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# Rapel: A 30 years temperate reservoir. Eutrophication or contamination?

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Abstract: Hydrologic conditions and an increase in incoming nutrients from human activities have enhanced the effect of copper sulfates from mine tailings flowing into the temperate monomictic lake Rapel (34° S), an hydroelectric reservoir constructed in 1968. Before copper additions, predictions pointed to rapid eutrophication processes. However, plankton community structure seemed to show conditioned responses to the presence of tailing metals, especially copper. An overall characterization of the lake showed major problems with continual hypolimnetic anoxia in summer during recent years. The sediments accumulating under these conditions exhibited elevated concentrations of methane: the intensive diffusive flux of this gas contributed to the anoxic conditions. It is also likely that substantial losses of sulfates and phosphates ocurred across the sediment-water interface. However, the presence of higher concentrations of copper in the water column prevented the dominance of specific algae such as bluegreens and some diatoms, and thus the general processes leading to rapid eutrophication were limited.

# Introduction

'ransport of allocthonous materials (both particulate and dissolved) is usually higher into reservoirs than in natural lakes. Shorter hydraulic residence times and higher particulate loadings and sedimentation rates, should lead to enhanced eutrophication in reservoirs (THORTON et al. 1990). Fluctuating water levels may significantly intensify sediment-water interactions, resulting in increased concentrations of particulates and nutrients. Thus, the recycling of externally-derived materials in the water column and sediments are increased by internal autochthonous processes. This is specially important in the Rapel Reservoir ecosystem. This hydroelectric reservoir located in Central Chile (34° S) was impounded in 1968 (BAHAMONDE & CABRERA 1984). Hydrological and bathymetric studies indicated the existence of three

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separate subbasins within the reservoir (Fig. 1). Of these, the Alhué basin exhibited an estimated renewal rate of 14 months, significantly slower than the rest of the reservoir where the residence time was about 28 days (CONTRERAS et al. 1994). Studies done by VILA & Soto (1981 a, b), MONTECINO & CABRERA (1982), ZUÑIGA & ARAYA (1982), SOTO et al. (1984), REYNOLDS et al. (1985) VILA et al. (1987) and MONTECINO (1991), of the Rapel reservoir ecosystem until the late 80's showed that physico-chemical characteristics, primary productivity values, and the structure and biomass of plankton and fish communities corresponded to a typical temperate mesotrophic system in the process of eutrophication.

Since 1988, in additon to the inflow of urban and agricultural waters to the main tributaries of the Rapel watershed, the Alhué sub-basin began to receive 'clear water tailings' from copper mining settling ponds via the Alhué stream. Copper tailings were treated and the 'clear water tailings' contained up to 1800 mg l<sup>-1</sup> of sulfates, copper and molybdenium along with other chemicals (VILA et al. 1997). With the influx of sulfates, two opposite limnological predictions for the future of the reservoir were proposed: i) Biotic abundance and composition would be drastically affected and primary productivity significatively lowered, or ii) hypereutrophication processes would rapidly occur in the lake (LAVANDEROS et al. 1990). However, long term, extensive monitoring and intensive sporadic research on this reservoir showed that neither of predictions occurred.

Soon after the introduction of waste water with mine tailings, there were massive fish kills of *Odontesthes bonariensis* VALENCIENNES, the dominant fish species, in the Alhué subbasin



Fig.1. Rapel reservoir morphology and main morphometric parameters. A=82.7 km<sup>2</sup>. V=0.667 km<sup>3</sup>. D<sub>1</sub>=6.94. (Modified from CONTRERAS et al. 1994).

during July 1989 and July 1990. Within the plankton, bluegreen algal blooms, observed annually during summer and autumn (VILA et al. 1987), disappeared at this time (VILA et al. 1997). Information on the chemical aspects of pollution and the increase of copper sulfates and nutrients are still not completely documented and evaluated. Acute toxicity tests, made with Rapel water using fish and the cladoceran, *Ceriodaphnia dubia* RICHARD, (collected from the reservoir) did not show negative effects. Nevertheless, long term studies undertaken at the Rapel reservoir ecosystem showed definite qualitative and quantitative effects on plankton and fish structure during the last 10 years (FRICK 1995, VILA et al. 1997).

