Ca\(^{2+}\) Budget, Factors of Calcite Precipitation in a High Altitude Himalayan Lake

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ABSTRACT

Hard water lakes are known to precipitate Ca\(^{2+}\) through a complex number of factors. Dal, a shallow Himalayan hard water lake was observed to remain saturated with respect to calcium carbonate CaCO\(^3\) ([S.I.] range: 0.1 – 0.7, avg. 0.3) throughout the study period of Sept. 1999 to Aug. 2000. CaCO\(^3\) precipitating tendency of lake waters primarily results from high surface loading of 422.7 g Ca\(^{2+}\) m\(^{-2}\) yr\(^{-1}\), which was mainly accounted by colossal export of 25.3 g Ca\(^{2+}\) m\(^{-2}\) yr\(^{-1}\) from its Telbal-Dachigham sub-catchment. Maximum saturation levels of lake waters were observed from mid spring through summer, and were concomitantly brought about by Ca\(^{2+}\) loading of 4169 tonnes (59.4% of total loading yr\(^{-1}\)), high temperatures and photosynthetic activity of dense macrophyte biomass (3.2 kg m\(^{-2}\)). Increase in the saturation level of lake waters during spring-summer period was observed to be a linear function of water temperature (\(r = 0.85, p <0.05\)) and hydraulic residence time (\(r = 0.93, p<0.05\)). Increase in the saturation levels of lake waters were observed to bring significant reductions in Ca\(^{2+}\) (\(r = -0.88, p<0.05\)) and PO\(_4\)-P (\(r = -0.93, p<0.05\)) through Ca-P precipitation. This loss of Ca\(^{2+}\) and PO\(_4\)-P was also confirmed by observing high retention of 2021.5 tonnes of Ca\(^{2+}\) yr\(^{-1}\), out of which about 1450 tonnes i.e. 72% flux was estimated during peak saturation levels. Keeping in view, the role of Ca\(^{2+}\) in lake management, this paper therefore, describes Ca\(^{2+}\) transport from various sub-catchment and inter alia interactions of Ca\(^{2+}\), macrophytes, PO\(_4\)-P, temperature, and hydraulic residence within the lake system. The sequence of these interactions is used for suggesting management options for the lake.

Keywords: Calcium, catchment exports, hydraulic residence, macrophytes, management, ortho-phosphate, saturation index, temperature

INTRODUCTION

Calcite precipitation either occurring naturally in hard water lakes or resulting from biogenic processes (Koschel et al. 1983; Stabel 1986; Thompson et al. 1997) has been considered as a self cleansing mechanism in lakes as it results in precipitation of phosphorus (P) with calcium (Ca\(^{2+}\)) (Rossknecht 1980; Koschel et al. 1983; Murphy et al. 1983), and consequent control of phytoplankton biomass production (Otsuki & Wetzel 1972; Solim & Wanganeo 2007). Development of eco-technologies based on naturally occurring calcite precipitation has a greater applicability for the restoration of eutrophic lakes. Although artificial calcite precipitation has been introduced as an eco-technological measure in a number of lakes (Cook et al. 1993) to control P concentrations and consequent phytoplankton blooms, yet, the effects have remained short-lived. Therefore, exploring feasibilities to enhance calcite precipitation in hard water lakes can prove a vital eco-technological tool in eutrophication control programme.

Dal, a high altitude Himalayan lake undergoes natural calcite precipitation during spring-summer, and this process accounts for considerable reduction in ortho-phosphate (PO\(_4\)-P) concentrations (Ishaq & Kaul 1988, 90; Solim & Wanganeo 2007) and also controls phytoplankton biomass development (Solim & Wanganeo 2007). This paper quantifies Dal Lake's major Ca\(^{2+}\) sources, describes the factors influencing calcite precipitation, and suggests the possibilities of utilizing the naturally occurring calcite precipitation in the lake as a tool for eutrophication control.

