 doi:10.20944/preprints202205.0210.v1

Article

Nitrogen and phosphorous mass balances show tropical eutrophic reservoirs behave as variable but persistent sinks of both elements: a case study using a long-term series to assess the effect of water level fluctuations

Mariel Barjau-Aguilar [1], Martín Merino-Ibarra[2*], Jorge A Ramírez-Zierold[3], Sergio F Castillo-Sandoval [2], Gloria Vilaclara-Fatjó[4], Andrea P Guzmán-Arias[1], Miroslav Macek[4], Rocío J Alcántara-Hernández[5], Salvador Sánchez-Carrillo[6], Patricia M Valdespino-Castillo[7], Arantxa Sacristán-Ramírez[8], José G Quintanilla-Terminel[1] , Emiliano Monroy-Ríos[1], Julio Díaz-Valenzuela[1], Julio A Lestayo-González[1], Oscar A Gerardo-Nieto[2], Roberto González- De Zayas[8]

[1] Posgrado de Ciencias del Mar y Limnología de la Universidad Nacional Autónoma de México, México; abmariel322@ciencias.unam.mx, andreaguzman07@gmail.com, josegqt@gmail.com, emiliano.monroy.rios@gmail.com

[2] Unidad Académica de Ecología y Biodiversidad Acuática, Instituto de Ciencias del Mar y Limnología, Universidad Nacional Autónoma de México, México; mmerino@cmairl.unam.mx, castillo@cmarl.unam.mx, oagerardon@gmail.com

[3] Patronato Pro-Valle de Bravo A.C, México; jramirezzierold@yahoo.com.mx

[4] FES Iztacala, Universidad Nacional Autónoma de México, México; vilaclara.gloria@iztacala.unam.mx, mmacek@live.co.uk

[5] Instituto de Geología, Universidad Nacional Autónoma de México, México; ralcantarah@geologia.unam.mx

[6] Departamento de Biogeoquímica y Ecología Microbiana, Museo Nacional de Ciencias Naturales, Consejo Superior de Investigaciones Científicas (MNCN-CSIC), España; sanchez.carrillo@mncn.csic.es

[7] Molecular Biophysics and Integrated Bioimaging Division, Lawrence Berkeley National Laboratory, Berkeley, CA, United States; PMValdespino@lbl.gov

[8] Department of Oceanography, College of Geosciences, Texas A&M University, College Station, TX 77843, USA; arantxa@tamu.edu

[9] Departamento de Ingeniería Hidráulica. Universidad de Ciego de Ávila.. Ciego de Ávila. Cuba.; cuba.robe@gmail.com

*Correspondence: mmerino@cmarl.unam.mx.

Abstract: Nitrogen and phosphorous loading drives eutrophication of aquatic systems. Lakes and reservoirs are often effective N and P sinks, but information is needed on the variability of their biogeochemical dynamics, especially for tropical systems. A long-term N and P mass balance (2003-2018) in a small tropical eutrophic reservoir lake, Valle de Bravo (VB), Mexico, showed it is a net sink of N (-41.7 g N m^{-2} y^{-1}), and P (-2.7 g P m^{-2} y^{-1}), mainly through net sedimentation, equivalent to 181% and 68% of their respective loading (23.0 g N m^{-2} y^{-1} and 4.2 g P m^{-2} y^{-1}). N mass balance showed that VB has a high net N atmospheric influx (31.6 g N m^{-2} y^{-1}), which was 1.3 times the external load, and likely dominated by N_2 fixation. During a period of high water level fluctuations (WLF), the net N atmospheric flux decreased by half compared to high level years. WLF can be a useful management tool to improve the trophic status of water bodies by decreasing anoxic conditions and net atmospheric fluxes, possibly through decreasing nitrogen fixation and/or promoting denitrification and other microbial processes that alleviate the N load.

Keywords: Nitrogen; mass balances; Nitrogen sink; sedimentation; nitrogen fixation; management; tropical reservoir.

1. Introduction

Industrial and agricultural activities have disturbed the global biogeochemical cycle of N overtaking the safe operating space for humanity [1,2].The increased availability of biological reactive N in aquatic ecosystems has led to its ecological deterioration [3] and has compromised its water quality [4]. Lakes and reservoirs have the potential to act as N

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 May 2022 doi:10.20944/preprints202205.0210.v1

removers, by burying it into the sediments or by permanently eliminating it through the production of gaseous species such as N_2, N_2O, via denitrification [5], anammox and DAMO [6,7].

It has been estimated that 19.7 x10^9 kg N y^{-1} are globally removed from watersheds by lentic systems every year [8]; 33%of which would take place in small reservoirs (surface area between 0.001- 50 km^2;Harrison et al. 2009b; Wollheim et al. 2008) despite they represent only 6% of the global lentic surface area [11]. This is attributed to their: 1) long residence times compared to rivers and streams, 2) high ratio of surface catchment area- lake surface area, 3) high apparent setting velocities for N, and 4) elevated average N loads [8,12]. This removal is enhanced in systems with conditions favorable for denitrification such as hypoxic or anoxic bottom water and/or sediments, and with a high content of organic carbon and nitrate [13,14].

An increasing number of dams and small reservoirs have been playing an important role in N cycling over the last 60 years [15] not only at the local scale but also at regional and global scales [8]. Globally, they exhibit important spatial variations on their N removal potential [13], but the regulation mechanisms need to be explored in detail. Furthermore, water level fluctuations (WLF), which are often common in reservoirs, can alter significantly the conditions that regulate the N cycling and therefore its removal [13,14]. The need to document N removal and mechanisms that affect it is paramount in tropical latitudes where aquatic systems are highly pressured by anthropic activities [16–18]. Because of the higher loads they receive, understanding the N dynamics of tropical reservoirs has become a priority.

To contribute to this goal, here use a mass balance approach to assess N and P retention, N and P net sedimentation and N net atmospheric fluxes at an ecosystem scale in a small eutrophic tropical reservoir lake along a 16 years long-term series, during which the reservoir underwent a period of important level fluctuations of up to 12 m. This long-term monitoring sheds light on the relative relevance of external load variations and water level fluctuations on these fluxes, and on the main N cycling processes.

2. Materials and Methods

2.1 Study area: Valle de Bravo

Valle de Bravo (VB) Lake (19º21'30" N, 100º11'00" W) is the biggest reservoir of the Cutzamala System (CS), formed by 7 reservoirs located in different basins (Figure S1, Suppl. Mat.), and which supplies water to Mexico City and its metropolitan area, to benefit 4.1 million inhabitants; [19]. The VB reservoir has a maximum capacity of 395.5 x10^3 m^3, mean surface area of 18.55 x10^6 m^2, and a mean depth of 21.1 m. However, when intense level fluctuations (1817.5 to 1830.0 m a.s.l) take place, its surface area can decrease down to 13.2x10^6 m^2. When it is required, water can be pumped back to VB from the reservoirs on the western part of the Cutzamala System (see [20] for details).

As many other reservoirs in Mexico, Valle de Bravo (VB) shows a detriment in water quality mainly due to is eutrophication since 1992 [21], and health risks due to the presence of cyanotoxins like microcystin and anatoxin-a [22–25]. For these reasons, information on nutrient (particularly N and P cycling) in this system has become a priority in recent years.

Water arrives to VB through 5 tributary rivers and 3 domestic sewage discharges (Figure S2, Supp. Mat.), among which the Amanalco river is the main source [20]. Agriculture in the Amanalco watershed drives increased N and P loads derived from the overuse of fertilizers. Upstream the Amanalco river, 94 trout aquaculture facilities operate and only 30 % of them dispose its wastewater under Mexican legislation [26]. All of the above have been identified as causes of the eutrophication of VB [20,27]

VB is as a warm monomythic water body with strong WLF linked to water management for supply purposes [27]. VB is located in a mountainous region where strong diurnal wind flows [28]. Both WLF and strong wind flows impact on diverse limnological and ecological aspects, such as: stability of stratification, nutrient exchange between the epilimnion and the hypolimnion [27], composition of phytoplankton and zooplankton community and ecosystem metabolism [18,29,30]. However, the effect of WLF on N net fluxes have not been studied, so far.

In a preliminary (2002-2005) mass balance assessment, Ramírez-Zierold et al. [20] estimated that N_2 fixation exceeded denitrification of VB, and that reservoirs net N_2 fixation doubled the N loading it received from rivers and sewage. However, important WLF have occurred since then, and their significant effect on vertical mixing has been outlined [27]. The aim of the present study is to improve the representativeness and the insight provided by the N and P mass balances, assessing it along a long-term series from 2003 to 2018, during which important WLF did take place in VB.

2.2 Samples and data

The data base comprised monthly samplings from January 2003 to December 2018, during which the VB reservoir, 5 rivers (Amanalco, Molino, González, Carrizal and Santa Monica) and the 3 sewage discharges (Tizates, embarcadero I and embarcadero II) were monitored every 30 ±1 days (N=200). Flow was measured at rivers and discharges using a drift buoy and cross section determinations (cf. [20]for details). For the reservoir, a single central station was monitored after 2006, as [29,31,32] found it to be representative of the reservoir because of its horizontal homogeneity.

Water samples were collected with a 1.5 L Uwitec sampling bottle at all rivers, sewage discharges as well at the central station of VB at depths: 0, 1, 2, 4, 8, 12 ,16 ,20 ,24 m and bottom. Samples for total nitrogen (TN) and total phosphorous (TP) determinations were collected by duplicate in 30 ml polypropylene bottles. Using a GF/F Whatman® filters, 60 mL of water were filtered and the filters were stored for particulate organic nitrogen (PON), and particulate organic phosphorous (POP) determinations. All samples were maintained at 4 °C and dark until its analysis. Additionally, at the central station, vertical profiles of temperature and dissolved oxygen (DO) were done using an Hydrolab DS4/SVR4 field probe from 2003 to 2009 and a multiparametric sonde YSI 6600 from 2009 to 2018.

