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Nutrients, conductivity and plankton in a landscape approach to a Pampean saline lowland river (Salado River, Argentina)

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Abstract. Nutrients, conductivity and other physical and chemical parameters were measured seasonally in the main channel and in tributaries of the Salado River basin during the period March 1997–June 1999. The sampling began in a low water period and later included flood events. High water events were associated with high proportions of allochthonous compounds (polyphenols, suspended solids and organic matter). Nutrients and conductivity were related to hydrological conditions and different land uses in the catchment. A relationship was found between the land-use and nutrient concentrations due to the inflow of diffuse sources from agricultural lands. High nutrient concentrations and conductivity recorded in the headwaters were, respectively, related to the intensive agriculture in this area and the inflow of saline groundwater, drained by canals from endorheic basin to the main channel. Their effects on the middle and lower reaches were related to the discharge and inputs of other sub-catchments. Nutrients, sulphates, alkalinity and conductivity declined downstream towards the river mouth. The consequences for the plankton community of these spatio-temporal changes in the chemical characteristics are discussed. The heterogeneity of the Salado River is related to seasonality, land use and the geomorphological features of the basin.

Introduction

Typically a longitudinal pattern can be recognised in rivers, which results from the interplay between physical processes and the biological responses and interactions, which determine a general downstream trend (Margalef 1983).

At the sub-catchment scale, specific hydrochemical processes control stream water chemistry. In general, a downstream increase is observed in the concentrations of the majority of determinants and at this scale, the major chemical constituents appear to originate from diffuse sources, such as weathering and agricultural inputs which implies that point-source pollution is not a major problem within the system (Plan Maestro Integral Cuenca del Río Salado 1999a). However, diffuse pollution sources, such as fertiliser-derived nitrate and phosphorus, can lead to localised pollution problems such as eutrophication. The main stream is, however, buffered against these problems due to further dilution of locally high nutrient concentrations by waters from other tributaries (Smart et al. 1998). The nutrient levels in a river may be augmented by irrational applications of chemical fertilisers, and increase in weathering and erosion may induce leaching of nutrients from soils, and hence augment riverine nutrient concentrations. Nutrient levels may also depend on climatic, geographic and tectonic conditions, as well as anthropogenic activities (Liu et al. 2003). Nutrient enrichment may degrade water quality and disturb the balance of species within a river and has been identified as a growing problem in many lowland rivers (Vandijk et al. 1994; Jarvie et al. 1998, 2002; Young et al. 1999). Riverine transport is the main pathway of suspended and dissolved elements from land to the sea and influences phytoplankton production rates (Liu et al. 2003). In particular, it has been suggested that heterogeneity of flow and river retentiveness are mechanisms that increase retention time and extend the opportunities for development of planktonic organisms (Reynolds and Descy 1996) in rivers. Negative correlations between discharge and chlorophyll '*a*' have been reported many times and related to the dilution effect (Everbcq et al. 2001). In a large river, processes at the catchment scale control plankton dynamics and determine the growth and losses in this community (Reynolds and Descy 1996). In the Salado River, the phytoplankton composition is mainly determined by the salinity, alkalinity and the trophic status of the water, with indicator species of both brackish and alkaline waters occurring. The cyanophyceae and chlorophyceae were dominant throughout the period with alternating maxima (O'Farrell 1993).

In previous investigations carried out on the lower reaches of the Salado River, physical and chemical changes were identified as factors controlling the plankton community within the main channel (Solari et al. 2002) and in a backwater pond (Gabellone et al. 2001). During low water periods, suspended solids increased, causing a decline in plankton density. Fluctuations in the discharge, conductivity and temperature were important as forcing variables on the plankton, within the annual cycle of different hydrological conditions. In high water periods the concentrations of phosphorus and polyphenols increased, with effects on the plankton community (dominance of euglenophytes, diatoms and ciliates). The alluvial valley of the Salado River is not extensive, but the associated shallow lakes, with different river connectivity, act as an alluvial valley, incorporating organisms as well as dissolved and suspended matter, into the river. The geomorphological features, conductivity and phosphorus fractions related to the hydrological cycle were recognised as the main factors that regulate the system, in particular those sectors of the Salado River that are connected to the backwater ponds.

Any attempt to understand the processes that regulate the concentrations of naturally occurring species within a major river system requires a more comprehensive analysis of river water samples than is usually available. Moreover, public bureaux involved in water resources management are increasingly interested in holistic catchment management strategies that need to be developed at a larger scale than that generally studied in scientific research (Smart et al. 1998).

The Salado River is the southernmost tributary of the Río de la Plata Basin and the major river arising within Buenos Aires province (Conzonno et al. 2001). The basin is considered to be the second South-American wetland in terms of rainfall accumulation. The more humid conditions in the second half of the last century promoted the formation of large wetlands in the Pampean plains, following a definite pattern (Iriondo 2004). The headwater reaches of the river are characterised by the presence of a sedimentary aquifer with high concentrations of sodium chloride, which originated during arid periods of the Pleistocene. The result of this salinisation is manifested by the presence of saline streams and shallow saline lakes, whose condition determines the salt balance of the Salado River. During flood periods, the salinization is diminished in the lower basin, as a result of the influx of runoff water. Surface waters receive salinity from groundwater, from evaporative salinisation, from dissolution of Post-Pampean materials along the course of the river, from catchment transfer and from land drainage. Good quality groundwater (up to 1000 mg l^{-1} of total dissolved solids) is present in the south of the area, adjacent to Tandil and Ventana mountains, and in the north along the catchment boundary. High salinity groundwater (up to 2000 mg l^{-1} of total dissolved solids) dominates the lower catchment area from Las Flores Lake to Samborombón Bay. Groundwater salinity increases rapidly where flows approach the Post-Pampean deposit from interfluves, suggesting hydrochemical mixing that is related to high river levels, with recharge entering the aquifer from the river. In the western endorheic zone, the regional groundwater salinities are in excess of 2000 mg l^{-1} of total dissolved solids for a large proportion of the catchment. In this area, the Pampean formation is shallow and the groundwater is influenced by the gypsiferous Araucana formation (Plan Maestro Integral Cuenca del Río Salado 1999b, c).

The Salado River basin is located in a dry, temperate flatland (Gustard 1994) and includes a large number of shallow lakes occupying 10,000 km^2 in normal conditions of river flow. These lakes have different degrees of connection with the river. In order to maintain their hydrometric levels and lower salinity values, gates regulate some of these lakes. Some of the lakes without regulation dry completely in summer when the flow in the river is very low and their inflow ceases. Evaporation and groundwater relationships also have an important effect in summer (Dangavs and Merlo 1980).

The regime of the Salado River is very variable. Its flow reaches no more than 100 m^3 s^{-1} in dry periods and increases up to as much as 1500 m^3 s^{-1} in flood periods, with consequent variations in conductivity and transport of dissolved and particulate materials. The flooding of large areas during weeks or months is one of the most important characteristics of the Pampean Plain.

Cattle rearing and agriculture are important economic activities in the catchment, and represent 30 and 27%, respectively of the national agriculture-cattle gross output (Indec 1988). The mouth of the Salado is located at Samborombón Bay, which is included in the Ramsar list of wetlands of international importance (Ramsar Convention Bureau 2004). The alternating conditions between dry and humid periods have allowed the development of some soil characteristics that permit intensive agricultural production and the existence of wetlands with a significant biodiversity. The presence or absence of water constitutes a key factor in the structure of ecosystems associated with the low slope and slow drainage that configure the characteristic landscape of this area. This situation demonstrates the importance of regional limnological studies, which indicate the causes, and consequences of changes in land-use.

Recent projects have proposed models for creating modifications to the drainage pattern in the basin, through dredging of the main channel to modify the variations in river discharge and, therefore, the connection conditions of the associated shallow lakes. For this reason, a holistic knowledge of the river is required now in order to predict likely future responses to geomorphological changes in different channel sectors, related to such hydraulic modifications. Furthermore, it is necessary to recognise the origins and dynamics of key factors such as salinity, nutrient inputs and the influence of land use, mainly in relation to flood and drought conditions. This paper reports the preliminary results of an investigation into the patterns and controls of conductivity, nutrients and plankton in the river at a range of spatial scales in this lowland river basin.

