

ACID MINE-WATER AND AGRICULTURAL POLLUTION IN A RIVER SKIRTING THE DOÑANA NATIONAL PARK (GUADIAMAR RIVER, SOUTH WEST SPAIN)*

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Abstract—An inventory of the pollution originated by a mining industry in its first stages of development and by a highly developed agriculture is carried out in a river skirting the Doñana National Park.

The pathway along the Guadamar river basin was studied for heavy metals derived from the opencast-worked polymetallic sulphide deposits and from the mine spoil heaps. The dynamics of N, P and herbicides in waters of urban and/or agricultural origin was also discussed.

Key words—acid mine water, agricultural pollution, *alpechines* (olive oil mill effluents), Doñana National Park, heavy metals

INTRODUCTION

South-west Spain is rich in sulphide deposits of different kinds some of them exploited since biblical times. Near the village of Aznalcóllar (Seville province) there are pyrite outcrops rich in zinc, lead, copper and manganese worked with different success. From 1977 to 1979, 12 million metric tons of mineral were extracted and a new factory was built to treat and concentrate the pyrites. In a second stage a sulphuric acid factory will be built to transform 2 million metric ton yr^{-1} of floated pyrite (Andaluz de Piritas, 1978).

The Agrio river receives the drainage waters from Aznalcóllar opencast-worked polymetallic sulphide deposits and the old mine spoil heaps. Some 7 km downstream, the Agrio river joins the Guadamar river which is the last tributary on the right of the Guadalquivir river, the most important andalusian course of water. In its last 60–70 km the Guadalquivir river is a low-land navigable river with large tidal influence.

The Guadamar river and all its tributaries stop flowing in the dry season which normally extends from May–June to September–October, although the rivers do not stop flowing till the end of June (Vannay, 1970). For this reason, the Agrio river has recently been dammed up near Aznalcóllar and its waters are used for processing the pyritic mineral. This has changed the normal water regime of the zone.

The Guadamar river runs across an ample agricultural region where the northern part is devoted to dry-land agriculture, irrigated fruit and olive tree orchards. In this area there are olive-oil manufacturing mills and some other smaller industries

related to olive, wine and fruit which effluents are discharged untreated to the water courses. Figure 1 shows the location of the more important outlets. Downstream, an area of some 20,000 ha of reclaimed marsh soils standing rice as the only crop, extends between the southern left bank of the Guadamar river and the right bank of the Guadalquivir river. The rice mean yield in this waste area is near 6 metric ton ha^{-1} supposedly the highest in the world.

The southern right bank of the Guadamar river includes the marshy part of Doñana National Park which extends westwards to the sea as shown in Fig. 2.

The utmost importance of Doñana National Park, which was founded by the World Wildlife Fund, is well known. Nowadays, the Doñana National Park is isolated from the waters of the Guadamar river by means of levees ("A" in Fig. 2). However, water from the Guadamar and Guadalquivir rivers can enter the Park at high tide levels across the spots indicated by arrows in Fig. 2, at the end of the levees.

It is suspected that the levees of the Guadamar river are altering the water regime of the Doñana National Park marshes causing drought and other problems of ecological significance. For this reason there exists a project to open the levees somewhere near point "B" in Fig. 2 and allow the waters of the Guadamar river to flood the marshes of the Doñana National Park again.

Guadamar river catchment supports a total population of approx. 40,000 living in villages which sewage outlets are discharged untreated to the river. The Guadalquivir river, just after receiving the Guadamar river, flows into the sea at Cadiz Gulf. Cadiz Gulf is rich in high quality shell—fishes and touristic resorts which are undoubtedly affected by the pollution.

The preceding description shows the importance of assessing the presence of pollutants from mine, olive-

oil mills, intensive agriculture and village sewages in the water courses of the region. The present work was made with this aim and carried out during 1978 and 1979 when the extraction of mineral from Aznalcóllar mine had just started again. Concentration and pro-

cessing of the mineral began only in late 1979. This study can be looked upon as an inventory of the pollution originated by a mining industry in its first stages of development and by a highly developed, very specialized agriculture.

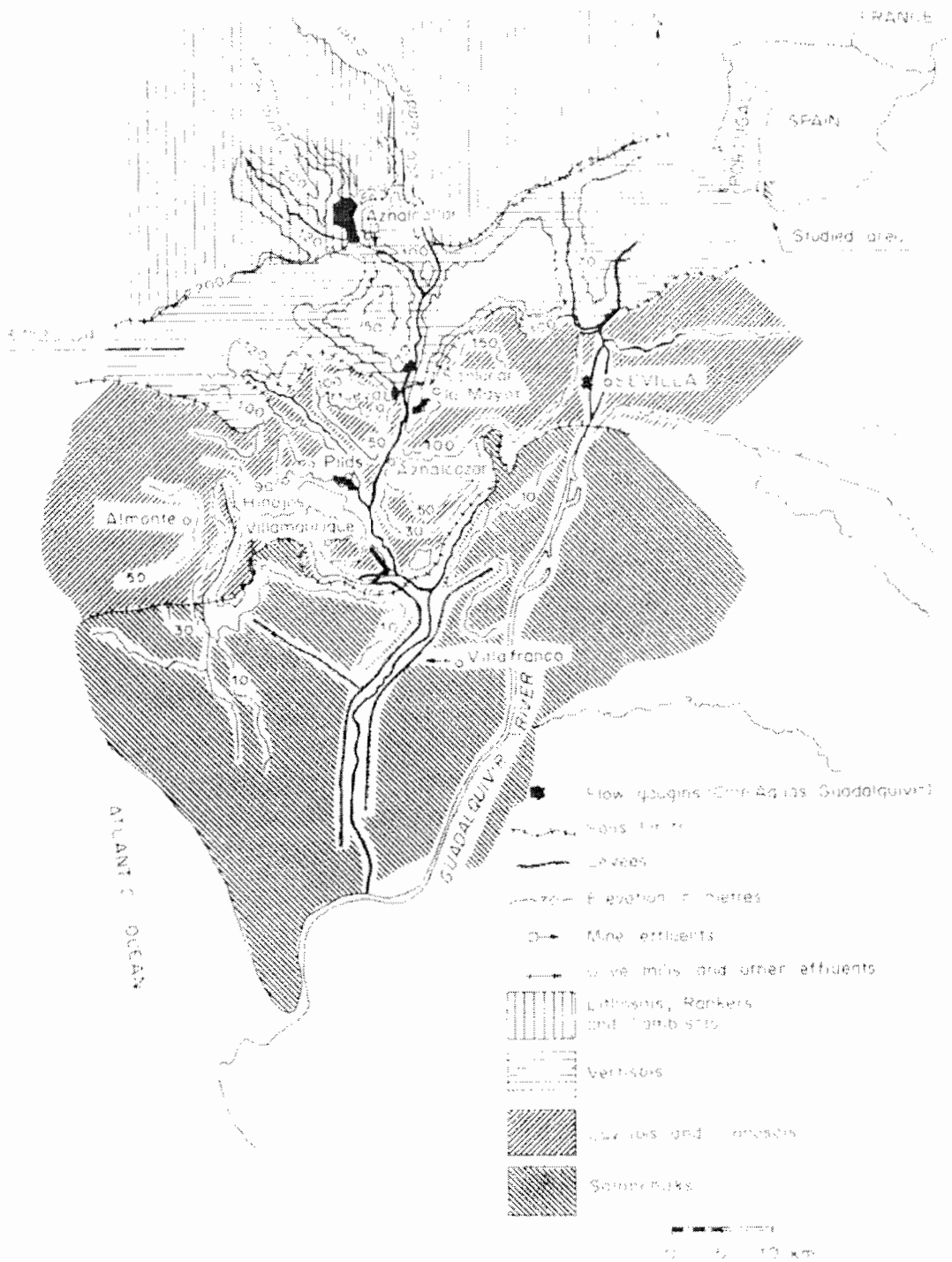


Fig. 1. Study area showing topography, soil distribution and location of the main waste effluents.

