Int. J. Environ. Res., 8(4):1203-1214, Autumn 2014
ISSN: 1735-6865

Estimating Sediment-water P exchange in Lake Rio Verde (Paraná State, Brazil)

Carneiro, C.[1,2,3*], Kelderman, P.[2], Kondageski, J. H.[1] and Irvine, K.[2]

[1] SANEPAR Water and Sanitation Company of Paraná State, Rua Eng. Antonio Batista Ribas, 151,
Rebouças, Zipcode 82800130, Curitiba, Brazil

[2] UNESCO-IHE Institute for Water Education, PO Box 3015, 2601 DA Delft, The Netherlands

[3] ISAE - Institute of Business Administration and Economics, Av. Visconde Guarapuava, 2943,
Centro, Zipcode 80010100, Curitiba, Brazil

Received 19 Jan. 2014; Revised 23 April 2014; Accepted 29 April 2014

ABSTRACT: Monthly and annual water and phosphorus mass budgets were set up over the year 2010 for the Lake Rio Verde, Brazil. Limited data for the water budget was compensated using an interpolation method with data water budget data of a nearby reservoir. Thus, errors of *ca.* 1.5% were estimated for the water budgets. Dominant P mass input terms were inflows from the rivers and direct run off into the reservoir. Main output terms were P outflow via rivers and industrial water abstraction. Equalizing the P inputs and outputs leads to a sediment phosphorus uptake term were estimated at 35% of the annual P inflow, but with a possible weak correlation between monthly P sediment/water exchange and monthly precipitation figures. Sediment characteristics likely play an important role in the P sediment-water exchange. High concentrations of P in sediment pore water, and seasonal reductions in the oxidized surface layer of sediment suggests reduction of the potential of the sediment to retain P under current and likely, increased, P loads to the reservoir. Future management of the reservoir, therefore, requires continued monitoring and catchment management to mitigate nutrient both point source and diffuse loads. This necessitates an integrated approach to reduce pressures on the reservoir. Failure to address potential problems can lead to reduced water quality, with associated increased treatment costs for water supply.

Key words: Water budget, Mass budget, Phosphorus, Sediment, Internal loading

INTRODUCTION

The use of nutrient mass balances to support catchment management (Bennett et al. 1999, Kelderman et al. 2005, Müller *et al.,* 2007, Maupin & Weakland 2009), depends on reliable and accurate hydrological data, in order to minimize measurement and interpretation errors (Winter 1981, Brown 1986, Neff & Nicholas 2005, Defew et al. 2013). For nutrient fluxes, sediments may either be a source or a sink depending on the relative importance of a number of mechanisms. These include *inter alia* diffusion of dissolved P through the sediment-water interface (Kleeberg 2010, Khalil & Rifaat 2013), resuspension of sediments by water turbulence (Scheffer 2004), bioturbation by benthic invertebrates and fish (Brabrand *et al.,* 1990, Hansen *et al.,* 1998), uptake by submerged macrophytes, and biotic excretion and decomposition (Reddy *et al.,* 1999, Brenner *et al.,* 1999, Baldwin *et al.,* 2005). The presence of 1:1 and 2:1 group clays and oxy-hydroxides, and binding with oxidized species of iron and manganese enhance P-adsorption and, hence, make the sediment more fit for storage P (Hingston *et al.,* 1974, Parfitt 1978, Monte et al. 2003), with adsorption or release of P strongly affected by redox conditions at the sediment-water interface and, thus, the sediment plays a key role for internal P loading.

Seasonal P cycling in reservoirs is driven by several abiotic and biotic processes regulated by temperature and climate. In tropical and sub-tropical regions, lower temperatures in winter are commonly linked with less rainfall and reduced run-off, lower organic loads and sedimentation rates. This will lead to enhancement of the thickness of the oxidising layer at the sediment-water interface due to lower oxygen and nitrate consumption which, in turn, enhances P retention (Kamp-Nielsen 1975, Jensen & Andersen, 1992). Less rainfall also leads to lower inflows into

---

*Corresponding author E-mail: charlesc@sanepar.com.br

lakes, resulting in lower throughflow and, hence, higher lake residence time. This, then, increases the probability of an anoxic hypolimnium (Esteves 1989, Jorgensen & Vollenweider 1989). Thermalredox-conditions at the sediment-water interface is, therefore, a crucial driver of P retention in lake sediments. Nitrate in the sediment promotes a thicker oxidised layer, while in the underlying anoxic layer; sulfate reduction facilitates FeS and FeS_2 bindings (Berner 1970, Caraco *et al.,* 1989, Slomp *et al.,* 2002). Phosphorus can be mobilized during mineralization of organic matter, or by methane/ hydrogen sulfide gas bubbles releasing nutrient-rich pore water from sediment (Kamp-Nielsen 1975, Christophoridis & Fytianos 2006). However, phosphorus released by this process may be rapidly re-adsorbed and precipitated into unavailable forms. Rates of P release are further influenced by phosphate concentrations in the overlying water (Kelderman 1984, Maasen 2003).

The Rio Verde reservoir (Fig. 1), commissioned in 1976, is located in the Metropolitan region of Curitiba, Paraná State, Brazil. The reservoir currently supplies water to the Presidente Getulio Vargas Refinery – PETROBRAS, but with plans for supplying drinking water for the population of the Curitiba and Metropolitan region. Increasing population, especially along a main highway, and agricultural expansion has increased point and diffuse inputs of N and P to the reservoir; contributing to increasing total phosphorus concentrations ranging from 7-27 µg/L between 2005 and 2008 (IAP 2009) to 10-40 µg/L in 2010. In 2005 a potentially toxic cyanobacteria *Cylindrospermopsis raciborskii* reached abundance of 96.500 cells/mL (IAP 2009). Effective management of the reservoir requires reliable monitoring to estimate nutrient inputs. Hydrological and nutrient mass balances can be used to estimate of the contribution of the sediment to reservoir P loads. The work presented here reports on annual and monthly P mass budgets for the Rio Verde Lake Basin for 2010, so as to determine internal P loading from the sediment and to identify the periods the reservoir is most vulnerable to algae blooms.

MATERIALS & METHODS

The Rio Verde Basin (Fig 1) has a drainage area to the reservoir of 159.4 km^2. The reservoir (25°31'30"S - 49°31'30"W) has a surface area of 6.5 km^2, a mean and maximum depth of, respectively, 5.6 m and 11 m, a volume of 34×10^6 m^3, and a mean residence time of 218 days (see Table 1 for complete morphometric and climate data). Water quality is fair-good according to the Brazilian water quality index (IQAR) (IAP 2009).

