Assessment of phosphorus behavior in sediments of Lake Sevan, Armenia

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ABSTRACT

Lake Sevan is the largest freshwater lake in the Caucasus region and one of Eurasia's largest alpine lakes. The lake has been experiencing growing cyanobacteria blooms; however, the relevance of external and internal phosphorus (P) loading to its eutrophication is still not known. We carried out a sediment investigation of Lake Sevan to estimate the potentially mobile P, which could be a source of internal total phosphorus (TP)-loading; we also estimated external TP-loading and retention. The study was carried out at four sampling points of different depths to determine the spatial variability of P in 2018. The sediments had elevated TP contents at the sediment surface; potentially mobile P ranged from 20 to 60% in the top 2 cm. The upper 4 cm sediment had an elevated content of TN (8 to 16.1 mg N g^{-1} dw) and TP (1.2 to 1.7 mg P g^{-1} dw). Spatial variability of most of the measured parameters was more prominent in the upper 3 cm. External TP loading was estimated to be 110 tons annually, and the TP retention was 85%. The estimated TP stored in the top cm of the sediment is 1,500 tons. The potential for P release is high; the short-term exchange between oxic and anoxic overlying water could release 0.01 to 0.02 mg P L^{-1} from the top cm of the sediment, and long-term diagenesis and burial could release about 0.12 mg P cm^{-2}. Internal P-loading in Lake Sevan may play an essential role in eutrophication, especially given the long flushing time of Lake Sevan. Internal P-loading in Lake Sevan may play an important role in eutrophication, especially given the long flushing time of Lake Sevan.

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Key words: Lake Sevan; mobile phosphorus; P-fractionation; internal/external P-loading; P-retention.

Contributions: all the authors made substantial contributions to the manuscript: Tallent Dadi, data acquisition, analysis, interpretation, manuscript writing, and revision; Wolf von Tümpling, data analysis, interpretation, manuscript writing, and revision; Chenxi Mi, data acquisition, analysis, interpretation, and manuscript writing and revision; Martin Schultze, idea conception, data acquisition, analysis, interpretation, and manuscript writing and revision; Kurt Friese, idea conception, data acquisition, analysis, interpretation, manuscript writing and revision. All authors have approved the manuscript version to be published and agree to be accountable for the accuracy and integrity of the manuscript.

Citation: Dadi T, von Tümpling W, Mi C, Schultze M, Friese K. Assessment of phosphorus behavior in sediments of Lake Sevan, Armenia. *J. Limnol. 2022;81(s1):2132.*

Edited by: Bardukh Gabrielyan, *Scientific Center of Zoology and Hydroecology of the National Academy of Sciences of Armenia, Yerevan, Armenia.*

Received: 7 March 2023.
Accepted: 21 September 2023.

J. Limnol., 2022; 81(s1):2132
DOI: 10.4081/jlimnol.2022.2132

INTRODUCTION

Eutrophication is a global problem threatening many lakes' ecosystem services; it has many undesirable effects, as summarized by Smith and Schindler (2009). The natural trophic state of a freshwater system is a function of volume, water residence time, and nutrient input from the surrounding watershed (Wetzel, 2001; Kalff, 2002). Moreover, human activity can modify the trophic status of such systems through anthropogenic loading (Klapper, 1991; Schindler *et al.*, 2016) and climate change (Allan *et al.*, 2005; Bertahas *et al.*, 2006; Lu *et al.*, 2019). Eutrophication is primarily due to the input of excess nutrients from urban and agricultural runoff or from sewage discharge (Lammens, 1990; Klapper, 1991; Karabin *et al.*, 1997; Nicholls, 1998; Withers *et al.*, 2014). Since eutrophication results from both external and internal loading; therefore, regular monitoring of the nutrient loading is essential, especially for lakes of great importance. Several of these lakes are monitored well, which helps the stakeholders and managers to make informed management decisions, *e.g.*, Lake Erie (Mohamed *et al.*, 2019; Watson *et al.*, 2016). On the other hand, we have lakes of high importance where there is still a lack of adequate data about nutrient loading, *e.g.*, Lake Sevan, which is the largest freshwater lake in the Caucasus region and one of the largest alpine lakes in Eurasia (Lehner and Döll, 2004; Wilkinson, 2020).

Lake Sevan experienced a substantial drawdown of its water level in the second half of the last century peaking at a ca. 19 m water level drop (1916 m asl in 1930; 1896 m asl in 2001; Gabrielyan *et al.*, 2022). The lowering of the water level resulted in enormous changes in the water quality, including eutrophication, reduction of macrophytes, blooms of cyanobacteria, and anoxia in the hypolimnion (Hovanesian and Bronozian, 1994; Gabrielyan *et al.*, 2022). Surprisingly, the concentration of phosphorus (P), which is usually considered the growth-limiting nutrient in freshwater lakes (Schindler *et al.*, 2016), dropped during the first decades of this development; the average concentration of total phosphorus (TP): 370 µg TP L^{-1} in the period 1930 to 1935; 60 µg TP L^{-1} in the period 1985 to 1996 (Hovhanissian and Gabrielyan, 2000). Stabilization of the water level by the reduction of water abstraction, installation of additional power generation plants, and diversion of additional river water into the lake and an increase up to currently 1900 m asl resulted in an intermediate improvement of water quality (Gabrielyan *et al.*, 2022). Ulyanova (1994) hypothesized that biologically induced calcite precipitation was the primary process of removing the P from the water column. Additionally, Gabrielyan *et al*. (2022) assume inadequate and incorrect sampling, preparation, and analytical techniques for P determination until the 1980s resulting in an overestimation of TP. In recent years, however, Lakes Sevan suffered from mass developments of cyanobacteria again (Aslanyan, 2020; Gevorgyan *et al.*, 2020; Khosrovyan *et al.*, 2023). Although the internal cycling of P is usually a key factor for eutrophication processes and the selection of optimal management strategies for lakes, none of the sediment investigations published so far (Nalbandyan *et al.*, 2006; Wilkinson and Gulakyan, 2010; Korzhenkov *et al.*, 2014; Gorbatov *et al.*, 2019; Nurgaliev *et al.*, 2019; Avagyan *et al.*, 2020; Gevorgyan *et al*., 2023) focused on sedimentary P and its speciation in Lake Sevan. In general, assessing potentially mobile P fractions in sediments is essential because benthic P can affect the trophic state of a lake.

Recently, fish farms and aquacultures are increasing in importance even in freshwater lakes, although being known as a potential source of P in lakes and having often been a driver of eutrophication (Gowen, 1994; Clerk *et al.*, 2004; Dauda *et al.*, 2019). Aquaculture is currently the fastest-growing sector in livestock production globally (Sampels, 2014), and fish protein is vital for the nutritional security of a substantial proportion of the world's population (Kawarazuka and Béné, 2011). Aquaculture in Lake Sevan was established in 2016. However, the purpose of that fish farm is not to produce as much fish as possible for the food market but to breed the endemic species "Sevan trout" (*Salmo Ischchan* Kessler, 1877) for stabilizing and increasing the almost completely extinct natural population of Lake Sevan. The Foundation for Sevan Trout Stocks and Development of Aquaculture (http://www.stf.am/en/home.html) was founded and operates the fish farm in Lake Sevan (Gabrielyan *et al.* 2022).

Besides external sources of nutrients like fertilizers and sewage discharge, the lake sediment may act as a sink or an internal source for the overlying water, depending on the quantity of P discharged into the lake, environmental conditions, and chemical forms of sediment-bound P. Many studies have investigated P dynamics in lakes of different trophic states (Hupfer *et al*., 1995; Kozerski and Kleeberg, 1998; Rydin, 2000; Dadi *et al*., 2020; Tu *et al*., 2020). Although the central processes which lead to P release from sediments have been known and studied for more than 70 years (Einsele, 1936; Mortimer, 1942), assessment of internal P load is still one of the most challenging subjects in lake and reservoir eutrophication and restoration (Nürnberg, 2009). Several methods were developed and applied to assess the amount and fate of nutrients (mainly P) released from lake sediments (Zamparas and Zacharias, 2014; Bormans *et al.*, 2016; Katsev, 2017). Sequential fractionation procedures have been essential in studying P dynamics in soils and sediments for over 50 years (Condron and Newman, 2011).

