ASSESSMENT OF METALS IN SEDIMENTS IN A TRIBUTARY OF GUADALQUIVIR RIVER (SPAIN). HEAVY METAL PARTITIONING AND RELATION BETWEEN THE WATER AND SEDIMENT SYSTEM

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Abstract. A physical-chemical characterisation of the sediments of the Guadaira River in Southwest Spain has been carried out, determining twenty-three parameters per sample. Non-treated urban sewage and industrial wastewaters from olive oil and table olives affect this river. The factor analysis of the data shows high organic matter contents with metallic pollution. Consequently, points downstream stand out because of very high organic and metallic pollution (Zn, Pb, Cr, Cu and Cd, in order of abundance, showing concentrations in sediments ranging from 50–7500 times those of waters). Heavy metals partitioning studies can be a good approach to show the real activity of these metals in the aquatic environment. We applied Tessier's analytical sequential extraction scheme to sediments. Sediments would be in general mildly hazardous because we found low levels of easily interchangeable metals in the first fraction. Nevertheless, that is not the case in the river's last stretch, precisely where sediments are most abundant, the heavy metal levels largest and dredgings are made periodically. Here, their disposal is of concern; since the actual use of these sediments as organic amendment for agricultural soils is unacceptable. Interaction between waters and sediments in the riverbed by means of correlation, factor and cluster analysis on waters and sediments data, was investigated. With this approach we concluded that in the final stretch there is a problem of contamination of both, sediments and waters. However, in the middle course only sediments are actually polluted. This corresponds to the previous research, when the situation of waters in this zone was even worse.

Keywords: analysis of river sediments, cluster analysis, correlation analysis, factor analysis, Guadaira River, metal partitioning, water-sediment interaction

1. Introduction

Pollution in river waters goes together with pollution of riverbeds, as a consequence of suspended solids sedimentation and fixation over these sediments of various pollutants. Thus, the organic or clay-like sludges that accumulate on the riverbed specially favour fixation to heavy metals, so sediments usually function as a trap, which removes some pollution from waters. In this way, sediment composition can indicate chemical forms that after dumping do not remain soluble in waters.

On the other hand, sediments can also act as a contamination source under other conditions, such as the appearance of strong currents, dredgings, the presence of

chelating agents, changes of pH, potential redox or salinity, etc. Then pollutants accumulated in sediments can return to waters in suspended or dissolved form. Therefore, they represent a potential risk for an aquatic environment and any water study ought to include an analysis of the sediment water comes into contact with.

Many works about heavy metals in sediments (Förstner and Wittmann, 1983; Salomons and Förstner, 1984; Birch *et al.*, 1996) refer to the overall metal concentration. These studies imply that all the existing forms of a metal in sediments have the same environmental effect and the same possibility of being extracted by waters, which is a long way from being true. Therefore, trace metals extraction studies gained in importance until 1990 (Samanidou and Fytyanos, 1987; Rauret *et al.*, 1988; Pardo *et al.*, 1990), on the basis of potential metals leaching, transport and bioavailability. Direct determination of specific sediment-trace metal associations is difficult, if not impossible, due to the great variety of solid phases that can bind trace metals, their amorphous character, and the low contents of metals involved. The partitioning of metals by a sequential extraction procedure is an alternative. Although the distribution of a metal does not reflect necessarily the association with discrete sediment phases, it can define the availability of some chemical entities by the analytical scheme itself. In this simple approach, the metals are analysed in-groups after a chemical scheme. There are several studies about sample integrity after sampling and during analysis. In order to guarantee accurate representation of the concomitant groups, it is necessary to take some experimental precautions (Thompson *et al.*, 1980; Saeki *et al.*, 1993). In this work we use the Tessier scheme considered as the most general (Tessier *et al.*, 1979) with recommended precautions for sample preservation and manipulations procedures to prevent exposure to atmospheric oxygen.

The sediments of the Guadaira River are studied in this work for the first time, implementing a former study method for waters (Enguix *et al.*, 1993). In the present paper, we establish the physical-chemical properties of the sediments and the availability to the environment of their trace metals. The interest of this work is to present the impact of very specific human activities on the sediment quality of a river in Southwest Spain in two clear recognisable areas. The first area is the upper and middle basin, with natural lands, agriculture and many olive industries, and the second is the lower basin, under the influence of important industrialised towns. An aim is also to know the interaction between waters and sediments by applying multivariate statistical analysis to waters and sediments data jointly. This approach demonstrated value for interpretation of pollution sources. This study also interfaces with policymakers involved at present with a Restoration plan in Guadaira's basin and specifically with the assessment for the potential environmental problems in the use of sediments for soil amendment.
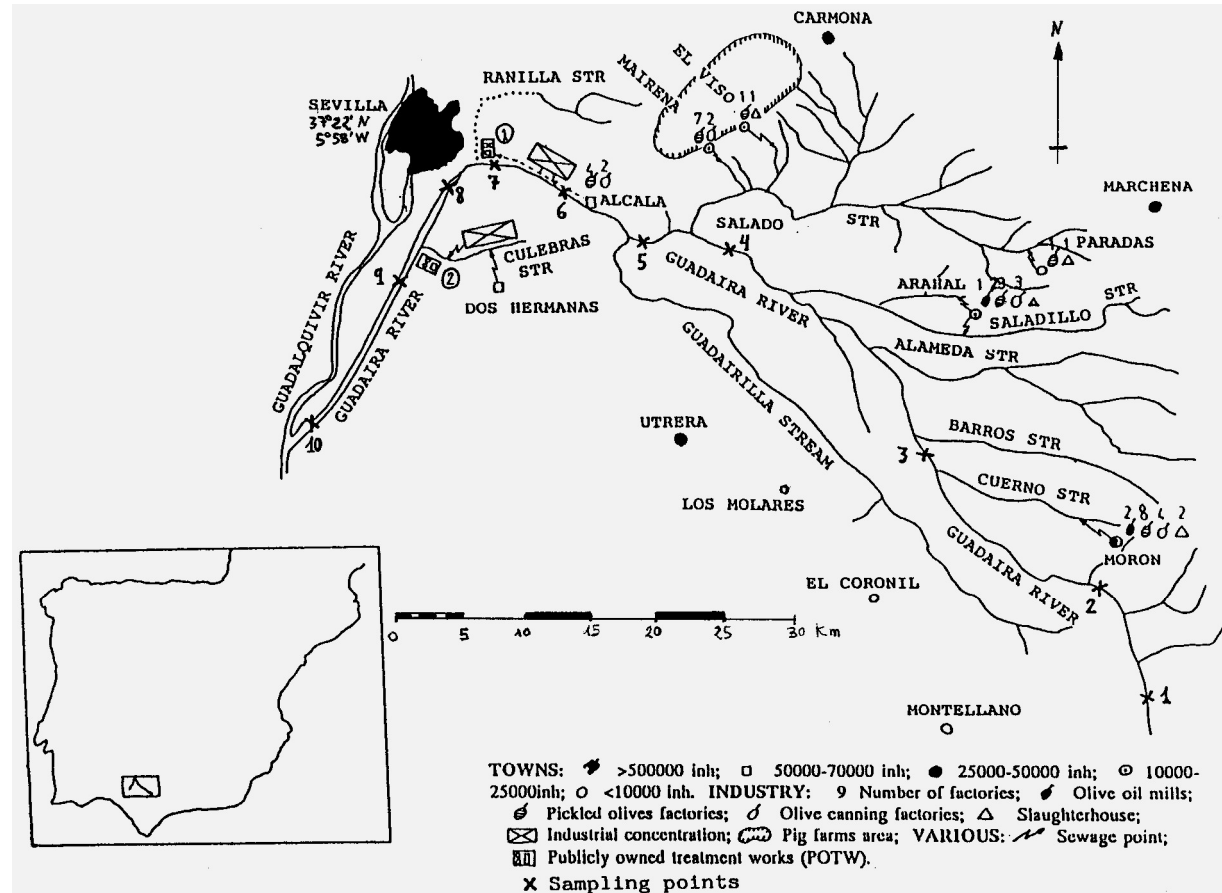
Figure 1. Map of the area with sampling points, human activities, effluents and discharge types.

