

## Communication

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# Phosphorous runoff risk assessment and its potential management using wollastonite according to geochemical modeling

<https://doi.org/10.1515/opag-2019-0075>

received August 27, 2019; accepted November 1, 2019

**Abstract:** Loss of phosphorus from agricultural land through water runoff causes serious detrimental effects on the environment and on water quality. Phosphorous runoff from excessive use of fertilizers can cause algal blooms to grow in nearby water systems, producing toxins that contaminate drinking water sources and recreational water. In this study, a risk analysis of the algal toxin microcystin-LR and the mitigation of phosphorus from agriculture runoff is discussed. A risk analysis was performed on the algal bloom toxin microcystin-LR considering the Lake Erie algal bloom event of 2011 as a case study. Toxicity risk analysis results show that relatively low concentrations of microcystin-LR compared to recent case studies pose an acute health risk to both children and adults, and a significant increase in the risk of developing cancer is suggested but subject to further study given the assumptions made. This study investigated the potential of using wollastonite to mitigate phosphorus pollution, considering thermodynamic conditions of a constructed wetland receiving influent water from agriculture runoff, by using geochemical modelling. Geochemical modelling results show that wollastonite can react with phosphorus and capture it in the stable mineral form of hydroxyapatite, offering a possible strategy for risk mitigation of phosphorous runoff. A removal efficiency of 77% of phosphorus using wollastonite is calculated with the help of geochemical modeling.

**Keywords:** Phosphorus runoff; Risk assessment; Algal toxin; Constructed wetland; Geochemical modeling

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## 1 Introduction

The occurrence of cytotoxic algal blooms is an increasing concern globally as the use of fertilizers increases (Fromme et al. 2007). Eutrophication, or the abnormally high richness of nutrients in a water source, is a main contributing factor to algal bloom growth. Cyanobacteria and blue-green algae (hereafter referred to as simply “algae”) can form large colonies known as “blooms” when stimulated by favourable growth conditions or eutrophication as a result of fertilizer runoff from agricultural application (Michalak et al. 2013). In Ontario, the incidence of algal blooms has increased significantly in recent decades (Winter et al. 2011). The algal blooms have the capacity to produce large quantities of diverse toxins, which can contaminate drinking water sources and can also pose a health hazard through recreational water activities by incidental ingestion and skin absorption (Koreivien et al. 2014).

Phosphorus fertilizers have been linked to increased incidence and severity of algal blooms by decreasing the N:P ratio, favouring growth of algae (Smith 1982). Numerous studies on mitigation strategies of reducing the amount of phosphorous from wastewater have been conducted, with several using industrial by-products like furnace slags, fly ash and natural minerals to capture the phosphorus. Calcium silicate slags are also used widely as a silicon source in agricultural applications (Chimney et al. 2007). In principle, phosphorous release may become trapped and reduced through chemical transformation of soluble phosphorous to the form of stable minerals such as hydroxyapatite (Brooks et al. 2000).

It is not known whether wollastonite ( $\text{CaSiO}_3$ ), which is a calcium silicate mineral, can reduce the amount of phosphorus in agriculture runoff. Wollastonite is a mineral mined in the Canadian province of Ontario, which faces algal bloom problems in several water bodies. This study investigated the use of wollastonite as a mitigation tool for reducing phosphorous from agriculture runoff assuming sedimentation within a constructed wetland,

and thus reducing risks to human health from algal bloom events. Geochemical modelling was used to simulate the wollastonite phosphorous run off mitigation strategy. Geochemical models are equilibrium models which can be very useful tools to understand the speciation and solubility of elements in matrixes like ash and soil, which can help us to understand how changing environmental conditions (e.g. pH, elemental concentrations or number of complexing surfaces) effect the mobility of trace elements. Furthermore, they can be used in evaluation of possible remediation strategies or risks associated with different management scenarios (Sjöstedt *et al.* 2018). The Geochemists Workbench uses a thermodynamics database to calculate chemical equilibriums and speciation of minerals.

## 2 Methodology

For the purpose of this study, health risks were assessed from the standpoint of a contaminated drinking water source as the result of an algal bloom. The symptoms of toxicity from most algal bloom toxins mimic that of common water pathogens, such as gastrointestinal problems, and therefore algal bloom toxins are usually overlooked until all other possible causes of a health crisis are ruled out, often long after an algal bloom event has occurred (Falconer and Humpage 2005). Therefore, it was assumed in the risk assessment that once an algal bloom event occurs, no water treatment mitigation strategies will be employed to reduce the concentration of toxins in the water. An individual has been assumed to be ingesting untreated water as a result of dietary or recreational activities, which contains a certain concentration of toxin.