A monomictic, mesotrophic to eutrophic lake until 1987, the Rapel reservoir ecosystem showed typical, seasonal successional dominance of diatoms-greens and blue-green algal populations from spring through autumn. The wind regime favored the dominance of Aulacoseira granulata (EHRENBERG) SIMONSEN all year round, (REYNOLDS et al. 1985, VILA et al. 987). Since 1987, the lake has received increasing amounts of nutrients along with the copper sulfate. This has caused a shift in phytoplankton as a response to these disturbances, with two main effects: i) it has slowed the natural seasonal replacement of algal associations normally found in temperate lakes (REYNOLDS 1997), and ii) it has decreased species diversity to a few species that reach high biomass. It is of importance to emphasize that all these species are cited in the literature as capable of generating Cu<sup>++</sup> resistant strains. (BOYD 1972, CHAPRA 1997). VILA et al. (1997) reported that the structure and composition of phytoplankton assemblages during 1992 showed the combined effects of the addition of nutrients and of the toxic copper sulfate from the mine tailings. There was an interruption in the continuity and successional processes of the lake biota. That was predicted by nutrient and chlorophyll relationships developed for temperate lakes and reservoirs. The phosphorous loading was not producing the algal biomass after 1987 (DILLON & RIGLER 1974, PETERS 1986, PRAIRIE et al. 1989, RYDING & RAST 1989). Copper toxicity to algae in natural and experimental fresh-water systems has been reported in the literature (KERRISON et al. 1988, LÜDERITZ & NICKLISCH 1989, HAVENS 1994, KNAUER et al. 1997). In spite of the buffering capacity described for fresh-water systems (JØRGENSSEN 1992), Rapel reservoir is presently changing, probably due to sustained perturbations resulting from the contaminating effect of copper sulfates and perhaps other metals associated with the mine tailing wastewaters.

# Lethods

### Water column collections

Available information for Rapel reservoir bathymetry and hydrology, obtained with a Furuno FE 420 echosounder and drift buoys (CONTRERAS et al. 1994), is shown in Fig. 1. Water quality data were obtained from the Program for Monitoring of Chilean lakes, sponsored by Dirección General de Aguas (Ministerio de Obras Públicas), and from other researchidone at the reservoir. Since 1987, water samples were obtained with a 3 l Van Dorn bottle for physical, chemical and biological variables at three depths from five stations for the three sub-basins (Fig. 1). P-PO<sub>4</sub> and N-NO<sub>3</sub> were measured according to ZAHRADNIK (1981); total P and total N were analyzed by the methodology of MÜHLHAUSER et al. (1986); sulfates were measured by turbidimetric method (GOLTERMAN et al. 1978) and copper by Atomic Absortion Spectroscopy (AAS). Chlorophyll-a determinations, performed according to MONTECINO & CABRERA (1982), were integrated from 0 to the euphotic depth ( $z_{en}$ ). Algae were collected monthly from

four stations at 0, 5 and 10 m with a 3 I Van Dorn bottle during 1975-1976 and 1991-1992. Identification was made on fresh and fixed 5% buffered preserved formaline samples. After oxidation, diatoms were mounted in Aroclor. Algae were counted as standard units (1 S.U. =  $400 \,\mu\text{m}^2$ ) on a one ml Sedgwick-Rafter cell in combination with a Whipple ocular micrometer. Following WOELKERLING et al. (1976), two fields in 12 subsamples were examined (VILA et al. 1987, 1997). During the last four years a Grant 3800 YSI multiparameter probe was used to obtain water profiles of temperature, pH and dissolved O<sub>2</sub> values during the summer at the dam and Alhue subbasins .

### Sediment pore/water metals and other chemical parameters

Measurements were made at the sediment-water interface for dissolved phosphate and metals (Fe, Mn, Mo). Sediment pore waters were collected using in situ samplers (pore water peepe cells that sampled pore water at 2 and 5 mm vertical resolutions) similar to those described by HESSLEIN (1976), CARIGNAN et al. (1984) and BELZILE et al. (1996). The samplers were filled with demineralized water placed in Plexiglas containers filled with demineralized water and bubbled with nitrogen for at least 48 hours before deployment. The samplers were inserted vertically by a diver at various water column depths in the reservoir. After a two week equilibration period, the samplers were retrieved from the sediment and sampled immediately. Pore water samples for dissolved Fe, Mn, Mo, P,  $NH_4^+$  and  $SO_4^{-2}$  were collected by piercing the peeper membrane with a micropipette and transferred to pre-acidified propyethylene tubes for further analyses. Nutrients were analysed in the laboratory by colorimetric methods and the concentration of total metals was measured by Inductively Coupled Plasma (ICP), (APHA 1995).