The P content of the sediment is primarily the result of the self-purification potential of the lake, *i.e.*, the sedimentation and retention of P depending on the import of P binding partners reflecting the geology and use of the catchment area. Phosphorus mobility or its partial release back to the water column is determined by the balance between the deposited amount of P and the retention capacity of the sediment, depending on the amount of respective P binding partners. In other words, a high sedimentary P content is also attributed to a relatively high input and supply of P-binding partners. However, the total P content of lake sediments does not correlate with the trophic state of the lakes or the extent of internal loading (Hupfer, 1995).

This work aimed to assess the nutrient status of the sediment of Lake Sevan by estimating the potentially mobile P-fraction as a source of internal P-loading since no information has been published so far. For this purpose, sediment cores were taken at four different points on the lake (Fig. 1) to investigate the variability and range of P content and spatial distribution. Furthermore, the different depths of the sediment cores were used to determine the mobile part of total P in an alternative way and to calculate the burial of P by diagenetic processes, respectively. We also estimated the external P loads and P retention to get an overview of the P budget of Lake Sevan.

METHODS

Study site

Lake Sevan is located in the northern part of the Armenian volcanic highlands, in Gegharkunik Marz province, 60 km north of Armenia's capital, Yerevan. It is the largest freshwater lake in the Caucasus region and one of Eurasia's largest freshwater high mountain lakes (volume of about 38 km³). The lake's surface is 1900 m above sea level, has a total area of 1278 km², a maximum depth of 80 m, an average depth of 29.7 m, a length of 75 km, and an average width of 19 km (Garibyan, 2007). Twenty-eight tributaries feed Lake Sevan, and an artificial tunnel that transfers water from two neighboring river catchments (Arpa and Vorotan) and has a single discharge outlet, the Hrazdan River (Gabrielyan *et al*., 2022). The average residence time (according to Vincent, 2018) is 42.4 years based on total annual inflow volume and the flushing time (according to Vincent, 2018) is 180 years based on annual average outflow (Shikhani *et al*., 2022). The flushing rate of 180 years (average outflow based) is caused by the lake's high evaporation rates and the more relevant quantity in the given context of eutrophication and contamination of Lake Sevan with nutrients. Lake Sevan has dimictic or monomictic mixing patterns depending on whether ice cover occurs in winter (Shikhani *et al*., 2022). In recent years, full ice cover occurred only exceptionally (ca. each 5th year; A. Misakyan, Hydrometeorology and Monitoring Center SNCO of the Ministry of Environment RA, *personal communication*).

Especially at Lake Sevan, the catchment's ratio to the lake's surface area is only 3:1, whereas the average for other lakes is 10:1 (Babayan *et al.*, 2005). The uniqueness of the lake is due to the combination of size, high mountain location, and comparatively "soft water" (total dissolved solids ca. 700 mg L^{-1}). Most large natural lakes in the region are salty, *e.g.*, the Caspian Sea, Lake Van, and Lake Orumiyeh (Babayan *et al.*, 2005). Lake Sevan is divided into two sub-basins, called the Small Sevan and Big Sevan, which are separated by a bedrock sill (Fig. 1). The Small Sevan is deeper (80 m) and smaller. At the same time, the Big Sevan is larger, shallower (32 m), and its bathymetry is comparatively flatter (Babayan *et al.*, 2005); more details are in Gabrielyan *et al*. (2022) and Wilkinson (2020).

Sediment sampling

Sediment depth profile samples were taken in April (cores BS_32m, SS_80m, SS_45m) and October (SS_62m) 2018 at four pre-defined sites (Fig. 1) by a modified Kajak gravity corer (UWITEC, Austria). The undisturbed sediment cores with an overlying water phase were sectioned immediately on the boat or at the shore. The sediment in the core was sliced into 1 cm thick layers from the top down to 6 cm and into 2 cm thick layers from 6 cm downwards using a simple core cutter (UWITEC, Austria) and stored

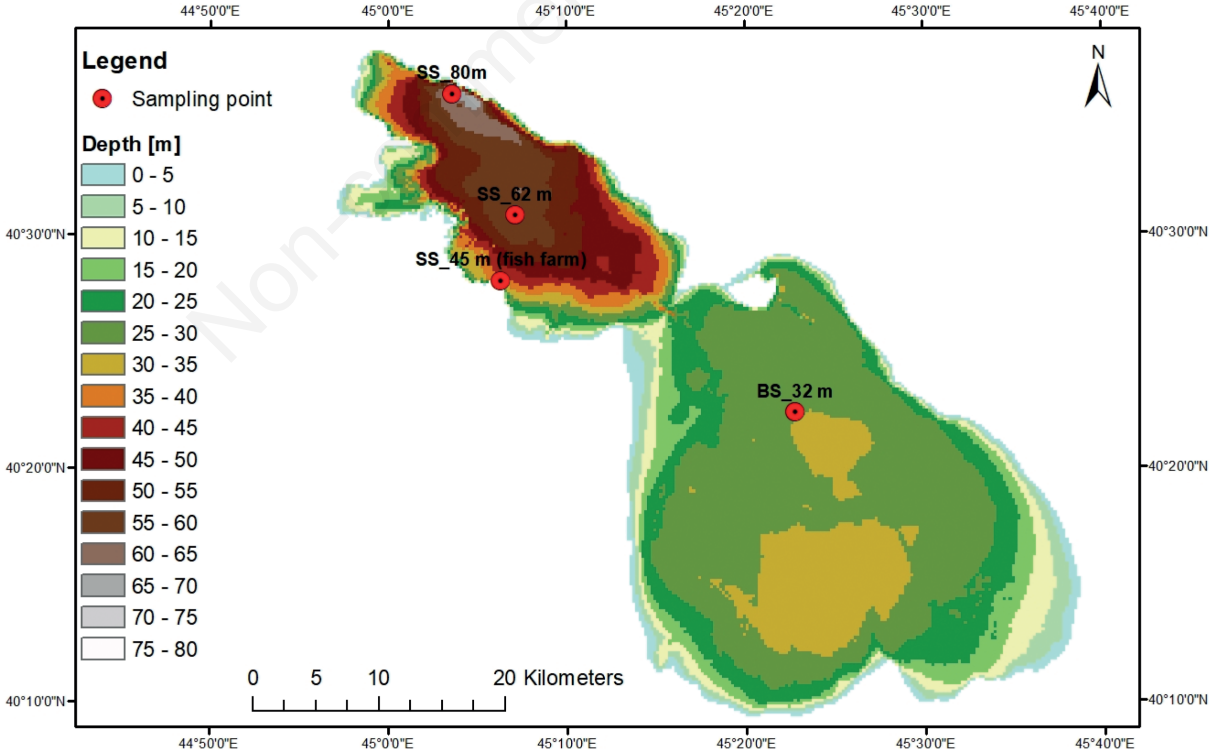

Fig. 1. Bathymetric map of Lake Sevan with sampling sites (based on data from the Hydrometeorology and Monitoring Center SNCO of the Ministry of Environment of the Republic of Armenia, Yerevan). SS_80m (40.600209 N 45.058649 E) is 80 m deep; SS_62m (40.513700 N, 45.117600 E) is 62 m deep; BS_32m (40.372611 N 45.378396 E) is 32 m deep; SS_45m (40.466837 N 45.103917 E) is 45 m deep and where the fish farm is located.

