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Quality evaluation of the surface waters entering the Doñana National Park (SW Spain)

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Abstract

Surficial waters entering the Doñana National Park were sampled and analysed for 20 parameters over 12 years at more than 30 sampling sites. Different types of pollution characterize the different water networks entering Doñana. The waters entering from the north are little polluted or only polluted by outlets from small villages and/or effluents from industries of transformation of agricultural products. Acid mine-waters with high heavy metal concentrations skirt and enter Doñana from the east. Finally waters of marine origin enter Doñana from the south. The eastern and northern water networks are very dynamic, and flood Doñana frequently. The importance and variation of the pollution carried through the various water networks under different flow conditions are discussed.

Keywords: Doñana National Park; Water pollution; Acid mine-waters; Heavy metals; Flow influence

1. Introduction

The existence of wetlands in the Mediterranean climates depends strongly on the changing and often extreme weather conditions. The Doñana National Park (DNP) receives surface waters through different nets of water courses—most of them altered by man (channels, levees, floodgates, agricultural and industrial pollution, etc.). The most important alteration are the levees of the Guadiamar river, which skirt the DNP, and which have changed the hydrology of the park by increasing the number of months with water deficit and preventing flooding. There is evidence that this factor leads to the progressive filling of the marshes and the decrease of nesting species in the DNP [1].

As a counter measure, a Hydrological Regulation Plan (HRP) has been designed that allows pumping of water from the Guadiamar river into the head of the 'Caño Guadiamar' or into the 'Caño Travieso' (Fig. 1) [2].

The DNP is considered as a dynamically very active system in a semi-steady state, depending on many factors, the most important of which are water quantity and quality. Thus the study of the

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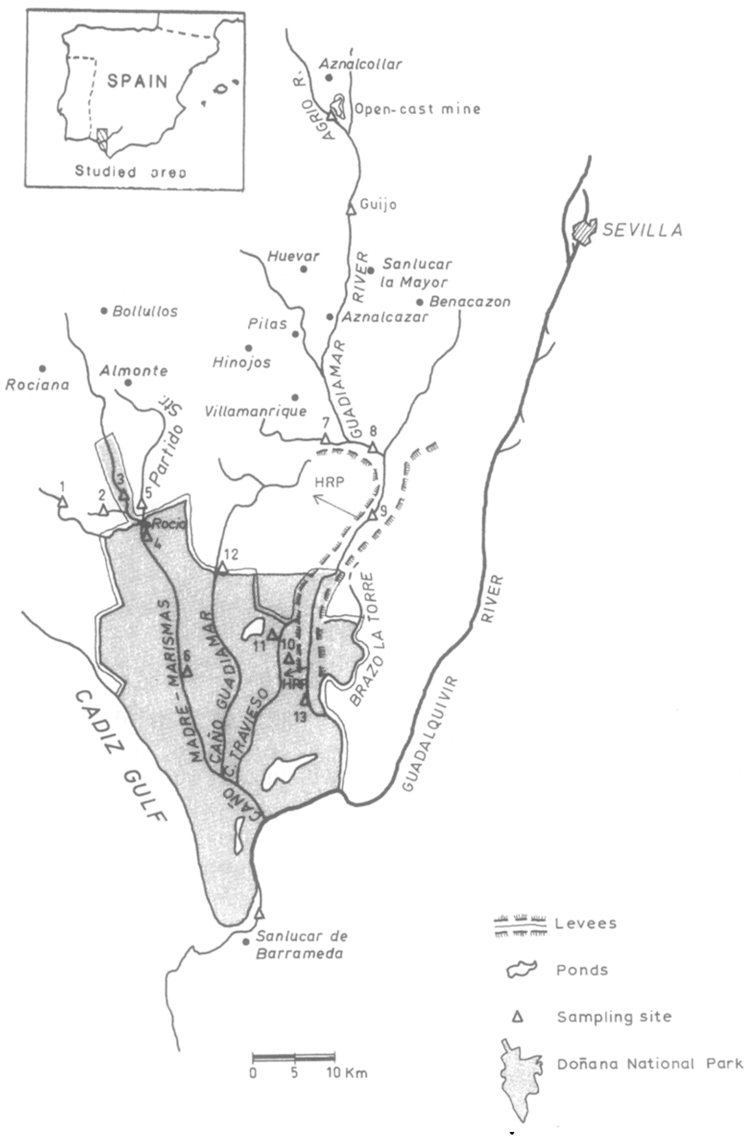

Fig. 1. General information and sampling sites during the 1982–1986 campaign.

composition of the water entering the park is the only sure way of conducting the HRP [3,4].