METHODS

Study site

Morphometric characteristics of Dal Lake are given in Fig. 1. Dal Lake is an urban, shallow eutrophic lake.
situated within Srinagar city of India. The lake is known for its tourist attraction in Asia, besides, also serves portable water, fish, vegetables, swimming and navigation purposes to the local population. The lake is divided into three basins i.e. Hazratbal, Bod-Dal and Nigeen. A large area of the lake (2.4 km$^2$) is covered by floating gardens, which are indigenously developed land masses used for vegetable cultivation. Solim and Wanganeo (2007) had reported that during growth season, dense macrophyte stands are the key factors for controlling phytoplankton biomass development in the lake. The authors had reported low chlorophyll $a$ [Chl $a$] (6.4 - 25.7 mg m$^-3$; avg. 14.1 ± 7.4 mg m$^-3$) values in the lake resulting from twin control mechanisms: (1) relative nitrogen deficits (lake water NP ratio of 2.1:1) induced by nitrogen uptake by macrophytes and (2) biogenic calcite precipitation.

Total catchment area of the lake is 337 km$^2$, and this is mainly comprised of five sub-catchments: (1) Telbal-Daghicham, (2) Srinagar Centre, (3) Srinagar North, (4) Lake Hillside, and (5) Lake Interior. Telbal-Daghicham is the largest (234 km$^2$) sub-catchment, and its drainage areas mainly feed the perennial Daghicham stream, which splits into four smaller streams in its lower reaches: (1) Boutkul, (2) Telbal, (3) Pishpuw, and (4) Meerakshah.

Figure 1: Base map of Dal Lake and its morphometric characteristics
These streams enter Hazratbal Basin of Dal Lake from the north-northeast. Lake interior sub-catchment is a unique nutrient source within the lake body itself. It inhabits a population of about 40,000, which live on hamlets and in permanently anchored boats. Dal Lake has two outlets, which drain the lake from its southern and western sides (Fig. 1).

**Sampling programme**

Water samples from various sources were collected from September 1999 to August 2000. Samples from 4 streams and 2 Lake outlets were collected weekly once in a day. Sewage samples were collected from 14 input points: 7 from Srinagar Centre, 6 from Lake Hillside, and 1 from Srinagar North twice/day (morning and afternoon) fortnightly. Dal Lake was sampled at 17 sites: 5 sites in the Hazratbal Basin, 4 sites in the Nigeen Basin, and 8 sites in the Bod Dal Basin (Fig. 1). Samples from these lake basins were collected near littoral (~1-1.5 m depth) and pelagic zones (up to 6-m depth in Nigeen basin and ~ 2.5 – 3.5 m in Hazratbal and Bod-Dal basins). For vertical concentration gradients, samples were collected at surface (0.25-m depth), mid-depth, and near bottom (~ 10 cm above lake bed) with a 1-L Ruttner water sampler. Samples from these sources were transported to the laboratory for immediate analysis. All samples (unfiltered) were analyzed for Ca²⁺ (EDTA titrimetric method; Eaton et al.1995) and PO₄-P (stannous chloride-molybedate blue calorimetric method; Eaton at.al.1995).

**Hydraulic characteristics**

Stream flows and lake outflows were measured at gauged stations continuously, once daily, while as water input from sewage channels was calculated during the periods of sample collection from flow calibrated V notch weirs. Precipitation (mm) and air temperature in (°C) data were collected from the local meteorological station. Water temperature was determined with a calibrated thermister.

**Evaluation of lake parameters**

Calcium load from surface inputs was estimated by their respective flow x concentration. Annual Ca²⁺ export from each sub-catchment was then obtained by dividing the Ca²⁺ load (tonnes yr⁻¹) by the area of the sub-catchment (km²).

Saturation index (S.I.) was calculated as:

\[
\text{S.I.} = \text{pH} - \text{pHs}
\]

Where, pH = measured pH, and pHs = pH of water if it were in equilibrium with calcium carbonate (CaCO₃) at the existing Ca²⁺ ion and bicarbonate ion (HCO₃⁻) concentrations.