Materials and methods

The Salado River is a typical lowland river with a watershed of approximately 150,000 km^2 (including the endorheic areas related to canals), length of approximately 600 km and a low slope (mean: 0.107 m km^{-1}).

Five zones (Figure 1) can be distinguished within the basin, which reflect geological, soil and agricultural influences, and have different parameters, such as concentration/flow relationships:

(1) A cattle-agricultural zone in the NE sector with clay-sandy and loess-clayey sediments, with a predominance of breeding and milk cattle (84% of the area), with summer cultivation (16%).

(2) An agricultural zone (70% of the region's area) in the N sector of the basin with similar sediments to the preceding zone, the main crops being wheat–soybean and corn–sunflower.

In this zone the following sampling stations were established: Station 1 (St 1) – Salado stream – originating in El Chañar, a shallow lake on the border with Santa Fe province, discharging into Mar Chiquita lake (flooded valley) at 662 km from the mouth; Station 2 (St 2) – Piñeiro stream is a first order stream, with aquatic macrophytes. It runs through soybean cultivation fields and discharges into Mar Chiquita lake; Station 3 (St 3) – Junín 1 – is located upstream of Junín city (at 592 km from the mouth); Station 4 (St 4) – Junín 2 – below the city. The site is at 567 km from the mouth, with a mean flow of 23.4 m^3 s^{-1}; Station 4–5r (St 4–5r) – Saladillo stream – is a right bank tributary at 478 km from the mouth. This stream receives the Jauretche – Mercante –

República de Italia canals which drain the Western internal basin and the Hinojo – Las Tunas complex which receives the Quinto River waters; a mean flow of 73.7 m^3 s^{-1} was estimated at this station; Station 5 (St 5) – Achupallas – the channel approximately 90 m wide and 1.8 m deep, at 458 km from the mouth; the mean flow was estimated as 23.6 m^3 s^{-1}.

(3) An agricultural (54% of the region's area) and cattle zone in the Middle West sector of the basin, with sandy clay sediments forming longitudinal dunes, with summer cultivation and cattle (wintering, livestock and milking cattle).

In this zone, the following sampling stations were established: Station 6 (St 6) – Ruta 30 – is located downstream of Chivilcoy city (more than 57,000 inhabitants and factories) and 408 km from the mouth; Station 6–7r (St 6–7r) is located at 284 km from the mouth at the confluence of Saladillo-Vallimanca

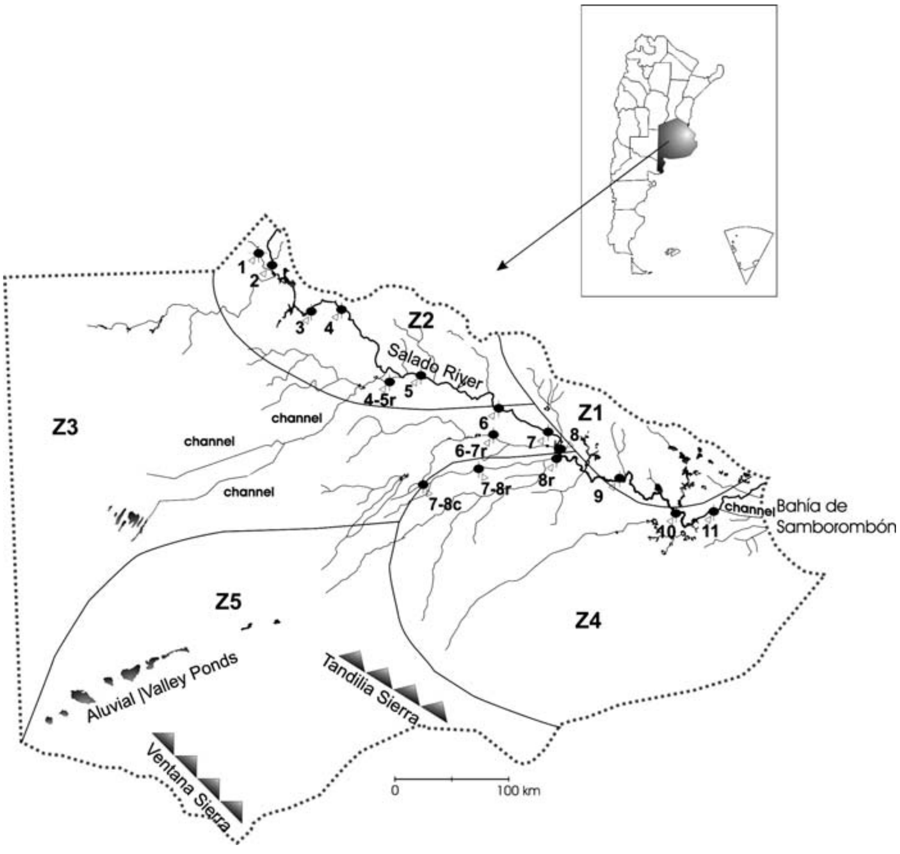


Figure 1. Map of the Salado River Basin, which shows the main channel, tributaries, sampling sites and the five zones of the catchment distinguished.

stream with the main channel. The Saladillo-Vallimanca stream (a sub-basin) is one of the main tributaries of the Salado River, originating in the Ventania Mountains and flowing more than 300 km to Las Flores Lake (a flushing lake of the Salado River). The stream has an extensive alluvial valley with a sinuous course and irregular meanders, with a mean flow of 14.6 $m^3 s^{-1}$; Station 7 (St 7) – Roque Pérez – at 348 km from the mouth this station is characterised by a change in the channel morphology of the river with interconnected depressions and an estimated mean flow of 93.6 $m^3 s^{-1}$.

(4) A cattle dominated zone (88%) with a few agricultural activities (12%) in the 'depressed pampa', with alluvial and eolian deposits.

In this zone the following sampling stations were established: Station 7–8r (St 7–8r) – Las Flores stream (sub basin) – has its source in the Tandilia Mountains and runs through 250 km with a mean flow of 9.71 $m^3 s^{-1}$. Its inflow to the Salado is located at the flushing lake Las Flores at 283 km from the mouth; Station 7–8c (St 7–8c) – Canal 16 – with a length of 120 km, joins Vallimanca stream at 182 km from the mouth before its inflow to Las Flores stream. This canal regulates the discharge of Vallimanca stream; Station 8 (St 8) – Gorchs left bank and Station 8r (St 8r) – Gorchs right bank – are situated downstream of Las Flores Lake at 273 km from the mouth. The characteristics of the water at each bank reflect the sub-catchment and headwater sources, respectively; Station 9 (St 9) – General Belgrano – with a mean flow of 167 $m^3 s^{-1}$ and located at 213 km from the mouth, is influenced by an important system of interconnected shallow lakes; Station 10 (St 10) – El Destino – The Salado River with a width of 114m and 3.8 m mean depth, can reach a depth of approximately 8.7 m during flood conditions; Station 11 (St 11) – La Postrera – 100 m wide and with a mean flow of 377 $m^3 s^{-1}$ is located at 84 km from the mouth; at this sampling point, the width of the river is restricted by the presence of a bridge.

(5) An agriculture (60% of the region's area) and cattle zone in the peri-mountain sector, with calcareous and coarse textured deposits, eolian sediments with clayey texture and a chalky crust in depressed areas.

No sampling stations were established downstream of Station 11 because, below here, 80% of the river discharge runs through two canals starting at 69 km from the mouth.

The sites were visited initially in March 1997, and then quarterly on a seasonal basis through to the autumn of 1999. On the first four occasions, 14 sampling stations were sampled. During the period May 1998–June 1999, two tributaries were also included because they bring in water from peri-mountain sub-basins (stations 7–8c and 7–8r). The incorporation of these sites improves the interpretation of the results.