It should be noted that there is an open-cast polymetallic sulphide mine which has been historically exploited and whose old spoil heaps (together with those from the newly built mineral concentration factory) discharge into the Agrio river—a tributary of the Guadiamar river (Fig. 1)—polluting its water with heavy metals [5,6]. Therefore, the possible influence of heavy metals on fauna, flora and soil should also be considered [7].

This paper presents data of the water quality in sampling sites of water courses related to the DNP over 12 years. Some 30 sampling sites were sampled every fortnight in the period 1978–1980

[5,6]. Other water samples were taken monthly at the flow gauging station of Guijo (Fig. 1) by the Water Authorities (Comisaría de Aguas del Guadalquivir, (CAG)), during 1979–1991 [8]. During 1982–1986 another 13 sites (Fig. 1) were sampled each year during the charge period (approximately from November to February), the retention period (March–June), and the discharge period (July–October) [9]. In the charge period of 1983, heavy rains occurred only for few days; a daily sampling was carried out at sites 1, 2, 3, 4, 5, 6, 8, 9, 10 and 11, to study the influence of flooding on water quality changes.

2. Experimental

2.1. Sampling sites

Fig. 1 shows the location of the sites sampled between 1982 and 1986. Site 1 is on a stream crossing a peat bog and receiving pollution from nearby recently graded soils (regosols or arenosols). Site 2 is on an irrigation channel. Site 3 is a pond or temporary rain-dependent lagoon at Rocio, a small village which has become a place of major religious pilgrimage. The possible influence of this village on the surface and ground water quality has not yet been studied. Site 4 is on a stream free of urban influence; while site 5 is on the Partido stream, which receives sewage from a wide area with a population of ca. 35 000, and in which there are small industries of preparation and transformation of agricultural products (mainly fruit juice, wine, table olive and olive oil). Site 6 is on the Madre de la Marisma stream which receives the waters of all the water courses previously referred to (Fig. 1).

Site 7 is on a stream receiving sewage from a village with 4000 inhabitants. Sites 8 and 9 are on the Guadiamar river between the levees constructed on both river banks to avoid unwanted flooding of the arable fields (Fig. 1). The Guadiamar river receives the sewage from a population of ca. 40 000 living in villages with olive-oil mills and other industries related with olive, wine and fruits, whose untreated effluents are discharged into the water courses. The Guadiamar river and its tributary the Agrio cross an important pyritic deposit of the Iberian Pyritic Belt, and receive waters polluted with heavy metals from erosion and from leaching of old spoil heaps [5,6,10]. The pyritic processing factory on the river Agrio has water treatment systems. Before the levees were built, the Guadiamar river joined a net of streams (often dry during summer and early autumn), called 'caños' (caño Guadiamar, caño Travieso and Madre de la Marisma being the most important), which discharged into the Guadalquivir river (Fig. 1). This net of 'caños' is of utmost importance to the DNP hydrological system [2]. Site 12 is at the place where the HRP waters enter the DNP.

Site 10 is on a man-made channel near the Brazo de la Torre; site 11 is in an unaltered zone of the Biological Reservation of the CSIC (the Spanish Science Research Council) inside the DNP, and site 13 is near the end of the levees. These last three sampling sites are affected by sea water from the Guadalquivir river at high tide.

2.2. Meteorological and hydrological data

The data of the six meteorological stations in the DNP show that the mean annual rainfall is 529.6 mm. The DNP has an area of ca. 60 000 ha, rainfall accounts for 315×10^6 m^3 of the total water entering the park annually. Other sources of water for the DNP are the Rocina and Partido streams (for which the CAG estimates ca. 12×10^6 m^3/year), the Guadiamar river and the Guadalquivir river. From the flow gauging data of the Guijo it can be estimated that a mean of 173×10^6 m^3/year entered the DNP through the Guadiamar during the period 1942–1975 [11]. This value decreased in the period 1979–1991 to ca. 70×10^6 m^3/year (CAG); these figures do not include the water brought by tributary streams downstream from the flow gauging station. The amount of water entering the DNP via the Guadalquivir river is unknown, but it can be considerable—especially at high tide and under west wind conditions—and is responsible for the ecology of the saline marshes of the DNP [12].

The potential evapotranspiration of this area of West Andalusia is considered to be ca. 900 mm

Table 1
Flow variations of the Guadiamar river at Guijo during the flood event of February 1982

Day	10	11	12	13	14	15	16	17	18	19	20
Flow (m^3/s)	0.55	0.30	102	40.4	34.6	10.5	3.7	2.8	1.1	0.82	0.82

Rainfall during 10–20 February: 101.4 mm (27.6% of the annual rainfall).