2.3 Nutrient analysis

Water samples for the determination of TN and TP, as well as filters for PON and POP, were subjected to high temperature persulfate oxidation to oxidize all the P and N species to nitrate and soluble reactive phosphorous (SRP), following [33]. Nutrient (SRP, ammonia, nitrite and nitrate) concentrations were determined using a Skalar San-Plus segmented-flow analyzer [34,35]. Dissolved inorganic nitrogen (DIN) was calculated as ammonia + nitrite + nitrate.

2.4 Mass balance approach

The water mass balance (equation 1) considered the reservoir as a single box and assumed that groundwater seepage was negligible [20].

$$\Delta V/\Delta t = \Sigma R_i + P_i - W - \Sigma(E - P) \text{ x } A \tag{1}$$

where ${}^{\Delta V}/_{\Delta t}$ is the volume change of the reservoir, R_i is the sum of all river and sewage inflow rates; Pi is pump-back inflow; W is the water withdrawal rate, E is evaporation, P is precipitation (m^3d^{-1} in all cases); and A is lake surface area (m^2).

While the volume change of the reservoir was available on a daily basis (provided by CONAGUA, National Water Commission), the rivers and sewage inflows could only be measured once a month, since there no government monitoring of the rivers was done at this time. Therefore, to improve the representativeness of our river discharge assessment, we calculated the water residuals ($Wres, equation$ 2) found using our monthly measurements and assuming a closed water mass balance (with no other significant inputs or outputs). These residuals were then used to correct the inflows ($\bar{R}_i$) by iteration (3), redistributing the $Wres$ water flow among the rivers according to each river´s contribution fraction (x_i, ranging between 0 and 1) to the total river input, which were assessed using the river´s average contribution fraction during the years for which the minimal deviations ($Wres$) were observed for the annual mass balances.

 doi:10.20944/preprints202205.0210.v1

$$Wres = {}^{\Delta V}/_{\Delta t} - (\Sigma R_i + P_i - W - \Sigma(E - P) * A) \quad (2)$$
$$\bar{R}_i = R_i + x_i(Wres) \quad (3)$$
$${}^{\Delta V}/_{\Delta t} = \Sigma \bar{R}_i + P_i - W - \Sigma(E - P)\ x\ A \quad (4)$$

$$(eq.1) Wres(\bar{R}_i) Wres\ {}^{\Delta V}/_{\Delta t} = \Sigma R_i + P_i - W - \Sigma(E - P)\ x\ AWres$$
$$= {}^{\Delta V}/_{\Delta t} - (\Sigma R_i + P_i - W - \Sigma(E - P) * A)\bar{R}_i = R_i + x_i(Wres)\ {}^{\Delta V}/_{\Delta t}$$
$$= \Sigma \bar{R}_i + P_i - W - \Sigma(E - P)\ x\ A\ {}^{\Delta V}/_{\Delta t}$$

2.5 Estimation of N and P Net Internal Fluxes

The Phosphorous and Nitrogen mass balances were represented by equation (5), as proposed by Ramírez-Zierold et al. [20] :

$${}^{\Delta M_{(P,N)}}/_{\Delta t} = \Sigma I_{(P,N)} - O_{(P,N)} \pm NIP_{(P,N)} \quad (5)$$

Where ${}^{\Delta M_{(P,N)}}/_{\Delta t}$ is the mass change of N or P in the reservoir between consecutive sampling surveys. P and N inputs ($I_{(P,N)}$) were calculated using the mean concentration of TP and TN determined on each source during both samplings multiplied by the corrected inflow ($\bar{R}_i$). Output($O_{(P,N)}$), was calculated using the TP and TN mean concentration near the bottom of the reservoir lake (from where the water is withdrawn, [20]) multiplied by the water withdrawal rate.

$NIP_{(P,N)}$ represents the net element flux due to all the biogeochemical processes that take place internally within the reservoir. Because there are not any processes that drive an exchange with the atmosphere, in the case of P, $NIP_{(P)}$ is the net exchange between the water column and the sediments. For N, nevertheless, $NIP_{(N)}$ includes the net N exchange with the sediments, but also the exchange between the water column and the atmosphere (equation 6) due to the input of N_2 fixation and the N emissions due to multiple processes such as denitrification, anammox and N-damo.

To estimate the N net flux between the water column and the sediments ($NIP_{(N)Sed}$), we used the P net sedimentation ($NIP_{(P)}$) and multiplied it by the particle N:P ratio (PON:POP) found in the hypolimnion of VB, as this is the lake's layer from which both sedimentation and exchange directly take place. This meant a refinement of the ($NIP_{(N)Sed}$) estimation, as compared to that of [20], where the full water column N:P ratio was used.

The net N flux between the atmosphere and the water column was the assessed from the $NIP_{(N)}$ after subtracting $NIP_{(N)Sed}$ from it in equation 6:

$$NIP_{(N)} = NIP_{(N)Atm} + NIP_{(N)Sed} \quad (6)$$

2.6 Data Statistical Analysis and data visualization

Pearson's correlations were used to find significant relationships between net N fluxes and water level, environmental parameters, and vertical fluxes of DIN [27]. Data rearrangement and their subsequent analyses were done using Microsoft Excel (King County, WA, USA) and ggplot 2 [36]and tidyverse [37] packages for R software [38].To visualize and assess interannual and long-term variations the data were integrated on a yearly basis. To help visualize the seasonal variations, the $NIP_{(N)Atm}$data series was smoothed with a three-phase moving average, until a clear seasonal pattern variation was revealed. Then, the data were averaged on a monthly scale to obtain a mean annual cycle of $NIP_{(N)Atm}$ on which the relative importance of the different N processes could be assessed.

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 May 2022 doi:10.20944/preprints202205.0210.v1

3. Results

3.1 Water budget

Throughout the full 2003-2018 period, the main water inflow to VB came from the rivers, mainly Amanalco and Molino, and the outflow was due to withdrawal (Figure 1). During the dry seasons (from November to May), rivers decreased their inflows while withdrawal increased to provide water to Mexico and other cities. During the rainy season the rivers input increased and the water withdrawal decreased. This caused a discrete seasonal oscillation of the reservoir´s water level, in the range of 4-6 m. However, as discussed by [27] , during some years the water imbalance was higher, causing higher WLF, of up to 12 m below the reservoir´s capacity.

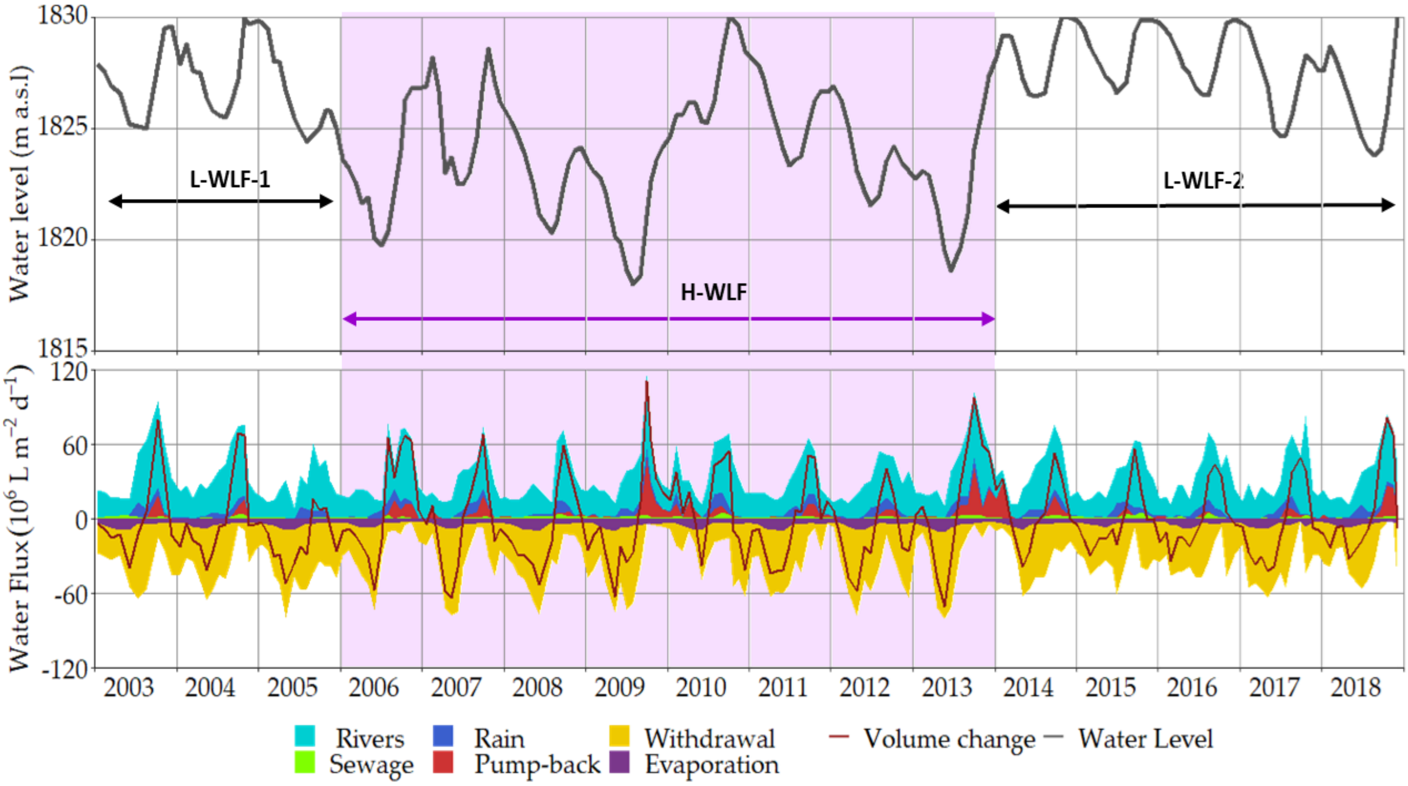

Figure 1. Water budget fluxes ($m^3 m^{-2} d^{-1}$) of Valle de Bravo and the its water level variations from 2003-2018. Purple shading outlines the higher water-level fluctuation (H-WLF) period.

