALS AND METHODS

Sixteen samples of sediments were collected along the lower Ulla River and its estuary. The surface sediment samples were taken with a grab sampler at 16 stations in the area (figure 1). Temperature and salinity were measured *in situ* with a thermometer and Arhen Chemical refractometer.

The grain-size fractions of the sediment samples below 500, 63 and, for selected samples, < 2 μm were separated, and their contents measured. The coarse fraction was dry-sieved with a 500-μm polyethylene sieve. The grain fraction below 63 μm was wet-sieved with a polyethylene sieve. The clay fraction (< 2 μm) was obtained by sedimentation of the bulk samples according to Stokes's law. Prior to sedimentation, the bulk samples were washed free from salt with Milli-Q water. The obtained wet fractions below 63 and 2 μm were dried at 100 °C and their contents were weighed.

The total contents of Cd, Mn, Ni and Pb in the sediment samples were determined following the method proposed by Loring and Rantala (1992):

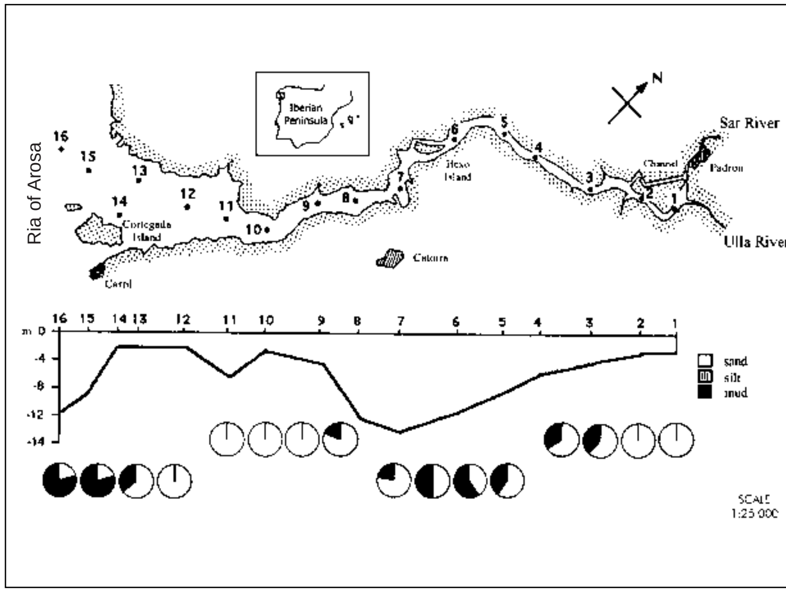

Figure 1. Sampling area and station locations

5 g of sediment was digested in Teflon pumps with a mixture of HF (6 cm^3) and aqua regia (HNO_3:HCl 1:3 v/v, 1 cm^3) at 130 °C for 2 h. The procedure was repeated to assure the complete digestion of the sediments. After cooling, the samples were diluted to 50 cm^3 and 5.6 g of H_3BO_3 was added. The obtained solutions were stored at 4 °C until chemical analysis by flame and graphite furnace atomic absorption spectrometry using an AA Varian Spectra AA BOO Z Plus. Reference material (MESS-1 sediments from the Miramichi River estuary obtained by MacLaren Plansearch Ltd., Dartmouth NS, National Research Council of Canada) were analysed in order to control the efficiency of the analytical procedure.