Most algal bloom toxins have both acute toxicity and exhibit carcinogenic properties (Falconer and Humpage 2005). If the use of a phosphorous runoff mitigation strategy decreases the size of toxic algal blooms, acute toxicity risk would be lowered. The analysis becomes more quantitative from a mitigation standpoint when considering the carcinogenic properties of many algal bloom toxins, where the concentration of algae in a water source can be lowered through reducing phosphorous runoff, therefore lowering exposure to the carcinogen and lowering cancer risk. Toxicity calculations were performed using Equations 1-4.

**Equation 1.** Intake of toxin from drinking water

$$Intake = \frac{C_{toxin} \times IR \times EF \times ED}{BW \times AT}$$

$C_{toxin}$  = concentration of toxin in water

$IR$  = intake rate, assumed to be 2 L/day for treated drinking water

$EF$  = exposure factor, residential, assumed to be 350 days/yr

$ED$  = exposure duration (yrs)

$BW$  = body weight, assumed to 70 kg for an adult, 15 kg for a child

$AT$  = averaging time

**Equation 2.** Hazard Quotient (HQ)

$$Hazard\ Quotient = \frac{CDI}{RfD}$$

$CDI$  = chronic daily intake as determined from summing Equation 1 from all sources

$RfD$  = reference dose

**Equation 3.** Incremental excess lifetime cancer risk

$$IELCR = Intake \times CSF$$

$IELCR$  = incremental excess lifetime cancer risk

$CSF$  = cancer slope factor

**Equation 4.** Cumulative target risk of cancer

$$CTR = IELCR_1 + IELCR_2 + \dots IELCR_n$$

$CTR$  = cumulative target risk of cancer

$IELCR$  = incremental excess lifetime cancer risk from source  $n$

The relationship between phosphorous levels and blue-green algae growth is complex and subject to many outside factors, including species of algae, temperature, salinity, bioavailability of nutrients, and latitudinal light intensity (Lukatelich and McComb 1986; McQueen and Lean 1987). However, based on several examples in the literature, it has been considered that the relationship between concentration of blue-green algae and phosphorous levels are roughly linear, given all other factors remain constant (Lukatelich and McComb 1986; Li *et al.* 2015). This relationship is shown in Equation 5. Therefore, a 10% reduc-

tion in phosphorous runoff will result in 10% fewer algae, and 10% fewer toxin, and 10% fewer risk of acute toxicity or cancer. Although this is simplified, it is a good starting point to quantify the benefit of a phosphorous runoff mitigation technique.

**Equation 5.** Relationship between phosphorous concentration and algae growth

$$C_{algae} = \alpha \times C_{phosphorous} + \beta$$

$\alpha$  = constant for an individual water source

$\beta$  = constant for an individual water source

$C_{algae}$  = concentration of algae in water source

$C_{phosphorous}$  = concentration of phosphorous in water source

The primary toxins of interest for algal blooms are microcystins, with the most potent being microcystin-LR (Hernández et al. 2009). The United States Environmental Protection Agency (US EPA) has determined a non-cancer reference dose (RfD) of 0.05 µg/kg/day for microcystin-LR (D'Anglada et al. 2015). As of this date, a cancer slope factor (CSF) has not been determined for microcystin-LR. However, there have been some laboratory scale studies in liver cell culture that have investigated carcinogenic effects (Nishiwaki-Matsushima et al. 1992). One study postulated from cell culture results that microcystin-LR is the most potent liver carcinogen discovered, and would have a much larger cancer slope factor than for those established liver carcinogens such as alpha-hexachlorocyclohexane, which has a CSF of 6.3 (mg/kg/day)<sup>-1</sup>. Drawing a direct comparison to other liver carcinogens is difficult for microcystin-LR, because the normally tested dose that results in carcinogenicity is a factor of 100-1000 times lower than other liver carcinogens such as alpha-hexachlorocyclohexane (Nishiwaki-Matsushima et al. 1992; Bradley et al. 2016). In this study, a conservative CSF of 10 times the CSF of alpha-hexachlorocyclohexane is assumed for microcystin-LR, considering differences in dosing. Therefore, the CSF of microcystin-LR has been assumed to be 63 (mg/kg/day)<sup>-1</sup>.

