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Swan Lake Reviews

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Memo

Subject: Calcium Peroxide and Biochar Proposals - Review

I have completed a technical review of proposals prepared for the Friends of Swan Lake Park (FSLP) to study the potential for using calcium peroxide and biochar to help address water quality issues in Swan Lake, including:

1. Calcium Peroxide: *Development of a Scope of Work for Research into Water Quality on Swan Lake*, prepared by Barbara Siembida-Lösch (Fleming College Centre for Advancement of Water and Wastewater Technologies)

This project proposes to perform laboratory-scale testing of chemical oxidation to increase dissolved oxygen (DO) concentrations in Swan Lake using calcium peroxide (CaO_2). The experimental design involves the comparison of water and sediment quality in a control tote and a treatment tote over a 4 to 6-week incubation period. The totes would be filled with surficial sediments (top 40 cm) and water collected from Swan Lake, with granular-grade CaO_2 added to the surface of the sediments in the treatment tote. Water and sediments would by analyzed for a comprehensive suite of water quality parameters to evaluate the effectiveness of the treatment to increase DO over time and changes in other key variables of interest including nutrients (phosphorus and nitrogen), metals, and pH.

2. Biochar: *Research Into Removal of Nutrients and Chlorides from Swan Lake,* prepared by Rama Pulicharla and Satinder K. Brar (York University), May 2, 2022.

This project proposes to develop and test biochar as an adsorption technology to remove nutrients (nitrogen, phosphorus, and chloride) from Swan Lake water. The experimental design includes monitoring and characterization of Swan Lake water over one month and a series of laboratory experiments to identify critical parameters to achieve optimal nutrient adsorption efficiency and determine potential of using biochar at scale for Swan Lake.

To support the review of the proposals, other related documents were reviewed including:

- *Literature Review of Potential Engineering Solutions for the Restoration of Swan Lake*, Report prepared by Barbara Siembida-Lösch, Fleming College, for Friends of Swan Lake Park, February 2021
- Memo from Gertrud Nürnberg, Freshwater Research (FWR) to Rob Grech, City of Markham dated 2021-04-08 (revised) regarding the *Evaluation of the recommendations by the Friends of Swan Lake Park, as summarized in an e-mail by Markham staff on March 25, 2021*

Review Comments – Calcium Peroxide Proposal

Rationale for Study

The proposal provides a review of background research on the use of CaO_2 as an oxygen release compound citing multiple research papers that document improved DO concentrations in surface water and sediments, as well as evidence for additional benefits including reduced organic matter in surface sediments, reduced phosphorus release from sediments, and precipitation of phosphate from water. The review also cited research on the need to modify the CaO_2 to cause the product to sink, release oxygen more gradually, and reduce high pH caused by the dissolution of CaO_2 in water.

Apart from one study on a pond in Finland, all the cited research was based on laboratory scale investigations and on water and sediment from "black water" waterbodies in Asia. These black water waterbodies are urban streams that receive domestic sewage and have exceptionally high concentrations of nutrients and bacteria which give the water its black colouring. The water and sediment quality of black water waterbodies differs substantially from that of Swan Lake, and therefore the cited research does not assess the feasibility of using CaO_2 at Swan Lake to increase dissolved oxygen (DO). The proposed research, therefore, would be needed to advance the understanding of the potential treatment capabilities of CaO_2 in Swan Lake, if warranted following ongoing measures that have increased DO concentrations.

Experimental Design, Chemistry and Potential Impacts

Overall, the proposed scope of work is well designed and is a common approach used to evaluate chemical treatments in a laboratory experiment. I offer the following comments on potential limitations of the proposed research and recommendations for consideration to improve the experimental design.

1. The study proposes to collect 1000 L of surface sediment (top 40 cm) from Swan Lake that will be transferred to two totes for the experiment. Mixing of the sediments during collection and transfer to the totes would homogenize spatial differences in sediment quality but would also alter the vertical sediment structure which could influence the results of the experiment with implications for the expected response of the treatment if it were to be applied to the lake. The geochemistry of Swan Lake sediments varies with depth from 0-10 cm as illustrated in the sediment quality/phosphorus fractionation analysis by Freshwater Research (2021). The sediment collection method would likely cause the loss of the highly flocculant and organic sediments at the sediment water interface in the lake. Furthermore, geochemical differences in the sediments at various depths due to previous chemical treatments [Phoslock® and polyaluminum chloride (PACL)] would be destroyed. As the CaO_2 will be applied to the sediment surface, the altered sediment characteristics due to mixing during sample collection may influence the results of the study.