[13] which amounts to a loss of ca. 540×10^6 m^3/year. Taking into account other water losses such as runoff and percolation (estimated at 300 mm/year [14]), the DNP has a very high negative hydrological balance which can extend from May to November.

The present study included dry and wet years, with the annual rainfall ranging between 367 and 828 mm. It is interesting to note that the uneven distribution of rainfall, peculiar to the Andalusian climate, causes the highly changing flow characteristics of the water courses of this area, as shown in Table 1. During the period of this study, flows as high as 150 m^3/s were recorded at Guijo on two occasions, and that 20 of the monthly mean records were 0 m^3/s. This variation in the flow of the water courses entering the DNP is another of the causes which configure its ecology.

2.3. Analytical methods

Surface water samples were collected in polythene acid-washed bottles and stored at 4°C. Dissolved oxygen (DO) was determined by the azide modification of the Winkler method [15] in water samples collected in glass bottles and fixed in situ. Electrical conductivity (EC) and pH were determined in unfiltered samples in the laboratory.

Total phosphorus and Kjeldahl nitrogen were determined after digesting the unfiltered samples by the method outlined by Nichols [16] and modified by Cabrera et al [17]. Total phosphorus in the digest was determined as ortho-phosphate by the Murphy and Riley method [18]. Kjeldahl nitrogen was determined as ammonium by the methods of Nessler [15] or Solorzano [19]. Potassium permanganate consuming capacity (PPCC) of unfiltered samples was determined by the method described by Rodier [20]. Nitrate was determined in filtered samples (0.45 μm) by the method of Scheiner [21].

Sodium and potassium were determined in filtered samples (0.45 μm) by flame emission spectrometry in a Perking Elmer AA 703 spectrophotometer. Dissolved heavy metals (iron, copper, manganese, lead, nickel, zinc and cadmium) were determined in filtered (0.45 μm) and acidified (3 ml of 1:1 HNO_3 per liter; pH < 2) samples. When metal concentrations were not sufficiently high to be determined directly, preconcentration of the sample was required (i) non-saline samples: by evaporation to dryness and subsequent dissolution of the residue with 2% (v/v) concentrated HCl [22] or (ii) saline samples: by extraction with ammonium pyrrolidine dithiocarbamate (APDC) in chloroform (pH 2.3), evaporation to dryness, digestion with concentrated HNO_3 and dissolution of the residues with 1:1 HNO_3 and deionized-distilled water [22]. At least, a twentyfold concentration was achieved by both methods. 'Total' heavy metals were determined in unfiltered, acidified (with 1:1 HNO_3 to pH < 2) samples, after evaporation to near dryness, subsequent dissolution of the soluble heavy metal with warm 1:1 HCl and dilution with deionised-distilled water. Heavy metals in solution were determined by flame atomic absorption spectrometry (FAAS) in a Perking Elmer AA 1100 B spectrophotometer. The operational detection limits for the metals were in mg/l were: Fe 0.12, Cu 0.1, Mn 0.05, Pb 0.5, Ni 0.15, Zn 0.02 and Cd 0.025. Quantification was accomplished using reference solutions of the corresponding metal (Titrisol, Merck) and spiked samples with known concentrations of each metal. Blank samples were made for each spectrophotometric analysis to account for any analytical and instrument error. Recoveries of the evaporation method were always > 95%. For the APDC-chloroform method recoveries ranged from 93% (Zn) and 103% (Fe).

Dissolved and suspended solids were determined by filtering known volumes of water

Table 2
Main characteristics of the waters entering the DNP from the north (sampling sites 1–6)

Flow	[Normal ($N = 43$)]				Flood ($N = 21$)
	Minimum	Maximum	Mean	Lowest mean	Mean
pH	6.3 (1)	8.6 (4)	7.6	6.9 (1)	7.4
EC (μS/cm)	92.4 (1)	2300 (5)	824	498 (3)	646
DO (mg O_2/l)	<DL (5)	17.1 (2)	7.2	2.7 (5)	—
PPCC (mg O_2/l)	5.6 (4)	296 (5)	47	13 (4)	66
Kjeld.-N (mg/l)	0.57 (4)	89 (5)	5.7	0.97 (4)	3.0
Dissol-(NO_3-N) (mg/l)	<DL (1–6)	3.28 (4)	0.63	0.18 (1,3)	1.46
Total-P (mg/l)	0.03 (2,4)	30 (5)	2.17	0.09 (1)	0.67
Chlorophyll (μg/l)	<DL (1,3)	357 (5)	51	6.8 (4)	30
Total-Fe (mg/l)	0.32 (4)	3.2 (5)	1.2	0.47 (1)	7.3
Total-Zn (mg/l)	0.02 (1–3)	1.3 (3)	0.18	0.05 (4)	0.07
Total-Cu (mg/l)	<DL (2)	0.08 (5)	0.05	0.01 (1)	0.06
Total-Mn (mg/l)	0.06 (4)	1.3 (6)	0.50	0.13 (4)	0.29
Total-Pb (mg/l)	<DL (1–6)	0.06 (6)	0.04	0.01 (1)	0.03
Total-Ni (mg/l)	0.01 (1–5)	0.09 (6)	0.04	0.02 (2–4)	0.03
Total-Cd (mg/l)	<DL (1–6)	0.010 (2,5)	0.001	<DL (1,6)	<DL
TIS (mg/l)	200 (1)	6324 (6)	875	300 (1)	678
DIS (mg/l)	28 (1)	1259 (5)	412	247 (1)	380
TOS (mg/l)	49 (2)	905 (6)	239	130 (2)	192
DOS (mg/l)	7.0 (2)	846 (5)	161	79 (2)	137