Geochemical modelling was performed using The Geochemist's Workbench (GWB v3.0) program to investigate the role of wollastonite for mitigating phosphorous runoff considering a constructed wetland conditions receiving agricultural influents. GWB capabilities include calculating the solubility, sorption, saturation indices and concentrations of different minerals and species at different temperatures, pressure and pH, including equilibrium and kinetic reactions (Shevalier et al. 2014).

Table 1 show the initial concentrations of species present in the sediment porewater of the constructed wetland before the addition of wollastonite. It has been assumed that there are 7 solutes (Na, K, SiO<sub>2</sub>, Ca, HCO<sub>3</sub><sup>-</sup>, Fe, HPO<sub>4</sub><sup>-</sup>), six of which are analysed with ICP-AES, and HPO<sub>4</sub><sup>-</sup> for which chemical extraction method is used. These data were obtained by using the soil composition reported by Devau et al. (2009) as the sediment solids composition and using GWB to calculate the porewater composition in equilibrium with these solids; then this porewater was used for subsequent modeling with wollastonite addition. For modelling, two possible minerals (whitlockite (Ca<sub>3</sub>(MgFe)(PO<sub>4</sub>)<sub>6</sub>PO<sub>3</sub>OH) and hydroxyapatite (Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>)) have been assumed to possibly form in the sediments of constructed wetland after addition of wollastonite (CaSiO<sub>3</sub>).

The geochemical modelling consists of several components. The equilibrium constant (K) has been calculated at 25°C to determine stability of wollastonite, hydroxyapatite and whitlockite, because the efficiency of adsorbent media is varied due to differences in mineral composition and their solubility (Uddin 2017). Different chemical reactions and their log K values were calculated using the GWB program Rxn at 25°C. It has been assumed that the constructed wetland is adjacent to the area of Lake Erie; agriculture runoff passes the small constructed wetland and then proceeds to a large water body and eventually into Lake Erie. For stability diagrams, pH was assumed to be in the range of 6-12, considering that soil (sediment) pH is often higher than 6 (Zeng et al. 2011). The GWB program Act2 has been used to determine the mineral stability/solubility by using log activity of Ca<sup>2+</sup> from -10 to 0. To measure concentrations of phosphorus before and after addition of

**Table 1:** Concentrations of sediment porewater species used as input in GWB

| Species                       | Concentration (mmol/kg) |
|-------------------------------|-------------------------|
| Na <sup>+</sup>               | 150                     |
| K <sup>+</sup>                | 0.35                    |
| SiO <sub>2</sub>              | 1.8                     |
| Ca <sup>2+</sup>              | 0.008                   |
| HCO <sub>3</sub> <sup>-</sup> | 1.8                     |
| Fe <sup>3+</sup>              | 33.7                    |
| HPO <sub>4</sub> <sup>-</sup> | 5.54                    |

wollastonite, the GWB program React was used. Removal efficiency of phosphorus was calculated using Equation 6.

**Equation 6.** Removal efficiency for phosphorous (Chen et al., 2004)

$$RE = \left[ 1 - \frac{C_e}{C_i} \right] \times 100$$

RE= Removal efficiency (%)

$C_i$  = Influent concentration (mol/m<sup>3</sup>)

$C_e$  = Effluent concentration (mol/m<sup>3</sup>)

## 3 Results and Discussion

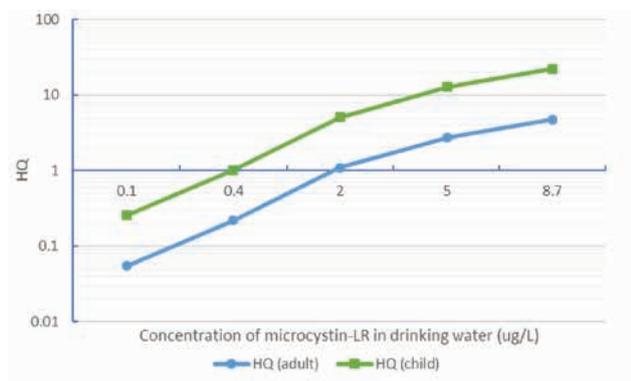
### 3.1 Risk analysis

Below are a series of calculations considering both acute toxicity and lifetime cancer risk from exposure to microcystin-LR in water. The scenarios are based on a 2011 algal bloom event in Lake Erie that caused concentrations of microcystin-LR in the range of 0.1-8.7 µg/L in water basins used for drinking water. Surface water concentrations were estimated to have reached a maximum concentration of 4500 µg/L (Michalak et al. 2013). The extremely high surface concentrations make acute toxicity calculation for recreational or accidental intake just as high, as a possible acute toxic dose for an adult “Hazard Quotient” (HQ) >1 is reached by ingesting only 0.78 ml of 4500 µg/L microcystin-LR surface water. Therefore, practically any amount of internal exposure to surface water with concentrations like that seen in the Lake Erie algal bloom exceeds acceptable risk. The length of time of one month was chosen to