TABLE I

General characterisitics of surface sediment samples taken from Guadaira river

Sampling site	pH	EC[a] (mS cm^{-1})	Carbonate (%)	OC[b] (%)	Grain size distribution		
					clay (%)	silt (%)	sand (%)
1	7.9	1.40	26.3	1.63	36.3	11.7	52.1
2	8.0	2.07	47.1	1.65	61.4	21.2	17.7
3	7.7	2.01	24.4	1.62	34.6	4.7	60.9
4	7.8	1.75	48.8	1.58	39.4	10.1	50.0
5	7.7	2.13	42.0	1.76	63.2	11.0	26.3
6	7.7	1.57	27.8	0.43	34.3	4.3	61.5
7	7.5	2.56	26.0	2.02	55.8	38.3	10.4
8	7.0	2.66	19.7	13.10	77.7	17.8	5.2
9	7.0	2.17	27.5	16.60	67.5	22.0	10.5
10	7.6	1.83	30.5	0.34	60.9	12.8	25.2

[a] Electrical conductivity.
[b] Organic carbon.

2. Materials and Methods

Ten sampling sites of sediment in the main river course were chosen (Figure 1). Water samples from the same points were also collected. In a previous study (Enguix *et al.*, 1993) using a 30 point network, waters were analysed for two years to gain a better idea about the environmental situation in the basin. A single field collection of sediment and water samples was carried out in February 1993. All the parameters considered for sediments and the main of waters (among the 30 analysed samples) appear in Tables I and II.

Sampling and analysis of sediments were done using standard methods (ASA-SSSA, 1982). Surface sediment grab samples were taken (0–10 cm). After sampling, samples were quickly packed in a propylene flask (about 1.5–2 kg in dry weight), hermetically closed and frozen as soon as they reached the laboratory. Subsamples were de-frozen, dried at ambient temperature and a fraction <2 mm was separated by sieving to determine granulommetry (Day, 1965) and total metal contents. Sample digestions for total metals determinations were performed using the method of Bello *et al.* (1994).

Referring to the partitioning of trace metals in sediments, we followed the sequential scheme of Tessier (Tessier *et al.*, 1979). Five fractions are obtained. These fractions related to metal leaching from sediments by successive extractants simulating stronger chemical conditions. These fractions can be operationally defined and obtained as indicated below:

TABLE II

Intervals values and average values of the parameters analyzed in sediments and waters of the Guadaira river

Parameter	Sediments		Waters	
	Interval	Average value	Interval	Average value
pH	7.0–8.0	7.6	7.2–7.8	7.5
Conductivity	1401–2664	2017 (μS cm^{-1})	2090–5720	3088 (μS cm^{-1})
Dampness at 105 °C	0.9–4.5	2.5 (%)	–	–
Losses at 500 °C	2.1–20.0	6.8 (%)	–	–
Losses at 800 °C	11.6–24.4	16.9 (%)	–	–
Carbonates	19.7–48.8	32.0 (%)	–	–
Bicarbonates	–	–	154–344	248 (mg L^{-1})
Sulphates	0.08–1.92	0.48 (%)	53–579	171 (mg L^{-1})
COD (chemical oxygen demand)	–	–	7–392	127 (mg L^{-1})
BOD$_5$ (biological oxygen demand)	–	–	2–362	82 (mg L^{-1})
Organic carbon	0.34-16.60	4.07 (%)	–	–
Ammonium	2.2–218.7	42.7 (mg kg^{-1})	0.1–19.0	8.2 (mg L^{-1})
Nitrites	0.00-19.22	4.31 (mg kg^{-1})	0.01–0.73	0.14 (mg L^{-1})
Nitrates	0.01–2.06	0.34 (mg kg^{-1})	0.1–17.1	5.6 (mg L^{-1})
Total Kjeldahl N	715–6548	2060 (mg kg^{-1})	–	–
Total phosphorous	653–5757	1861 (mg kg^{-1})	0.1–9.4	5.0 (mg L^{-1})
Iron	11.14–33.71	20.21 (g kg^{-1})	0.06–0.40	0.21 (mg L^{-1})
Aluminium	101.3–50.4	72.3 (g kg^{-1})	0.05–1.44	0.14 (mg L^{-1})
Manganese	27.4–754.2	336.0 (mg kg^{-1})	0.109–0.276	0.156 (mg L^{-1})
Zinc	43.1-1033.0	233.6 (mg kg^{-1})	0.02–0.19	0.04 (mg L^{-1})
Lead	15.8–388.7	68.9 (mg kg^{-1})	0.036–0.0205	0.0081 (mg L^{-1})
Chromium	17.0–188.8	64.1 (mg kg^{-1})	0.0–0.05	0.02 (mg L^{-1})
Copper	13.9-142.6	43.2 (mg kg^{-1})	0.01–0.02	0.01 (mg L^{-1})
Nickel	18.1–46.7	32.1 (mg kg^{-1})	0.001–0.021	0.007 (mg L^{-1})
Cadmium	2.0–9.1	3.7 (mg kg^{-1})	0.00	0.0006 (mg L^{-1})
Arsenic	0.7–5.2	1.9 (mg kg^{-1})	0.0001–0.0033	0.0019 (mg L^{-1})
Mercury	0.0–0.059	0.014 (mg kg^{-1})	0.0005–0.0020	0.00 (mg L^{-1})

