

Nitrogen and phosphorus transport in the Bermejo River (South America)

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ABSTRACT

The transport of the inorganic nitrogen and phosphate and the suspended and dissolved matters were studied. Suspended matter transport was estimated 1200 t km⁻² y⁻¹ and dissolved matter transport in 41 t km⁻² y⁻¹. High relief, seasonal distribution of precipitation and large temperature variations in the upper basin contribute to high erosion rates. Transport of inorganic nitrogen was a moderate 76 kg km⁻² y⁻¹. Total P transport was high (313 kg km⁻² y⁻¹) while that of soluble reactive phosphorus was comparatively low (3.3 kg km⁻² y⁻¹). The waters were supersaturated with calcium carbonate throughout the whole year related to the basin lithology being dominated by calcium-rich rocks (marl, dolomite, limestone). The calcium-carbonate system seems the main phosphate regulating system. A pH decrease released phosphate by seston dissolution in laboratory experiments.

KEY WORDS : Exportation rates — Nitrogen transport — Phosphorus transport — South America — Rivers.

RÉSUMÉ

LE TRANSPORT D'AZOTE ET DE PHOSPHORE DANS LA RIVIÈRE BERMEJO (AMÉRIQUE DU SUD)

Nous avons étudié l'exportation annuelle d'azote, de phosphore, de matière dissoute et de matière en suspension de la rivière Bermejo. Les variations de concentration avec le débit sont considérées. On a estimé l'exportation des matières en suspension à 1 200 tonnes km⁻² an⁻¹ et celle des matières dissoutes à 41 tonnes km² an⁻¹. L'érosion est très importante en raison d'un relief accidenté, des grandes amplitudes thermiques et des précipitations saisonnières qui caractérisent le haut bassin. Le transport d'azote est modéré : 76 kg km² an⁻¹. Le transport de phosphore total a été très important (313 kg km⁻² an⁻¹) alors que celui de phosphate fut comparativement réduit (3,3 kg km² an⁻¹). Les eaux du Bermejo sont sursaturées en carbonate de calcium à longueur d'année. La lithologie du haut bassin présente une prédominance de matériaux sédimentaires avec une proportion élevée de calcaire (dolomite, calcite, marne). Le carbonate de calcium semble être le principal système régulateur du phosphate dans ce milieu. La diminution du pH, en laboratoire, aboutit à une dissolution du seston et à l'augmentation du phosphore et du calcium dissous.

MOTS-CLÉS : Exportation — Transport — Azote — Phosphore — Rivières — Amérique du Sud.

RESUMEN

TRANSPORTE DE NITRÓGENO Y FÓSFORO EN EL RÍO SUDAMERICANO : BERMEJO

Se estudió el transporte de nitrógeno inorgánico, fósforo, sólidos disueltos y sólidos suspendidos del río Bermejo. Se discuten las variaciones de concentración en función del caudal. La tasa de transporte de los sólidos suspendidos fue evaluada en 1200 t km⁻² año⁻¹ y la de sólidos disueltos en 41 t km⁻² año⁻¹. El relieve accidentado, las precipitaciones distribuidas estacionalmente y las marcadas amplitudes térmicas predominantes en la alta

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cuena, condicionan tan elevada tasa de erosión. La carga anual de nitrógeno inorgánico resultó moderada (76 kg km⁻² año⁻¹). La carga de P total resultó elevada (313 kg km⁻² año⁻¹), mientras que, por el contrario, el de fósforo soluble reactivo resultó comparativamente bajo (3.3 kg km⁻² año⁻¹). Las aguas del Bermejo estuvieron sobresaturadas con carbonato de calcio durante todo el año. La litología de la cuena superior muestra el predominio absoluto de rocas sedimentarias con elevada proporción de rocas ricas en calcio, tales como limolita, dolomita y marga. El carbonato de calcio parece ser el principal sistema regulador del fosfato. En experimentos de laboratorio se observó liberación de fosfatos y calcio por disolución del seson, en respuesta a una disminución del pH.

PALABRAS CLAVES : Tasa de transporte — Transporte de nitrógeno — Transporte de fósforo — Ríos — America del Sur.

INTRODUCTION

There is lack of adequate data for the transport of solutes and particulates in tropical rivers (LESACK *et al.*, 1984). Within South America, most information comes from the Amazon catchment (GIBBS, 1967, 1972). In the Río de la Plata, the second largest hydrographic system in the continent, nitrogen and phosphorus transport rates are thus far unreported.

