HEAVY METAL POLLUTION IN THE GUADAMAR RIVER AND THE GUADALQUIVIR ESTUARY
(SOUTH WEST SPAIN)

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INTRODUCTION

The Guadalquivir river is the most important course of water of South West Spain. Its tributary, the Guadamar river, joins the Guadalquivir near its mouth at Cádiz Gulf in the Spanish South Atlantic coast, just after skirting the marshy part of the Doñana National Park.

The upper Guadamar river receives through its tributary the Agrio river the drainage water from an opencast-worked polymetallic sulphide deposit and the effluents from a plant for the treatment and concentration of mineral. Guadamar river also receives sewages outlets from villages supporting a population of ca. 40000 and diffuse land pollution. Untreated effluents from olive-oil manufacturing mills were also discharged into the river during the first part of the period of this study.

To preserve the Doñana National Park from water pollution, Guadamar river flows between levees in the neighbourhood of the Park, what causes droughts and other problems of ecological significance. However, there exists a project to allow Guadamar river to flood the marshes of the Park again.

Cádiz Gulf is rich in high quality fish and shell-fish and touristic resorts. Also Cádiz Gulf and Guadalquivir estuary are important areas for the development of aquaculture.

The Doñana National Park, the Guadalquivir estuary and the Cádiz Gulf, are very fragile ecosystems which can be greatly altered by inflow of sewage and industrial effluents.

The present paper summarizes the work carried out from 1978 to 1984 on water, sediment, flora and fauna of the Guadamar river and the Guadalquivir estuary.

METHOD AND MATERIALS

Heavy metals were determined in acidified filter water samples by AAS (U. S. EPA, 1979).

Digestion of soil, sediment and plant samples for total metal determinations were carried out by the dry-ashing method described by Ritter *et al.*¹

Available heavy metals in soils and sediments were determined by the DTPA method.²

Digestion of dried samples of marine animal tissues (liver and dorsal muscle) were carried out by the methods described by Ritter *et al.*¹, Lytle and Lytle³ and Salánki *et al.*⁴

RESULTS AND DISCUSSION

During 1978-79 a study on the heavy metal content of Guadamar water was carried out.^{5,6} Several sampling stations were established in order to determine heavy metal pollution originated by the mine industry in its first stage of development. Table I shows that water from stations 1, 3 and 8, beyond the influence of the polymetallic sulphide deposit, had pH values and heavy metal concentrations within the range of the U. S. EPA quality criteria.⁷

Table I.- Mean values of pH and heavy metal concentrations (mg l^{-1}) of water from Agrio, Guadamar and Guadalquivir rivers (1978-79).

Sampling station	Location	Period	pH	Fe	Cu	Mn	Pb	Zn
1	Agrio reservoir (up stream from mine)	wet	7.0	0.23	0.01	0.24	0.01	0.09
		dry	7.2	0.26	0.01	0.03	0.01	0.07
2	Agrio river (1 Km downstream from mine)	wet	3.6	195	17.2	21.6	1.0	114.4
		dry	3.3	253	15.2	29.6	0.5	111.1
3	Guadamar river (up stream from mine)	wet	7.9	0.58	0.03	0.06	0.03	0.28
		dry	7.9	0.53	0.03	0.12	0.04	0.52
5	Guadamar river (13 Km downstream from mine)	wet	7.8	0.15	0.04	0.55	0.04	1.81
		dry	8.0	0.09	0.01	0.25	0.05	0.75
6	Guadamar river (25 Km downstream from mine)	wet	7.8	0.14	0.02	0.48	0.04	1.10
		dry	8.0	0.08	0.01	0.23	0.05	0.25
7	Guadamar river (40 Km downstream from mine)	wet	7.9	0.30	0.02	0.58	0.05	0.24
		dry	8.1	0.06	0.02	0.15	0.07	0.06
8	Guadalquivir river before confluence Guadamar	wet	7.9	0.12	0.01	0.04	0.05	0.04
		dry	8.2	0.08	0.01	0.01	0.04	0.03

Wet period: May-September (reinfull 48.8 mm 1978; 14.0 mm 1979)

Dry period: January-April, October-December (rainfull 368.3 mm 1978; 509.4 mm 1979)

In general, both in wet and dry periods, sampling stations 2, 5, 6 and 7 showed heavy concentrations higher than those in stations 1, 3 and 8, showing the influence of the mine industry.

