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Multivariate Analysis of Water Contamination by Heavy Metals at Doñana National Park

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Trace metals have recently come to the forefront of dangerous substances causing serious health hazards in human and other organisms. Joint investigations of trace elements given off in aquatic environment, are being carried out in many parts of the world to determine their concentrations and to establish their pathways in the environment. Cd, Hg, Pb, Cu and Zn are among the most dangerous of these elements. The problems of trace metals are especially alarming in the inmediate vicinity of smelters (Swaine 1981, Zowzdziak and Zowzdziak 1982, Nriagu 1982).

Doñana National Park is a natural park about 60,000 Ha. It is a very important stopping ground and winter habitat for migratory birds that breed in northern Europe. The park is located in the SW of Spain on the west bank of the delta of the Guadalquivir river, where two main areas, marshes and stabilized sands can be easily distinguised.

One of the most important water-supplies for the survival of the park is the Guadiamar river. The Agrio river is a tributary of the Guadiamar river and it flows across an important mining field which is operation at present.

We sampled the watershed to determine any possible contamination alongside the mine, and we analysed heavy metal concentrations at each point. The multivariate analysis method is applied to determine the relationships of heavy metals with each other and with geographic region.

MATERIALS AND METHODS

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

On 14th April 1984, 27 samples of two liters of waters each were collected: five near the mine, 16 from the marshes and 6 from the stabilized sands.

All the samples were stored at 4-5º C. until preanalytical treatment

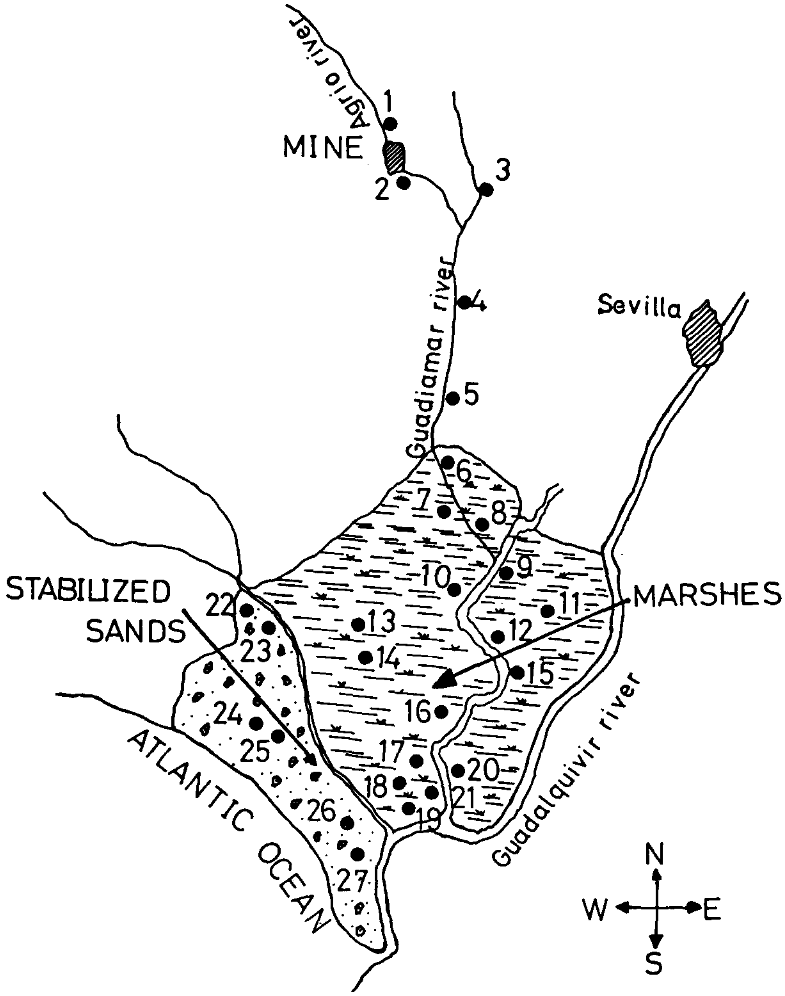

Figure 1. The study area and sampling locations

of 3 ml of aqueous solution of nitric acid (1:1) per litre of water were added. Water was filtered before testing. The mercury concentration was determined by the flameless atomic absorption method of Uthe et al (1970). Lead, cadmium, copper and zinc were analyzed by flame atomic absorption according to the method of Brown (1968). Analyses were duplicated and recoveries of Hg, Cd, Pb, Cu and Zn were in a range of 87-99 %.

RESULTS AND DISCUSSION

Metal concentrations varied with the sampling site and the specific metal (table 1).

The mining area contains the highest values, particularly sample 2, which is nearest the mining work. Pollution at point 2 exceeds

Table 1. Levels of Hg, Cd, Pb, Cu and Zn in ug/l in waters of Doñana National Park and arounds.

