ORGANOCHLORINATED COMPOUNDS AND SELECTED METALS IN WATERS AND SOILS FROM DOÑANA NATIONAL PARK (SPAIN)

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(Received May 30, 1991; revised December 19, 1991)

Abstract. A study on contamination levels by organochlorinated compounds (pesticides and PCBs) and heavy metals (Hg, Cd, Pb, Cu and Zn) in Doñana National Park (Spain) area and its surrounding region has been carried out. Residue levels of xenobiotics were determined in water and soils samples from seventeen sites selected through the park and nearest surrounding farm lands affecting to the inner Park. Also we analyzed some stations along the Guadiamar Basin in the north of Doñana region to determined the movement and influence of one mine situated over 40 km away, in Aznalcóllar, where the commercial expoitation of pyrites ores rich in Zn, Pb and Cu is being operated.

1. Introduction

Even though the use of organochlorinated insecticides have been banned in numerous countries, a large number of papers have been published on contamination by DDT, its derivatives, and other persistent related compounds with similar chemical and physical properties, such as polychlorinated biphenyls, and heavy metals (King *et al.*, 1991 Marchand, 1989; Ford and Hill, 1991; Steeves *et al.*, 1991). There are also several papers on pollution by these chemicals in Doñana National Park (González *et al.*, 1990; Rico *et al.*, 1989).

This park is situated in the south-western part of the Iberian Peninsula, between 37 °7′ and 36 °48′ north latitude and 6 °12′ and 6 °34′ west longitude, at the delta of the Guadalquivir River on the right bank. With an extension of 50 720 ha, this park shows three clearly distinguished parts: dunes, stabilized sands and marshes. The first parts are disposed along the coast of the Atlantic Ocean. Stabilized sands are situated in the west part of Doñana, contain low hills and natural lagoons. Marshes are the typical landscape of the region and extend over 27 000 ha.

The aquatic system in Doñana consists of small streams, lagoons and artificial channels. In late winter or spring, commonly with large precipitation events the stream system partially disappears and the inner area is mostly covered by water. The annual rainfall averages 600 mm and 80% of the rainfall takes place between October and March (Llamas, 1990). In late summer, with the very intense heat, the marshes dry out and the remaining water is retained in several isolated ponds called 'lucios'. These particular forms make Doñana the most important winter habitat for migratory birds which breed in Northern Europe. As a consequence, any modification of the water quality may be of major concern in view of the impact on the inhabitant species.

A feature of this Natural Park is the agricultural activities in the north surrounding

Water, Air, and Soil Pollution **65**: 293–305, 1992.

areas, centred almost exclusively in rice cultivation, with 20 000 ha bordering the north-eastern, where high quantities of pesticides are used. This is one of the most important threats from human activities, but not the only, because the products of the pyrite ores rich in Zn, Pb and Cu are transported by the Guadiamar River. Also, the Guadalquivir River is one vehicle of input for the waste products along its basin, since it runs through large centers of industries and people, such Sevilla or Córdoba.

The importance of the Doñana National Park makes necessary an evaluation of the pollution in abiotic substrates, water and soils, in order to assess the influence on birds and wildlife in this area.

2. Materials and Methods

The sampling points for water and soils were divided in two parts: marshes and stabilized sands (Figure 1). The geographic location and description are: (1) Madre de las Marismas, (2) Laguna de Santa Olalla, (3) Arroyo de la Rocina, (4) Arroyo Marin, (5) Arroyo del Partido, (6) Caño Guadiamar at Food and Agriculture Organization wall, (7) Quema, (8) Lucio de Vetas Altas, (9) Vuelta de las Arenas,

