Optimal Control of Lake pH for Mercury Bioaccumulation Control

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Abstract

Mercury is recognized internationally as an important pollutant, since mercury and its compounds are persistent, bioaccumulative and toxic, and pose human and ecosystem risks. Although mercury can cycle in the environment in all media, an important aspect of this cycling is the bioaccumulation of mercury along the aquatic food chain. Mercury, in the form of methylmercury, bioaccumulates up the aquatic food chains so that organisms in higher trophic levels have higher mercury concentrations. This leads to humans getting exposed to mercury through contaminated fish consumption. Since methyl mercury is the primary bioaccumulative form of mercury, controlling the conversion of mercury in water bodies to methyl mercury is a possible option to control bioaccumulation. Since lake acidity (pH) is correlated with mercury methylation, this work proposes to reduce bioaccumulation by controlling water pH. This is to be achieved through time dependent liming strategy, derived using optimal control theory. The work incorporates uncertainty for a robust and realistic analysis. This calls for effective uncertainty modeling using stochastic processes from real options theory and efficient solution techniques using stochastic optimal control. The work also presents results for a multi-objective problem highlighting the tradeoff between good control and liming cost. The analysis is expected to make liming operation more reliable, thereby presenting one more tool to manage the harmful effects of mercury pollution.

1 Introduction

Mercury is recognized internationally as an important pollutant and is fast becoming a major concern to the environmentalists, primarily due to a better understanding of its harmful environmental and health impacts. For humans, the primary targets for toxicity of mercury and mercury compounds are the nervous system, kidney, and developing fetus. Other systems in the human body that may be affected include respiratory, cardiovascular, gastrointestinal, hematologic, immune and reproductive [1].

Mercury can cycle in the environment in all media as part of both natural and anthropogenic activities. Figure 1 gives a pictorial representation of the atmospheric mercury cycling. Majority of mercury is emitted in air, coal fired power plants being the major source. Other polluters include waste incinerators, chlor-alkali plants etc. However, most of the mercury present in air (in elemental or inorganic form) is deposited into various water bodies such as lakes, rivers and oceans. This transfer of mercury is attributed to the processes of dry and wet deposition. In addition, the water bodies are enriched in mercury due to direct industrial waste water discharge, storm water runoffs, agricultural runoffs etc. Once present in water, mercury is highly dangerous not only to the aquatic communities but also to humans through direct and indirect effects [2]. Inorganic mercury in water is converted into organic methylmercury through the process of methylation. Methylmercury accumulates up the aquatic food chains, so that organisms in higher trophic levels have higher mercury concentrations [3, 4]. The consumption of these aquatic animals by humans and wild animals further aids bioaccumulation along the food chain. As a result, contaminated fish consumption is the most predominant path of human exposure to mercury. This has resulted in fish consumption advisories at various water bodies throughout the US.

Owing to such a complex cycling, successful management of mercury pollution should consider management strategies at various stages of the cycle. While doing so, it is essential to juxtapose the environmental, economic and social objectives. One option is to restrict mercury bioaccumulation in the water bodies. Although the exact mechanism of mercury methylation is not well understood, literature based on experimental studies shows that acidic lakes (low pH lakes) have high mercury bioaccumulation rates. Hence, controlling the lake/river pH is an option to minimize harmful effects. This idea is investigated in the presented work. Since natural systems are dynamic in nature, time dependent liming is expected to result in more accurate control of lake pH. This work uses optimal control theory to derive the time dependent liming strategy. It is well known that natural systems such as lakes are not very well understood. Hence there are considerable uncertainties associated with the liming operation. To make the analysis more realistic, this work incorporates uncertainty in the analysis. This calls for effective uncertainty modeling techniques. Real options theory is used for the same. The resulting stochastic control problem is solved using the stochastic maximum principle. The work also formulates a multi-objective control problem, including the economic objective in addition to the environmental objective. The aim is to understand various tradeoffs associated with the liming operation. The work discussed here is expected to make the liming operation more reliable, thereby presenting one more tool to manage the harmful effects of mercury pollution.

The article is arranged as follows. The next section gives an overview of mercury bioaccumulation and reasons out the basis for lake liming operation. Section 3 explains the liming operation while section 4 justifies the use of a systematic approach to decide the liming strategy. Section 5 described the various forms of lake liming model, including the stochastic model which is used for further analysis. This is followed by section 6 presenting the optimal control theory aspects relevant for this problem and section 7 discussing the results for the control problem. Section 8 presents the multi-objective liming problem results and the article ends with conclusions presented in section 9.

2 Mercury bioaccumulation overview

Figure 2 represents the overall mercury cycling in water bodies such as lakes and rivers. As shown in the schematic, mercury can exists in various forms, mainly, elemental mercury (Hg), inorganic mercury (Hg(II)), organic methyl mercury (CH_3Hg) and complexes of these with dissolved organic carbon. There are number of pathways by which mercury can enter freshwater environment: Hg(II) and methylmercury from atmospheric deposition (wet and dry) can enter bodies directly; Hg(II) and methylmercury can be transported to water bodies in runoff (bound to suspended soil/humus or attached to dissolved organic carbon); or Hg(II) and methylmercury can leach into the water body from

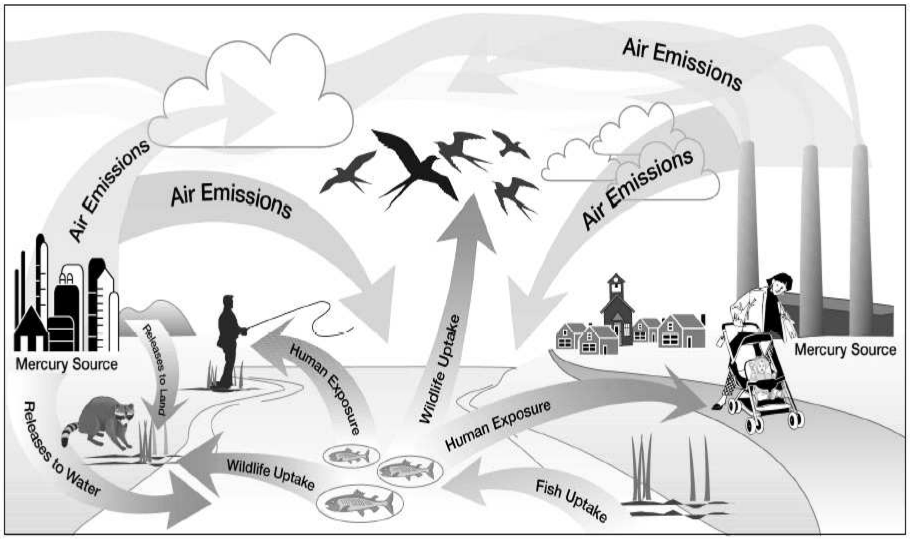

Figure 1: Environmental cycling of mercury

groundwater flow in the upper soil layers [1]. Mercury and its compounds exist in different segments of the water body such as the water column, sediment (active and passive), and the biota (fish).