Retention of Ca²⁺ in the lake was estimated as a difference between Ca²⁺ Input – Ca²⁺ Output – Δ lake Ca²⁺, where Δ lake Ca²⁺ = change in Ca²⁺ content of the lake from one month to the next.

**Statistical analysis**

Two way ANOVA was carried out between surface and mixed-depth Ca²⁺ and PO₄-P concentrations to ascertain the extent of influence of calcite precipitation on vertical concentrations gradients. Except for Ca²⁺-hydraulic input and temperature-pH relationships, correlations, regressions and significance derivations of various attributes were determined for the average monthly data sets from April 2000 to August 2000. For prediction of S.I. values, Ca²⁺ load from various sub-catchments and sources was first pooled and then plotted against the average Lake S.I. values. Significance (p) levels of 0.05, 0.01 and 0.001 were reported in the regression analysis.

**RESULTS**

Total water input to Dal Lake from various sources was of the order of 195.62 x 10⁶ m³ yr⁻¹, and out of this, 163.21 x 10⁶ m³ yr⁻¹ (83.4 %) was contributed by its Telbal-Dachigham sub-catchment. This hydraulic input from Telbal-Dachigham was observed to carry a Ca²⁺ load of 5918 tonnes yr⁻¹, which also accounted for 84.3% of total Ca²⁺ loading yr⁻¹ to the lake. Maximum total Ca²⁺ loading of 4169.1 tonnes was recorded from April to August 2000, and this was brought about by corresponding hydraulic input of 125.6 x 10⁶ m³. Total water residence in the lake was estimated of 20.5 days, and out of which, 4.8 days was observed from April to August, with a maximum of 2.1 and 1.0 days being recorded in June and July, respectively. Volume weighted average Ca²⁺ mass in the lake was of the order of 513.1 tonnes yr⁻¹. Significant reductions in the Ca²⁺ mass of the lake were observed to occur from March to June. The loss of Ca²⁺ through outlets was of the order of 4987.3 tonnes yr⁻¹. Maximum losses of 951 and 784.8 tonnes of Ca²⁺ were recorded during April and May, respectively. Positive retention of Ca²⁺ was recorded in most of the months except during January and March, wherein negative flux was observed. The total flux of Ca²⁺ to sediments was 2021.5 tonnes yr⁻¹ (i.e. 28.8% of total external loading yr⁻¹). Moreover, the flux of Ca²⁺ was observed to increase progressively from April to August, and was estimated to account for 72% of the total flux yr⁻¹ (Table 1).

Mixed column Ca²⁺ concentrations in the lake was 25.9 – 49.4 (range) mg l⁻¹; 36.8 ± 8.4 (average ± 1 SD) mg l⁻¹ yr⁻¹. Minimum and maximum values in this range were observed in June and January, respectively. No significant difference (ANOVA; p>0.05) was observed
in mixed column and surface Ca\(^{2+}\) concentrations of the lake either during the entire study year or during the peak growth phase of the year i.e. from April to August. At surface, Ca\(^{2+}\) concentrations were of the order of 24.4 – 49.1 mg l\(^{-1}\); 36.3 ± 9.4 mg l\(^{-1}\) yr\(^{-1}\). Minimum Ca\(^{2+}\) concentrations of 25.4 and 24.4 mg l\(^{-1}\) were recorded in June and July (Fig. 2).

No significant difference (ANOVA; \(p>0.05\)) was observed in mixed-depth and surface PO\(_4\)-P concentrations. The mixed depth and surface PO\(_4\)-P concentrations in the lake were observed as 31 – 99.5 μg l\(^{-1}\); 64.8 ± 26.9 μg l\(^{-1}\) yr\(^{-1}\) and 22.3 – 108.9 μg l\(^{-1}\); 61.9 ± 26.9 μg l\(^{-1}\) yr\(^{-1}\), respectively. Moreover, from April to August, the mixed column and surface PO\(_4\)-P concentrations depicted similar fluctuations with values in April and May being almost similar, and thereafter decrease considerably till June, followed by progressive increase in July and August (Fig. 2).