The Bermejo River is an affluent of the Paraguay River, which merges with the High Parana River to form the Middle Parana System. The latter provides 75 % of the Río de la Plata discharge (23 000 m³ s⁻¹) (BONETTO, 1975). The Bermejo River drains the eastern slope of the Andes chain and provides 49 % of the Río de la Plata suspended load (DEPETRIS, 1968). The interest in the Bermejo river was stimulated in recent years by feasibility studies on potential investment for hydrologic multipurpose projects on the basin (Organization of American States, 1975). Plans have been proposed to dam the river at Zanja del Tigre, in the upper, hilly region. Another large dam is projected in the Middle Parana stretch. The lake would inundate 8 000 km² of the flood valley (Agua y Energía Eléctrica, 1983). It is thought that the dams would alter the silt and nutrient flux to the delta ecosystem, an area close to Buenos Aires city, where important paper and timber industries are developed. Concern has also arisen about the trophic status of the future man-made lakes.

This paper evaluates the nitrogen and phosphorus transport of the Bermejo River, examines its seasonal variation as a function of discharge and relates the measured exportation rates with the main environmental factors prevailing in the basin.

STUDY AREA

The Bermejo River originates in the Santa Victoria Mountains (22°23' S; 65°00' W) close to the Argentine-Bolivian border. The basin comprises three different environments: the Santa Victoria Mountains, the Puna Plateau and the Chaco Plain (Fig. 1). The first

of these ranges from 300 to 2 500 m and represents the eastern slope of the Andes Mountain chain. Local orographic processes determine intense summer precipitations (600-1 000 mm). Temperatures range from -10 to 45 °C (Organization of American States, 1969). Vegetation is mainly forest (CABRERA and WILLINK, 1973).

The Puna Plateau is high, cold and dry. Altitudes range from 1 000 to 4 400 m. Annual precipitation ranges from 200 to 600 mm with most in summer. Temperature ranges from -15 to 27 °C (Servicio Meteorológico Nacional, 1975). The vegetation is an arbustive steppe and most of the soil surface remains uncovered (CABRERA and WILLINK, 1973). In both environments the lithology is sedimentary rocks (90 %), 38 % calcareous (limestone, calcite, dolomite, marl, etc.) (Organization of American States, 1969).

Coming down from the Mountains the river enters into the Chaco Plain where it runs about 800 km without receiving any affluents until its confluence with the Paraguay River. Within the Chaco Plain there is an extended climatic gradient, to the West it is arid (600 mm) with strong temperatures changes (-5 to 45 °C) changing gradually to the East where it is humid (1 400 mm) and milder (0.1 to 41 °C) (Servicio Meteorológico Nacional, 1975). The vegetation is a xerophytic deciduous forest with an herbaceous layer (CABRERA and WILLINK, 1973). Along the river sides a narrow strip of dense riparian forest is found.

The Bermejo River hydrological regime follows the precipitation pattern, with a low water phase from May to December. Minimum discharges of about 40 m³ s⁻¹ are observed during October. The flood period lasts from January to April, with maximum discharges of about 2 000 m³ s⁻¹ during February (SOLDANO, 1947). Population density within the basin is very low. With the exception of Jujuy city (about 100 000 inhabitants) only small settlements are found in the upper basin valleys and agriculture accounts for less than 5 % of the surface (Organization of American States, 1969).

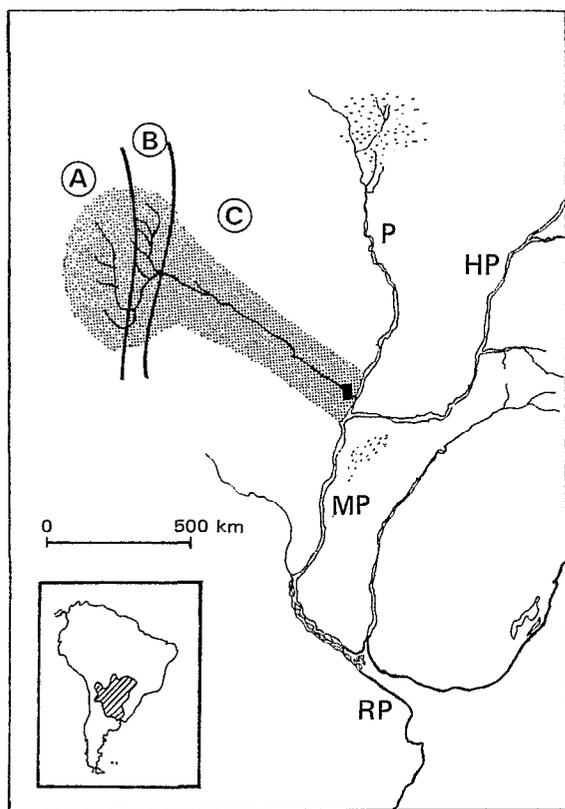


FIG. 1. — Map of the Bermejo river basin. Three different environments are marked. A : Puna Plateau; B : Santa Victoria Mountains; C : Chaco Plain. The black dash shows the sampling point. The Paraguay (P), High Parana (HP), Middle Parana (MP) and Río de la Plata (RP) Rivers are also marked. Inset : position of the Río de la Plata basin in South America