Location	Sample	Hg	Cd	Pb	Cu	Zn
Mine	1	0.79	1.61	11.20	40.46	112.10
"	2	3.92	690.00	712.50	5000.50	3925.00
"	3	1.13	0.61	5.91	29.46	12.10
"	4	2.29	19.55	32.20	322.55	2755.00
"	5	1.48	8.36	6.80	70.89	2591.33
Marshes	6	1.71	1.66	5.25	53.81	546.87
"	7	2.50	2.16	6.37	27.00	677.53
"	8	2.13	1.85	6.48	25.24	895.37
"	9	2.26	2.84	23.17	22.87	418.58
"	10	2.50	0.27	22.96	18.37	136.82
"	11	0.69	0.22	2.09	15.26	19.50
"	12	0.55	0.21	3.64	14.85	43.77
"	13	1.85	0.09	3.85	17.71	10.06
"	14	3.11	0.12	2.23	18.08	10.06
"	15	2.40	0.15	1.60	18.44	22.14
"	16	3.84	0.11	1.41	13.51	17.50
"	17	3.22	0.19	1.04	13.57	12.10
"	18	3.60	0.17	2.62	21.03	7.45
"	19	3.68	0.16	2.54	16.08	8.70
"	20	1.63	0.16	1.73	19.42	11.97
"	21	2.58	0.13	1.78	17.37	12.66
Stab. sands	22	2.53	0.26	1.82	15.26	23.76
"	23	2.44	0.29	3.09	17.20	16.24
"	24	1.16	0.14	1.48	12.15	16.62
"	25	1.99	0.22	1.86	7.96	11.53
"	26	1.76	0.78	1.95	11.43	9.63
"	27	0.60	0.14	3.08	14.67	11.67

the detected pollution at point 1 by 4.96 times in Hg, 428 in Cd, 64 in Pb, 123 in Cu and 35 in Zn. Point 1 has been taken as a reference for the pollution of these metals in the proximity of the smelter and point 3 has been taken as a reference for the natural pollution of these metal in the mining area (zone I), which are geologically different from areas II and III, which are typically sedimentary.

Values found in the northern side of the marshes (points 6, 7, 8, 9 and 10) show lower levels than those found in the mining area. The values detected in the sothern side of the marshes (points 16, 17, 18, 19 y 20) are lower than those found in the northern side of the marshes and similar, though a little higher than, the corresponding values of the stabilized sands (zone III).

The SIMCA method of pattern recognition (Albano et al 1981) classifies all the points as belonging to a unique class, the modelling power for the variables Hg, Cd, Pb, Cu and Zn being

Table 2. Correlation coefficients matrix for metals[1]

	Hg	Cd	Pb	Cu
Cd	0.090			
Pb	0.035	0.932		
Cu	0.048	0.830	0.773	
Zn	0.110	0.993	0.923	0.798

[1] Significant at $p < 0.01$ for $r > 0.487$

0.61, 0.74, 0.74, 0.77 and 0.72 respectively, all of them highly significant.

The correlation coefficients matrix of metal contents show many significant relationships existing between pairs of metal contents

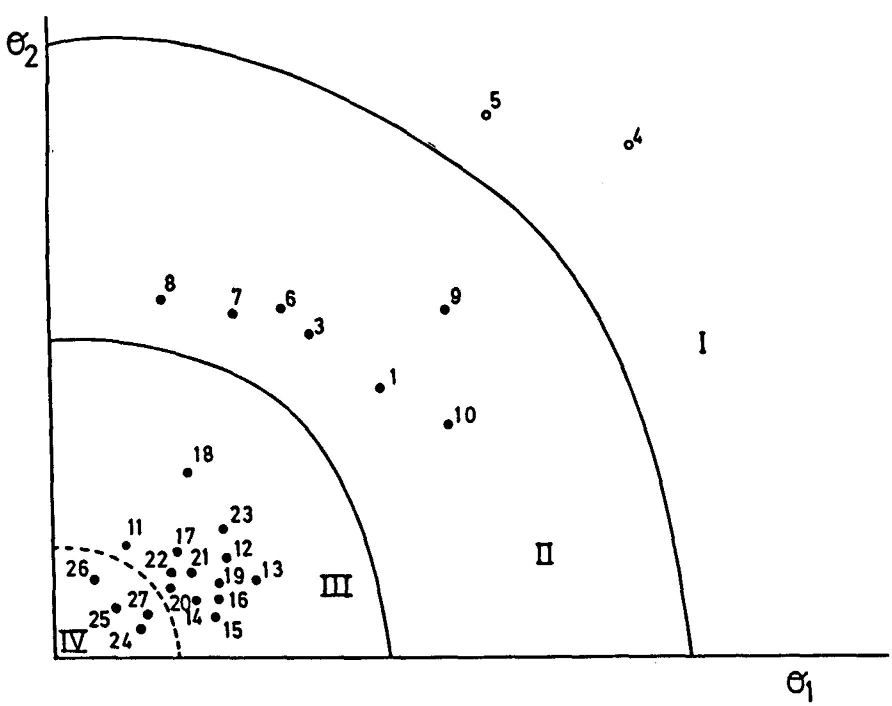

Figure 2. Plot of the metal data set, excluding point 2, on the plane defined by the two principal components.