– Interchangeable metal (FI) (treating sediment with 50 mL of Mg$_2$Cl 1 M and agitation during 60 min at room temperature).

– Metal linked to carbonates (FII) (treating the beforehand residue with 25 mL of acetic acid 0.11 M with agitation during 60 min at room temperature).

- Metal linked to iron and manganese oxide (FIII)(extract the residue agitating with 25 mL of hydroxylammonium chloride 0.1 M in acetic acid 25% (v/v) during 2 hr at 96 °C).
- Metal bound to organic matter and sulphides (FIV) (adding 25 mL of HNO_3 0.02 M and 15 mL of 30% (v/v) H_2O_2, heating at 85 °C under agitation for 2 hr).
- Residual metal (FV) (treat with 10 mL of concentrated HF, 15 mL of concentrated HNO_3 and 1 mL of concentrated $HClO_4$ in a teflon vessel. Heat for 5 hr at 140 °C on a stove).

Tessier's scheme was applied directly on duplicates of defrozen samples (wet subsamples of about 1 g on dry basis) taking into account the precautions proposed by Rapin *et al.* (1986). Thus, the samples were manipulated throughout under oxygen-free conditions to suppress the anoxic character of sediments. The extracting solutions were previously deaerated by N_2 gas bubbling, shakings and centrifugations as fractions I to IV were made under N_2 atmosphere. The centrifugal tubes were closed with a rubber stopper with small connecting tubes to withdraw the air in the upper part of the tube with N_2 and to remove through them the supernatants. Immediately after this, the residue from the previous step is added through the connections with the next extracting solution.

Metals concentrations in the whole sample and the lechates were determined by hydride generation (As) and flame atomic absorption spectrometry, when concentrations were close to detection limits Graphite Furnace atomic absorption was used (PERKIN ELMER 2380 spectrometer and HGA programmer-300). The analysis procedures have been validated by estuarine sediment certified sample (CRM 277).

Conventional and multivariate statistical techniques for data treatment were used, such as correlation between parameters, Factor Analysis (Principal Components Analysis followed by varimax rotation) and Cluster Analysis (Single linkage of nearest neighbour) for both variables and cases. Water data (Enguix, 1995) and sediment data (present work) were submitted to the aforementioned statistical techniques in the waters-sediments interaction study. We considered the average results of seven samplings of river water (taken from 1990–1993) and one sample of sediment (taken in February 1993). The water average values were considered more representative because they are less sensitive to actual pluviometry. The statistical studies were performed by means of a set of computer programs (CCSS-Statsoft version 3.1, Statsoft Tulsa, Oklahoma).

3. Area Description

Guadaira River is one of the last tributaries of the Guadalquivir River from its east (Figure 1). Its length is 130 km and the extension of its drainage basin is about 1360 km^2 with a population density of 150 inh km^{-2}. On its banks, Sevilla, Dos

Hermanas and Alcalá de Guadaira are the largest populated towns and the most industrialised areas in the basin. There are many medium size factories on their outskirts, which imply potential sources of pollutants: cement, building materials, glass, pottery, painting, chemicals and especially food and drink processing industries. Along its middle and upper basin are another six main towns with an economy based mainly on agriculture and farming. Here, the river has been traditionally polluted with alpechines (olive-oil mill effluents), and other effluents from a very specific industry in the Guadaira basin: that is a pickled olives factory (including its canning). Nevertheless, the pollution caused by sewage waters from all towns in the basin is even worse than industrial pollutants (Enguix, 1995).

The Guadaira River system is mainly made up of little streams originated by superficial run-off, that generally only run in the rainy season. In the upper (sampling points Nos. 1–3) and middle (Nos. 4–6) basin the Guadaira River has noticeable ecological and landscape values despite the present pollution, remarkable by a gallery forest along it. In the lower basin (Nos. 7–10) the river is channelized until it empties into Guadalquivir estuary (the marine flood enters the Guadaira River's last stretch). This 22 km long channel must be dredged completely every ten years due to the large amount of sediments that form an artificial swampy area across which waters flow very slowly. The sediment disposal is of great concern, because agricultural destination is prefered.

In summer or periods of persistent draught, it can be said that the Guadaira River is made up almost entirely of sewage waters (river flow of 2 m^3 s^{-1}). It can be described in several spots as a real outdoor sewer with foams. Stinking water problems are common in the area. In fact, the painful situation of the Guadaira River has often been published in the press.

4. Results and Discussion

The inclusion of all considered analytical results is not considered necessary. Table I shows the most general characteristics of all sediment samples. Nevertheless, the most relevant individual results of sediments (referred to dry weight of sediment) will be commented. Average values and intervals of studied parameters are shown in Table II to give a global idea of the Guadaira's waters (Enguix *et al*., 1993) and sediments.

4.1. GENERAL CHARACTERISTICS OF SEDIMENTS

Samples 1, 3, 4 and 6 have sandy/clay-like textures, and the others are predominantly clay-like, especially 7–10. Samples 8 and 9 stand out by extremely rich organic matter (Table I).