Two statistically different (t(9)=4.75, p=0.001) water-level patters were identified for 2003-2018: 1) Low water level fluctuations (L-WLF) periods, when water level remained within 4 to 6 m of the capacity level (1830.0 m a.s.l), which occurred from 2003 to 2005 (L-WLF-1) and from 2014 to 2018 (L-WLF-2) (M=1827.4, SD=0.81), and 2) a high water level fluctuations (H-WLF) period that occurred from 2006 to 2013, when the reservoir lake's water level decreased farther below from the historic mean (M=1824.0, SD=1.88). Water budget means for each of the periods can be found in Table S1 (Supp Mat). During the H-WLF period, the input of rivers and sewages decreased ~16% overall compared to the L-WLF periods, and the water-level reached extraordinary minima (<1820 m a.s.l) in 2006, 2009 and 2013 (Figure 1). Water management during this period implied a decrease (by 21 %) of withdrawal and an increase in pump-back from other reservoirs (from <4% to >10% of the inputs) in order to recover the water level. As a result, a recovery of the reservoir water-level to its average level was achieved in ~5 months, particularly during 2009 and 2013.

3.3 N and P mass budgets

As previously found by [20] both the N and P budgets, and the resulting NIPs varied significantly at the monthly scale. Therefore, to smooth out the short-term variability and to facilitate the visualization of the long-term trends as well as the net differences among years, and among different WLF periods (Table 1), we integrated the N and P budgets on the annual scale (Figures 2 and 3). The H-WLF period is shaded in purple (as in Tables 1 and 1S, Supp Mat) to ease the identification of the high WLF.

P budget (Figure 2) shows that VB received an average P load of 68.6 x 10^3 Kg P y^{-1} during 2003-2018. Most of the P input to VB (73% overall mean) arrived through the rivers, but the input from sewages and pump-back from other reservoirs of the Cutzamala System were also significant. Withdrawal of water from the reservoir removed on average 19.6 x 10^3 Kg P y^{-1} during the same period, only about one third (29% overall mean) of the P arriving to VB, so the rest of the P load (68% overall mean), would have been incorporated into the sediments as a result of the net P sedimentation flux $NIP_{(P)}$, Figure 2 which averaged 46.9 x 10^3 Kg P y^{-1} for the full sampling period.

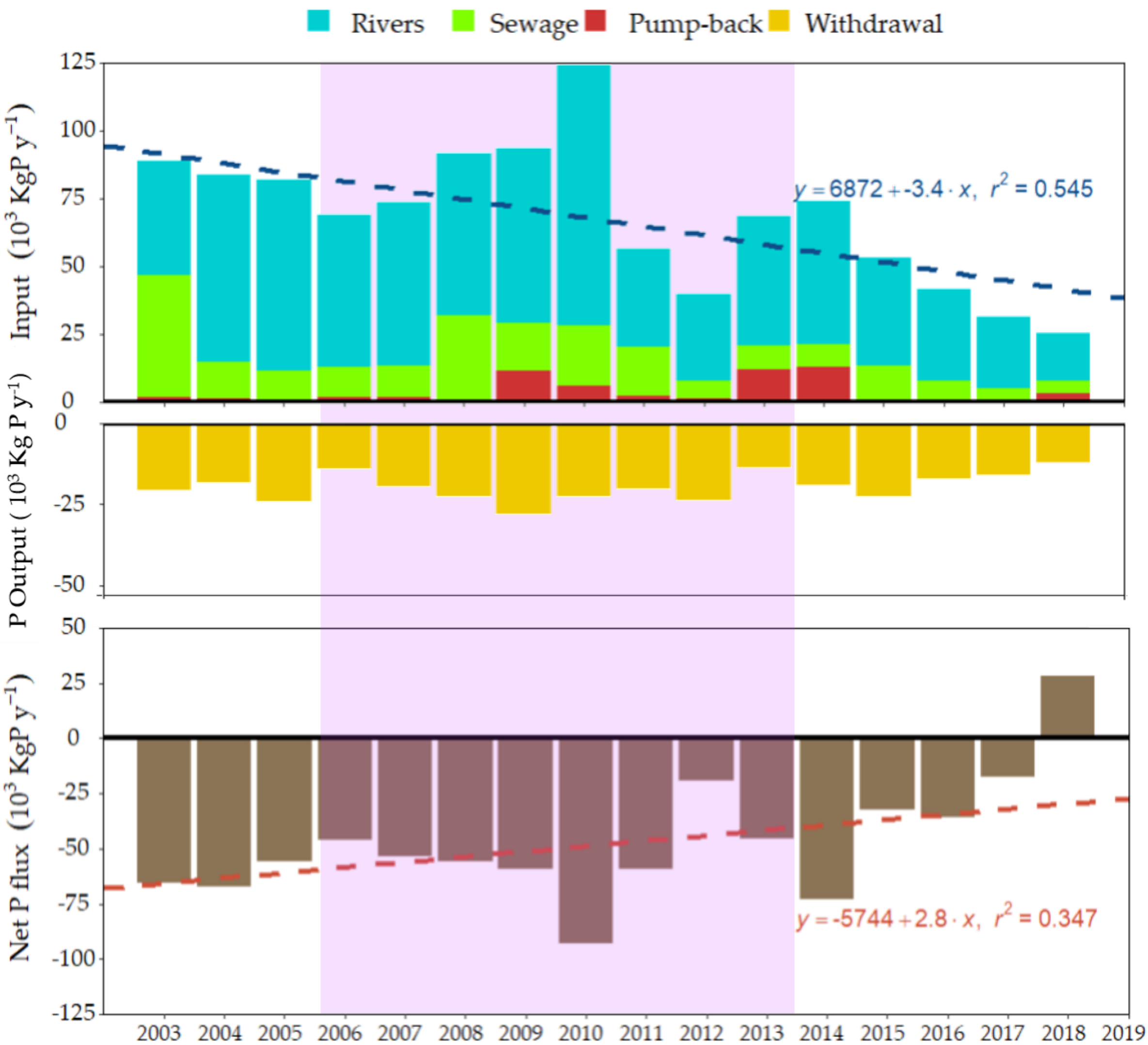

Figure 2. Annual P budgets for VB from 2002-2018. Top panel shows the inputs from rivers, sewages and pump-back from the other reservoirs of the Cutzamala System. Middle panel depicts the output through water withdrawal. Bottom panel shows the $NIP_{(P)}$ yielded by the P budget, which correspond to the net P annual flux to the sediments or P net sedimentation. Dashed line in top and bottom panels indicate the input and $NIP_{(P)}$ trend for the 2003-2018 period overall. The equation corresponds to a linear regression of this trend, together with its correlation coefficient.

Overall, P phosphorous inputs to VB decreased throughout 2003-2018, at an average rate of -3.4 x 10^3 Kg P y^{-1}. As a result, and because the amount removed from the lake by water withdrawal remained nearly constant, the amount of P removed into the sediments also decreased throughout the period, at a mean rate of -2.8 x 10^3 Kg P y^{-1}. The yearly

 doi:10.20944/preprints202205.0210.v1

variations observed in the inputs were reflected in the net P sedimentation, outstanding 2010 with the maximum P input and sedimentation annual rates, and 2018 with the lowest rates, when the P budget even yielded a net P efflux of P from the sediments to the water column on an annual basis. The H-WLF period did not show an important difference when compared to the L-WLF periods, and the mean annual fluxes were within 10% of the mean values for the previous L-WLF-1 (Table 1). Nevertheless, after the H-WLF period, the P net sedimentation flux was on average 26.1 x 10^3 Kg P y^{-1}, less than half of those of during the two previous periods, either under low WLF (62.7 x 10^3 Kg P y^{-1}, L-WLF-1) or high WLF (53.9 x 10^3 Kg P y^{-1}, H-WLF).

Table 1. Phosphorous and nitrogen budgets for Valle de Bravo during 2003-2018. Mean annual phosphorous (TP) and nitrogen (TN) budget components of Valle de Bravo are shown for: the low water level fluctuations-1 (L-WLF-1) period (2003-2005), the high-water level fluctuations (H-WLF) period (2006-2013) −for better visualization shaded in purple−, the water level fluctuations-2 (L-WLF-2) period (2014-2018), the overall means for the full studied period (2003-2018) as well as the percentage of each flux relative to the total input. The net internal fluxes of P and N are shaded in orange, the net sedimentation fluxes are shaded in yellow and the atmosphere- water fluxes of N are shaded in blue.

TP	L-WLF (2003-2005)	H-WLF (2006-2013)	L-WLF-2 (2014-2018)	Overall (2003-2018)	
Mean Mass reservoir (10^3kg P)	26.3	30.8	26.5	28.6	
Δ mass (10^3kg P y^{-1})	1.3	2.7	1.7	2.1	
Fluxes (10^3kg P y^{-1})					**% Input**
Rivers	60.7	56.4	34.0	50.2	73%
Sewage	23.2	15.9	7.5	14.7	21%
Pump back	1.1	4.7	3.7	3.7	5%
Total Input	**85.0**	**77.1**	**45.2**	**68.6**	**100%**
Output	**-21.0**	**-20.5**	**-17.4**	**-19.6**	**-29%**
Input-Output	64.0	56.6	27.8	49.0	71%
Net Internal Flux	-62.7	-53.9	-26.1	-46.9	-68%
Net Sedimentation	**-62.7**	**-53.9**	**-26.1**	-46.9	-68%
TN					**% Input**
Mean Mass reservoir (10^3kg N)	382.6	289.0	288.6	306.4	
Δ mass (10^3kg N y^{-1})	65.1	-22.7	-0.3	0.8	
Fluxes (10^3kg N y^{-1})					
Rivers	354.6	293.3	281.0	300.9	80%
Sewage	51.7	58.5	46.0	53.3	14%
Pump back	8.0	27.7	26.0	23.5	6%
Total Input	**414.3**	**379.5**	**353.0**	**377.7**	**100%**
Output	**-286.4**	**-194.0**	**-194.7**	**-211.6**	**-56%**
Input-Output	127.9	185.4	158.3	166.2	44%
Net Internal Flux	**-62.8**	**-208.2**	**-158.5**	-165.4	-44%
NOP: POP_{hipo}	36	26	33	29.9	8%
Net Sedimentation	**-1049.9**	**-662.4**	**-497.4**	-683.5	-181%
Atmosphere-Water fluxes	**987.2**	**454.2**	**338.8**	518.1	137%

N loading to VB was also high during 2003-2018, when it received an average of 377.7 x 10^3 Kg N y^{-1} through the water inputs to the reservoir (Table 1). The main nutrient input was from rivers (80 % overall) and sewages (14 % overall). Nevertheless the increase in

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 May 2022 doi:10.20944/preprints202205.0210.v1

the pump-back operations from other reservoirs during the H-WLF period meant almost a 4-fold increase in the N input to VB through this source, which passed from being < 2% of the total N input during the L-WLF-1 to < 7% during the H-WLF period (Figure 3), and remained near this proportion during the rest of the time of our study (L-WLF-2). In spite of this, N inputs from the water sources showed an overall decreasing trend (-6.5 x 10^3 Kg N y^{-1}) throughout the studied period, likely as a result of the management actions taken on the rivers and sewages inputs [20,25].

