

Phosphorus Speciation of Sediments of a Meso-eutrophic Lake in Quebec, Canada

Dileep Palakkeel Veetil¹, Catherine N Mulligan and¹ * and Sam Bhat²

¹ Concordia University, Montreal QC H3G 1M8, CANADA

² Titan Environmental Containment Ltd, MN, Canada

* Email: mulligan@civil.concordia.ca

Abstract. Sediment phosphorus (P) release is one of the main reasons for eutrophication in many shallow lakes. This present study examines sediment samples collected from Lake Johanne, a shallow, meso-eutrophic lake in Canada for sediment P concentration and its speciation to understand the potential of sediment phosphorus for release into the lake water. Speciation of the sediment phosphorus was performed according to the SMT sequential extraction technique. Sediment analysis showed a relatively high P concentration (1186-1451 mg/kg) across the lake. Speciation of P in the two core sediments (Stations 4 and 7) was found to be significantly different. Inorganic phosphorus (IP) was the major form of P in both core sediment samples. Non-apatite inorganic phosphorus (NAIP) and organic phosphorus (OP) were the major phosphorus forms present in the St.4 core sediment. Heavy metal concentrations in the lake sediments were within the acceptable levels. Significant content of readily available P forms (NAIP and OP), and the high P concentration in the sediment core from St.4 pointed out to the outflow from its neighboring wetland that carries nutrients and organic matter into the lake.

Keywords: Sediment, Phosphorus, Speciation, and Eutrophication.

1 Introduction

Eutrophication is a serious environmental issue in many freshwater systems around the world. Phosphorus (P) is a key growth-limiting nutrient that controls primary production in freshwater systems [1]. Its excess concentration in freshwater through natural and anthropogenic activities causes eutrophication- a state of increased primary production and occurrence of floating algal blooms [1, 2]. Eutrophication can occur in any lakes, irrespective of how deep or shallow they are [3]. High turbidity, reduced aquatic biodiversity, low dissolved oxygen and the release of toxins from a certain type of cyanobacteria (blue-green algae) are some of the potential issues associated with lake eutrophication [2, 3].

Sediment P is one of the potential sources of P in the overlying water in many shallow lakes [3, 4]. Due to the sediment P release, many lake restoration projects have been delayed and failed to achieve desired surface water quality and to reduce eutrophication, even after eliminating the external P input into the lakes [3, 5, 6]. In

shallow lakes, due to the lower water column depth and very high dynamic conditions, sediment nutrients are easily available to the photic zone of the shallow lake water and this provides favorable conditions for algae to grow [4]. Sediment P release into the overlying water occurs through different mechanisms such as desorption and dissolution of P-associated with fine particulate matter and inorganic materials (Fe, Al, Mn, and Ca), microbial mineralization of organic matter and dead algae in sediment and the diffusion of dissolved P from sediment pore water [7,8].

Lake Johanne is a shallow lake located in the Sainte-Anne-des Lacs municipality in Quebec, Canada. The government of Quebec has been monitoring the lake water quality for many years as a part of the Quebec Volunteer Lake Monitoring Program (VLMP) to assess the changes in the lake's water quality. However, very limited information is available about the lake sediment quality. Thus, the present study evaluates the sediment quality of Lake Johanne, especially for phosphorus concentration and its speciation in the sediment.

2 Materials and Methods

2.1 Study Area

Lake Johanne ($45^{\circ}50'23''$ N; $74^{\circ}08'19''$ W) is a shallow lake with maximum and average depths are 3.1 and 1.7 m, respectively. The lake has a surface area of 44,910 m² and the average water volume is about 76,300 m³ [9]. Though the lake is currently not included in the MDDEP (Ministère du Développement Durable de l'Environnement et des Parcs) list of lakes in Quebec having algal blooms, it was exposed to algal blooms in the past during 2004-10 [10]. The lake's watershed is occupied with wild trees, and a few privately owned houses with lawns. The main sources of water in the lake include precipitation, snow, surface runoff and an outflow from its neighboring, small, wetland. Fig 1 shows the map of Lake Johanne with sampling stations.