Table 1. Passaúna Lake Basin - main features

Items	Information
Morphometric	
Total area basin (km^2)	166
Drainage area to reservoir (km^2)	159
Surface area (km^2)	6.5
Creager spillway at cote (m)	885.5
Dam length (m)	600
Hydrological	
Maximum volume (m3)	$34 \,.\, 10^6$
Maximum depth (m)	11
Mean depth (m)	5.6
Mean retention time (days)	218
Weather	
Climate zone	humid temperate
Mean minimum temperature (ºC)	18
Mean maximum temperature (ºC)	22
Historical annual average precipitation (mm)	1500
Total precipitation 2010 (mm)	1803 (+ Jan 333, - Sep 45)

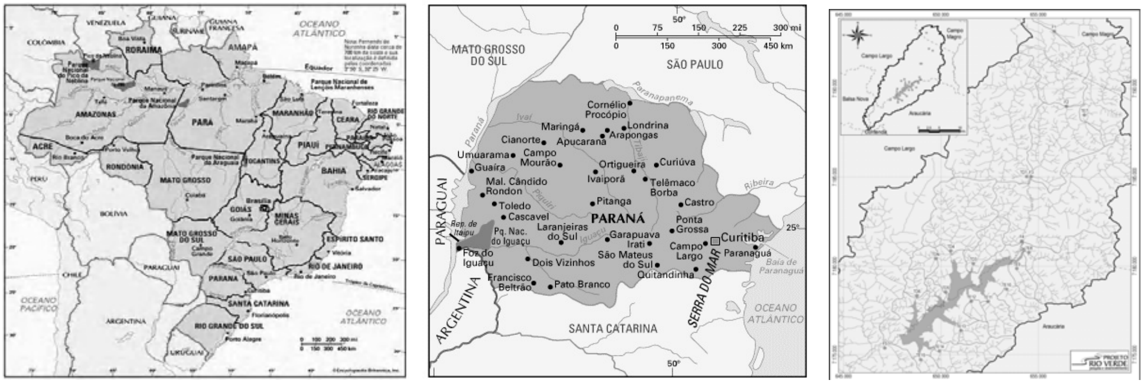

Fig.1. Location of the Rio Verde Lake Basin in Brazil

The catchment area is dominated by clay minerals as important components of three geological compositions: i) Crystalline Basement: rocks with a high degree of metamorphism (migmatites), with silicates: iron-magnesium aluminosilicate as main mineralogical composition; ii) Açungui Group, which main mineralogical composition is: a) aluminosilicate, viz. minerals of the mica family (phyllosilicates), kaolinite (in altered materials), b) Ca and Mg carbonates; c) silicates; d) oxides (primary altered materials); and iii) Guabirotuba Formation of sedimentary rocks, with main mineralogical composition of: a) aluminosilicate, viz. kaolinite and montmorillonite; b) silicates; c) oxides and hydroxides and oxy-hydroxides like goethite and gibbsite (Bigarella 1962; MPS, 1994).

The main types of soil found in the basin are: i) ultisols; ii) oxisols; iii) association oxisols + ultisols; iv) ultisols + inceptisols; and v) entisols (additional information is given by Embrapa 1999). Mean composition, and range, of soils found in profile samples of the basin is as follows: pH – 5.00 (4.1-6.1); P_{labile} – 13 mg/kg (2-170); Ca^{2+} – 3.5 $cmol_c$/kg; Mg^{++} – 1.6 $cmol_c$/kg; K^+ - 0.20 $cmol_c$/kg; medium texture (20–40% clay) – (Doetzer et al. 2011). The basin land use is comprised mainly of mixed forests, and agriculture. Urban areas comprise 15 km² (9%). For further details on land use of the Rio Verde basin, see Caneparo et al. (2011). The water quality in the tributaries and reservoir can be described as "good", with mean BOD values < 5 mg/L in all the tributaries, within the limit accepted by the Brazilian legislation (CONAMA 357/2005). The ratio between the COD and BOD was found to be high in 2008 and 2009 in the main tributary (Carneiro et al, 2011), suggesting industrial effluent discharges. In the reservoir, pH values range from 6.4 to 7.1, and are comparatively high in warmer months, likely linked with increasing phytoplankton production, while the maximum EC values were 199 and 7.9 µS/cm, in 2008 and 2009, respectively. The highest value of dissolved oxygen at the surface (9.5 mg/L) was observed in July 2009, when water temperature was around 16°C. Concentrations of dissolved oxygen close to zero are usually observed at depths near the bottom during warm months (December to April), when mean water temperature reaches 20°C, which is commonly followed by thermal stratification (Fernandes *et al.,* 2011).

Over 2010, mean silicate concentration was > 450 µg/L, chlorophyll-a values ranged from 2.5 µg/L to 120 µg/L (mean value: 13 µg/L) in the deepest part of the lake (10.5 m). Total phytoplankton abundance in the overlying water column was between 1,000 and 10,000 cells/mL, with mean values around 3,800 cells/mL, with diatoms, flagellates and especially chlorophytes usually dominating the phytoplankton community (Fernandes *et al.,* 2011).

The sediment was analysed in October 2009 and June 2010 in three different layers: 0–10 cm, 10–30 cm, and 30–50 cm. The assessments revealed a sediment primarily of clay (66-87%), with organic matter varying from 3 to 10%. TP varied across the lake, with high values in stations close to tributary discharges (24-27 µg/g), where the organic fraction ranged 50-77%; labile P ranged from 90 to 110% of inorganic portion (5-7 µg/g); pH 6.6-7.1 and ORP from -142 to -177 mV. TP contents in the sediment-water interface were 70-206 µg/L and orthophosphate 6-15 µg/L; while in the pore water P values were higher, with TP between 270-364 µg/L and orthophosphate 238-286 µg/L (Carneiro et al. 2011 b).

In order to estimate the phosphorus mass budget (P-budget) in the reservoir, it is necessary to first determine the water balance (W-budget). There are different approaches to evaluate W-budgets (see e.g. Lencastre & Franco 1984; Jorgensen & Vollenweider 1989; Kelderman et al. 2005; Raghunath 2006). Here, the lake Rio Verde W-budget equation was defined as:

$$V_b + P_r\Delta t + I\Delta t + R\Delta t = V_e + U\Delta t + M\Delta t + D\Delta t + E\Delta t \tag{1}$$

Where:
V_b and V_e as the lake volumes at the beginning and end of period, Δt, respectively (m³);
P_r as the amount of precipitation in the lake surface area (m³/day);
I and U as the amount of inflowing and outflowing water respectively (m³/day);
R as the amount of run-off from areas and incremental sub-basins around the lake < 1 km² (m³/day);
M as the amount of industrial water abstractions (m³/day);
D as the amount of dam percolation (m/day);
E as the amount of evaporation (m/ay);

Estimates were based on extensive data collected in 2010, taking into account monthly values to estimate W-budget and P sediment-water exchange. The variable in the Equation 1 were obtained as follows:

i)Volume V, measured by metric gauge (beginning and end of period, i.e. January and December of 2010); for monthly measurements by interpolation: $\Delta_{month} = [(V_> - V_<)/(n-1)]$, where $V_>$ is the month with highest value, $V_<$ as the month with the smallest value, and n is the observation number. This interpolation method was used after comparison with a nearby reservoir (6 km distance) with similar land use and weather conditions and showing a progressive decrease in the volume over the year (*r* for reservoirs volumes = 0.73). This procedure will be discussed further below.

ii) Precipitation P_r, was obtained using data of a weather station located close to the dam, at 15 minutes intervals. Rainfall comprises lake surface area;

iii) Inflow I and outflow U, using data from two full-time gauging stations placed upstream in the main tributary (F4 – 60% of basin total area) and downstream immediately after the spillway, and to smaller tributaries (of which the summation corresponds to 28% of basin total area), were estimated with the SWAT2005 model® (developed by USDA - United States Department of Agriculture) based on data obtained from gauging stations and flow measurements in previous years (Soares et al 2011). The Nash-Sutcliffe coefficient, used to assess the predictive power of hydrological models (Machado *et al.,* 2003), was 0.79, indicating a high concordance between measured and estimated data (Soares *et al.,* 2011). The catchment was sub-divided into 11 sub-basins covering 88% of total area basin (See Fig. 2);

iv) Runoff R estimates employed the Rational Method [Q_r = C.i.A]??where Q_r is the flow rate; C is runoff coefficient, of 0.35 (dimensionless) as intermediate value between 0.2, for sandy, and 0.5, for clay cultivation soils (Das & Saikia 2009); i as mean rainfall intensity; and A as the considered drainage area (8.1% of the total area basin).