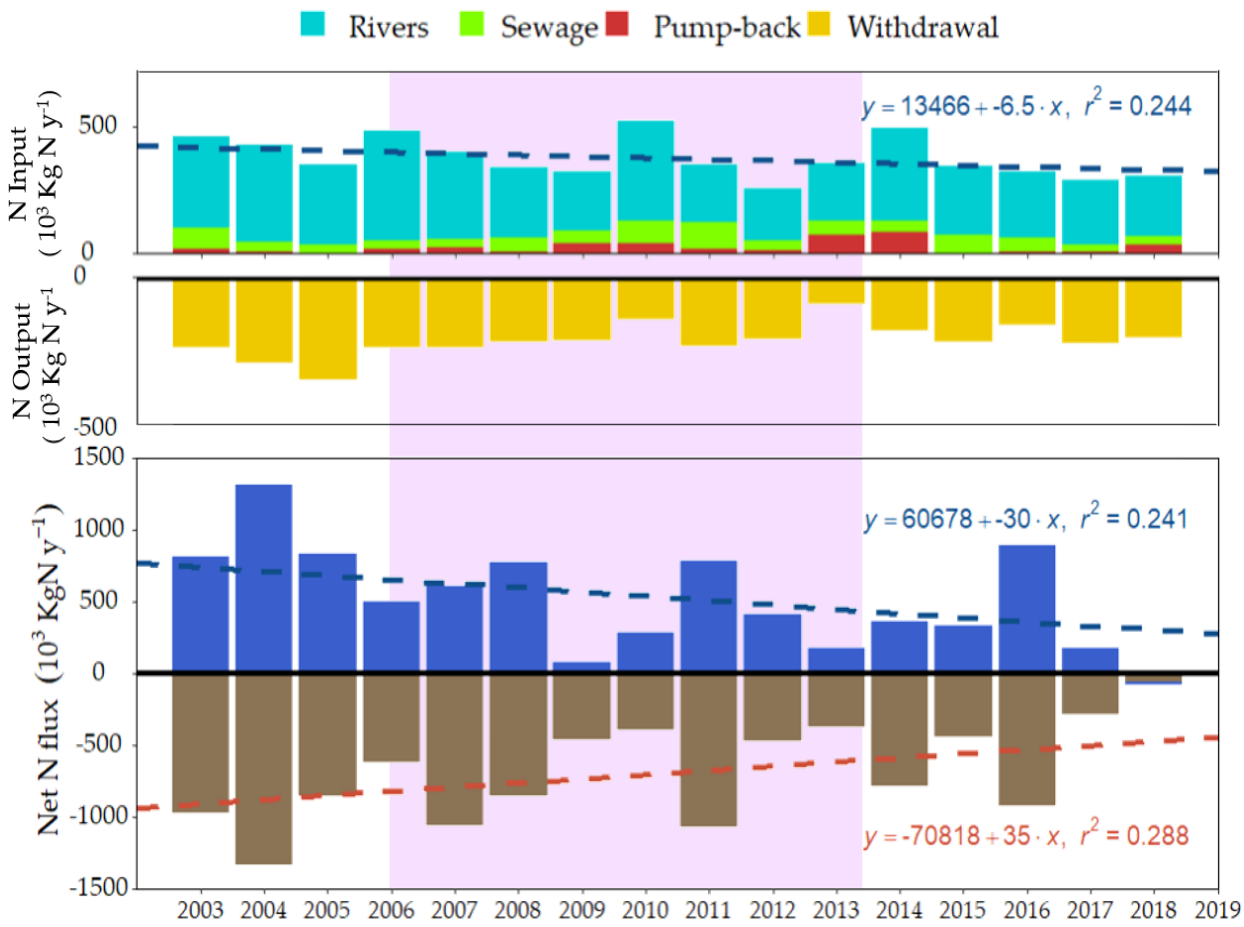

Figure 3. Annual N budgets for VB from 2002-2018. Top panel shows the inputs from rivers, sewages and pump-back from the other reservoirs of the Cutzamala System. Middle panel depicts the output through water withdrawal. Bottom panel show $NIP_{(N)}$ yielded by the N budget. The full bar depicts $NIP_{(N)}$, the total net change in N in the reservoir due to both atmospheric and sedimentary exchange fluxes. Brown bars correspond to the net N annual flux to the sediments $NIP_{(N)Sed}$ as assessed from the P net sedimentation shown in figure 2. Blue bars show the net N atmospheric flux, $NIP_{(N)Atm}$, calculated after subtracting $NIP_{(N)Sed}$ from the total $NIP_{(N)}$. Dashed lines in top and bottom panels indicate the input and $NIP_{(N)}$ trend for the 2003-2018 period overall. The corresponds to a linear regression of this trend, together with its correlation coefficient.

N internal ($NIP_{(N)}$) varied significantly during 2003-2018 as compared to P, although VB also retained N (i.e., input > output) throughout 2003-2018, behaving as a N sink (Table 1; Figure 3). VB had a net N flux to the sediments ($NIP_{(N)Sed}$) and a net N flux from the atmosphere ($NIP_{(N)Atm}$) throughout the sampled period, but the magnitude of these fluxes changed markedly among years. Both net fluxes decreased significantly during the H-WLF period, particularly in the lowest level years (2006, 2009 and 2013). As a result, $NIP_{(N)Sed}$ decreased on average by 37% during the H-WLF period relative to average of the previous years (L-WLF-1), and $NIP_{(N)Atm}$ decreased to around almost half (54%) compared to the same years (Table 1). In spite of the return to low level fluctuations after 2013, both net N fluxes remained as low on average during L-WLF-2, and in fact continued decreasing. Overall, $NIP_{(N)Sed}$ decreased on average by 35 x 10^3 Kg N y^{-1}, and $NIP_{(N)Atm}$ by

 doi:10.20944/preprints202205.0210.v1

30 x 10^3 Kg N y^{-1} throughout the 2003-2018 period, an impressive decrease of about 3% per year in the nitrogen fluxes of the system (Figure 3).

Correlation analysis (Figure 4) shows that the variations of the net N atmospheric flux $NIP_{(N)Atm}$, were closely related with the water level changes that occurred in VB during the H-WLF period. $NIP_{(N)Atm}$ decreased significantly as the water level drooped and stability of the water column diminished. It also correlated significantly, but inversely, with the oxygen concentration and the DIN vertical flux, which increased as the level dropped and vertical mixing between the epilimnion and the hypolimnion was intensified [27], particularly during the H-WLF years.

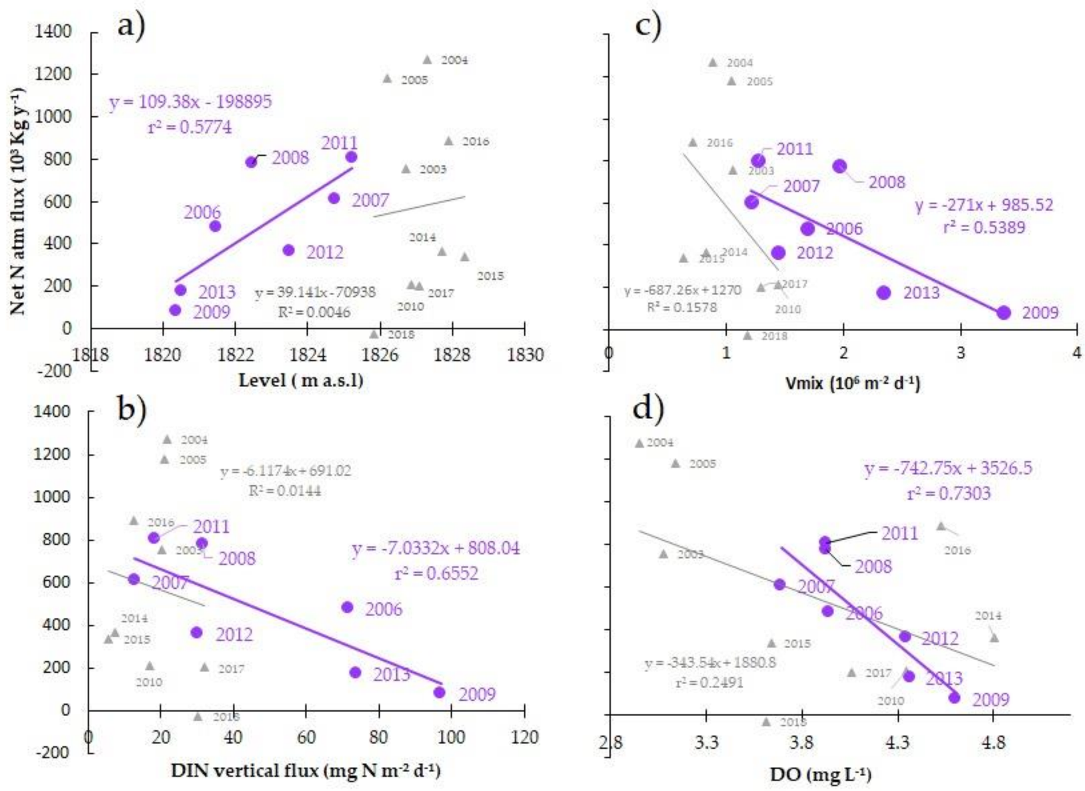

Figure 4. Relationships between net N atmospheric flux and: a) water level, b) volume of water mixed (Vmix) between the epilimnion and the hypolimnion, c) DIN vertical flux to the epilimnion, and d) mean dissolved oxygen (DO) throughout the water column in VB for 2003-2018. Purple dots and numbers designate the years of the period with high WLF (H-WLF). The low WLF years are depicted by grey numbers and triangles. Linear regressions and correlations for both sets of years are also shown in the corresponding color. Vmix and DIN vertical Flux after [27].