Fig. 1. Lake Johanne with sampling stations.

The wetland is connected to the lake via a drainage pipe, through which some of the nutrients and organic matter enter into the wetland, from its surrounding forest area, is finally end up into the lake water.

2.2 Sediment and Chemical Analysis

Sediment sampling was performed at the different selected stations across the lake during the summer of 2017. Sampling locations (Stations 2, 3, 4, 7, and 11) were selected based on their proximity to the wetland and to the road as sediments from these stations might have affected by external activities. Surface sediments were collected using a Birge-Ekman grab surface sediment sampler. A hand sediment corer of 50.8 cm long and 5.08 cm diameter was used to collect sediment cores from St.2 and St.7. Both surface and core sediments were collected where the outflow from the wetland mixes with the lake water (St.4). The surface sediments were stored in closed plastic containers at 4°C, whereas the sediment cores were freeze-dried. Sediment organic matter (loss on ignition at 440 °C) was determined according to the ASTM D2974-87 method [11]. Sediment particle size analysis (PSA) was performed with a laser diffraction particle analyzer (LA-960 Horiba laser particle size analyzer). Elemental analysis of sediment samples was performed by using ICP-MS (Inductively coupled plasma mass spectrometer, Agilent 7700 Series) after a partial acid-peroxide digestion ($\text{HNO}_3\text{-H}_2\text{O}_2$) of powdered sediment sample [12]. The freeze-dried sediment core was sectioned every 4 cm in length for chemical analysis.

2.3 Phosphorus Speciation

Speciation of P in the surface sediments was determined by using the SMT extraction technique [13]. This method allows the quantification of P associated with different geochemical phases as follows: (i) P associated with Al, Mn, and Fe oxides/hydroxides, called non-apatite inorganic phosphorus (NAIP), (ii) P associated with Ca, called apatite inorganic phosphorus, (AIP), (iii) inorganic P (sum of NAIP and AIP), (iv) organic phosphorus (OP), and total phosphorus (TP, sum of IP and OP). NAIP and AIP were extracted by 20 ml of 1M NaOH and 1M HCl, respectively. In a separate extraction step, IP was first extracted from the sediment using 1M HCl and the resulted residual sediment was dried at 450°C for a given time and then extracted for OP using 1M HCl. For TP, original sediment was dried at 450°C for a given period of time and then extracted with 3.5M HCl. [13]. The P extract obtained from each extraction step was centrifuged and filtered through 0.20 µm syringe filters for P analysis using ICP-MS.

3 Results and Discussion

3.1 Sediment Characterization

The organic matter (OM) content was found very high (28-47%) in sediments collected from all stations, especially from St.4 and St.11. The high organic matter in St.4 (32%) sediment could be related to the outflow from the wetland and dead aquatic organisms that settled at the bottom of the lake. St.11 was located close to a small lake island with vegetation, debris and runoff from the island could be a reason for the very high sediment OM (47%) observed at this station. The sediment pH varied from 6.9 to 7.4. Among the samples tested, sediment from St.3 contained more fine sediment particles than others. About 50% of the sediment from St.3 was under $51\mu\text{m}$. The sediment samples were dominated with silt fraction (26-52%) followed by fine sand (19-31%) and very fine sand (18-28%). The content of clay fraction ranged between 0.5-1.1% of the total particle size. Among the major elements analyzed, Al and Fe concentrations were found to be relatively very high in all the sediments analyzed, in a range of 12287-19808 mg/kg and 17480-33932 mg/kg, respectively. Fe concentration was found to be high for the samples from St.7 and St.11. The concentration of Ca was relatively low, ranging between 1249-1717 mg/kg, compared to Fe and Al concentrations in the sediment. Fig 2 shows the vertical distribution of Cu, Zn, and Pb in the sediment cores sampled from St.4 and St.7.