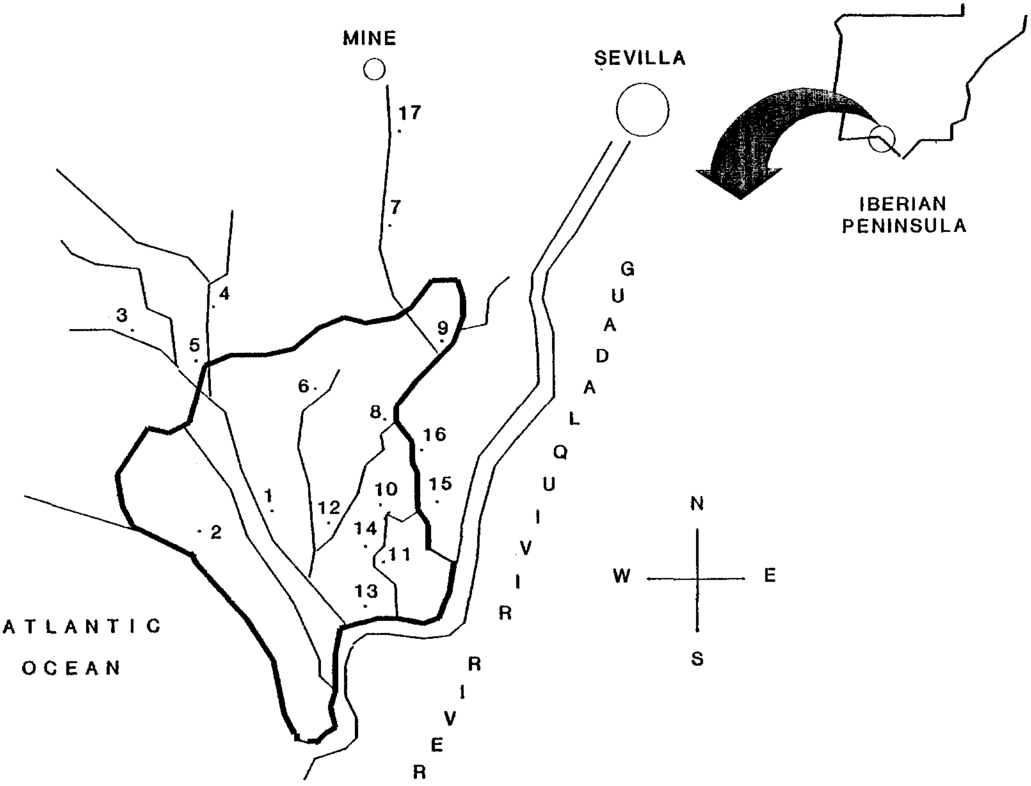

Fig. 1. Study area and sampling locations. Gross line is the limit of the park.

(10) Lucio del Cangrejo Grande, (11) Brazo de la Torre, (12) Lucio de Marilópez, (13) Lucio de los Ansares, (14) Caño Travieso, (15) Puente de Cantaritas (16) Canal de aguas mínimas, and (17) Cortijo de los Pobres.

Water was collected in 2 L clean bottles stored at 4 to 5 °C until preanalytical treatment. Metals were determined in acidified (3 mL of aqueous solution of HNO_3 (1:1) per liter of water) and filtered samples (Whatman F/C glass fiber filter). Soil samples were collected by manual coring (0 to 5 cm) and stored frozen in clean glass jars until analysis. Soil samples were dried at 60 °C for 24 hr and sieved.

Samples were analyzed for α, β, τ and δ hexachlorociclohexanes, aldrin, dieldrin, heptachlor epoxide, dichlorobenzophenone, pp′-DDT, pp′-TDE, pp′-DDE and PCBs and their congeners number 101, 151, 153, 138, 180, 170 and 194 (Ballschmiter and Zell, 1980) as chlorinated compounds, and Hg, Cd, Pb, Cu and Zn.

Organochlorinated compounds were extracted from duplicate water samples (1 L) three times with 100 mL diethyl ether and once with 100 mL hexane and then concentrated to 1 mL in a Kuderna-Danish concentrator. Fifty g of dried soil were extracted in Sohxlet apparatus with 200 mL of hexane for 12 hr and then evaporate to 1 mL. Both water and soil concentrated extracts were cleaned-up over Florisil column, eluated with hexane-diethyl ether (75:25) and later evaporated to 1 mL and analyzed using gas chromatography. Two different gas-chromatographs equipped with ^{63}Ni electron capture detectors were used. First, a Hewlett-Packard 5890 Series II with a Non-Pakd column (Alltech) of 30 m long, 0.54 mm inner diameter and thickness film was 5.0 μm of AT-5 formerly RSL-200. Second, a Perkin-Elmer 8600 with a capillary column covered with BP-5 of 50 m long, 0.22 mm i.d. and 0.25 μm of thickness film to confirm. Chromatographic conditions were as follow: detector, 300 °C; injector, 280 °C; temperature program, isothermal phases at 180 °C (1 min) and 250 °C (30 min), with intermediate temperature increase rate of 2 °C min^{-1}. Peaks were identified on the integrator by retention times; tolerance allowed was ± 0.05 min. The peaks were measured by area counts (minimum count 500) given by the integrator. Recoveries of organochlorines ranged between 84 and 104%, but residue data in the tables were not adjusted on the basis of these recoveries. Total PCBs were estimated by comparing the total peak areas with that of Aroclor 1260. PCB congeneres were calculated by comparing the peak area with that of single congeners for PCB.

For Cd, Pb, Cu and Zn a flame atomic absorption spectrometer was used according to the method of Brown (1968); duplicate samples, consisting of 300 mL of water were extracted with isobutyl ketone (MIBK). Metals from soils were determined by the same technique after HNO_3-$HCLO_4$ digestion. Mercury was analyzed by flameless atomic absorption using an amalgam attachment, adjusting samples to pH = 3.6 in water samples. Ten mL of water was added to 0.5 mL HNO_3 (30%) and H_2SO_4 (30%) acids for direct reading. In soils, 0.2 g of sample are added to 3 mL of HNO_3, held in an oven at 90 °C for 2 hr and measured using a Hg hidride system coupled to AAS. Recoveries of Hg, Pb, Cd, Cu, and Zn ranged from 87 to 96%. The resiude data in the tables were not adjusted on the basis of these recoveries.