#### Sediment coring and sediment gas sampling and measurements

Bottom sediments were mostly collected by hand gravity coring to a sediment depth of 50-70 cm with a small Phleger core (MUDROCH & MACKNIGHT, 1994), modified to accept 4.4 cm i.d. acrylic plastic liners without a metal barrel. Cores were collected from the Rapel subbasins during the summer and some of the winter periods from 1995 through 1998. Cores we also periodically collected by Scuba divers from the Alhue sub-basin. The cores were processed in an oxygen-free glove bag by transferring sediments at 1-2 cm depth intervals. A core adapter syringe sampling (CASS) system (ADAMS 1994) was used to transfer sediment samples directly from core liners to 25 ml Sarstedt (Sarstedt, Numbrecht-Rommelsdorf, Germany) syringes and glass scintillation vials. During this operation the glove bag was continually flushed with helium. and the internal contents of the glove bag were kept at about 0.2-0.5 ppm O, during sediment processing (FENDINGER & ADAMS 1986). All sediment gas syringes were immediately stored on ice in helium-filled, heavy-duty freezer bags for transport. Scintillation vials were tightly closed and kept on ice to minimise water loss. These techniques for processing cored sediments decreased the possibility of introducing atmospheric contamination so that Ar and N<sub>2</sub> gases could be measured in sediment pore waters (ADAMS 1994). Analysis of sediment gases usually took place 1 to 2 days after coring and immediate glove bag operations. At this time sediment gas syringes were submerged in a water bath at constant temperature (20 °C) and 5 ml of helium was added to each syringe; manipulations took place under water

to avoid atmospheric contamination. Extraction of sediment gases into helium headspace of each syringe was facilitated by mechanical shaking for 3.5 to 4 minutes followed by removal of 0.8 ml helium headspace with a gas tight syringe. A model 8610 SRI gas chromatograph (GC), using Peak 2 software (SRI Instruments, Torrance, CA) and a laptop computer for gas area integration and data storage, were employed to measure the following gases: headspace extractable argon (Ar), oxygen (O<sub>2</sub>), nitrogen (N<sub>2</sub>), methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). The GC was equipped with a flame ionization detector (FID) for measuring carbon (with a C-H bond) gases and an in-line methanizer [(operated at 380 °C with H<sub>2</sub>) to convert CO<sub>2</sub> to CH<sub>4</sub> for measuring with the FID and to remove O<sub>2</sub> for Ar analyses] to measure low levels of CH<sub>4</sub> and CO<sub>2</sub>. An in-line thermal conductivity detector (TCD), also used with the methanizer, was employed to measure Ar (with or without O<sub>2</sub>), N<sub>2</sub>, CH<sub>4</sub> and CO<sub>2</sub>.

# Results

The morphology of Rapel reservoir is characterized by three sub-basins, two shallow (Alhué and Las Balsas) and one deep (Dam), with maximum depths of 11, 25 and 80 m respectively (Fig. 1). In this temperate monomictic aquatic ecosystem the water temperature ranged from 7° to 25 °C. Most data presented here represent average values for sub-basins. Total monthly rainfall, flow rates and the retention time (in days) are shown in Fig. 2. Rainfall and flow rates showed important inter-annual and intra-annual differences causing significant differences of retention time. Average values of surface pH varied between 8 to 9 and the conductivity oscillated between 200 and 500  $\mu$ S cm<sup>-1</sup>. Total phosphorous values corresponded to those of eutrophic systems (Fig. 3A). Total N and nitrate-N (Fig. 3B), progressively increased each year with maximum values reaching 1800  $\mu$ g l<sup>-1</sup> and 700 $\mu$ g l<sup>-1</sup>, respectively. Both parameters showed large temporal fluctuations, but it is possible to identify a tendency of increasing values with time. There was a tendency of copper concentrations to increase in water column between the

Table 1. Autumn and winter phytoplankton total abundance (in Standard Units, S. U.x10) at the different basins in Rapel reservoir and three sampling depths (1 is surface, 2 is limit of the euphotic zone and 3 is the deep sample) in 1977 and 1992.