v) Industrial abstraction M as a constant daily volume uptake;

vi) Dam percolation D estimated by the formula: [Q_{perc} = k H_L (N_f/N_d) B], where Q_{perc} is the percolation flow; k is soil hydraulic conductivity ($3*10^{-6}$ m/s - medium-textured); H_L is reservoir hydraulic load, N_f/N_d as aspect ratio between hydraulic equipotential lines; and B as length of the dam (Gobbi & Nocko, 2011); this percolation value D would then be 0.012 m^3/s;

vii) The equation of Penman, modified by Doorenbos & Pruit (1977), was applied to estimate daily evaporation E at the lake surface, as follows: E_t = C [W.R_n + (1-W) f(u) (e_a – e_d)], where:

•E_t is the potential evapotranspiration (mm/day);

•C as an adjustment factor to compensate for the effect of day and night weather conditions (dimensionless) (Doorenbos & Pruit, 1977); a value of 1.10 is estimated for this region;

•W is a weighting factor related to the effect of radiation, elevation and temperature (dimensionless) given by the equation: W = Δ/(Δ+¥), where Δ is the rate of change of the saturation vapour pressure with temperature, obtained by: Δ = [4098/(T_a+273.2)^2] $6.11^{[(17.27.Ta)/(Ta+237.3)]}$ and ¥ is the psychometric constant (kPa/°C) calculated from ¥= $\{1-[0.0065/(273+T_a)].h\}^{5.2586}$ / [1.5156–(0.00143307.T_s)], T_a and T_s as the daily mean air and water temperature, respectively (^{0}C) and h as altitude (m) (Theocharis, 2009);

•R_n is daily net radiation (mm/day) given by R_n = R_{ns} - R_{nl}, where R_{ns} is the incident radiation, given by R_{ns} = (1"β) R_s, where β is reflectance coefficient (0.05 for open water surfaces – Penman, 1948); R_s is achieved by the Angströn-Prescott equation: R_s = [a+b (n/N)] R_a, where a and b are linear and angular coefficients (in this region a=0.21 and b=0.42, Lech et al. (2009); n is the number of actual sunshine hours, measured by a heliograph; N is maximum possible sunshine hours and R_a is a value related to latitude and month (both N and R_a found from Doorenbos & Pruit, 1977). R_{nl} is the reflected radiation, given by R_{nl} = f(t) f(e_d) f(n/N), where f(t) = 0.2109 T_{mm}+10.42, with T_{mm} as mean maximum temperature; f(ed sub) = 0.34-0.044 "e_d, with e_d as mean actual vapour pressure of air, given by e_d = e_a.(RH/100), where e_a is the water vapour saturation pressure, according to Ometto (1981), RH is mean relative humidity, and f(n/N) = 0.1+0.9 (n/N);

•f(u) as function related to the wind (dimensionless) given by f(u) = 0.27 [1+(U_{2m}/100)], where U_{2m} is mean day time wind speed (km/h);

Groundwater flows were not considered because the soils over the lake area are permanently saturated and strongly gleying. In this way, capillary ascension is practically nonexistent. There could be an exception for quite dry periods, but these were not observed in this study, when rainfall exceeded the norm (Carneiro *et al.,* 2011 a).

To evaluate the reliability of the W-budget and quantify the associated error related to inflows and discharges, a simple comparison was made between total inflow (Eq. 1, left had side) and outlet (Eq. 2, right hand side) over of the year: ε = 100 [(ΣIn–Σout) / (ΣIn+Σout)].

TP budget was calculated as the summation of water flux and TP concentrations: *'P-budget' = 'P load*$_{in}$ *- P load*$_{out}$*'* ± *'sediment-water exchange'*, obtained by including the various P concentrations and the net P sediment–water exchange term (F) as:

$$V_bc_b + Pc_p\Delta t + Ic_i\Delta t + Rc_r\Delta t = V_ec_{e\,+}\,Mc_u\Delta t + Dc_d\Delta t + E.0\Delta t + F\Delta t,$$

where F (g/day) denotes internal P-accumulation into the sediment as a positive F value, and release as a negative one (Kelderman *et al.,* 2005).

Sampling and laboratory procedures followed "Standard Methods for the Examination of Water and Wastewater" (APHA/WEF/AWWA, 2005). Sampling locations represented reservoir hydrological features, so that the lotic region was represented by station R1, while R2 and R3 characterized the intermediate regions,

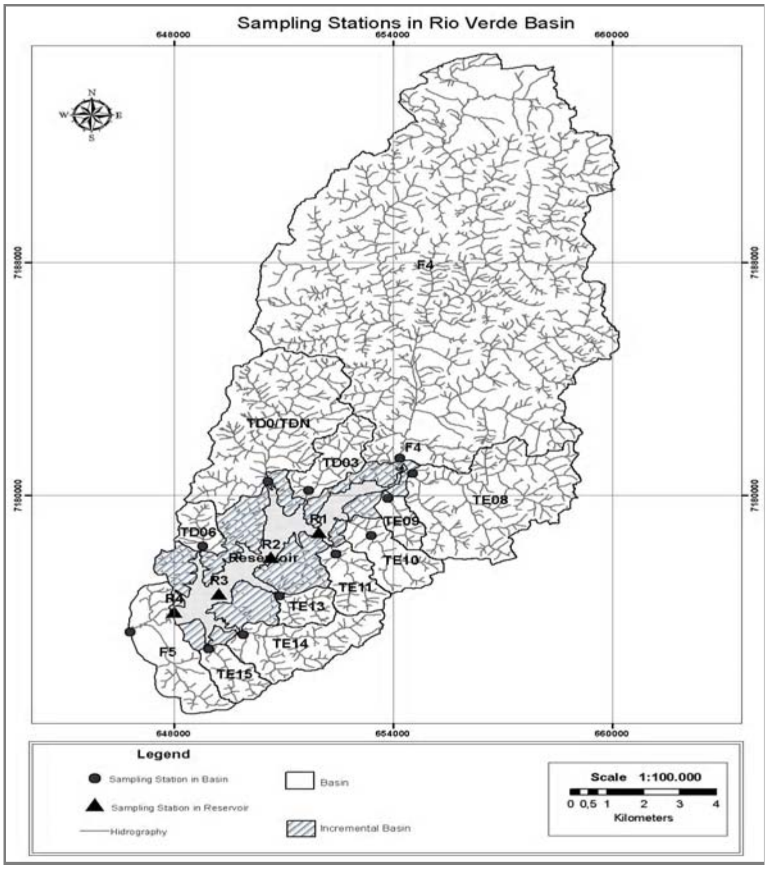

Fig. 2. Sampling Stations in Rio Verve Lake Basin (reservoir and tributaries)

and R4 the lentic and deeper region (close to the spillway - see Fig. 2). However, from July/2009 onwards, only station R4 was maintained, so that the P-budget for 2010 considers just station R4, which is the most representative for general reservoir conditions, with the largest water volume and less lakeshore influences (as outlined by the SisBAHIA® model; Cunha *et al.,* 2011). In 2010 the main tributaries were monitored (representing 94.1% of basin total flow), and used to extrapolate the concentration of smaller inlet streams. Sampling points were always situated at the river mouths.