in water-tight plastic bags. Each sediment sample was used for general assessment (*e.g.*, dry weight, loss on ignition, and nutrient contents), pore water analysis, and sequential P-fractionation. During sediment slicing, pH and oxidation, and redox potential (ORP) were immediately measured from each sediment depth using conventional handheld electrodes (WTW®, Xylem Analytics; Weilheilm). The ORP values were converted to the standard hydrogen electrode (SHE) ORP, *i.e.*, Eh, using an online calculator (Wolkersdorfer, 2023). The online calculator uses Equation 1 (Wolkersdorfer, 2008).

$$E_{0(25^{\circ}C)} = E_t - 0.198 \times (T - 25) + \sqrt{(a - b \times T)} \quad \text{(eq. 1)}$$

where:

$E_{0(25^{\circ}C)}$ converted ORP at 25°C in mV

E_t is the measured ORP at temperature T in mV

T is the temperature in °C

a and b are coefficients specific to the type of electrode used

Sample preparation and analyses

Basic characterization and nutrients

Sediments were analyzed for their dry weight (DW), loss on ignition (LOI), total contents of carbon (TC), total organic carbon (TOC), total nitrogen (TN), and total phosphorus (TP). TC, TOC, and TN were measured with a CN-elemental analyzer (vario EL cube; Elementar Analysensysteme GmbH, Hanau, Germany) according to DIN ISO 10694 (1995). Subsamples for TOC were acidified by adding sulphuric acid (Suprapure®; Merck KGaA, Darmstadt, Germany) to eliminate inorganic carbon if present before measuring. Total inorganic carbon (TIC) was calculated by subtracting the total organic carbon (TOC) amounts from the total carbon amount (TC). The method was calibrated using sulfanilic acid p.a. TP was analyzed photometrically (DR5000; Hach Lange GmbH, Düsseldorf, Germany) after ignition of the sediment at 550°C in a muffle oven and digestion with 1M hydrochloric acid (Supraprure®) at 100°C for 15 min, according to the German standard method DIN 38414-12, 1986.

Porewater analysis

The sediment was centrifuged (3500 rpm at 6°C). The raw porewater samples were filtered using a 0.45 µm syringe filter (Sartorius, Göttingen, Germany). Afterwards, the samples were analyzed for soluble reactive phosphorus (SRP), NH_4^+-N, Fe (dissolved), and SO_4^{2-}. SRP and NH_4^+-N were analyzed photometrically with an SFA (Skalar, Breda, The Netherlands), Fe was determined by ICP-OES Optima 7300 DV (Perkin Elmer, Rodgau, Germany), and SO_4^{2-} was analyzed by ion-chromatography with an ICS 6000 system (Thermo Fisher Scientific, Waltham, MA, USA). The limits of quantification (LOQ) for parameters are TP (0.006 mg L^{-1}), SRP (0.003 mg L^{-1}), SO_4^{2-} (0.8 mg L^{-1}), NH_4^+-N (0.01 mg L^{-1}), and Fe (0.01 mg L^{-1}). Further details on the methods are described in Herzsprung *et al.* (2006) and Herzsprung *et al.* (1998).

P-fractionation

Phosphorus fractionation was performed for the top 0 to 10 cm of sediment according to the method described by Psenner *et al.* (1984) and modified by Hupfer *et al.* (1995). This fractionation divides the sediment P into i) easily soluble; ii) reductant soluble; ii) NaOH-P (referred to as aluminum bound P, ligand exchangeable phosphate, mineral $FePO_4$ and humic acid bound P); iv) apatite; and v) refractory P (Tab. 1), the latter often described as poorly soluble organic P compounds by Hupfer *et al.* (1995).

Sediment samples were stored in a fridge at 4°C until transported to Germany; after that frozen (-18°C) until used for the extraction. Approximately 2 g of sediment was weighted into 50 mL centrifuge tubes to obtain a defined dry matter-to-solute ratio.

All solutions were freshly prepared using laboratory-standardized chemicals. Volumetric flasks were washed with P-free laboratory rinsing fluid and rinsed with high-purity water. The solutions of NH_4Cl and BD were stored in one liter bottles and degassed with nitrogen for one hour to remove oxygen. Degassing is essential for the glove box extraction steps to prevent sediment oxidation.

TP was analyzed for the extracts, except for the NaOH fraction, for which SRP was also determined. Within all ex-

Tab. 1. Specific P-pools received from the applied P fractionation scheme, according to Psenner *et al.* (1984), modified by Hupfer *et al.* (1995).

Extracting agent (P-pool)	Analysis	Compound
Ammonium chloride (NH_4Cl-P)	TP	Interstitial water P, loosely bound P
Bicarbonate dithionite (BD-P)	TP	Reductively soluble P, bound to Fe- or Mn- oxides
Sodium hydroxide (NaOH-NRP)	TP	P in microorganism, detritic P, humic bound P
Sodium hydroxide NaOH-SRP	SRP	P bound to metal oxides (Al, Fe, ...)
Hydrochloric acid (HCl-P)	TP	P bound to carbonate, apatite, acid labile P
Sulphuric acid (residual P)	TP	Refractory organic P

tracts, TP can be divided into soluble reactive P (SRP) and non-reactive P (NRP). The NRP fraction is predominantly organic bonded phosphorus mainly extracted by NaOH hence the need to differentiate the SRP and NRP for the NaOH fraction. For all other fractions, the NRP concentration is relatively insignificant (Hupfer *et al*., 1995).

The Al and Fe in the extract from sediment P-fractionation (only SS_62m) were determined by ICP-OES Optima 7300 DV (Perkin Elmer). The limits of quantification were Fe (0.01 mg L^{-1}) and Al (0.02 mg L^{-1}). Refer to Baborowski *et al*. (2012) for more details on the method.

Calculation of potentially mobile phosphorus

The potentially mobile and probably available (for organisms) part of TP ($P_{-mobile}$) within the sediment was estimated by two approaches: i) as described in several studies, the phosphorus found within the NH_4Cl-P, BD-P, and NaOH-NRP fractions can be seen as potentially mobile (Reitzel *et al.*, 2005; Wauer *et al.*, 2005); ii) the potentially mobile part of sedimentary P can be alternatively calculated by the so-called "gradient method" (Hupfer and Lewandowski, 2005; Grüneberg *et al.*, 2014; Hupfer *et al.*, 2020). Assuming steady-state conditions for burial and release (Jørgensen *et al.*, 1975; Schauser *et al.*, 2006), $P_{-mobile}$ is defined as the sum of TP mass differences for each sediment layer between the measured TP mass (in mg g^{-1}) and minimal TP background value (given by the lowest TP value at the deepest layer = permanent P mass) acc. to equation 2 (see also Hupfer *et al*., 2020):

$$P_{-mobile} = \sum_{i=1}^{n}(TP_i - TP_{min}) * x_i * dd \qquad \text{(eq. 2)}$$

where:
P_{mobile} = potentially mobile P (mg cm^{-2})
TP_i = TP mass content of a layer (mg g^{-1} dw)
TP_{min} = TP mass content permanently fixed (minimum background mg g^{-1} dw)
x_i = thickness of layer (cm)
dd = dry density (g cm^{-3}: measured as the dry mass of a given volume)

Total phosphorus loads

We used three methods, recommended by Hilden (2003) to calculate TP loads into Lake Sevan from each inflow; standard method (eq. 3), discharge-corrected standard method (eq. 4), and generalized additive model (GAM) regression method (eq. 5) below. The calculations were done for the period from 2010 to 2020. The data for discharge and concentration of TP in the rivers flowing into Lake Sevan were provided by the Hydrometeorology Center state non-commercial organization of the Ministry of Environment RA. Inflow discharge was measured at daily resolution, and samples for measuring TP concentration were taken at monthly resolution:

$$L = \frac{364 * 86400\,s}{1000 * 1000} * \frac{1}{n}\sum_{i=1}^{n}(c_t * Q_t) \qquad \text{(eq. 3)}$$

where:
L is the annual TP load (tons $year^{-1}$)
n is the annual measured times for inflow TP concentration
c_t is the monthly TP concentration (mg L^{-1})
Q_t is the daily discharge (m^3 s^{-1})

