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Sources and Transport of Organochlorine Compounds and Heavy Metals into Waters of the National Park of Doñana

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In earlier papers (Baluja et al. 1977, 1978, 1983; F.-Aceytuno et al. 1984) results were reported on the pollution by organochlorine pesticides, PCBs, and heavy metals of abiotic material and plants and fauna of the biological reserve of the National Park of Doñana. This park 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, between 37° 7′- 36° 48′north latitude and 6° 12′- 6° 34′west longitude. Two main areas can be easily distinguished, the marshes, and the shore and moving dunes (Fig.1). The aquatic system of the park consists of small streams, lagoons, and artificial channels. One of the streams descends from the northern side where a mine is located, at a distance of about 40 km (25 miles) from the northern boundary of the park. The mine is very old, since the Romam Empire, and was inactive for a long time. At present it is being operated to extract large quantities of copper, zinc, and lead. Another stream comes from the NW where some farms outside the park are cultivated. These streams are tributaries of the main river Guadalquivir which flows out into the Atlantic Ocean.

In winters with large precipitation events the stream system partially disapperars and the interior area is mostly covered by water. In situations of drastic dry weather, which have been occurring throughout the sampling period (1981 to 1983) the marsh was exhausted and large volumes of water had been pumped from the Guadalquivir river and from underground water. The current study was designed to see if hexaclorocyclohexanes (HCHs), total DDTs and PCBs, and mercury, cadmium, lead, copper and zinc were being transported into the water system of the park, and to elucidate the sources of these pollutants, taking into account the mine location and the cultivated lands outside the park.

MATERIALS AND METHODS

Water sampling was made on surface waters from lagoons, channels and streams. At times of drastic dry weather conditions some sampling was in small pools left by the streams. 800 samples of water were taken in 30 locations of the park and adjacent

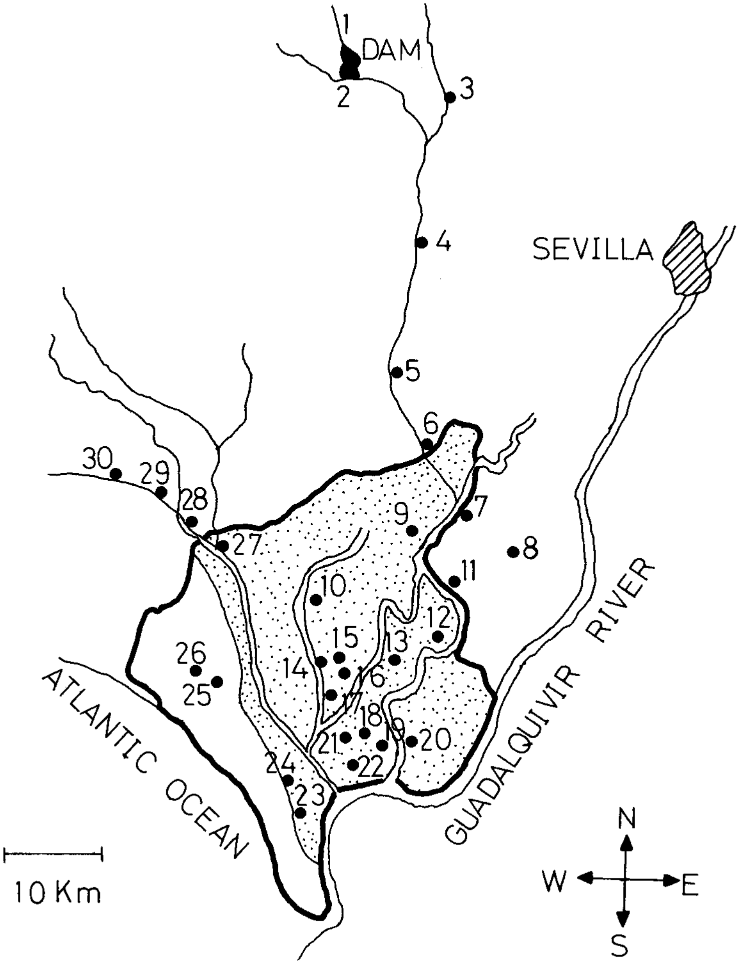

Figure 1. Study area and sampling locations. Gross line is the limit of the park, dotted zone is the marsh area, white zone is the dune area.