3. Discussion

3.1. WATER SAMPLES

3.1.1. *Organochlorinated Compounds*

Data on residue levels obtained for organochlorine compounds in water are presented in Table I. Isomers β and δ of HCH has been detected in 89 and 100% of samples with mean value of 0.031 µg L^{-1} (range non detected-0.148 µg L^{-1}) and 0.032 µg L^{-1} (range 0.002 to 0.134 µg L^{-1}), respectively, but the presence of α and τ isomers were more erratic. Heptachlor epoxide was the only ciclodienic pesticide, quantified in 89% of samples with an average of 0.008 µg L^{-1} (range N. D.-0.051 µg L^{-1}). DDT compounds were determined as pp′-DDE (in 56% of samples) and dichlorobenzophenone (in 67% of samples) metabolites. Their mean levels were 0.005 µg L^{-1} (range N. D.-0.040 µg L^{-1}) and 0.004 µg L^{-1} (range N. D.-0.041 µg L^{-1}), respectively. pp′-TDE and pp′DDT were not detected in samples. More frequent and important quantitatively were polychlorinated biphenyls, with a mean value of 0.237 µg L^{-1} (range 0.076 to 1.448 µg L^{-1}). Gathering all chemicals by structural affinity can be arranged in decreasing level as follow: PCBs (mean 0.237 µg L^{-1})>HCHs (0.046 µg L^{-1})>DDTs (0.009 µg L^{-1})>CDs (0.008 µg L^{-1}).

In any case the limit of 0.1 µg L^{-1} established by WHO (1984) for isomer τ-HCH (lindane) was exceeded. No sample was higher than 0.1 µg L^{-1} that WHO (1984) proposes as a guideline value for heptachlor epoxide. All residues of DDT

TABLE I

Concentrations of chlorinated pesticides and PCBs in waters from Doñana, expressed in µg L^{-1}

Site	αHCH	βHCH	τHCH	δHCH	DBF	H.Ep	DDE	PCBs
1	*	*	*	0.018	*	0.009	0.008	0.103
2	*	0.039	*	0.042	0.002	0.001	0.001	0.115
3	*	0.048	*	0.024	0.001	0.017	0.001	0.134
4	0.001	0.005	0.005	0.134	0.004	0.051	0.001	0.282
5	*	0.022	*	0.017	0.004	0.001	*	0.136
6	*	0.024	*	0.039	0.002	0.022	*	0.114
7	0.001	0.001	*	0.005	0.004	0.002	0.026	0.206
8	*	0.148	*	0.057	0.005	0.001	0.006	0.250
9	*	0.073	0.001	0.019	0.002	0.001	*	0.092
10	*	0.008	*	0.005	0.001	0.010	*	0.076
11	*	0.067	*	0.041	*	0.021	0.040	1.448
12	0.001	*	*	0.002	*	0.001	*	0.223
13	*	0.022	*	0.007	0.001	*	0.001	0.170
14	*	0.030	*	0.013	0.001	0.005	*	0.121
15	*	0.009	*	0.004	0.041	*	*	0.086
16	0.003	0.059	*	0.036	*	0.001	*	0.166
17	*	0.005	*	0.007	*	0.004	0.001	0.179

* = Not detected (<0.001 µg L^{-1}).

group were lower than the guideline value by WHO (1984) of 1 μg L^{-1}. Only one sample exceeded 0.5 μg L^{-1} that WHO (1976) considers as a limit for very polluted water, and the remaining samples may be considered as moderately polluted waters (0.05 to 0.5 μg L^{-1}, WHO 1976).

Pollution in all samples from Doñana National Park did not vary significantly from one site to another ($p > 0.05$). In Doñana National Park there exists background contamination in all areas sampled. It is not possible to distinguish significantly between sample stations. It is necessary to add that station number 2 is an isolated lagoon, independent from other superficial flows, where rain and groundwater are its sources. This can be a perfect example of the atmospheric transport of chlorinated pollutants referred by several authors as an important way of widespread (Hasset and Lee, 1975; Manchester-Neesvig and Andren, 1989).

The most polluted site was number 11 at Brazo de la Torre flow, whereas the rest of stations were similar. However, there are significant differences between the chemicals ($p < 0.001$), and PCBs are the major pollutants.

3.1.2. *PCB Congeners Composition*

Seven congeners of PCBs were analyzed, but number 194 never was detected. Residue levels for isomers number 101, 151, 153, 138, 180 and 170 are shown in Table II. Different values for each one can be noticed. The maximum levels were found in congeners number 180 and 138. The averages for each chemical in decreasing quantitative order are as follow: 180> 138> 101> 153> 151> 170. In Table II between brackets are shown the percentage for individual compounds relative to the total PCBs, and the addition of the six congeners. This is 21.44 (± 3.87) of total PCBs, determined in Arclor 1260 basis.