The discharge-corrected TP loading L_Q (eq. 4) was used to take non-representative sampling of the discharge dynamics into account.

$$L_Q = L\frac{\overline{Q}}{\overline{Q_S}} \qquad \text{(eq. 4)}$$

where:
L_Q is the discharge corrected annual TP load (tons $year^{-1}$)
L is the annual TP load (tons $year^{-1}$)
$\overline{Q}$ is the mean annual discharge (m^3 s^{-1})
$\overline{Q}_s$ is the mean sampled discharge (m^3 s^{-1})
The generalized additive model (GAM) regression method was used to capture the response of TP concentration C_t to the dynamics of years, Julian days, and discharge, and then calculated annual load L_{GAM} (eq. 5):

$$L_{GAM} = \frac{84600s}{1000*1000}\sum_{i=1}^{N}(C_t * Q_t) \qquad \text{(eq. 5)}$$

where:
N is the number of Julian days in a year (*i.e.*, 366 for leap years and 365 for the others)
L_{GAM} is the annual TP load (tons $year^{-1}$)
C_t is the monthly TP concentration (mg L^{-1})
Q_t is the daily discharge (m^3 s^{-1})

We calculated the TP load by each inflow and got the total annual load into the lake. The same methods were used to calculate outflow TP mass. Due to the lack of measured TP concentration at the outflow Hrazdan River, as an alternative, we put the surface concentration of Small Sevan into three equations and quantified the mass by combining it with the daily outflow discharge. Finally, TP retention was calculated using Equation 6. The surface TP concentration of Lake Sevan was monitored on a monthly sequence only from 2018 to 2020, so the retention calculation only covered these 3 years. The discharge and concentration data were provided Hydrometeorology Center state non-commercial organization of the Ministry of Environment RA:

$$R = \frac{(L_{inflow} - L_{outflow}) * 100}{L_{inflow}} \qquad \text{(eq. 6)}$$

where:
R is the TP retention (%)
L_{inflow} is the annual inflow TP load (tons $year^{-1}$)
$L_{outflow}$ is the annual outflow TP load (tons $year^{-1}$)

Statistical analysis

In general, the explorative factor analysis concentrates significant proportions of the total variance of many variables on a few factors with specific, interpretable structures and may help identify sources. As a data pre-processing, all used independent parameters were auto-scaled. The principal axis factor analysis combined with a varimax rotation was used to minimize an over-extraction (Wood *et al.*, 1996). For the analysis, Statistica^{TM} Version 13.3 was used. Figures were prepared using R (R-Core-Team 2018) and SigmaPlot (Systat Software, San Jose, CA, USA).

RESULTS

Basic sediment characterization

Although sediment cores of various lengths up to 38 cm were retrieved at different sites, only the top 10 cm of sediment were considered for this study since this is the main depth interval where the exchange of lake water and sediment solutes of the porewater can interfere if oxygen concentration and redox potential allow bioturbation (Hupfer and Lewandowski, 2005). The pH was measured in a narrow range between 7.2 and 7.9 (Fig. 2), and all cores had the highest pH at the top surface layer or immediately below. At BS_32m, SS_80m, and SS_62m, we detected a very uniform pH below 2 cm sediment depth. At SS_45m, the pH value increased from 7.2 to 7.7 at 2 and 10 cm sediment depth, respectively. In-situ Eh values ranged from -150 to 70 mV; they were similar and coherent throughout the depth distribution, except at SS_62m 3 to 4 cm (Fig. 2). In general, dry weight (DW) increased with depth from 5 to 10 wt-% at the top surface towards 15 to 20 wt-% at 10 cm sediment depth (Fig. 2). LOI (wt-%) decreased from 15 to 20 wt-% at the top surface layer to 10 wt-% in 10 cm depth of sediment (Fig. 2).

Nutrient analyses

The depth distribution of TOC in the sediment was similar for all sites showing highest concentrations at the top two layers and lowest concentration in 10 cm sediment depth; highest concentrations at SS_62m and SS_45m in the 1 to 2 cm sediment depth (Fig. 2). The absolute values were also quite similar in between the different sites (40 to 80 mg TC g^{-1} dw) except for SS_80m where considerably higher concentrations of TOC occurred in the top layer (110 mg TC g^{-1} dw). In all sediment samples, relatively high amounts of inorganic carbon were observed (Fig. 2). Lowest contents were detected for the Big Sevan (BS_32m), varying between 15 and 25 mg g^{-1} TIC dw, at all three sites of Small Sevan maximum content of TIC reached 60 mg g^{-1} dw (SS_80m), nearly 60 mg TIC g^{-1} dw (SS_62m), and nearly 50 mg TIC g^{-1} dw (SS_45m) at 10 cm depth, respectively. However, the depth distribution was different at all three sites (Fig. 2). In contrast, at SS_80m, the content increased steadily from the surface layer (15 mg TIC g^{-1} dw) towards 10 cm depth (61 mg TIC g^{-1} dw), the depth distribution at SS_62m was scattered showing no clear tendency. At SS_45m, the depth distribution of TIC

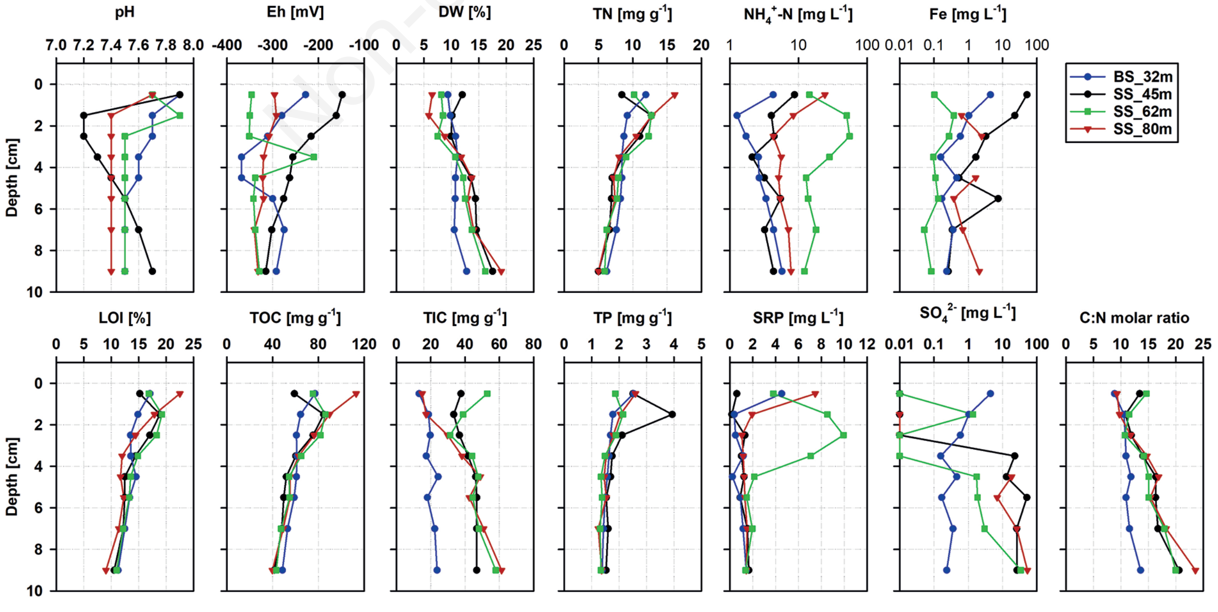

Fig. 2. Depth distribution of various sediment and pore water parameters within the top 10 cm sediment depth of Lake Sevan. Note that NH_4^+-N, Fe, and SO_4^{2-} have a logarithmic x-axis scale.

was more or less homogenous, with values between 34 and 47 mg TIC g^{-1} dw.

Magnitude and distribution of TN in the sediments were similar for all four sites, with maximum values ranging from about 8 to 13 mg g^{-1} TN dw (SS_80m even 16 mg TN g^{-1}) top 3 cm of the sediment cores and lowest values of 5 to 6.2 mg TN g^{-1} dw at 10 cm sediment depth (Fig. 2).