Bassin de la rivière Bermejo. Les trois types de paysage sont notés : A, Plateau de Puna; B, Montagnes de Santa Victoria; C, Plaine de Chaco. Le carré noir près de la confluence situe le point de prélèvements. Différents symboles correspondent aux autres fleuves : Paraguay (P), Haut Parana (HP), Moyen Parana (MP) et Río de la Plata (RP). Encart : le bassin du Río de la Plata

METHODS

Between 1984 and 1986 twelve samples were taken at Puerto Velaz, 20 km upstream the confluence with the Paraguay River, from the surface layer (0.5 m); they were transported in dark cold boxes to the laboratory. Conductivity was measured with a conductivity meter (Yellow Spring Instruments) at 25 °C and pH was measured with an Orion 407 pH meter. Oxygen and alkalinity were determined by titration (APHA, 1980). Calcium was determined by titration with EDTA (APHA, 1980). Iron was determined by the phenanthroline method (APHA, 1980).

The chemical oxygen demand was measured by the dichromate method (GOLTERMAN *et al.*, 1978). Nitrate was estimated by reduction with a cadmium column followed by colorimetry as for the nitrite (APHA, 1980), and ammonia by the indophenol blue method (MACKERETH *et al.*, 1978). Soluble reactive phosphorus (SRP) was measured by the molybdate blue method according to GOLTERMAN *et al.* (1978). All the analysis of dissolved components were on 0.45 μ pore filtered water.

Chlorophyll *a* was extracted with 90 % acetone (APHA, 1980). Total phosphorus (TP) was determined by acid digestion with potassium persulfate followed by SRP determination, and total dissolved phosphorus (TDP) by a similar digestion after membrane filtration. Total particulate phosphorus (TPP) was estimated as the difference between TP and TDP.

The phosphorus fractionation of the suspended matter sampled on 20 March 86 was carried out following the method described by HIELTJES and LIJKLEMA (1980). A wet sediment corresponding to 10 mg dry weight was extracted twice with 10 ml of 1M ammonium chloride in centrifuge tubes shaken for 2 hours at 20 °C. After centrifugation SRP was determined in the supernatant and the sediments were extracted with 10 ml 0.1M NaOH for 17 hours with shaking. After centrifugation and neutralization SRP was determined in the supernatant and the sediments extracted with 10 ml 0.5M HCl for 24 hours. After centrifugation and neutralization SRP was determined. On the same sample one liter water was acidified with 0.05N HCl until the original pH (7,9) was decreased to 7,6. After stabilization with magnetic stirring for 24 hours, calcium, iron and SRP analysis were repeated.

Total dissolved plus suspended matter was determined by evaporation and subsequent dry weight determination.

River discharge rate were measured by the Electricity State Enterprise at Fortin Lavalle. Since the Bermejo River receives no affluent in the stretch concerned no changes in discharge are expected in the lower course. Loads (metric tonnes day⁻¹) were calculated as the product of discharge by concentration on each sampling date. Loads were plotted as a function of time for the period January 1984-March 1985 and the corresponding area integrated by planimetry. Export rates were obtained as the ratio of the annual load and the total area of the basin (131 000 km²) (SOLDANO, 1947).

The surface covered by different rock formation were calculated by planimetry on a geological map of the Río de la Plata basin (Organization of American States, 1969).

TABLE I
Summary of main water chemistry measurements in the Bermejo River
Principales características químicas de la rivi re Bermejo

	1 9 8 4							1 9 8 5				1986
	26 Jan	15 Mar	15 May	17 Jul	22 Aug	25 Oct	19 Nov	1 Mar	4 Jun	12 Set	11 Dec	20 Mar
Discharge ($\text{m}^3 \text{s}^{-1}$)	1252	1475	675	293	293	66	209	1772	595	60	560	1680
Temperature ($^{\circ}\text{C}$)	28	27	20	18	19	26.5	25	26	20	24	28	27
pH	8.7	8.5	8.5	8.6	8.7	8.8	8.5	8.6	8.5	8.3	8.3	7.9
Conductivity ($\mu\text{S cm}^{-1}$)	370	115	430	580	615	850	450	120	450	640	400	330
Suspended matter (mg l^{-1})	7730	9390	3960	1170	620	320	480	11930	790	143	4680	11400
Total P ($\mu\text{g l}^{-1}$)	2147	2535	1176	331	213	194	251	3256	310	103	1216	4850
Particulate P ($\mu\text{g l}^{-1}$)	2116	2508	1107	252	138	84	152	3221	208	21	1177	--
Total dissolved P ($\mu\text{g l}^{-1}$)	31	27	69	79	75	110	99	35	102	82	39	--
Soluble reactive P ($\mu\text{g l}^{-1}$)	29	26	64	78	71	104	88	30	92	78	35	36
N- NO_3 ($\mu\text{g l}^{-1}$)	576	158	729	212	77	120	253	130	110	228	200	193
N- NH_3 ($\mu\text{g l}^{-1}$)	25	250	84	125	21	86	47	180	105	85	11	500
N- NO_2 ($\mu\text{g l}^{-1}$)	2	1.5	0.5	n.d.	0.7	1	1	1	0.5	1.6	0.5	0.5
Inorganic N ($\mu\text{g l}^{-1}$)	603	410	814	337	99	207	301	311	216	315	212	364
HCO_3 (mg l^{-1})	126	206	147	186	207	185	135	--	153	200	100	128
Ca (mg l^{-1})	38.3	56.4	43.4	41.1	58.2	56.0	40.3	--	39.2	41.5	28.6	29