The conductivity of sediments is, in general, high and pH is close to 7.7 except for samples 8 and 9 (Table I).

The organic carbon contents reach the highest values in points 8 and 9 (13.1 and 16.6% respectively), and these samples had a lower pH (about 7) and higher dampness (about 4.2% w/w). In these two points, phosphorus, ammonium and total nitrogen readings are especially high. Elevated values for ammonium in sediments (average 42.7 mg L^{-1}) reveal organic pollution caused by sewages in practically the whole river, especially for point Nos. 3, 6, 8 and above all for point 9 (42, 36, 62 and 220 mg L^{-1} of NH_4^+, respectively).

The high result for sulphate in the source of the Guadaira River (No. 1) points out the presence of gypsum ground in the area. With regards to the carbonate contents, the high values in points 2, 4 and 5 stand out (>42%).

Therefore, the pollution in Guadaira's sediments is mainly organic, increasing downwards because of the degradation of the waters, stagnation and abundant sedimentation of the waterborne particles.

On the basis of water and sediment data, in agreement with suspected pollution sources, we conclude that the pollution can be described in the following way. The high contents of sulphate, calcium and magnesium and secondarily of chloride and sodium at the river source, show the natural influence of gypsum and saline grounds. After the initial impact of some tributaries with olive related and urban wastewaters, the river becomes polluted. The river recovers partially by self-depuration at the middle basin (Nos. 4–6); yet, this does not happen in the lower basin in a similar way after the last discharges (POTWs and Las Culebras Stream) from which point the Guadaira River literally becomes a sewer (Nos. 7–10).

4.2. POLLUTION LEVELS AND PARTITIONING OF HEAVY METALS

Table III presents the natural background contents of heavy metals for the Guadaira and other two rivers in the nearby area in order to have a reference. In Table III the maximum enrichment factors (EF) of heavy metals in sediments are also reported. EFs have been calculated normalizing them with respect to Al to make data comparable (enrichment factor = $[X_i]/[Al_i]$: $[X_o]/[Al_o]$; where $[X_i]$ and $[X_o]$ are the concentrations of a metal at a point and the first one, considering this sample as background).

In our study, we found low trace metal contents in the Guadira's sediment according to the sparse metal-based industries or the lack of mining activities in the basin (Figure 1). Exceptionally high concentrations are located, however, in the lower river (points 7, 8 and 9), which presents EFs up to 18 for Pb and Zn, about 5 for Cu and Cr and 2 for Cd and As (see Table III). The Guadaira's situation is between that of the Tinto river (example of one crossing a rich calcopyritic metallogenic region) and the Guadalete (example of a less polluted one). Although the Guadaira sometimes shows higher EF than Tinto, it does not reach the pollution of the latter. The Tinto river just flows through an important mining area and starts from a higher background.

TABLE III

Heavy metals background levels and maximum enrichment factors (EF) for Guadaira sediments and other two rivers in the near zone

	Al	Fe	Mn	Zn	Pb	Cr	Cu	Ni	Cd	As
	(g kg^{-1})					(mg kg^{-1})				
Guadaira river										
Background	91	25	477	51	20	38	25	37	3.0	2.0
EF	–	1.6	1.9	18	17	4.7	5.0	1.3	2.7	1.5
Guadalete river[a]										
Background	34	18	316	53	11	–	22	31	0.4	–
EF	–	2.0	1.9	0.8	1.0	1.1	2.3	2.1	4.0	–
Tinto river[b]										
Background	0.6	105	58	250	1400	11	221	18	2.1	605
EF	–	0.9	5.3	3.3	10	3.7	23	1.0	2.8	6.2

EF = Enrichment factor for the metal along the river bed in relation to source.
[a] Adapted from Pinto *et al*., 1996.
[b] Adapted from Campos *et al*., 1990.

Metals fixation in sediment by the abundant clayey materials, organic matter, phosphate and sulphides present in the Guadaira's lower stretch, dominated by an anaerobic ambient, is considerable. Metal fixation from the upstream sewage effluents will preferably take place in point No. 8. Sediment here reaches the maximum pollution due to the most favourable conditions (Clay >75% and organic carbon 13.1%). Also, point No. 8 picks up the old contamination from Alcalá before the treatment of urban and industrial effluents of this important town began in 1987. The trace metal content in point No. 7 is somewhat less, being now mainly manganese and iron oxides as well as carbonate, responsible for fixation. The following leaching study supports this conclusion. Point No. 7 represents a transition between the oxidative settlement of some metal traces that dominates in the midbasin and the reductive one at the lower stretch. This oxidative mechanism of fixation competes for this stretch with the solving ability of alpechines (olive oil liquid wastes) present in waters during the manufacturing season, which can solubilize them from sediments (Bejarano and Madrid, 1995). Alpechines show pH values 4.2–5.2, with 0.7–4.0% polialcohols and/or polyphenols, and 0.2–1.0% policarboxylic organic acids. The latter ones act as the main complexing agents of these liquid discharges. The much lower heavy metals concentrations in sediments

Nos. 3, 4, 5 and 6 are, despite less industrialization of the area, presumably due to this action of alpechines.

Metal speciation in sediments was performed following Tessier's sequential scheme. The values for each metal in each fraction of the partitioning scheme reflect its distribution in the different sediment chemical phases. We have not considered appropriate, due to lack of room, the inclusion here of all results of this partitioning study. In order to give a global idea of the ten sediment samples, only average values of total metal contents and metal percentages in each fraction are displayed in Figure 2.

The metal fraction FI in sediment corresponds to metals species with the highest trend to leach and thus most hazardous. The values found for this fraction in almost all the points are low, except for manganese (the most abundant trace metal in this fraction, mean >15 mg kg^{-1}, 5%); also zinc (20 mg kg^{-1}) and cadmium (0.2 mg kg^{-1}) stand out in FI at point No. 8. If we consider the sum of fractions FII and FIII (metals that can be released when changing waters pH or potential redox), the greatest risks due to higher toxicity and percentages on the total content are showed by lead (mean 30 mg kg^{-1}, 63%) and by cadmium (mean 2.2 mg kg^{-1}, 63%) and in less extent arsenic (0.9 mg kg^{-1}, 30%). In Point No. 7, high contents in FII + FIII (Mn 70%, Pb 67%, Cd 51%, Zn 49%, As 42% and Ni 34%) indicate that here the fixation by carbonates and oxides prevails.