Within the annual scale, after the smoothing of short-term variations, the net N atmospheric flux $NIP_{(N)Atm}$ showed a clear seasonal pattern associated to the annual stratification- circulation cycle of this monomictic lake (Figure 5). Overall, $NIP_{(N)Atm}$ increased during the stratification period, when the conditions are likely most favorable for N_2 fixation, peaking during June. In contrast, $NIP_{(N)Atm}$ was lowest during the circulation period, particularly during its second half, in the first months of this year. At this time, nitrate peaks in VB, so when stratification begins denitrification is likely favored, delaying the evident increase of $NIP_{(N)Atm}$ until May, when the stratification is clearly stablished and nitrate has been depleted. As the cycle proceeds, small observed decrements in $NIP_{(N)Atm}$ (as observed in April, July and September) may be due to other processes that might cause the efflux of N form the system, such as Annamox and Damo, as suggested by unpublished data [39] Finally, because ammonia is accumulated in the epilimnion during the stratification period, and $NIP_{(N)Atm}$ decreases sharply as its annual circulation begins, it is posed that significant emissions of ammonia [40] may occur at this time of the year in VB.

 doi:10.20944/preprints202205.0210.v1

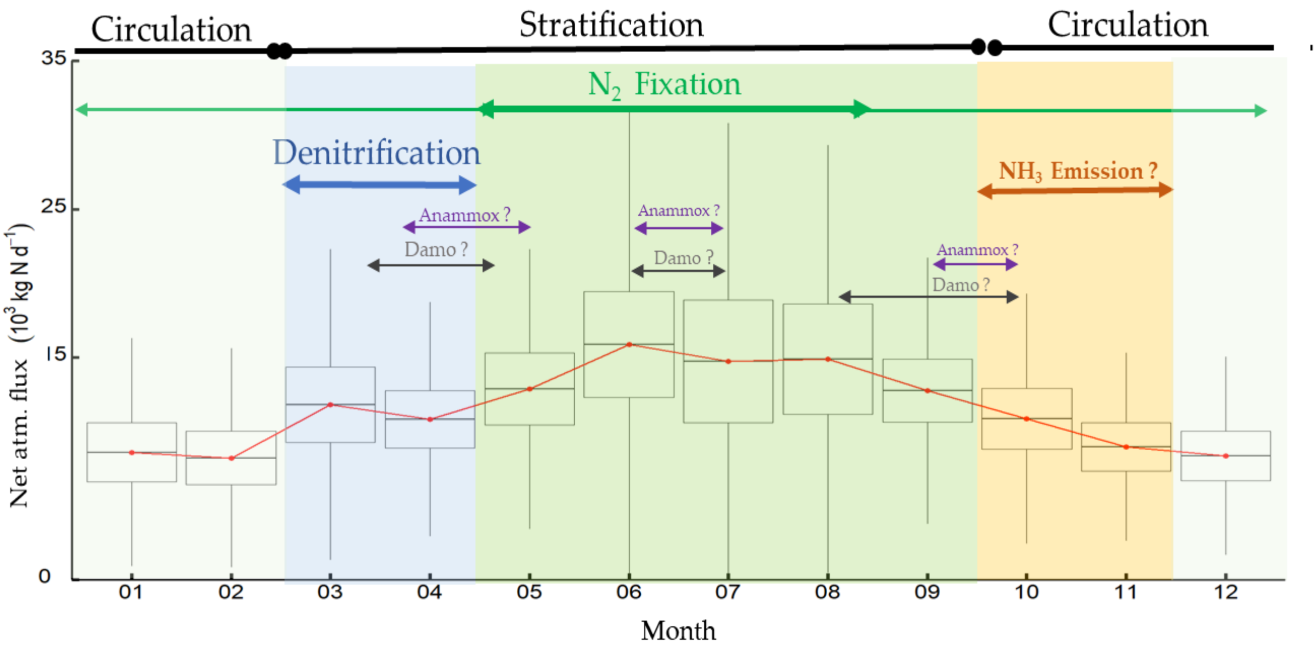

Figure 5. Mean annual evolution of the net N atmospheric flux (10^3 Kg N d^{-1}) in VB during the period 2003-2018. Box plots depict SE and SD. The main N processes that affect the atmospheric flux and the proposed periods when they become more important are signaled along the annual evolution of the net N atmospheric flux and the circulation and stratification cycle of the lake (shown on top).

Independently of these variations, the mean values of all the components of the N budget are useful to make a graphical summary and compare their relative magnitudes (Figure 6). As done in Table 1 and Table S2 (Supp. Mat.) and in previous assessments (i.e., [20] we compared the N fluxes with the external loading to the system. It is interesting to note that on the average VB transferred to its sediments 683.5 x 10^3 Kg N y^{-1} (181 % of the external load it received), while 211.6 x 10^3 Kg N y^{-1} (56 % of this load) was removed by the water withdrawal. The apparent deficit of N this could suggest is covered by the high net N influx from the atmosphere (518.1 x 10^3 Kg N y^{-1} on average) that is about 137 % higher that the external N loading (Figure 6).

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 May 2022 doi:10.20944/preprints202205.0210.v1

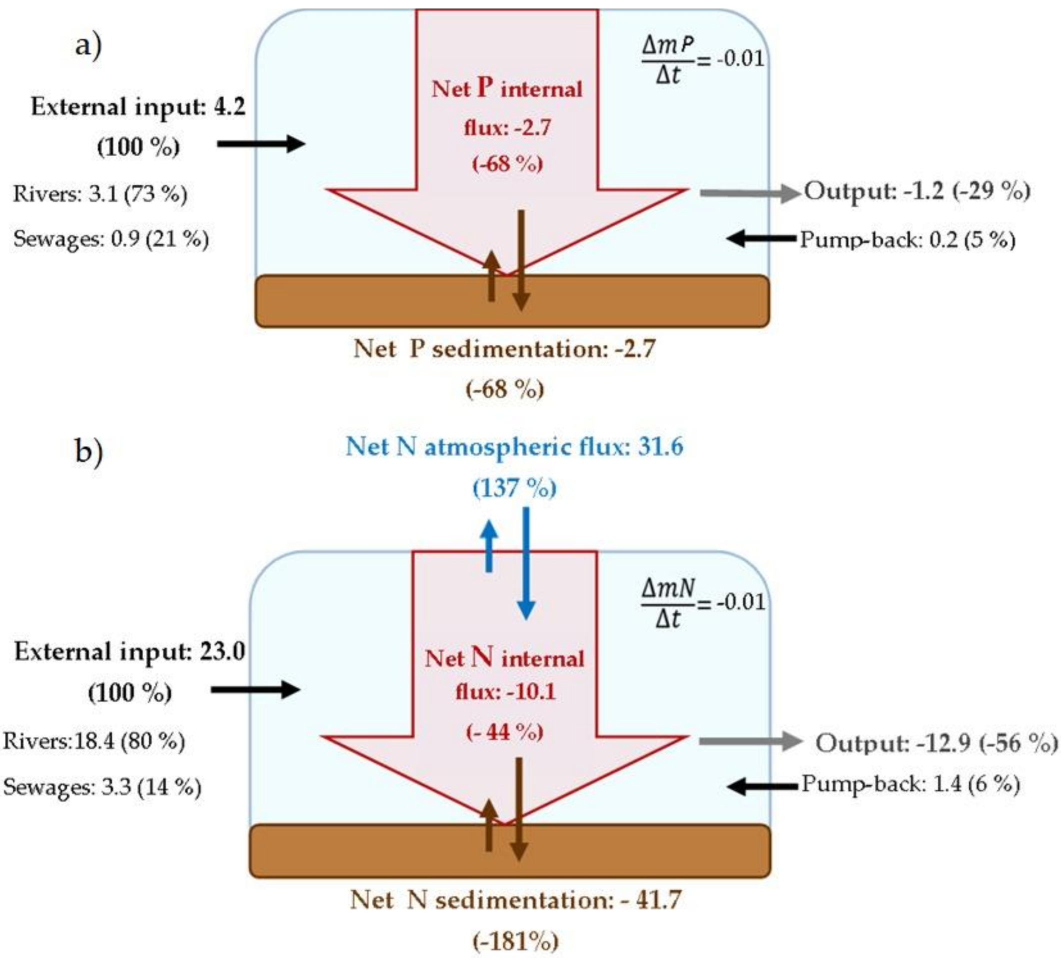

Figure 6. Graphical Summary of the mean annual a) P and b) N fluxes (10^3kgN y^{-1}) in the VB reservoir for the period 2003-2018. The percentage of each flux relative to the total annual load of each element through water sources (rivers and sewages) is shown in parenthesis.

4. Discussion

Sustained monitoring of VB lake showed that during the 16-year period of 2003-2018, this tropical reservoir of the CS continued receiving important loads of P and N from human activities on its basin, mainly through rivers and sewages, but also, occasionally, through pump-back operations from other reservoirs of the CS. These loads, which averaged 68.6 x 10^3 Kg P y^{-1} and 377.7 x 10^3 Kg N y^{-1}, represented 239% in the case of P and 123% for N of the total mass of these nutrients contained in the water of the lake (28.6 x 10^3 Kg P y^{-1} and 306.4 x 10^3 Kg N y^{-1} respectively) on average during this period. So, on a yearly base, the system received almost 2.5 timed the P it already contained, and 1.2 times the N that was already there. These proportions help visualize the magnitude of the environmental pressure VB has to handle as an ecosystem, as a biogeochemical processor.