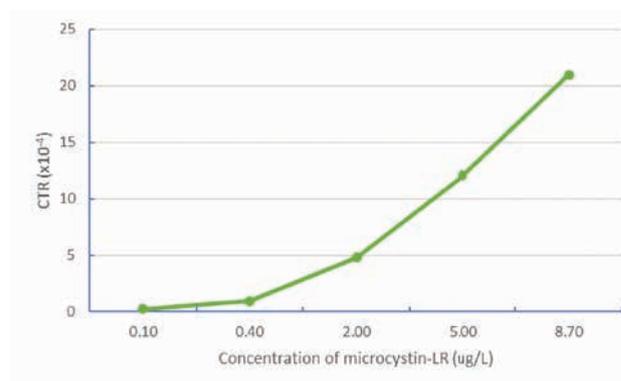
represent an estimated algal bloom event. For cancer risk calculations, a lifetime of living in an area with drinking water containing microcystin-LR has been investigated.

Acute toxicity requires further investigation when a risk assessment points to HQ values above 1.0. The results in Figure 1 show that the hazard of acute effects begin to become a significant concern (HQ > 1.0) at concentrations above 0.4 µg/L for children, and concentrations above 2.0 µg/L for adults. These levels are relatively low compared to the water maximum in the Lake Erie algal bloom event of 8.7 µg/L (Michalak et al. 2013). Calculations were based on contaminated water consumed at 2 L/day for 30 days every year to simulate an algal bloom occurring in a nearby water source. It has been assumed that an adult has a weight of 70 kg and a child 15 kg. Moreover, the calculated HQs for non-treated water containing microcystins-LR, for both children and adults, show values greater than 1.0 when considering the acceptable level of microcystins is suggested to be 1 µg/L for different water sources in household drinking water (Mokoena et al. 2016). This is very concerning and highlights the importance of mitigating health impacts, especially for children who drink water containing relatively low levels of microcystin-LR.

Figure 2 shows the cumulative target risk of cancer as a result of drinking microcystin-LR contaminated tap water as a result of an algal bloom event occurring every year throughout an entire lifetime. It has been statistically assumed that contaminated water is ingested at 2 L/day for 30 days every year to simulate an algal bloom re-occurring annually in a nearby water source. Age 0-12 were calculated as a child of 15 kg, ages 13-70 were calculated as an adult of 70 kg. A concentration of 0.4 µg/L microcystin-LR corresponds with a CTR of 1. Concentrations of microcystin-LR greater than 0.4 µg/L result in a CTR of greater than  $1 \times 10^{-4}$ , representing a significant and unacceptable risk



**Figure 1:** Hazard Quotient (HQ) for drinking water contaminated with microcystin-LR



**Figure 2:** Cumulative target risk of cancer from microcystin-LR in drinking water throughout a 70-year lifetime

of cancer that requires further investigation. This analysis is limited due to the variety of assumptions used, but it provides a good estimate at the considerable risk for cancer, as well as acute toxicity caused by the algal bloom toxin microcystin-LR. In vivo experiments have revealed that some changes in body weight, liver histology and liver enzymes can cause liver cancer due to continuous exposure to microcystin-LR at 1 µg/L in drinking water for seven months (Labine et al. 2015).

### 3.2 Geochemical modeling

Table 2 shows the equilibrium reactions for wollastonite, hydroxyapatite and whitlockite at 25°C and pH 6.5, which have been calculated using GWB. Hydroxyapatite has a lower solubility product (log  $K_{sp}$ ) value as compared to other minerals, which shows that it is a more stable mineral in relation to wollastonite and whitlockite. Log  $K_{sp}$  values also indicate potential to undergo dissolution and

precipitation mechanisms. In literature, log  $K_{sp}$  values for wollastonite and hydroxyapatite are reported as -7.60 and -58.6, respectively at 25°C (Dai et al. 2018; Sun et al. 2016). This is due to the crystalline structure of hydroxyapatite that also depends on the thermodynamic properties (i.e. pH and temperature) (Suchanek and Yoshimura 1998).