In Aroclor 1260 the percentage composition for each congener was approximatley 1.4%, 2.7%, 6.5%, 5.8%, 8.3% and 4.8% for 101, 151, 153, 138, 180 and 170 PCBs, obtained using a capillary column. We quantified in water samples the following mean percentages: 4.2%, 1.5%, 2.1%, 5.8% and 1.4%, respectively, for the same congeners. The number of chlorines and obviously their chemical and physical properties derivated, specially water solubility, condition the behavior of the congeners in different way. The percentage of congener number 101 was increased in water respect to % in Aroclor 1260, mostly due to its solubility in water (log $K_{o/w} = 6.38$) (Hodson and Williams, 1988), the highest of all congeners studied.

In Figure 2, total PCBs which represents the total PCBs in water samples, expressed as Aroclor 1260, is plotted *vs* total PCB congeners, which represents the total PCB congeners in water samples, expressed as sum of concentrations of the six congeners investigated. The correlation is good, with a correlation coefficient of 0.991.

3.1.3. *Heavy Metals*

Table III shows data of selected metals, Hg, Cd, Pb, Cu and Zn determined in waters from Doñana. Their mean values and ranges were respectively: 4.07 μg L^{-1} (2.80 to 5.70), 0.59 μg L^{-1} (0.32 to 1.04), 4.24 μg L^{-1} (2.01 to 5.87), 18.81

TABLE II

Levels of PCBs congeners in waters and total PCBs, expressed in μg L^{-1} and percentage of total PCBs between brackets

Site	101	151	153	138	180	170	ΣISOM
1	0.006	0.001	0.001	0.006	0.006	0.003	0.023
	(5.83)	(0.97)	(0.97)	(5.83)	(5.83)	(2.91)	
2	0.005	0.003	0.002	0.006	0.009	*	0.025
	(4.35)	(2.61)	(1.74)	(5.22)	(7.83)		
3	0.007	0.003	0.004	0.007	0.008	0.003	0.032
	(5.22)	(2.24)	(2.99)	(5.22)	(5.97)	(2.24)	
4	0.017	0.008	0.008	0.015	0.016	0.006	0.070
	(6.03)	(2.84)	(2.84)	(5.32)	(5.67)	(2.13)	
5	0.006	0.004	0.003	0.008	0.008	*	0.029
	(4.41)	(2.94)	(2.21)	(5.88)	(5.88)		
6	0.009	0.002	0.003	0.006	0.006	0.002	0.028
	(7.89)	(1.75)	(2.63)	(5.26)	(5.26)	(1.75)	
7	0.007	0.002	0.004	0.013	0.014	0.002	0.042
	(3.40)	(0.97)	(1.94)	(6.31)	(6.80)	(0.97)	
8	0.006	0.002	0.011	0.015	0.016	0.006	0.080
	(2.40)	(0.80)	(4.40)	(6.00)	(6.40)	(2.40)	
9	0.004	0.001	0.001	0.005	0.006	0.002	0.019
	(4.35)	(1.09)	(1.09)	(5.43)	(6.52)	(2.17)	
10	0.002	0.001	0.001	0.004	0.005	0.001	0.014
	(2.63)	(1.32)	(1.32)	(5.26)	(6.58)	(1.32)	
11	0.085	0.006	0.020	0.095	0.071	0.003	0.280
	(5.87)	(0.41)	(1.38)	(6.56)	(4.90)	(0.21)	
12	0.004	0.001	0.002	0.015	0.013	0.003	0.038
	(1.79)	(0.45)	(0.90)	(6.73)	(5.83)	(1.35)	
13	0.008	0.001	0.002	0.010	0.008	0.004	0.033
	(4.71)	(0.56)	(1.18)	(5.88)	(4.71)	(2.35)	
14	0.005	0.002	0.003	0.009	0.008	*	0.027
	(4.13)	(1.65)	(2.48)	(7.43)	(6.61)		
15	0.002	0.002	0.003	0.007	0.006	0.002	0.022
	(2.33)	(2.33)	(3.49)	(8.14)	(6.98)	(2.33)	
16	0.004	0.003	0.004	0.009	0.008	0.002	0.030
	(2.41)	(1.81)	(2.41)	(5.42)	(4.82)	(1.20)	
17	0.008	0.003	0.004	0.009	0.008	0.002	0.034
	(4.47)	(1.68)	(2.23)	(5.03)	(4.47)	(1.12)	

* = Not detected (<0.001 μg L^{-1}).

μg L^{-1} (9.10 to 31.80), and 96.47 μg L^{-1} (27.93 to 426.97).