The highest values of metal virtually bound to organic matter or sulphide (FIV) are found in most of cases, at points 8 and 9 (relative amounts about 70, 52, 50 and 50% for Cu, Cr, Pb and As, respectively), where sulphides, organic and clay contents are the most abundant. This metal fixation in sediments is typical for a reductive ambient dominated by sewage waters. The residual fraction (FV), obtained after the overall sediment extraction, logically the most inert one, presents the lowest average proportions for manganese, lead and cadmium (17.1, 20.3 and 31.1%, respectively). Therefore, this reflects certain remobilization danger under favourable conditions (especially in points No. 9 and even more No. 8), which could be a serious problem because of Pb and Cd toxicity. Even more, the danger is worse because sediment dredgings at these points are used for agricultural soil amendments.

5. Statistical Analysis for Sediments

5.1. Correlation between analysed parameters

The correlation matrix of the different variables has allowed us to verify that there is very high negative correlation between pH and dampness at 105 °C, losses at 500 °C, organic carbon, ammonium, total phosphorous, nickel, chromium, copper, zinc, lead and cadmium, which consequently are strong correlated among themselves. The conductivity is specially linked to dampness at 105 °C. High
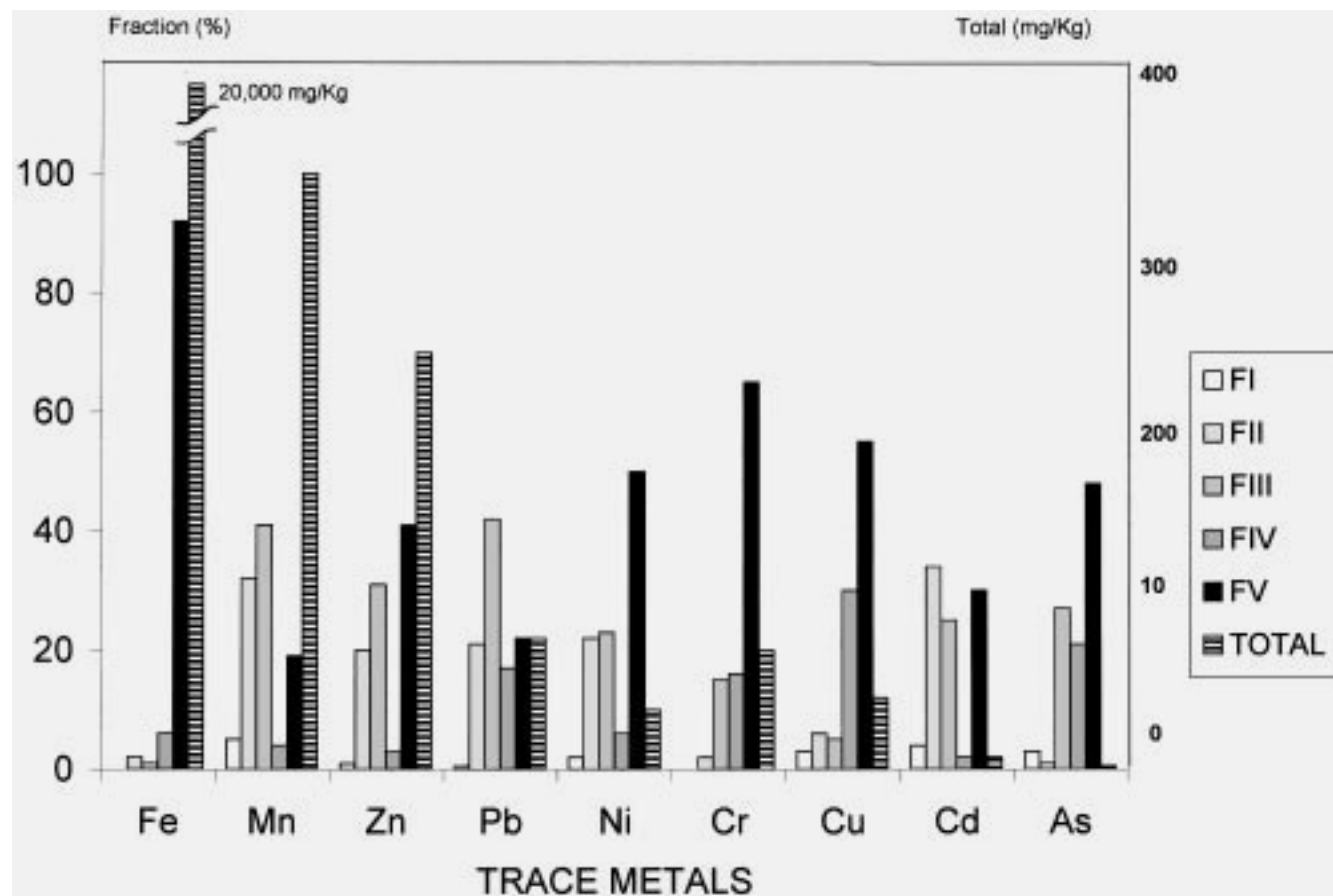
Figure 2. Average values for the partitioning (%) and for total contents (mg kg^{-1}) of metals in sediments.