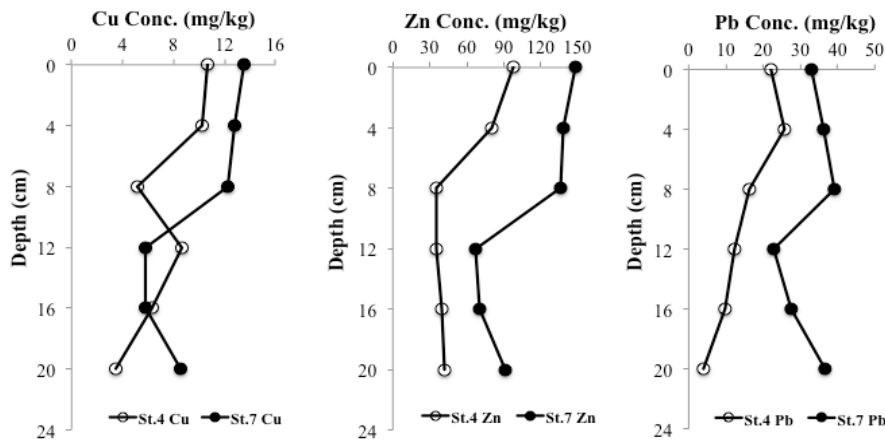


Fig. 2. Vertical concentration of heavy metals in Lake Johanne core sediments (St.4 and St.7)

The Cu, Zn, and Pb concentrations were found to be slightly high for upper sediments (0-4 cm) and then declined with depth for both sediment cores. The high metal concentration in the upper sediment shows the possibility of recent contaminations that occurred through surface runoff and other human activities including road constructions, transportation and use of de-icing salts on the lake shore road in the winter. In some areas, the lakeshore is very close to the road and there is more chance for de-icing salts to runoff into the lake water. It was observed that a salt-like precipitate was

found when the surface sediments were dried at 105°C. Heavy metal concentrations in surface sediment samples across the lake were under the acceptable maximum levels. All sediments contain a relatively high concentration of zinc (Zn), in the range of 169-271 mg/kg. The concentrations of chromium (Cr), copper (Cu) and arsenic (As) in the sediment samples were below the threshold effect level (TEL), whereas Zn and lead (Pb) concentrations were slightly above the TEL, norm set for freshwater sediment quality, for the protection of aquatic organisms, by MDDEP and Environment Canada. TEL is the level below that adverse effects are rarely observed and above which adverse effects are occasionally observed [14].