4.1 Most of the external load translates into net sedimentation

The main consequence of the external load of N and P to VB -besides eutrophication and all its associated impacts and risks [28]- is a high net sedimentation flux of P and N to the sediments of the lake, which we estimate is the destiny of 68% of the P load and is equivalent to 44% of the N load on average. The rest of the external load to the reservoir is removed by water withdrawal, and so 29% of the P load and 56% of the N load are transferred to the water supply processing system of the CS.

Although these loads are still very high, they likely evidence an improvement as compared to the loads of 120.8 x 10^3 Kg P y^{-1} and 591.8 x 10^3 Kg N y^{-1} assessed by [20] in a preliminary assessment of 2002-2005 conditions. In fact, the detailed monitoring of P and

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 May 2022 doi:10.20944/preprints202205.0210.v1

N that has proceeded since then, allowed the verification of a decreasing trend of external inputs o P (~ 5% per year) and N (~ 2%) to VB for the 2003-2018 period overall. This trend was particularly evident after 2010, when the preliminary assessment was published, and its results promoted the actions of emerging non-governmental organizations like Pro-Valle (e.g. [41] and the onset of citizen science actions in the basin, which in turn spurred a series of management actions directed to reduce the external loads to VB, included waste water treatment from agriculture, livestock and aquaculture activities on the Amanalco and Tizates river basins [25,42,43]

Our results also show that a sustained decrease of the net sedimentation fluxes occurred in a concomitant way and a trend parallel to the decrease of the loads, particularly in the case of P. In this case, the average decrease rate is about ~ 6% of the net P sedimentation rate, relatively slightly higher than the average P load decrease rate. This is an encouraging finding that is backed up by the consistency of our estimates of net P sedimentation with. Our mean net P sedimentation of 2.9 Kg P m^{-2} y^{-1} is quite close to the average of 3.3 Kg P m^{-2} y^{-1} reported for tropical reservoirs [17] and for other aquatic systems such as Lake Kariba [44] and Lake Xuanwu [45]. At the same time, our estimates for the initial 2003-2005 period also match very well with the P sedimentation rates in VB estimated for those years (2.0 to 4.2 g $m^{-2}y^{-1}$) by [46], who used radiochronology studies to asses sedimentation in VB from 1992 to 2006. These results also sustain that the net P sedimentation preliminary assessed by [20] for 2002-2006 (~ 6 g $m^{-2}y^{-1}$) was probably an overestimation as suspected.

Similarly, in the case of the net N sedimentation rate, our estimates for 2003-2005 also indicate an overestimation in the preliminary assessment (75 g $m^{-2}y^{-1}$) of [20] for the period 2002-2005, and yield a much lower overall mean (41.9 g $m^{-2}y^{-1}$) for the full 2003-2018 period. This difference is likely partially due to improvements on the assessment approach here made, both on the water balance (i.e. the residual redistribution on the river inputs) and on the use of the hypolimnetic PON:POP proportion instead of the proportion within the full water column . This second modification may be relevant because some important groups of the epilimnetic phytoplankton biomass, like cyanobacteria, might not reach the sediments as much as other like diatoms, as explained later. In any case, these new estimates are much closer to the N sedimentation estimated by radiochronology [46], which ranged from 4.9 g $m^{-2}y^{-1}$ as a basal value before 1992 to 48 g $m^{-2}y^{-1}$ in 2005, solving much of the suspected overestimation problem. In any case, the direct measurements of sedimentation rates could help to further confirm these results.

4.2 Net N atmospheric fluxwas lower during high water level fluctuations

As previously described, net N atmospheric flux decreased drastically (by 54 %) and significantly during the high WLF period as compared to the previous low WLF period (Table S2, Supp. Mat.). Furthermore, within the H-WLF, net N atmospheric flux correlated significantly with the water level change among the years (n=9, r^2=0.58; Figure 4a). In a detailed analysis of the effects of high WLF in VB, Merino-Ibarra et al. [27] found that during the high WLF years, as the water level decreased, vertical mixing between the epilimnion and the hypolimnion of VB intensified through boundary mixing events without breaking the stratification. This enhanced mixing would imply an important vertical exchange of nutrients and oxygen between these two layers.

The input of oxygen to the otherwise anoxic hypolimnion, and the vertical input of nutrients to the impoverished epilimnion could certainly affect in different ways the multiple processes involved in N cycling. We can identify three mechanisms that may be occurring in VB when vertical mixing intensifies and the net N atmospheric flux decreases.

One mechanism would be the direct inhibition of N_2 fixation due to the additional input of DIN to the epilimnion (Figure 4b). When the availability of inorganic nitrogen species in the epilimnion is high N_2 fixation decreases, as cyanobacteria (e.g. Nostocales, found in VB, [29]) suppress the synthesis of new nitrogenase. Another mechanism driving a decrease in N_2 fixation could be the effect of mixing on the abundance of N fixers. It has been demonstrated that the increase of turbulence in the water column plays a profound impact on phytoplankton composition, including the promotion of non-cyanobacterial

Preprints (www.preprints.org) | NOT PEER-REVIEWED | Posted: 16 May 2022 doi:10.20944/preprints202205.0210.v1

phytoplankton (e.g., diatoms and chlorophyta [29]. In VB, diatoms such as Cyclotella ocellata, *Fragilaria crotonensis* were abundant during the low-level stratifications of 2008 and 2009, while, Cyanophyta was notoriously abundant during high-level 2001-2002, 2010 and 2017 stratifications [23,24,47–49]. Additionally, zooplankton community composition changes (i.e. increasing abundance of cladocerans and copepods assemblages during low-level stratifications instead of rotifer-dominated zooplankton communities) could also impact phytoplankton through herbivory but also sedimentation, primary and secondary production [50]

The other way mixing could have decreased the net N atmospheric flux is through favoring or enhancing the diverse processes that can cause N loss to the atmosphere. The exchange of oxygen, ammonium and nitrate between the oxic and anoxic layers during stratification creating suitable conditions for nitrification coupled with denitrification and other microbial processes, promoting N loss from the water column to atmosphere, as observed in several aquatic ecosystems [7,51,52]. Denitrification strongly depends on the nitrate availability in the water column [13,53], which could increase associated the inputs of oxygenated water to the hypolimnion of VB which has a high ammonium content, favoring denitrification episodes. In this study, using a mass balance approach we cannot estimate denitrification rate itself, but the inverse correlation between net N atmospheric flux and the oxygen content in the water column (Figure 4d), as well as its direct correlation with the mean nitrate concentration in water column (not shown) supports this possibility in VB.

Although the net sedimentation fluxes also diminished from the first low WLF period (L-WLF-I) to the high WLF period (H-WLF) it was much lower than that of net N atmospheric flux (54%), particularly for net P sedimentation (only 14%). This decoupling of the two fluxes could be explained by the enriched abundance of diatoms as a response to the turbulence rising during H-WLF [29]. Diatoms have been cited to exhibit higher sedimentation rates than other phytoplankton species [54,55]. In contrast, diverse species of cyanobacteria [56], in particular some of the genus *Microcystis* are known to possess gas vacuoles to regulate their buoyancy [57] Additionally, cyanobacterial taxa are known to produce mucilage or polysaccharide-rich extracellular polymeric substances (EPS) that also contribute to buoyancy [58,59]. So, the decrease of cyanobacteria dominance during the H-WLF period would diminish the part of the biomass that is mineralized in the water column, rather than settling in the lake sediment [56] and would therefore also contribute to a relatively smaller decrease of net sedimentation. The bigger decrease in net N sedimentation (47%) as compared to the P decrease (14%) could be due in part to the relative impoverishment in N of the planktonic community concomitant with the decreased N_2 fixation during this period.

Overall, our results also arise interesting possibilities and questions that might deserve further analysis and complementary investigations. For example, both the net sedimentation and net atmospheric fluxes were relatively low during the second low WLF period (L-WLF-2) as compared to the first low WLF, suggesting that some of the changes that occurred during the H-WLF period may have prevailed or may have modified the ecosystem in a lasting way. Alternatively, this may be the result of the long-term decrease on the external loads derived from the social demand of management actions.

In any case, our results in VB suggest that strong water level fluctuations affect, not only their temperature, oxygen, nutrients and planktonic composition, but they also impinge on N cycling, particularly by decreasing the net N atmospheric flux in the water column, so they are a potentially valuable management tool, and should be considered in water management plans to relieve eutrophic conditions in the reservoir. In any case, further studies addressed to assess specifically N_2 fixation, nitrification, denitrification, and other N processes will be useful to further examine our preliminary conclusions.

5. Conclusions

We found that during the 16 years of this long-term study this tropical reservoir lake was a sink of N (-41.9 g N m^{-2} y^{-1}), and P (-2.9 g P m^{-2} y^{-1}), mainly through net flux to its sediments. A high net N atmospheric flux of 31.6 g N m^{-2} y^{-1}, contributed to N sedimentation, while the P net sedimentation flux was mainly due to the external load. The N net atmospheric exchange was likely dominated by N_2 fixation over the processes that drive N loss, such as denitrification. Nevertheless, during a period the period of high the N atmospheric flux decreased by half. Vertical mixing during low water level years likely enhanced denitrification through the oxygenation of the water column, and inhibited N_2 fixation through the injection of inorganic N from the hypolimnion into the epilimnion. We propose that WLF can therefore be used as a useful management tool to decrease N_2 fixation and/or promoting denitrification and other microbial processes to alleviate the N load in VB and in similar aquatic systems.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Figure S1: The Cutzamala System, Figure S2: Bathymetric map of Valle de Bravo (VB) reservoir showing the main inputs (rivers and sewages), and water withdrawal route, Table S1: Water Budget of Valle de Bravo.

Author Contributions: Conceptualization, M.M-I. and J.A.R-Z..; methodology, M.M-I., J.A.R-Z, F.S.S-C., M. B-A, .;validation, M.M-I and F.S.C-S; formal analysis, M.B-A.; investigation, F.S.C-S, A.P.G.-A., A.S.-R., J.G.Q.-T., P.M.V-C.; resources, M.M-I.; data curation, F-S.C-S, A.P.G.-A.,M.B-A., A.S-R., P.M.V-C., G.Q-T., E.M-R., J.A.R-Z., writing—original draft preparation, M.B-A.; writing—review and editing, M.B-A. ,M.M-I., J.A.R-Z., P.M.V-C., G.V-F., M.M,R.J.A-H, S.S-C.; visualization, M.B-A.; supervision, M.M-I.; project administration, M.M-I.; funding acquisition, M.M-I. and J.A.R-Z. All authors have read and agreed to the published version of the manuscript."