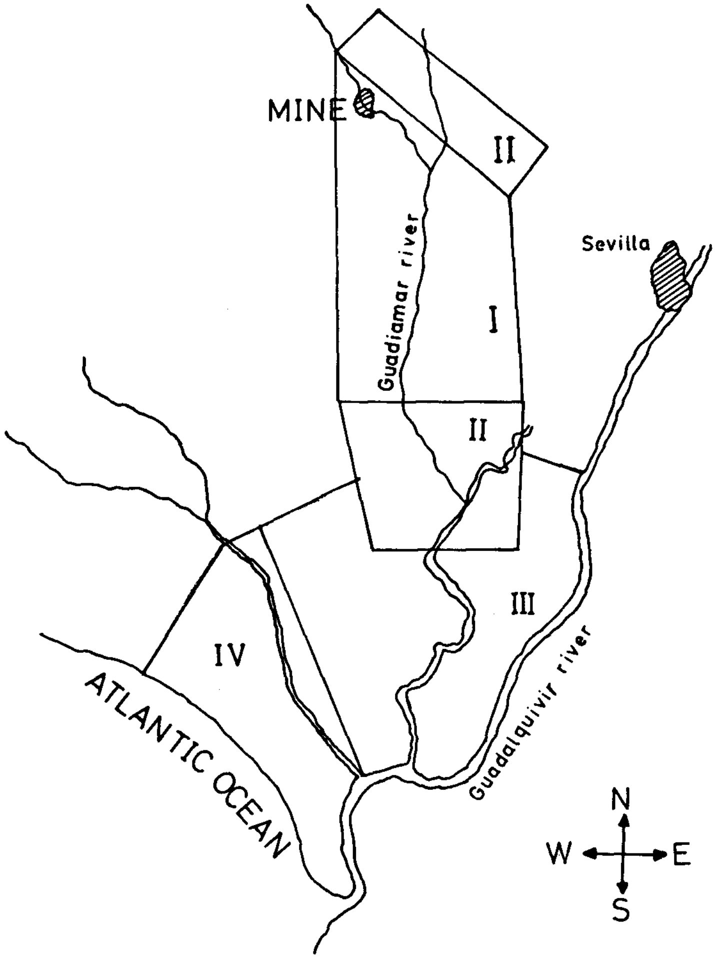

Figure 3. Distribution of the area according its degree of contamination

(r 0.478; p 0.01) corresponding to Cd-Pb-Cu-Zn (table 2). Hg is independent from the other metals. The highly correlated metals support the theory that the principal source of these metals in the area studied is the mining field of Aznalcollar. Another source could be the Guadalquivir river which is remarkable, mainly due to its tides.

It is evident that there is more than one way of penetration of mercury into the Doñana National Park. Possibly one entryway is via the Guadalquivir river. Mercury has the highest values in in the southern side of the marshes, which is the nearest one to the mouth of the Guadalquivir river. However, mercury varies within a narrow range of values (0.55-3.92) as opposed to the other four metals. The natural level of Hg in fluvial waters is 0.1 ug/l and in rain waters it is 0.2 ug/l (Saha 1972). By comparison, the examined waters contain a load 20 times higher than natural levels. Consequently these samples should be considered as overpolluted.

The points of the originally four dimensional-space (Cd, Pb, Cu and Zn) have been projected onto the plane surface defined by the eigenvectors of the two principal components (Kowaski and Bender 1973). These components explain 96.25% of the total variability (figure 2), being split into four region taking as a basis the module of the four-dimensional vectors which measure boundary between regions II and III coincides aproximately with the value above which deleterious effects on aquatic living organism could begin to appear (EPA 1973).

If the values of pollution in figure 2 are assigned to the corresponding points on the map of figure 1 it is verified that they still remain grouped into four different classes, these can be identified with four geographical regions as shown in figure 3, although region III and IV are not clearly separated.

The main conclusion of this study is the existence of Cd, Pb, Cu and Zn pollution in the waters of the studied area. Contamination was very high in the mining area (I), high in the northern side of the marshes (II), moderate in southern side of the marshes (III) and low in the stabilized sands (IV). This conclusion is linked with the fact that the hydraulic system of the stabilized sands is independent from that of the marshes. The stabilized sands only depend on the rain and the subterranean waters. High Hg pollution was found throughout the area studied.

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