DL, detection limit. Figures in brackets show the sampling site where the values were attained. N, number of samples.

through pre-ignited Whatman GF/C glass filters (1.2 μm) and evaporating the filtrates. Evaporated filtrates and filters were heated to constant weight at 110°C and later at 525°C. Dissolved inorganic solids (DIS) were considered to be the residue of the filtrate at 525°C, and dissolved organic solids (DOS) were calculated by the difference between the weights at 110 and 525°C. Suspended inorganic and organic solids (SIS and SOS) were calculated in a similar way from the weights of the filters. Total inorganic and organic solids (TIS and TOS) were calculated by the sum of the dissolved and suspended solids.

Chlorophyll content was determined by the trichromatic method [15]. Samples of surface sediments were air-dried and ground to pass through a 0.5 mm sieve. Total iron, copper, manganese, lead and zinc contents were assayed by FAAS after HNO_3-$HClO_4$ digestion of the ground samples. An estuarine sediment (CRM 277) [23] was used as reference material. Recoveries ranged from 77% (Cu) to 103% (Fe) of the certified contents and 81% (Cu, Mn) and 115% (Cd) of the uncertified data of aqua regia-soluble metals in the reference sediment given in the BRS report [23,24].

A general index for water quality (GQI) was calculated from the concentration of the pollutants, as established by Water Authorities of the Ministry of Public Works. The GQI has values between 0 and 100, with the score 60 being defined as the lowest value of 'acceptable quality' [25].

3. Results and discussion

3.1. General water quality

Tables 2–4 show maximum, minimum and mean values of the parameters analysed to characterize waters entering the DNP from the north (sampling sites 1, 2, 3, 4, 5 and 6), through the Guadiamar river (sites 7, 8 and 9), and from the south (sites 10, 11, 12 and 13), respectively. These tables also show the lowest mean values for the

Table 3
Main characteristics of the waters entering the DNP through the Guadiamar river (Sampling sites 7–9)

Flow	[Normal ($N = 24$)]				Flood ($N = 6$)
	Minimum	Maximum	Mean	Lowest mean	Mean
pH	7.4 (7–9)	8.4 (7)	7.8	7.7 (9)	7.8
EC (μS/cm)	386 (9)	3600 (9)	1652	1052 (7)	386
DO (mg O_2/l)	<DL (8)	13.5 (8)	6.0	5.3 (8)	6.7
PPCC (mg O_2/l)	6.4 (8)	93 (8)	21	14 (7)	13
Kjeld.-N (mg/l)	0.67 (9)	12.6 (8)	3.76	2.62 (7)	0.67
Dissol-(NO_3-N) (mg/l)	<DL (8,9)	2.26 (8)	0.74	0.60 (7)	0.75
Total-P (mg/l)	0.08 (9)	5.13 (9)	1.13	1.06 (7)	0.43
Chlorophyll (μg/l)	1.5 (7,8)	399 (9)	63.7	26.3 (7)	2.7
Total-Fe (mg/l)	0.61 (8)	35.3 (9)	3.56	1.95 (8)	22.7
Total-Zn (mg/l)	0.05 (9)	2.40 (8)	0.73	0.62 (8)	1.04
Total-Cu (mg/l)	0.01 (8)	0.10 (9)	0.05	0.03 (8)	0.10
Total-Mn (mg/l)	0.52 (8)	3.55 (8)	1.68	1.48 (7)	0.81
Total-Pb (mg/l)	0.01 (7)	0.07 (9)	0.04	0.02 (7)	0.05
Total-Ni (mg/l)	0.02 (7,8)	0.06 (9)	0.03	0.02 (7)	0.05
Total-Cd (mg/l)	<DL (7,9)	0.020 (9)	0.003	<DL (7)	0.020
TIS (mg/l)	240 (7)	2536 (9)	1182	610 (7)	559
DIS (mg/l)	227 (9)	2514 (9)	1128	574 (7)	227
TOS (mg/l)	68 (7,8)	404 (9)	198	124 (7)	111
DOS (mg/l)	54 (7)	392 (9)	172	106 (7)	59