Table I. Textural composition of the surface sediments: Grain-size fractions content (dry weight %). (Rsd): 5 %

Station	> 500 µm	< 500 µm > 63 µm	< 63 µm > 2 µm	< 2 µm
1	99.6	0.4		
2	99.5	0.5		
3		60.7	33.3	6.0
4		64.3	28.7	7.0
5		60.3	36.5	3.2
6		40.9	48.5	10.6
7		49.2	39.2	11.6
8		77.5	20.9	1.6
9		80.8	12.2	7.0
10		79.0	21.0	
11		65.3	34.7	
12		72.6	27.4	
13		58.2	41.8	
14		64.3	28.3	7.4
15		20.4	67.1	12.5
16		21.5	63.1	15.4

RESULTS

The textural composition of the sediment samples are illustrated in figure l. Table I shows the percentages of the grain-size fractions: coarse sand (> 500 µm), sand (500-63 µm), silt (63-2 µm) and clay (< 2 µm). Coarse material is found at the upper part of the river and at the river mouth. The content of fine sediments composed by mud and black mud increases along the river and towards the sea. In deposition areas (stations 6, 7, 15, 16), the content of the clay fraction in sediments ranges between 10-15 %.

The total content of Cd, Mn, Ni and Pb in surface sediments, as well as their distribution pattern along the low part of the Ulla River and its estuary, are illustrated in table II and figure 2. The highest metal concentrations correspond to Mn and Ni at river station 3, near industrial sources and wastewater discharges, with values of 720 and 357 mg kg^{-1} respectively. An extremely high value of Mn was detected at station l. The concentrations of both metals show a decrease along the river down to its mouth, where the lowest values of Mn and Ni were found: 122-174 mg kg^{-1} for Mn and 7-60 mg kg^{-1} for Ni. On the contrary, an enrichment in the Mn and Ni contents was found in the sediments of the

Table II. Total metal content (mg kg^{-1}) in the surface sediments. (ND): not detected. (Rsd): 5 %

Station	Fraction	Cd	Ni	Pb	Mn
	< 500 µm				
1		nd	8	47.6	2 110
2		0.05	27	37.0	391
10		0.14	8	30.5	261
11		0.06	7	36.9	174
12		0.19	8	25.6	170
13		0.01	60	28.5	122
	< 63 µm				
3		0.03	357	50.9	720
4		0.05	86	47.3	332
5		0.04	68	36.2	336
6		0.09	69	41.6	327
7		0.05	55	29.6	306
8		0.35	75	51.7	269
9		0.09	72	32.7	304
14		0.47	54	39.5	257
15		0.05	63	61.4	212
16		0.06	57	55.3	223
	< 2 µm				
3		0.17	125	60.6	314
9		0.92	42	57.2	204
15		nd	36	68.2	144

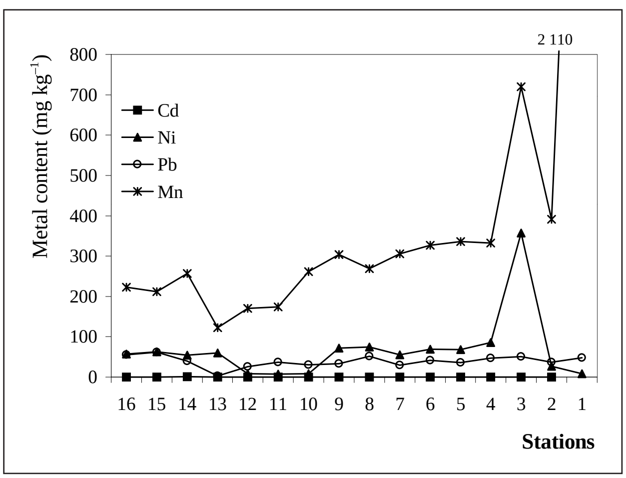

Figure 2. Distributions of Cd, Ni, Pb and Mn along the lower Ulla River

Ulla estuary, with Mn concentrations ranging from 212 to 257 mg kg^{-1}, and Ni concentrations from 54 to 63 mg kg^{-1}. The behaviour observed for Cd and Pb is different. These metals show a homogeneous distribution pattern along the lower river and its estuary (figure 2). Cadmium presents low contents in the sediments, being 0.92 mg kg^{-1} the highest value found, at station 9. The Pb values range from 25.6 to 61.4 mg kg^{-1} (at the estuary). We found that the metal content correlates with the sediments' grain-size distribution. The Pb and Cd concentrations in the clay fraction (< 2 µm) of selected samples (stations 3, 9, 15) was higher than in the silty fraction (63-2 µm) (figure 3). Furthermore, the estuarine sediments at the head of the ria, which have more than 75 % of the fine fraction, presented high Ni and Mn contents.