For TP, a similar distribution with the highest values (1.9 to 2.6 mg TP g^{-1} dw) at the top surface layer of the sediment and the lowest content (1.3 mg TP g^{-1} dw) at 10 cm sediment depth was found at all sites. However, the highest TP content (3.86 mg TP g^{-1} dw) was measured at the 1 to 2 cm sediment depth of SS_45m (Fig. 2). Calculated C:N molar ratios increased with depth; they varied between 9 to 15 at the surface layer and 12 to 24 at 10 cm sediment depth at all four sites (Fig. 2). The porewater of the sediment is rich in NH_4^+-N; both the SRP and NH_4^+-N were elevated at SS_62m (Fig. 2). Dissolved Fe concentration was variable; SS_62m had very low concentration while the other sites had concentrations between 0.1 to 1 mg Fe L^{-1} in the 10 cm sediment, except for BS_32m and SS_45m which had elevated concentrations in the upper sediments. Sulphate was generally not detected or very low in the upper sediments of SS_45m, SS_62m, and SS_80m; in contrast, BS_32m has very low sulfate in the lower sediments and slightly elevated concentration in the upper sediment.

Phosphorus-fractionation

The sum of P fractions decreased with depth at all sites; BS_32m and SS_80m had a relatively higher sum of P fractions in comparison to SS_62m and SS_45m (Fig. 3). In terms of P-fractions BS_32m and SS_80m had the most similar trend; they had the highest percentage of P in the NaOH-NRP fraction (20 to 35%) and the residual refractory fraction depending on sediment depth (Fig. 3).

The NH_4Cl-P fraction was mostly the least fraction at all sampling points; depth distribution showed a slight elevation in the upper 2 cm and was constant from 3 to 10 cm at all sampling points. The percentages of the NH_4Cl-P and BD-P fractions were less important at these sites (at most depths, values below 5% for NH_4Cl-P and below 10% for BD-P) than the other fractions. The BD-P was elevated in the upper 3 cm at all sampling points, with the most distinct elevation at SS_62m. The sum of NH_4Cl-P and BD-P fractions was relatively more prominent in the top cm of the sediment at site SS_62m with values of 11% and 25%, respectively. The NaOH-NRP distinctly decreased with depth at all sites. At BS_32m, SS_80m, and SS_45m, the NaOH-NRP was the predominant fraction in the upper 2 cm sediment layer. At SS_80m, the NaOH-fractions and the HCl-fraction had the highest percentages of P-bonding with decreasing percentages of the NaOH-NRP-fraction from the top layer (36%) to 10 cm sediment depth (15%).

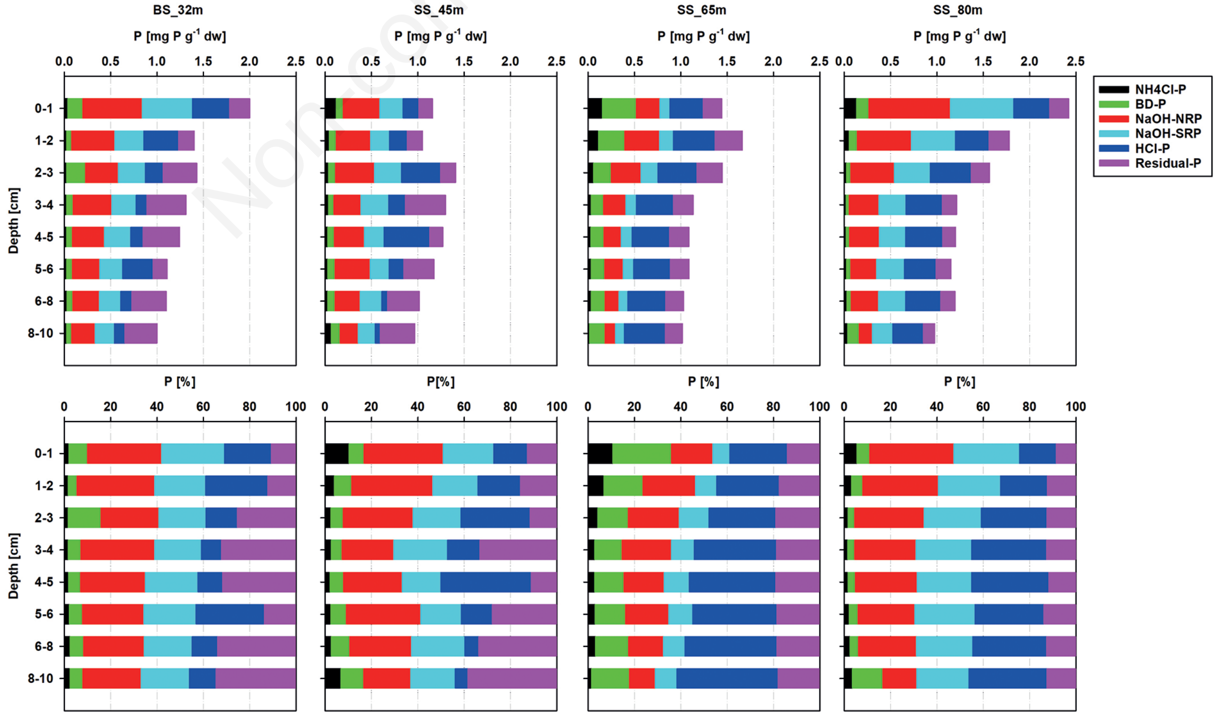

Fig. 3. Distribution of P-fractions with sediment depths at all four sediment sites of Lake Sevan.

The NaOH-SRP (P preferentially bound to Al-oxides) was the 3rd most dominant P-fraction at BS_32m, SS_45m and SS_80m. It remained nearly constant throughout the top 10 cm at percentages of 23% to 26%, with slightly higher percentages of 28% and 27% at the top two centimeters. In contrast, NaOH-SRP at SS_62m was much smaller compared to the other sites exhibiting values between 7% and 13%. In contrast, the refractory-P had constant percentages between 17% and 19%, except for the top layer (14%). The NaOH-NRP fraction showed an explicit depth dependency with NaOH-NRP percentages decreasing from 23% at 1 to 2 cm sediment depth to 11% at 10 cm sediment depth.

The HCl-P was relatively high at all sampling points; at SS_62m, it was the major P-fraction. The percentages of the HCl-P-fraction increased from top to down (16% at 0 to 1 cm to 34% at 10 cm sediment depth). The depth distribution of the HCl-P fraction was irregular; it showed higher percentages as the residual P-fraction at the top 2 cm and 5 to 6 cm sediment depth of BS_32m and 2 to 3 cm and 4 to 5 cm sediment depth of SS_45m, respectively. The residual-P was the fourth dominant P-fraction at all sampling sites. It showed an increasing trend with depth at BS_32m and SS_45m and a decreasing trend at SS_80m and SS_62m.

Aluminum and Fe distribution throughout the P-fractions for SS_62m were different. The NaOH extracted more than 87% of the Al, and HCl extracted the rest; BD extracted less than 0.5% Al (Fig. 4). More than 52 to 74% of the Fe was extracted by HCl, 10 to 32% was extracted by BD, and 10 to 29 % was extracted by NaOH (Fig. 4).

The behavior of the P group speciation was determined using a factor analysis with a simple varimax rotation based on the auto-scaled absolute values. Three factors were extracted by factor analysis. They describe more than 82 % of the total variance. The results of the first two extraction steps are highly correlated to factor 3. Both NaOH fractions have high loadings in factor 1. The HCl-P is highly correlated to factor 2, while residual-P fraction was highly anticorrelated to factor 2 (Tab. 2). The first two P-fractions are the most mobile P-fractions with similar behavior and NaOH fractions with less mobile bonded P. The strong anticorrelation of the HCl-P and residual-P results in factor 2 indicates that the HCl-P extraction is incomplete in all samples.