   An alternative study design could be to collect the samples with sediment core tubes and to perform the experiment on the undisturbed sediments in the tubes. This approach, however, may limit the volume of sediment and water needed to perform the full suite of chemical analyses that is proposed. Core tube incubation studies could also be done alongside the totes with the analysis of a reduced set of parameters to document potential differences between the intact and mixed sediments.

2. Granular grade CaO_2 will be applied to the surface of the sediments in the totes. Calcium peroxide increases pH when added to water, which may have unintended consequences for aquatic toxicity and increased internal phosphorus loading.

   – Swan Lake has elevated pH that has exceeded the Provincial Water Quality Objective of 8.5, in part due to high photosynthetic activity of algae. A further increase in pH can therefore be detrimental to aquatic life.

   – Aluminum (Al) and lanthanum (La, in Phoslock) form a stable bond with phosphorus in sediment and water that is not sensitive to anoxia, but dissolution of these compounds occurs at high pH. Aluminum can be mobilized at a pH ~>8.5 (Reitzel et al., 2013) and the phosphorus adsorption capacity of lanthanum decreases at a pH >9 (Ross et al., 2008). Increasing pH at the sediment-water interface with the addition of CaO_2 could promote this dissolution causing the release of phosphorus from the sediments and potential toxicity due to dissolved aluminum (and other pH sensitive metals). Furthermore, the potential for mobilization of these metals at high pH is increased in shallow lakes that are prone to sediment resuspension like Swan Lake. The mixing of the sediments and the resultant dilution of La and Al in the proposed experimental design may mask the potential negative effect of the treatment on the phosphorus binding capacity from previous chemical treatments in the lake.

- Using a modified CaO_2 product that buffers pH may be appropriate for the experiment to avoid potential issues with high pH.

3. Calcium peroxide is a strong oxidant. When added to water, it dissociates to produce oxygen gas (O_2) that could help to prevent anoxia. While the dissociation of CaO_2 directly produces O_2, it may also produce H_2O_2 (peroxide):

$$CaO_2 + H_2O \rightarrow Ca(OH)_2 + \tfrac{1}{2}O_2 \qquad \text{(Equation 1)}$$

$$CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2O_2 \rightarrow Ca(OH)_2 + H_2O + \tfrac{1}{2}O_2 \qquad \text{(Equation 2)}$$

- Peroxide at the sediment surface could negatively impact the microbial community. Bacteria are highly susceptible to oxidation by peroxide, which is why peroxide has been used as an algaecide to treat cyanobacteria blooms. Heterotrophic bacteria play an important role in aquatic ecosystems, thus changes in the abundance or composition of microbial communities could potentially affect biogeochemical cycles, nutrient availability, and water quality. At high concentrations, peroxide can also potentially affect benthic invertebrates and zooplankton.
- Peroxide would degrade organic matter in the sediments, which would release phosphate. It is not clear from the research presented in the background review whether or not the calcium hydroxide ($Ca(OH_2)$) released by the CaO_2 dissolution would be sufficient to bind the phosphorus that is released.
- It is noted that peroxide production by the dissolution of CaO_2 declines as pH (and temperature) increases, therefore if a buffered CaO_2 is used to prevent potential toxicity and nutrient release at elevated pH, higher concentrations of peroxide could be generated with negative impacts on aquatic biota.

4. The dosage that will be used in the experiment has not been well defined with a proposed dosage of 100 g CaO_2/m^2 or 1000 g CaO_2/m^2. These doses appear to be based on the background research projects on sediments and water from black water waterbodies, which may not be appropriate for use in this experiment. Calculations using oxygen demand of the sediments and water in Swan Lake, or jar tests may be helpful to determine dosages specific to Swan Lake.
5. High phytoplankton concentrations in Swan Lake can cause large diurnal changes in pH and dissolved oxygen of the water and contribute to the deposition of organic matter to the sediments as cells die and sink to the bottom. These effects could affect the dosage and efficacy of the CaO_2. Swan Lake also undergoes mixing that can cause sediment resuspension, potentially causing the CaO_2 granules to become suspended or redistributed, which would also affect dosage and efficacy. The study design cannot account for the effects of phytoplankton, mixing and sediment resuspension, and other lake processes that vary over time, supporting the need for future study if the results of this project are positive.

The proposal includes optional bench-scale testing to determine the different phosphorus forms that are present in the sediments, through a bioavailable phosphorus assay (or phosphorus fractionation). In 2020, multiple lake cores were collected from Swan Lake, and this analysis was performed at a laboratory in Germany (Freshwater Research, 2021). The results of this study were then used to determine the necessary dosages for the chemical treatment of the lake in 2021. It would be preferred if the researchers at Fleming College could conduct this analysis in the future, rather than sending core samples to Germany. The next chemical treatment is scheduled for 2024, and there is likely to be minimal sediment accumulation since the previous analysis. Therefore, repeating the analysis before the 2024 chemical treatment would not yield much benefit. The 2020 cores showed that La from the Phoslock treatment in 2013 was mostly present in the upper 5 cm of the sediment cores, indicating an accumulation of only ~5 cm of sediment over seven years. The mobile sediment fraction in the recently deposited sediments (~2.5 cm) for dosing requirements in 2024 could be approximated using the 2020 results.