The ecotoxicologic significance of those residues may be derivated from the natural levels in freshwater (Forstner and Wittman, 1979) for heavy metals, 0.01 for Hg, 0.07 for Cd, 0.20 for Pb, 1.80 for Cu and 10.00 for Zn, expressed in μg L^{-1}. All of metal concentrations were exceeded in our samples. All water samples contained concentrations of Hg higher than 1 μg L^{-1}, guideline value of health significance proposed by WHO (1984). However, none of the water samples exceeded the guideline values by this organization for Cd, Pb, Cu and Zn, established in 5, 50, 1000 and 5000 μg L^{-1}.

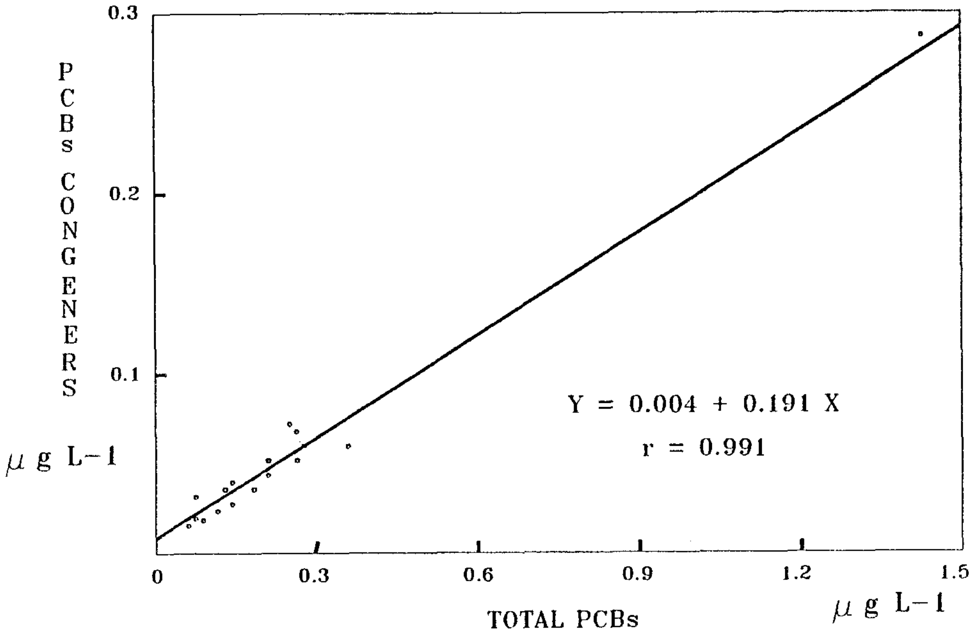

Fig. 2. Relationship between total PCBs and total congeners in waters from Doñana National Park.

TABLE III

Residue levels of heavy metals in waters from Doñana, in $\mu g\ L^{-1}$

Site	Hg	Cd	Pb	Cu	Zn
1	3.00	0.47	5.24	13.42	56.81
2	3.50	0.63	2.81	14.58	77.70
3	3.91	0.50	5.87	19.63	54.37
4	3.00	0.59	3.78	9.10	27.93
5	4.00	1.01	5.27	14.99	89.46
6	5.11	0.85	5.35	31.80	93.48
7	2.80	1.04	5.81	18.40	98.56
8	4.97	0.62	5.74	15.67	426.97
10	5.70	0.36	2.01	20.56	75.12
11	4.40	0.39	3.18	11.79	65.92
12	3.05	0.67	4.30	25.47	65.15
13	4.30	0.32	5.35	20.83	44.55
14	5.20	0.56	3.02	21.96	87.70
15	5.40	0.34	4.31	18.36	66.68
16	4.57	0.66	4.40	25.56	178.00
17	2.89	0.37	2.55	12.62	66.55

It is noteworthy that the most probable origin for Hg may be its use as mercurial insecticide in surrounding fields. The other metals have their main source in the mine situtated in Aznalcóllar by a mobilization process already pointed out (González *et al.*, 1990).

Significant differences in metals concentration were observed ($p<0.001$) with Zn as the most important metal due to its concentration. However, there is no evidence of differences by points of sampling, and station number 9, located at Brazo de la Torre, was the most polluted. Stations nearest to the input of waterflows are more contamined, specially by Zn, that is very illustrative of the descending movement of metals along the north-south axis from the mining area in Aznalcóllar.