Once in the water bodies, mercury can exist in dissolved as well as particulate form and it can undergo following different transformations: Elemental Hg can be oxidized to Hg(II) or volatilized to the atmosphere; Hg(II) can be methylated in sediments and water column to form methylmercury; methylmercury can be alkylated to form dimethylmercury; and Hg(II) and methylmercury can form organic and inorganic complexes with sediment and suspended particular matter. All these transformations are simultaneously observed in a given water body. The concentration of each chemical form depends on the extent of various reactions, which can differ for different water bodies.

Of the various chemical forms of mercury, methylmercury (MeHg) is considered to be the most dangerous due to the following reasons:

- All forms of mercury can be converted to methylmercury by natural processes in the environment.
- Methylmercury bioaccumulates and biomagnifies in aquatic food webs.
- Methylmercury is the most toxic form of mercury.

Owing to its high bioaccumulative potential, the concentration of methylmercury in large aquatic animals (such as predatory fishes) is many times more than the water column or sediment concentration. Generally, methylmercury fraction in a water column is not more than 25% of the total mercury content. In lakes without point source discharges, this fractions is typically less than 10% [1]. However, it has been observed that almost all of the mercury present in fish tissues is as methylmercury, confirming its preferential bioaccumulation.

"Bioaccumulation" refers to the net uptake of a contaminant from the environment into biological tissue via all pathways. It includes the accumulation that may occur by direct contact of skin

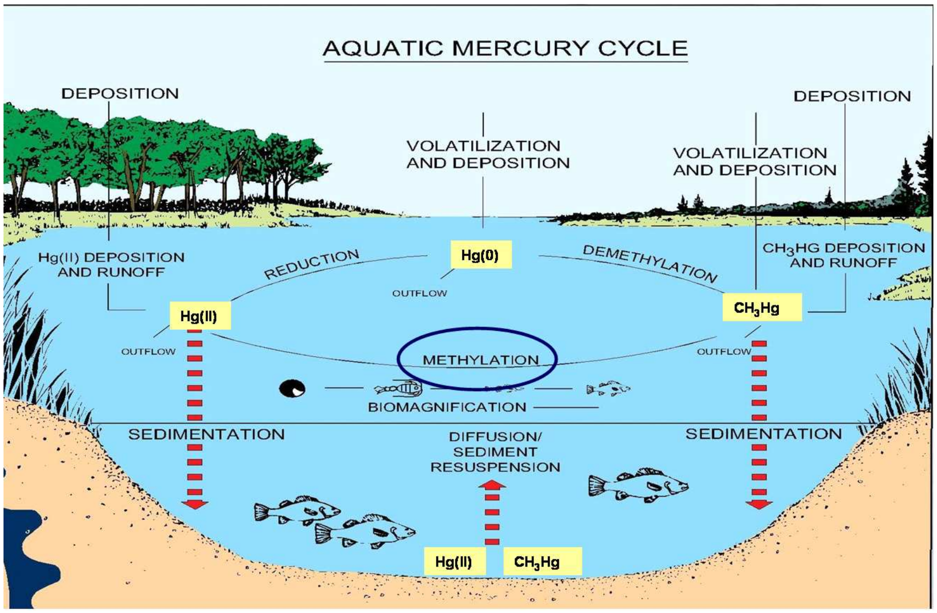

Figure 2: Mercury cycling in water

or gills with mercury-contaminated water as well as ingestion of mercury-contaminated food. “Biomagnification” refers to the increase in chemical concentration in organisms at successively higher trophic levels in a food chain as a result of the ingestion of contaminated organisms at lower trophic levels. The reason for the strong toxicity of methylmercury is its strong affinity for sulfur containing compounds (e.g. proteins). Biological membranes, including the blood-brain barrier and the placenta, that tend to discriminate against other forms of mercury allow relatively easy passage of methylmercury and dissolved mercury vapor [5]. This leads to the harmful effects that have been previously mentioned.

Thus, methylation of mercury to MeHg is a key step in the bioaccumulation of mercury in aquatic food chains [6]. The concentration of MeHg in water depends on the equilibrium between the methylation and demethylation reactions, which occur in the water column as well as the sediments. The exact mechanism of the methylation reaction is not well understood. Various mechanisms have been proposed in the literature for the formation of methylmercury. The proposed mechanisms include abiotic and biotic. Abiotic methylation includes photochemical and due to the presence of humic and fulvic acids in the solution [7]. However abiotic methylation is considered to be insignificant in most cases. Biotic methylation is due to the presence of bacteria that excrete methylcobalamine (Vitamin B_{12}) [3]. It can be enzymatic [8] as well as non-enzymatic [9]. It has also been shown that biotic methylation can take place in sediment [10] and water column [11]. It has also been proposed that sulfate reducing bacteria mediate mercury methylation [12]. This illustrates that there is considerable uncertainty over the exact methylation mechanism. Studies have also been carried out to understand the effect of physical and chemical conditions such as pH, dissolve oxygen, dissolved organic carbon (DOC), temperature, salinity etc., on methylation [10, 13]. These studies have shown a strong correlation between acidic conditions, i.e. low pH values and high mercury bioaccumulation in fish. This correlation could be due to higher concentration of bioavailable methylmercury in the ecosystems caused by altered chemical partitioning of methylmercury across the sediment water interface, increased inputs of methylmercury to lakes from the terrestrial ecosystems or precipitation, or increased in-lake production of methylmercury [10]. Even though the exact contribution of each of these factors is not accurately known, the strong correlation between pH and mercury concentration suggests a possible option to reduce mercury bioaccumulation. This idea forms the basis of lake liming operation which is described in the next section.

3 Lake liming

The process of lowering of the pH of a lake is known as lake acidification. The primary reason for lake acidification is burning of different fossil fuels (coal, oil, petrol). The resulting emissions of different types of compounds (sulphur dioxide and nitrogen oxides) oxidize in the atmosphere giving rise to the deposition of hydrogen, that is, to acidification. Acidifying substances, which are mainly S and N, are deposited on land and water as wet and dry deposition. Some other natural processes such as degradation of organic matter or weathering of base rock can also affect lake acidity. However, these are shown to be secondary in most cases. Since gases emitted due to anthropogenic activities can travel a long distance before getting deposited, acidification problem as assumed global scale.

The previous section discussed the correlation between pH and mercury bioaccumulation. There are also direct effects of the acidic conditions on lake biota. Very acidic lakes (i.e. pH below 4) are often devoid of fish, frogs, salamanders, crayfish, insects, and plankton. Certain fish types are sensitive to changes in pH and prefer lake waters with pH values ranging from 7 to 9. Because very acidic surface waters can have toxic concentrations of aluminum in solution, aquatic animals may be subjected to a potentially lethal double dose of poisonous acid and metals. Acidic conditions have also been shown to affect the reproductive processes in aquatic animals. Therefore, control of lake pH and hence its acidification can be an effective method to avoid such undesirable effects.