Frequency interval of sampling for TP was monthly for the reservoir stations and tributaries. The samplings covered normal as well as under drought conditions and periods of intense and long lasting rains. Precipitation values of P collected randomly over a three year period were always < 0.02 mg/L (LOQ); likewise, it was decided to use a minimum value of 0.01 mg P/L. A generalized export coefficient of 1.05 kg P/ha/yr, proposed by PLUARG (1978) and used by Reckhow et al. (1980), was used to estimate runoff loads across the catchment.

P evaporation term was considered to be zero;

P values for industrial water abstractions and dam percolation were represented by values obtained from station R4 due to the location nearby for those points.

RESULTS & DISCUSSION

Reservoir volume was measured only twice, but volumes were monitored continuously at a reservoir 6 km away, with similar land use and weather conditions. Using the two existing volume data (January and December of 2010), other monthly measurements were estimated by interpolation: $\Delta_{month} = [(V_{>} - V_{<})/(n-1)]$, where: $V_{>}$ as the highest month value, $V_{<}$ as the smallest month value, and n is the measured interval (Fig. 3). This produces a progressive variation based on the reservoir dynamics of the nearby analogue reservoir. The correlation coefficient between both volume fluctuations was $r = 0.73_{0.05}$, resulting in an annual error of -1.6%, with some monthly errors >2%. Estimating reservoir volumes from satellite images, in which reservoir areas can be obtained using an 'elevation-area-volume' curve of the reservoir, was not possible because of insufficient serial imaging data. The water budget, presented in Table 2, showed maximum water input to the reservoir during the warm months (Dec-May), while the outlet volumes were higher in colder months (Jun-Nov). February was the month with largest input/output difference (Fig. 4). The monthly imput/output is equivalent to the lake volume, demonstrating the large importance of rainfall rates and land use over the lake water amount.

Dingman (2008) suggested that errors in water balances should be lower than 2%, even though uncertainties between 15 and 30% are not uncommon (Brown 1986, Neff & Nicholas 2005); and the scale factor needs to be considered as well. The calculated residual value in this W-budget (-1.6%) corresponds to a volume of 5.7 x 10^6 m^3 (+ outlet). This difference can be associated with either the inflow values obtained by modeling or groundwater fluxes. Tributaries represented the main inputs in the W-budget (68%), while spillway was the main output (60%), followed by industrial use (17%).

Monthly variation for TP contents and annual TP load in all tributaries and reservoir is shown in Fig. 5. The TP concentrations were low, varying from 14 to 55 µg P/L (mean 30 µg P/L). Only one tributary (F4) comprised 58% of all TP load via tributaries (mean: 5.6

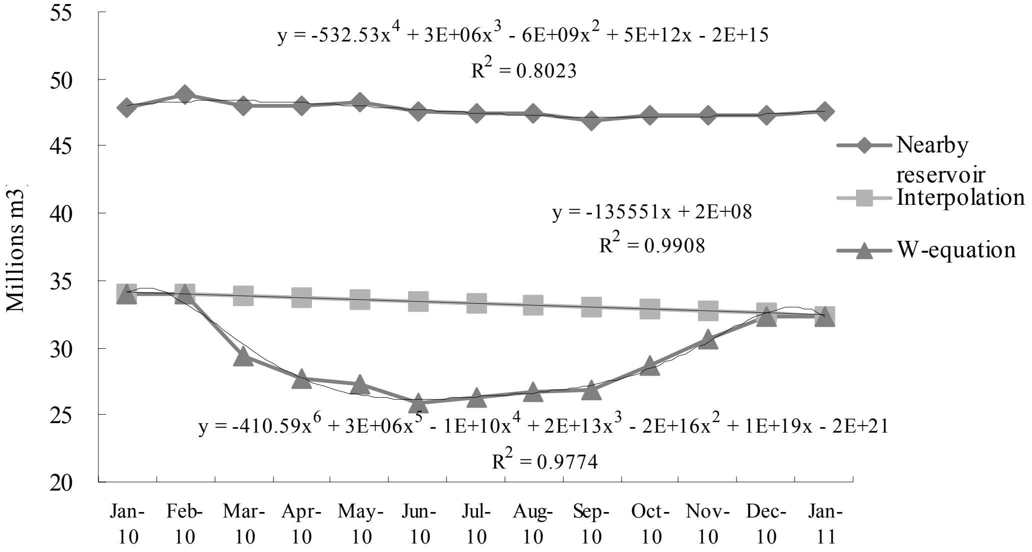

Fig. 3 . Volume values and respective regression equations for the Passaúna Reservoir (closest to Lake Rio Verde), and attempts for interpolation and water balance estimates (W-equation)

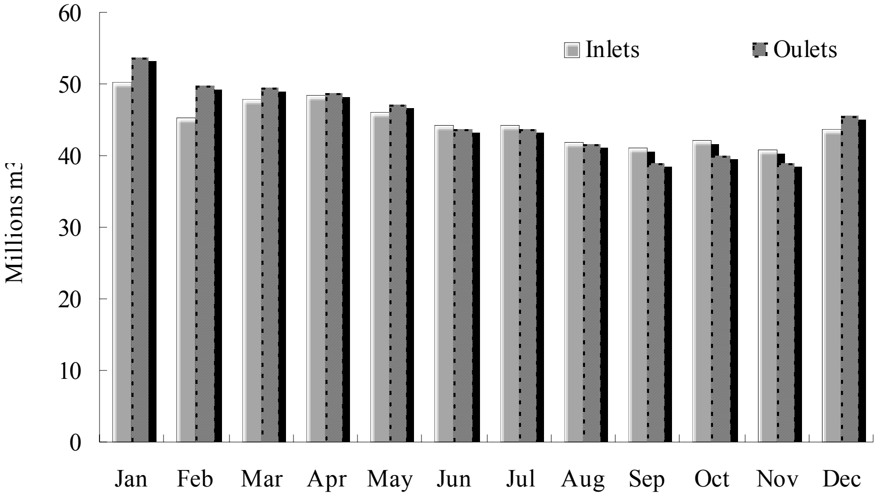

Fig. 4. Effect of increasing sampling resolution from 1.0 mm/sample to 0.4 mm/sample on the amplitude of the coral $\delta^{13}C$, $\delta^{18}O$, and Sr/Ca signals over annual cycles of 2009 and 2010.

kg/day SD ± 0.8 kg/day), mainly due to its large flow (55% of mean total tributaries-inflow). Nevertheless, high loads were also estimated from the TDN/TD4 and TE8 sub-basins. The daily mean TP load observed over 2010 was 9.6 kg/day, while in a study carried out in 2008/09 this value was 10.4 kg/day (Carneiro *et al.,* subm.). Another important aspect illustrated in Fig. 5 is the close match between loads and flows. Evidence on that also might be realized later on through the monthly TP sediment-water exchange and precipitation rates (Fig. 6).