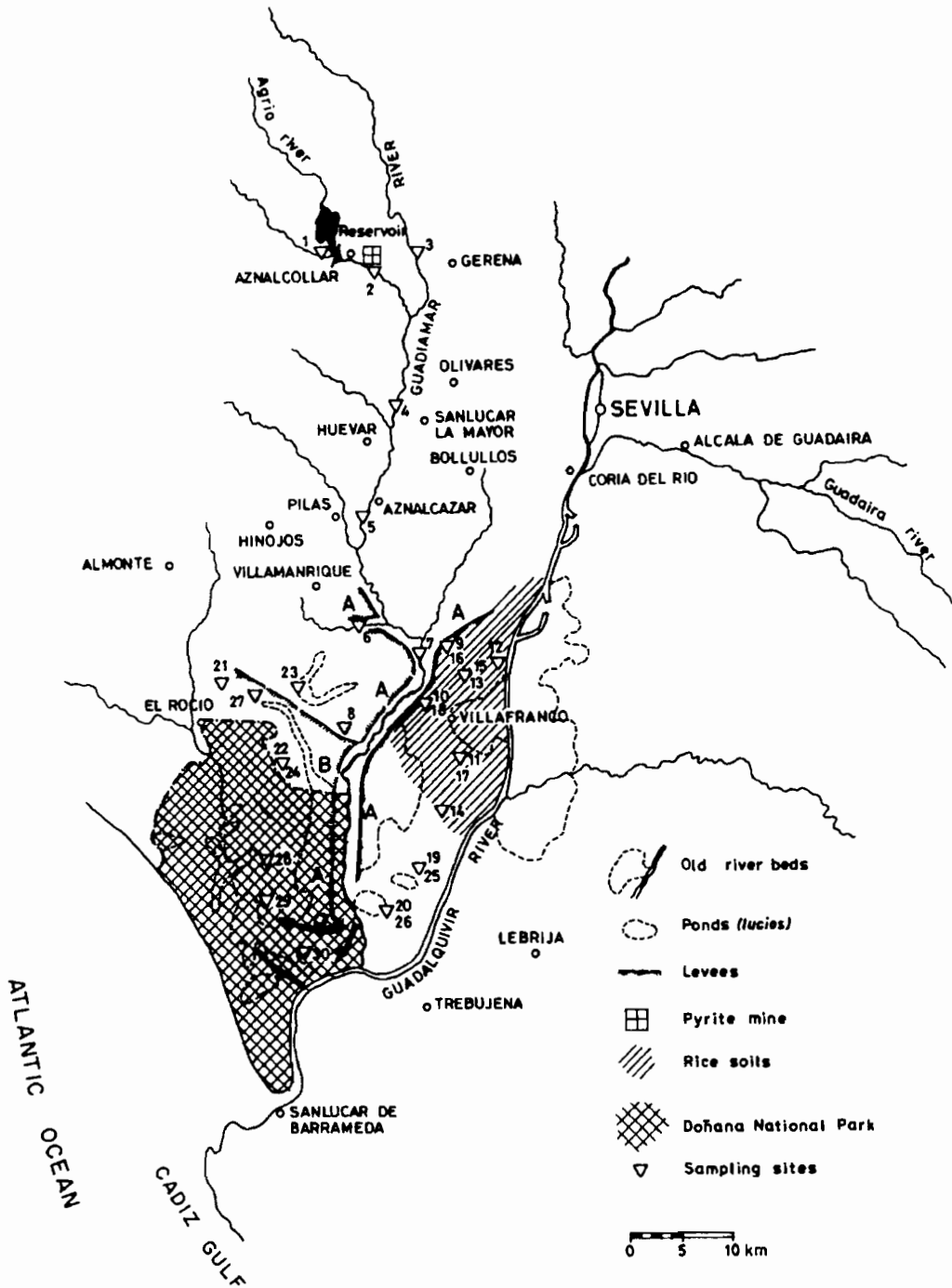


Fig. 2. Study area showing location of sampling sites.

MATERIALS AND METHODS

Sampling sites and description of the area

Location of sampling sites are shown in Fig. 2. Sampling site 1 is on the Agrio reservoir upstream from the mine influence. Site 2 is on the Agrio river downstream from the sulphide deposits and the waste effluent of the processing factory. Sites 3 and 4, 5 and 7 are situated respectively before and after the confluence of the Agrio river with the Guadamar river. Sites 4, 5 and 7 are the most affected by the effluents from olive-oil mills and village sewages. Sampling sites 6 and 8 are near the confluences of the Gua-

damar river with two canals collecting drainage waters from marsh soils under reclamation. Site 6 also receives the influence of dry-land agriculture and villages. Sampling sites 9, 10, 11 and 13 are on rice field drains and sites 12 is on the Guadalquivir river.

Water samples from sites 1 to 13 were collected 48 times during 1978 and 1979, approximately every fortnight.

Additional sampling sites 14 and 19-23, situated on marshes, were sampled for water and sites 24-27, situated on shallow ponds of salty water (*lucios*) of the Doñana National Park, were sampled for sediments in September 1978 and 1979. Samples of water from sites 15-18, located

on the rice field, and 28–30, on the *lucios*, were collected in June and July 1979 for pesticides determinations.

Sampling sites 1, 2 and 3 were located on mountain, poorly developed soils (Lithosols, Rankers and Cambisols on slates and schists and Dystric Cambisols on spilites). Sites 4, 5 and 7 are in a different scenery of small, round topped hills. Site 4 is surrounded by Chromic Vertisols and Vertic Cambisols developed on marls and Calcareous marls. Sampling sites 5 and 7, located on Calcareous Fluvisols and on Alluvial sediments, are surrounded by Chromic Luvisols on calcarenites, Planosols and calcareous sediments.

All remaining sampling sites are located on flat open marshes with gleyic and takinic Solonchaks on fluvio-marine clay sediments (Centro de Edafologia, 1979). Figure 1 shows the distribution of the main groups of soils.

As previously mentioned, the flow of Agrio and Guadamar rivers changes very much depending on the contrasting Andalusian weather. Table 1 shows mean monthly flows of the Guadalquivir and Guadamar rivers mean monthly discharge of the Agrio reservoir as well as the monthly rainfall in the region during the 2 years of study. A dry and a wet period may be considered, a dry period extending over May–September (cumulative rainfall 48.8 mm in 1978 and 14.0 mm in 1979), and a wet period comprising from January to April and from October to December (cumulative rainfall 368.3 mm in 1978 and 509.4 mm in 1979).

Water temperature changes from 9 to 31°C being the 20% of the recorded values $\geq 25^\circ\text{C}$. The mean air temperature varies from 4.7°C, January 1978 and 5.8°C, December 1979, to 35.2°C, July 1978 and 34.8°C, August 1979. Maximum temperatures during summer were 42.6°C in 1978 and 41.0°C in 1979. Minimum temperature was -1.0°C in both winters.

Analytical methods

Water samples were surface collected in polythene acid-washed bottles and stored at 4°C before analysis.

Dissolved oxygen was determined by the azide modification of the Winkler method (APHA, 1971) on water samples collected in glass bottles and fixed *in situ*.

Measurement of pH of unfiltered waters were made in laboratory using a glass–Ag/AgCl combination electrode.