Although, reduction in the emission of these gases is the ultimate solution of acidification, this will be a slow process and will take time to implement. Therefore, more immediate methods need to be resorted to. One such method is lake liming. Liming is the addition of a base, such as limestone, to the water body to neutralize acid waters and soils and buffer them from rapid fluctuations in pH. Liming is an established practice with its origins in the Roman era. Soil liming has been extensively practised in the U.S. and U.K. The treatment of surface waters to control acidity (surface water liming) began in Norway in 1920s [14]. Since then, the use of liming as a mitigative techniques has been widespread in the Scandinavian countries. Approximately 8000 lakes and 6000 km of running water have been limed in Sweden during the last two decades at an annual cost of about USD 20 million. This makes liming one of the most extensive activities applied to preserve and restore threatened environments [15]. Considerable research on lake liming has been conducted in United State, Canada, United Kingdom, Finland and Sweden in the past few years, increasing the overall understanding about the liming operation.

Base treatment neutralizes acidity in surface water and increases the supply of basic cations, thereby improving water quality and fostering the presence of a broader array of organisms than found in acidic waters. The possible liming agents include: limestone minerals such as calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$), hydrated lime ($Ca(OH)_2$) and soda ash (Na_2CO_3). Limestone has been the preferred material because: (1) it neutralizes acidity without causing excessively high or rapidly changing pH; (2) it increases acid neutralizing capacity (ANC) with high buffer capacity at typical ambient pH; (3) it increases the amount of divalent cations, which are physiologically important to fish and may competitively inhibit the uptake of toxic metal ions; (4) it provides flexibility in treatment design owing to its pH solubility relationship; and (5) it is inexpensive, readily available, and usually contains few toxic contaminants [14]. In Sweden, more than 95% of liming operations are carried out using limestone and dolomite [16]. Finely ground calcite, usually less than 0.2 mm in diameter, is an effective liming agent. Porcella et al. [14] discuss the water chemistry related to lake liming operation in detail. In summary, the deacidification is due to the rapid reaction of calcite with hydrogen ions and aqueous carbon-di-oxide, increasing the pH value.

Two important questions related to liming operation are:

- What are the cost effective ways of liming?
- What are the ecological effects of liming?

The cost depends primarily on the method of liming. There are various ways to carry out liming operation: (1) direct addition of lime to the water body; (2) wetland liming, generally by helicopter, to create a smoother influence on lake pH and prolong the duration of the liming; (3) fullscale drainage area liming to influence the entire catchment area and obtain long-term effects; and (4) by dosers in the tributaries to the lake [15]. Although the last three methods often result in more effective liming, they are considerably more expensive than direct addition of lime in water. There are various options to carry out direct lime addition, such as: boat or barge, surface ice (snowmobile), shoreland (tractor), feeder stream, and air (helicopter, plane). Liming by boat or barge is the most popular liming method. Lime is usually distributed in the form of slurry which aids its dissolution leading to more immediate impact on the lake pH. The selection of a particular method often depends on criteria such as budget, accessibility to the site, weather conditions, geographical details etc.

To answer the second question, many experimental studies have been conducted to determine the effect of lime addition on aquatic biota [17, 18, 19, 20, 21, 22, 23]. Since these case studies and observations are site specific, it is difficult to make generalized conclusions about the effect of liming on lake biota. The important conclusions can be summarized as:

- Response to acidic conditions and liming is species specific. There are species that thrive on acidic conditions.
- The biomass and diversity of a particular trophic level may not always be correlated while liming [22].
- Recovery to preacidification stage might take a long time after the initial improvements.
- pH value above 6 often ensures the survival and reproduction of most species.

This information is used in the subsequent sections to formulate the lake liming problem.

4 Systematic approach to lake liming

Since liming entails considerable costs, it is essential that the liming operation is optimized so as to reduce expenses. Even though the liming technique is the major factor deciding the expenses, efficient implementation of the selected technique can reduce expenses. Previous work in this area includes [17] and [24]. Currently, most of the liming decisions are based on rule of thumb. The amount of lime to be added is decided using parameters such a lake volume, current lake pH, targeted pH, water salinity etc. [25]. These are mostly static decisions and do not take into account the dynamic nature of the natural system (lake). It is obvious that such heuristics based decisions do not maximize the benefit. An effective approach is to use time dependent liming where liming decisions (amount of lime to be added) change with time based on the current lake conditions. In engineering field, such problems are commonly solved and come under the aegis of control theory applications. Control theory has been developed with engineering applications in mind. However, natural systems also present an interesting avenue to implement these ideas. Recent examples of such applications include Shastri and Diwekar [26, 27], Ludwig et al. [28], Chukwu [29] and Kolosov [30] among others. This work proposes to use control theory to achieve time dependent liming of a lake. There are different types of control techniques that might be applicable to a control problem (e.g. optimal control, model predictive control, linearized control etc.). In this work, optimal control theory has been used. The fundamentals of optimal control theory have been well established. The main advantages of using optimal control theory are: it does not make any assumption about the structure of the controller (control law), and it theoretically works for all types of systems, including nonlinear. Due to these advantages, most of the control theory applications in natural systems use optimal control theory. The theoretical details are skipped here for brevity and interested readers are referred to texts such as Kirk [31] and Lewis [32].

There are other issues that complicate the liming operation. The primary issue is the presence of various kinds of uncertainties, such as lack of information on the exact pH of the lake, seasonal variations in lake pH, and topological effects of liming. Moreover, the spatial and temporal effects of liming on lake biota are subjective. As a result, lake liming has not been a widespread practice in north America even though it has been relatively successful in Scandinavian countries. In order to make liming implementable, one needs to incorporate these uncertainties in the analysis. Uncertainty can be of two types: time independent (static) and time dependent (dynamic). Many of the uncertainties associated with natural systems are dynamic in nature. Moreover, static uncertainties in dynamic systems can often lead to time dependent uncertainties. Hence this work will focus on incorporating dynamic uncertainty in control problem formulation.

The primary requirement to formulate and solve a control problem is a model for the liming operation. Ottosson and Håkanson [33] present a simplified deterministic model to simulate lake pH in the presence of natural inputs and liming actions. The inclusion of uncertainty in the analysis however necessitates uncertainty modeling. Real options theory has dealt with time dependent uncertain variables and proposes efficient methods to model those. The modeling basics can be found in Dixit and Pindyck [34] and Diwekar [35] and are omitted here for the sake of brevity. Environmental related applications of these stochastic modelling techniques can be found in Shastri and Diwekar [27] and Diwekar [36]. Those ideas are used here to model uncertain parameters associated with the liming operation.

The next section presents the liming model in detail. The basic deterministic model is first discussed followed by the stochastic model which is later used to formulate and solve the optimal control problem.