On the other hand, when unit-area (TP ha/year) was considered, P loads in other smaller sub-basin (TE10) were roughly double the values observed in the F4 sub-basin (~ 23 % of TP), indicating a more intensive land-use. The neighboring sub-basins TE13, TE14 and TE15, which overall had reduced loads, sometimes showed high P concentrations, indicating a need for careful further monitoring.

In the reservoir, the mean TP concentrations were 25 µg/L (range 10 - 40; SD ± 12 µg/L; Fig 5). Fernandes et al. (2011), observed that for much of the year the N:P ratio in the reservoir much higher than the Redfield ratio of 16:1, suggesting phytoplankton to be limited by P.

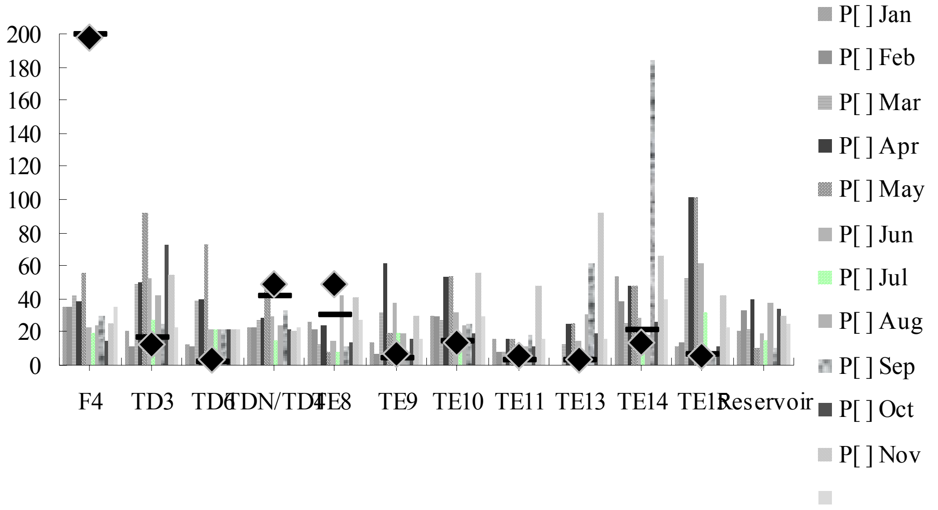

Fig. 5. Tributaries and reservoir behavior taking account: the monthly TP contents (P[ ] in µg/L), the annual TP load (t-Load . 10 kg/year), and the daily mean flow (m-Q . 10 L/s) - Rio Verde Lake Basin – 2010

Table 2. Input (+) and output (-) terms for the water budget in Lake Rio Verde in 2010 (m^3/yr)

Variables	**Values**	**%**
INPUTS		
Lake volume - beginning of the year (+)	$34 . 10^6$	20
Inflow from tributaries (+)	$114.5 . 10^6$	68
Precipitation lake area (+)	$11.7 . 10^6$	7
Runoff from incremental sub-basins (+)	$8.5 . 10^6$	5
OUTPUTS		
Industrial water abstraction (-)	$29.7 . 10^6$	17
Outflow by spillway (-)	$105 . 10^6$	60
Evapotranspiration (-)	$7 . 10^6$	4
Dam percolation (-)	$377 . 10^3$	0.2
Lake volume - end of the year (-)	$32.4 . 10^6$	19
Σ -Input – Σ _Output	**$- 5.7 . 10^6$**	

Table 3 summarizes results from the P-budget of 2010. Summed inflow by tributaries and runoff comprised about 86% (~ 5 x 10^3 kg) of the total P load. In contrast, the addition of all outflow contributions is < 3 x 10^3 kg, meaning that in 2010 about 35% (~ 2 . 10^3 kg) of the incoming TP was retained in the reservoir. As the water quality of Lake Rio Verde is still relatively good, P retention into sediment is clearly limiting the impact of the P loads on the Rio Verde reservoir. Although the mean daily P load had decreased in 2010 compared with 2008/2009, the future water quality is likely to be vulnerable with large P retention suggestive of P-saturation of the sediment.

Other factors of importance are urban expansion associated with a main highway (BR277), and high labile-P contents of the catchment soil (2-170 mg P/kg – Doetzer et al. 2011). This can result in high P loadings to the reservoir from erosion and diffuse run-off.

Estimated net P accumulation into the sediment (2010: ~ 2 x 10^3 kg P) was highest during high rainfall months (Fig. 6). An exception was seen in February, which although a typically rainy month, had reduced rainfall in 2010. This resulted in increased P concentration in the lake owing to a constant industrial abstraction and spillway discharge that led to P discharge in February 2-3 times above the annual average. An opposite situation was observed in May, where even under small precipitation the largest P accumulation was found, with high concentration in most of tributaries. It is speculated this was a result of winter phosphate fertilizing; a possible concentration effect cannot be considered, as a significant decrease in the lake volume was not observed. The correlation coefficient for precipitation and P accumulation was $0.38_{0.05}$

Table 3. TP mass budget (kg) of Lake Rio Verde - 2010

Loads	**Values**	**%**
INPUTS		
Lake volume - beginning of the year (+)	680	12
Tributaries (+)	3,502	61
Precipitation lake area (+)	117	2
Runoff from incremental sub-basins (+)	1,416	25
OUTPUTS		
Industrial water abstraction (-)	726	20
Outflow by spillway (-)	2,172	58
Dam percolation (-)	9	0.2
Lake volume - end of the year (-)	810	22
Σ -Input – Σ _Output		
Net accumulation of TP into the sediment of Lake Rio Verde	**1,998**	

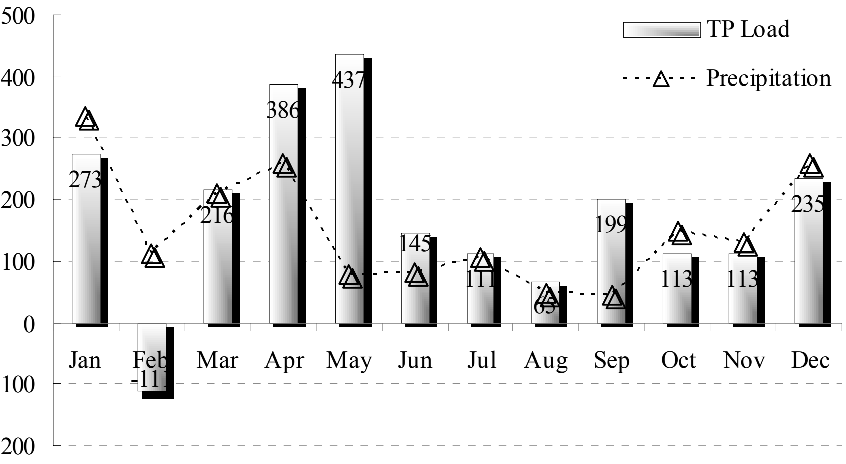

Fig. 6 . Monthly TP sediment-water exchange (kg) and monthly precipitation (mm) in Lake Rio Verde – 2010 ('+values' = P accumulation to the sediment, while '-values' = release from the sediment)

The sediment in the Rio Verde Basin is dominated by clays (65 - 87%) with moderate organic matter content (3.3 - 7.4%), high capacity for P adsorption onto clay minerals, as well as complex organic compounds. This promotes P retention. Orthophosphates bonded to a protonated hydroxyl group become one a more complex molecule, hampering the releasing (Hingston et al. 1974, Barrow 1983, Bohn *et al.,* 1985). On the other hand, a sediment pH of around 7.0 over the sampling years, largely favours P-Al and P-Fe bindings; under this pH range the point of zero charge (pzc) of oxides is higher than clays (Bohn et al. 1985, Stumm & Morgan 1996). In addition, pH in overlying water column (6.4–7.1) was similar to sediment pH (6.6–7.1), suggesting P-Al and P-Fe precipitation as a relevant P retention mechanism. Then, Al and Fe content in the water column as well as their oxidation state assume a large importance on keeping P in precipitate forms. The biogeochemistry of Fe and SO_4^{2-} perform an important function for sediment release or retention of P (Hingston *et al.,* 1967, Ruttenberg 1992, Suzumura & Kamatani 1995). Ferrous-Fe precipitates easily into ferrosulphides (FeS or FeS_2), enhancing ortho-P content in interstitial water (Berner 1970, Caraco et al. 1989, Roden & Edmonds 1997), then available toward water column.