Total phosphorus and total Kjeldahl nitrogen were determined after digesting unfiltered samples by the method outlined by Nichols (1975) and modified by Cabrera *et al.* (1981). Total phosphorus in the digest was determined as *ortho*-phosphate by the Murphy and Riley method (1962). Total Kjeldahl nitrogen as ammonia was determined by the method of Nessler (APHA, 1971) or by the Solorzano method (1969).

Potassium permanganate-consuming capacity (PCCC) of unfiltered waters was determined by the method described by Rodier (1971).

Dissolved phosphorus, ammonia, nitrate and nitrite were determined in filtered samples. Phosphorus and ammonia were analysed by the methods referred to above, and nitrate and nitrite by the method of Scheiner (1974) and Stainton *et al.* (1977) respectively.

Potassium, iron, copper, manganese, lead and zinc were determined in filtered samples. Potassium was analysed by emission spectrophotometry and Fe, Cu, Mn, Pb and Zn by flame atomic absorption spectrophotometry. Determination of Fe, Cu, Mn, Pb and Zn required sometimes the previous concentration of the samples by evaporation to dryness and subsequent dissolution of the residue with 2% conc. HCl (U.S. EPA, 1979).

Dissolved and suspended solids were obtained by filtering known volumes of water through preignited Whatman GF/C glass fibre filter paper and evaporating the filtrates. Evaporated filtrates and filters were heated up to constant weight at 110 and later at 525°C. Dissolved inorganic solids (d.i.s.) were considered to be the residue of the filtrate at

Table 1. Flows of the Guadalquivir and Guadamar rivers, discharge of the Agrio reservoir and rainfall distribution

Site	Year	J	F	M	A	M	J	J	A	S	O	N	D
Guadalquivir	1978	89	289	484	113	208	74	40	42	39	33	23	71
	1979	550	1285	359	440	69	49	39	41	52	160	71	61
Guadamar	1978	7.0	0.5	13.1	0.6	0.5	0.5	0.0	0.0	0.0	—	—	—
	1979	0.7	16.2	0.3	0.5	0.3	0.2	0.0	0.0	0.0	0.0	0.3	0.1
Agrio reservoir	1978	11.6	1.3	18.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	9.1
	1979	16.8	26.4	6.4	1.5	0.1	0.1	0.0	0.0	0.7	9.1	5.2	3.4
Zone of study	1978	7.5	100.0	26.5	43.2	0.0	42.7	0.0	0.0	6.1	39.2	21.1	130.8
	1979	168.0	118.4	77.4	13.9	1.3	0.0	5.5	0.0	7.2	122.0	1.6	8.1

525°C, and dissolved organic solids (d.o.s.) were calculated by difference between weights at 110 and 525°C. Suspended inorganic solids (s.i.s.) and suspended organic solids (s.o.s.) were calculated in a similar way from the weights of the filters.

For the herbicide Ordram or Molinate (5-ethyl hexahydro-1H-azepine-1-carbothionate) determination, unfiltered waters were acidulated with conc. HCl and extracted with hexane (Zweig and Sherma, 1972). For the determination of the Chlorophenoxy herbicides 2,4-D(2,4-dichlorophenoxy acetic acid) and 2,4,5-TP (2,2,4,5-trichlorophenoxy propionic acid), unfiltered waters acidulated with conc. H₂SO₄ were extracted with dichloroethane and methylated with diazomethane (Chacko and Gummer, 1980). Herbicide extracts were analysed by liquid-gas chromatography using lindane (gamma isomer of the hexachlorocyclohexane) as internal standard.

Samples of superficial sediments were air-dried and ground to pass a 0.5 mm sieve. Analysis of their Fe, Cu, Mn, Pb and Zn contents were carried out by flame atomic absorption spectrophotometry after HNO₃-HClO₄ digestion of the ground samples.

RESULTS AND DISCUSSION

Mining pollution

Figure 3 shows the mean values of pH, heavy metals and suspended inorganic solids (s.i.s.) contents in sampling sites 1, 2, 3, 4, 5, 7 and 12 during wet and dry periods of 1978 and 1979. The corresponding standard deviations (not shown) are of the same order as the mean values. The time distribution of some of the considered parameters shown in Figs 4, 5 and 6 gives their variation ranges.

Sites 1, 3 and 12, beyond the influence of the pyrite deposits, the spoil heaps and the mineral processing factory, show pH values and heavy metal concentrations within the range of the U.S. EPA (1977) quality criteria. Low levels of heavy metals in the Guadalquivir river (site 12) is of great importance because its waters are used for flooding the rice fields. Consequently, heavy metal contents in water of the rice fields and irrigation canals (data not shown here), represented by sites 9, 10, 11 and 13 (Fig. 2) are of the same order as those in the waters of the Guadalquivir river. In a few occasions, as will be shown later, this is not true because water from the Guadamar river was pumped into sampling site 10.

The s.i.s. contents in site 12 are higher in wet than in dry period mainly due to the runoff of the agricultural smectitic rich soils in the middle course of the Guadalquivir river, and to a lesser extent due to the resuspension of deposited sediments.

In general, sites 2, 4, 5 and 7 show heavy metal concentrations higher than those in sites 1, 3, and 12, showing the influence of the polymetallic sulphide deposits.

The oxidation of sulphides upstream of site 2 causes the high pollution by heavy metals and the low pH and dissolved oxygen values (Thompson, 1980). The higher values of pH and dissolved oxygen in site 4 could mean that those oxidation reactions have taken place before this site (Table 2). The dissimilarities

between sites 2 and 4 are further evidenced from Fig. 4 which shows the variation along the 2 years of study of the PPCC and Fe content in both sampling sites. In site 2 PPCC and Fe curves show a similar pattern from mid-summer 1978 onwards, corresponding in time with the start of the high scale mineral extraction. Correlation between PPCC and Fe can be explained accepting that PPCC values reflect the presence of reduced ionic species in water (i.e. Fe²⁺). The different pattern of PPCC and Fe in site 4 shows on the other hand that the oxidation processes of reduced inorganic species practically come to an end before this sampling site.

Changes in flow of Agrio and Guadamar rivers have important effects on the pollution of the sampling sites located downstream of site 2. During wet period of 1978 and 1979 the Agrio reservoir had to be discharged (Table 1 and Fig. 5) causing dramatic changes in the flows of both Agrio and Guadamar rivers and abrupt changes in the dissolved metal contents (see Fig. 4 for Fe variations), in t.i.s. and pH values of sampling site 2 (Fig. 5). Minimum values of t.i.s. in site 2 appear at high pH values and correspond with heavy rainfall and/or reservoir releases (Fig. 5).

Table 3 shows the pH values and contents in Fe and total and suspended solids of water sampled immediately before and after two marked increases in flow of Agrio and Guadamar rivers. This data corresponds with two of the most conspicuous minima shown for site 2 in Fig. 5. Site 1 only shows an increase of total organic solids (t.o.s. = d.o.s. + s.o.s.) in the high flow periods possibly due to runoff of the vegetable cover of the poorly developed soils of the area. The arrival of the reservoir-discharged water to site 2 produces a sharp increase in pH and a decrease of the Fe and t.i.s. contents. The increase of flow resuspends river sediments, carrying them downstream and increasing the contents in metal and suspended matter as shown by Symader (1980) elsewhere. Accordingly, site 4, 5 and 7 show a proportionally important increase in the contents of metals, s.i.s. and t.o.s. in high flow periods (Table 3).