5 Lake liming model

5.1 Basic Deterministic model

The basic lake liming model is presented in Ottosson and Håkanson [33] and further discussed in [25] and [15]. It is a mixed model consisting of both statistical regression and dynamic interactions. An empirical model is used to predict the initial pH (mean annual pH). The model also includes a regression that predicts natural pH. In addition to these empirical submodels, the lake liming model

consists of dynamic (time dependent) interactions. It is a compartmental model with three different compartments, namely, water, active sediment and passive sediment. Accordingly, the three model variables are: lime in water, lime in active sediment and lime in passive sediment. Four continuous flows of lime connect the three compartments: sedimentation to active sediments, internal loading from active sediments to water, outflow from the lake water and transport from active to passive sediments. In addition, two flows give the inflow of lime from the liming, one to the lake water and one directly to the active sediments. The model is easy to handle since all input data can be obtained from maps and no field measurements are necessary. The necessary input parameters in the equation are: lime distribution coefficient (Dc), internal loading rate (ILR), dynamic ratio (Dr), lake water retention time (Rt), sedimentation rate (Sr) and active sediment age (ASA). These parameters are dependent on other basic lake chemical and physical properties such as: lake area, lake mean depth, lake maximum depth, lake color, lake total phosphorous concentration, drainage area, mean annual precipitation. The model variables are:
y_1: Lime in water
y_2: Lime in active sediment
y_3: Lime in passive sediment
The governing ordinary differential equations for the model are:

$$\begin{aligned} f_1 = \frac{dy_1}{dt} &= \text{Lime input}.Dc.(0.422 * 0.712) \\ &\quad + y_2.ILR.Dr - \frac{y_1}{Rt.52} - y_1.Sr \qquad (1) \\ f_2 = \frac{dy_2}{dt} &= y_1.Sr + u.(1 - Dc).(0.422 * 0.712) \\ &\quad - y_2.ILR.Dr - \frac{y_2}{ASA} \qquad (2) \\ f_3 = \frac{dy_3}{dt} &= \frac{y_2}{ASA} \qquad (3) \end{aligned}$$

The change in lake pH value is computed from the lime in water variable of the model using a logical condition given below.

$$\Delta pH = \begin{cases} log_{10}(LC + 0.01) - AC & \text{if } log_{10}(LC + 0.01) - AC > 0 \\ 0 & \text{if } log_{10}(LC + 0.01) - AC \leq 0 \end{cases}$$

where,
AC = Additive constant,
LC = Lime concentration = Lime in water/Lake volume, and
Lake pH = Lake initial pH + ΔpH

Extensive discussion of the model and its validation can be found in Ottosson and Håkanson [33] and Hakanson and Boulion [25] and hence skipped in this text. The next section explains a modification to the basic model in order to make it suitable for optimal control application.

5.2 Modified lake liming model

In the deterministic lake liming model, the computation of the lake pH from lime in water is through a logical condition. However, the presence of a logical condition is problematic in the formulation and solution of the control problem. The logical condition therefore must be eliminated, which is done here through an approximation.

The modified model assumes, for the sake of mathematical representation, that the base pH value of the lake is a result of the presence of lime in water. Any additional lime, which represents the actual lime added in the liming operation, increases the lake pH above the base pH value. A continuous function relates the lake pH value and the total lime quantity in water (which includes the lime quantity corresponding to the base pH value). The variation in pH with base concentration is often represented in chemistry literature by a well known sigmoidal function. The general equation for the sigmoidal curve is given as:

$$f(x) = Vmin + \frac{Vmax - Vmin}{1 + 10^{[log_{10}(E_{50}) - x]}} \tag{4}$$

Here, $Vmin$ and $Vmax$ are the minimum and maximum values of the dependent variable, respectively, E_{50} is the 50% value in the given range (where the steepest part of the curve is situated), and x is the value of the independent variable. It is assumed that such a sigmoidal curve governs the relationship between lake pH and lime in water (the steepest part of the sigmoidal curve being around pH 7). Accordingly, the dependent variable is lake pH while the independent variable is lime quantity in water. The pH range of interest for liming operation is take as 0-10. Thus, $Vmin = 0$, $Vmax = 10$. Let u be the quantity of lime in water, u_{max} being the maximum quantity of lime expected in water, u_{min} being the minimum quantity of lime in water (taken as zero), and u_{mean} be the lime quantity in water corresponding to the initial lake pH. The range of independent variable in the actual sigmoidal equation is $v_{min} = -10$ and $v_{max} = +10$, which corresponds with u_{min} and u_{max}, respectively and therefore $u_{mean} = 0$. The resulting pH equation is given as:

$$pH = \frac{10}{1 + 10^{[k.(\frac{u_{mean}}{u})^4.(log_{10}(E_{50}) + 10 - 20.\frac{u}{u_{max}})]}} \tag{5}$$

where, k is a tuning parameter for better approximation. The value of E_{50} is adjusted to ensure that simulation results for the approximate model matches those for the original model reasonably well. Values for u_{mean} and u_{max} will depend on the properties of the lake being limed. The lake pH is thus calculated as a function of u, and the actual lime addition is given by $u - u_{mean}$.

5.3 Stochastic lake liming model

It has been mentioned before that the lake liming operation is complicated due to the presence of various uncertainties. Natural pH of a lake varies seasonally and hence constitutes an uncertain parameter. Typical seasonal fluctuations in natural lake pH are reported in Ottosson and Håkanson [33]. The data gives fractional change in lake pH for a particular month over the annual average lake pH value. To include these variations, the modified lake pH equation is written as:

$$pH = \frac{10}{1 + 10^{[k.(\frac{u_{mean}}{u})^4.(log_{10}(E_{50}) + 10 - 20.\frac{u}{u_{max}})]}}(1 + \delta pH) \tag{6}$$

where, δpH is the fractional variation in lake pH value for that time period.

However, fluctuations represented by δpH can vary for different lakes (due to geographic location, land use practices and other geochemical properties). Determination of the exact values of δpH for each lake is not practical. Since this is a parameter that changes randomly with time, time dependent uncertainty modeling techniques can be used. A generalized representation of δpH in Eq. 6 using a stochastic process will also make the liming model flexible for application to different lakes.

