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Water Contamination by Heavy Metals (Hg, Cd, Pb, Cu and Zn) in Doñana National Park (Spain)

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Pollutants of major concern in aquatic ecosystems are (1) produced and reach the environment in large amount (2) toxic to aquatic organisms (3) concentrated within organisms to levels greater than in the environment and (4) persistent for long period of time and increased concentrations (McIntyre and Mills 1975). Heavy metals fit each of the above categories.

Trace metals have recently come to the forefront of dangerous substances causing serious health hazards in human and other organisms. Hg, Cd, Pb, Cu, and Zn are among the most dangerous of these elements. The problems of trace elements are specially alarming in the inmediate vicinity of smelters (Swaine et al. 1981; Zwozdziak and Zwozdziak 1982; Nriagu et al. 1982).

The National Park of Doñana has an expanse of 50,720 ha and is located in the SW of Spain on the right bank of the delta of the Guadalquivir river. The aquatic system of the Park consists of small streams, lagoons and artificial channels. One of the streams, the Guadiamar river, descend from the Northern side where a mine is located, at a distance about 40 km from the Northern boundary of the Park. The mine is very old and was inactive for a long time. At present it is being operated in the commercial exploitation of pyrite ores rich in Zn, Pb, Cu and Mn.

We sampled the watershed of Doñana and mining area to determine any possible contamination alongside the mine and we analysed heavy metal concentrations at each point.

MATERIALS AND METHODS

The sampling points were located in three areas (figure 1): the mining area, the marshes and the stabilized sands.

Samples of water were in ten different locations of the Park (Canal de Casa Riera (1), Huerta de las Arenas (2), Lucio del Cangrejo

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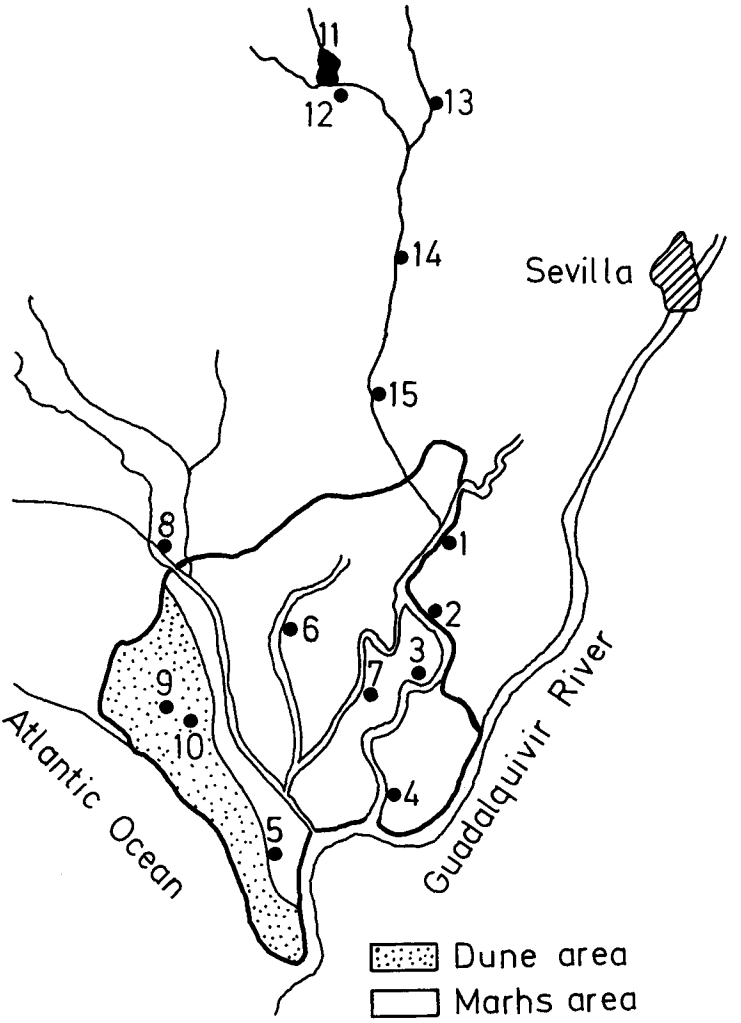

Figure 1. Study area and sampling locations.

(3), Canal del Cherry (4), Lucio del Membrillo (5), Caño Guadiamar (6), Lucio de Mari López (7), La Rocina (8), Laguna Dulce (9) and Laguna de Santa Olalla (10); and five locations of the mining area; this locations are: sampling site 11 is on the Dam of Aznalcollar, site 12 is on the Agrio river downstream from the waste effluent of the processing factory, site 13 is situated before the confluence of the Agrio river with the Guadiamar river and sites 14 and 15 are located after the confluence of the Agrio river with the Guadiamar river.