Ionic products were calculated with the measured ionic concentration without ionic strength correction in order to compare our data with that in rivers where ionic analysis are incomplete. The ionic product (IP) for calcium and carbonate was calculated as follows:

$$\text{IP} = [\text{Ca}^{2+}] [\text{HCO}_3^-] k_2 / [\text{H}^+]$$

where $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ are the calcium and bicarbonate concentrations; $[\text{H}^+]$ was estimated as $10^{-\text{pH}}$; k_2 is the second ionization constant of the carbonic acid. It was interpolated from the figures given by STUMM and MORGAN (1970) for the different temperatures at each sampling date.

The hydroxyapatite ionic product was calculated as:

$$\text{IP} = [\text{Ca}^{2+}]^5 [\text{PO}_4^{3-}]^3 k_w / [\text{H}^+]$$

where $[\text{Ca}^{2+}]$ is the measured calcium concentration; k_w is the ionization constant of water; H^+ was estimated as $10^{-\text{pH}}$ and $[\text{PO}_4^{3-}]$ stands for real trivalent o-phosphate concentration and was calculated as:

$$[\text{PO}_4^{3-}] = \text{o-P} / \{1 + [\text{H}^+] / k_3p + [\text{H}^+]^2 / k_2p k_3p\}$$

where k_2p and k_3p are the second and third ionization constants of the o-phosphoric acid; o-P is the concentration of o-phosphate as measured with the molybdate reaction method. k_w , k_2p and k_3p are temperature dependent, their values were calculated using the formula proposed by GOLTERMAN and MEYER (1985b).

Maximum theoretical soluble reactive phosphorus concentrations in equilibrium with hydroxyapatite were calculated following the algorithm proposed by GOLTERMAN (1982):

$$A = \{10^{-32} + 2.8 [\text{H}^+] + 1.4 \cdot 10^7 [\text{H}^+]^2\}$$

$$\text{o-phosphate} \leq A \sqrt{\frac{[\text{H}^+]}{[\text{Ca}^{2+}]^2}} \cdot 31 \text{ (g l}^{-1}\text{)}$$

RESULTS AND DISCUSSION

Table I summarizes the results. The temperature was high throughout the entire year, ranging from 18 to 28 $^{\circ}\text{C}$ with a mean of 24.3 $^{\circ}\text{C}$. Secchi disc depths were low because of the high sediment load. Less than 7 cm were recorded year round and figures less than

2 cm were recorded during flood periods. Oxygen content ranged from 51 to 95 % saturation. Conductivity showed an inverse relationship with discharge. The dilution fitted an exponential type equation of the form $Cd = a Q^b$ where Cd is conductivity ($\mu\text{S cm}^{-1}$) and Q is discharge ($\text{m}^3 \text{s}^{-1}$) and where $a = 5\,274$ and $b = -0.425$ ($r = -0.79$; $p < 0.01$). Such an exponential pattern is commonly interpreted as dilution of ground waters by much less mineralized rain water.

The waters were alkaline with pH values ranging from 7.9 to 8.8. No seasonal pattern was observed. Calcium concentration ($28.6\text{--}58.2 \text{ mg l}^{-1}$) showed variations related to those of bicarbonate ($100\text{--}207 \text{ mg l}^{-1}$) fitting a linear regression line ($r = 0.82$; $p < 0.01$). There was no obvious relation with discharge although low water periods were associated with high concentration. Table 2 shows the water temperature, pH, calculated calcium and carbonate ionic product and the corresponding theoretical solubility product for calcium carbonate (STUMM and MORGAN, 1970) on each sampling date. As may be seen, the water was always supersaturated with calcium carbonate. Supersaturation increased with increasing pH, and fitting an equation of the type $IP = a \text{pH}^b$, where $a = 3 \times 10^{-34}$ and $b = 28$ ($r = 0.92$; $p < 0.01$). GOLTERMAN and MEYER (1985a) also found correlation between the calcium and carbonate ionic product and the pH in the rivers Rhône and Rhine. Although coefficients a and b for the mentioned rivers were different from those calculated for the Bermejo River, the regression lines do not differ considerably.