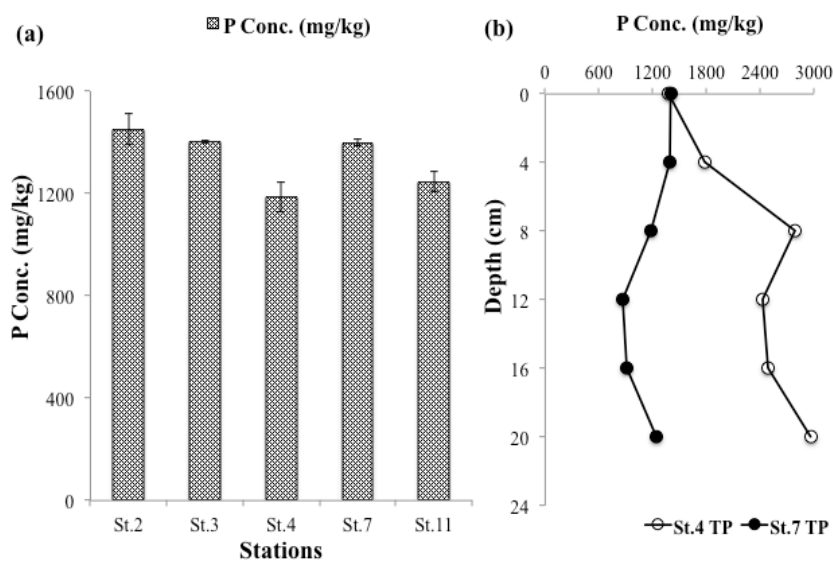


Fig. 3 Concentration of P in Lake Johanne (a) surface and (b) core sediments

The sediment P concentration was high, in a range of 1186-1451 mg/kg, in all sediment samples collected across the lake (Fig. 4a) Concentrations of P in Lake Johanne sediments were slightly higher than those reported in a shallow, eutrophic lake, Lake Caron (769-1298 mg/kg), in the same location [15] The vertical concentrations of P in the two core sediments analyzed were different. The P concentration increased with sediment depth for St.4 core sediment. P concentrations in the top (0-4 cm) and bottom of the sediment core (20-24 cm) were 1375 ± 64 and 2962 ± 87 mg/kg, respectively. The high vertical P concentration in St.4 sediment indicates the enrichment of P in the sediment in the past, possibly from surface runoff and discharge from the neighboring wetland located next to St.4. The upper sediment P concentration was the same for both cores. In the case of St.7 core sediment, the P concentration was consistent at depths of 0-4 cm (1400 ± 25 mg/kg) and 4-8 cm (1396 ± 62 mg/kg) and then gradually reduced at depths of 8-12 cm (1181 ± 12 mg/kg). In St.7, a similar P distribution pattern was observed compared to St.4 core sediment at depths of 8-24 cm.

3.2 Phosphorus Speciation

In soil and sediments, P is associated with different geochemical phases and release of P from these fractions is significantly controlled by different in-situ physical, chemical and microbiological conditions. The vertical distribution of different geochemical forms of P in St.4 and St.7 sediment core is given in Fig.4. Inorganic phosphorus (IP) was the major P form (65-84%) in all vertical sediment fractions (St.4) and found increased with increasing depth up to 0-12 cm and then decreased slightly at depths of 12-20 and thereafter the concentration significantly increased at depths of 20-24 cm. About 84% of the TP at depths of 20-24 cm was accounted by IP, mainly by P associated with Ca (74%, AIP) (Fig. 4a).

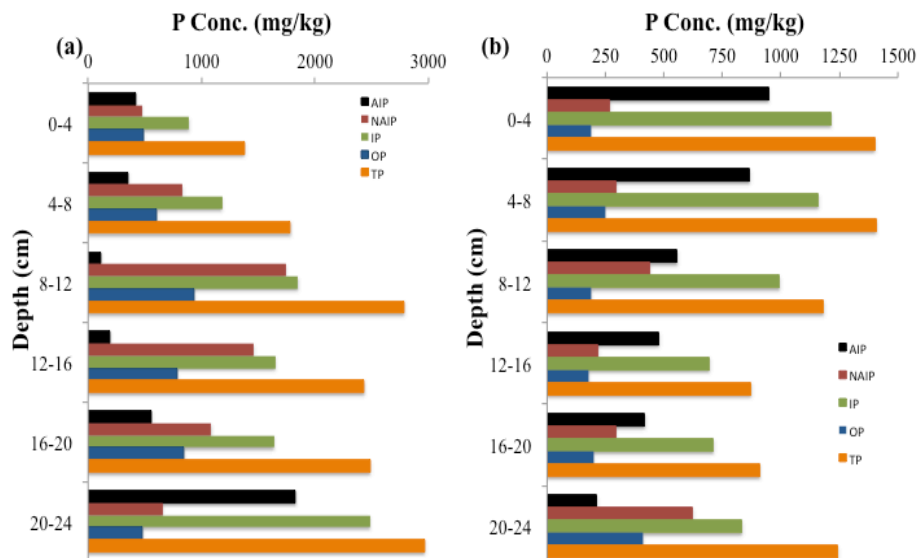


Fig. 4. Speciation of P in core sediments from Lake Johanne (St.4 (a) and St.7 (b)).