The oxidation of sulphides causes low pH values and high heavy metal concentrations in station 2. Most heavy metals are precipitated before station 5 as shown by the appearance of hydrous oxide precipitates on the Agrio and Guadamar river beds. Precipitation is mainly caused by the neutralization of water due to the change of soil parent materials from acid to calcareous along the Guadamar river basin, and by dilution of acid mine effluents by water from Agrio reservoir and Guadamar river. Consequently, Fe, Cu and Pb concentrations decrease downstream from station 2 down to levels found in Guadalquivir river. Manganese and Zn concentrations also decrease downstream but in station 7 are still 12 and 6 times respectively those in Guadalquivir river.

Generally in wet periods mean concentrations of heavy metals in water from stations 5, 6 and 7 are higher than expected from the respectively hydrous solubilities.⁸ This fact can be explained by the resuspension of sediments caused by heavy rains and water discharged from Agrio reservoir. The appearance of inorganic and organic complexing agents, especially olive oil manufacturing mill effluents called "alpechines", can alter the normal precipitation-adsorption pathway of deposition of metal into sediments. Alpechines have high content in organic matter (4-12 %, BDO_5 23-33 g l^{-1}) rich in alcoholic and polyphenolic compounds which are active chelating agents.

In laboratory experiments,⁹ it was confirmed that alpechines have high ability to dissolve

and complex heavy metals from sediments. Solid residues from a water sample polluted by alpechines were found to absorb $128 \mu\text{g Cu mg}^{-1}$ from solution. Maximum complexing ability of soluble fraction of alpechines were determined by Zunino *et al.* method ¹⁰, and amounted to 42, 21 and $10 \mu\text{g mg}^{-1}$ for Cu, Zn and Mn respectively.

From 1980 to 1984 the region suffered a severe drought. In the same period the plant for concentration of the mineral started using SO_2 derivatives as floating agents and the metal contents of water greatly increased.

During those years, studies on water, sediments, soils and vegetation of the river banks of Agrio and Guadamar rivers were carried out.¹¹ The trend of the water results (Table II) was very similar to that observed in 1978-79 (Table I), although mean values of pH and metal concentrations in station 5 showed that the pollution had increased respect to 1978-79. This can probably due to the discharge of floating agents composed by thiosalts which acidified water and dissolved metals from sediments.

Table II.- Mean values and ranges of pH and heavy metal concentrations (mg l^{-1}) of water from Agrio and Guadamar rivers (1980-84).

Sampling station	Location	Range	pH	Fe	Cu	Mn	Pb	Zn
2	Agrio river (1 Km downstream from mine)	Mean	4.4	50.2	5.03	11.6	0.21	34.1
		Min	3.3	13.0	0.08	1.9	0.10	0.9
		Max	6.1	81.0	19.22	19.0	0.31	78.0
3	Guadamar river (up stream from mine)	Mean	7.7	0.78	0.01	0.10	0.003	0.07
		Min	7.3	0.05	0.00	0.06	0.000	0.04
		Max	8.1	2.00	0.02	0.13	0.005	0.10
4	Guadamar river (6 Km downstream from mine)	Mean	4.4	10.8	1.78	8.9	0.04	14.5
		Min	3.5	0.12	0.08	5.2	0.03	2.8
		Max	5.7	21.2	7.65	19.3	0.05	32.8
5	Guadamar river (13 Km downstream from mine)	Mean	6.1	4.0	1.54	3.3	0.005	7.5
		Min	3.1	0.01	0.02	0.04	0.000	0.05
		Max	7.8	12.6	7.57	10.0	0.016	33.5

Mean concentrations of total and available heavy metals in sediments and soils from stations 2, 4 and 5 were higher than those in the reference station 3 (Table III). Mean values of total concentrations of Cu, Pb and Zn in both sediments and soils from stations 2, 4 and 5 exceeded the values indicative of intermediate level of contamination ($25\text{--}50 \mu\text{g Cu g}^{-1}$, $40\text{--}60 \mu\text{g Pb g}^{-1}$, $90\text{--}200 \mu\text{g Zn g}^{-1}$).¹² However, pH and metal concentration values in soils and sediments did not change regularly with distance to the mine. This could be due to the drastic changes in the river flows. Agrio and Guadamar rivers stop flowing in the dry season, and water remaining in the river beds evaporates producing salty crusts and hydrous deposits. In periods of heavy rains, flow increases, salty crusts are dissolved and sediments are suspended and transported downstream, polluting water, sediments and soils located far away from where they were first deposited.