Total inorganic solids in sites 3 and 4, located before and after the mine effluent outlets respectively, shows less rainfall or reservoir release dependence than site 2 (Fig. 5) and small changes of pH values (site 3: max. 8.4, min. 7.3, mean value 7.9; site 4: max. 8.5, min. 7.2, mean value 7.9). On the other hand it can be deduced from Fig. 5 that t.i.s. in site 7 are independent of both rainfall and water pH; maximum values of t.i.s. will be commented later.

Results in Figs 3 and 4 indicate that most of the suspended or dissolved metals coming from the mine effluents are sedimented or precipitated before site 4, which is plainly shown by the appearance of the so-called "yellow boy" and other hydrous oxides on the Agrio and Guadamar river beds. Precipitation is mainly caused by the neutralization of water due to the change of the soil parent materials from acid to

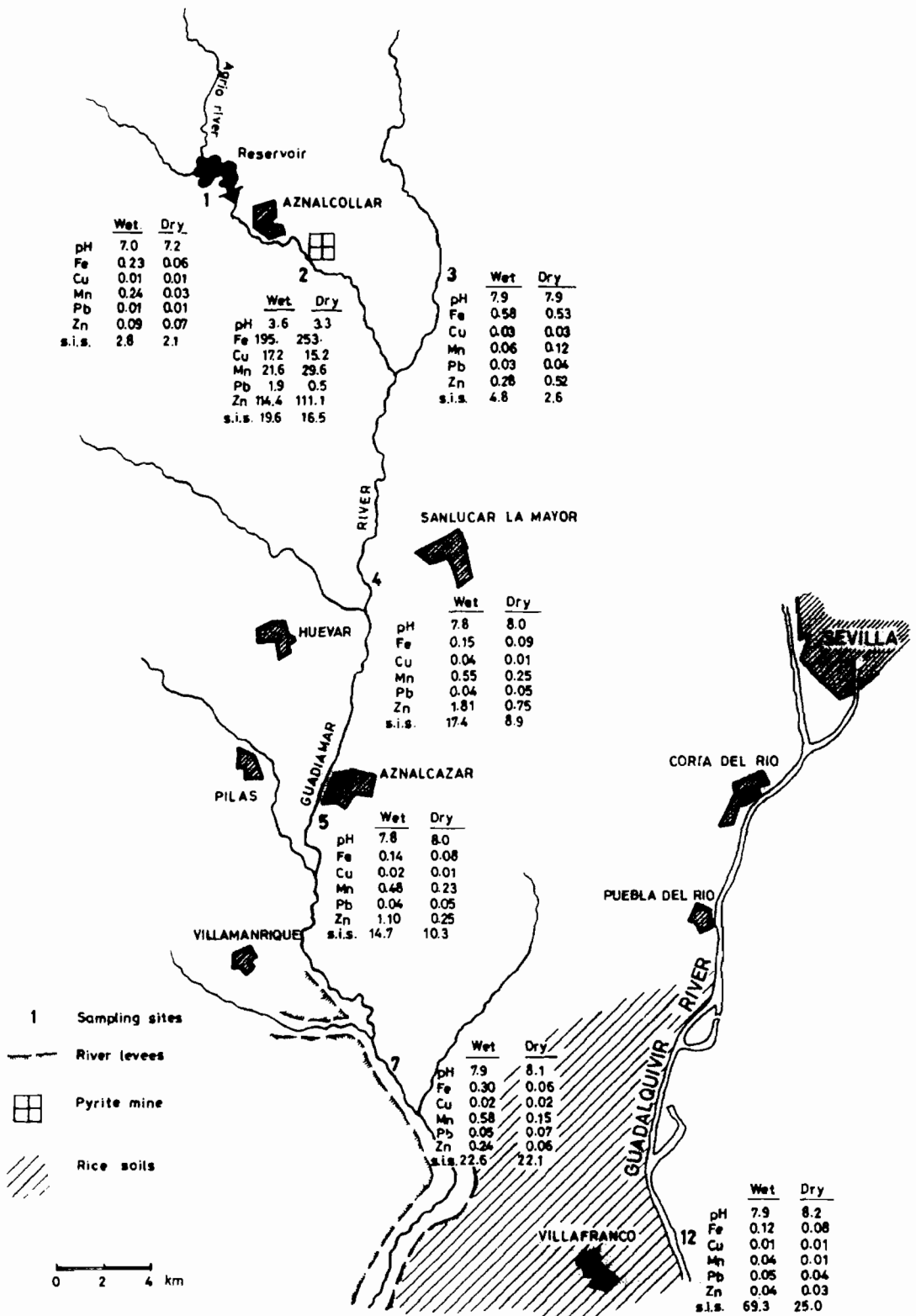


Fig. 3. Mean values of pH, heavy metals and suspended inorganic solid (s.i.s.) contents in sampling sites 1, 2, 3, 4, 5, 7 and 12 during wet and dry periods of 1978 and 1979 (concentrations in mg l^{-1}).

calcareous along the Guadiamar river basin just after joining the Agrio river (Fig. 1). Dilution of acid mine effluents by water from Agrio reservoir and Guadiamar river also contributes to the water neutralization.

Water neutralization causes the concentration of Fe, Cu and Pb in solution to decrease downstream from site 2 up to the levels found in the Guadalquivir river (site 12, out of the influence of the mine) (Fig. 3). Manganese and Zn concentrations also decrease

Table 2. Values pH and dissolved oxygen in sampling sites 2 and 4 during 1978 and 1979

Sampling site	pH			Dissolved oxygen (mg O ₂ l ⁻¹)		
	Mean	Max.	Min.	Mean	Max.	Min.
2	3.5	7.5*	2.7	2.7	12.8*	0
4	7.9	8.5	7.2	9.5	13.3	6.5

*Exceptional values registered in winter 1979 during a reservoir discharge.

downstream but their values in site 7 are still 12 and 6 times respectively those in site 12. The same differential behaviour of these metals was found by other workers (Norris *et al.*, 1981; Young and Blevins, 1981; Filippek *et al.*, 1981).

Generally in wet periods mean concentrations of heavy metals in waters from sites 4, 5 and 7 (Fig. 3) are higher than expected from the respective hydrous oxide solubilities (Pagenkoff and Cameron, 1979). This fact can be explained accepting that heavy rains and water discharges from the Agrio reservoir not only cause the resuspension of the sediments but also the appearance of organic and inorganic complexing agents which alter the normal precipitation-adsorption pathway of deposition of metals into the sediments.

On the other hand, in autumn the olive-oil manufacturing mills start working and their effluents called *alpechines* enter into the river without treatment through points shown in Fig. 1, giving a noticeable black colour to the water. The *alpechines* have high K, P and organic matter contents (average BOD,

33,000 mg l⁻¹) (Fiestas *et al.*, 1979). *Alpechines* organic matter are rich in polyphenols which are known to be active chelating agents. The biggest olive-oil mill of this zone is in the village of Pilas and its effluents (approx. 3×10^6 m³ total discharge, in the grinding season which lasts from October to January) are discharged into the Guadiamar river between sampling sites 5 and 7. Figure 6 shows two noticeable peaks of K in site 7 and only a smaller one in site 5. Potassium peaks are supposed to show the relative importance of the *alpechines* presence in site 5 and 7. If that is so, the increase of Fe and Mn in solution shown in Fig. 6 must be due to the complexing action of *alpechines*. From December to March 1978 there is no available data for site 7 (Fig. 6) because the Guadiamar flood cut the land access to this sampling site.