Figure 3 explains the presence of different minerals within the wetland sediment without and with wollastonite, respectively. Figure 3a shows log[a], which is the ionic activity of  $Ca^{2+}$  ions as a function of pH. It can be seen in Figure 3a that quartz is the dominant mineral in the normal pH range (pH 6-9). Beyond the normal pH range, some forms of wollastonite can be seen in the more alkaline conditions. When wollastonite is reacted, geochemical modeling shows two different mineral phases forming according to Figure 3b. In the normal pH range, whitlockite is a dominant mineral with low log activity of calcium (log[a]  $Ca^{2+}$ ) in the form of  $H_2PO_4^-$  and  $HPO_4^{2-}$ . Whitlockite is a mineral in an alternate form of calcium phosphate (Jang et al. 2014). As ionic activity of  $Ca^{2+}$  increases, the

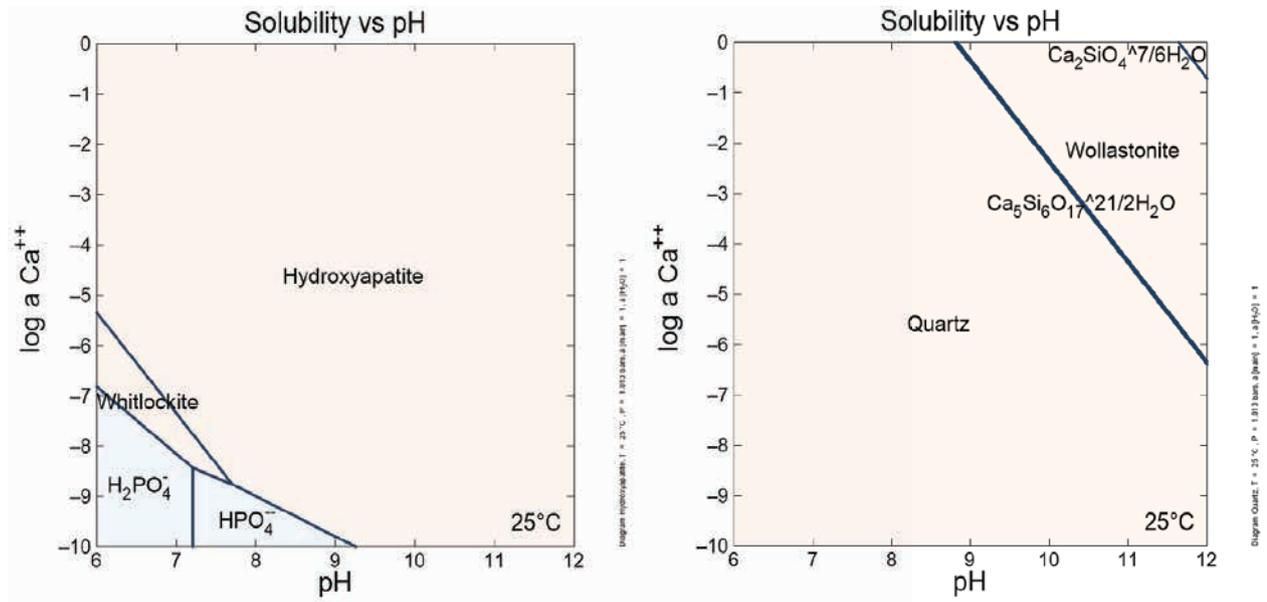


Figure 3: (a) Left: Presence of minerals in sediments without incorporation of wollastonite; (b) Right: Presence of minerals in sediments with incorporation of wollastonite. T = 25°C, P = 1.013 bar