DL, detection limit. Figures in brackets show sampling site where the values were attained. N, number of samples.

individual sampling sites. The last column in the tables presents mean values during flood events. The figures in brackets show the sampling site where the maximum, minimum or lowest values were attained.

Table 2 shows that the Partido stream (sampling site 5) provides the DNP with more polluted water than the other streams from the north (sites 1–4). The mean value of the GQI at site 5 is 33.8, characteristic of very poor quality water, while the mean value for sites 1–4 is 74.4, showing an acceptable quality water. Comparison of the mean values during normal flow period and flood events, in which the flow can be up to 2 m^3/s (10 times more than the mean flow value) [11] shows that heavy rain does not substantially improve the water quality.

The results given in Table 3 show the concentration of heavy metals, the EC values and the content of inorganic residues (TIS and DIS) in the waters of the Guadiamar river (sampling sites 8 and 9). These values are higher than those in the Partido stream (Table 2) and than those entering from the south (Table 4). Comparing normal flow and flood events it can be observed that heavy rain decreases the content of both inorganic and organic residues (measured by EC, PPCC, TIS, TOS, DIS and DOS) of the waters, as well as the concentration of P and N. However, total heavy metals increase, especially Fe and Mn, because of the increase of SIS. The mean value of GQI rises from 54.3 in the normal flow period to 65.4 in the high flow event.

Table 4 shows that the waters to the south of DNP have high values of pH and dissolved oxygen, which may be due to a carbonic–carbonate imbalance. They also have high values of EC and DIS and low heavy metal contents, showing the marine influence. At high flow the saline characteristics decrease, and the Guadiamar river influence is shown by the increase in the total heavy metal contents.

At normal flow, mean values of chlorophyll, Kjeldahl-N and total-P in Tables 2–4 are typical of eutrophic waters [26]. During the flood event, waters entering DNP from the north are also

Table 4
Main characteristics of the waters entering the DNP through the Guadalquivir and/or the Guadiamar rivers (sampling sites 10–13)

Flow	[Normal ($N = 22$)]				Flood ($N = 20$)
	Minimum	Maximum	Mean	Lowest mean	Mean
pH	7.5 (13)	9.7 (11)	8.6	7.8 (13)	7.6
EC (μS/cm)	1700 (13)	34510 (11)	9607	4046 (13)	2940
DO (mg O_2/l)	7.2 (12)	13.7 (10)	10.2	10 (10)	–
PPCC (mg O_2/l)	6.6 (13)	241 (12)	43	8.9 (13)	12
Kjeld.-N (mg/l)	0.69 (11)	12.8 (11)	2.68	1.00 (13)	1.29
Dissol-(NO_3-N) (mg/l)	0.25 (10,11)	10.8 (13)	1.76	0.38 (11)	2.87
Total-P (mg/l)	0.09 (11)	0.71 (10)	0.25	0.15 (13)	0.32
Chlorophyll (μg/l)	1.1 (12)	236 (10)	49	31 (12)	–
Total-Fe (mg/l)	0.38 (11)	7.80 (13)	2.36	0.91 (12)	10.1
Total-Zn (mg/l)	0.02 (10,12)	0.93 (13)	0.11	0.03 (10)	0.42
Total-Cu (mg/l)	0.01 (10–12)	0.04 (11,12)	0.03	0.02 (13)	0.03
Total-Mn (mg/l)	0.02 (10,11)	1.18 (13)	0.23	0.12 (10)	1.47
Total-Pb (mg/l)	<DL (10,11)	0.29 (11)	0.08	0.04 (13)	0.05
Total-Ni (mg/l)	<DL (10,11)	0.12 (11)	0.04	0.03 (13)	0.03
Total-Cd (mg/l)	<DL (10–13)	0.020 (10–13)	0.007	0.004 (13)	0.001
TIS (mg/l)	895 (13)	20379 (11)	5592	2182 (13)	1803
DIS (mg/l)	857 (13)	20192 (11)	5563	2131 (13)	1562
TOS (mg/l)	166 (10)	5120 (11)	1238	531 (13)	403
DOS (mg/l)	159 (10)	5044 (11)	1216	525 (13)	372

DL, detection limit. Figures in brackets show sampling site where the values were attained. N, number of samples.

eutrophic (Table 2), but those from the Guadiamar river are not (Table 3).