Before the levees marked "A" in Fig. 2 were built, the Guadiamar river entered into the Doñana National Park and the heavy metal pollution reached as far as sampling sites 24, 25 and 26 (Fig. 2). This is shown by the fact that sediments in sites 24, 25 and 26 are richer in metals than both the soils of the Guadalquivir marshes (Aubert and Pinta, 1977) and sediments at site 27, the latter being located near to, but out of reach of the effect of the Guadiamar river floods (Table 4). Despite that sites 24-26 are located about 50 km downstream from the mine, the found metal contents are even higher than values given by other workers for sediments close to similar pollution sources (Hutchinson and Whitby, 1974; Moore, 1980; Say and Giami, 1981; Norris *et al.*, 1981).

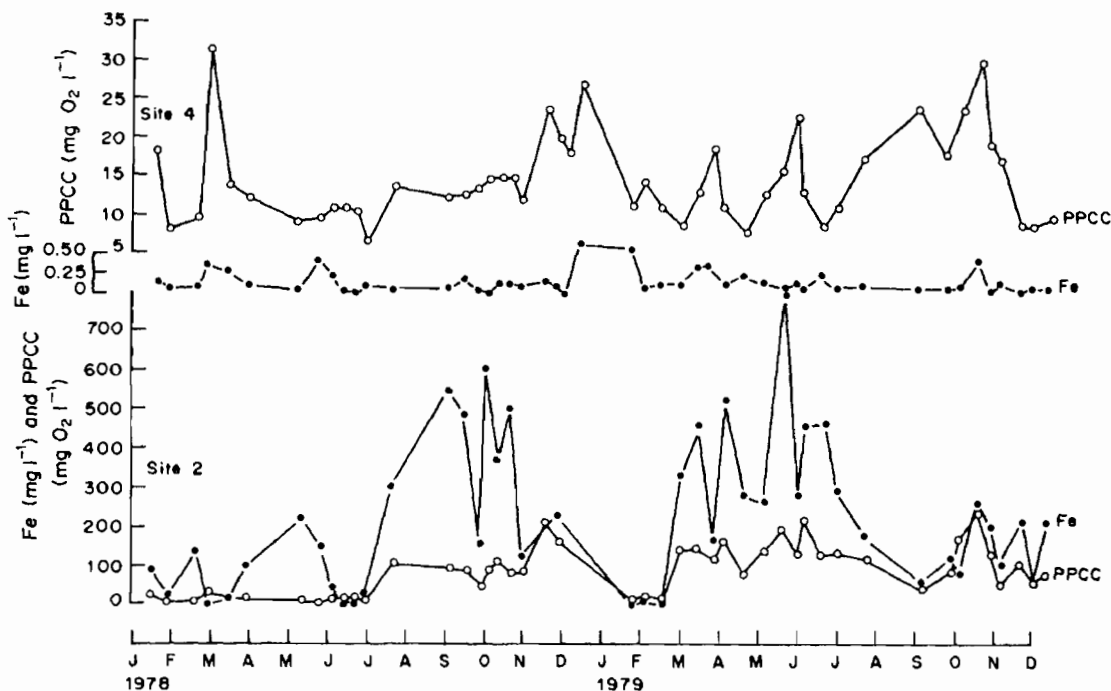


Fig. 4. Variations of Fe concentration and potassium permanganate consuming capacity (PPCC) in sampling sites 2 and 4 during 1978 and 1979.

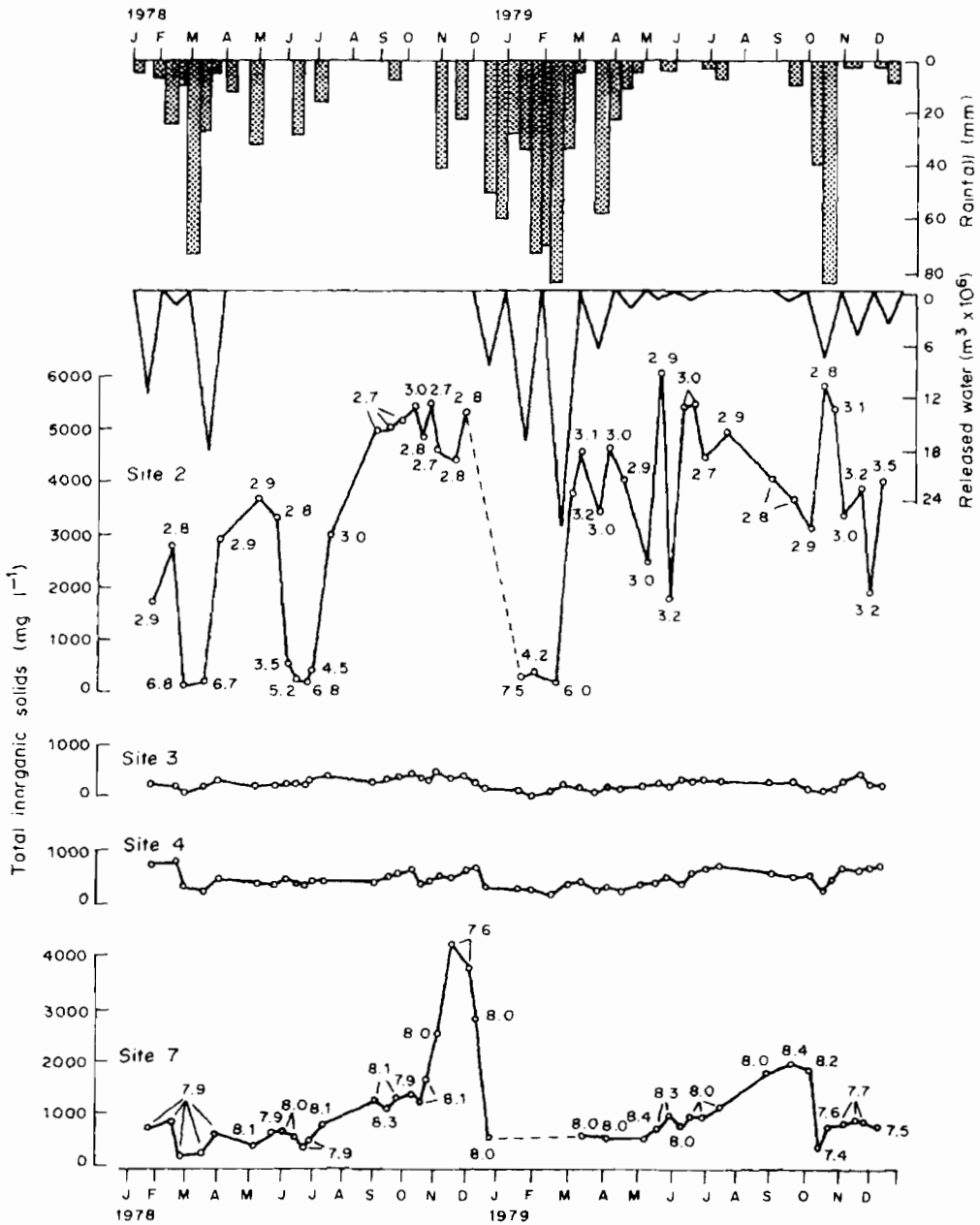


Fig. 5. Variations of total inorganic solid (t.i.s.) contents and pH in sampling sites 2, 3, 4 and 7, rainfall and reservoir discharge during 1978 and 1979. Figures near the experimental points are pH values (concentrations in mg l^{-1}).

Agricultural pollution

As described above olive-oil mill wastes called *alpechines* are discharged into the Guadiamar river causing a pollution that may be considered of agricultural origin. The presence of *alpechines* in water of site 7 during October–December 1978 decreases the dissolved oxygen content and increases the PPCC and the t.o.s., K, Fe and Mn contents (Fig. 6). The peak of t.i.s. for site 7 in winter 1979 (Fig. 5) is also related to the *alpechines* appearance. As a result of the *alpechines* pollution, the fish population dies every year in the lower course of the Guadiamar

river, particularly in the zone between levees. On the other hand, these polluted waters can enter the National Park of Doñana as a consequence of the high tide and floods. It has been also observed that waters from Guadiamar river were sometimes pumped into a nearby rice field irrigation canal (sampling site 10); consequently, in autumn, the olive grinding season, concentrations of Fe, Mn, Zn and K as well as PPCC in site 10 are higher than in spring, while the dissolved oxygen values are lower (Table 5).