At each visit the following measurements were made: temperature, pH, dissolved oxygen, conductivity and turbidity, with a Horiba Multimeter U-10, and water velocity. The water samples were collected in 1 l acid-cleaned polyethylene bottles, transported back to the laboratory in an ice-cooled isolation box and stored in the dark at 5–8 °C prior to the analysis.

Total phosphorus (TP) was determined by the ascorbic acid method after digestion with acidic persulfate (method 4500-PB, APHA 1995). Dissolved polyphenols and chloride were determined according to methods 5550 B and 4500-Cl B recommended by APHA (1995), respectively. Whatmann GF/C filters were used for spectrophotometric determination of chlorophyll '*a*' concentration (method 10200 H, APHA 1995). The concentrations of total suspended solids were measured according to method 2540 D as recommended by APHA (1995). The concentrations of particulate organic matter were determined by loss on ignition at 550 °C (method 2540 E, APHA 1995). Nitrate, plus nitrite, was determined by the hydrazine reduction method (4500-NO3 H, APHA 1995) and sulphates by the turbidimetric method described by Tabatabai (1974).

Replicate phytoplankton samples were collected with a 2 l Van Dorn bottle. Replicate zooplankton samples were obtained by filtering 100 l through a 30 μm mesh net. Phytoplankton populations were enumerated, using the settling technique (Utermöhl 1958). Protozoans and rotifers were counted in a Sedgwick–Rafter chamber, while a Bogorov chamber was used for crustaceans.

Representative time series of rainfall for the basin were taken from the Servicio Meteorológico Nacional. Monthly deposition estimation was based on an integrated network of storage rain gauges. The time series for Junín, 9 de Julio-Bolivar, Monte and Las Flores were selected as representatives for zones 2, 3, 4 and 5, respectively. Data on discharge is scarce both in terms of frequency and location. There are only four gauges with a few available data taken from Dirección de Hidráulica of Buenos Aires province.

Some variables were transformed, to ensure that frequency distributions of the parameters were normal, by the Kolmogorov–Smirnov test: square-root transformation for phytoplankton density and organic matter concentration; log 10 transformations for nitrates plus nitrites, chlorophyll '*a*', total phosphorus and zooplankton density. Relationships among parameters were examined using Pearson product–moment correlation.

Multivariate analyses of clusters and principal components were performed using principal component analysis (PCA) and cluster analysis (CA) with a standardised matrix. Complete linkage and Euclidean distance were used in the cluster analysis.

Results

Physical and chemical characteristics

The 1997 annual mean rainfall for the whole catchment was 1057 mm. It decreased to 921 mm in 1998 and to 749 mm in 1999. The seasonal rainfall regime has an autumn–spring maximum and a winter minimum. The months with most rainfall were December 1997, in the lower basin with 330 mm (historical maximum value recorded in the sector since 1911), April 1998 with

208.4 mm and March 1999 with 270.3 mm, both in the middle basin (Figure 2). The mean annual rainfall (1911–1996) was 870 mm and the mean annual temperature (1911–1996) was 14 °C.

An inverse relationship between conductivity and discharge was observed in the lower basin (site 9) (Figure 3). The highest conductivity measured

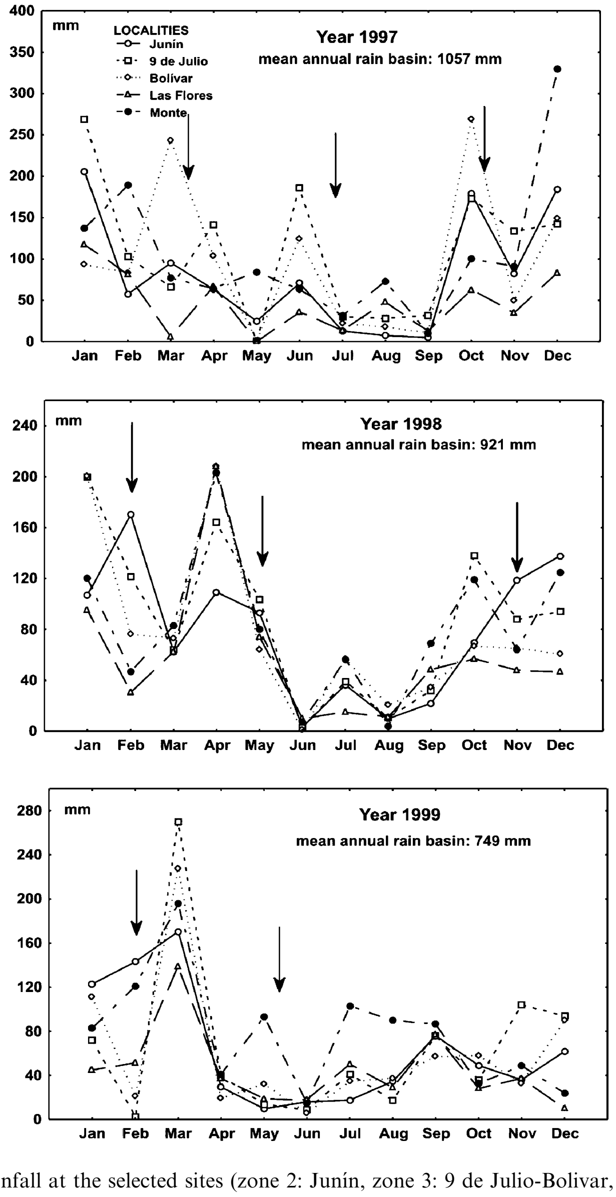


Figure 2. Rainfall at the selected sites (zone 2: Junín, zone 3: 9 de Julio-Bolivar, zone 4: Monte; zone 5: Las Flores) within the basin during the sampling period: 1997–1999 (the arrows indicate the sampling dates).

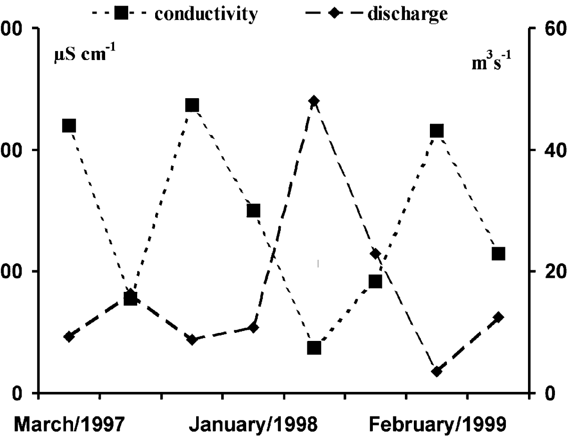


Figure 3. Conductivity vs. discharge during the sampling period in the lower basin sector (St 9: Belgrano).

(5910 μS cm^{-1}) in October 1997 was associated with a discharge of 87 m^3 s^{-1} while the lowest (934 μS cm^{-1}) in May 1998, was associated with the maximum discharge (481 m^3 s^{-1}).

The whole basin is characterised by highly mineralised and alkaline waters (Tables 1–3). pH values ranged between 7.6 (St 7–8c in autumn 1999) and 9.7 (St 3 in summer 1998) (Figure 4). The values of total alkalinity decreased from the headwaters to the middle sector of the river and remained fairly stable from there to the mouth (Figure 4). A similar pattern was observed in the distribution of total phosphorus, with the maximum values in the headwater sectors and the minima in the low basin tributaries (St 6–7r, 7–8c and 7–8r) (Figure 4c). The sulphates and alkalinity showed a tendency to decrease towards the mouth but the tributary inputs varied (Tables 1–3). The sulphate concentrations of the headwater tributaries, such the Salado stream (St 1) and Saladillo stream (St 4–5r), were higher than those of the sub-basin tributaries (St 6–7r, 7–8c and 7–8r). Thus, sulphate concentration in the lower basin responds to the influence of each stream, and that depends on hydrometeorological conditions, explaining the large standard deviation among the lower basin sampling stations (Figure 4). The Piñeiro stream (St 2) is the exception, showing the lowest sulphate values in the basin (Figure 4). The influence of this tributary on the basin is, however, negligible due to the small size of its catchments.