The redox potential of sediment was quite low and similar between stations (-172 and -151 mV as mean values for R4 and R1, respectively). This provides a reducing character to sediment, affecting the P bindings, as reduced Fe and Mn are not able to precipitate P. Under anoxic conditions, depletion of oxidised substances may explain the high P values in pore water (270-364 µg TP/L and 239-286 µg ortho-P/L - Carneiro *et al.,* 2011 b). Usually, release of sorbed P and Fe compounds can already occur below +200 mV (Dillon & Rigler, 1974; Boers *et al.,* 1993, Stumm & Morgan 1996). In addition, these values refer to the winter, when the water column was well mixed (hypolimnion - 7 mg O_2/L) and probably with oxidised upper sediment. In contrast, reducing condition might be intense in the summer, a period with strong stratification and a clear separation of epi and hypolimnia (Fernandes *et al.,* 2011). Under these conditions the upper sediment oxidised layer may be thin, or periodically reduced, further enhancing the P release potential.

Although the P concentration is significantly higher in the pore water rather than water phase, it represents a small fraction (< 1%) of the sediment TP pool. Organic decomposition and reduction of iron oxy-hydroxides represent main mechanisms for release of sediment P. The organic P pool in Lake Rio Verde was 50-77% of TP, which implies a large P stock. Cunha et al. (2011) clearly showed larger TP accumulation in the lake-tributaries confluence area, indicating recent contributions.

No information about the type of P bindings in the sediment of Lake Rio Verde is available, but compared with other Brazilian reservoirs of comparable age, with sediment TP concentrations of up to 1,200 µg/g (Franzen, 2009), sediment concentrations in Lake Rio Verde are low and within guidance values (e.g. as for instance, Sediment Quality Guideline of Ontario (SQGC, 1993) and Brazilian National Council of Environment guidance – CONAMA, 2012]. Nevertheless, evidence of seasonal P-release and reduced P-binding potential during periods of stratification provide early warning signs that capacity of the sediment to retain P is reducing. Given the persistence, or increase, of current P loading, this provides a high potential for periodic large release of P into the water column with consequential deterioration of water quality and a prognosis of more difficult and expensive reservoir management.

CONCLUSION

Application of mass-balance to the Rio Verde reservoir, based on monthly monitoring in 2010 of the main inlets indicated a loading of 31 kg P/km^2/year, from a drainage area comprising mainly forest but with increasing urbanization and agricultural land use. Low data frequency of reservoir volume was compensated by use of continuous monitoring from a nearby reservoir, and interpolation using the limited volume data from Rio Verde. The 2010 P-budget indicated a TP retention of 35%, but with release of P from the sediment to the water column in February. Assessment of sediment chemistry indicated P values in the water, sediment and at the sediment-water interface to be relatively low, but with high concentrations in the pore water. Under temporary anoxic conditions in the hypolimnium, pore water orthophosphate can diffuse to the overlying water and contribute to reservoir nutrient loadings. Increased, or maintenance of, nutrient loadings to the reservoir will inevitably lead to increased organic loading to the sediment and reduction of capacity of the sediment to retain P. This enhances the risk of sediment P-release to the water column, especially during periods of water column stratification. Accumulating P load to Lake Rio Verde makes it susceptible to algae blooms. Management of the reservoir, therefore, requires not only further monitoring of inlet water chemistry and hydrological load, but attention and response to P management in the catchment. In particular this should include assessment of P reservoirs in the soil and measures to limit diffuse pollution contributing to the reservoirs loading. Point sources for industry and, especially, an increasing urban population are, in principle, easier to control but require effective water treatment facilities.

ACKNOWLEDGEMENTS

All data employed in this work were produced by the researchers of the group "Eutrophication Interdisciplinary Studies in the Rio Verde Lake Basin". Sincere thanks are given to colleagues: Nicolas Lopardo, Aldo Fernandes, Cynara Cunha, Fernanda Achete, Christine Xavier; to colleagues from SANEPAR (especially DMA, APD, USHI and USPD departments), to CAPES for financial support; and also thanks to institutions: Águas Paraná, SIMEPAR and SANEPAR, for availability of data; distinguish appreciation to the last, by allowing exclusive dedication time to this work, and UNESCO-IHE for kindly welcoming me to Postdoctoral Programme.

REFERENCES

APHA, (2005). American Public Health Association American Public Health Association, American Water Works Association, Water Environment Federation Standard methods for the examination of water and wastewater, 21th edn, Washington, USA.

Baldwin, D. S., Howitt, J. A. and Beattie, J. K. (2005). Abiotic degradation of organic phosphorus compounds in the environment. (In: Turner BL, Frossard E, Baldwin DS (ed), Organic phosphorus in the environment (pp 75–88). UK: CABI Publishing)

Barrow, N. J., (1983). A mechanistic model for describing the sorption and desorption of phosphate by soil. J. Soil Sci. **34,** 733–750.

Bennett, E. M., Reed-Andersen T., Houser, J. N., Gabriel, J. R. and Carpenter, S. R. (1999). A Phosphorus Budget for the Lake Mendota Watershed. Ecosyst., **2**, 69–75.

Berner, R. A. (1970). Sedimentary pyrite formation. Am. J. Sci., **268**, 1–23.

Bigarella, J. J. and Salamuni, R. (1962). Caracteres texturais dos sedimentos da bacia de Curitiba (*Textural characters of sediments in the Curitiba basin*). Bulletin of Federal University of Paraná State – Geologia., **7**, 1-164.

Boers, P. C. M., Van Raaphorst, W. and Van Der Molen, D. T. (1998). Phosphorus retention in sediments. Wat. Sci. Tech., **37 (3)**, 31-39.

Bohn, H. L., McNeal, B. L. and O'Connor, G. A. (1985). Soil Chemistry (2nd ed, New York: John Wiley & Sons Ltd)

Brabrand, Å., Faafeng, B. and Nilssen, J. P. (1990). Relative importance of phosphorus supply to phytoplankton production: fish excretion versus external loading. Can. J. Fish. Aquat. Sci., **47**, 364-372.

Brenner, M., Whitmore, T. J., Lasi, M. A., Cable, J. E. and Cable, P. H. (1999). A multi-proxy trophic state reconstruction for shallow Orange Lake, Florida, USA: possible influence of macrophytes on limnetic nutrient concentrations. J. Paleolimnol., **21**, 215-233.