The calculated ionic product of hydroxyapatite ranged from 5.9×10^{-53} to 4×10^{-46} with a mean value of 5×10^{-49} through the studied period. GOLTERMAN and MEYER (1985b) estimated a mean value of 10^{-50} in the rivers Rhone and Rhine, and proposed this value as the solubility product. Reported values of the hydroxyapatite solubility product in the literature range between 10^{-50} and 10^{-57} (GOLTERMAN and MEYER, 1985b). The sources of uncertainty are discussed by the authors.

Precision and accuracy of the ionic product determination was discussed by CLYMO and GOLTERMAN (1985). In spite of some admitted ambiguity, the large difference between the calculated ionic products and the reported solubility products suggests that the Bermejo River waters are supersaturated with respect to hydroxyapatite year round. Table 3 shows that the measured soluble reactive phosphorus concentration was normally higher than the calculated soluble reactive phosphorus in equilibrium with hydroxyapatite (GOLTERMAN, 1982). The three occasions when this was not so coincided with three of the four lowest pH recorded in the period.

It is unlikely that photosynthetic shifting of pH was responsible for calcium carbonate and hydroxyapatite supersaturation. Bermejo River phytoplankton primary production is low. Phytoplankton production has previously been shown to be limited by turbidity to the point of undetectability by ^{14}C fixation (BONETTO *et al.*, 1984). Also phytoplankton biomass, as chlorophyll *a* determination, was undetectable during the flood period and increased up to 3 mg m^{-3} during the low water period. Organic matter was therefore mainly allochthonous. Dissolved organic carbon ranged from 0.44 to 3.98 mg C l^{-1} with a mean of 2.25 mg C l^{-1} . This range lies amongst the lowest values in the literature and close to the mean reported for semiarid regions (MEYBECK, 1982).

The amount of suspended matter was high at all times ($320\text{--}11\,930 \text{ mg l}^{-1}$). It was correlated to discharge and fitting an exponential equation: $Cs = a Q^b$, where Cs is suspended matter (mg l^{-1}), Q is discharge ($\text{m}^3 \text{s}^{-1}$), $a = 7.5 \times 10^{-4}$ and $b = 1.28$ ($r = 0.94$; $p < 0.01$). Granulometry was dominated by the silt fraction (66 %), while clay accounted for 28 % and sand for 6 % by weight (BONETTO and ORFEO, 1984). Illite was the main clay component (45 %) followed by montmorillonite (30 %) and kaolinite (25 %). Only traces of chlorite were observed (BONETTO and ORFEO, 1984).

Total phosphorus concentration showed variations linearly related to those of discharge ($r = 0.98$; $p < 0.01$). Both, total and particulate phosphorus, showed positive linear relationship to suspended matter ($r = 0.990$ and 0.996 respectively; $p < 0.01$). The percentage of particulate phosphorus within the total was exponentially related to the discharge ($r = 0.94$; $p < 0.01$) ranging from 43 % during the low water phase to 99 % during the flood. The suspended matter phosphorus content ranged from 0.150 to $0.426 \text{ mg P g}^{-1}$ (dry wt) sediment. Such values are low when compared with those of the literature. According to MEYBECK (1982, quoting also MARTIN and MEYBECK, 1979; and GORDEN and LISITZIN, 1978) values often approximate $1.150 \text{ mg P g}^{-1}$ (dry wt). The low suspended matter phosphorus content suggests a largely geochemical origin for the particulate phosphorus. The suspended matter coarse grain size may also be related to the low phosphorus content. VINER (1982) showed that clay size suspended matter can bear orders of magnitude greater amounts of phosphorus per gram than larger sizes. The phosphorus fractionation of the suspended matter sampled on 20 March 86 showed that the loosely bound phosphorus, amounted to $12 \mu\text{g P g}^{-1}$ (dry wt) sediment (3 % of the total extracted phosphorus). The NaOH extractable phosphorus, supposed to extract iron and aluminium bound phosphorus, amounted to $91 \mu\text{g P g}^{-1}$ (dry wt) sedi-

TABLE 2

Water temperature, pH, calculated ionic product of calcium and carbonate (IP) and the theoretical solubility product for calcium carbonate (SP) (STUMM and MORGAN, 1970) in the Bermejo River on each sampling date

Température de l'eau, pH, produit ionique calculé d'après les analyses de calcium et de carbonate (IP) et produit de solubilité théorique du carbonate de calcium (SP) (STUMM et MORGAN, 1970) dans la rivière Bermejo

Date	Temperature (°C)	pH	$10^8 \times \text{IP}$	$10^8 \times \text{SP}$
26 Jan 84	28	8.7	4.5	0.41
15 Mar 84	27	8.5	7.3	0.43
15 May 84	20	8.5	3.0	0.52
17 Jul 84	18	8.6	4.5	0.56
22 Aug 84	19	8.7	10.0	0.54
25 Oct 84	26.5	8.8	12.8	0.44
19 Nov 84	25	8.5	3.3	0.46
04 Jun 85	20	8.5	3.3	0.52
12 Sep 85	24	8.3	3.1	0.47
11 Dec 85	28	8.3	1.1	0.41
20 Mar 86	27	7.9	0.52	0.43