The Salado basin is divided into two distinct geographic regions in terms of land use, which produce clear differences in water chemistry. The concentrations of TP were highest, including a wide standard deviation, in the headwater sector (Table 1). Values decreased markedly towards the mouth (St 9, St 10 and St 11) in response to the low TP input of the middle sector sub-catchments (St 6–7r, St 7–8c and St 7–8r) (Tables 2–3). In the headwater sector, agriculture is the principal activity and the use of fertilisers at different times, plus the

Table 1. Mean and standard deviation (in parentheses) of parameters and variables of sampling stations located in zone 2 of Salado River basin.

	Salado stream	Piñeiro stream	Junín 1
Temperature (°C)	19.0 (6.8)	19.8 (6.2)	18.8 (5.9)
pH	9.3 (0.3)	8.6 (0.4)	9.2 (0.3)
Dissolved oxygen (mg l^{-1})	9.1 (2.2)	9.5 (4.0)	8.7 (3.5)
Conductivity (μS cm^{-1})	5514 (3080)	911 (189)	4718 (1652)
Alkalinity (mg l^{-1})	663 (265)	463 (110)	810 (189)
Chloride (mg l^{-1})	850 (381)	202 (238)	901 (302)
Sulphates (mg l^{-1})	813 (391)	100 (12)	655 (180)
Total phosphorus (μg l^{-1})	715 (341)	587 (217)	670 (312)
Nitrates plus nitrites (μg l^{-1})	923 (1,522)	622 (703)	493 (379)
Suspended solids (g l^{-1})	0.25 (0.2)	0.08 (0.1)	0.07 (0.02)
Dissolved polyphenols (mg l^{-1})	2.1 (0.8)	1.9 (1.8)	1.6 (0.5)
Particulate organic matter (g l^{-1})	0.06 (0.05)	0.02 (0.03)	
Chlorophyll *a* (mg m^{-3})	50.7 (43.2)	4.97 (1.86)	88.97 (130.6)
Phytoplankton (ind. ml^{-1})	64363 (66576)	2 905 (1407)	35691 (23152)
Zooplankton (ind. l^{-1})	691 (584)	111 (54)	827 (762)
	Junín 2	Saladillo stream	Achupallas
Temperature (°C)	18.9 (5.9)	18.5 (6.3)	18.1 (6.6)
pH	8.90 (0.3)	8.70 (0.3)	8.6 (0.3)
Dissolved oxygen (mg l^{-1})	6.0 (2.4)	8.5 (4.0)	5.8 (3.7)
Conductivity (μS cm^{-1})	3666 (1218)	6388 (1525)	6005 (2452)
Alkalinity (mg l^{-1})	740 (169)	607 (142)	555 (149)
Chloride (mg l^{-1})	734 (293)	1670 (384)	1294 (433)
Sulphates (mg l^{-1})	558 (220)	869 (186)	708 (199)
Total phosphorus (μg l^{-1})	1090 (657)	633 (534)	444 (146)
Nitrates plus nitrites (μg l^{-1})	1429 (1335)	894 (1205)	263 (147.7)
Suspended solids (g l^{-1})	0.1 (0.07)	0.07 (0.04)	0.08 (0.07)
Dissolved polyphenols (mg l^{-1})	1.98 (0.7)	2.5 (0.9)	2.1 (0.7)
Particulate organic matter (g l^{-1})	0.04 (0.03)	0.02 (0.02)	0.03 (0.03)
Chlorophyll *a* (mg m^{-3})	115 (197.5)	79.5 (86.0)	52.97 (65.3)
Phytoplankton (ind. ml^{-1})	75194 (65977)	83440 (47816)	68823 (64178)
Zooplankton (ind. l^{-1})	730 (628)	2619 (1723)	858 (560)

timing of rainfall, determined the high concentrations of TP in the river (Figure 4).

Seven sampling stations ((St 1, St 2, St 4, St 4–5r, St 7, St 6–7r, St 9) were selected as representative sites for the basin in relation to their physical and chemical characteristics. Over the entire basin, low conductivity values occurred in autumn, coinciding with high rainfall Figure 5). The Salado stream (St 1) showed the highest values of conductivity (11200 μS cm^{-1}) and Piñeiro stream (St 2) the lowest. This tributary is different from the other sites analysed in respect of its low mineral content (Figure 5), despite its extremely low discharges. The influence of tributaries such Saladillo stream (St 4–5r) (Figure 5) is evident and significant in recent decades, with increasing conductivity values in the main channel because this stream incorporates water from endorheic zones into the system – endorheic catchments – (zone 3) by means of artificial

Table 2. Mean and standard deviation (in parentheses) of parameters and variables of sampling stations located in zone 3 of Salado River basin.

	Ruta 30	Roque Pérez	Saladillo-Vallimanca
Temperature (°C)	19.5 (6.4)	19.4 (6.9)	18.8 (6.6)
pH	8.6 (0.4)	8.6 (0.4)	8.6 (0.5)
Dissolved oxygen (mg l^{-1})	7.6 (2.4)	8.4 (3.1)	7.6 (2.2)
Conductivity (μS cm^{-1})	5380 (2793)	5245 (2150)	3098 (1485)
Alkalinity (mg l^{-1})	532 (209)	480 (191)	424 (166)
Chloride (mg l^{-1})	1301 (661)	1110 (479)	663 (296)
Sulphates (mg l^{-1})	683 (321)	636 (292)	462 (228)
Total phosphorus (μg l^{-1})	579 (367)	481 (191)	233 (89)
Nitrates plus nitrites (μg l^{-1})	565 (913)	266 (134)	272 (149)
Suspended solids (g l^{-1})	0.14 (0.2)	0.1 (0.1)	0.07 (0.06)
Dissolved polyphenols (mg l^{-1})	2.54 (1.2)	2.1 (0.6)	2.01 (0.7)
Particulate organic matter (g l^{-1})	0.06 (0.07)	0.04 (0.04)	0.017 (0.02)
Chlorophyll a (mg m^{-3})	34.1 (34.8)	80.4 (83.5)	45.3 (34.6)
Phytoplankton (ind. ml^{-1})	83420 (105547)	94287 (78680)	66899 (50462)
Zooplankton (ind. l^{-1})	1274 (875)	1177 (717)	1492 (1544)

channels. This influence is maintained into the middle basin, prior to the incorporation of a right bank tributary (Figure 5) which (St 6–7r) rises in zone 5, and is characterised by an intermediate salinity that causes a decrease in conductivity in the lower basin (Figure 5). The lower basin showed intermediate values due to the mixing of surface and groundwater (St 9) (Figure 5). The basin is characterised by high concentrations of chloride related to sedimentary aquifer with high concentrations of sodium chloride. The spatial and temporal pattern of chloride is coincided with conductivity (Figures 5 and 7). Chloride is considered the principal ion that determines water salinity.

The source of dissolved polyphenols is considered to be allochthonous and related to land use such that the substances are incorporated by run off. The dissolved polyphenols showed maximum values in Piñeiro stream (St 2) with 4.7 mg l^{-1}, in Saladillo stream (St 4–5r) with 4.2 mg l^{-1} and in the upper sector of the river (St 4) in spring with 2.9 mg l^{-1} (Figure 5).

Marked spatial and temporal differences in nutrient concentrations were observed, with high values in the headwaters during spring. The highest concentrations of nitrates plus nitrites were 4350 μg l^{-1} (St 1) and 4179 μg l^{-1} (St 4) in spring 1997 (Figure 5). The highest TP concentration (2237 μg l^{-1}: St 4) (Figure 5) was detected in summer 1997. The lowest nutrient concentrations were recorded in the lower basin, but maintained the same trend as the headwater stations, with TP values lower than 600 μg l^{-1} (St 9) (Figure 5).