Funding: This research was funded by UNAM, PAPIIT-IN207702 and CONACYT-SEMARNAT, C01-1125 projects to M.M-I.

Acknowledgments: We thank all the Aquatic Biogeochemistry Lab collaborators including Lourdes N. Murueta, Flor Arcega, Irina Cruz, Sofía Montalvo, Rebeca Sánchez, Claudia N. Saavedra, Patricia Memije, Alfredo Gallardo, Felipe Solís, Federico Serna Blanco, Arturo Alvarez, Felipe Solis, Mónica Olson, Karina Castro, Abraham Vargas and to all the students that have assisted us, both in the field and in the laboratory, during these 18 years of monitoring and analyses. We also acknowledge the support from VB lovers, including Alberto Dana and Tito Benítez, Provalle A.C., the Marina Azul and Naútico Avandaro Sailing Clubs.

Conflicts of Interest: The authors declare no conflict of interest

References

1. Rockström, J.; Steffen, W.; Noone, K.; Persson, Å.; Chapin, F.S.; Lambin, E.F.; Lenton, T.M.; Scheffer, M.; Folke, C.; Schellnhuber, H.J.; et al. A Safe Operating Space for Humanity. *Nature* **2009**, *461*, 472–475, doi:10.1038/461472a.
2. Mackenzie, F.T.; Ver, L.M.; Lerman, A. Century-Scale Nitrogen and Phosphorus Controls of the Carbon Cycle. *Chemical Geology* **2002**, *190*, 13–32, doi:https://doi.org/10.1016/S0009-2541(02)00108-0.
3. Gruber, N.; Galloway, J.N. An Earth-System Perspective of the Global Nitrogen Cycle. *Nature* **2008**, *451*, 293–296, doi:10.1038/nature06592.
4. Ward, M.H. Too Much of a Good Thing? Nitrate from Nitrogen Fertilizers and Cancer: President's Cancer Panel-October 21, 2008. *Rev Environ Health* **2009**, *24*, 357.
5. Saunders, D.L.; Kalff, J. Nitrogen Retention in Wetlands, Lakes and Rivers. *Hydrobiologia* **2001**, *443*, 205–212, doi:10.1023/A:1017506914063.

6. Kuypers, M.M.M.; Marchant, H.K.; Kartal, B. The Microbial Nitrogen-Cycling Network. *Nature Reviews Microbiology* **2018**, *16*, 263–276, doi:10.1038/nrmicro.2018.9.
7. Thamdrup, B. New Pathways and Processes in the Global Nitrogen Cycle. *Annual Review of Ecology, Evolution, and Systematics* **2012**, *43*, 407–428, doi:10.1146/annurev-ecolsys-102710-145048.
8. Harrison, J.A.; Maranger, R.J.; Alexander, R.B.; Giblin, A.E.; Jacinthe, P.A.; Mayorga, E.; Seitzinger, S.P.; Sobota, D.J.; Wollheim, W.M. The Regional and Global Significance of Nitrogen Removal in Lakes and Reservoirs. *Biogeochemistry* **2009**, *93*, 143–157, doi:10.1007/s10533-008-9272-x.
9. Harrison, J.A.; Maranger, R.J.; Alexander, R.B.; Giblin, A.E.; Jacinthe, P.A.; Mayorga, E.; Seitzinger, S.P.; Sobota, D.J.; Wollheim, W.M. The Regional and Global Significance of Nitrogen Removal in Lakes and Reservoirs. *Biogeochemistry* **2009**, *93*, 143–157, doi:10.1007/s10533-008-9272-x.
10. Wollheim, W.M.; Vörösmarty, C.J.; Bouwman, A.F.; Green, P.; Harrison, J.; Linder, E.; Peterson, B.J.; Seitzinger, S.P.; Syvitski, J.P.M. Global N Removal by Freshwater Aquatic Systems Using a Spatially Distributed, within-Basin Approach. *Global Biogeochemical Cycles* **2008**, *22*, doi:10.1029/2007GB002963.
11. Downing, J.A.; Prairie, Y.T.; Cole, J.J.; Duarte, C.M.; Tranvik, L.J.; Striegl, R.G.; McDowell, W.H.; Kortelainen, P.; Caraco, N.F.; Melack, J.M. The Global Abundance and Size Distribution of Lakes, Ponds, and Impoundments. *Limnology and Oceanography* **2006**, *51*, 2388–2397.
12. Seitzinger, S.; Harrison, J.A.; Böhlke, J.K.; Bouwman, A.F.; Lowrance, R.; Peterson, B.; Tobias, C.; Van Drecht, G. Denitrification across Landscapes and Waterscapes: A Synthesis. *Ecological Applications* **2006**, *16*, 2064–2090, doi:10.1890/1051-0761(2006)016[2064:DALAWA]2.0.CO;2.
13. Piña-Ochoa, E.; Álvarez-Cobelas, M. Denitrification in Aquatic Environments: A Cross-System Analysis. *Biogeochemistry* **2006**, *81*, 111–130, doi:10.1007/s10533-006-9033-7.
14. Seitzinger, S.; Harrison, J.A.; Böhlke, J.K.; Bouwman, A.F.; Lowrance, R.; Peterson, B.; Tobias, C.; Van Drecht, G. Denitrification across Landscapes and Waterscapes: A Synthesis. *Ecological Applications* **2006**, *16*, 2064–2090, doi:10.1890/1051-0761(2006)016[2064:DALAWA]2.0.CO;2.
15. Berga, L.; Buil, J.M.; Bofill, E.; De Cea, J.C.; Perez, J.A.G.; Mañueco, G.; Polimon, J.; Soriano, A.; Yagüe, J. *Dams and Reservoirs, Societies and Environment in the 21st Century, Two Volume Set: Proceedings of the International Symposium on Dams in the Societies of the 21st Century, 22nd International Congress on Large Dams (ICOLD), Barcelona, Spain, 18 June 2006*; CRC Press, 2006; ISBN 1482262916.
16. Lewis, W.M. Tropical Lakes: How Latitude Makes a Difference. *Perspectives in tropical limnology* 1996, 43–64.
17. Kunz, M.J.; Anselmetti, F.S.; West, A.; Wehrli, B.; Vollenweider, A.; Thüring, S.; Senn, D.B. Sediment Accumulation and Carbon, Nitrogen, and Phosphorus Deposition in the Large Tropical Reservoir Lake Kariba (Zambia/Zimbabwe). *Journal of Geophysical Research: Biogeosciences* **2011**, *116*, 1–13, doi:10.1029/2010JG001538.
18. Ramírez-Zierold, J.A. *Variabilidad de La Mezcla Vertical y El Flujo de Nutrientes Asociado En Un Embalse Estratificado, Valle de Bravo, México*; 2015; ISBN 9786070271991.
19. CONAGUA Estadísticas DEL AGUA EN. **2017**.
20. Ramírez-Zierold, J.A.; Merino-Ibarra, M.; Monroy-Ríos, E.; Olson, M.; Castillo, F.S.; Gallegos, M.E.; Vilaclara, G. Changing Water, Phosphorus and Nitrogen Budgets for Valle de Bravo Reservoir, Water Supply for Mexico City Metropolitan Area. *Lake and Reservoir Management* **2010**, *26*, 23–34, doi:10.1080/07438140903539790.
21. Olvera Viascán, V. Estudio de Eutroficación de La Presa Valle de Bravo, México. *Ingenieria Hidráulica en México* **1992**, 148–161.
22. Gaytan-Herrera, M.L.; Martinez-Almeida, V.; Oliva-Martinez, M.G.; Duran-Diaz, Á.; Ramirez-Garcia, P. Temporal Variation of Phytoplankton from the Tropical Reservoir Valle de Bravo, Mexico. *Journal of Environmental Biology* **2011**, *32*, 117–126.