areas (Fig.1) throughout July and November 1981, March, April and November 1982, and February and May 1983. Preanalytical treatment of samples and the analysis of organochlorine compounds by GLC-EC (Ni-63) were carried out according to a method described in a previous paper (Hernández et al. 1976). Mercury was analyzed by the flameless atomic absorption method of Uthe et al. (1970). Lead, cadmium, copper and zinc were analyzed by the flame atomic absorption using the method of Brown (1968). Duplicate analysis were made and recoveries of organochlorine residues were in a range of 90-95 %, 87-99 % for Hg, Pb and Cu, and 87 % for Zn.

RESULTS AND DISCUSSION

The area where the park is located suffered a very dry climate during the sampling period (Fig.2). Evaporation had been much

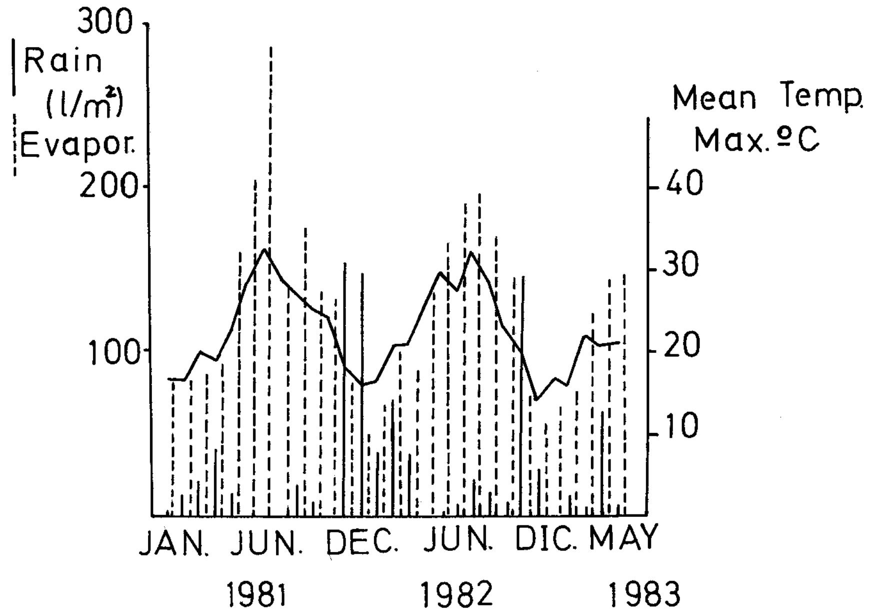

Figure 2. Rainfall, evaporation and mean of the maximum temperatures registered during the sampling period.

greater than rainfall except in December of 1981 and January and November of 1982. The mean maximum temperatures are shown by the continuous transversal line. The water body of the subsoil of the area has great significance in this high evaporation process. According to theoretical estimations, about 20 million cubic metres of water annually flush-up to the upper ground surface. The pH mean of all water samples from locations 6 to 30 throughout the sampling periods vary between 7.1 and 7.9. The water showed a slight saline character where sodium and calcium are abundant cations, but the water samples taken in the vicinity of the mine works had a pH mean of 2.8 (SD ± 0.4).

In Fig.3 are the mean results of the analysis of organochlorines in the water of the eight locations sampled. It is observed that most of the results fluctuate in a small range around the mean line, which suggests that a rather homogeneous distribution of residues is occurring there. Mean levels were calculated from 6 to 8 analytical values. Location 25 is a shallow lagoon located at the N of the dune area where the water body is fed by rainfall and infiltration waters, and is independent of the stream system.