In this work, mean revering Ito process is used to model δpH owing to its success in modeling various time dependent stochastic parameters [36, 27, 37]. The stochastic liming model is then represented as:

$$f_1 = \frac{dy_1}{dt} = (u - u_{mean}).Dc.(0.422 * 0.712) + y_2.ILR.Dr - \frac{(y_1 - k(4))}{Rt.52} - (y_1 - k(4)).Sr \tag{7}$$

$$f_2 = \frac{dy_2}{dt} = (y_1 - k(4)).Sr + (u - u_{mean}).(1 - Dc).(0.422 * 0.712) - y_2.ILR.Dr - \frac{y_2}{ASA} \tag{8}$$

$$f_3 = \frac{dy_3}{dt} = \frac{y_2}{ASA} \tag{9}$$

$$pH = y_4 = \frac{10}{1 + 10^{[k.(\frac{u_{mean}}{u})^4.(log_{10}(E_{50})+10-20.\frac{u}{u_{max}})]}}(1 + y_5) \tag{10}$$

$$f_{ito} = \frac{dy_5}{dt} = \eta(d\bar{pH} - y_5) + \frac{\sigma\ \epsilon}{\sqrt{\Delta t}} \tag{11}$$

Here, the parameter representing natural pH fluctuations (δpH) becomes the additional state variable (y_5), which is modelled as a stochastic process represented by equation f_{ito}. $d\bar{pH}$ is the mean value of fractional natural pH variation. The stochastic lake liming model is used further in this work to formulate and solve optimal control problem.

6 Optimal control problem

Optimal control problems require establishing an index of performance for the system and designing the course of action so as to optimize the performance index. The goal in the lake liming operation is to maintain the pH value at some desired level or within a desired range. Let $\bar{pH}$ represent the targeted pH value, which can be a constant or a time dependent parameter. The objective is to achieve target pH value as closely as possible, or alternately, to minimize the variance of the actual lake pH value around the targeted pH value. Accordingly, the time dependent objective is mathematically represented as:

$$J = \int_0^T (y_4 - \bar{pH})^2\ dt \tag{12}$$

where, T is the simulation time horizon.

The presented lake liming problem is a stochastic optimal control problem. Deterministic optimal control problems are common, and well established methods exist to solve these problems. These include Dynamic programming (Hamilton-Jacobi-Bellman equation), calculus of variation (Euler Lagrange equation) and Pontryagin's maximum principle. Stochastic dynamic programming has been proposed to solve the stochastic optimal control problems. However, this method is known to be computationally taxing. Recently, stochastic maximum principle has been proposed by Ramirez and Diwekar [38, 39], which is an extension of the maximum principle. The method is shown to have a distinct computational advantage over the stochastic dynamic programming approach. The mathematical details can be found in [39] and are omitted here. The application of this method results in the formulation of a two point boundary value problem consisting of algebraic and ordinary differential equations. Since the resulting boundary value problem is complex, analytical solution is very difficult. Hence, computational technique of steepest ascent of Hamiltonian is used. The problem details and equations are omitted here for the sake of brevity. The next section discusses the important results of the problem.

7 Lake liming problem results

The methodology explained in the previous sections is applied on a case study lake liming problem. The parameter values for the case study lake, based on the values reported in Håkanson and Boulion [25], are:

Initial lake pH = 6.15
Lake area = 1.26 km^2
Lake mean depth = 8.5 m
Lake maximum depth = 26.2 m
Drainage area = 51.5 km^2
Mean annual precipitation = 602 mm/year
Active sediment age = 519.6 weeks
Internal loading rate = 0.001 (1/month)
Distribution coefficient = 0.5
Settling velocity = 0.074 meter/week
Additive constant = 2.375

The other parameters are computed using these basic parameters as per the following relationships [25]:

Lake volume = Lake area * Lake mean depth
Water discharge = 0.01*DrainageArea*Precipitation/600
Lake water retention time = Lake volume/(Water discharge*60*60*24*365/7) (weeks)
Sedimentation rate = Settling velocity/Lake mean depth (1/week)
Dynamic ratio = Lake area$^{0.5}$/Lake mean depth

Ottosson and Håkanson [33] report the typical natural lake pH variation for a lake. As described in section 5, a mean revering Ito process is used to model the natural lake pH variation for the stochastic optimal control problem. Figure 3 shows a comparison between the predefined natural variation and the variation modeled using mean reverting Ito process. The targeted pH value to be used in the time dependent objective function is 7.0. The simulation time horizon is 1000 weeks. The upper limit on the control variable (lime addition rate) is 100 T/week. Such an upper limit is expected to be present in actual implementations due to logistic or equipment limitations.

Figure 4 presents the result of the control problem solution, indicating that the targeted lake pH is effectively achieved. The lake pH rises very quickly within about one year and then fluctuates around the targeted pH for the remaining time horizon. The control variable profile for this result is shown in 5. The lime input for the initial part of the simulation is high to raise the lake pH value to the targeted value as quickly as possible. After the targeted range has been achieved, lime addition settles at a non-zero value for the remaining time horizon. The value fluctuates continuously to account for the variation in natural lake pH.

To ascertain the importance of using stochastic maximum principle, the stochastic model is solved using deterministic optimal control technique. Thus, the natural lake pH variation is represented using the mean reverting Ito process. However, the control problem is solved using the deterministic techniques, i.e. the natural pH variations do not affect the optimal control problem solution. This is equivalent to ignoring natural pH variations while taking liming decisions. The result for this problem, along with the result for the stochastic problem is shown in Figure 6. The

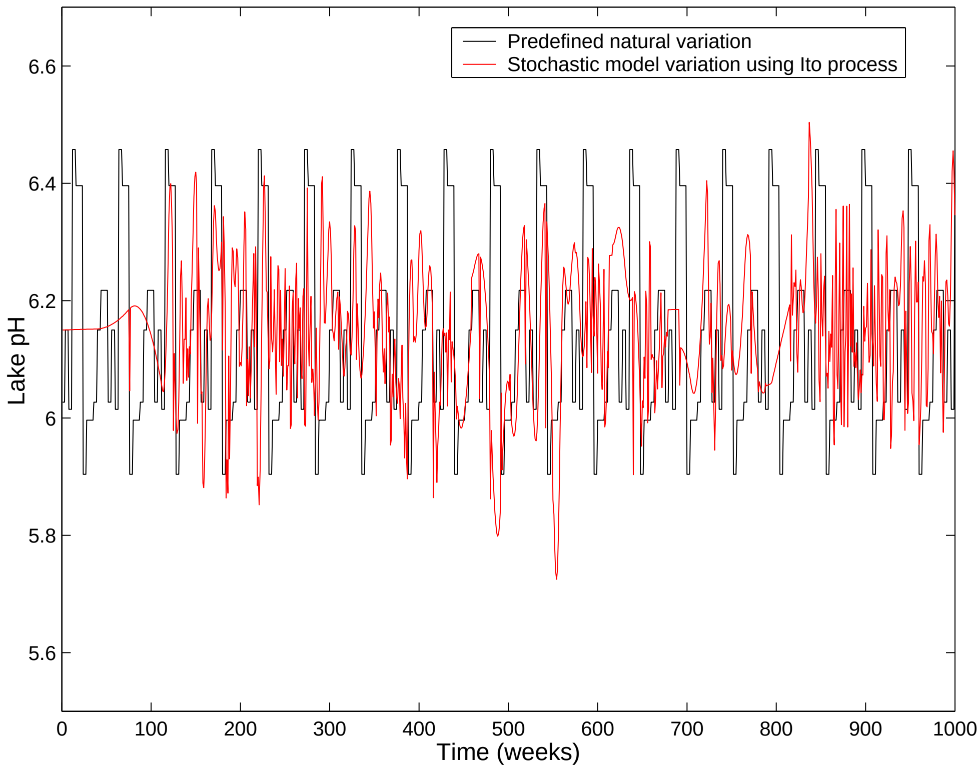

Figure 3: Natural lake pH variation: Comparison between predefined and Ito process variation

use of stochastic optimal control (stochastic maximum principle) clearly leads to much better lake pH control, emphasizing that taking liming decision while ignoring natural pH variations will lead to suboptimal results. These results therefore highlight the importance of uncertainty consideration in decision making.