Trends of TP inputs varied during the seasonal cycle and were related to distance from the river mouth (md). Mean values of TP at each sampling station, taking into account all sampling occasions, showed a significant correlation with md ($r = 0.78$, $p < 0.05$, $n = 16$). Examining each season separately, high correlations were observed in spring and autumn (Figure 6) related to the influence of headwater inputs throughout the main channel. In contrast,

Table 3. Mean and standard deviation (in parentheses) of parameters and variables of sampling stations located in zone 4 of Salado River basin.

	Canal 16	Las Flores stream	Gorchs LB	Gorchs RB
Temperature (°C)	18.9 (7.3)	18.2 (5.8)	19.5 (7.5)	18.8 (9.8)
pH	8.3 (0.4)	8.1 (0.3)	8.7 (0.6)	8.7 (0.0)
Dissolved oxygen (mg l^{-1})	8.2 (0.9)	8.1 (0.8)	8.5 (4.9)	9.13 (1.6)
Conductivity (μS cm^{-1})	2495 (1481)	1455 (687)	4524 (2455)	3360 (1846)
Alkalinity (mg l^{-1})	451 (185)	324 (64)	370 (137)	384 (168)
Chloride (mg l^{-1})	517 (381)	239 (101)	1007 (468)	526 (301)
Sulphates (mg l^{-1})	405 (151)	299 (65)	518 (254)	456 (208)
Total phosphorus (μg l^{-1})	265 (124)	298 (224)	474 (231)	390 (152)
Nitrates plus nitrites (μg l^{-1})	306 (77)	297 (152)	354 (339)	209 (132)
Suspended solids (g l^{-1})	0.04 (0.03)	0.05 (0.05)	0.13 (0.09)	0.19 (0.2)
Dissolved polyphenols (mg l^{-1})	3.04 (0.28)	2.79 (0.88)	1.95 (0.78)	2.1 (0.6)
Particulate organic matter (g l^{-1})	0.0164 (0.01)	0.023 (0.005)	0.036 (0.03)	0.040 (0.03)
Chlorophyll *a* (mg m^{-3})	20 (4.6)	42 (4.5)	53 (72)	13 (8.4)
Phytoplankton (ind. ml^{-1})	90192 (19694)	67842 (57162)	29221 (19694)	13678 (3811)
Zooplankton (ind. l^{-1})	103 (59)	209 (308)	1405 (550)	1100 (193)
	Belgrano	Destino	La Postrera	
Temperature (°C)	18.5 (5.9)	17.7 (5.6)	17.1 (5.5)	
pH	8.3 (0.3)	8.3 (0.4)	8.5 (0.5)	
Dissolved oxygen (mg l^{-1})	6.9 (2.6)	7.6 (2.5)	7.6 (2.1)	
Conductivity (μS cm^{-1})	3573 (1864)	3731 (1970)	3998 (2229)	
Alkalinity (mg l^{-1})	353 (129)	393 (108)	383 (134)	
Chloride (mg l^{-1})	767 (409)	825 (479)	920 (518)	
Sulphates (mg l^{-1})	499 (271)	533 (266)	538 (278)	
Total phosphorus (μg l^{-1})	351 (147)	326 (149)	353 (88)	
Nitrates plus nitrites (μg l^{-1})	417 (411)	282 (120)	471 (410)	
Suspended solids (g l^{-1})	0.09 (0.05)	0.09 (0.06)	0.12 (0.08)	
Dissolved polyphenols (mg l^{-1})	2.02 (0.54)	1.94 (0.57)	1.84 (0.63)	
Particulate organic matter (g l^{-1})	0.027 (0.02)	0.028 (0.02)	0.033 (0.03)	
Chlorophyll *a* (mg m^{-3})	50.4 (56.9)	51.8 (57.3)	52.6 (36.7)	
Phytoplankton (ind. ml^{-1})	50255 (41415)	46786 (48311)	65613 (79809)	
Zooplankton (ind. l^{-1})	1113 (696)	673 (447)	437 (305)	

in the summers, the TP/md relationship was not significant, although in the first summer a clear relationship of TP and distance from the mouth was detected in the middle and lower sectors (Figure 6).

The maximum values of suspended solids were detected in spring 1997 in those sectors sampled after a rainfall event, with the highest value at St 6 (0.656 g l^{-1}).

Plankton

The phytoplankton contained 237 species. Marked spatio-temporal differences of phytoplankton richness were observed with a maximum mean richness of 55

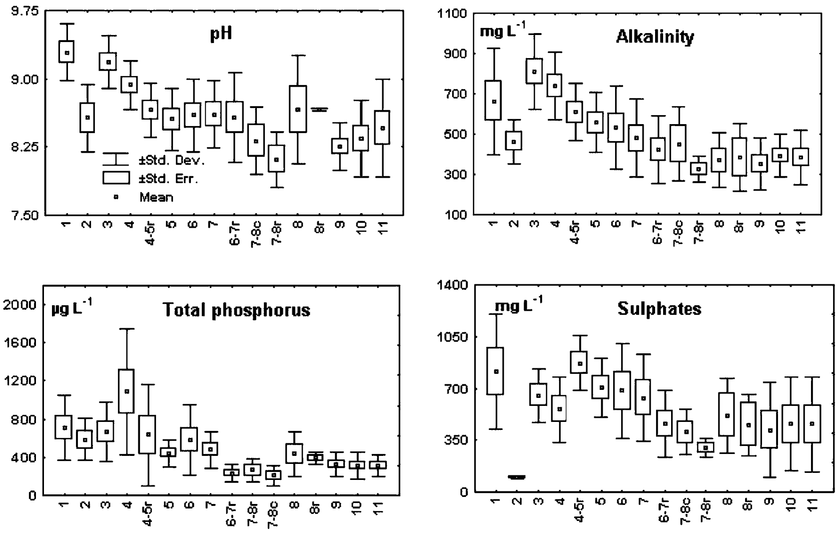


Figure 4. Spatial variation of pH, alkalinity (mg l^{-1}), total phosphorus (μg l^{-1}) and sulphates (mg l^{-1}) in the Salado River basin during the sampling period: 1997–1999 (95% confidence interval).

species in summer, and minimum in winter (23 species). Phytoplankton richness in spring and autumn was similar, with 41 and 40 species, respectively. A mean richness of 46 species was detected in the middle sector of the river and similar values were estimated for tributaries and the mouth sector (42 species). In comparison, the headwater sector was distinguished by its low richness (28 species) and the conspicuous presence of filamentous cyanophytes (*Raphidiopsis mediterranea*, *Oscillatoria* spp, *Aphanocapsa delicatissima*, *Anabaena aphanizomenoides*, among others). Density peaks occurred during spring in the middle sector when chlorophytes dominated. The maximum was recorded at St 6 in spring 1998, with 311436 individuals ml^{-1} while the minimum occurred at St 2 in autumn 1998, with 1231 individuals ml^{-1} (Table 1–3). The concentration of chlorophyll '*a*', as an estimation of phytoplankton biomass, showed maximum values in the spring–summer periods (599 mg m^{-3}) in the headwaters of the basin (St 4) (Figure 7) while minimum values were recorded during autumn–winter. The values for Piñeiro stream (St 2) were 3 or 4 times lower than the other sampling stations and this was associated with the importance of non-planktonic algae (diatoms) in this stream (Tables 1–3) (Figure 7).

Statistical analysis

In the PCA analysis, the first three axes explained 58% of the total variance. Factor 1 was negatively correlated with conductivity (−0.89), chloride (−0.81) and sulphates (−0.84) and positively with dissolved polyphenols.