TABLE 3

Calcium concentration, pH, measured soluble reactive phosphorus and calculated soluble reactive phosphorus in equilibrium with hydroxyapatite (GOLTERMAN, 1982)

Concentration en calcium, pH, phosphore soluble réactif mesuré et calculé d'après l'équilibre avec l'hydroxy-apatite selon GOLTERMAN (1982)

Date	Calcium (mg l^{-1})	pH	Measured SRP ($\mu\text{gP l}^{-1}$)	Calculated SRP ($\mu\text{gP l}^{-1}$)
26 Jun 84	38.3	8.2	29	110
15 Mar 84	56.4	8.5	26	23
15 May 84	43.3	8.5	64	35
17 Jul 84	41.1	8.6	78	28
22 Aug 84	58.2	8.7	71	12
25 Oct 84	56.0	8.8	104	9
19 Nov 84	40.3	8.5	88	39
04 Jun 85	39.2	8.5	92	42
12 Sep 85	41.5	8.3	78	72
11 Dec 85	28.4	8.3	35	132
20 Mar 86	29	7.9	36	457

ment (21 % of the total extracted phosphorus). The HCl extractable phosphorus, supposed to extract the calcium bound phosphorus, amounted $322 \mu\text{g P g}^{-1}$ (dry wt) sediment (76 % of the total extractable phosphorus).

Total dissolved phosphorus represented between 1 and 57 % of the total phosphorus. It showed

an inverse exponential relation to discharge ($r = -0.93$; $p < 0.01$). As between 86 and 99 % of the dissolved phosphorus was present in the form of soluble reactive phosphorus, this also showed an inverse exponential relation to discharge ($r = -0.82$; $p < 0.01$). The phosphorus fractionated sample was also analysed for soluble reactive phosphorus, calcium

and iron, after the pH was reduced from the original 7.9 value to 7.6 and allowed to stabilize for 24 hours with magnetic stirring. Soluble reactive phosphorus concentration increased from 36 to 186 $\mu\text{g l}^{-1}$, calcium increased from 28.4 to 48.4 mg l^{-1} and iron increased from 80 to 90 $\mu\text{g l}^{-1}$. OTZUKI and WETZEL (1972) observed phosphate disappearance from solution by co-precipitation with calcium carbonate as a response to a pH increment in hard water from Lawrence Lake. Inversely, both calcium and soluble reactive phosphorus increased in solution in response to acidification coupled with calcium carbonate dissolution in the Bermejo River.

Neither nitrate nor ammonia showed any single relationship to discharge. Nitrate was usually the main inorganic nitrogen component. Low nitrate concentrations occurred both during floods and low water phases while high concentrations were associated with fast changes of discharge, which suggests

an influence of soil conditions. Soil nitrate is hardly adsorbed onto soil particules whereas ammonia is largely absorbed. Hence, during rapid increase of discharge, mainly nitrate appears in the river until the soil source is exhausted, which can be quite rapid, while soil ammonia leaches out slowly. Longer water residence times during low water period enables nitrification of ammonia to nitrate which accumulates in the soil. Ammonia concentrations in the river were below 100 $\mu\text{g N l}^{-1}$ most of the year, reaching highest figures in the flood peaks. High ammonia concentrations seem to be related to decomposition of litter material from the riparian forest inundated during the flood. Nitrite was always below 2 $\mu\text{g N l}^{-1}$. No relationship with discharge was observed.

The estimated Bermejo transport and export rates are summarized in Table 4. Suspended matter is 30 times higher than dissolved matter transport.

TABLE 4

Transport rate of phosphorus, nitrogen, dissolved and particulate matter of the Bermejo River
Transport de phosphore, d'azote, de matière dissoute et particulaire, dans la rivière Bermejo

	Transport t y^{-1}	Exportation rate $\text{kg km}^{-2} \text{y}^{-1}$
Suspended matter	157 10 ⁶	1 200 10 ³
Dissolved matter	5.4 10 ⁶	41 10 ³
Dissolved Organic Carbon	5.5 10 ⁴	420
Inorganic nitrogen	10 000	76
Total P	41 000	313
Particulate P	40 600	310
Total dissolved P	460	3.5
Soluble reactive P	430	3.3