X-ray analysis showed the existence of metallic sulphides (pyrite, marcasite, etc.) in the sediments, and hydroxides, gypsum and other sulphates of Al, Fe, Zn, Cu, Ca, K, etc. (alunite, pisanite, sepielite, etc.) in the salty crusts.

Heavy metal contents in foliage of three naturally occurring plants species (Holoschoenus

vulgaris, Thypha latifolia and Mentha rotundifolia) collected in the river banks of the sampling stations 2, 4 and 5 were higher than the general background ones in the reference station 3 (Table IV). For M. rotundifolia positive linear correlations were found between Fe, Cu and Zn concentrations in foliage and their available levels in soils (Fe $r=0.760$ $P<0.05$; Cu $r=0.887$ $P<0.01$; Zn $r=0.986$ $P<0.001$).

Table III.- Mean values of pH and total available heavy metal concentrations of sediments and soils. Concentrations are in $\mu\text{g g}^{-1}$, except for Fe, Cu and Zn (*) which are mg g^{-1} .

Sampling station		pH	Sediments						pH	Soils					
			Fe	Cu	Mn	Pb	Zn	Fe		Cu	Mn	Pb	Zn		
2	Total	5.9	121.3*	1.1*	420	1966	4.3*	7.4	39.3*	0.42*	719	289	0.97*		
	Avail.		82.3	106	50.8	4.8	293		36.0	118	21	37.0	136		
3	Total	7.2	30.3*	0.01	283	28	0.05*	8.6	22.4*	0.01*	250	28.0	0.05*		
	Avail.		24.0	3.0	17.0	1.0	2.0		24.0	2.00	8.0	1.0	1.0		
4	Total	6.6	42.9*	1.1*	594	172	2.3*	6.8	54.8*	2.19*	623	112	3.13*		
	Avail.		52.3	132	43.0	9.0	212		8.0	265	11.0	1.0	142		
5	Total	7.4	40.8*	6.2*	1744	387	4.5*	7.2	30.4*	0.32*	500	220	1.00*		
	Avail.		3.0	344	22.7	1.7	203		37.0	70.0	18.0	24.0	83		

Table IV.- Average metal concentrations ($\mu\text{g g}^{-1}$) in foliage of Holoschoenus vulgaris, Typha latifolia and Mentha rotundifolia.

Sampling station	Fe	Cu	Mn	Pb	Zn
<u>Holoschoenus vulgaris</u>					
2	165	12.4	65	2.0	85
3	103	4.0	16	3.0	14
4	132	11.3	97	4.0	94
5	85	7.9	38	0.0	41
<u>Typha latifolia</u>					
2	699	15.0	724	8.5	202
3	111	4.0	289	0.0	26
4	--	--	--	--	--
5	115	13.0	422	0.0	105
<u>Mentha rotundifolia</u>					
2	1950	45.0	59	51	272
3	803	14.0	60	15	45
4	709	25.0	78	25	107
5	1720	28.0	75	28	101

During the autumn 1983 and the spring 1984, water, sediments and three animal species of commercial interest (Crassostrea angulata, filter feeder; Dicentrarchus labrax, predator; and Mugil auratus, detritus feeder) were examined in the Guadalquivir estuary.¹² Results were compared with those from the Barbate estuary, also in the Cádiz Gulf, but only affected by diffuse agricultural pollution and small village sewages.

Mean concentrations of Fe, Cu, Mn, Pb and Zn in water from both estuaries (Table V), were within the same range, and generally lower than those found upstream in the Guadalquivir river (Table I).

Table V.- Mean values and ranges of heavy metal concentrations in water (mg l^{-1}) and sediments ($\mu\text{g g}^{-1}$, except for Fe which is mg g^{-1}) from Guadalquivir and Barbate estuaries.