8 Multi-objective liming problem

The previous section presented the optimal control analysis of a stochastic lake liming problem. The objective for the control problem is to achieve the target pH as closely as possible for the complete time duration under consideration. The only restriction on the control variable is an upper bound to account for logistical and equipment limitations. However lake liming is expensive. Hence, financial aspect will have a definite impact on the decisions related to liming. This represents an additional objective for the control problem. Such problems appear in almost all real life decisions and are known as multi-objective problems in optimization and control theory terminology. Quite often these multiple objectives are conflicting and a tradeoff exists between them. The decision maker first has to decide the importance of each of the objectives and then solve the control problem that optimizes the objectives according to the given weights. The more difficult task for the decision maker is then to decide the appropriate weights for the objectives. Quite often the approach to solve the problem for different weights on the objective and generate a Pareto surface [35]. For the lake liming problem, the objectives are to achieve the target lake pH and minimize the liming expenses, which are conflicting. To formulate the multi-objective optimization problem though, the liming cost function has to be finalized.

The cost of liming depends on the method used for liming. The costs incurred for liming using different methods have been reported in Riely and Rockland [24] based on experimental studies.

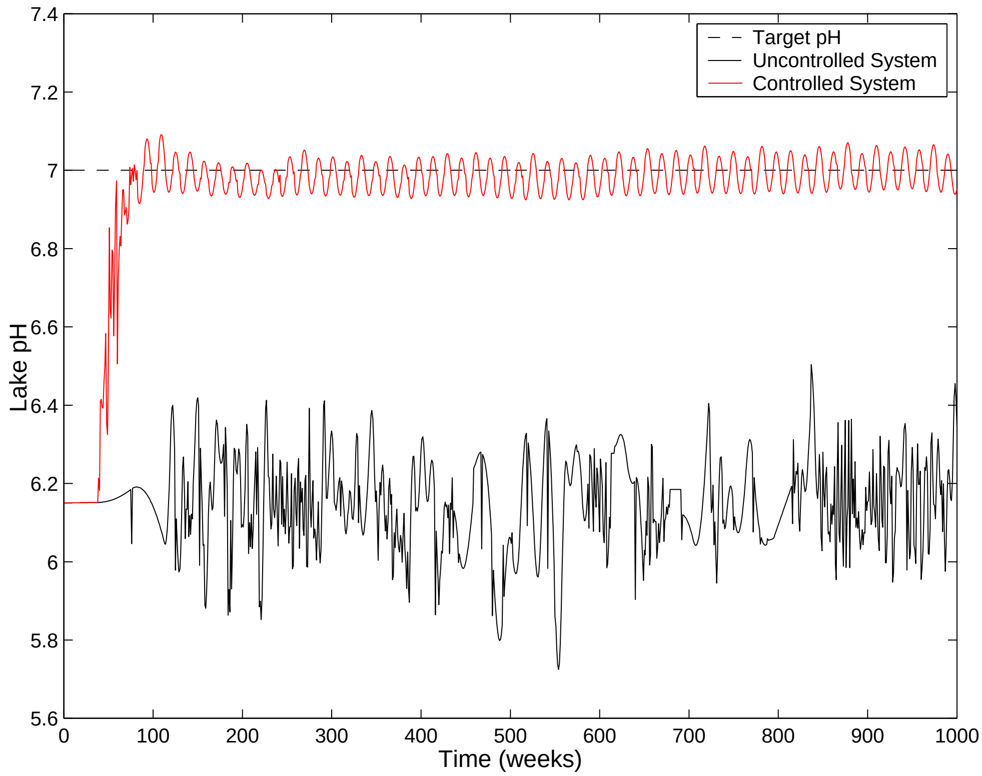

Figure 4: Lake pH variation: Controlled and uncontrolled system

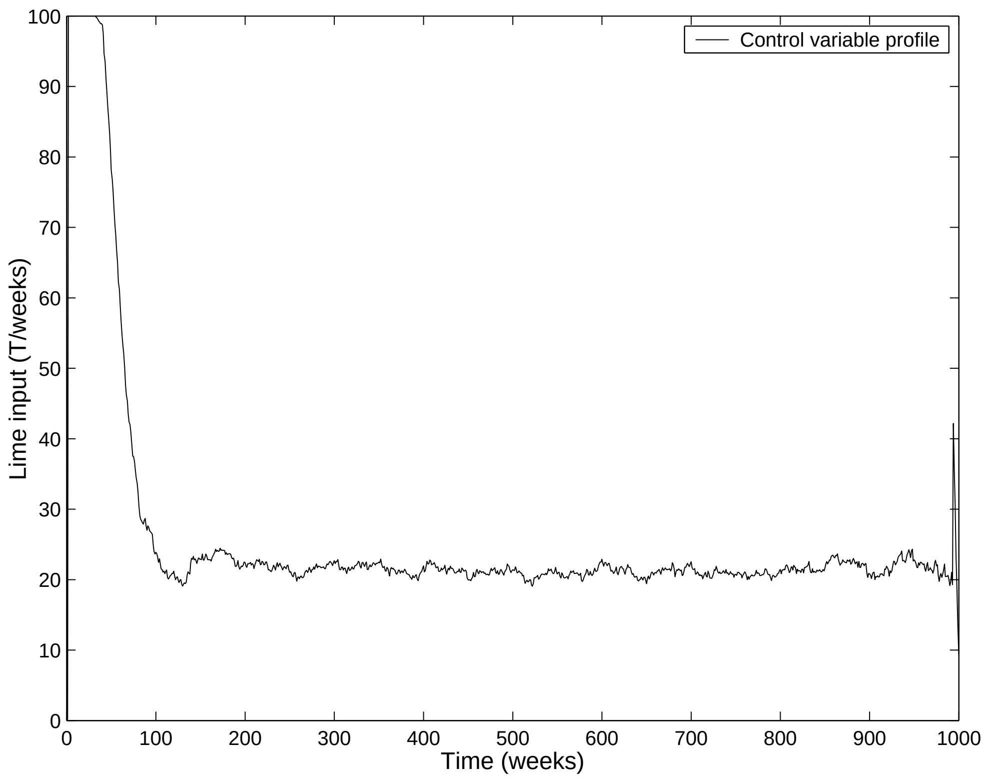

Figure 5: Control variable (lime addition) profile for the stochastic lake pH control