About 98 % of the estimated total phosphorus transport (41 000 t y^{-1}) is in particulate form. Because of the particulate matter dependency upon discharge, about 87 % of the annual phosphorous load is provided by the flood. Of interest are the high suspended matter export rates. Present estimations are similar to the 1 100 $\text{t km}^{-2} \text{y}^{-1}$ calculated in previous studies (BONETTO *et al.*, 1984; BONETTO, 1982). According to HOLEMAN (1968), few rivers in the world show higher figures (Yellow, Ganges, Bramaputra and some of their affluents). These Asian rivers and the Bermejo

are characterized by the high relief and seasonally distributed precipitation in the upper basin. Within the Bermejo upper basin, the Puna Plateau contributes with 20 % of the sediment load with an estimated export rate of 611 $\text{t km}^{-2} \text{y}^{-1}$ (Agua y Energía Eléctrica, 1981). About 70 % of the rainfall fell between December and January. The soil is mostly uncovered by the steppe vegetation. The Santa Victoria Mountains contribute with 80 % of the sediment load. About 60 % of the precipitation fell between January and March. The steep slopes of

unconsolidated material produce an export rate of 2 500 t km² y⁻¹ (Agua y Energía Eléctrica, 1981) in spite of the forest cover.

Relief, climate and lithology have been repeatedly shown to be important in determining riverine transport rates (MEYBECK, 1976, 1982; GIBBS, 1967; DILLON and KIRCHNER, 1975; LESAK *et al.*, 1984). Within the Amazon tributaries, GIBBS (1967) showed that the variability of the concentration of the suspended solids was accounted for by the relief of each watershed while the composition of the suspended solids was controlled by the lithology of each basin. DILLON and KIRCHNER (1975) determined the phosphorus export rate in 34 watersheds and reviewed the literature on the subject, and reported that sedimentary watersheds exported more phosphorus than igneous ones. LESAK *et al.* (1984) interpreted the low Gambia River export rates as the result of a basin lithology dominated by quartzitic sandstones and dolerites combined with a semi-arid climate in an area of gentle slopes.

CONCLUSIONS

Within the Bermejo River upper basin conspicuous temperature changes and seasonally distributed rainfall occurring as discrete storm events of concentrated energy determine intense weathering processes. These processes operating in an area of strong slopes and sedimentary lithology determine high erosion rates. Both, suspended matter and total phosphorus export rates lies among the highest recorded (MEYBECK, 1976; DILLON and KIRCHNER, 1975; HOLEMAN, 1968). Phosphorus is transported mainly in particulate form. High export rates are attained in spite of the low phosphorus content per unit weight of sediment. Phosphorus in the sediments

are considered to be of geochemical origin. Inorganic nitrogen export rates lie in the middle of the range in the literature while both dissolved organic carbon and soluble reactive phosphorus are closer to the lower part of the published ranges (MEYBECK, 1982). Bermejo waters are supersaturated with calcium carbonate and hydroxyapatite. Measured phosphate concentrations are usually higher than those theoretically in equilibrium with hydroxyapatite. The phosphorus fractionation of the suspended matter revealed that so-called calcium-bound phosphate accounts for 76 % of the extractable phosphorus, while the so-called iron-bound phosphate represents only 21 %. Dissolution of sestonic calcium carbonate by pH reduction is coupled with a phosphate increment in solution. Present evidence, therefore, suggests that the calcium carbonate is the main phosphate controlling system in the Bermejo waters. STUMM and BACCINI (1978) showed that predominance of iron or calcium-bound phosphate is very sensitive to pH. At the pH and calcium concentrations prevailing year round it is believed that the iron system is of less importance than that of calcium, a characteristic related to the lithology of the upper basin rich in calcareous sedimentary rocks.

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REFERENCES

- AGUA Y ENERGÍA ELÉCTRICA, 1981. — Estadística hidrológica. Buenos Aires. 183 p.
- AGUA Y ENERGÍA ELÉCTRICA, 1983. — Aprovechamiento integral Paraná Medio. Agua y Energía Eléctrica. Santa Fe, Argentina. 15 p.
- APHA, 1980. — Standard methods for the examination of water. 15th edition. American Public Health Association. Washington. 1134 p.
- BONETTO (A.), 1975. — Hydrologic regime of the Paraná river and its influence on ecosystems. *In*: Hasler (A.) (Ed.) Coupling of Land and Water Systems. Springer-Verlag. Berlin, New York : 175-197.
- BONETTO (A.) and ORFEO (O.), 1984. — Caracteres sedimentológicos de la carga en suspensión del río Paraná entre Confluencia y Esquina (Prov. Corrientes). *Asoc. Arg. de Mineralog. Petrolog. y Sedim.*, 15 (3-4) : 51-61.
- BONETTO (A.), ZALOGAR (Y.), PEDROZO (F.) and BONETTO (C.), 1984. — Contribución al conocimiento limnológico del río Bermejo en su tramo inferior. *Ecosur*, 11 (21-22) : 61-74.
- BONETTO (C.), 1982. — Producción primaria del fitoplancton, concentración de pigmentos, materia orgánica y nutrientes, en la caracterización limnológica de los cuerpos de agua regionales del nordeste argentino. Ph. D. dissertation. University of Buenos Aires. 185 p.