Brown, R. G. (1986). Errors in estimating ground-water components of hydrologic and phosphorus budgets of lakes. (In Subitzky S (ed) Selected papers in the hydrologic sciences: U.S. Geological Survey Water-Supply, Paper 2310-D pp 53-64.

Caneparo, S. C., Frick, E. C. L., Pereira, G.H.A., Druszcz, M. B. and Silva, J. J. I. (2011). Base de dados para o diagnóstico e análise ambiental da bacia do Rio Verde - o modelo digital do ambiente (*Data base for environmental diagnosis and assessment in the Rio Verde Basin – the environmental digital model*). (In: Cunha C. L. N., Carneiro C., Gobbi E. F. and Andreoli C. V. (ed) Eutrofização em Reservatórios: Gestão Preventiva - Estudo Interdisciplinar na Bacia do Rio Verde, PR (*Reservoir Eutrophication: Preventive Management. An applied example of Integrated Basin Management interdisciplinary research*), (pp 59-86) Curitiba, Brazil)

Caraco, N. F., Cole, J. J. and Likens, G. E. (1989). Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. Nature, **341**, 316–318.

Carneiro, C., Andreoli, C. V., Gutseit, K. C., Kondageski, J. H., Lagos, P. E. D. and Okumoto, H. H. (2011 a). Avaliação do potencial poluidor de bacias de reservatórios artificiais: concentrações e cargas (*Assessment of pollution potential in artificial reservoir basins: concentrations and loads*). (In: Cunha C. L. N., Carneiro C., Gobbi E. F. and Andreoli C. V. (ed) Eutrofização em Reservatórios: Gestão Preventiva - Estudo Interdisciplinar na Bacia do Rio Verde, PR (*Reservoir Eutrophication: Preventive Management. An applied example of Integrated Basin Management interdisciplinary research*), (pp 187-218) Curitiba, Brazil)

Carneiro, C., Gutseit, K. C., Andreoli, C. V. and Lima, R. L. D. (2011 b). Análise do sedimento (*Sediment analysis*). (In: Cunha C. L. N., Carneiro C., Gobbi E. F. and Andreoli C. V. (ed) Eutrofização em Reservatórios: Gestão Preventiva - Estudo Interdisciplinar na Bacia do Rio Verde, PR (*Reservoir Eutrophication: Preventive Management. An applied example of Integrated Basin Management interdisciplinary research*), (pp 219-244) Curitiba, Brazil)

Christophoridis, C. and Fytianos, K. (2006). Conditions Affecting the Release of Phosphorus from Surface Lake Sediments. J. Environ. Qual., **35**, 1181-1192.

CONAMA, (2012). National Council of EnvironmentResolução nº 454/2012 diretrizes gerais e os procedimentos referenciais para o gerenciamento do material a ser dragado em águas sob jurisdição nacional. Resolution 454/2012 - general guidelines and procedures for the management dredged material in waters under national jurisdiction) Brazilian Official Dairy, Brasília, Brazil.

Cunha, C. L. N., Franz, G., Soares, A. P. K., Gonçalves, J. E. and Rosman, P. C. C. (2011) Hidrodinâmica e transporte no reservatório Rio Verde (*Hydrodynamic and transport in the Lake Rio Verde*). (In Cunha C. L. N., Carneiro C., Gobbi E. F. and Andreoli C. V. (ed) Eutrofização em Reservatórios: Gestão Preventiva - Estudo Interdisciplinar na Bacia do Rio

Verde, PR (Reservoir Eutrophication: Preventive *management. Interdisciplinary studies in the Rio Verde lake basin*), (pp 245-280), Curitiba, Brazil.

Das, M. M. and Saikia, M. D. (2009). Hidrology. Nova Dehli: PHI Learning Private Ltd.

Defew, L., May, L. and Heal, K. (2013). Uncertainties in estimated phosphorus loads as a function of different sampling frequencies and common calculation methods. Mar & Freshw Res. Accepted 21 January 2013.

Dillon, P. J. and Rigler, F. H. (1974). The phosphorus chlorophyll relationship in lakes. Limnol and Oceanogr, **19**, 767-773.

Dingman, S. L. (2008). Physical Hydrology. 2nd edn, Long Grove, IL: Waveland Press.

Doetzer, B. H. W., Berthol, O. and Zavelinski, C. (2011). Pedologia e aptidão de uso do solo (*Pedology and suitability of land use*). In: Cunha C. L. N., Carneiro C., Gobbi E. F. and Andreoli C. V. (ed) Eutrofização em Reservatórios: Gestão Preventiva - Estudo Interdisciplinar na Bacia do Rio Verde, PR (*Reservoir Eutrophication: Preventive Management. An applied example of Integrated Basin Management interdisciplinary research*), (pp 93-110), Curitiba, Brazil.

Doorenbos, J. and Pruit, W. O. (1977). Crop Water Requirement. (Rone: FAO Irrigation and Drainage, Paper 24)

Embrapa, (1999). Brazilian Agricultural Research Corporation Sistema Brasileiro de Classificação de Solos *Brazilian system of soils classification*). (Rio de Janeiro, Brazil: Embrapa Solos.

Esteves, F. A. (1998). *Fundamentos de limnologia (Fundaments of limnology).* 2nd edn, Rio de Janeiro, Brazil

Fernandes, L. F., Gutseit, K. C., Wojciechowski, J., Lagos, P. E. D., Xavier, C. F. and Wosiack, A. C. (2011). Ecologia do fitoplâncton no reservatório Rio Verde (*Phytoplankton ecology in the Rio Verde reservoir*). (In: Cunha C. L. N., Carneiro C., Gobbi E.F. and Andreoli C.V. (ed) Eutrofização em Reservatórios: Gestão Preventiva - Estudo Interdisciplinar na Bacia do Rio Verde, PR (*Reservoir Eutrophication: Preventive Management. An applied example of Integrated Basin Management interdisciplinary research*), (pp 283-304), Curitiba, Brazil)

Franzen, M. (2009). Dinâmica do fósforo na interface água sedimento em reservatórios (*Phosphorus dynamic in water-sediment interface in reservoirs*). Doctorate theses, Federal University of Rio Grande do Sul State, Brazil.

Gobbi, M. F. and Nocko H. (2011). Capacidade de abastecimento do reservatório Rio Verde (*Supply capacity of the Rio Verde reservoir*). (In: Cunha C. L. N., Carneiro C., Gobbi E.F. and Andreoli C.V. (ed) Eutrofização em Reservatórios: Gestão Preventiva - Estudo Interdisciplinar na Bacia do Rio Verde, PR (*Reservoir Eutrophication: Preventive Management. An applied example of Integrated Basin Management interdisciplinary research*), (pp 143-166), Curitiba, Brazil)

Hansen, K., Mouridsen, S. and Kristensen, E. (1998). The impact of Chironomus plumosus larvae on organic matter decay and nutrient (N, P) exchange in a shallow eutrophic lake sediment following a phytoplankton sedimentation. Hydrobiol., **364**, 65-74.

Hingston, F. J., Atkinson, R. J., Posner, A. M. and Quirk, J. P. (1967). Specific adsorption of anions. Nature, **215**, 1459–1461.

Hingston, F. J., Posner, A. M. and Quirk, J. P. (1974). Anion adsorption by goethite and gibbsite. II. Desorption of anions from hydrous oxides surfaces. J. Soil Sci., **25**, 16-26.