Samples consisting in two liters of waters each collected in all of the sampling points.

Table 1. Levels of heavy metals (Hg, Cd, Pb, Cu and Zn) found in waters of Doñana National Park in the period 1982-1986

Year	S.P.*	Hg	Cd	Pb	Cu	Zn
1982	1	0.7	2.2	27.0	50.2	86.2
1983	1	4.1	0.7	1.7	15.9	70.1
1984	1	0.8	4.2	18.0	25.8	842.9
1985	1	2.4	0.5	4.9	26.3	47.8
1986	1	2.9	0.8	41.6	18.3	74.0
1982	2	1.4	1.6	23.9	42.4	50.3
1983	2	3.0	0.2	1.4	10.5	72.1
1984	2	1.1	0.4	13.8	19.4	189.0
1985	2	2.5	0.4	5.4	36.6	45.7
1986	2	2.5	1.1	13.7	13.5	92.6
1982	3	2.0	0.6	5.4	23.1	20.7
1983	3	3.3	0.2	6.1	20.3	70.4
1984	3	2.3	0.3	2.6	15.6	33.6
1985	3	2.6	0.2	2.4	31.3	42.0
1986	3	2.7	0.7	12.9	11.7	44.5
1982	4	1.9	1.1	8.0	48.7	52.0
1983	4	4.4	0.3	5.8	20.7	103.9
1984	4	0.9	0.2	2.8	17.4	22.9
1985	4	1.0	0.5	5.5	17.3	45.5
1986	4	2.7	1.0	26.6	33.0	34.0
1982	5	1.7	0.9	10.3	21.1	52.2
1983	5	2.9	0.9	28.0	33.3	38.0
1984	5	0.6	0.1	3.1	14.7	11.8
1985	5	2.2	1.9	8.8	19.1	54.0
1986	5	1.8	0.8	7.5	19.7	71.4
1982	6	0.9	0.8	8.9	22.6	46.4
1983	6	2.7	0.4	11.2	20.1	60.1
1984	6	1.6	0.2	3.4	16.8	9.1
1985	6	2.6	0.4	2.5	22.0	36.3
1986	6	2.3	1.9	14.9	16.0	46.5
1982	7	6.0	0.4	8.6	41.9	66.7
1983	7	2.0	0.1	5.3	19.3	56.7
1984	7	1.1	0.3	4.0	14.0	5.4
1985	7	2.2	0.3	11.8	30.0	23.5
1986	7	3.9	0.9	7.8	16.1	42.6
1982	8	3.1	0.7	30.2	35.9	71.8
1983	8	3.4	1.0	7.8	27.2	83.8
1984	8	1.3	0.4	3.1	16.1	26.7
1985	8	2.7	0.9	13.2	15.7	50.1
1986	8	4.8	0.8	27.8	50.7	57.6

Table 1. (Continued)

Year	S.P.*	Hg	Cd	Pb	Cu	Zn
1982	9	3.3	0.2	9.9	25.5	42.7
1983	9	3.3	0.1	8.6	35.1	87.6
1984	9	1.2	0.1	1.5	12.2	16.6
1985	9	2.7	2.2	21.6	18.5	72.7
1986	9	1.0	1.0	8.9	11.5	44.0
1982	10	1.8	0.4	12.3	34.0	26.7
1983	10	5.3	1.0	9.8	27.0	92.1
1984	10	1.2	0.4	3.5	11.3	13.9
1985	10	2.3	1.0	6.7	25.6	55.8
1986	10	N.D.	1.0	6.9	9.6	43.6
1982	11	0.3	2.0	2.5	114.4	243.1
1983	11	2.0	0.6	3.4	56.7	91.4
1984	11	0.8	1.6	11.2	40.6	112.1
1985	11	3.1	0.8	4.9	49.9	77.4
1986	11	2.0	1.1	9.8	35.3	138.4
1982	12	7.2	432.3	462.0	11979.0	142890.0
1983	12	3.4	196.6	2072.3	3221.3	41985.8
1984	12	1.8	583.3	646.0	4973.5	3211.4
1985	12	2.5	361.6	232.9	55033.7	16061.3
1982	13	0.8	1.0	5.0	33.0	75.0
1983	13	1.0	0.3	2.6	58.2	19.2
1984	13	1.1	0.6	5.9	29.5	12.1
1985	13	2.8	0.5	3.1	51.4	47.8
1986	13	4.3	0.8	6.2	8.7	59.3
1982	14	3.0	1.8	12.4	41.8	399.0
1983	14	4.2	13.4	56.9	132.0	1781.0
1984	14	1.3	19.6	32.4	322.6	2775.4
1985	14	2.5	10.0	8.8	54.8	1705.3
1986	14	2.9	9.5	10.0	25.3	2622.5
1982	15	2.8	0.9	9.5	45.6	106.4
1983	15	3.3	2.1	15.7	75.9	161.1
1984	15	1.5	8.4	6.8	70.9	2591.9
1985	15	3.1	3.2	14.7	57.1	486.6
1986	15	2.4	3.4	8.3	22.3	2314.3