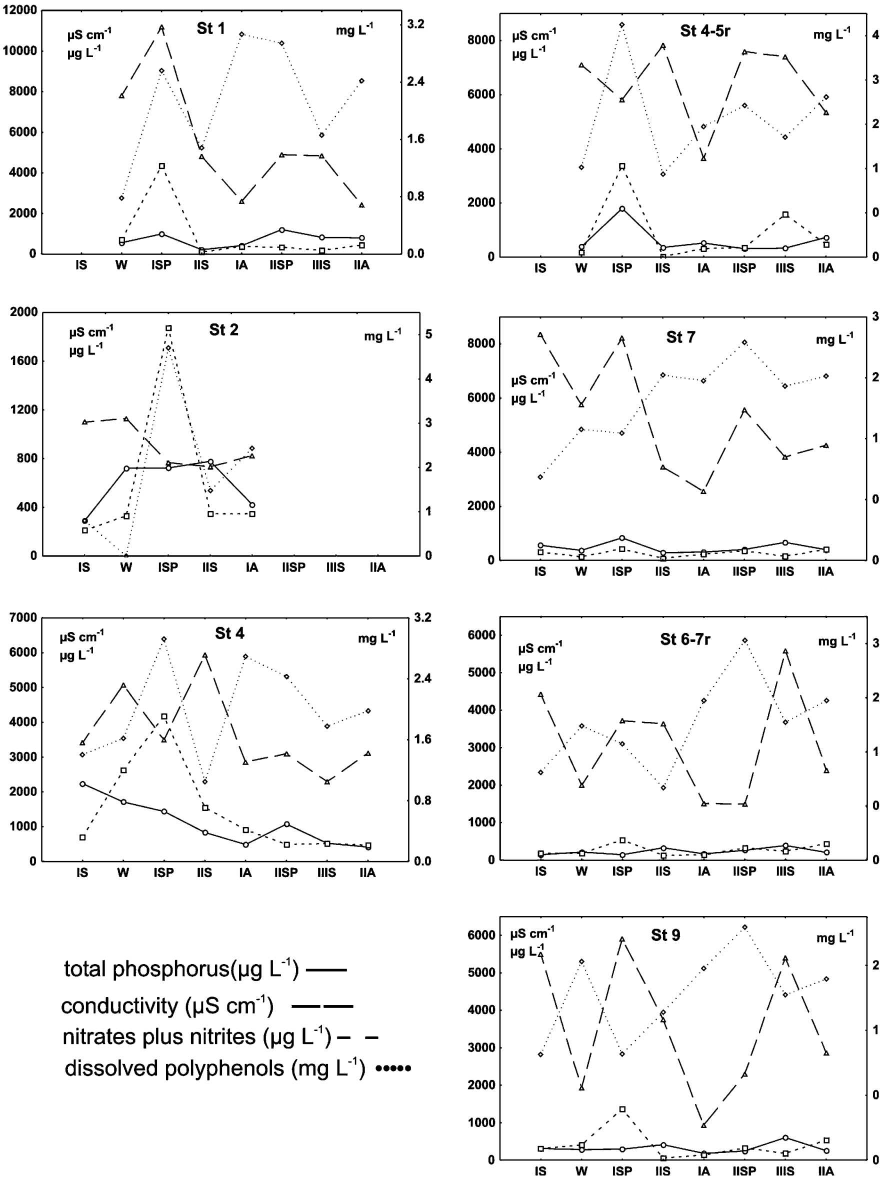


Figure 5. Temporal variation of total phosphorus (μg l^{-1}), nitrates plus nitrites (μg l^{-1}), dissolved polyphenols (mg l^{-1}) and conductivity (μS cm^{-1}) at sites representative of the Salado River basin (St 1: Salado stream, St 2: Piñeiro stream, St 4: Junín 2, St 4–5r: Saladillo stream, St 7: Roque Pérez, St 6–7r: Saladillo-Vallimanca stream and St 9: Belgrano). (IS: March 1997, W: July 1997, ISP: October 1997, IIS: January 1998, IA: May 1998, IISP: October 1998, IIIS: February 1999, IIA: May 1999).

Factor 2 was positively correlated with zooplankton density (0.45) and chlorophyll '*a*' concentration (0.48) but negatively with nitrates plus nitrites (−0.64), organic matter (−0.61) and suspended solids (−0.62). Factor 3 was defined by phytoplankton density (0.72) in the positive sector and in the negative sector by temperature (−0.35) and suspended solids (−0.052) (Figure 8).

In the cluster analysis, two main groups of samples (A and B) were clearly identified. Group A included 54 of 107 sampling occasions characterised, in comparison with group B, by high concentrations of dissolved polyphenols and phytoplankton density, low values of conductivity and organic matter. The subgroups (A1 and A2) were defined by dissolved polyphenols, suspended solids, nutrients and organic matter. Those sampling occasions with higher values of conductivity, nutrients, chloride, alkalinity and organic matter than A1, but lower dissolved oxygen concentration, formed the subgroup A2. Group B included two subgroups (B1 and B2) whose arrangement was defined by seasonality of water temperature and a spatial differentiation was noted between the tributaries and the main channel stations. Those sampling occasions with lowest temperatures formed subgroup B1, whereas subgroup B2 included the majority of the sampling stations/occasions of summer 1998 (Figure 9).

Discussion

During the study period, the Salado River showed a spatio-temporal heterogeneity related to its physical and chemical characteristics and plankton dynamics. Differences in land-use and geomorphological features determined these changes in space and time. The temperature, as a seasonal factor, and salinity (represented by conductivity, chloride and sulphates), as the hydrological factor, were the main factors that defined the pattern of these changes. Nutrients and dissolved polyphenols were found to be a relevant indication of land-use combined with different hydrological events. These factors were responsible for the arrangement of different river sectors and sampling occasions within the cluster analysis.

In the Salado River, the degree of human impact is in inverse relationship to the direction of water flow and the spatio-temporal variation of the parameters and variables is less significant at the sampling stations in the lower basin sector and the main tributaries. Conditions are more similar among these sites than among those located in the headwater and middle sectors and this could be associated with two processes (dilution of salts and nutrients, and the metabolism of nutrients) that result in the headwater inputs being associated in the analysis with the low human activity in this sector. This characteristic will be lost when it is taken into account that the main objective of the proposed drainage projects is the rapid diversion of rainfall from upper basin agricultural lands to the lower basin sector.