DISCUSSION

In surface sediments, the highest Mn and Ni content was found in the Ulla River, near the town of Padrón, caused by the wastewater discharges from that area. Thus, these metals, transported by suspended particulates, are mechanically deposited on the bottom sediments after crossing a channel located in the upper section of the river (figure l). Based on salinity data obtained for the Ulla River and its estuary in May 1995, 1 psu for station 1 and 24 psu for station 4 (Belzunce-Segarra, Helios-Rybicka and Prego, 1997b), it can be assumed that a change in the pH at the upper part of the river could cause the precipitation of Mn and Ni associated with and transported by particulate material (Förstner, 1989).

In riverine sediments, a decrease in metals content towards the Atlantic Ocean is the result of increasing the distance from industrial sources and the sandy fraction of the bottom sediments. In the estuarine sediments (samples 14, 15, 16), the observed increase of metals content is due to polluted fine materials which are incorporated into the sediments when they reach the estuarine systems (Turekian, 1977; Hunter, 1983)

Cadmium and Pb present conservative behaviour throughout the studied area. As noted previously by several authors (Luoma and Bryan, 1981; Tessier, Rapin and Cariganan, 1985), Cd and Pb are adsorbed in the fine particles of the sediments, showing a positive correlation with the clay fraction (figure 3), which indicates a natural origin of these metals, mainly detrital inputs from soils and weathered rocks. Furthermore, Cd and Pb were found in concentrations comparable with the natural metal levels given for granite (Carral *et al.*, 1995), schists (Turekian and Wedepohl, 1961) and sub-recent Rhine sediments (Förstner and Müller, 1974).

Carral *et al.* (1992) have established the background levels of metals in sediments of the Galician rias, which are given in table III. Based on