Another source of pollution to be considered on the lower course of the Guadiamar river is that produced by urban sewages, application of fertilizers,

Table 3. Influence of changes in flow of Agrio and Guadimar rivers on pH values and contents in Fe, total inorganic solids (t.i.s.), total organic solids (t.o.s.) and suspended inorganic solids (s.i.s.)

Sampling site	Low flow 20 Feb. 1978 (mg l ⁻¹)					High flow 27 Feb. 1978 (mg l ⁻¹)				
	pH	Fe	t.i.s.	t.o.s.	s.i.s.	pH	Fe	t.i.s.	t.o.s.	s.i.s.
1	6.5	0.10	70	22	10	6.7	0.20	21	69	7
2	2.8	135.5	2817	647	15	6.8	0.14	69	404	9
4	7.9	0.07	377	97	1	7.9	0.33	141	662	84
5	7.8	0.05	506	105	0	7.8	0.11	106	379	45
7	7.9	0.07	758	160	32	7.9	0.20	89	343	33

Sampling site	Low flow 24 Nov. 1978 (mg l ⁻¹)					High flow 26 Jan. 1979 (mg l ⁻¹)				
	pH	Fe	t.i.s.	t.o.s.	s.i.s.	pH	Fe	t.i.s.	t.o.s.	s.i.s.
1	7.2	1.00	103	29	0	7.0	0.00	90	64	0
2	2.8	225.0	5248	678	1	7.5	0.08	295	153	85
4	8.0	0.06	532	57	0	7.7	0.52	198	109	83
5	7.9	0.02	931	46	3	7.7	0.16	214	131	26
7	8.0	1.00	3825	780	0	*	*	*	*	*

*The access to sampling site was cut off due to floods of the Guadimar river.

pesticides, etc., which has an important influence on the N and P contents of waters. Figure 7 shows the mean values of organic-N, NH₃, NO₃, total-PO₄ and dissolved-PO₄ contents in sampling sites 6–13. The corresponding coefficients of variation, not shown here, are in all cases close to 100%.

The mean values of organic-N and NH₃ both in wet and dry periods in sites 9, 10, 11 and 13 are very similar to those in site 12. These results cannot be only due to rice fields being irrigated with waters taken from the Guadalquivir river, since rice is heavily fertilized with ammonium or urea fertilizers. In a previous study (Peris, 1982) it was observed that Sevilla, with a population of 600,000, originates a remarkable increase in the contents in organic-N and NH₃ of waters of the Guadalquivir river. This pollution decreased gradually downstream and after 10 km past Sevilla, the values were again similar to those found upstream immediately before the city. At the

same time the concentration of NO₃ increased. In the present work, concentrations of organic-N and NH₃ at site 12, located approx. 30 km downstream from Sevilla, are similar to those found by Peris (1982) at 10 km from the same city. These values are also similar to those found at site 8 in which organic-N and NH₃ can only arise from the biotic activity and soil organic matter evolution as this sampling site is located in a canal receiving runoff and drainage water from virgin saline soils under reclamation. Similar results were found by Reinhorn and Arnimeloch (1974). Because of the uniformity of climatic factors and the low content in, well humified, organic matter (approx. 2%) of the Western Andalusian soils (Martín and González Vila, 1981), it could be inferred that the levels of organic-N and NH₃ found in the Guadalquivir river and rice soil drains of the studied zone are those corresponding to the ecological semi-equilibrium state and will change only where they receive exogenous effluents.

Figure 8 shows the direct relationship between organic-N content and rainfall in site 8; only during July 1978 and 1979 organic-N peaks do not correspond with rainfall but are caused by the preceding springtime microbiologic activity. The behaviours of organic-N contents with time in sites 6, 7 and 8 exhibit a narrow similarity (Fig. 8; data for site 6 not shown). Therefore, organic-N in sites 6 and 7, re-

Table 4. Heavy metal contents in sediments of sampling sites 24–27

Sampling site	24	25	26	27
	(mg kg ⁻¹)			
Metal content				
Fe	36,000	31,900	35,250	11,900
Cu	40	50	40	0
Mn	660	490	660	90
Zn	110	111	100	—

Table 5. Effect of pumping waters from the Guadimar river into sampling site 10 during spring and autumn of 1978 and 1979 (olive mills and pumps work only in autumn)

	Spring			Autumn		
	1978	1979	Mean (13 samples)	1978	1979	Mean (17 samples)
Fe (mg l ⁻¹)	0.05	0.11	0.08	0.17	0.11	0.14
Cu (mg l ⁻¹)	0.01	0.02	0.02	0.00	0.01	0.01
Mn (mg l ⁻¹)	0.06	0.07	0.06	0.18	0.45	0.31
Zn (mg l ⁻¹)	0.03	0.04	0.03	0.05	0.17	0.11
K (mg l ⁻¹)	8.0	8.5	8.3	23.4	12.7	18.4
Dissolved oxygen (mg l ⁻¹)	7.3	6.4	6.9	2.1	3.0	2.5
PPCC in O ₂ (mg l ⁻¹)	22.6	45.3	33.9	86.0	67.3	77.2