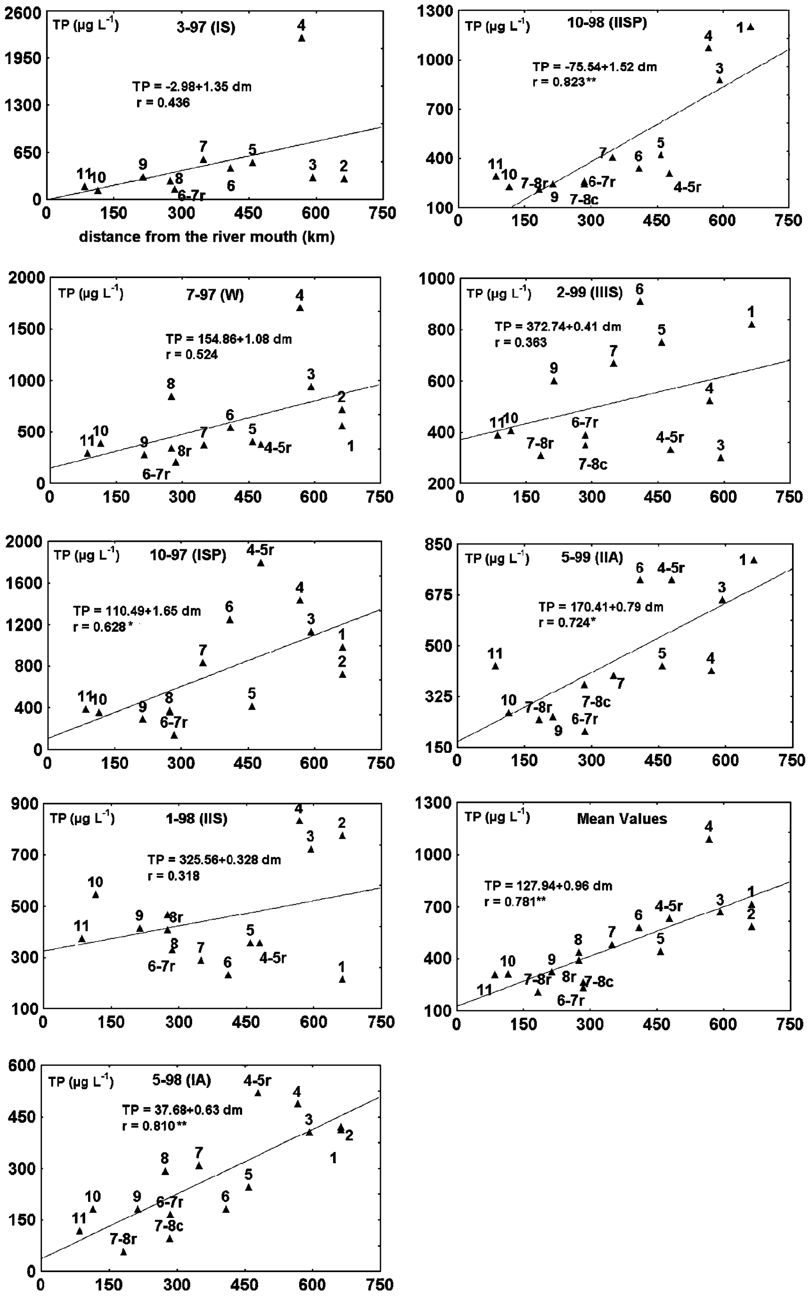


Figure 6. Plots of each sampling occasion and mean total values showing the relationship of total phosphorus (μg l^{-1}) to distance from the river mouth (dm: km) for all sampling stations (ns: non significant, $*p < 0.05$, $**p < 0.01$). (IS: March 1997, W: July 1997, ISP: October 1997, IIS: January 1998, IA: May 1998, IISP: October 1998, IIIS: February 1999, IIA: May 1999).

In the Salado River basin, a relationship was detected between the land-use and nutrient concentrations due to diffuse inflows from agricultural lands. This effect has also been observed in other basins (Edwards et al. in Scotland (2000), May et al. in the R. Cherwell, UK (2001), Liu et al. (2003) in the Yangtze River, Pieterse et al. (2003) in the Dommel River, Belgium and Netherlands). Similarly, the variation of nutrient concentrations, related to the mixed agriculture developed in this sector, agrees with the results of House et al. (1997) from British rivers. The increase of material input detected after storm flow in the Salado River coincides with results found in other lowland rivers (May et al. 2001; Jarvie et al. 1997). In contrast, however, House et al. (1997) observed in the River Humber that nutrient concentrations, especially of nitrogen, diminished due to dilution by a storm discharge.

During spring 1997, following recent local rainfall, the upper basin sampling stations of the Salado River showed similar physical and chemical characteristics. On this sampling occasion, the highest phosphorus and nitrogen concentrations occurred in this agricultural zone. The nutrient concentrations in the river would be associated with their increased input due to runoff and to the use of fertilisers (diammonium phosphate and urea) in the headwater sector of the catchment (soybean, and corn seed sowing, with an annual average input of commercial fertilisers of 100 kg ha^{-1} (Melgar 2003)). The increase of dissolved polyphenols, nitrates plus nitrites, suspended solids and organic matter also generally reflected high water events with a high proportion of allochthonous compounds, which had a negative effect on the plankton community. The plankton community also showed marked signs of stress, in the headwater sector of the basin, which were related to the high nutrient concentrations that on certain sampling occasions reached values of 1 mg l^{-1}. A decrease of species richness, an increase of biomass and the dominance of certain species (cyanophytes) favoured by these nutrient conditions were observed at the same time. Downstream, in response to changes in the land use, the plankton community reached higher values of specific richness and more typical potamoplankton characteristics (Neschuk et al. 2002).

When discharge was low, high conductivity values were measured in the middle and lower basin sectors, in agreement with the earlier observations of O'Farrell (1994) and the results of Jarvie et al. (1997) in the River Humber. The main channel and its principal tributaries showed fluctuations from oligohaline to mesohaline states, closely related to the balance between surface and groundwater. Also, the main channel receives inflows of saline groundwater drained from internal basins to the Saladillo stream (St 4–5r) due to elevation of the water table after large precipitation events (40 years). This particular process has a similar consequence to that observed in the lower Murray River, but in that case as a result of drainage from irrigation areas (Jolly et al. 2001). The Piñeiro stream (St 2) was the only headwater tributary with oligohaline water throughout the sampling period. Nevertheless, the influence of this stream is insignificant due its small catchment.

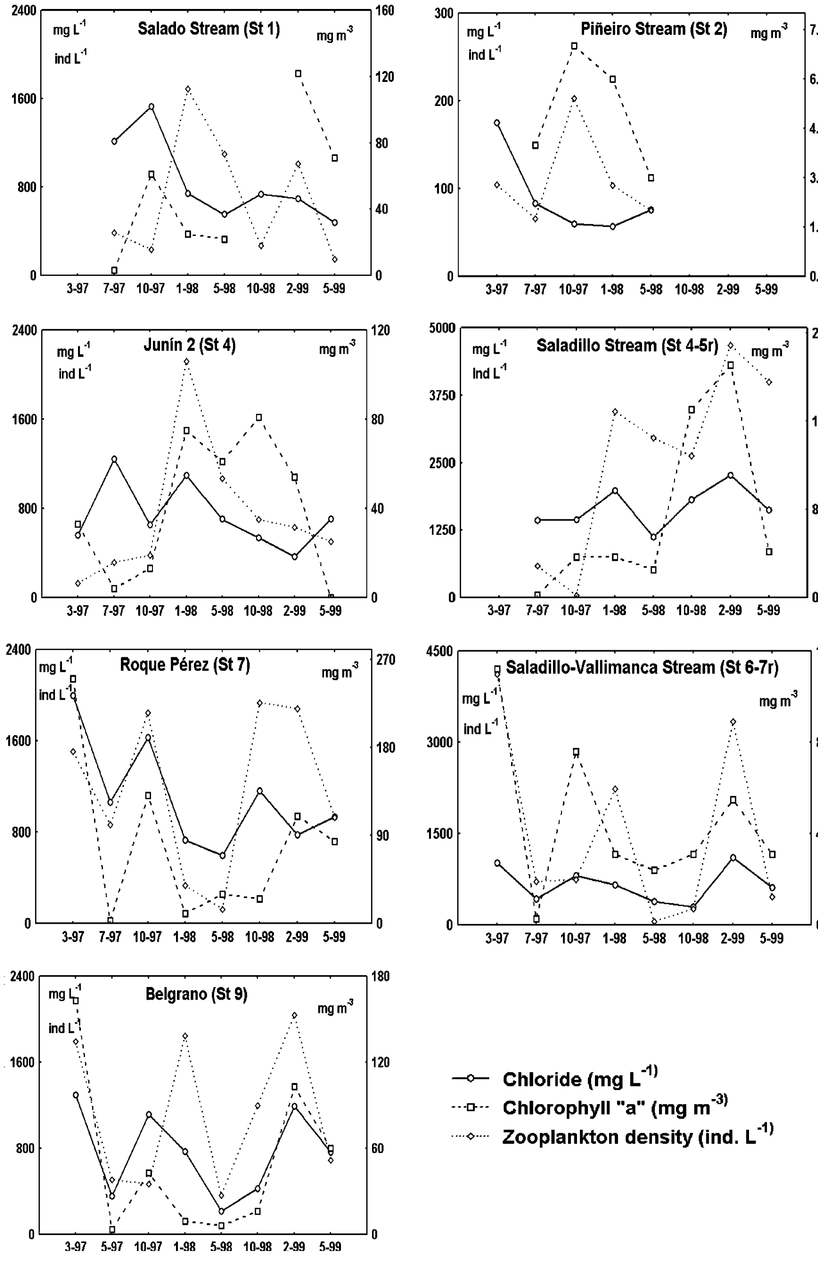


Figure 7. Temporal variation of chloride (mg l^{-1}), chlorophyll '*a*' (mg m^{-3}) and zooplankton density (individuals l^{-1}) at representative sites of the Salado River basin (St 1: Salado stream, St 2: Piñeiro stream, St 4: Junín 2, St 4–5r: Saladillo stream, St 7: Roque Pérez, St 6–7r: Saladillo-Vallimanca stream and St 9: Belgrano). (IS: March 1997, W: July 1997, ISP: October 1997, IIS: January 1998, IA: May 1998, IISP: October 1998, IIIS: February 1999, IIA: May 1999).