3.2. SOIL SAMPLES

3.2.1. *Organochlorinated Compounds*

In Table IV are shown data of organochlorinated pesticides and PCBs of the seventeen stations. Heptachlor and aldrin were not detected in any case. In HCHs group α and β isomers were quantified just in three samples with mean levels of 0.004 μg g^{-1} (range: N.D.-0.017) for α and 0.120 μg kg^{-1} (range: N.D-0.439) for β. However τ and δ isomers are more constant, detected in 85.7% and 100% of soil samples, respectively, with mean levels of 0.019 μg kg^{-1} (range: N.D.-0.057) for τ and 0.884 μg kg^{-1} (range: 0.376 to 1.940) for δ. Heptachlor epoxide and dieldrin were the two only ciclodienic pesticides detected, the first in 64.5% and the second in 35.3% of samples. Their mean values and ranges were 0.027 μg kg^{-1} (N.D.-0.073) and

TABLE IV

Concentrations of chlorinated pesticides and PCBs in soils from Donaña, expressed in μg k^{-1}

Site	τHCH	δHCH	DBF	H.Ep	DDE	DIEL	TDE	DDT	PCBs
1	*	*	*	0.038	0.201	* *	* *	* *	1.911
2	*	*	*	0.018	0.127	* *	* *	* *	0.897
3	0.009	0.973	0.119	0.033	0.081	* *	* *	* *	0.973
4	0.016	1.110	0.223	0.073	0.139	* *	* *	0.026	0.763
5	0.008	0.988	0.126	0.040	0.032	* *	0.032	* *	0.982
6	0.057	1.940	0.321	0.072	0.060	* *	0.047	* *	1.716
7	*	*	*	0.002	0.913	0.200	* *	* *	2.155
8	*	*	*	* *	0.150	0.081	0.002	* *	0.570
9	*	*	*	* *	0.496	0.109	0.038	0.025	0.726
10	*	*	*	* *	0.445	0.128	0.090	0.018	0.464
11	*	*	*	0.038	5.145	* *	0.106	0.058	4.570
12	*	*	*	0.022	0.399	0.158	0.008	0.001	1.752
13	0.004	0.419	0.377	0.043	0.191	* *	* *	0.004	1.452
14	*	*	*	0.009	0.104	0.024	* *	* *	0.592
15	0.042	0.376	0.479	0.070	0.381	* *	0.002	* *	4.209
16	* *	0.382	0.184	* *	2.644	* *	0.129	* *	18.561
17	*	*	*	* *	3.739	* *	0.081	0.016	4.289

* = Not analyzed. * * = Not detected. (<0.001 μg kg^{-1}).

0.041 (N.D.-0.200). The four metabolites of dichlorodiphenylethanes group were detected, although in differents appearance degree. So, whereas TDE (mean: 0.031 μg kg^{-1}; range N.D.-0.129) and DDT (mean: 0.009 μg kg^{-1}; range N.D.-0.058) were detected in 58.8% and 41.2% of samples, DDE (mean: 0.892 μg kg^{-1}; range: 0.032 to 5.145) and DBF (mean: 0.256 μg kg^{-1}; range: 0.119 to 0.479) were in 100% of cases. Also PCBs were determined in all samples, ranging from 0.464 to 18,561 μg kg^{-1}, mean 2.521 μg kg^{-1}.

As well as in water samples ANOVA reveals in soils that PCBs are significantly the most important contaminant organochlorinated chemicals in Doñana soils ($p<0.05$). This is logical if we keep in mind all the years ruined from the ban of chlorinated pesticides in Spain. But there are no significative differences between the seventeen stations, and sampling points number 16 and 11 are the most polluted, both located along the Brazo de la Torre basin.

Organic chemicals are commonly adsorpted by particles falling into the sediments of the bottom. In soils from Doñana this process is carried out. So, the accumulation derived is displayed by factors of concentration representing the [soil]/[water] ratio of a contaminant. Geometric means of these factors in all sites for pesticides and PCBs taken by structural affinity are 103.24 for DDTs, 16.57 for HCHs, 13.77 for CDs and 9.86 for PCBs. These factors are directly related with some physical-chemical properties, mainly K_{OC}, that are pointed out with data from Hodson and Williams (1988) for DDT and a pentabiphenyl congener with K_{OC} values of 5.63 and 4.02, taking in mind that this parameter is the μg of adsorpted sustance per