Basin	Depth	April		May		June		July		August	
		1977	1992	1977	1992	1977	1992	1977	1992	1977	1992
Dam	1	49	474	26	882	1113	416	2	505	11	75
	2	44	408	218	1356	2490	235	-	550	43	130
	3	39	469	251	2811	2579	88	-	208	47	143
Confluence	1	78	573	446	1296	546	925	1	270	, 114	447
	2	2	783	-	1848	-	439	-	240	4 .	335
	3	1	543	1	2455	-	1582	2	195	-	248
Las Balsas	1	96	-	484	2201	3	69		527	1	155
	2	84	-	805	3364	5	5		412	1	95
	3	90	-	1076	1169	5	35		143	1	119
Alhue	1	89	413	588	1268	4780	1156		461	100	151
	2		443		1200	-	1217		683	1.70	1390
	3	8	620	-	1358	-	1774		1326	-	-



. A. Total monthly rainfall (mm); B. Flow rate (m<sup>3</sup> s<sup>-1</sup>); C. Retention time (days) at Rapel reservoir.





Fig. 3. A. Total P-PO<sub>4</sub> values ( $\mu$ g l<sup>-1</sup>); B. Total N-NO<sub>3</sub> ( $\mu$ g l<sup>-1</sup>), average values at Rapel reservoir. (Vertical line=1 S.D.)

1980-1987 and 1988-1997 periods (Fig. 4). Summer temperature and dissolved oxygen profiles are detailed in Fig. 5. In addition to physical and chemical temporal variations, Rapel reservoir showed vertical thermal stratification during the summer periods with development of an anoxic hypolimnion during the last three years of observation. Previously the entire water column had remained oxic (VILA et al. 1987). Autumn and winter values of total monthly abundances of algae for the periods 1976-1977 and 1991-1992 are given in Table 1. High algal values were maintained during the autumn and winter periods in 1992. During the first period there was a significative dominance by *A. granulata* ( $F_{1.48} = 102.0$ , P<0.001); during the second period this dominance changed to *Pediastrum simplex* MEYEN, *Closterium* 



Fig. 4. Total sulphates and total copper (mg 11) values at Rapel reservoir

aciculare T. WEST and Dictyosphaerium pulchellum NAEGELI (Table 2). As seen in Fig. 6, integrated values of chlorophyll-a (mg Chl m<sup>-2</sup>) profiles significantly changed between the periods 1980-1987 and 1988-1997 (p<0.037; t 2.17 paired samples). The relatively shallow euphotic zone ( $z_{eu}$ ) had a mean depth of 4.8 m (MONTECINO 1991), as confirmed by later work (VILA, unpublished data). The concentrations of pore water phosphates, sulfates and ammonium for the last three summer periods are shown in Fig. 7. Enhanced organic matter decomposition, was reflected by the high concentration of phosphates,  $CO_2$  and  $CH_4$  produced in the surface sediments as compared to values measured in the water column during the summers of 1995 to 1998 (Fig. 8). Important diffusive fluxes to the water column of phosphate and gases such as methane were calculated. When comparisons are made with other natural aquatic systems, calculated methane fluxes were substantially higher at the Rapel reservoir (See Table 3).

Table 2. Aulacoseira granulata: relative abundance in percentage (%) for autumn and winter periods at different depths and different basis at Rapel reservoir in 1977 and 1992.

Basin	Depth	April		Mai		June		July		August	
		1977	1992	1977	1992	1977	1992	1977	1992	1977	1992
Dam	0	49	39	88	35	97	41	98	1	86	12
	5	44	20	85	30	97	74		2	99	7
	10	39	10	87	25	96	33	-	6	95	55
Confluence	0	78	30	79	51	90	43	94	26	92	46
Las Balsas	0	96	2	94	9	81	54	:21	66	46	50
	5	84	4	96	12	82	55	-	69	79	0
Alhue	0	90	3	85	34	85	54	343	66	44	50



Fig. 5. Temperature and dissolved oxygen profiles.  $S_1$  dam site;  $S_2$ : 1000 m upstream;  $S_3$ : 2,500 m upstream.

# Discussion

Different scales of perturbation have affected Rapel reservoir. Interannual drought and flood periods from ENSO events, together with annual hydrological regulation for electricity production during the winter and autumn seasons, have decreased the lake volume and produced periods of higher water retention time in the lake. Retention time showed large temporal changes. The reservoir represents a repository for inflowing sediment, flushed from the two main Andean



Fig. 6. Chlorophyll-a values (mg Chl m<sup>-2</sup>) at Rapel reservoir.

rivers, Cachapoal and Tinguiririca. Resuspension and erosion of shore sediments, and phytoplankton growth from imported and recycled nutrients also contribute to the sediment loading. In addition, sustained import of copper sulfates has greatly increased since 1987.