The sulphates, alkalinity and conductivity showed a clear tendency to decrease towards the mouth, which is explained by the inputs from tributaries (sub-basins) on the right bank. The same spatial pattern was observed for TP concentrations (Figure 10) but was more evident in autumn and spring, during high water periods when phosphorus inputs from the headwaters could be transported downstream. In summer, the relationship between TP and distance from the mouth was irrelevant due to low discharge and the decrease in agricultural activities, but inputs from urban areas in the headwaters were always evident.

Thus, the basin of the Salado River includes two contrasting areas based on their land use and the geomorphological features of the alluvial valley. The natural systems in the lower basin are in a good state of conservation, buffering the effects of anthropogenic impacts in the headwaters. This buffer effect has, however, limitations related to the intensity of human activities (seasonal agricultural activities) and river transport characteristics. The interaction with lentic environments in the river valley, inputs of organisms and dissolved and

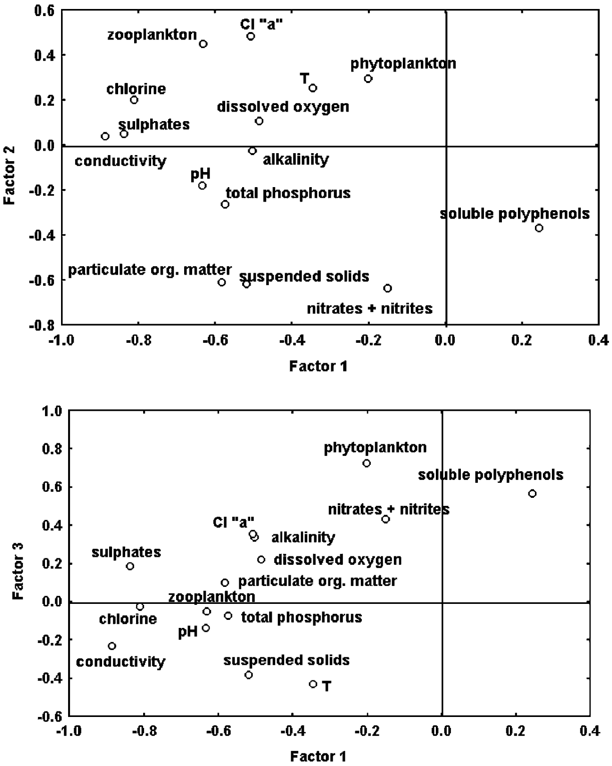
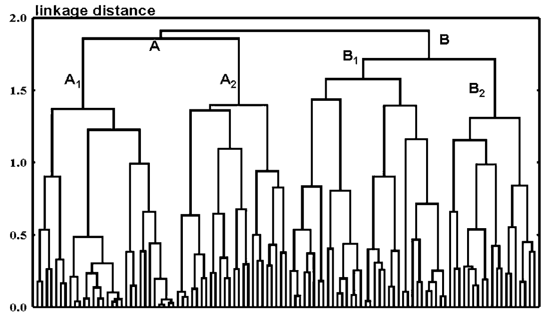


Figure 8. Bidimensional principal components analysis (PCA) representation of parameters and variables at all sampling stations (main channel and tributaries) obtained during the study period (T: temperature, Cl '*a*': chlorophyll '*a*').



Subgroup A1: IIIS7, IIIS5, IIIS7-8R, IIIS4, IISP11, IISP6, IISP7, IIA7-8R, IA7-8R, IA7-8C, IISP10, IISP9, IA11, IA10, IA9, IISP7-8R, IISP7-8C, IISP6-7R, IA6-7R, IIS7-8C, IA7, IA6, IA3, IA1, IA2, W8R,W9, W10, W6-7R
Subgroup A2: IIA11, IIA10, IIA9, IIA7, IIA6, IIA6-7R, II5, IIIS6,IA8, IIIS7-8C, IIS7, IIS6, IISP5, IA5, IIS5, ISP3, IIA1, IIA4, IA4, ISP4-5R, ISP4, ISP2, W4, IS4
Subgroup B1: ISP10, ISP11, ISP9, IIIS11, ISP7, ISP5, ISP6, ISP1, W8, W2, W5, W4-5R, W3, W7, W6, W1, IIA4-5R, IA4-5R, IIIS6-7R, IIIS4-5R, IIS4-5R, IIIS10, IIIS9,IS9, IIA3, IISP3, IISP4-5R, IS8, IS6-7R, IS11, IS9, IS6, IS7, IS5
Subgroup B2: IISP1, IISAP4, IIS2, IIS10, IIS8R, IIS11, IIS8, IIS9, IIS6-7R, ISP8, ISP8R, ISP6-7R, IIS4, IIS3, IIS1, IIIS3, IIIS1, IS3, IS2

Figure 9. Grouping of samples by cluster analysis according to their physical and chemical characteristics, plankton abundance and hydrological conditions during the study period (the first letters indicate the sampling occasions: IS: March 1997, W: July 1997, ISP: October 1997, IIS: January 1998, IA: May 1998, IISP: October 1998, IIIS: February 1999, IIA: May 1999, the last numbers indicate the sampling stations: 1 Salado stream, 2 Piñeiro stream, 3 Junín 1, 4 Junín 2, 4–5r Saladillo stream, 5 Achupallas, 6 Ruta 30, 7 Roque Pérez, 6–7r: Saladillo-Vallimanca stream, 7–8c Canal 16, 7–8r Las Flores stream, 8 Gorchs left bank, 8r Gorchs right bank, 9 Belgrano, 10 Destino, 11 La Postrera).

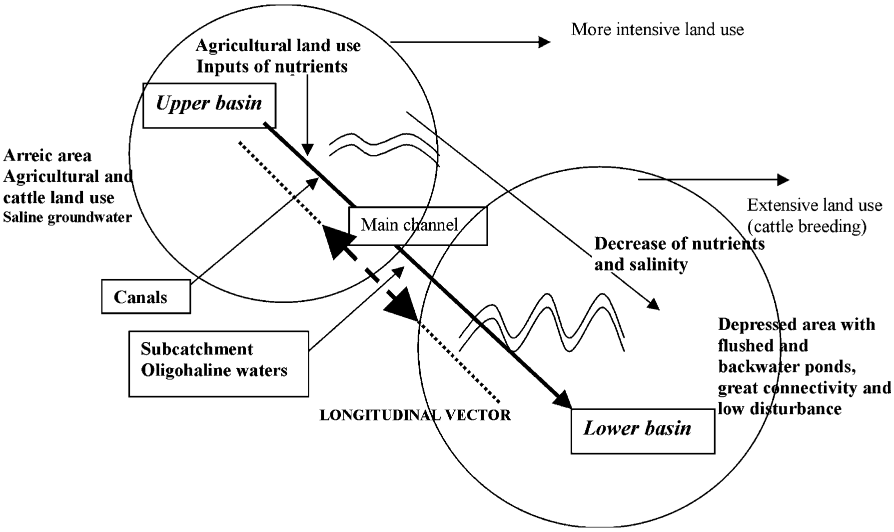


Figure 10. Proposed scheme showing the influence of land use on the nutrient concentrations and salinity of the Salado River basin.

particulate material (organic and inorganic), the inflow of tributaries with different degrees of salinity, comprised a spatially dynamic vector, with a longitudinal dimension that could change over brief time intervals (Figure 10).

In summary, we can conclude that the river characteristics respond mainly to hydrological random patterns rather than deterministic conditions. These changes in the river must be considered as basic information needed for its ecological management, in order to maintain the structure and function of the Salado River system as a whole, allowing a balance between land for food (agriculture and cattle) production and the natural conservation of zones with high biodiversity, including Samborombón Bay which has been declared a Ramsar site.

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