### Table 1. Hydraulic characteristics and calcium mass balance of Dal Lake.

<table>
<thead>
<tr>
<th>Month</th>
<th>Hydraulic characteristics</th>
<th>Calcium mass balance (tonnes)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydraulic inputs (x 10(^6) m(^3))</td>
<td>Residence time (days)</td>
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<tr>
<td>-------</td>
<td>--------------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>Sept. 99</td>
<td>13.5</td>
<td>15.3</td>
</tr>
<tr>
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<td>6.5</td>
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</tr>
<tr>
<td>Nov</td>
<td>3.8</td>
<td>5.5</td>
</tr>
<tr>
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<td>4.9</td>
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</tr>
<tr>
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<td>26.6</td>
</tr>
<tr>
<td>Total</td>
<td>163.2</td>
<td>195.6</td>
</tr>
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</table>

* Average

Figure 2: Temporal variations in surface and mixed depth Ca\(^{2+}\) and PO\(_4\)-P concentrations in the lake.
Annual average surface water temperature of 16.2 °C was recorded in the lake, with a minimum of 5.6 °C recorded in February and, a maximum temperature of 25.2 °C being recorded in June. Maximum temperatures were recorded from April to August (Fig. 3), which also represents the period of minimum Ca²⁺ concentrations/mass in the lake.

The lake was observed to remain saturated with respect to calcium carbonate (CaCO₃) throughout the study year, and higher levels of saturation were recorded from April to August, with maximum saturation index (S.I.) values of 0.7 and 0.5 being recorded in June and July, respectively, (Fig. 3).

**Ca²⁺ correlates during calcite precipitation**

Calcium loading from Telbal-Dachigham sub-catchment was significantly ($r^2 = 0.77, p < 0.000$) (Fig. 4a) related to its hydraulic inputs. Ca²⁺ concentrations and Ca²⁺ mass in the lake from April to August were low in relation to the Ca²⁺ loading observed during this period (Table 1). Statistically Ca²⁺ concentrations in the lake could also not be significantly ($p > 0.05$) predicted from the Ca²⁺ loading either occurring from Telbal-Dachigham or from cumulative inputs occurring from all sub-catchments and sources. This being on account of the fact that higher levels of Ca²⁺ loading results in higher CaCO₃ saturation of lake waters, and consequent reductions in Ca²⁺ concentrations due to calcite precipitation. Accordingly, during spring-summer, saturation of lake waters with CaCO₃ was significantly predicted from Ca²⁺ loading of Telbal-Dachigham ($r^2 = 0.83, p < 0.05$) (Fig. 4b), and this was also 11% more than the predictions ($r^2 = 0.72, p < 0.05$) achieved from cumulative Ca²⁺ inputs occurring from all sources (Fig. 4c). In addition, increase in saturation levels of lake waters from April to August was a result of (1) increasing temperatures, (2) high photosynthetic activity, and (3) hydraulic residence time. Series of regression analysis showed a complex number of interactions occurring between various lake variables. From April to August, Lake S.I. values were significantly related to temperature ($r^2 = 0.73, p < 0.05$) (Fig. 4d), pH values ($r^2 = 0.74, p < 0.05$) (Fig. 4e), and hydraulic residence time ($r^2 = 0.86, p < 0.05$) (Fig. 4f). Water temperature was observed significantly related to pH values ($r^2 = 0.62, p < 0.02$) (Fig. 4g), Ca²⁺ ($r^2 = 0.95, p < 0.01$) (Fig. 4h), and PO₄-P ($r^2 = 0.87, p < 0.05$) (Fig. 4i) concentrations of the lake. The reductions observed in Ca²⁺ and PO₄-P concentrations could in turn be significantly predicted ($r^2 = 0.77, p < 0.05$) (Fig. 4j) and ($r^2 = 0.91, p < 0.05$) (Fig. 4k), respectively, from S.I. values of lake waters.
Figure 4a-k: Relationship between various lake variables: (a) Hydraulic and Ca²⁺ loading from Telbal-Dachigham sub-catchment, (b) Lake S.I. values in relation to Ca²⁺ loading from Telbal-Dachigham catchment, (c) Lake S.I. values in relation to Ca²⁺ loading to the lake from all sources, (d) Variations in Lake S.I. values in relation to water temperature, (e) Variations in Lake S.I. values in relation to pH, (f) Variations in Lake S.I. values in relation to hydraulic residence time, (g) Variations in Lake pH values in relation to water temperature, (h) Variations in Lake Ca²⁺ values in relation to water temperature, (i) Variations in Lake PO₄-P values in relation to water temperature, (j) Variations in Lake Ca²⁺ values in relation to Lake S.I. values, and (k) Variations in Lake PO₄-P values in relation to Lake S.I. values. For $r^2$ and significance ($p$) values see text.
Calcium loading of 5918 tonnes yr\(^{-1}\) from Telbal-Dachigham accounted for an export of 25.3 g Ca\(^{2+}\) m\(^{-2}\) yr\(^{-1}\), which in turn resulted in surface loading of 422.7 g Ca\(^{2+}\) m\(^{-2}\) yr\(^{-1}\) (~84% of total yr\(^{-1}\)) to the lake. This high catchment export per unit area can be attributed to highly buffered nature of catchment soils, and discharge has been observed to play an important role in the process (Fig. 4a). Ishaq and Kaul (1988) had also reported that the soils of this catchment are richly buffered and contribute to maximum levels of Ca\(^{2+}\) loading of all the sub-catchment to the lake. The higher (83%) predictability of CaCO\(_3\) saturation of lake waters from Ca\(^{2+}\) loading of Telbal-Dachigham also highlights the importance of this sub-catchment for having a major role in calcite precipitation.