Table 2: Equilibrium reactions for minerals dissolution and precipitation

| Minerals       | Equilibrium Reactions                                     | Temp (°C) | Log K  |
|----------------|---|-----------|--------|
| Wollastonite   | $CaSiO_3 + 2H^+ = Ca^{2+} + SiO_{2(aq)} + H_2O$           | 25        | 13.63  |
| Hydroxyapatite | $Ca_5(PO_4)_3(OH) + 4H^+ = 5Ca^{2+} + 3HPO_4^{2-} + H_2O$ | 25        | -11.53 |
| Whitlockite    | $Whitlockite + 2H^+ = 3Ca^{2+} + 2HPO_4^{2-}$             | 25        | -3.99  |

dominant mineral form is hydroxyapatite due to higher precipitation. Hydroxyapatite is a stable and dominant phase that lengthens the retention of phosphorus in the sediments. Dissolution and precipitation can also be altered with increasing or decreasing activity of  $\text{Ca}^{2+}$ . Precipitation in the form of hydroxyapatite is the main mechanism of phosphorus removal, which depends on the  $\text{Ca}^{2+}$  ion availability from the wollastonite (Dupraz *et al.* 2009). Lowering the pH can change the extent of saturation, as shown in Figure 3. Solubility highly depends on pH, temperature and ionic activity because these parameters affect the reaction path and surface morphology (Abiola *et al.* 2017).

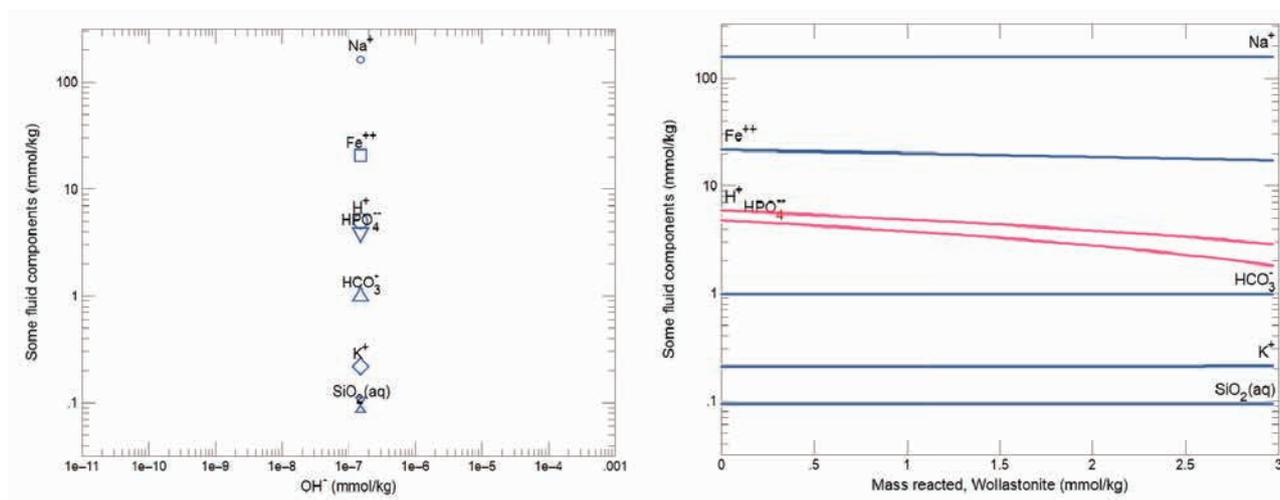
Figure 4a and 4b show initial concentrations of species present in the sediments in the aqueous form, and concentrations after amendment of wollastonite, respectively. It is evident from Figure 4b that phosphorus species and hydrogen ion concentrations decrease as the concentration of wollastonite increases. Phosphorus species are reacting with wollastonite to form the stable mineral, i.e. hydroxyapatite. The concentration of  $\text{H}^+$  is decreasing due to the alkalinity of wollastonite.

Removal efficiency for phosphorus has been calculated from Equation 6. Influent concentrations are the initial concentrations of the species in the sediments and effluent concentrations are taken from the GWB after the addition of wollastonite. Removal efficiency was calculated as 77%. For comparison, a 57% removal efficiency of phosphorus has been calculated using transport modelling in a constructed wetland in a previous study (Braskerud 2002). Also, laboratory scale tests were carried out by Brooks *et al.* (2000) in which 39%-80% removal efficiency of phosphorus by using wollastonite was observed in

columns, depending on the residence time for the wastewater treatment.