S.P.* = Sampling points; N.D. = Not determined; all levels are expressed in ppb.

All the samples were stored at 4-5ºC; until preanalytical treatment of 3 ml of aqueousus solution of nitric acid (1:1) per liter of water was added. Water was filtered before testing.

The mercury concentration was determined by flameless atomic

absorption method of Uthe et al. (1970); duplicate samples were dissolved with 10 ml of 3:1 sulphuric and nitric acid mixture for 2 h at 60ºC, followed by 15 ml of 6% MnO_4K_2, and analyzed by the flameless atomic absorption.

Lead, cadmium, copper and zinc were analyzed by flame atomic absorption according to the method of Brown (1968); duplicate samples, consisting in 300 ml of water, were extracted with methyl isobutyl ketone (MIBK) and analyzed by atomic absorption.

Recoveries of metals studied were in a range of 87-99%. All of residues are expressed as ppb.

RESULTS AND DISCUSSION

All heavy metals concerned were found in every analyzed samples (Table 1).

In all cases cadmium showed the lowest mean levels with a range from 0.1 to 4.2 ppb, followed by mercury with a range from 0.3 to 6.1; lead range 1.4 to 41.6; copper, range 10.5 to 50.2 and zinc, range 5.4 to 842.9. Levels shown in table 1 great to the maximum level of range corresponding to the mining area.

With regard to the evolution that levels of heavy metals follow, in function of time, can be verified an increase for mercury in the period of study, but for cadmium, lead, copper and zinc is not clearly directed in only one way.

The natural levels in freshwater (Fornstner and Wittman 1979) and the maximum allowable levels in water (U.S.E.P.A. 1979) of metals are detailed in table 2.

All of samples analyzed exceeded the natural levels in freshwater for heavy metals; 6% of samples for Hg, 9.5% for Cd, 6.8% for Pb, 5.4% for Cu and 4.1% for Zn exceeded the maximum allowable levels; in all of cases, except for Hg, this levels corresponding to the mining area.

Table 2. Maximum allowable levels in water (U.S.E.P.A. 1979) and natural levels in freshwater (Fornstner and Wittman 1979) of heavy metals, in ppb.

	Maximum allowable levels	Natural levels
Mercury	2.00	0.01
Cadmium	10.00	0.07
Lead	50.00	0.20
Copper	1000.00	1.80
Zinc	5000.00	10.00

Table 3. Results of one-way analysis of variance on concentrations of heavy metals in waters, Doñana National Park (Spain).

	F	
	Years F=2.5252; α=0.05 df1=4 df2=69	Locations F=1.8360; α=0.05 df1=14 df2=59
Mercury	5.560**	0.798
Cadmium	0.353	31.590**
Lead	0.653	5.465**
Copper	0.792	3.131**
Zinc	0.724	3.419**

Table 4. Correlation among residues of heavy metals detected in waters from Doñana National Park.

	Cd	Pb	Cu	Zn
Hg	0.317	0.468	0.093	0.358
Cd		0.822**	0.866**	0.996**
Pb			0.597*	0.809**
Cu				0.864**

** α = 0.01; * α = 0.05

A one-way analysis of variance (ANOVA I) with stations was used to test the null hypotheses: there was no significant difference in pollutant residue concentrations due to location.

ANOVA I with years was used to test the null hypotheses: there was no effect due to time.

The results of one way analysis of variance are detailed in table 3.

Significant difference were observed in mercury concentration from the five years; the major level of Hg was observed in 1982 and 1985. Significant difference were observed in cadmium, lead, copper and zinc concentrations due to location. No significant difference could be observed in Hg residue due to location or in Cd, Pb, Cu and Zn levels due to time.

Correlations among residues of heavy metals were calculated and are presented in table 4. There are highly significant or significant correlations between heavy metals except to mercury; this may be that emission source of Cd, Pb, Cu and Zn, but no Hg, is located at the mine of Aznalcollar. The origin of mercury pollution is in agricultural and industrial activities in the proximity of the Park.

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