The occurrence of high Ca\(^{2+}\) loading result in high within Lake Ca\(^{2+}\) concentrations and accordingly, render Lake waters saturated with CaCO\(_3\). Increase in the S.I. values from April to August was in tandem brought about by high Ca\(^{2+}\) loading, temperatures, hydraulic residence, and high macrophyte density. Solim and Wanganeo (2007) had also reported that high macrophyte density of 3.2 kg m\(^{-2}\) in the lake was responsible for triggering biogenic calcite precipitation. Temperature had an instantaneous dual in the process: (1) by directly promoting calcite precipitation as also observed from its significant relationship with S.I. values of the lake and (2) by promoting the biogenic factor i.e. photosynthetic activity. Significant relationship of temperature with S.I., pH, Ca\(^{2+}\) and PO\(_4\)-P values substantiates the viewpoint. Brunskill (1969) had considered temperature as a primary factor to stimulate calcite precipitation, while photosynthetic activity was reported to rank second. Though the lake waters remain saturated with CaCO\(_3\) through out the year, and had tendency to precipitate Ca\(^{2+}\), however, main effect of calcite precipitation was observed in remains from April to August, while in rest of the months, the effect was not pronounced to account for significant reductions of Ca\(^{2+}\) and PO\(_4\)-P concentrations. During March low water temperature is held responsible (Fig. 3), and small reduction in the volumetric value of Ca\(^{2+}\) from 630.2 tonnes in February to 621.0 tonnes in March confirms low precipitation activity. Similarly, during September, the onset of macrophyte senescence is being held responsible, and this becomes apparent by observing increase in the Ca\(^{2+}\) mass and decrease in the flux rate of Ca\(^{2+}\) in the lake during this month (Table 1). Moreover, stepwise significant regression relationships between various variables were observed from April to August, while, including values of other months destabilized the relationships.