- CABRERA (L.) and WILLINK (A.), 1973. — Biogeografía de América Latina. *Monogr. Cient. Org. Am. States* (13) : 1-120.
- CLYMO (R.) and GOLTERMAN (H.), 1985. — Precision and accuracy of the determination of the ionic product of hydroxy-apatite. *Hydrobiologia*, 126 : 31-34.
- DEPETRIS (P.), 1968. — Algunas consideraciones sobre la velocidad de la erosión en la República Argentina. *Rev. Asoc. Geol. Arg.*, 23 (3) : 237-245.
- DILLON (P.) and KIRCHNER (W.), 1975. — The effects of geology and land use on the export of phosphorus from watersheds. *Water Res.*, 9 : 135-148.
- GIBBS (J.), 1967. — The geochemistry of the Amazon river system. Part. I. The factors that control the salinity and the composition and concentration of the suspended solids. *Geological Soc. Am. Bul.*, 78 : 1203-1232.
- GIBBS (J.), 1972. — Water chemistry of the Amazon river. *Geochimica and Cosmochimica*, Acta 36 : 1061-1066.
- GOLTERMAN (H.), 1982. — Loading concentration models for phosphate in shallow lakes. *Hydrobiologia*, 91 : 169-174.
- GOLTERMAN (H.) and MEYER (M.), 1985a. — The geochemistry of two hard water rivers : the Rhine and the Rhône. Part 2 : the apparent solubility of calcium carbonate. *Hydrobiologia*, 126 : 11-19.
- GOLTERMAN (H.) and MEYER (M.), 1985b. — The geochemistry of two hard water rivers, the Rhine and the Rhône. Part 4 : the determination of the solubility product of hydroxy-apatite. *Hydrobiologia*, 126 : 25-29.
- GOLTERMAN (H.), CLYMO (R.) and OHNSTAD (M.), 1978. — Methods for physical and chemical analysis of freshwaters. IBP Handbook No. 8. Blackwell, London 156 p.
- GORDEEN (V.) and LISITZIN (A.), 1978. — Average chemical composition of suspended solids in world rivers and river particulate inputs to oceans. *Akad. Nauk. SSSR Doklady.*, 238 (1) : 225-228.
- HIELTJES (A.) and LIJKLEMA (L.), 1980. — Fractionation of inorganic phosphates in calcareous sediments. *J. Environ. Qual.*, 9 (3) : 405-407.
- HOLEMAN (J.), 1968. — The sediment yield of major rivers of the world. *Water Res. Research.*, 4 (4) : 737-747.
- LESÁK (L.), HECKY (R.) and MELACK (J.), 1984. — Transport of carbon, nitrogen, phosphorus, and major solutes in the Gambia river, West Africa. *Limnol. Oceanogr.*, 29 (4) : 816-830.
- MACKERETH (F.), HERON (J.) and TALLING (J.), 1978. — Water analysis : some methods for limnologists. *Freshwater Biol. Ass. Sc. Public.* No. 36, England. 120 p.
- MARTIN (J.) and MEYBECK (M.), 1979. — Elemental mass-balance of material carried by world major rivers. *Marine Chemistry*, 7 : 173-206.
- MEYBECK (M.), 1976. — Dissolved and suspended matter carried by rivers : composition, time and space variation and world balance. In: Golterman (H.) (Ed.), *Interactions between sediments and freshwater*. Junk Publ., The Hague, Holland : 25-36.
- MEYBECK (M.), 1982. — Carbon, nitrogen and phosphorus transport by world rivers. *Am. J. Sci.*, 282 : 401-450.
- ORGANIZATION OF AMERICAN STATES, 1969. — Cuenca del Río de la Plata. Estudio para su planificación y desarrollo. Washington D.C., 273 p.
- ORGANIZATION OF AMERICAN STATES, 1975. — Estudio de la cuenca inferior del río Bermejo. Tomo II : Recursos Hídricos. Washington D.C. 538 p.
- OTZUKI (A.) and WETZEL (R.), 1972. — Coprecipitation of phosphate with carbonates in a Marl lake. *Limnol. Oceanogr.*, 17 (5) : 763-767.
- SERVICIO METEOROLOGICO NACIONAL, 1975. — Estadísticas climatológicas 1951-1960. Servicio Meteorológico Nacional. Buenos Aires. 156 p.
- SOLDANO (F.), 1947. — Régimen y aprovechamiento de la red fluvial argentina. Címera. Buenos Aires. 277 p.
- STUMM (W.) and BACCINI (P.), 1978. — Man-made chemical perturbation of lakes. In: Lerman (Ed.), *Lakes: chemistry, geology, physics*. Springer-Verlag. New York: 91-126.
- STUMM (W.) and MORGAN (J.), 1970. — Aquatic chemistry. Wiley. New York. 583 p.
- VINER (A.), 1982. — A quantitative assessment of the nutrient phosphate transported by particles in a tropical river. *Rev. Hydrobiol. Trop.*, 15 (1) : 3-8.