General Comments and Recommendations

The proposed scope of work has technical merit, and the study would help to advance the understanding of the capability of CaO_2 to increase DO in water from Swan Lake. While the research would answer many questions about the treatment potential of CaO_2, it is anticipated that additional study will be required to fully understand the advantages of the treatment and potential negative effects on aquatic biota and nutrient cycling before this product could be considered for full scale use at Swan Lake. The additional research may include more laboratory-scale testing and lake mesocosm studies. The latter would likely be needed to account for the complex physical, chemical, and biological processes in Swan Lake that could affect, or be altered by, the treatment, and the lack of such studies in other similar waterbodies. This means that it could be some time (several years) before all the necessary research is completed and enough data could be gathered to support the use of CaO_2 in Swan Lake.

A key consideration for the feasibility of using CaO_2 in Swan Lake is its impact on prior and future chemical treatments involving Phoslock and/or PACL. The previous chemical treatments were highly successful in decreasing total phosphorus levels in Swan Lake, and the binding of phosphorus by La and Al in the sediment remained stable under anoxic conditions, which reduced internal phosphorus loading from the sediment. However, as previously mentioned, the high pH generated by CaO_2 may cause the release of previously immobilized phosphorus in the sediment. While the proposed experiment will provide some data on the pH effects at the tested CaO_2 dosage, core incubation studies and/or lake mesocosm studies would be necessary to confidently assess the potential mobilization of La and Al-bound phosphorus from the previous chemical treatments in the lake.

The proposal correctly notes that anoxia is a primary driver of internal phosphorus loads from sediments such that preventing anoxia through chemical oxidation could help to reduce phosphorus concentrations in the lake. Following the PACL application in 2021, however, anoxia was not detected during the City's water quality monitoring in 2022, and water column DO concentrations were improved over pre-treatment conditions to above water quality minimum guidelines for the protection of aquatic life on all but two sampling events. It is possible that anoxia develops at night due to respiration of algae or during extended periods of calm weather that were not captured by the monitoring. The City plans to install continuous data loggers to document the occurrence of anoxia more fully. If oxygen levels/anoxia is not problematic, or only occasionally problematic, then chemical oxidation using CaO_2 may not provide substantial benefit. As the City continues to implement nutrient reduction strategies, it is anticipated that DO issues will continue to decline as algae levels are reduced over time. It should also be recognized that anoxia is not the only driver of internal phosphorus loading. Decomposition of newly deposited organic matter to the sediments by bacteria (or degradation by peroxide) can also cause the recycling of phosphorus.

If the ongoing efforts to improve DO concentrations fail to meet the approved targets, and if the City decides to move forward with the proposed scope of work, it is recommended that the study consider a core tube incubation approach instead of, or in addition to, the tote reactors. Also, initial jar testing or other bench-scale test could be completed before moving forward with the experiment to first determine the potential impacts of the CaO_2 on pH at the dosages needed to produce enough oxygen to prevent anoxia in the Swan Lake water. If elevated pH is found to be problematic, then the researchers could consider a buffered CaO_2 product for testing.

Review Comments – Biochar Proposal

Rationale for Study

The research proposal's introduction presents a summary of nutrient pollution, its sources, and its impact on water quality, emphasizing the need for the development of innovative technologies to reduce nutrient pollution. However, biochar is not described and only one refence is provided on the use of biochar, and it was a lab-scale study that examined nitrogen and phosphorus removal by magnesium-amended biochars. A rationale for the potential use of biochar to remove chloride was not provided.

Biochar is a type of charcoal that is produced by heating organic material, such as wood, municipal sludge, or agricultural waste, in the absence of oxygen at high temperatures. It is known to have a range of beneficial effects on soil health, including improving nutrient retention and reducing soil erosion, and for removing a variety of contaminants such as volatile organic compounds, heavy metal ions, pesticides, pharmaceuticals, dyes, and polycyclic aromatic hydrocarbons from soils and wastewater (Qiu et al., 2022).