It was generally assumed that surface washoff from soils and airborne are the most widespread sources of low level contamination of surface waters by pesticides (Risebrowgh 1969; Hasset and Lee 1975). Airborne dispersion can be, however, more involved in the spread of organochlorine residues in this area. This assumption is supported by the occurrence of pesticides in the shallow water of the lagoon at location 25, which is isolated

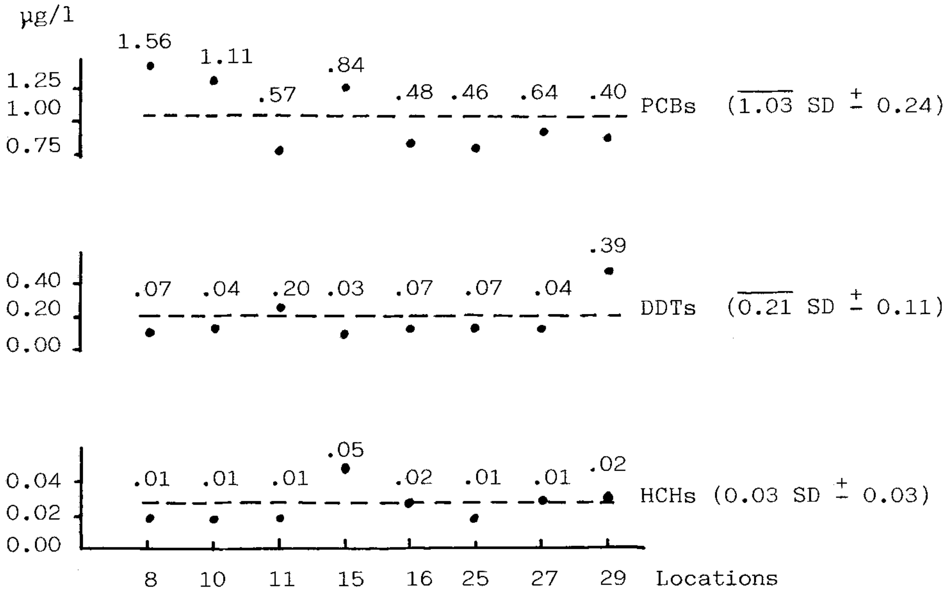

Figure 3. Mean concentrations of organochlorine residues (µg/l) in water from each location. Dashed line is the general mean, and numerals on dots are the SD of mean for each location. (HCHs = α-HCH + γ-HCH; DDTs = pp′-DDE + pp′-TDE + pp′-DDT).

from any contribution of surface waters, as well as the more or less homogeneous distribution of residues in the whole area of the park. The organic matter in these streams may contribute to the solubilization of the organochlorine compounds (Wershaw and Goldberg, 1972), and the saline character of this water with Na^+ as a predominant cation (Arambarri et al. 1980) contributes to the stability of the organic matter-pesticide complex.

More than 1,000 analytical values were computed for metals. The estimated mean levels in Fig.4 were calculated from 5 to 8 analytical values for each location in each sampling period. An extremely high concentration was found in the water from location 2, which is close to the mine (ranges in µg/l are: Hg 3.4-7.2; Cd 196-432; Pb 908-2,072; Cu 3,200-22,000; Zn 42,000-167,400). Other locations in the nearby area do not have these unusual metal levels. The metal load in a stream around the mine can vary considerably in a short time, as shown by Larsen et al. (1983). The results also showed that the highest metal concentrations in water were Pb, Cu and Zn. They are the main metal constituents of the native ore whilst the more toxic Hg and Cd appear to behave as trace metals resulting from the mineral refining.

Though the mean levels reported here do not vary much, a few high values were found in some locations inside de park and these seem to be annomalies. This situation might be attributed to local concentrations of these metals related with chemical