Retention of 1449.6 tonnes (~72% of total retention yr\(^{-1}\)) of Ca\(^{2+}\) in the lake from April to August accounted for a loss 87.4 g Ca\(^{2+}\) m\(^{-2}\) yr\(^{-1}\), which is mainly being attributed to calcite precipitation.

The role of calcite in rendering P inactive as Ca-P complex was noticeable in significant reductions observed in Lake Ca\(^{2+}\) and PO\(_4\)-P concentrations. Moreover, the increasing S.I. values were observed to increase the rate of precipitation, and result in binding of Ca\(^{2+}\) and PO\(_4\)-P as Ca-P. This was confirmed by observing significant relationship of the lake S.I. values with Ca\(^{2+}\) and PO\(_4\)-P concentrations. Reductions in soluble reactive phosphate concentrations during calcite precipitation has been reported earlier also, and has been regarded as the natural cleansing process in lakes (Brunskill 1969; Otsuki & Wetzel 1972; Kelts & Hsu 1978; Scavia 1979; Rossknecht 1980; Murphy et al. 1983; Koschel et al. 1983; Yin & Johnson 1984; White & Wetzel 1985). Maximum Ca\(^{2+}\) and PO\(_4\)-P concentrations of 36.3 mg l\(^{-1}\) and 101.9 \(\mu\)g l\(^{-1}\), respectively recorded in April are in relation to the lowest hydraulic residence (0.5 days) and S.I. (0.2) values, while as substantial reduction to 25.9 mg l\(^{-1}\) and 34.2 \(\mu\)g l\(^{-1}\), respectively in June are in relation to maximum hydraulic residence time (2.1 days) and S.I. (0.7) values. Significant relationship observed between hydraulic residence and S.I. values of the lake waters substantiates the viewpoint. This reduction till June accounts for a removal of 28.8 % of Ca\(^{2+}\) and 66.5 % of PO\(_4\)-P from the water column, and highlights the importance of hydraulic residence in calcite precipitation, and that of latter in regulating the nutrient balance of the lake. Calcite precipitation has a significant role in the nutrient budgets and has been reported in a number of cases (Rossmann 1980; Rossknecht 1980; Murphy et al. 1983; Stabel 1986).

**Management Implications**

The naturally occurring high % reduction in PO\(_4\)-P concentrations of lake waters signifies the importance of calcite precipitation in regulating P concentrations in the lake. The governing factors i.e. temperature, macrophyte density and hydraulic residence time, accordingly become viable tools for achieving maximum possible reductions in P concentrations. Although temperature is an unpredictable variable, however, determination of: (1) macrophyte density, which is acceptable for the lake in terms of minimum nutrient pool additions to sediments on their senescence and (2) hydraulic residence time which is acceptable for the lake as greater stagnation can increase the rate of internal TP loading, will help in developing a natural eco-technology for Dal Lake eutrophication control.
Solim and Wangen (2007) had reported Dal Lake as a high input regulated system, subjected to external and internal TP loading of ~5 and 1 g m⁻² yr⁻¹, respectively, with an average mixed-column Lake TP concentration of 296.8 µg l⁻¹ yr⁻¹. The internal TP loading was reported to co-occur during the periods (i.e. from April to July) of calcite precipitation in the lake. In addition, municipal sewage inputs contribute 12.5 x 10⁶ m³ of hydraulic inputs to the lake and an associated TP load of 18.2 tonnes yr⁻¹ (Solim S. U., Dove P. M. and Hochella M. F. Jr. (1993) Calcite foster the rate of CaCO₃ precipitation as per the basis. While as determination of permissible precipitating tendency of the lake waters on a long term rate of P elimination through enhanced calcite and sewage input, calcite precipitation is still taking place in the lake to account for significant reductions in PO₄-P concentrations. Therefore reduction in the P and organic loading to the lake is expected to increase the rate of P elimination through enhanced calcite precipitating tendency of the lake waters on a long term basis. While as determination of permissible macrophyte biomass and hydraulic residence time can be utilized as natural eco-technological measures to foster the rate of CaCO₃ precipitation as per the requirements.

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