Ratios of TIS/TOS are ca. 3 in the Partido stream (Table 2), ca. 6 in the Guadiamar river (Table 3), and intermediate in waters entering DNP from the south, indicating the mineral characteristics of Guadiamar river water. EC and PPCC values of the Guadiamar (Table 3) are typical of mineralized waters.

3.2. Heavy metal pollution

Table 5 compares water quality data at three different sampling sites in the Guadiamar catchment. The flow gauging station of Guijo is some 15 km downstream of the Agrio river close to the village and mines of Aznalcóllar, and some 35 km upstream of sampling site 9 (Fig. 1). It is interesting to note the strong heavy metal pollution of the Agrio river water (agrio means sour), its low pH values and its high values of PPCC (indicative of the presence of oxidizable metallic compounds) and of dissolved solids (typical of highly mineralized waters). The influence of this acid mine-water can be detected 15 km downstream at the Guijo flow gauging station, where the monthly average pH was still 3.8 and 5.9 in June 1988 and January 1991 respectively, despite the measures taken by the Aznalcóllar mine exploiters to reduce heavy metal pollution [8]. Natural water neutralization and consequent lowering of the heavy metal content observed at Guijo (Table 5) may be due in part to the change of the Guadiamar river bed soils from Ranker (on slates and schists) and Dystric cambisols (on spilites) in the Agrio river to Chromic vertisols (on calcareous marls) in the Guadiamar near Guijo [6]. The Agrio and Guadiamar rivers stop flowing in the dry season and during the long periods of drought. Water remaining in the river banks evaporates producing crusts of mixtures of hydroxides, gypsum and other sulphates (alunite, melanterite, etc.) and sulphides (pyrite and marcasite) that are found on the river banks between the Agrio river and the sampling site of Guijo [27]. These crusts are dissolved and/or suspended and transported down-

Table 5
Comparison of some water properties at three sampling sites affected by acid mine-waters

Sampling sites	[Agrio river (1) ($N = 48$)]			Guijo flow gauging station (2) ($N = 85$)			Sampling site No. 9 (3) ($N = 72$)		
	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean
pH	2.7	7.5	3.4	3.1	8.5	6.9	7.4	8.4	7.9
DIS (mg/l)	183	7075	3934	265	8579	2095	313	9056	2139
DO (mg O_2/l)	<DL	12.8	2.4	<DL	12.5	5.6	<DL	19.2	6.1
PPCC (mg O_2/l)	7.2	239	79	1.5	390	22	12	702	96
Dissol-Fe (mg/l)	0.1	800	219	0.2	12	1.1	<DL	1.2	0.2
Dissol-Zn (mg/l)	3.5	200	113	0.1	210	6.2	0.02	0.9	0.2
Dissol-Cu (mg/l)	<DL	76	16	<DL	1.27	0.04	<DL	0.08	0.02
Dissol-Mn (mg/l)	<DL	100	25	0.08	29	4.3	<DL	1.9	0.39
Dissol-Pb (mg/l)	<DL	2.0	0.95	<DL	0.09	0.05	<DL	0.32	0.07

DL, detection limit. N, number of samples.
(1) Period 1978–1980, fortnightly sampling [5].
(2) Period 1979–1991, monthly sampling [8].
(3) Period 1978–1980, fortnightly sampling [5] and 1982–1984 seasonal sampling [9].

stream during flood periods, giving rise to the increased heavy metal concentration in water during floods (Table 3). Thereafter heavy metal concentration decreases and water quality improves. Similar results were found by Wilson [28].

Fig. 2 shows the evolution of Guadiamar water flow (sampling site 9) during the flood event of November 1983. Two peaks can be observed in the hydrograph corresponding with two storms. For EC, TIS and DIS there is a general trend towards lower values at higher flows. SIS reflects the dredging effect of the stream flow in the bank soils and sediments and shows higher values at higher flows. This trend is less noticeable during the second flow peak since readily suspendible material was flushed during the first flow increase. A very good linear correlation was found between SIS and total-Fe values ($r^2 = 0.98$) as these soils and sediments are rich in Fe [27]. Generally, concentrations of total Mn, Zn, Cu, Pb, Ni and Cd increase during the flood event, showing a peak related to the second peak of the flow. Similar trends were reported by Hart et al. [29].