The behavior of TP is not strongly related to one of the factors because of the differences in the TP values and the sum of P fractions. The sum P fractions were less than the TP values by 22 ± 2 % (BS_32m), 39 ± 16% (SS_45m), 22 ± 4% (SS_62m), and 16 ± 8% (SS_80m).

Potentially mobile phosphorus

The potential mobile-P calculated by adding the first three P-fractions shows a decreasing trend with depth and is similar at all sampling points. It ranged from 54% in the upper sediment to 29% in the lower sediment (Fig. 5, left). The potentially mobile-P calculated by the "gradient method" (eq. 1) showed a similar decreasing trend with depth; it ranged from 52% in the upper sediment to 0.3% in the lower sediment (Fig. 5, right). Interestingly, both methods show similar results in the upper 2 cm (Fig. 5),

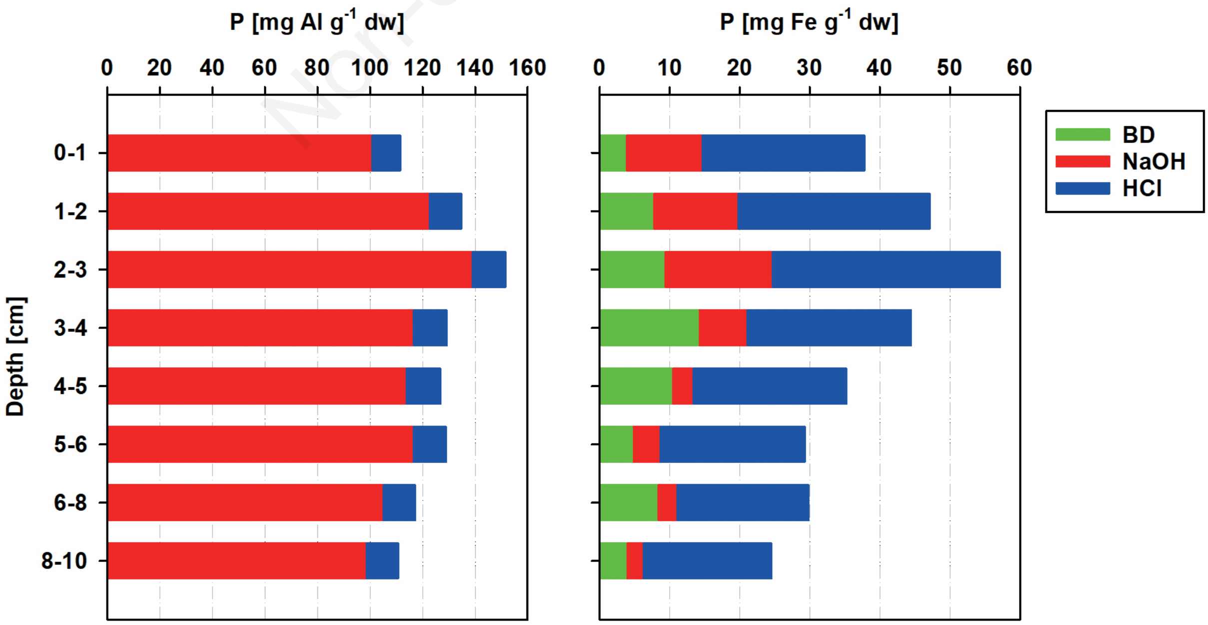

Fig. 4. Fate of aluminum (Al) and iron (Fe) in the P-fractionation solutions (BD, NaOH, and HCl) for the sampling point SS_62m.

which is the sediment layer likely to contribute to releasing nutrients into the water column due to its proximity to the sediment-water interface.

Phosphorus loads and retention

Estimated annual average loads of total P ranged between 102 to 113 t TP y^{-1}, with a gradual increase from 2011 on (Fig. 6). Most of the TP (85%) from the inflow is retained in the lake. The retention from the three methods [standard method (eq. 3), discharge-corrected standard method (eq. 4), and generalized additive model (GAM) regression method (eq. 5)] was similar (Fig. 6). The most remarkable difference of 9% in 2019 was between the standard and GAM regression method (Fig. 6).

DISCUSSION

Characteristics of the sediments and their phosphorus content

The pH ranged from 7 to 8; in the top 2 cm of sediment, the pH was more spatially variable, probably due to diagenetic and microbial processes. The pH was, however, uniform below 2 cm except for SS_45m, which showed a slight decrease in pH with depth. Since the Eh-values for most sediment depths were negative (Fig. 2), a strongly reduced neutral environment was indicated during sampling. At the very negative Eh-values found in the sediments, bioturbation, if occurring at all, was restricted to the top surface layer of the sediment. In some lakes, bioturbation is essential in oxygenating lower sediments (Lewandowski *et al.*, 2007). However, in Lake Sevan, the role of bioturbation was not prominent since we did not observe any burrows. The recently proven occurrence of sulfate reduction at the bottom of Lake Sevan (Avetisyan *et al*., 2021) additionally supports this interpretation.

The LOI indicated moderate organic matter in the sediments with the highest value (23 wt%) at SS_80m. A typical decrease from higher LOI values in the upper 3 cm towards lower values with increasing water depth is attributed to diagenetic microbial degradation of organic matter and physical consolidation ("funnel effect"). The TOC content was about 50% of LOI, as observed in several soil and sediment studies (Sutherland, 1998; Jensen *et al.*, 2018).

The relatively high amount of TIC (30 to 50% of TC) suggested calcite precipitation from lake water and porewater (Fig. 2). This fits the observation of calcite crusts at ropes exposed in Lake Sevan. Ulyanova (1994) proposed that calcite precipitation occurred in Lake Sevan and was the primary process for removing P from the lake water, as Hovhanissian and Gabrielyan (2000) described. Furthermore, Sahakyan *et al*. (2019) reported on microbialites in Lake Sevan, fossil and recent ones indicating that calcite precipitation is a typical, long-lasting process in Lake Sevan. This observation supports the idea that the organic matter enriched layer at the top 2 to 3 cm of the sediment is mainly derived from dead algae. However, the visual inspection of the sediment cores within the used transparent liners did not show varve-like layers, and our investigations were not detailed enough (no age determination; thickness of the analyzed sediment layers 1 cm or more) to separate single years or even seasons of sedimentation. Part of the initially precipitated calcite was probably later re-dissolved by CO_2 from the decay of organic matter, while the P may have been transferred into other binding forms. This is particularly likely in the location of the highest organic matter accumulation. Unfortunately, it remains to be seen if our investigations included the sediments from the 1940s to the 1970s when the main reduction of P in the water of Lake Sevan occurred, according to Hovhannissian and Gabrielyan (2000).

The TP content in Lake Sevan sediment was on the lower side of the range of 0.1 to 7 mg TP g^{-1} dw, which has been observed in other lakes (Hupfer, 1995). The TP content range of 1.3 to 3.9 mg TP g^{-1} dw was similar to that of other deep lakes, *i.e.*, ~1 to 3 mg TP g^{-1} dw in Lake Stechlin (Gonsiorczyk *et al*. 2001), 1 to 2 mg TP g^{-1} dw in the Rappbode Reservoir (Dadi *et al.*, 2020), which both were oligotrophic at the time of the study. The TP values within the top 2 cm of site SS_45m near the fish farm showed an extraordinary enrichment by doubling these values (Fig. 5).

Tab. 2. Loadings of the factors from a factor analysis simple varimax rotated.

Variable	Factor 1	Factor 2	Factor 3
NH_4Cl-P	-0.288	0.020	0.871
BD-P	0.228	0.097	0.900
NaOH-SRP	-0.922	0.032	-0.165
NaOH-NRP	-0.956	0.037	0.097
HCl-P	0.002	0.928	0.123
Residual-P	0.065	-0.922	0.018
Total-P	-0.667	0.010	0.378
Explained portion of the total variance	0.336	0.246	0.252

Studies about C, N, and P in fish farms showed that up to 80% of the original P input is usually released from fish cage farms and lost in the marine or lake environment (Dauda *et al*., 2019). The production process releases a large amount of residual food and excreta into the water, which can be oxidized to soluble substances and partially consumed by lake plankton. Most of these by-products would become part of the sediment, ultimately leading to long-term accumulation (Gowen, 1994; Clerk *et al.*, 2004; Dauda *et al.*, 2019).