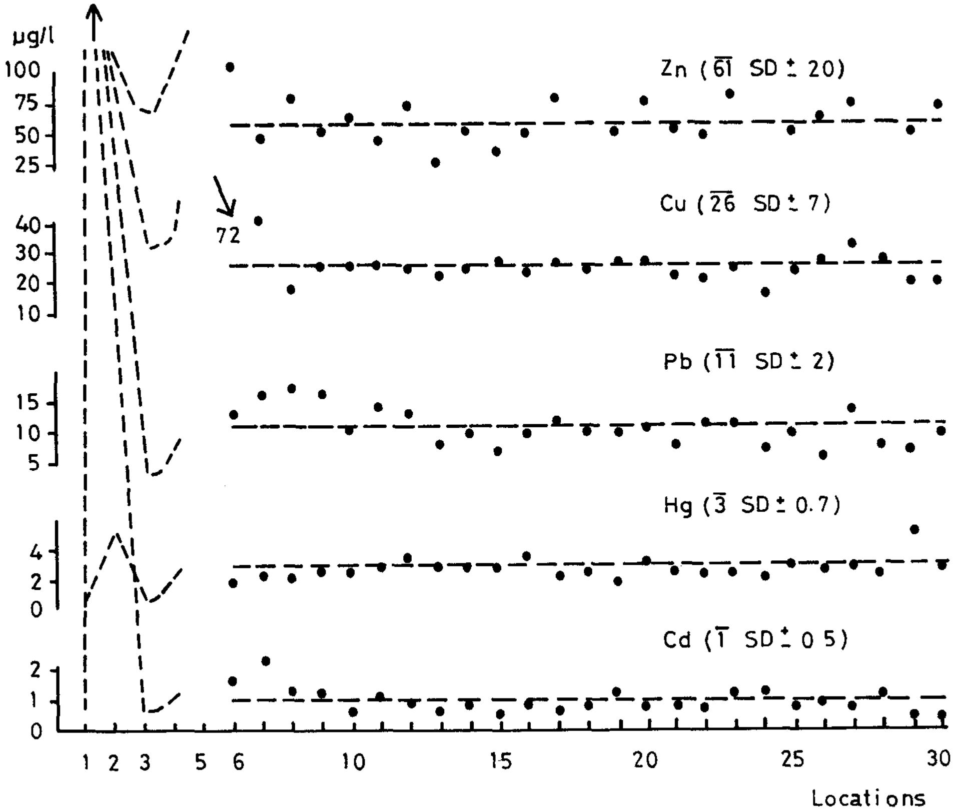

Figure 4. Mean concentrations of metals in water (µg/l) from locations 6 to 30. Dashed line represents the general mean for each metal and SD of mean. The mine site shows the highest variation

and/or physical interactions. However, November 1982 had been a rainy month, with nearly 150 $1/m^2$ of rainfall (Fig.2) and this event could mobilize the copper, for instance, though the lead would not have increased comparatively. The summer and autumn of 1981 were quite dry and in spite of this the lead increased significantly in November but not copper. Consequently, a clear relationship between the rainfall and the metal load in the streams was not found. The pH of water during the sampling periods vary between 7.1 and 7.9, which means that a dissolution process of metals was not favoured. The low pH (2.4-3.3) of waters in the neighbourhood of the mine allows the dissolution of metal-oxide complexes to liberate the metals to the aqueous media. Furthermore, as it is known the transport of heavy metals in the aquatic system is significantly influenced by the dissolved organic matter (Craig 1980). As much as we Knoow the water of these streams is abundant in organic material, because, according to the data reported by Arambarri et al. (1980) for the years 1978 and 1979 the COD ranged between 18 and 195 mg/l, and the organic nitrogen between 3 and 8 mg/l, depending of the season of the year. This means that through the formation of soluble organic complexes the adsorption of these metals by clays and metal-oxyhydroxides is inhibited.