TABLE IV

Factor analysis of the analyzed parameters for sediments and for the waters-sediment study

Factors	Selected variables (loadings $\geq$ 0.5)	Explained variance (%)
Study of sediments		
F1S (sediments)	[a] dampness at 105 °C, losses at 500 °C, organic carbon, ammonium, total nitrogen, total phosphorous, chromium, copper, zinc, lead and cadmium [b] pH	53.6
F2S (sediments)	[a] iron, manganese and arsenic	15.4
F3S (sediments)	[a] losses a 800 °C and carbonates	10.9
F4S (sediments)	[a] sulphates	6.6
Total		86.5
Study of waters-sediments		
F1WS (sediments)	[a] copper, lead, nickel, chromium, zinc, cadmium, conductivity, dampness at 105 °C, organic carbon, ammonium, total nitrogen and total phosphorous	35.9
F2WS (waters)	[a] dry residue, sulphates, calcium, magnesium, lithium, copper and dissolved oxygen [b] silica, potassium, bicarbonates, arsenic, colour, total phosphorous and ammonium	18.4
F3WS (waters)	[a] solids suspended, colour, COD, BOD, lead, cadmium, zinc, chromium, antimonium, sulphides and detergents	14.3
F4WS (waters)	[a] iron, aluminium and nickel	11.3
F5WS (waters)	[a] chlorides, sodium and carbonates	6.9
Total		86.8

[a] Variables positively selected.
[b] Variables negatively selected.

correlations among most of heavy metals can be observed: chromium and nickel (r = 0.99); Cu, Zn, Pb and Cd (r > 0.9); aluminium with iron, manganese, and arsenic (natural oxides)(r > 0.8); and all together (r > 0.7).

5.2. FACTOR AND CLUSTER ANALYSES

The factor analysis led to a reduction of the dimensionality of the matrix data from 23 to 4 significative factors, accounting for 86.5% of the total variance. Factors explaining variance percentage lower than 6% have been rejected. Aiming at interpreting the significance of factors in an easier way, all maps representing variable position vs. factors were obtained. From these maps, we can infer the variables selected by each factor that appear in Table IV (loading >0.5).

Factor F1S can be considered as a factor of both organic and metallic pollution related to waste dumpings made into the river. Factors F2S, F3S and F4S can be considered respectively as representative of the oxides, carbonates and sulphates present in sediments.

The position maps for observations corresponding to all possible pairs of factors, as well as factor profiles along the river (Figure 3) points out the relationship existing among the different sampling sites. These graphs show that sediment quality is similar in most points, standing out mainly in points Nos. 8 and 9 for their high organic and metallic pollution (F1S), point No. 7 for natural oxides (F2S), Nos. 2, 4 and 5 in carbonate (F3S) and No. 1 in sulphate (F4S). The situation in point Nos. 2, 4, 5 and 6 corresponds to the exhaust of the organic carbon as carbonate in the sediment after the river recovery by some aerobic biodegradation that follows to the impact of very polluted tributaries. In the stretch of points 4–6 the stream suffers a good aeration by several old milldams nowadays out of use.

Cluster analysis of variables confirms some conclusions extracted from correlation and factor analysis. For instance, the grouping of parameters that suggests the presence of organic matter and metallic elements (variables selected by factor F1S) or the grouping of the elements related to natural oxides (factor F2S) can be distinguished. The cluster analysis of cases clearly shows the grouping made by sediments 8 and 9, as response to its peculiarities, and a rather uniform situation for other samples.

6. Statistical Analysis for Waters

To obtain global conclusions about waters, we used the same statistical multivariate techniques for water data as above for sediments. Data matrix is composed by the values of water parameters for the same ten sampling points in the river. Water values correspond to the average values of seven samplings (1990–1993) (these data are presented in Enguix (1995)). Results of these analyses are substantially the same as those obtained for one more extent 30 points net including main course and tributaries, which have been already published (Enguix, 1993). Therefore they are not given here, although that study was kept in mind to interpret the relation between waters and contacting sediments. Besides, this relation is undertaken in the following item.

7. Joint Statistical Analysis for Waters and Sediments

A global study of the water-sediment interaction was carried out for the ten selected points with the experimental data of sediments and these ones corresponding to their contacting waters (average values). Correlation, factor and cluster analysis were applied. Results from the different leachable metallic fractions in sediments
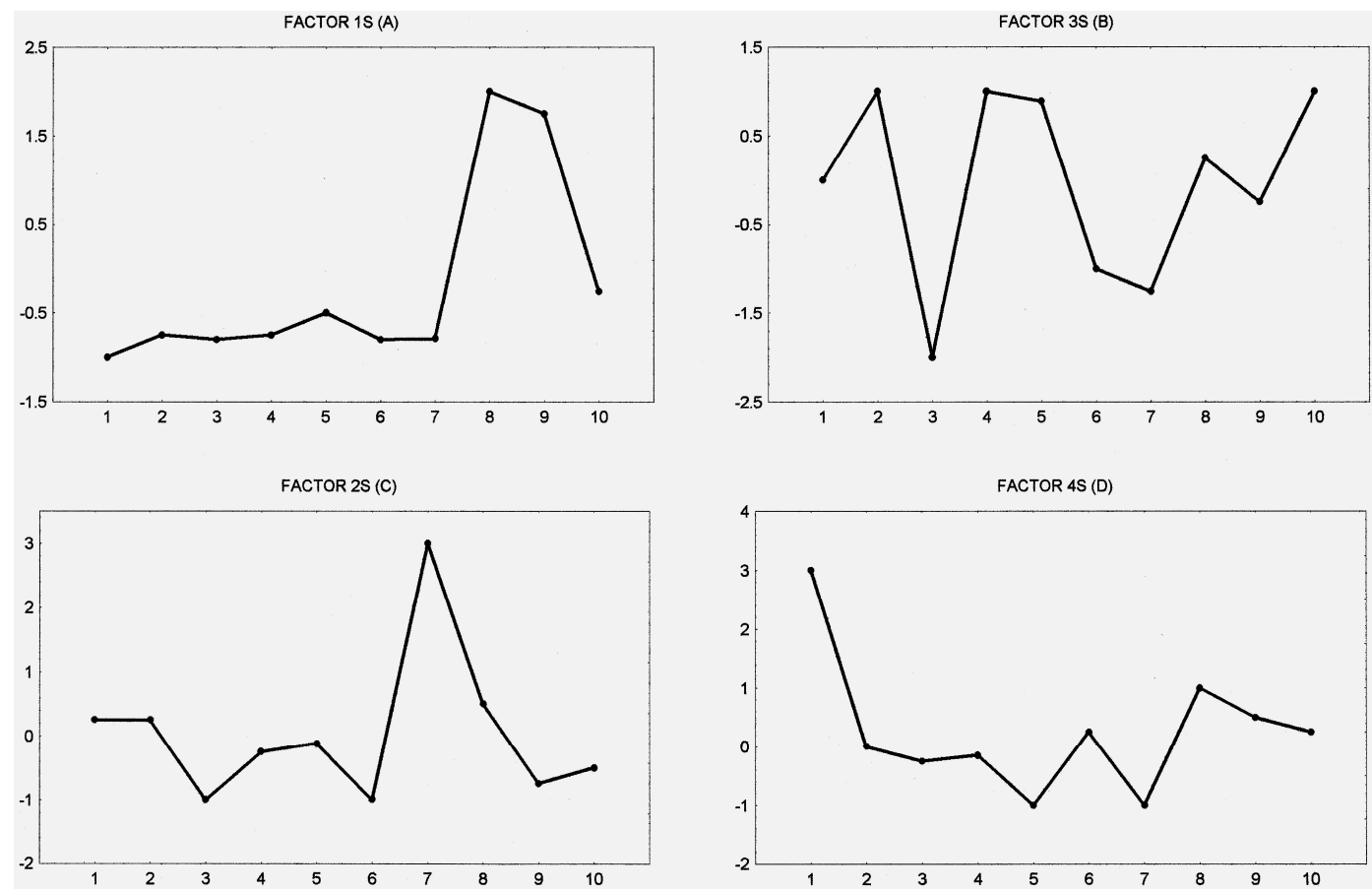
Figure 3. Spatial evolution of the factors in the factor analysis of the sediments.