IAP, (2009). Environmental Institute of Paraná State, Monitoramento da qualidade das águas dos reservatórios do estado do Paraná, no período de 2005 a 2008, *Monitoring of reservoir water quality in the Paraná state, period 2005 – 2008*. (Curitiba, Brazil).

Jensen, H. S. and Andersen, F. Ø. (1992). Importance of temperature, nitrate, and pH for phosphate release from aerobic sediments of 4 shallow, eutrophic lakes. Limnol. Oceanogr., **37**, 577-589.

Jorgensen, S. E. and Vollenweider, R. A. (1989). Guidelines of lake management – v.1. Principles of lake management. Otsu, Japan: ILEC – UNEP.

Kamp-Nielsen, L. (1975). A kinetic approach to the aerobic sediment-water exchange of phosphorus in Lake Esrum. Ecol. Model., **1**, 153-160.

Khalil, M. K. and Rifaat A. E. (2013). Seasonal fluxes of phosphate across the sediment-water interface in Edku Lagoon, Egypt. Oceanol., **55 (1)**, 219–233.

Kelderman, P. (1984). Sediment-water exchange in Lake Grevelingen under different environmental conditions. Neth. J. Sea Res., **18**, 286-311.

Kelderman, P., Wei, Z. and Maessen, M. (2005). Water and mass budgets for estimating phosphorus sediment–water exchange in Lake Taihu (China P. R.). Hydrobiol., **544**, 167–175.

Kleeberg, A., Herzog, C., Jordan, S. and Hupfer, M. (2010). What drives the evolution of the sedimentary phosphorus cycle? Limnologica, **40 (2)**, 102–113.

Lencastre, A. and Franco, F. M. (1984). Lições de Hidrologia (Lessons of Hydrology). (Lisboa, Portugal: Universidade Nova de Lisboa – Sciences and Technology Faculty.

Lech, L. R., Jerszurki, D. and Souza, J. L. M. (2009). Ajustamento entre equações de estimativa da temperatura média do ar em distintas regiões brasileiras (*Adjustment between estimating equations for average air temperature in different regions of Brazil*). (In: Annals of XVII workshop of scientific initiation – UFPR, Curitiba, Brazil.

Maasen, S., Roske, I. and Uhlmann, D. (2003). Chemical and microbial composition of sediments in reservoirs with different trophic state. Int. Rev. Hydrobiol., **88**, 508-518.

Machado, R. E., Vettorazzi, C. A. and Cruciani, D. E. (2003). Simulação de escoamento em uma microbacia hidrográfica utilizando técnicas de modelagem e geoprocessamento (*Runoff* *simulation in a watershed using modeling techniques and GIS*). Rev. Bras. Rec. Hídr., **8 (1)**, 147-155.

Maupin, M. A. and Weakland, R. J. (2009). Water Budgets for Coeur d'Alene Lake, Idaho, Water Years 2000–2005. Geological Survey, Reston, Virginia, US: Report 2009–5184.

MPS, (1994). Minerals of Paraná State Mineropar, – Mapeamento geológico-geotécnico na região do Alto Iguaçu (*Geological and geotechnical mapping in the Alto Iguaçu region*). Curitiba, Brazul: Report v2.

Müller, B., Finger, D., Sturm, M., Prasuhn, V., Haltmeier, T., Bossard, P., Hoyle, C. and Wüest, A. (2007). Present and past bio-available phosphorus budget in the ultra-oligotrophic Lake Brienz. Aquat. Sci., **69**, 227-239.

Neff, B. P. and Nicholas, J. R. (2005). Uncertainty in the Great Lakes Water Balance. (Geological Survey, Reston, Virginia, US: Report 2004-5100.

Ometto, J. C. (1981). Bioclimatologia Vegetal (Vegetable Bioclimatologic). São Paulo, Brazil: Agronômica Ceres.

Parfitt, R. L. (1978). Anion adsorption by soils and soil materials. Adv. in Agron., **30**, 1-50.

Penman, H. L. (1948). Natural evaporation from open water, bare soil and grass. In: Proceedings of the Royal Society A – Series, **193,** (pp 120-145), London, United Kingdon.

PLUARG, (1978). International Reference Group on Great Lakes Pollution from Land Use Activities Environmental management strategy for The Great Lakes System. (Final Report to the International Joint Commission (IJC). Windsor, Ontario, Canada)

Raghunath, H. M. (2006). Hydrology: Principles, Analysis, and Design. (2th edn, New Delhi, India)

Reckhow, K. H., Beaulac, M. N. and Simpson, J. T. (1980). Modeling phosphorus loading and lake response under uncertainty – a manual and compila1ion of export coefficients. Department of Resource Development, Michigan State University / U.S. Environmental Protection Agency, Washington, US.

Reddy, K. R., O'connor, G. A. and Schelske, C. L. (1999). Phosphorous biogeochemistry in subtropical ecosystems. Boca Raton, Florida, US: CRC Press LLC.

Roden, E. E. and Edmonds, J. W. (1997). Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe (III) oxide reduction versus iron-sulfide formation. Arch. Hydrobiol., **139 (3)**, 347– 378.

Ruttenberg, K. C. (1992). Development of a sequential extraction method for different forms of phosphorus in marine sediments. Limnol. Oceanogr., **37 (7)**, 1460–1482.

Scheffer, M. (2004). Ecology of Shallow Lakes. Kluwer Academic Publishers Dordrecht, Netherlands.

Slomp, C. P., Thomson, J. and De Lange, G. J. (2002). Enhanced regeneration of phosphorus during formation of the most recent eastern Mediterranean sapropel (S1). Geochim. Cosmochim. Acta**, 66 (7)**, 1171-1184.

Soares, A. P. K., Cunha, C. L. N. and Caneparo, S. C. (2011). Estudo da influência da urbanização na disponibilidade de água em bacias rurais: o caso do Rio Verde – PR (*Study about the influence of urbanization on water availability in rural basins: the Rio Verde case– PR*). In: Annals of XIV Water World Congress, Porto de Galinhas, Brazil.

SQGC, (1993). Sediment quality guidelines Canadian, for the protection of aquatic life (Hull: National Guidelines and Standards Office.

Stumm, W. and Morgan, J. J. (1996). Aquatic Chemistry – Chemical Equilibria and Rates in Natural Waters, 3th Edition, New York, US: John Wiley & Sons Inc.

Suzumura, M. and Kamatani, A. (1995). Mineralization of inositol hexaphosphate in aerobic and anaerobic marine sediments: implications for the phosphorus cycle. – Geochim. Cosmochim. Acta, **59 (5)**, 1021–1026.

Theocharis, M. (2009). A computer system of estimating reference crop evapotranspiration using the modified Penman's (FAO-24) method. (In: Christodoulou S (ed) Proceedings of 7th International Conference in Water Resources Conservancy and Risk Reduction Under Climatic Uncertainty - EWRA (pp 215–222), Greece)

Wetzel, R. G. (1999). Organic phosphorus mineralization in soils and sediments. (In: Reddy KR, O'connor GA, Schelske CL (ed) Phosphorus Biogeochemistry in Subtropical Ecosystems (pp 225-245), Boca Raton, Florida: CRC Press LLC.

Winter, T. C. (1981). Uncertainties in estimating the water balance of lakes. Water Resources Bulletin - American Water Resources Association, **17 (1)**, 82-115.