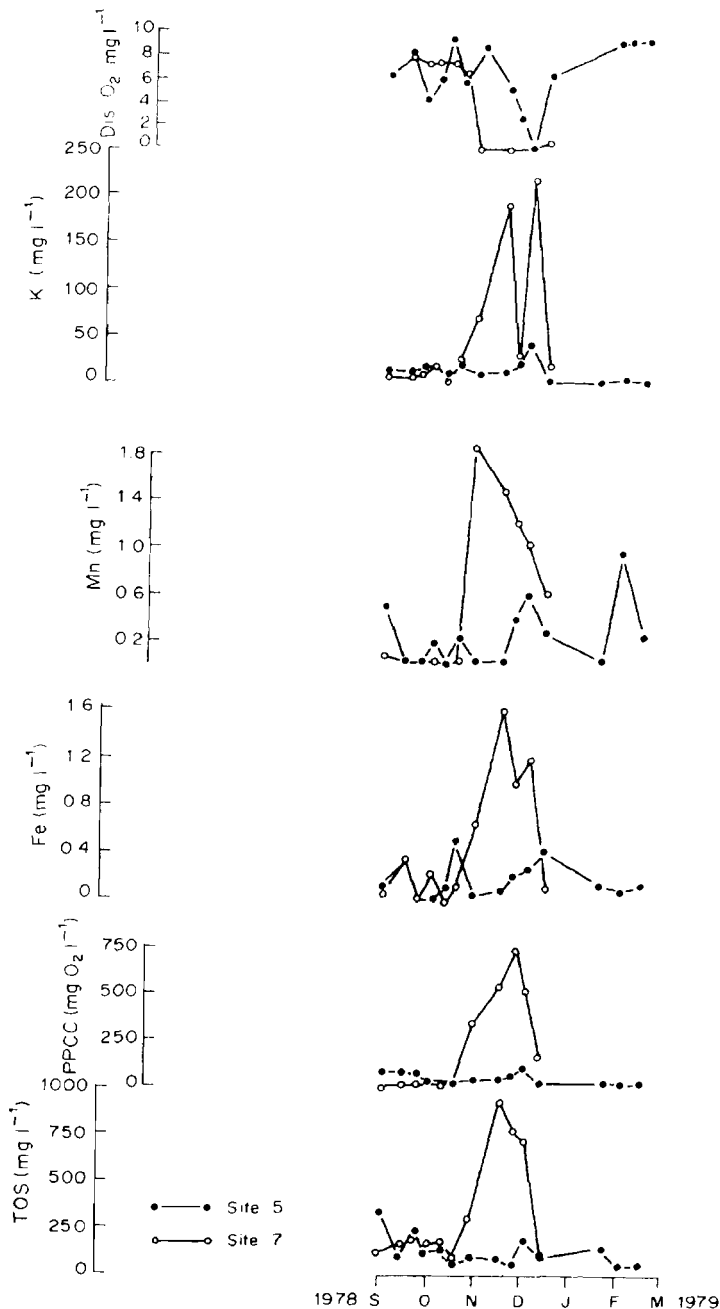


Fig. 6. Variations of dissolved oxygen, total organic solid (t.o.s.), Fe, Mn and K contents and potassium permanganate consuming capacity (PPCC) in sampling sites 5 and 7 from September 1978–March 1979.

ceiving village sewages, seems to be more influenced by the evolution of the organic matter of soil than by that of urban origin. The possible influence of village sewages in sites 5, 6, 7 and 12 is shown by NO_2 contents (Table 6), as large amounts of NO_2 are considered as an indication of sewage effluents (Hannan *et al.*, 1973).

The NO_3 content in waters from site 12 can be due to the evolution of the organic-N compounds present in Sevilla sewages, as said before, and also to the leaching of the NO_3 -N fertilizers used in dry-land agriculture in the Guadalquivir valley. The lower

NO_3 mean values found in sites 9, 10, 11 and 13 show that rice fields behave as NO_3 sinks.

Total and dissolved PO_4 values in site 7 are high especially in wet period due to the presence of *alpechines*. This fact can be seen in Fig. 8 in which total- PO_4 values in site 7 reach a maximum, $42.6 \text{ mg PO}_4 \text{ l}^{-1}$ corresponding with K concentrations as high as 218 mg K l^{-1} (Fig. 6).

Influence of *alpechines* is also noticed in site 12 although the PO_4 values are lower than in site 7 (Fig. 7), what can be explained considering that Guadalquivir river receives olive mill effluents far

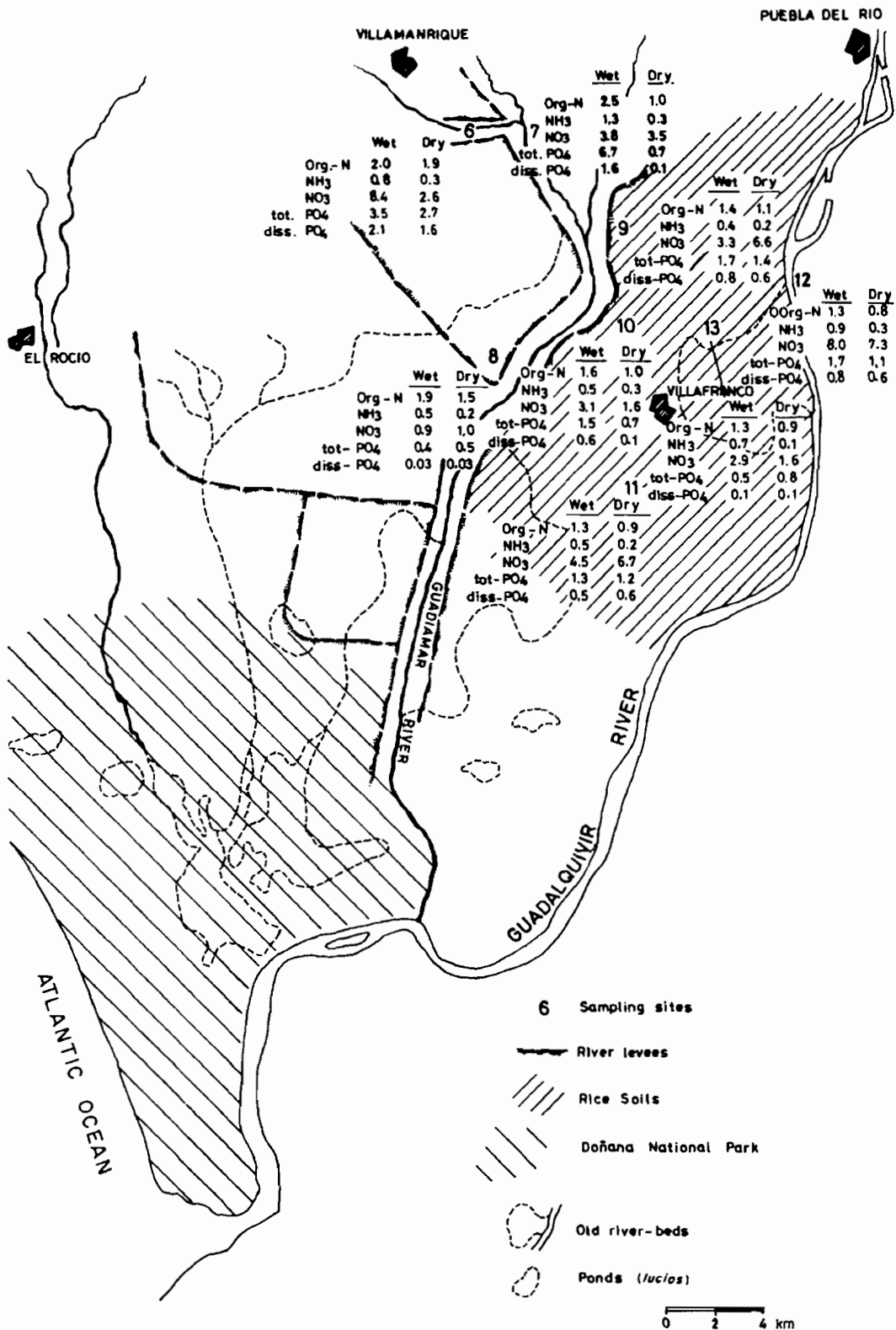


Fig. 7. Mean values of organic-N, NH₃, NO₃, total-PO₄ and dissolved-PO₄ contents in sampling sites 6–13 during wet and dry periods of 1978 and 1979 (concentrations in mg l⁻¹).

upstream from site 12 and that it carries much more water than the Guadalquivir river.

In rice field canals (site 9, 10, 11 and 13) total and dissolved PO₄ mean values are equal or even lower than those in site 12. As the main sources of P in the

rice fields are fertilizers and irrigation waters from Guadalquivir river (site 12) and occasionally from Guadalquivir river (site 7), it can be concluded that rice fields behave as P sinks. Since the first step of the transformation of P fertilizers in calcareous soils is