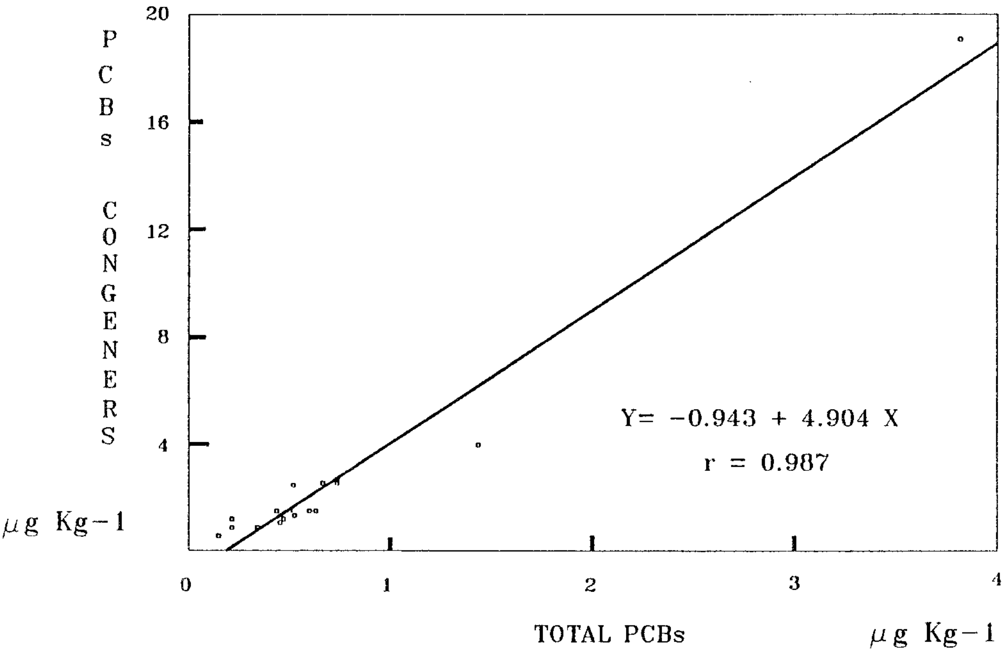

Fig. 3. Relationship between total PCBs and total congeners in soils from Doñana National Park.

gram of organic C and concentration of the sustance in water expressed in μg mL^{-1} ratio.

3.2.2. *PCBs Congeners Composition*

In table V are presented levels of congeners of PCBs, numbers 101, 151, 153, 138, 180, 170 and 194, and total PCBs, with the percentage referred to the total PCBs between brackets. One can arrange the congeners in decreasing mean concentration order as follow: 180> 101> 138> 153> 151> 170> 194>, and their mean concentrations percentages or total PCBs are 0.203, 0.177, 0.134, 0.126, 0.071, 0.045, and 0.010.

TABLE V

Levels of PCBs congeners in soils and total PCBs, in μg kg^{-1} and percentage of total PCBs between brackets

Site	101	151	153	138	180	170	194	ΣISOM
1	0.172	0.016	0.098	0.132	0.169	0.015	0.032	0.634
	(9.00)	(0.84)	(5.13)	(6.91)	(8.84)	(0.78)	(1.67)	
2	0.129	0.028	0.021	0.055	0.071	0.044	*	0.348
	(14.4)	(3.12)	(2.34)	(6.13)	(7.92)	(4.91)		
3	0.114	0.032	0.053	0.056	0.071	0.027	0.020	0.373
	(11.7)	(3.29)	(5.45)	(5.76)	(7.30)	(2.77)	(2.06)	
4	0.191	0.073	0.060	0.008	0.010	0.022	*	0.364
	(25.0)	(9.57)	(7.86)	(1.05)	(1.31)	(2.88)		
5	0.138	0.069	0.024	0.052	0.066	0.003	*	0.352
	(14.1)	(7.03)	(2.44)	(5.30)	(6.72)	(0.31)		
6	0.251	0.075	0.054	0.096	0.123	*	*	0.599
	(14.6)	(4.37)	(3.15)	(5.59)	(7.17)			
7	0.028	0.004	0.082	0.064	0.083	*	*	0.261
	(3.22)	(0.46)	(9.44)	(7.36)	(9.55)			
8	0.012	0.011	0.054	0.037	0.048	*	*	0.162
	(2.11)	(1.93)	(9.47)	(6.49)	(8.42)			
9	0.038	0.053	0.075	0.030	0.039	*	*	0.235
	(5.23)	(7.30)	(10.3)	(4.13)	(5.37)			
10	0.026	0.083	0.077	0.060	0.078	*	*	0.324
	(2.53)	(8.07)	(7.49)	(5.84)	(7.59)			
11	0.304	0.246	0.463	0.451	0.490	0.338	0.076	2.368
	(5.03)	(4.07)	(7.66)	(7.46)	(8.11)	(5.59)	(1.26)	
12	0.196	0.080	0.220	0.095	0.128	0.002	0.001	0.722
	(11.2)	(4.57)	(12.6)	(5.42)	(7.31)	(0.11)	(0.06)	
13	0.194	0.077	0.090	0.068	0.092	0.040	0.024	0.585
	(13.4)	(5.30)	(6.20)	(4.68)	(6.34)	(2.75)	(1.65)	
14	0.018	0.037	0.059	0.036	0.048	*	*	0.199
	(3.04)	(6.25)	(9.97)	(6.08)	(8.11)			
15	0.496	0.073	0.139	0.287	0.388	0.068	*	1.451
	(11.8)	(1.73)	(3.30)	(6.82)	(9.22)	(1.62)		
16	0.379	0.226	0.492	0.846	1.665	0.183	*	3.791
	(2.04)	(1.22)	(2.65)	(4.56)	(8.97)	(0.99)		
17	0.398	0.165	0.404	0.239	0.322	0.024	0.017	1.569
	(9.28)	(3.85)	(9.42)	(5.75)	(7.15)	(0.56)	(0.40)	

* = Not detected. (<0.001 μg kg^{-1}).