A striking result of our study was the increase of the C:N ratio in the sediments with depth (Fig. 2). We attribute this phenomenon to the preferential early diagenetic loss of N, as known from many lakes (Talbot, 2001). The eutrophication of Lake Sevan and, thus, the increase of autochthonous production of organic matter and, in turn, the decrease of the relative contribution of terrestrial organic matter with higher C:N ratios (Meyers and Ishiwatari, 1993) may have also contributed to that. However, the relevance of the latter effect strongly depends on the time represented by our sediment samples which is still unknown.

Spatial differences in sediment composition

The spatial variability was relatively more prominent in the upper 3 cm. As expected, the sampling point SS_80m had an elevated TOC content because it was the deepest

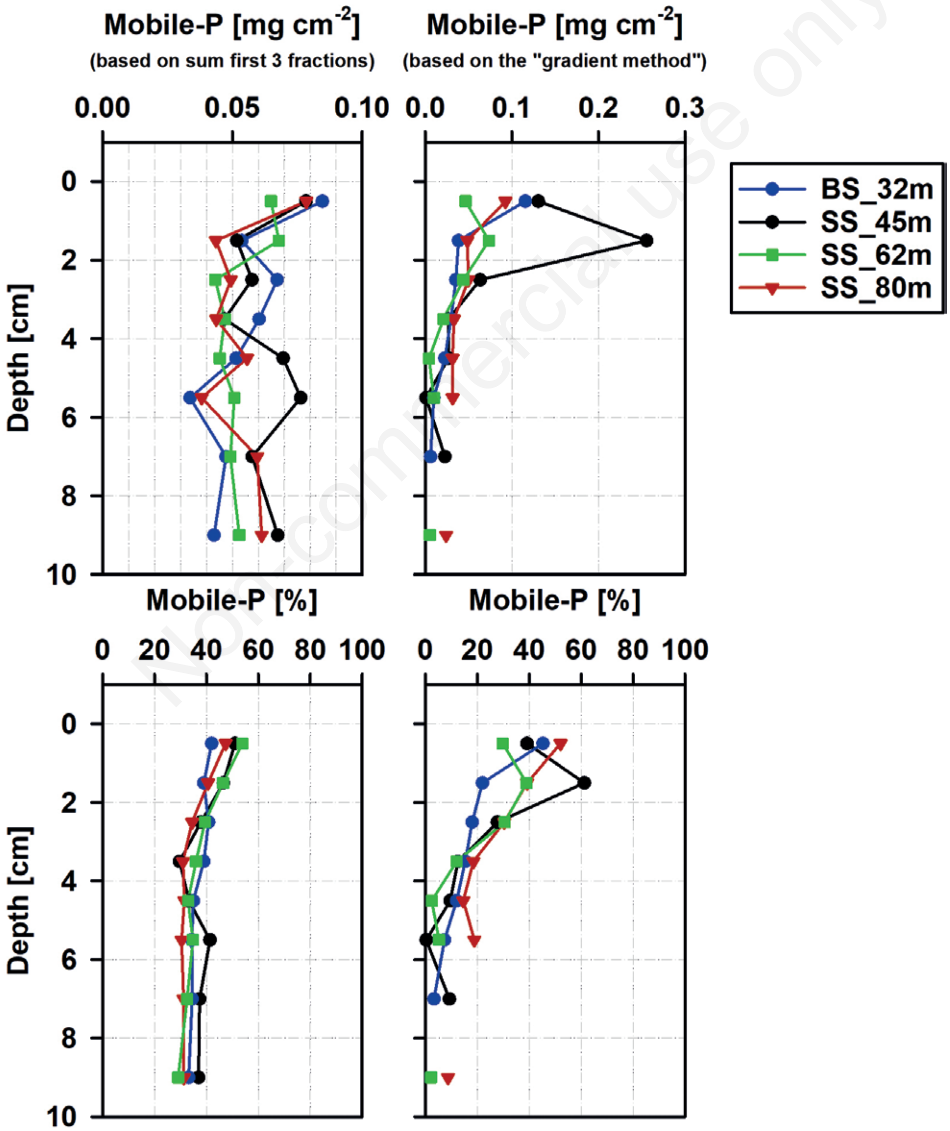

Fig. 5. Potentially mobile P-pool ($P_{\text{-mobile}}$) in the sediments calculated using two methods; left panels based calculated as the sum of the first three P-fractions (NH_4Cl-P, BD-P, and NaOH-NRP), right panels based on the "gradient method" calculated according to Equation 1. Please note that for both methods, the contents have been multiplied by the dry density and thickness of the respective sediment layers.

sampling point where most of the finest lake particles settled. Such accumulation, so-called "sediment focusing" (*i.e.*, the gradual transport of the sediment to the deepest sites of lake basins and accumulation there), is well-known in many lakes (Edington and Robbins, 1990; Bloesch, 1995; Lin *et al.*, 2018). In contrast, SS_62m showed a lower TOC content in the upper layer but an elevated TIC content. SS_62m was sampled at the end of the vegetative season of 2018, and a cyanobacterial bloom occurred in July 2018 (Gevorgyan *et al*., 2021). It is plausible to assume that the calcite, which was precipitated due to phytoplankton growth during the summer of 2018, was not yet re-dissolved by CO_2 resulting from the microbial decay of the freshly settled biomass in the top layer of the sediment at the time of sampling SS_62m. The bottom temperatures at both sites remain relatively constant in Lake Sevan throughout the year (Poddubny, 2010), so the decay of organic matter can continue in winter, and the quality of organic matter is the most likely factor influencing the mineralization rate. It is well known that autochthonous organic matter is degraded faster (Burdige, 2007). This explains why the calcite originating from the summer of 2017 could have been the subject of re-dissolution by CO_2 resulting from the microbial decay already in the spring of 2018 when SS_80m was sampled. Sampling point SS_62m also had a lower TP content in the upper layer in comparison to SS_80m. The lower TP content could be due to the "dilution" by the not-yet re-dissolved calcite and the mobilization of P through both mineralization (Hupfer and Lewandowski, 2008) and reductive dissolution of Fe hydroxides (Einsele, 1936; Mortimer, 1971) as evidenced by the elevated concentration of the labile BD-P and NH_4Cl-P fractions (Fig. 3).

There was a high spatial variability of the redox potential. The trend was apparently influenced by depth, *i.e.*, the shallower points SS_45m and BS_32m had a higher redox potential as compared to the more profound points SS_80m and SS_62m (Fig. 2). The difference in the redox potential of SS_62m and SS_80m could be a seasonal effect because SS_80m was sampled in April and SS_62m was sampled in October. Generally, after summer, the redox potential in the sediment can be expected to be very low due to the supply of fresh settling biomass (*e.g.*, from algal blooms), its mineralization, and other biogeochemical reduction processes. This assumption is supported by detecting elemental sulfur and hydrogen sulfide in the

Fig. 6. Inflow total phosphorus (TP) loads into Lake Sevan from 2010 to 2020 (top) and TP retention rate from 2018 to 2020 calculated by three methods; method 1 (standard method, eq. 3), method 2 (discharge-corrected standard method, eq. 4), and method 3 (generalized additive model regression method, eq. 5).

lower parts of the hypolimnion of both Small and Big Sevan (Avetisyan *et al.*, 2021).