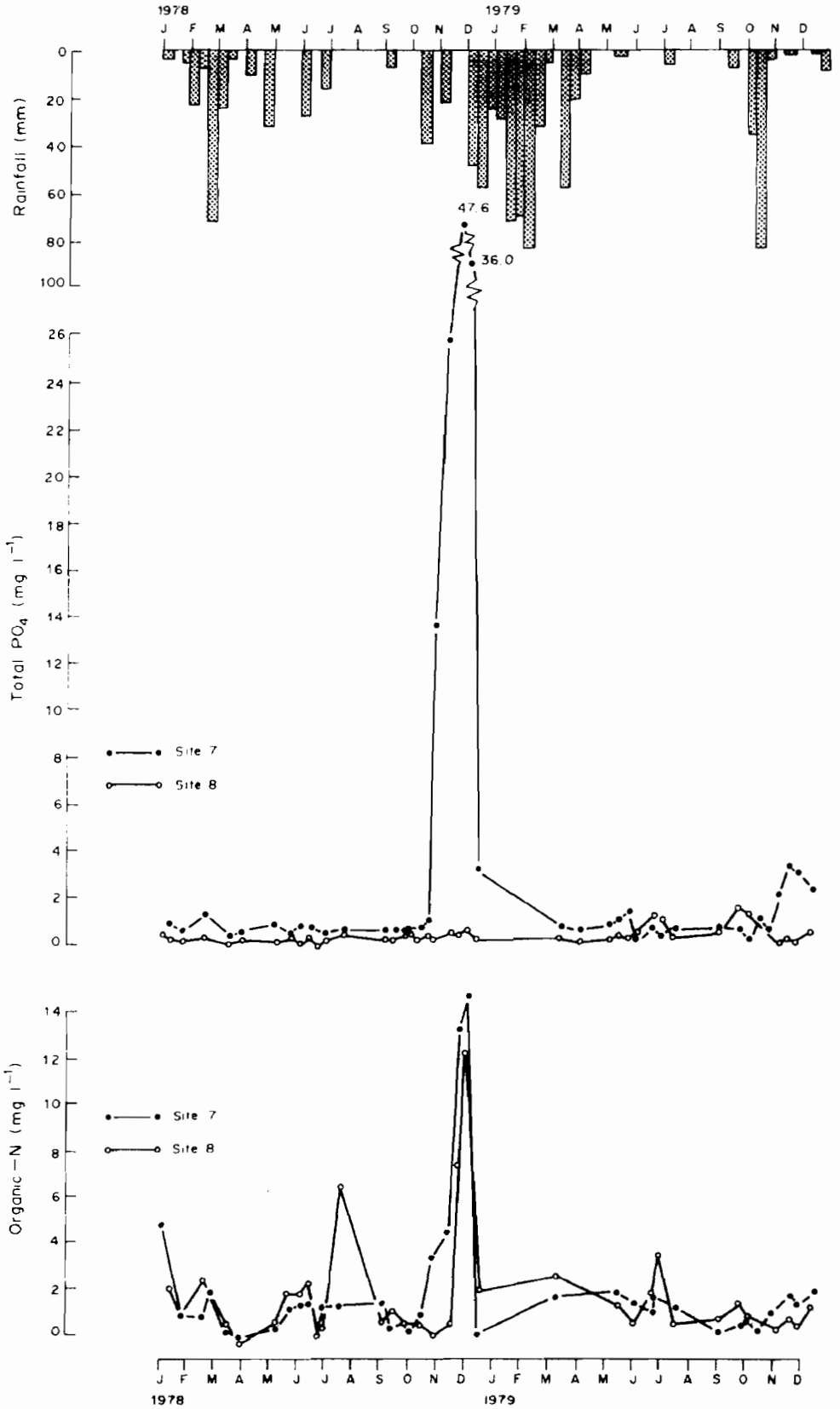


Fig. 8. Variations of rainfall, organic-N and total-PO₄ in sampling sites 7 and 8 during 1978 and 1979.

Table 6. Mean, maximum and minimum values of NO_2^- content in sampling sites 5-13 during 1978 and 1979

Sampling site	NO_2^- (mg l^{-1})		
	Mean	Max.	Min.
5	0.39	5.36	0.00
6	0.75	2.14	0.00
7	0.27	4.90	0.00
8	0.01	2.40	0.00
9	0.22	2.00	0.00
10	0.10	5.40	0.00
11	0.24	2.70	0.00
12	0.50	2.00	0.00
13	0.18	1.70	0.00

dicalcium phosphate dihydrate releasing approx. $200 \text{ mg PO}_4 \text{ l}^{-1}$ to the soil solution (Moreno *et al.*, 1960; Arambarri and Madrid, 1971), PO_4 concentration in rice field canals seems to be governed by either the pseudo-equilibrium of more insoluble soil phosphates (i.e. octocalcium phosphate) or by hydrolysis of poly and organic phosphates.

On the other hand, mean values of total and dissolved PO_4 in site 8 (Fig. 7) have the expected equilibrium values for unfertilized soils in the Guadalquivir valley in which the residual P is in apatite-like forms (García de Leániz and Arambarri, 1975; Madrid *et al.*, 1977).

The dissolved oxygen values in rice field canals are normally high enough for aquatic life, with mean values approx. $7 \text{ mg O}_2 \text{ l}^{-1}$ in wet period and slightly smaller in dry period, approx. 4.9. Only when waters from site 7 are pumped into those canals the dissolved oxygen reaches low values (Table 5).

Table 7 shows the Ordram, 2,4-D and 2,4,5-TP maximum contents in different sites. The 2,4-D and 2,4,5-TP herbicides were found to be ubiquitous along the studied zone, as found by Chacko and Gummer (1980) and in some instances reach values considered as the limit of safety (U.S. EPA, 1977). Pollution by 2,4-D and 2,4,5-TP is bigger in site 30 than in sampling sites 28 and 29 in most occasions, which can be taken as an indication that the polluted waters enter the Doñana National Park from south to north in the direction shown by the arrows in Fig. 2.

Ordram concentrations found after application were maximum and similar to those found in the rice fields of Camargue, France (Podlejski, 1978). After-

wards the concentration decreases in such a way that this herbicide has not been detected in sites 28-30 in the Doñana National Park (Table 7). Similar results were reported by Soderquist *et al.* (1977).

CONCLUSIONS

Drainage waters from polymetallic sulphide deposits and old mine spoil-heaps originate high concentrations of heavy metals in water and sediments of Agrio and Guadamar rivers. When river flows increase because of heavy rains or reservoir discharges, sediments are resuspended and transported downstream. The presence of other effluents rich in organic matter with active chelating agents (*alpechines*) facilitate the metal dissolution and transport. Consequently 30 km downstream from the mine heavy metal concentrations in Guadamar river are still higher than those in other unpolluted rivers of this zone. The progression of the heavy metal pollution in the Guadamar river can be prevented controlling the mine effluents and sudden flow increases of Agrio and Guadamar rivers.

Pollution by olive mill effluents (*alpechines*) is important during the grinding season (autumn and winter). It originates increases in the K, P and organic matter contents of water as well as decreases in dissolved oxygen to levels inadequate for aquatic life. Therefore, discharge of *alpechines* should not be allowed without a pretreatment whose nature will be established in subsequent research works.

Nitrogen and P fertilization of rice fields is not at the moment producing abnormal increases in the concentration of these elements in water. However, it has been found that concentrations of 2,4-D and 2,4,5-TP in waters of both the rice field canals and Doñana National Park reach in some occasions values considered as the limit of safety for aquatic life. That means that rice fields are not isolated from Doñana National Park so the conditions of fertilizers and pesticides applications must be controlled (e.g. wind direction and velocity must be monitored previous to each application of chemicals by aircraft, and other factors like drain leakage must be avoided).

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Table 7. Maximum values found for herbicides contents in rice fields and in the National Park of Doñana

Sampling site	Date	Ordram (mg l^{-1})	2,4-D ($\mu\text{g l}^{-1}$)	2,4,5-TP ($\mu\text{g l}^{-1}$)
18	June 1978	4.1	—	—
15	June 1979	5.2	25.3	16.5
17	June 1979	4.5	17.2	6.3
18	June 1979	2.5	47.2	—
28	July 1979	ND	45.5	7.1
29	July 1979	ND	47.8	10.2
30	July 1979	ND	34.1	10.9

ND—not detected.

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