The geometric mean factors for six congeners were 29.73 for 153 PCB, 24.14 for 151 PCB, 17.63 for 101 PCB, 11.86 for 170 PCB, 11.43 for 180 PCB and 8.60 for 138 PCB. For congener number 194 there are no factors due to the lack of detected residues of this biphenyl in waters.

In Figure 3 total PCBs which represents the total of PCBs in soil samples, expressed as Aroclor 1260 is plotted *vs* total PCBs congeners, which represents the total PCBs congeners in soils expressed as sum of concentrations of the seven congeners investigated. A good correlation has been obtained with a correlation coefficient of 0.987.

3.2.3. *Heavy Metals*

Table VI shows levels of heavy metals in soils. Mean values and ranges for the five metals are: Hg, 0.38 μg g^{-1} (0.22 to 0.70); Cd, 1.24 μg g^{-1} (0.25 to 4.97); Pb, 14.84 μg g^{-1} (1.35 to 31.26); Cu, 48.47 μg g^{-1} (0.11 to 538.35); and Zn, 700.30 μg g^{-1} (4.29 to 5402.00). The following metal levels in soil samples from rather unpolluted regions are cited in literature (Uthe *et al.*, 1972; Anderlini *et al.*, 1982): 1082 Hg, 0.30 μg g^{-1}; Cd, 0.06 μg g^{-1}; Pb, 10.0 μg g^{-1}; Cu, 20.0 μg g^{-1}; and Zn, 50.0 μg g^{-1}. With these premises it is possible observe the contamination process carried out in Doñana, especially strong for Zn and Cd in points situated near the mine. Zn may serve to monitorize the phenomenon of mobilization of metals already commented on before. The residue levels of Zn in soils decreased with increasing distance from the mine of Aznalcóllar. So the most polluted point is the nearest to mine, in Cortijo de los Pobres, with 5402.00 μg g^{-1}, and in accordance

TABLE VI

Levels of heavy metals in soils from Doñana, expressed in μg g^{-1}

Site	Hg	Cd	Pb	Cu	Zn
1	0.41	0.43	20.49	13.16	172.31
2	0.33	0.28	8.24	0.61	5.09
3	0.37	0.25	1.35	0.11	5.13
4	0.31	0.28	4.22	2.26	17.84
5	0.42	0.31	2.83	1.29	4.29
6	0.38	0.57	15.15	19.01	59.40
7	0.36	3.09	28.15	32.91	2368.30
8	0.45	0.87	14.16	13.60	169.56
9	0.46	1.39	14.42	35.78	571.96
10	0.26	4.01	15.49	47.95	2153.00
11	0.70	0.86	14.83	22.36	226.01
12	0.44	0.55	13.28	12.14	58.80
13	0.28	0.49	12.02	9.18	46.56
14	0.23	0.64	23.67	12.25	64.68
15	0.35	0.83	20.56	30.90	152.00
16	0.22	1.23	12.10	31.45	428.09
17	0.43	4.97	31.26	538.35	5402.00

TABLE VII

Factors of correlation between metals in soils

	Cd	Pb	Cu	Zn
Hg	-0.046	0.028	0.1161	0.0221
Cd	0.644[a]	0.7455[a]	0.9480[a]	
Pb		0.5646[b]	0.6555[a]	
Cu				0.8956[a]

[a] = $p<0.001$.
[b] = $p<0.05$.

with Guadiamar River descends to the south, levels are decreasing up to 2368.3 $\mu g\ g^{-1}$ at Vado de la Quema and 571.96 $\mu g\ g^{-1}$ at Vuelta de las Arenas, becoming lost in the rest of the Park.

One can notice significant differences between the metal contamination ($p<0.001$), being Zn the major metal. However no significant differences by stations of sampling ($p>0.05$) has been found, although points number 17, 7 and 10 are more polluted than the rest considered as background levels.

High correlations exist between Cd, Pb, Cu and Zn (Table VII). However coefficients for Hg are very low. This can be explained by the similar sources and dynamics of distribution for Cd, Pb, Cu and Zn, while Hg has an agricultural origin due to its use in mercurial pesticides in rice fields around Doñana.

Data from analysis indicate an accumulation process of heavy metals in soils derivated from their adsorptive capacity to retaine chemicals (Connel, 1990). The geometric means of the factors of concentration from water to soil are arranged in decreasing order as follow: Pb (3500.45) > Zn (1458.63) > Cd (1422.59) > Cu (623.57) > Hg (91.97).

4. Conclusions

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 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 metal comes from the soil in the park, taking into account that the south-west area of soil in the peninsula is abundant in metallic ores. If 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 occured (Hernández *et al.*, 1988, 1989).

Acknowledgements

Supported by CICYT and CSIC. The authors acknowledge the assistance in collecting samples of Mrs. Blanca Ramos Losada, from Doñana National Park, ICONA.

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