Location	Range	Fe	Cu	Mn	Pb	Zn	Fe	Cu	Mn	Pb	Zn
Water						Sediments					
Guadalquivir	Mean	0.089	0.011	0.013	0.006	0.023	27.3	63.2	481	65.5	126.4
	Min	0.023	0.003	0.005	0.002	0.010	24.4	55.0	347	60.8	110.0
	Max	0.250	0.040	0.030	0.013	0.035	28.5	72.8	562	70.0	143.4
Barbate	Mean	0.174	0.009	0.029	0.008	0.033	28.8	36.6	293	33.1	83.7
	Min	0.038	0.003	0.004	0.002	0.012	15.8	22.7	224	26.0	48.0
	Max	0.444	0.018	0.065	0.016	0.049	38.8	47.2	363	40.8	131.1

Mean total concentrations of heavy metals in the Guadalquivir estuary sediments were higher than those in the Barbate estuary (Table V). However, in both estuaries Cu, Mn, Pb and Zn mean values were higher than those in the reference station 3 in the Guadamar river, but much lower than those in the polluted stations 2, 4 and 5 (Table III). Only Cu and Pb in the Guadalquivir estuary sediments exceeded the values indicative of intermediate level of contamination.¹³

Comparing specimens of *C. angulata* within the same range of weight ($\leq 10\text{g}$) (Table VI), the specimens from the Guadalquivir estuary had 1.09, 5.47, 1.03 and 2.18 time more Fe, Cu, Mn and Zn respectively than those from the Barbate estuary, differences being statistically significant for Cu and Zn ($P < 0.001$). Copper concentrations of *C. angulata* from the Guadalquivir estuary were always higher than the recommended concentration for human consumption ($1000 \mu\text{g Cu g}^{-1}\text{d.w.}$).¹⁴

No significant differences were found between mean values of either Fe, Mn or Zn in liver of *D. labrax* (total weight ≤ 500) from Guadalquivir and Barbate estuaries (Table VI). However, mean values of Cu in liver of specimens from Guadalquivir were 3.03 times greater ($P < 0.01$) than those from Barbate. In dorsal muscle tissue, significant differences were only found for Cu ($P < 0.001$) and Zn ($P < 0.05$) which were slightly higher in specimens from Barbate estuary.

Mean concentrations of Fe, Cu and Zn in liver of *M. auratus* (total weight ≤ 700) from Guadalquivir estuary were respectively 1.73, 22.67 and 1.57 times greater ($P < 0.001$) than those from Barbate. In dorsal muscle tissue, Fe, Mn and Zn were higher ($P < 0.001$, $P < 0.05$ and $P < 0.01$ respectively) in the Guadalquivir specimens.

CONCLUSIONS

Heavy metal pollution of Guadamar river mainly extends by the drastic changes in the river flow and the dissolving, adsorbing and complexing ability of organic effluents (e.g. *alpechines*). Also the discharge of floating agents (e.g. thiosalts) contributes to the progression of metal pollution.

To prevent the progression of the metal pollution, effluents from mineral treatment plant must be oxidized and neutralized before being discharged into the river.

In addition, the water Authorities should establish a continuous water quality and flow control station to determine the effluent variable permits of the industries, in accordance with statistical minimum stream flow.

To regenerate the hydrological status of the Doñana National Park, water from Guadamar river must be received in aeration lagoons before allow it to enter into the Park.

Table VI.- Mean values and ranges of heavy metal concentrations ($\mu\text{g g}^{-1}$ dry wt.) in *Crassostrea angulata*, *Dicentrarchus labrax* y *Mugil auratus* from the Guadalquivir and Barbate estuaries.

		Guadalquivir				Barbate			
		Fe	Cu	Mn	Zn	Fe	Cu	Mn	Zn
<i>C. angulata</i>	Mean	741	2979	44.3	9729	681	545	43.1	4457
	Min	342	1034	19.5	2422	257	302	19.5	2895
	Max	2082	5952	85.0	20742	1600	1520	76.1	8333
<i>D. labrax</i> liver	Mean	919	291	9.5	164	1036	96.0	13.3	116
	Min	410	84.1	4.7	116	206	14.5	0.0	97.2
	Max	1949	634	12.2	259	2664	920	25.0	310
dorsal muscle	Mean	23.2	4.84	0.88	23.5	19.7	8.15	0.82	28.1
	Min	9.2	3.88	0.00	18.6	6.2	2.89	0.00	12.7
	Max	35.7	6.40	1.55	32.6	32.9	23.77	1.35	51.5
<i>M. auratus</i> liver	Mean	2277	6234	14.3	321	1313	275	14.4	205
	Min	1282	726	1.7	132	445	22.5	4.4	125
	Max	3820	19444	43.3	588	3181	1078	47.2	307
dorsal muscle	Mean	54.5	8.55	1.64	40.5	31.3	6.78	0.95	31.8
	Min	16.5	4.50	0.46	22.2	12.5	3.72	0.00	22.3
	Max	124	17.10	3.85	71.5	86.1	19.50	4.08	50.0

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