have been discarded, because that would add unnecessary complexity to the data set and to the interpretation.

7.1. CORRELATION BETWEEN SEDIMENT AND WATER PARAMETERS

According to the correlation matrix, it stands out that ignition losses at 800 °C and carbonates in sediments are negatively correlated with the following parameters of waters: COD, BOD_5, ammonium, phosphates, oils and fats, and others; that is, waters with urban sewage pollution. This is because the points, whose sediments have higher levels of carbonates, correspond to situations where the organic pollution of their waters has been already degraded by oxidation. Likewise, carbonates in sediments correlate well positively with some natural components of the waters: chlorides, bicarbonates, sodium and lithium.

Ammonium in sediments is correlated with water parameters such as colour, COD, BOD_5, oxidability, ammonium, phosphates, sulphates and certain metals, and negatively with pH, dissolved oxygen, redox potential and nitrates. In general, total phosphorus and ammonium in sediments behave in the same way. This points out the permanence in sediments of faecal contamination in river stretches where the stream is steadily polluted. An analogue conclusion is valid also with respect to metals, because the anoxic stretches ease also their retention in sediments with levels up to ten thousand times greater than in waters.

These correlations let us check that a high pollution of some sediments corresponds parallel to a highly polluted stream, clearly with regard to organic matter and sometimes to trace metals. Cd and Pb in waters are well correlated with Cr, Cu and Zn in sediments. This reveals, that although all of them have same sources, Cd and Pb are more leachable from sediments and in fact are present mostly in fraction FII and FIII, while Zn is preferably found in FIII and FIV, and finally Cr and Cu have affinity for fractions FIV and FV (according to the earlier partitioning study in sediments).

7.2. FACTOR AND CLUSTER ANALYSIS APPLIED TO SEDIMENTS AND WATERS RESULTS

Factor analysis applied to the ten sampling sites renders five factors, which explain 86.8% of the total variance (Table IV study of waters-sediments). Maps with variable positions for all different pairs of factors have been evaluated, considering the sediments and/or waters parameters picked up by each of them.

Factor F1WS is the only one related to sediment contamination, by means of organic and metallic components, since it comprises only sediment parameters. Factor F2WS shows waters hardness associated largely with gypsum coming from the southwest of Guadaira's basin, corresponding also to absence of urban or industrial pollution. Factor F3WS represents the stream pollution from urban sewages and Factor F5WS the salinity related now to the predominant natural sodic chlorided chemical facies of river waters. Finally, Factor F4WS, which gathers
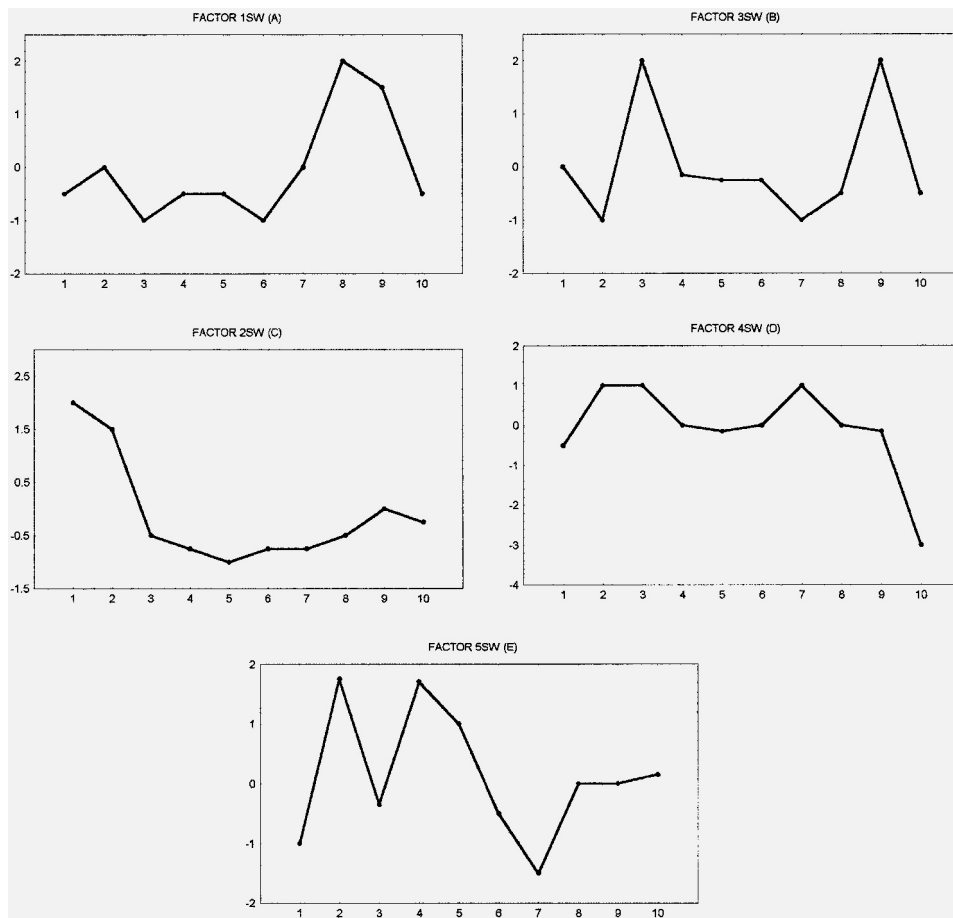
Figure 4. Spatial evolution of the factors in the waters-sediments joint study.

iron, aluminium and nickel in waters, stands out in point 10, maybe because of elemental resolubilization into the stream from the associated sediments under the saline flood influence this site.