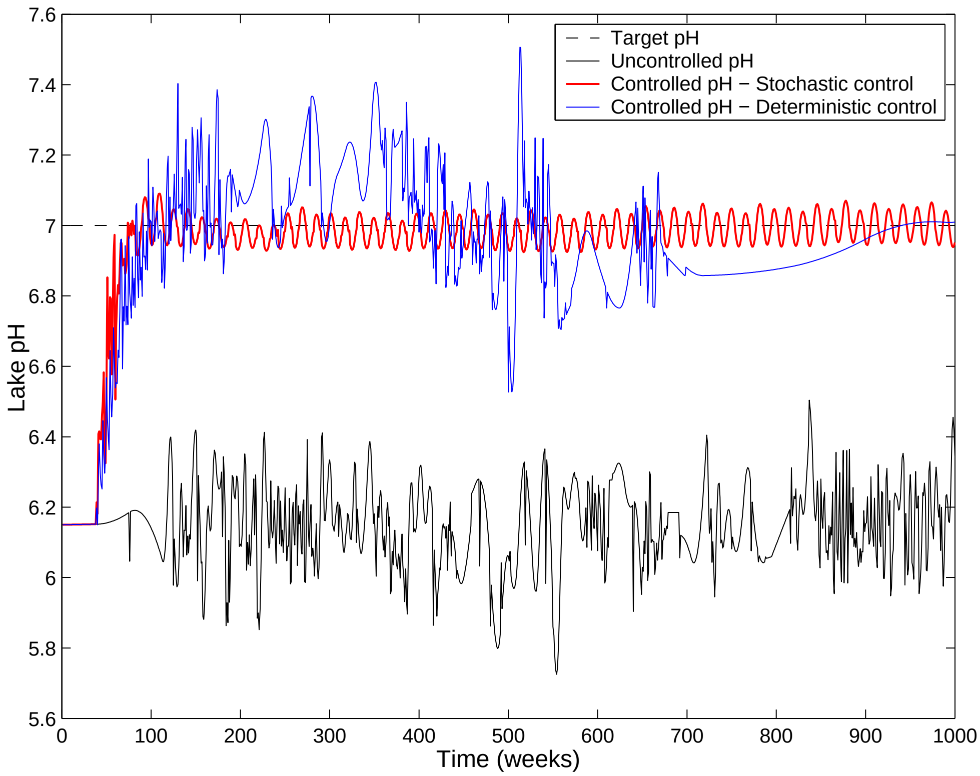

Figure 6: Comparison between stochastic and deterministic control problem result

Since liming by boat or barge is the most popular method, it is assumed to be the method employed in this analysis. Based on the values reported in Riely and Rockland [24], the average liming cost is $236 per unit Ton of lime. However, it must be noted that there is a minimum cost of liming irrespective of the quantity of lime added. This represents the basic logistic and equipment expense. The fraction of this cost in the total expenditure typically reduces as the quantity of lime added is increased. Thus, cost and lime quantity are nonlinearly related. Here, $236 is assumed to be the minimum required cost for any non-zero lime addition. This discontinuous function is approximated using a power law as given below:

$$\text{Liming cost} = 236.u(t)^{0.25} \tag{13}$$

where, u is the quantity of lime added at any instant. This equation is the mathematical representation of the second objective function. For the multi-objective problem, the combined objective function is therefore defined as:

$$J = \int_0^T \left[w_1.(y_4 - p\bar{H})^2 + w_2.236.u(t)^{0.25} \right] dt \tag{14}$$

where, w_1 and w_2 represent the weights given to each objective function.

The stochastic optimal control problem solved in the previous section represents the solution with no importance to the economic objective, i.e. with $w_2 = 0$. To find the tradeoff between the two objectives, the problem is solved with a non-zero weight on the economic objective function. The comparative results are shown in figure 7. The comparison shows that the inclusion of economic objective degrades the quality of pH control. In the multi-objective case, the lake pH is constantly fluctuating and never settles around the targeted pH value. A comparison of the numerical values suggests that there is about 50% reduction in the liming cost from the single objective solution. However, this is accompanied by about 50% deterioration in the liming objective (variance around

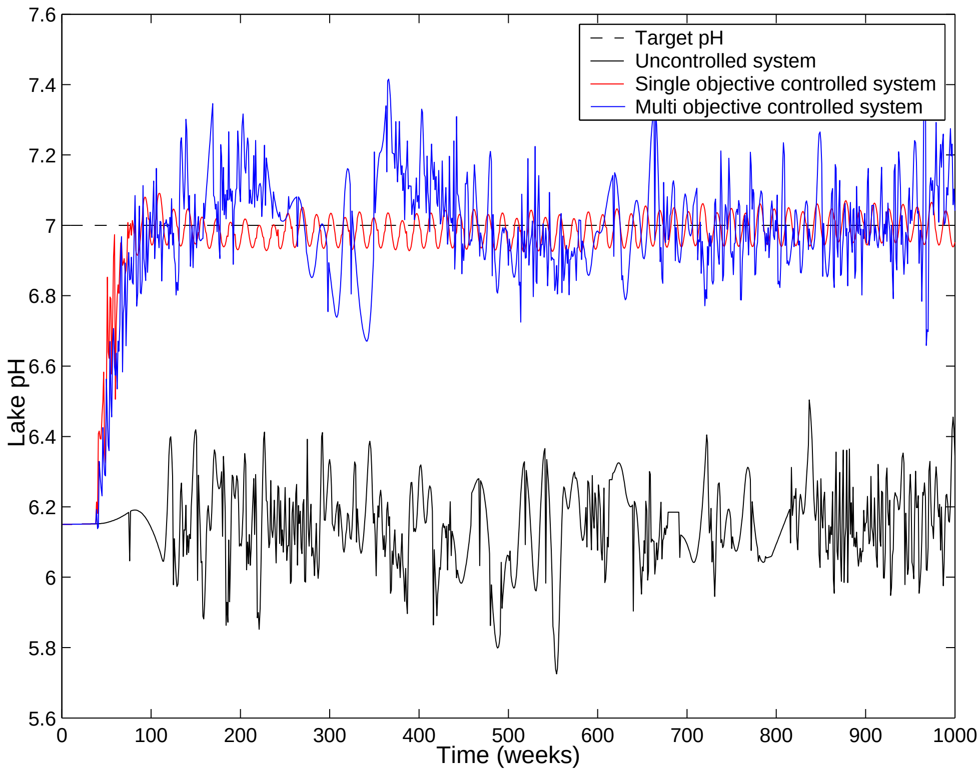

Figure 7: Comparison between single objective and multi-objective liming problem solution

the target value).