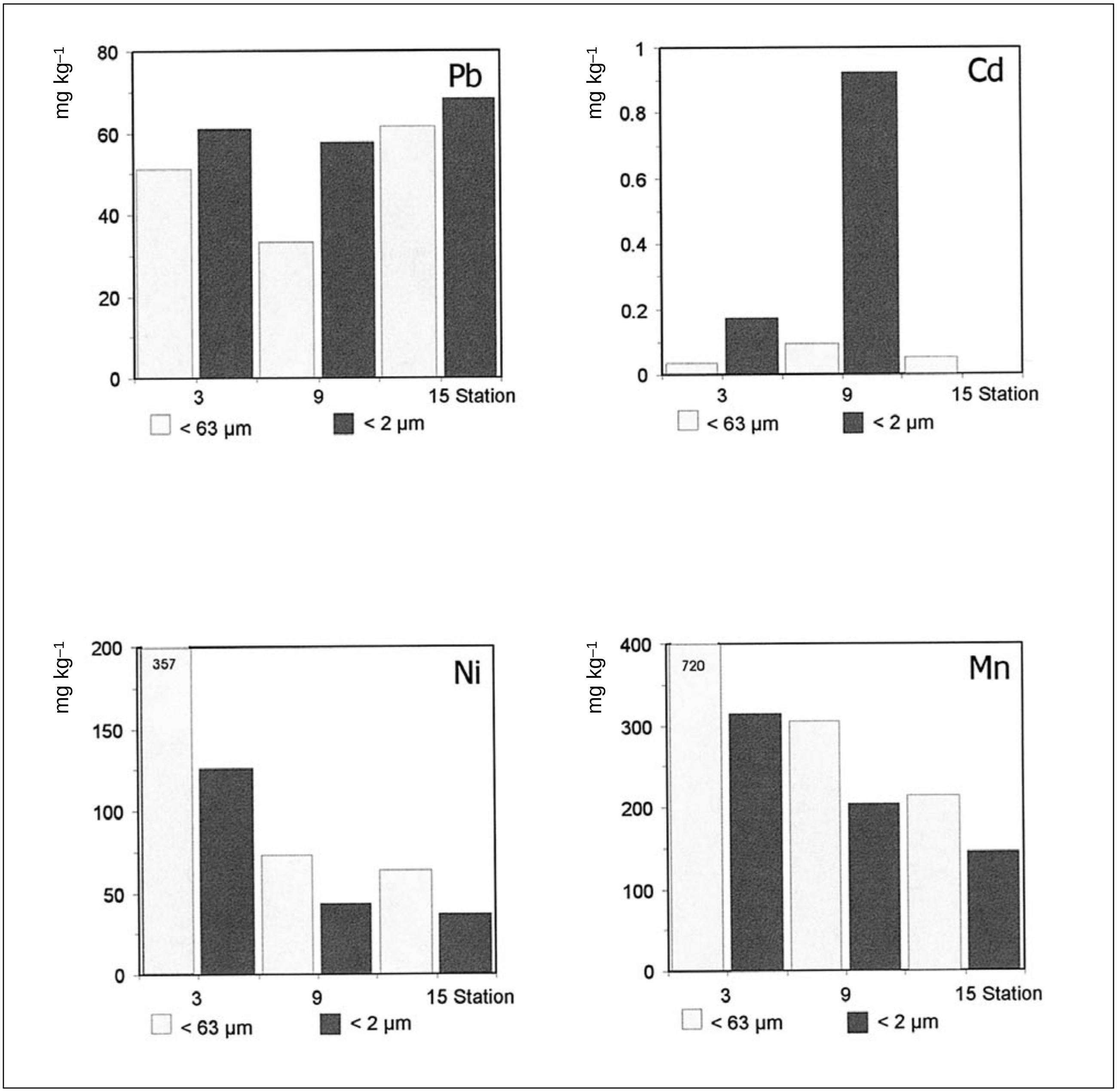

Figure 3. Content of Cd, Ni, Pb and Mn in the fine fractions (< 63 μm and < 2 μm) of the surface sediments at stations 3, 9 and 15

Table III. Background concentrations (ppm) of heavy metals in sediments of the Galician rias. (*): Average value from background given for shale and clays (Turekian and Wedepohl, 1961), river sediments (Förstner and Müller, 1974), lacustrine sediments (Förstner, 1978) and soils (Ure and Berrow, 1982)

Metal	Barreiro (1991)	Carral *et al.* (1992)	
Ni	30	31	
Pb	25	43	
Mn	225		
Cd			0.38*

these data, Carral *et al.* (1992) have calculated the enrichment factors (EF) of metals in the Galician rias and have defined four levels of contamination:

1) low or null (EF < 1)
2) mild (EF > 1 < 3)
3) high (EF > 3 < 6)
4) very high (EF > 6)

According to these authors and based on the EF values obtained for the metals studied, we found that:

– Mn and Ni generally presented mild contamination indices, with EF varying between 1 to 1.50 for Mn and 1.80 to 2.50 for Ni. Sandy sediments had no Mn pollution. However, near the industrial area, Mn and Ni were found at high and very high pollution levels
– Pb was classified in the mild pollution level at the upper part of the river and in the estuarine fine sediments (EF: 1.09-1.41)
– In the case of Cd, no contamination levels were found whose EF values were < l. However, at stations 8 and 14, the presence of a clay fraction explains the higher contribution of Cd

In summary, the lower Ulla River and its estuary present:

- moderate to high contamination levels of Mn and Ni
- moderate Pb pollution levels
- no Cd contamination

The highest concentrations of metals were obtained in the river, near the wastewater discharges, and in the estuary, associated with fine particles.

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