## 4 Conclusion

The risk analysis of acute toxicity and cancer risk from the algal bloom toxin microcystin-LR in drinking water is indicative of a serious threat to human health. Concentrations as low as  $0.4 \mu\text{g/L}$  microcystin-LR have been calculated to be acutely hazardous to children drinking contaminated water. An unacceptable risk of cancer is exceeded at a concentration of  $0.4 \mu\text{g/L}$  for an individual living for 70 years and drinking contaminated water for one month per year. The danger of algal bloom toxicity from microcystin-LR can be affirmed considering recent case studies in the literature. The significant public health risk of algal bloom toxins is highlighted in this report and provides a motive for implementing mitigation strategies to reduce the risk. Risk reduction can be assumed to be linear in relation to the reduction of phosphorous runoff and therefore so are algae concentration as well as eventually toxin concentration, providing a clear payoff in terms of risk reduction potential for any mitigation strategy. Geochemical modelling results show the basis of using wollastonite applied to the sediments within a constructed wetland to mitigate phosphorous runoff, highlighting the ability to capture phosphorous as hydroxyapatite in the sediments for a longer time period due to its stability. A theoretical maximum of 77% removal of phosphorous was calculated, translating to a risk reduction of 77% through the linear relationship outlined previously. This lays a



**Figure 4:** a) Left: Initial concentrations of species in sediments of constructed wetland from agriculture runoff; b) Right: Concentrations of species in sediments of constructed wetland after addition of wollastonite

solid foundation for further work analyzing the use of wollastonite-amended constructed wetlands as a mitigation strategy to prevent phosphorous runoff and therefore decrease human health risks associated with cytotoxic algal blooms.