The total volume discharged by the Guadiamar river during the flood event was 87×10^6 m^3, of which 31×10^6 m^3 were discharged from 16 to 23 November 1983. During the latter period it was possible to calculate the total heavy metal loads transported by the river which amount to 580×10^3 kg Fe, 73×10^3 kg Zn, 43×10^3 kg Mn, 5.0×10^3 kg Cu, 2.1×10^3 kg Pb, 1.8×10^3 kg Ni and 0.71×10^3 kg Cd.

The total amount of heavy metals entering the HRP from the Guadiamar river through sampling site 12 during the time span of the present study, can be estimated through the mean flow 70×10^6 m^3/year and the mean values of heavy metals in Table 3: 2990×10^3 kg Fe, 613×10^3 kg Zn, 1411×10^3 kg Mn, 42×10^3 kg Cu, 34×10^3 kg Pb, 24×10^3 kg Ni and 2.5×10^3 kg Cd. These heavy metal loads could contribute to the pollution of the waters, soils and sediments of DNP.

At the end of the levees there are 6000 ha. of marshes that are put in danger by the heavy metals carried down by the Guadiamar waters. As a consequence of the high values of heavy metals in water, sediments of the Agrio river and of the Guadiamar at Guijo are highly polluted. Table 6 shows values of enrichment factors of heavy metals in sediments ($EF = HM_{sediment}/HM_{average\ shale}$, where $HM_{sediment}$ and $HM_{average\ shale}$ are the concentrations of heavy metals in the sediment and in

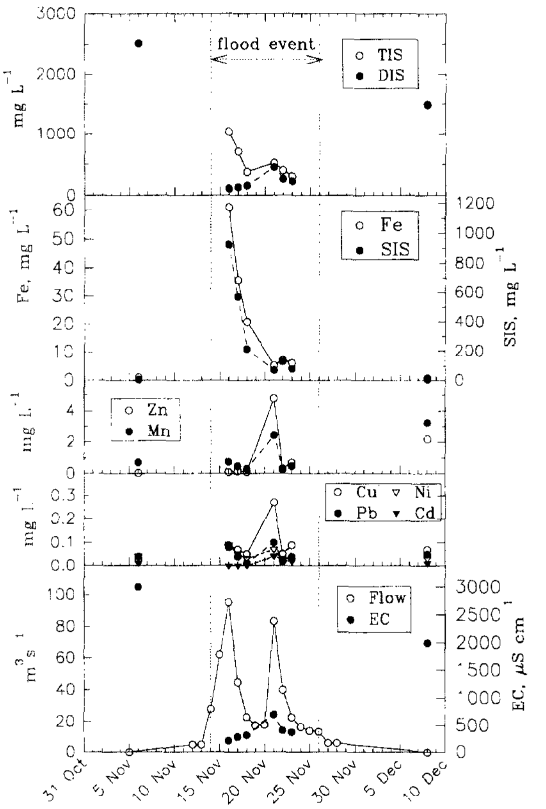

Fig. 2. Variation of water flow, EC, heavy metals, TIS and DIS in Guadiamar river water during the flood event of November 1983.

the average fossil shale [30], respectively) and values of the pollution load index ($PLI = (\Pi EF_i)^{1/n}$, where n is the number of heavy metals considered), calculated after Tomlinson et al. [31]. Agrio and Guadiamar river EF and PLI values are

Table 6
EF and PLI of heavy metals in sediments

	($EF = HM_{sediment}/HM_{average\ shale}$)		
	Agrio	Guadiamar	Guadalquivir
Mn	0.5	2.1	0.6
Zn	45	47	1.5
Cu	24	138	1.4
Fe	2.6	0.9	0.6
Pb	98	19	3.5
PLI	10.8	11.9	1.2

compared with those of the Guadalquivir river mouth at Sanlúcar de Barrameda [32] as representative of the situation to the south of the DNP (Fig. 1).

Sediments of the Agrio and Guadiamar show high EF values for Zn, Cu and Pb which are indicative of pollution. It is worth noting that for the same heavy metals, the sediments of the Guadalquivir have EF values > 1, which may be due to the influence of the Guadiamar river which joins the Guadalquivir river close to its mouth [32].

The value of PLI for the Guadalquivir estuary sediments is close to unity—that of sediments with the same heavy metal contents as the average fossil shale [30]. PLI values for Agrio and Guadiamar river sediments (8.9 and 9.8 times higher than that for the Guadalquivir estuary) are indicative of high heavy metal pollution. During the periods of heavy rains, these highly polluted sediments are resuspended and transported downstream [6,27], representing a real hazard for the DNP.