23. Valeriano-Riveros; Gloria, Vilaclara–Fatjó, Jorge, R.-Z.; Martín, M.-I.; Sergio, C.-S.F.; Emiliano, M.-R.; Luz, L.-G.; José, Q.-T.; Patricia, V.-C.; Jorge, J.-C.; María Variabilidad de La Mezcla Vertical y El Flujo de Nutrientes Asociado En Un Embalse Estratificado, Valle de Bravo, México. *Tendencias de Investigación* **2010**, 39.
24. Alillo-Sánchez, J.L.; Gaytán-Herrera, M.L.; Martínez-Almeida, V.M.; Ramírez-García, P. Microcystin-LR Equivalents and Their Correlation with Anabaena Spp. in the Main Reservoir of a Hydraulic System of Central Mexico. *Inland Waters* **2014**, *4*, 327–336, doi:10.5268/IW-4.3.573.
25. Calderón Cendejas, J.; Madrid Ramírez, L.; Ramírez Zierold, J.; Díaz Valenzuela, J.; Merino Ibarra, M.; Morató Sánchez de Tagle, S.; Chino Téllez, A. Evaluation of the Impacts of Land Use in Water Quality and the Role of Nature-Based Solutions: A Citizen Science-Based Study. *Sustainability* **2021**, *13*, 10519, doi:10.3390/su131910519.
26. Pichardo Pagaza, I. *El Agua Ciclo de Un Destino*; 1ª.; Biblioteca Mexiquense del Bicentenario: Estado de México, 2007; ISBN 9684846630.
27. Merino-Ibarra, Martín.; Ramírez-Zierold, J.A.; Valdespino-Castillo, P.M.; Castillo-Sandoval, F.S.; Guzmán-Arias, A.P.; Barjau-Aguilar, M.; Monroy-Ríos, E.; Gómez, L.M.L.-; Sacristán-Ramírez, A.; Quintanilla-Terminel, J.G.; et al. Vertical Boundary Mixing Events during Stratification Govern Heat and Nutrient Dynamics in Windy Tropical Lakes with High Water-Level Fluctuations: A Long-Term (2001-2018) Study. **2021**, doi:10.20944/PREPRINTS202105.0721.V2.
28. Merino-Ibarra, M.; Monroy-Ríos, E.; Vilaclara, G.; Castillo, F.S.; Gallegos, M.E.; Ramírez-Zierold, J. Physical and Chemical Limnology of a Wind-Swept Tropical Highland Reservoir. *Aquatic Ecology* **2008**, *42*, 335–345, doi:10.1007/s10452-007-9111-5.
29. Valeriano-Riveros, M.E.; Vilaclara, G.; Castillo-Sandoval, F.S.; Merino-Ibarra, M. Phytoplankton Composition Changes during Water Level Fluctuations in a High-Altitude, Tropical Reservoir. *Inland Waters* **2014**, *4*, 337–348, doi:10.5268/IW-4.3.598.
30. Guimarais-Bermejo, M.O.; Merino-Ibarra, M.; Valdespino-Castillo, P.M.; Castillo-Sandoval, F.S.; Ramírez-Zierold, J.A. Metabolism in a Deep Hypertrophic Aquatic Ecosystem with High Water-Level Fluctuations: A Decade of Records Confirms Sustained Net Heterotrophy. *PeerJ* **2018**, *2018*, doi:10.7717/peerj.5205.
31. Gutiérrez, S.G.; Sarma, S.S.S.; Nandini, S. Seasonal Variations of Rotifers from a High Altitude Urban Shallow Water Body, La Cantera Oriente (Mexico City, Mexico). *Chinese Journal of Oceanology and Limnology* **2017**, *35*, 1387–1397, doi:10.1007/s00343-017-6101-x.
32. Barjau-Aguilar, M. Estimación de Los Procesos Internos Netos (NIP) de P y N Mediante Balances de Masa En El Embalse Tropical de Valle de Bravo Durante 2011-2015., Universidad Nacional Autónoma de México, 2018.
33. Valderrama, J.C. The Simultaneous Analysis of Total Nitrogen and Total Phosphorus in Natural Waters. *Marine Chemistry* **1981**, *10*, 109–122, doi:https://doi.org/10.1016/0304-4203(81)90027-X.
34. Kirkwood, D.S. Sanplus Segmented Flow Analyzer and Its Applications. Seawater Analysis. *Skalar. Amsterdam* **1994**.
35. Grasshoff, K.; Ehrhardt, M.; Kremling, K. Sea Water Analysis. **1983**.
36. Wickham, H. *Ggplot2*; 2nd ed.; Springer New York: New York, NY, 2009; ISBN 978-0-387-98140-6.
37. Wickham, H.; Averick, M.; Bryan, J.; Chang, W.; McGowan, L.; François, R.; Grolemund, G.; Hayes, A.; Henry, L.; Hester, J.; et al. Welcome to the Tidyverse. *Journal of Open Source Software* **2019**, *4*, 1686, doi:10.21105/joss.01686.
38. RStudio Team RStudio: Integrated Development for R Available online: http://www.rstudio.com/ (accessed on 11 May 2022).
39. Gerardo-Nieto, O.; Merino-Ibarra, M.; Sanchez-Carrillo, S.; Guzmán-Arias, A.; Castillo-Sandoval, S.F.; Barjau-Aguilar, M.; Valdespino-Castillo, P.M.; Lestayo-González, J.A.; Díaz-Valenzuela, J.; Ramírez-Zierold, J.; et al. *Limnological Dynamics of Methane and Carbon Dioxide Emissions from a Tropical Hypertrophic Reservoir*; Mexico City , 2022;

40. Chen, J.; Li, W.; Qiao, P.; Li, Y.; Zheng, K.; Wang, Y.; Dong, X.; Wang, S.; Tan, L.; Chu, F.; et al. Characterizing Ammonia Emissions from Water Bodies Using Dynamic Floating Chambers. *Science of The Total Environment* **2021**, *796*, 148978, doi:10.1016/j.scitotenv.2021.148978.
41. Ramírez-Zierold, J.; Merino-Ibarra, M.; Castillo-Sandoval, F.S.; Vilaclara-Fatjó, G.; Monroy-Ríos, E.; Gallegos, M.; Olson, M.; López-Gómez, L.M. *Boletín del Patronato Pro-Valle de Bravo*. Valle de Bravo 2007, pp. 6–9.
42. IMTA *Plan Estratégico Para La Recuperación Ambiental de La Cuenca Amanalco-Valle de Bravo: Actualización*; 2012;
43. Ramírez-Zierold, J.; Merino-Ibarra, M.; Valdespino-Castillo, P.; Castillo-Sandoval, F.S.; Ardiles, V.; Monroy-Ríos, E.; López-Gómez, L.M.; Quintanilla-Terminel, J.G.; Jiménez, J.; Valeriano-Riveros, M.; et al. *Boletín del Patronato Pro-Valle de Bravo* . Valle de Bravo 2013, pp. 2–12.
44. Kunz, M.J.; Wüest, A.; Wehrli, B.; Landert, J.; Senn, D.B. Impact of a Large Tropical Reservoir on Riverine Transport of Sediment, Carbon, and Nutrients to Downstream Wetlands. *Water Resources Research* **2011**, *47*, 1–16, doi:10.1029/2011WR010996.
45. Wu, Y.; Wen, Y.; Zhou, J.; Wu, Y. Phosphorus Release from Lake Sediments: Effects of PH, Temperature and Dissolved Oxygen. *KSCE Journal of Civil Engineering* **2014**, *18*, 323–329, doi:10.1007/s12205-014-0192-0.
46. Carnero-Bravo, V.; Merino-Ibarra, M.; Ruiz-Fernández, A.C.; Sanchez-Cabeza, J.A.; Ghaleb, B. Sedimentary Record of Water Column Trophic Conditions and Sediment Carbon Fluxes in a Tropical Water Reservoir (Valle de Bravo, Mexico). *Environmental Science and Pollution Research* **2015**, *22*, 4680–4694, doi:10.1007/s11356-014-3703-0.
47. Gaytan-Herrera, M.L.; Martinez-Almeida, V.; Oliva-Martinez, M.G.; Duran-Diaz, Á.; Ramirez-Garcia, P. Temporal Variation of Phytoplankton from the Tropical Reservoir Valle de Bravo, Mexico. *Journal of Environmental Biology* **2011**, *32*, 117–126.
48. Valadez, F.; Oliva, G.; Vilaclara, G.; Caballero, M.; Rodríguez, D.C. On the Presence of Stephanodiscus Niagarae Ehrenberg in Central Mexico. *Journal of Paleolimnology* **2005**, *34*, 147–157, doi:10.1007/s10933-005-0810-4.
49. Nandini, S.; Sánchez-Zamora, C.; Sarma, S.S.S. Toxicity of Cyanobacterial Blooms from the Reservoir Valle de Bravo (Mexico): A Case Study on the Rotifer Brachionus Calyciflorus. *Science of the Total Environment* **2019**, *688*, 1348–1358, doi:10.1016/j.scitotenv.2019.06.297.
50. Valdespino-Castillo, P.M.; Merino-Ibarra, M.; Jiménez-Contreras, J.; Castillo-Sandoval, F.S.; Ramírez-Zierold, J.A. Community Metabolism in a Deep (Stratified) Tropical Reservoir during a Period of High Water-Level Fluctuations. *Environmental Monitoring and Assessment* **2014**, *186*, 6505–6520, doi:10.1007/s10661-014-3870-y.
51. Canfield, D.E.; Erik Kristensen; Bo Thamdrup The Nitrogen Cycle. In *Aquatic Geomicrobiology*; Canfield, D.E., Kristensen, E., Thamdrup, B.B.T.-A. in M.B., Eds.; Academic Press, 2005; Vol. 48, pp. 205–267 ISBN 0065-2881.
52. Peters, B.D.; Babbin, A.R.; Lettmann, K.A.; Mordy, C.W.; Ulloa, O.; Ward, B.B.; Casciotti, K.L. Vertical Modeling of the Nitrogen Cycle in the Eastern Tropical South Pacific Oxygen Deficient Zone Using High-Resolution Concentration and Isotope Measurements. *Global Biogeochemical Cycles* **2016**, *30*, 1661–1681, doi:10.1002/2016GB005415.
53. Rysgaard, S.; Christensen, P.B.; Nielsen, L.P. Seasonal Variation in Nitrification and Denitrification in Estuarine Sediment Colonized by Benthic Microalgae and Bioturbating Infauna. *Marine Ecology Progress Series* **1995**, *126*, 111–121.
54. Heiskanen, A.; Kononen, K. Sedimentation of Vernal and Late Summer Phytoplankton Communities in the Coastal Baltic Sea. *Archiv Fur Hydrobiologie* **1994**, *131*, 175.
55. Sommer, U. Sedimentation of Principal Phytoplankton Species in Lake Constance. *Journal of Plankton Research* **1984**, *6*, 1–14, doi:10.1093/plankt/6.1.1.
56. Walsby, A.E.; McAllister, G.K. Buoyancy Regulation by Microcystis in Lake Okaro. **1987**.

 doi:10.20944/preprints202205.0210.v1

57. Walsby, A.E. Cyanobacteria: Planktonic Gas-Vacuolate Forms BT - The Prokaryotes: A Handbook on Habitats, Isolation, and Identification of Bacteria. In; Starr, M.P., Stolp, H., Trüper, H.G., Balows, A., Schlegel, H.G., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, 1981; pp. 224–235 ISBN 978-3-662-13187-9.
58. Li, H.; Song, C.L.; Cao, X.Y.; Zhou, Y.Y. The Phosphorus Release Pathways and Their Mechanisms Driven by Organic Carbon and Nitrogen in Sediments of Eutrophic Shallow Lakes. *Science of the Total Environment* **2016**, *572*, 280–288, doi:10.1016/j.scitotenv.2016.07.221.
59. Liu, L.; Huang, Q.; Qin, B. Characteristics and Roles of Microcystis Extracellular Polymeric Substances (EPS) in Cyanobacterial Blooms: A Short Review. *Journal of Freshwater Ecology* **2018**, *33*, 183–193, doi:10.1080/02705060.2017.1391722.