Organic phosphorus (OP) content was also high (32-35%) and consistent up to sediment depths of 0-20 cm, and then decreased, accounting for only 16 % in the 20-24 cm fraction. The low OP in the bottom sediment could be due to the conversion of OP to IP by anaerobic mineralization [16]. The high OP content in the surface sediments can be related to high OM (32%) found in the surface sediment at St.4. OP can be bioavailable to algae as mineralization of organic matter results in the release of P associated with it. In shallow lakes, due to the small water column depth, dead algae and other organic matter rapidly settle and incorporate in the bottom sediment where mineralization of this organic matter and dead algae leads to the release of P into the overlying water [4]. Rydin [17] reported that about 50-60% of the OP in sediments could be decomposed into bioavailable P. The vertical concentration of OP in the sediment core (St.4) was found to be high in all sediment fractions, except for the bottom sediments varying between 499-931 mg/kg.

Among the different forms of IP, NAIP was P-associated with Al, Fe, and Mn, the major inorganic P form (54-94%) in all sediment depths (0-20 cm), except for the lowest (20-24 cm) fraction in which P was mainly in AIP (74%) form. The vertical concentration of major elements showed high Al and Fe concentrations, compared to Ca (638-771 mg/kg), in the St.4 sediment core. The high content of NAIP in the St.4 core sediment can be related to the high Al (15530-26329 mg/kg) and Fe (8195-10953 mg/kg) concentrations in sediments at the depths of (0-20 cm). A linear relationship found between the concentration of Al and P associated with NAIP fraction indicates the significant role of Al oxides and hydroxides on P binding in the NAIP fraction. NAIP is a redox-sensitive fraction and P associated with this fraction can be released into the overlying water through adsorption/desorption process and thus allows P available to algae and other microorganisms in the water column. Reduction of Fe^{3+} to Fe^{2+} in anoxic sediments can result in the release of P that adsorbed on Fe oxides and hydroxides into the overlying water [3, 4]. Since Fe oxides and hydroxides in the sediment can provide new adsorption sites for P, a strong relationship exists between the sediment Fe content and its capacity to bind P [4, 5]. Jensen et al. [5] reported a strong negative correlation between sediment Fe:P ratio and soluble reactive phosphorus concentration in the lake water, suggesting that sediment with a high Fe:P ratio (>15) could have strong sediment P retention capacity. However, the vertical Fe:P ratio for St.4 core sediment was low (3 to 9) and was found to decline towards the bottom of the core sediment. AIP is a stable form of P and is not bioavailable under normal environmental conditions. Though NAIP was the major inorganic P form in St.4 core sediment, AIP content was significant at the top and bottom of the core sediment (St.4) (Fig. 4a).

The vertical distribution of different P forms in St.7 core sediment is given in Fig. 4b. IP was the major P form in the core sediment (67-87%), with a very low OP content (13-33%). The IP content decreased with increasing depth. Unlike the sediment core from St.4, the OP content in St.7 core sediment was very low and this can be related to the low sediment OM content at St.7 (22%). However, the OP concentration in the lower sediment fractions (20-24cm) was almost the same for both core sediments, unlike the upper fractions. P-associated with AIP was the major IP form in all core sediment fractions (0-20 cm), except for the lower fraction (20-24 cm) in which NAIP was the major IP form. Compared to the St.4 core sediment, the concentration of Ca and Fe in the St.7 core sediment was very high. A very high Fe:P ratio (16-19) in St.7 core sediment indicates the strong P retention capacity of the sediment.