The BS_32m sampling point differed (for most of the parameters) from the other points, which can be attributed to BS_32m being located in Big Sevan, whereas the other three sampling points were in the Small Sevan. The majority of rivers flow into Big Sevan; its catchment is larger than that of Small Sevan, and the intensity of land use is also higher in the catchment of Big Sevan (European Union Water Initiative Plus, 2020), even resulting in a slightly higher trophic state of Big Sevan compared to Small Sevan in the past (Hovhannissian, 1994). Further research should focus on determining water current velocities to ascertain the potential exchange of water and their constituents between the Small and Big Sevan to verify whether both basins are similar or behave more as two separate water bodies, especially regarding nutrients.

Different sedimentation conditions at all four sample sites may have contributed to different distribution patterns of P-bonding. Generally, unusually low P-bonding at reducible Fe phases occurred at sites BS_32m, SS_80m, and SS_45m (Fig. 3) despite having higher Fe content (Fig. 2). Only site SS_62m in the central part of Small Sevan showed Fe-bound P of about 10 to 20% of TP. The low P-bonding might be due to iron (III) immobilization by forming iron (II) sulfides. We observed depleted sulfate in the upper sediments, indicating sulfide formation from sulfate reduction; sulfate reduction has also been demonstrated recently in Lake Sevan (Avetisyan *et al.*, 2021). In contrast, at sites BS_32m, SS_80m, and SS_45m, a larger part of P was stored in organic and detrital material that might have been mobilized by microbial degradation of organic matter and contributed to the potentially mobile pool of P.

Evaluation of the potential mobility of sedimentary phosphorus

This potentially mobile P pool refers to the sum of P stored within the NH_4Cl-P, BD-P, and NaOH-NRP fractions (paragraph "Calculation of potentially mobile phosphorus"). It can be seen as P available on a short-term perspective, *e.g.*, on a seasonal release at changing redox conditions (oxic/anoxic). The upper 2 cm of the sediment is more likely to contribute the highest portion of the potentially mobile P released from the sediment. The average values of the potentially mobile-P pool in the 2 cm layer ranged from 34 to 50 % of TP. It should be noted that a release of P from the first three fractions does not necessarily occur at the same conditions and time. Whereas P related to the NH_4Cl-P fraction might be available at any time and condition as part of the porewater, P from the BD-P fraction represents that part of P, which only occurs at reduced anoxic conditions. For the NaOH-NRP fraction, a release of P might be possible either at oxic or anoxic conditions, but the amount of bacterial degradation of organic matter is seen more pronounced at oxic conditions (Bastviken *et al.*, 2004).

An alternative and more robust method to assess the potentially mobile part of sedimentary P is the so-called "gradient method" (Hupfer and Lewandowski, 2005; Grüneberg *et al*., 2015; Hupfer *et al*., 2020). This method can be used if the TP profiles follow the theoretical curve of declining TP contents with depth due to diagenetic P loss with time, as it occurs at all four Lake Sevan sampling sites. Applying this method to the TP distribution of Lake Sevan sediments by using Equation 1 (section 2.4) yields a mobile P (P_{mobile}) range of 0.04 mg P_{mobile} cm^{-2} (BS_32m) to 0.26 mg P_{mobile} cm^{-2} (SS_45m); this is based on a long-term diagenetic perspective for the top 2 cm (Fig. 5). Considering the amount of TP cm^{-2} in the top 2 cm of sediment these values represent between 22% (BS_32m) and 61% (SS_45m) of TP as potentially mobile P on a long-term view; this is comparable with the findings based on sequential extraction (34 to 50%; Fig. 5).

A simple conservative estimation was applied to assess the ecological impact of internal TP load on Lake Sevan's nutrient status. Assuming that about 50% of the TP stored only within the first cm of sediment is released to the lake water (about 0.115 mg TP cm^{-2} on average of the four core sites) at a specific time, this would sum up to 1,470 t of TP over the whole lake sediment surface (1278 km^2). Divided by the lake water volume of 38 km^3, it would yield an increase of about 0.04 mg L^{-1} P to the lake water concentration. If we apply the average sediment accumulation rate in lakes of 0.3 cm y^{-1} (Baud *et al*. 2021), then the TP in the top cm of Lake Sevan would have accumulated in 3 to 4 years. The 3 mm y^{-1} is applicable for Lake Sevan because an investigation in the 1920s or 1930s estimated the sediment accumulation rate to be ca. 1 mm y^{-1} (Gulakyan and Wilkinson, 2002) while the most recent study (Nalbandyan *et al*. 2006) estimated sediment accumulation to be ca. 5 mm y^{-1}.

This potentially mobilized sedimentary TP equals ca. 15 years of nutrient loads from the surrounding catchment. The results from the three methods of external load calculations were quite close to each other, with the annual average value ranging from 102 to 113 t P y^{-1}; this confirms the robustness of our calculation (Fig. 5). Over 85 % of inflow TP was retained within the lake, which served as an important source for the mobile P trapped in sediment, as shown by the internal P load estimation above.

Of course, this part of P in the sediment surface would not be released spontaneously at one given point in time but more continuously over a certain period, *e.g.*, during summer stratification when oxygen was consumed in the hypolimnion and anoxic conditions at the water-sediment interface were set up. Nevertheless, if not only the first top cm of the sediment layer is considered but also the 1 to 2 cm of sediment layer, the release amount of P would be doubled. Since it is not very likely that P from all three potentially mobile fractions is released at the same time and conditions, a more conservative calculation based on the sum of the NH_4Cl-P and BD-P fractions (10 to 36% of mobile P from the top cm, see Fig. 3) would yield a release by only 0.007 to 0.019 mg P L^{-1} from the top cm on a short-term view. Nevertheless, this concentration of internal P release is calculated for the whole water body. Of course, it will not occur homogeneously in the water body. An enrichment of the mobilized P can be expected for the hypolimnion. The P accumulated in the hypolimnion will be transported into the photic zone only during the mixing period, *i.e.*, once or twice per year, since the lake exhibits both dimictic and monomictic mixing patterns in different years. In addition, part of the P immobilized goes back to the sediments due to the redox-dependent adsorption and precipitation of P by Fe (III) hydroxides during the mixing (Skoog and Arias-Esquivel, 2009).

CONCLUSIONS

Our study provides first insights into the magnitude and proportion of sedimentary TP fractions in Lake Sevan. Lake Sevan has a high TP retention (85%). In general, sedimentary TP in Lake Sevan showed elevated contents near the sediment surface, with the maximum within the top layers of SS_45m, probably due to the nearby fish farm operation. From a long-term perspective, we estimated the potential mobile P in Lake Sevan in the top 2 cm to be 20 to 60%. Given the high content of potentially mobile P within the top sediment layers, a potential release of 40 to 50% is plausible, and the long flushing time of Lake Sevan adds to that. This potential P release applies to short-term exchange between oxic and anoxic overlying water, long-term diagenesis, and permanent burial from the top cm of sediment. To reliably define the eutrophication risk of the internal loading, additional studies should focus on determining exact sediment accumulation rates and benthic nutrient fluxes at different times of the year, *e.g.*, by use of sediment traps and sediment pore water samplers.

ACKNOWLEDGEMENTS

This work was funded by the Federal Ministry for Education and Research of Germany (BMBF) under the German-Armenian projects SevaMod (Project ID 01DK17022) and SEVAMOD2 (Project ID 01DK20038). The latter project is co-funded by the Republic of Armenia, Ministry of Environment. The water quality data for Lake Sevan used in this study were also produced within this project. We are grateful to the Hydrometeorology and Monitoring Center, a state non-commercial organization of the Republic of Armenia, Ministry of Environment, for providing data on discharge and water quality on Lake Sevan and the connected rivers. We acknowledge the Captain and Crew of the research vessel GIDROLOG for navigating us to the sampling points and their support during sampling. We thank Vahe Melkonyan for helping take the sediment cores and handle the rubber boat. Many thanks to Burkhard Kuehn and Michael Herzog for their assistance during the sampling campaigns and for preparing and analyzing the samples; Armine Hayrapetyan and Gor Gevorgyan for the logistics, their help during the campaigns and for doing the water sampling from Lake Sevan within the projects SevaMod and SEVAMOD2.

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