There is a growing interest in the potential use of biochar as a management tool to address nutrient enrichment in surface waterbodies based on laboratory research documenting its ability to adsorb nitrogen and phosphorus (Jiang et al., 2019; Zhu et al., 2020; Wang et al., 2021; Qin et al., 2022; Xu et al., 2022). This research has determined that pristine biochar typically has a low capacity to adsorb phosphate, however, the adsorption capacity can be increased significantly by modifying the biochar with metal oxides of aluminum, iron, magnesium, and others. Similarly, recent laboratory testing and modeling suggest that biochar can adsorb chloride ions and the adsorption capability depends on the type and density of functional groups on the biochar surface (Phalavan et al., 2023).

Research, such as the proposed study, is needed to evaluate the effectiveness of biochar in reducing phosphorus, nitrogen, and chloride levels in surface water that considers several factors including the specific characteristics of the water source, the type and amount of biochar used, and the application method. Additionally, research will be needed to investigate potential environmental concerns such as toxicity of aging biochar and the desorption of adsorbed pollutants (Qiu et al., 2022). Biochars can contain high levels of heavy metals and free radicals that can pose a threat to the environment, which also needs to be tested before its usage (Srivatsav et al., 2020).

Experimental Design, Chemistry and Potential Impacts

Overall, the researchers have presented a well-designed experiment that will answer key questions on the use of biochar to remove nutrients. I have some remarks on the proposed study and suggestions for the experimental design for your consideration, as follows:

1. The project includes monitoring at Swan Lake (twice a week for one month) to characterize water quality. The City has been monitoring water quality at Swan Lake for several years, and the monitoring has included most of the parameters that are proposed for the study. The City's data set would provide a better representation of the variability in water quality characteristics of Swan Lake over the growing season than intensive monitoring over one month and may be more relevant to evaluate biochar treatment needs. To reduce costs, the proposed monitoring could be scaled back to capture parameters not regularly monitored by the City or to include fewer sampling events. Alternatively, the City's program could also be expanded in the proposed study year to fill in data gaps, if necessary.
2. The study proposes to analyze nitrogen, phosphorus, and chloride, in the Swan Lake water and in the influent/effluent of the lab-scale filter experiment. The analytical methods for these parameters, the nitrogen and phosphorus species to be analyzed, and the laboratory detection limits were not provided. It is recommended that the analysis include total phosphorus, soluble reactive phosphorus, ammonia-N, nitrate-N, nitrite-N and total Kjeldahl nitrogen which are relevant to eutrophication, with methods and detection limits suitable for lake water.
3. The proposed biochar testing methods (characterization, dosing, and column tests) have been used previously by Dr. Brar for similar research projects that have been published in peer-reviewed scientific journals, providing confidence that the project will provide the data needed to answer the proposed research questions. However, for the lab-scale filter test, Swan Lake water samples will be spiked with nutrients (N, P, Cl^-), which is reasonable to test the biochar performance at higher nutrient concentrations that could occur in the Lake. The proposed concentrations (1 – 10 mg/g), however, are exceptionally high and not representative of the concentrations in Swan Lake. It is recommended that the test be run on Swan Lake water without nutrient spiking and spiked with a much lower concentration of nutrients. While it is understood that the goal of this test is to determine the normalized concentration (i.e., % removal efficiency)

which can be done with high spiked concentrations, the removal efficiency of the biochar may be different at the lower concentrations observed in lake water. It is also noted that the test may not determine the removal efficiency of different nitrogen and phosphorus compounds, depending on the spike compounds, which could have implications for assessing its effectiveness for application in a lake setting.

4. The aim of the research project is to examine the effectiveness of biochar on Swan Lake water. However, for potential future applications, it may be pertinent to also conduct the test on stormwater runoff to the lake, particularly if the biochar is shown to effectively remove chloride. Removing chloride before it enters the lake during high chloride loading events, such as the spring thaw, would be highly beneficial in preventing elevated chloride concentrations in the lake.
5. Biochar can contain heavy metals that if released in water, could pose a concern for environmental toxicity. The biochar characterization and adsorption capacity tests could include analysis of heavy metals to evaluate the potential for metals release to water.

General Comments and Recommendations

The proposed scope of work is well designed, and the results of this research would be valuable to determine the effectiveness of the biochar product to remove nutrients under real water conditions at Swan Lake. The researchers have rightfully pointed out that this type of study is necessary before conducting pilot or field-scale experiments or contemplating the product's full-scale application in a lake. If the results indicate good nutrient removal capability of the biochar, additional research could lead to the development of a valuable lake management tool. This is especially the case for chloride removal as there are presently no cost-effective and feasible technologies to remove chloride from freshwater bodies.

If the City decides to move forward with the proposed scope of work, it is recommended that the project be revised to study both the lake water (to remove existing chloride) and runoff (to control runoff input). Furthermore, it would be of interest to include a desorption test to evaluate the potential for the release of nutrients, metals, or other contaminants of concern from the biochar with aging in Swan Lake water and stormwater.

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