4 Conclusions

The concentration of TP was found very high and ranged between 1186-1451 mg/kg, in all surface sediments, irrespective of sampling stations, collected across the lake. Sediment core analysis showed significantly very high P concentration in the lower layer of the sediment core from St.4. P speciation was found to be significantly different in both core sediments tested. The IP fraction was the major P form in sediment cores from St.4 and St.11. While NAIP was the main IP form in St.4 core sediment,

AIP was the major IP form in St.7 core sediment. A direct correlation was found between OM content and OP fraction in both core sediments. St.4 sediment contained a significant amount of NAIP and OP fractions, which can be a potential source of P in the overlying water under specific redox conditions.

References

1. Schindler, D.W.: Evolution of Phosphorus Limitation in Lakes. *Science*, 195:260 (1977).
2. Chislock, M.F., Doster, E., Zitomer, R.A., Wilson, A. E.: Eutrophication: Causes, Consequences, and Controls in Aquatic Ecosystems. *Nature Education Knowledge* 4(4), 10 (2013).
3. Sondergaard, M., Jensen J.P., Jeppesen, E.: Retention and Internal Loading of Phosphorus in Shallow, Eutrophic Lakes. *Review Article The Scientific World* 1 (2), 427-442 (2001).
4. Sondergaard, M., Jensen J.P., Jeppesen, E.: Role of Sediment and Internal Loading of Phosphorus in Shallow Lakes. *Hydrobiologia* 506-509, 135-145 (2003).
5. Jensen, H.S., Kristensen, P., Jeppesen, E., Skytthe, A.: Iron: Phosphorus Ratio in Surface Sediment as an Indicator of Phosphate Release from Aerobic Sediments in Shallow Lakes. *Hydrobiologia* 235:236, 731-743 (1992).
6. Welch, E.B., Cooke, G.D.: Internal Phosphorus Loadings in Shallow Lakes: Importance and Control. *Lake and Reserve Management* 11(3), 273-281 (1995).
7. Moore, Jr. P. A., Reddy, K.R.: Role of Eh and pH on Phosphorus Geochemistry in Sediments of Lake Okeechobee. *Journal of Environmental Quality* 23 (5), 955-964 (1994).
8. Pettersson, K.: Mechanisms for Internal Loading of Phosphorus in Lakes. *Hydrobiologia* 373/374, 21-25 (1998).
9. ABVLACS (Agence des Bassins Versants de Sainte-Anne- des-Lacs) <http://abvlacs.org/lac-johanne> last accessed 2018/2/20.
10. MDDELCC, http://www.mddelcc.gouv.qc.ca/Eau/rsvl/rsvl_details.asp?fiche=497, last accessed 2018/01/20.
11. ASTM D2974-87.: Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils. D2974-87, 1-3 (1993).
12. USEPA, <https://www.epa.gov/.../epa-method-3050b-acid-digestion-sediments-sludges-and-soils>, last accessed 2018/01/20.
13. Ruban, V., Lo'pez-Sa'nchez, J.F., Pardo, P., Rauret, G., Muntauc, H., Quevauviller, Ph.: Selection and Evaluation of Sequential Extraction Procedures for the Determination of Phosphorus Forms in Lake Sediment. *Journal of Environmental Monitoring* 1, 51-56 (1999).
14. Environment Canada., Ministère du Développement durable, de l'Environnement et des Parcs du Québec. : Criteria for the Assessment of Sediment Quality in Quebec and Application Frameworks: Prevention, Dredging and Remediation, 1-37, (2007).
15. Veetil, D.P., Mulligan, C.N., Bhat, Sam. : Sediment Characterization and Speciation of Phosphorus in Lake Sediments in Quebec, Canada. 16th Joint Seminar on Geo-Environmental Engineering (GEE), pp. 1-6. Seoul, Korea (2017).
16. Wang., Liang T.: Distribution Characteristics of Phosphorus in the Sediments and Overlying Water of Poyang Lake. *PLoS ONE* 10 (5), 1-12 (2015).
17. Rydin, E.: Potentially Mobile P in Lake Erken Sediment. *Water Research* 34 (7), 2037-2042 (2000).