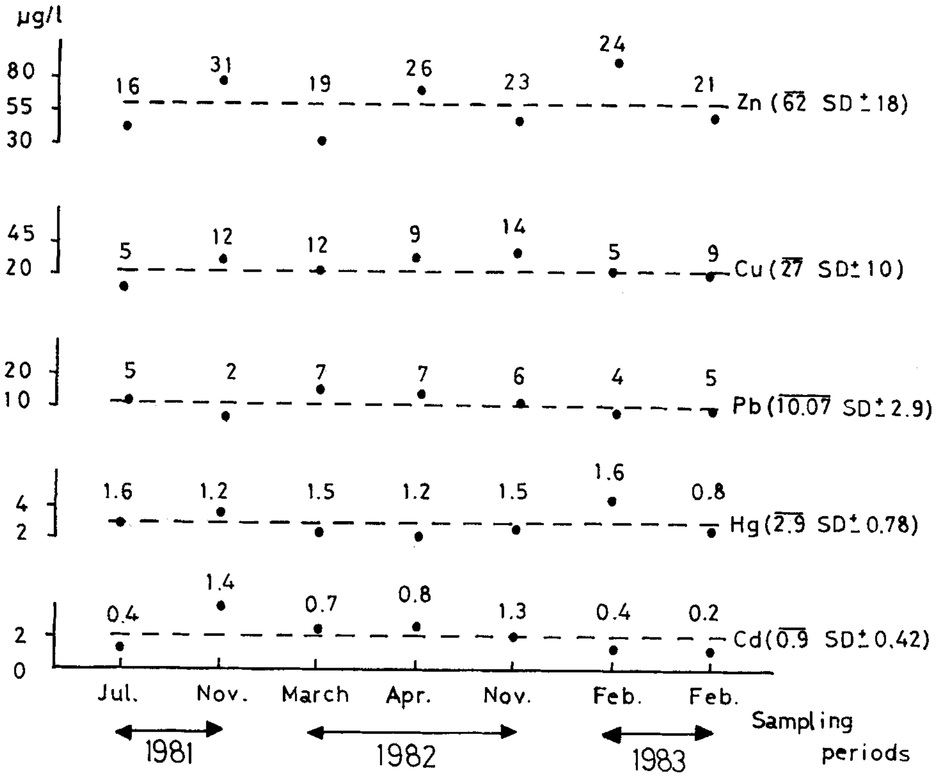

Figure 5. Mean concentrations of metals (µg/l) and SD of mean in the water from 25 (6 to 30) locations along the north-south stream system in each sampling period. Numerals on dots are the SD of mean of 25 analytical values for each sampling period.

The mean levels for each sampling period shown in Fig.5 include 25 (6 to 30) locations following the predominant north-south stream flow, the first being location 6. If these mean levels are compared it appears there are no differences among the concentrations of heavy metals along the stream flow, signifying the metals are distributed more or less homogeneously in the whole aquatic system. The deposition is very fast around the mine, according to the data previously shown for location 2 and the sketched lines in Fig.4, but as they are relatively volatile metals can also be transferred by air to other remote zones of the area (Craig 1980). This is shown since locations 25 and 26 are lagoons which are independent of surface waters of the stream system and in spite of this the metal content in their shallow waters is not dissimilar to the levels found in other sites. Furthermore, location 1 (a dam 3 km away from the north of mine), and location 3 (in the main stream 5 km away from the east of mine) are not influenced by the drainage of the mine, but the concentration range of metals is not very different to that found in other sites of the marsh. The estimations of Zwozdziak (1982) to determine which portion of the total amount of a metal contained in the water in the vicinity of a copper smelter has contributed by fallout and which portion by soil show that nearly 9 % of Cu, 15 % of Pb and 22 % of Zn came from dust fallout. Also, the background concentration level of Cu in soil was reached at a distance of 8 km from the emission source, whereas those of Pb, Zn and Cd surpassed a distance of 10 km. The present day atmospheric concentration of Hg, Pb and Zn in remote areas have a mean value of 4, 3 and less than 10 ng/m^3 respectively, and the average residence time in the atmosphere appears to be 11 days for Hg and 14 days for Pb (Craig 1980).

The aquatic system of the park is evidently polluted by low levels of organochlorine pesticides and PCBs, as well as by relatively significant levels of Hg, Cd, Pb, Cu and Zn, but a gradient in the concentration range in any direction either north-south or northwest-south, following the predominant stream flow inside the marsh, was not observed. It may be that the supposed emission sources located at the mine and the farm lands are partially responsible for this pollution, and other natural mechanisms such as fallout may be involved in this process. It is conceivable that a fraction of the metals comes from the own soil of the park, taking into account that the south-west soil of the Peninsula is abundant in metalic ores. If the pollution levels detected are deleterious to the ecology of the park there are actually no certain solutions to this question. Since they are cumulative poisons some effect is expected to occur and may have already occurred (Hernández et al. 19882; González et al. 1983; Baluja et al. 1983).

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