Several studies on the levels of heavy metals of soils from DNP and its surrounding region illustrate that river bank soils from the Agrio and Guadiamar (up to 13 km from the mine) are severely polluted [27,32–35]. Concentrations of Zn, Cu, Pb, and Cd of soils inside the park are lower than those from the Agrio and Guadiamar river banks outside the park, although soils in the zone of influence of the river generally show levels of these metals over the background levels. The situation is different for Hg, that besides its mine origin has an agricultural source, due to its use in mercurial pesticides in rice fields around. Therefore Hg enters the DNP both through the Guadalquivir river inlet and by fallout [32–34].

Heavy metal levels related with pollution were only found in some aquatic organisms [32,35], especially in tissue muscle samples of crayfish (*Procambus clacrkii*) and eel (*Angilla angilla*). Perhaps, higher heavy metal contents could be found by analysing filter-feeding organisms or fish accumulator organs [27,36]. Cabrera et al. [27] and Cordón et al. [36] reported considerable heavy metal pollution in organisms of the Guadalquivir estuary, very close to the DNP, in which levels of heavy metals in water and sediments are of the same order as those found in DNP. They found mean concentrations of Cu and Zn in oyster (*Crassostrea angulata*), a filter-feeding organism, 5.5 and 2.2 times, respectively, higher than the background. Also, mean concentrations of Cu and Zn over the background levels were found in liver of sea bass (*Dicentrarchu labrax*) (3.0 and 1.4 times for Cu and Zn) and of grey mullet (*Mugil auratus*) (22.7 and 1.6 times for Cu and Zn).

No contamination was found in samples of the terrestrial fauna of DNP. Concentrations of heavy metals in muscle and liver of birds and mammals of DNP are generally below levels known to have a direct effect on survival or reproduction [32,37]. Also, concentrations of heavy metals in eggs of falconiform and ciconiforme of DNP are generally at the background levels and, therefore, it seems to have no detrimental effect on hatchability and nesting survival [38,39].

Data of heavy metal in plants of DNP are scarce. Levels of Cu and Zn in *Halimium halimifolium*, *Erica scoparia*, *Juncus maritimus* and *Carex divisa* from sandy areas and marshes of DNP were found to be on the normal range for these species [41]. Perhaps the more relevant information on this subject are the papers of Soldevilla et al. [10] and Cabrera et al. [27] carried out outside the DNP in the Agrio and Guadiamar river banks (up to 13 km from the mine). They reported that mean concentrations of Fe, Cu, Zn, Mn and Pb of three plant species (*Mentha rotundifolia*, *Typha latifolia* and *Holoschoenus vulgaris*) growing in soils and sediments very polluted by heavy metals are 2–6 times over the levels in unpolluted sites.

Therefore, from the existing data of heavy metal in the biotic compartment of DNP it is not clear whether the levels of heavy metal pollution detected in waters, sediments and soils are deleterious to the ecology of the park. Nevertheless, heavy metals accumulate in DNP soils and sediments in the zone of influence of the Guadiamar river. Soils and sediments are not permanent 'chemical sinks' of heavy metals, because they have a finite carrying capacity that does not guarantee that heavy metals are safely stored forever [41,44]. The capacity of soils and sediments to adsorb and immobilize heavy metals is strongly influenced by certain prevailing properties, mainly pH, redox potential, salinity and organic matter content, which are very dependent on climate. Therefore, soils and sediments could became a source of mobilized heavy metals under changed climatic conditions, if the new conditions lead to a shrinkage of the system' capacity to absorb heavy metals. This is an example of the so-called chemical time bombs (CTBs) defined by Stigliani et al. [42] and DNP could be a paradigmatic scenario in which these CTBs could 'explode'.

4. Conclusions

There are three main sources of surficial water in the DNP, each of them supplies water with different characteristics.

The waters entering from the north, except that of the Partido stream, generally show an acceptable quality. The Partido stream waters, affected by urban and by food and agriculture industrial effluents, are characterized mainly by their high concentrations of organic matter, dissolved inorganic salts and substances rich in nitrogen and phosphorus. Therefore, the waters of the Partido stream are potentially hazardous and should be treated before joining the other streams of the north of DNP.

Waters of the Guadiamar river, skirting and entering the DNP through the Hydrological Regulation Plan, are characterized by their high heavy metal contents which increase in the flood events due to the transport of heavy metal rich solids precipitated upstream on the Guadiamar river bed. The pumping of these waters into the DNP may constitute a hazard of heavy metal pollution for soils and sediments, especially during flood events. A continuous assessment of the water quality of the Guadiamar river should allow cessation of pumping when increasing the heavy metal concentration because of flood or accident in the pyritic processing factory at Aznalcóllar.

The waters entering DNP from the south do not show any environmental problem; salinity is their main characteristic due to the marine influence of the tidal Guadalquivir river.

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