Fig. 8. Sediment vertical profiles for pore water gases:  $CH_4$ ,  $CO_2$ ,  $N_2$  and sediment water content at Rapel dam sub-basins during winter time.

Concentrations of nutrients and chlorophyll-a are similar for each of the Rapel reservoir subasins, but deoxygenation now occurs from the dam into the upstream reservoir areas; these changes are extreme compared with other reservoirs (KIMMEL et al. 1990). It is notable that the gas production values at the sediment water interface were higher than reported for other eutrophic systems (ADAMS et al. in press). Anoxia occurred near the dam (50-60 m depth) during the summer 1995-1996, zero oxygen was measured at ca. 40 m depth. Again in 1997, a similar condition of anoxia occurred, but this time at a depth of 15 m. Also, methane was usually high in surface sediments at the dam site, where it was normally supersaturated, and was also de-

**Table 3.** Calculated diffusive flux of oxygene and methane for different aquatic environments and Rapel reservoir. Units are in mM m<sup>-2</sup> day<sup>-1</sup>.

Lake	Depth (m)	Oxygen flux	Methane flux	Data source		
Taupo (oligo) 83-155		2.8-4.7	1-1.4	D. ADAMS unpubl.		
Constance (oligo)	147	9.4-0.4	9.0	FRENZEL et al. 1990		
Vechten (meso)	10	O- 29	O-9.4	SWEERTS et al. 1991		
Washington (meso) 65		4.3-8.8	0.6	KUIVILA et al. 1988		
Sempach (eutro)	87	11-16	0.4-1.2 (PEPPER)	WEHRLI pers. comm		
			0.5 (CORE)	7		
Lake Erie (eutro)	24	8.8-11	1.9 (CORE)	ADAMS et al. 1982		
RAPEL (eutro)	53-70	11.5-25	5.9	Present work		

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tected in the water column during anoxia. High sediment methane was also observed at the Alhué site even though the overlying water column was continuously oxygenated.

Seasonal values of dissolved oxygen are highly dependent on the hydrology, stratification pattern and volume of the reservoir, and these are the forcing factors which determine the oxic characteristics of the entire water column in Las Balsas and dam basins. Nevertheless the high amounts of organic matter resulting from eutrophication should cause a high demand for dissolved oxygen, especially at the sediment-water interface. The processes of organic matter decomposition in the surface sediments produced high levels of  $CO_2$  CH<sub>4</sub> and PO<sub>4</sub>, which were recycled by diffusion from the sediments to overlying waters, mainly in Alhué and dam basins.

The concentrations of nutrients and chlorophyll-a correspond to typical eutrophic systems, but the algal assemblages in these aquatic systems are different from the associations and seasonal successions described for the Rapel reservoir (VILA et al. 1987). Furthermore, chlorophyll-a levels were lower than expected from the nutrient concentrations as described by PRAIRIE et al. (1989) and RYDING & RAST (1989) for other aquatic systems ( $\bar{x} = 40$  mg Chl l<sup>-1</sup> compared with  $\bar{x} = 22$  mg Chl l<sup>-1</sup> for Rapel).

In addition to the hydrological conditions, there is a question whether the sustained input of copper is a "disturbance" factor for these reservoir waters. The combined effects of high nutrient and copper inputs could be important in determining the composition and temporal succession of algae. The transport and eventual remobilization of affecting copper could be an important factor affecting algal composition and succession, but copper availability would be related to the presence or absence of organic ligand molecules (SUNDA 1994, XUE et al. 1995, 1997, KERNER & GEISLER 1995). Algae also have an important role in removing metallic elements by biological uptake (REYNOLDS et al. 1985, VILA et al. 1987). *A. granulata* constituted up to 95% of the algal biomass at Rapel reservoir before the mine tailings were introduced to the watershed. These algal tend to sink to the sediments but may be resuspended during mixing. Thus, copper toxicity in the water column could also affect live *A. granulata* cells brought into the reservoir. The result is that this species has significantly decreased in the reservoir in recent years.

The deoxygenation of the hypolimnetic waters during summer stratification is likely to become a major water quality problem in this reservoir in the future. The increased development of anoxic water could result in further chemical and biological problems. Larger different sive fluxes of reduced chemicals and phosphorous from the sediments and increased toxicity from sulfide production will increase the polluted state of this system. As a result, the responses of the biological community to the continuous inflow of copper sulfate might be changed.

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