In this study position maps of the observations for all possible factor pairs have been represented, although not showed here. Factor variations (scores) along the river are showed in Figure 4. Thus, the sediment pollution in points 8 and 9 are confirmed (F1WS high scores). However it might be emphasised that point No. 8 does not presently show water contamination (F3WS low scores). Point Nos. 1 and 3 have similar characteristics, because of significant hardness in the waters (F2WS high scores), and subsequent lack of pollution in sediments and waters (F1WS low scores). The high pollution level that waters reach at points 3 and 9 (high F3WS values) is consistent with their respective situation after the two most degraded tributaries of Guadaira River. Other sites present some uniform characteristics.
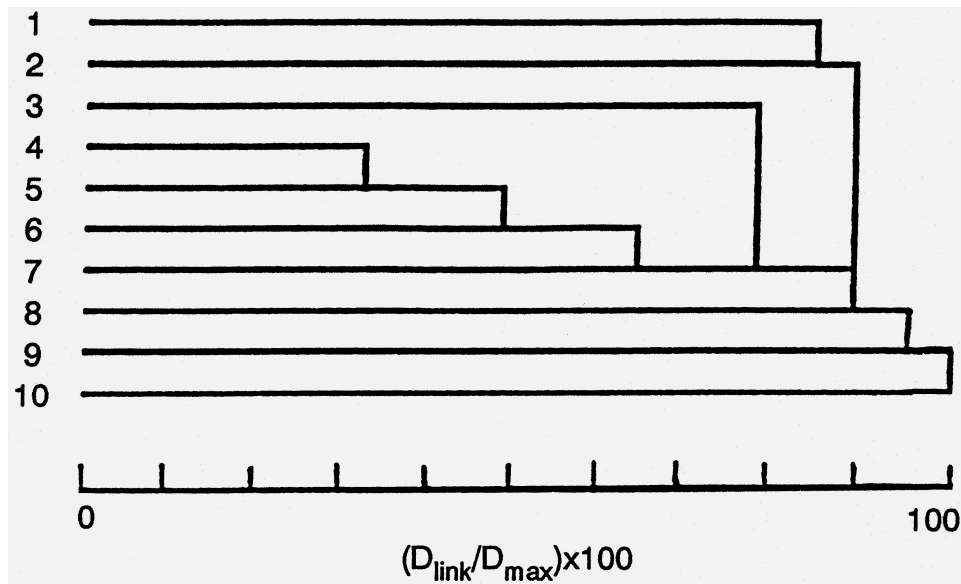
Figure 5. Dendrogram of sampling points obtained from a Cluster analysis on water and sediment data.

The dendrogram, corresponding to the cluster analysis of the cases applied to the waters and sediments, reinforces the factor analysis conclusions (Figure 5). Points 8 and 9, and points 1 and 2 make well-defined clusters because of their respective aforementioned similarities and the remaining points constitute another cluster, except point No. 3 which has a slightly different character because of its water pollution.

8. Conclusions

The methodology applied in this study has proven to be adequate for sediment quality and aquatic pollution assesement of a river in South West Spain. It is at present subjected to a Corrective Plan.

Sediments for points located in the upper basin show salinity (sulphates and chlorides) due to lithological causes. On the other hand, the most polluted sediments are in the river's final stretch, showing high values for many parameters owing to the progressive river degradation.

Heavy metal average levels reveal that sediments according to USEPA disposal criteria (Salomons and Förstner, 1984) are moderately polluted for Cd, Cr, Ni and Cu. The tolerable limits are surpassed for Pb and Zn. River sediments in the final stretch (Nos. 8, 9, 10) have to be dredged periodically and they are used nearby as organic amendment for agricultural soils. Our study reveals that this practice is environmentally unacceptable.

The partitioning study of heavy metals reveals that contents in the first fractions, which are the most hazardous from the environmental point of view, are imperceptible in most of the samples. Lead and cadmium, which present the lowest values in the residual fraction, would represent the highest danger of leaching.

The statistical multivariate analysis applied to the sediments analytical data has led to recognition of points 8 and 9 as the most polluted by organic contamination and secondarily by heavy metals; mainly Zn, Pb, Cr, Cu and Cd, in this order. The presence of a great amount of phosphorus and ammonium in these sediments proclaims their source in sewage waters, but to a lesser extent the influence of industrial wastewaters containing metals can be observed.

The influence of the polluted stream over sediments has been confirmed through a multivariate analysis applied now to both analytical data from sediments and from their contacting waters. This has let us classify the sampling points depending on its analytical characteristics. Points 1 and 2 show a high salinity in waters related to their respective natural sulphated and chlorided facies. They have also a remarkable absence of pollution in waters and sediments. Other points stand out for water pollution (point Nos. 3 and 9), because they directly receive the influence of very polluted streams. Points 7, 8 and 9 show sediment pollution (the water anaerobiosis increases in this order). Point 7 and even more 8 reflect pollution above all in sediment, possibly due to an old contamination before installation of treatment plants in this area, as well as vegetation contributing to settle the suspended matter in the stream. Thus, waters are not so polluted as sediments are. Sediment No. 9 shows the worst situation and reveals that the river flows there permanently with an excessive faecal and, in small measure, industrial contamination. Finally in point No. 10, since it is located in a zone affected by Guadalquivir's estuarine flood, the sediment is frequently removed and does not show the characteristics of the former points 8 and 9.

Acknowledgements

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