**Conflicts of interest:** The authors declare no conflict of interest.

## References

- [1] Abiola O., Ruizhong H., Philips F., and Olugbenga O., Geochemical and Mineralogical Investigation of Kaolin Occurrence around Ugiamen Area, Southern Nigeria, *Int. J. Sci. Eng. Res.*, 2017, 8, 635–658
- [2] Bradley A.E., Shoenfelt J.L., and Durda J.L., Carcinogenicity and mode of action evaluation for alpha-hexachlorocyclohexane: Implications for human health risk assessment, *Regul. Toxicol. Pharmacol.*, 2016, 76, 152–173
- [3] Braskerud B.C., Factors affecting phosphorus retention in small constructed wetlands treating agricultural non-point source pollution, *Ecol. Eng.*, 2002, 19, 41–61
- [4] Brooks A.S., Rozenwald M.N., Geohring L.D., Lion L.W., and Steenhuis T.S., Phosphorus removal by wollastonite: A constructed wetland substrate, *Ecol. Eng.*, 2000, 15, 121–132
- [5] Chen Y., Randall A.A., and McCue T., The efficiency of enhanced biological phosphorus removal from real wastewater affected by different ratios of acetic to propionic acid, *Water Res.*, 2004, 38, 27–36
- [6] Chimney M.J., Wan Y., Matichenkov V.V., and Calvert D.V., Minimizing phosphorus release from newly flooded organic soils amended with calcium silicate slag: A pilot study, *Wetl. Ecol. Manag.*, 2007, 15, 385–390
- [7] D'Anglada L.V., Donohue J.M., Strong J., and Hawkins B., United States Environmental Protection Agency: Health Effects Support Document for the Cyanobacterial Toxin Microcystins, June 2015, EPA-820R15102
- [8] Dai, H., Tan, X., Zhu, H., Sun, T., Wang, X., Effects of commonly occurring metal ions on hydroxyapatite crystallization for phosphorus recovery from wastewater. *Water*, 2018, 10, 1619
- [9] Devau N., Cadre E.L., Hinsinger P., Jaillard B., and Gérard F., Soil pH controls the environmental availability of phosphorus: Experimental and mechanistic modelling approaches, *Appl. Geochemistry*, 2009, 24, 2163–2174
- [10] Dupraz S., Parmentier M., Ménez B and Guyot F., Experimental and numerical modeling of bacterially induced pH increase and calcite precipitation in saline aquifers, *Chem. Geol.*, 2009, 265, 44–53
- [11] Falconer I.R., and Humpage A.R., Health Risk Assessment of Cyanobacterial (Blue-green Algal) Toxins in Drinking Water, *Int. J. Environ. Res. Public Heal.*, 2005, 2, 43–50
- [12] Fromme H., Kohler A., Krause R., and Fuhrling D., Occurrence of Cyanobacterial Toxins — Microcystins and Anatoxin-a — in Berlin Water Bodies with Implications to Human Health and Regulations, *Environ. Toxicol.*, 2007, 15, 120–130
- [13] Hernández J.M., López-Rodas V., and Costas E., Microcystins from tap water could be a risk factor for liver and colorectal cancer: A risk intensified by global change, *Med. Hypotheses*, 2009, 72, 539–540
- [14] Jang H.L., Jin K., Lee J., Kim Y., Nahm S.H., Hong K.S et al., Revisiting whitlockite, the second most abundant biomineral in bone: Nanocrystal synthesis in physiologically relevant conditions and biocompatibility evaluation, *ACS Nano*, 2014, 8, 634–641
- [15] Koreivien J., Anne O., Kasperovicene J., and Burskyte V., Cyanotoxin management and human health risk mitigation in recreational waters, *Environ. Monit. Assess.*, 2014, 186, 4443–4459
- [16] Labine M.A., Green C., Mak G., Xue L, Nowatzki J., Griffith J., et al., The geographic distribution of liver cancer in Canada does not associate with cyanobacterial toxin exposure, *Int. J. Environ. Res. Public Health.*, 2015, 12, 15143–15153
- [17] Li J., Wang Z., Cao X., Wang Z., and Zheng Z., Effect of orthophosphate and bioavailability of dissolved organic phosphorous compounds to typically harmful cyanobacterium *Microcystis aeruginosa*, *Mar. Pollut. Bull.*, 2015, 92, 52–58
- [18] Lukatelich R.J., and McComb A.J., Nutrient levels and the development of diatom and blue-green algal blooms in a shallow australian estuary, *J. Plankt. Res.*, 1986, 8, 597–618
- [19] McQueen D.R.S., and Lean D.J., Influence of Water Temperature and Nitrogen to Phosphorus Ratios on the Dominance of Blue-Green Algae in Lake St. George, Ontario, *Can. J. Fish. Aquat. Sci.*, 1987, 44, 598–604
- [20] Michalak A.M., Anderson E.J., Beletsky D., Boland S., Bosch N.S., Bridgeman T.B., et al., Record-setting algal bloom in Lake Erie caused by agricultural and meteorological trends consistent with expected future conditions, *Proc. Natl. Acad. Sci. U.S.A.*, 2013, 110 6448–6452
- [21] Mokoena M.M., Mukhola M.S., and Okonkwo O.J., Hazard assessment of microcystins from the household's drinking water, *Appl. Ecol. Environ. Res.*, 2016, 14, 695–710
- [22] Nishiwaki-Matsushima R., Ohta T., Nishiwaki S., Suganuma M., Kohyama K., Ishikawa T., et al., Liver tumor promotion by the cyanobacterial cyclic peptide toxin microcystin-LR, *J. Cancer Res. Clin. Oncol.*, 1992, 118, 420–424
- [23] Shevalier M., Dalkha C., Humez P., Mayer B., Becker V., Nightingale M., et al., Coupling of TOUGHREACT-geochemist workbench (GWB) for modeling changes in the isotopic composition of CO<sub>2</sub> leaking from a CCS storage reservoir, *Energy Procedia*, 2014, 63, 3751–3760
- [24] Sjöstedt C., Löf, Å., Olivecrona Z., Boye K., Kleja D.B., Improved Geochemical Modeling of Lead solubility in contaminated soils by considering colloidal fractions and solid phase EXAFS speciation, *Appl. Geochemistry*, 2018, 92, 110–20
- [25] Smith V.H., The nitrogen and phosphorus dependence of algal blooms in lakes: An empirical and theoretical analysis, *Limnol. Oceanogr.*, 1982, 27, 1101-1111
- [26] Suchanek W., and Yoshimura M., Processing and properties of hydroxyapatite-based biomaterials for use as hard tissue replacement implants, *J. Mat. Res.*, 1998, 13, 94–117
- [27] Sun H., He S., Wu P., Gao C., Feng P., Xiao T., Deng Y., Shuai C., A novel MgO-CaO-SiO<sub>2</sub> system for fabricating bone scaffolds with improved overall performance, *Materials* 2016, 9(4), 287

- [28] Uddin M.K., A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade, *Chem. Eng. J.*, 2017, 308, 438–462
- [29] Winter J.G., DeSellas A.M., Fletcher R., Heintsch L., Morley A., Nakamoto L., et al., Algal blooms in Ontario, Canada: Increases in reports since 1994, *Lake Reserv. Manag.*, 2011, 27, 107–114
- [30] Zeng F., Ali S., Zhang H., Ouyang Y., Qiu B., Wu F., et al., The influence of pH and organic matter content in paddy soil on heavy metal availability and their uptake by rice plants, *Environ. Pollut.*, 2011, 159, 84–91