This comparison thus illustrates the tradeoff between accurate pH control and liming cost. Problem solution for different weights on the objectives will generate the complete tradeoff surface (Pareto surface). The decision maker can then chose the right combination of the weights and use the corresponding lime input profile for implementation.

9 Conclusion

Mercury as a pollutant is highly dangerous to humans mainly due to its bioaccumulative nature. Mercury methylation is an important step in the process. Since acidic conditions aid methylation, control of lake pH through external lime addition, known as lake liming, is a possible solution to minimize the adverse effects. To maximize the benefits from lake liming, this work proposes time dependent liming, and use of systems theory based technique of optimal control for decision making. The basic lake liming model from literature is modified to formulate the optimal control problem. However, there are considerable uncertainties associated with the liming operation, mainly due to the unpredictable natural fluctuations in lake parameters. This work proposes to use efficient uncertainty modeling techniques from finance literature, resulting in a stochastic optimal control problem. A case study problem, considering natural lake pH variation as an uncertain parameter, is discussed. The results show that use of time dependent liming is a worthwhile option and highlight the importance of considering uncertainty in taking liming decisions. The multi-objective problem results illustrate the trade-off between the liming and financial objectives. The results should generate more interest in lake liming operation, thereby presenting an additional tool to minimize the harmful effects of mercury pollution.

References

[1] USEPA. Mercury study report to congress. Report to congress: EPA-452/R-97-003, United States Environmental Protection Agency, 1997.

[2] USEPA. Mercury research strategy. Technical report: EPA/600/R-00/073, United States Environmental Protection Agency, Office of Research and Development, Washington DC 20460, 2000.

[3] S. Jensen and A. Jernelöv. Biological methylation of mercury in aquatic organisms. *Nature*, 223:753–754, 1969.

[4] R.E. DeSimone, M.W. Penley, L. Charbonneau, G.M. Smith, J.M. Wood, H.A.O. Hill, J.M. Pratt, S. Ridsdale, and R.J.P. Williams. The kinetics and mechanism of cobalamine-dependent mthyl and ethyl transfer to mercuric ion. *Biochimica et Biophysica Acta*, 304:851–863, 1973.

[5] R. Eisler. Mercury hazards to fish, wildlife, and invertebrates: A synoptic review. Publication no. 85 (1.10), U.S. Fish and Wildlife Service, Department of the Interior, Washington, DC, 1987.

[6] J. Sorensen, G. Glass, K. Schmidt, J Huber, and G. Rapp. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton and fish of eighty northern minnesota lakes. *Environmental Science and Technology*, 24:1716–1727, 1990.

[7] H. Nagase, Y. Ose, T. Sato, and T. Ishikawa. Methylation of mercury by humic substances in an aquatic environment. *Science of Total Environment*, 32:147–156, 1982.

[8] J.M. Wood, F.S. Kennedy, and C.G. Rosen. Synthesis of methyl-mercury compounds by extracts of a methanogenic bacterium. *Nature*, 220:173–174, 1968.

[9] L. Bertilsson and H.Y. Neujahr. Methylation of mercury compounds by methylcobalamin. *Biochemistry*, 10(14), 1971.

[10] M. R. Winfrey and J. W. M. Rudd. Environmental factors affecting the formation of methylmercury in low ph lakes. *Environmental Toxicology and Chemistry*, 9:853–869, 1990.

[11] L. Xun, N. Campbell, and J.W. Rudd. Measurements of specific rates of net methyl mercury production in the water column and surface sediments of acidified and circumneutral lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 44:750–757, 1987.

[12] C.C. Gilmour, E.A. Henry, and R. Mitchell. Sulfate stimulation of mercury methylation in freshwater sediments. *Environmental Science and Technology*, 26:2281–2287, 1992.

[13] C.T. Driscoll, V. Blette, C. Yan, C.L. Schofield, R. Munson, and J. Holsapple. The role of dissolved organic carbon in the chemistry and bioavailability of mercury in remote adirondack lakes. *Water, Air and Soild Pollution*, 80:499–508, 1995.

[14] D.B. Porcella, C.L. Schofield, J.V. DePinto, C.T. Driscoll, P.A. Bukaveckas, S.P. Gloss, and T.C. Young. *Acidic precipitation*, volume Volume 4: Soils, aquatic processes, and lake acidification of *Advances in Environmental Science*, chapter Mitigation of acidic conditions in lakes and streams, pages 159–186. Springer-Verlag, 1989.

[15] L. Håkanson. A general management model to optimize lake liming operations. *Lakes & Reservoirs: Research and Management*, 8:105–140, 2003.

[16] L. Henrikson and Y.W. Brodin. *Liming of acidified surface waters*. Springer, Berlin, 1995.

[17] L. Håkanson. Consequences and correctives related to lake acidification, liming and mercury in fish - A case-study for lake Huljesjön, Sweden, using the LakeWeb-model. *Environmental Modeling and Assessment*, 8:275–283, 2003.

[18] G. Morabito. Six years (19921997) evolution of phytoplankton communities after recovery by liming in Lake Orta, northern Italy. *Lakes & Reservoirs: Research and Management*, 6:305–312, 2001.

[19] E.E. Prepas, B. Pinel-Alloul, P.A. Chambers, T.P. Murphy, S. Reedyk, G. Sandland, and M. Serediak. Lime treatment and its effects on the chemistry and biota of hardwater eutrophic lakes. *Freshwater Biology*, 46:1049–1060, 2001.

[20] A. Erikkson. Are the effects of acidification postponed and aggravated by lake liming? - a laboratory study on a re-acidification of the limed lake gårdsjön, SW Sweden. Technical report, Department of Physical Geography, Göteborg, 1998.

[21] S.S. Hincks and G.L. Mackie. Effects of pH, calcium, alkalinity, hardness, and chlorophyll on the survival, growth, and reproductive success of zebra mussel (Dreissena polymorpha) in Ontario lakes. *Canadian Journal of Fisheries and Aquatic Sciences*, 54:2049–2057, 1997.

[22] D.L. Findlay. The effect of incremental pH recovery on the lake 223 phytoplankton community. *Canadian Journal of Fisheries and Aquatic Sciences*, 53:856–864, 1996.

[23] A. Hindar, F. Kroglund, E. Lyderson, A. Skiple, and R. Høgberget. Liming of wetlands in the acidified Lake Røynelandsvatn catchment in southern Norway: effects on stream water chemistry. *Canadian Journal of Fisheries and Aquatic Sciences*, 53:985–993, 1996.

[24] P.L. Riely and D.B. Rockland. Evaluation of liming operations though benefit-cost analysis. *Water, Air and Soil Pollution*, 41:293–228, 1988.

[25] L. Håkanson and V. Boulion. *The lake foodweb*. Backhuys Publishers, Leiden, 2002.

[26] Y. Shastri and U. Diwekar. Sustainable ecosystem management using optimal control theory: Part 1 (deterministic systems). *Journal of Theoretical Biology*, 241:506–521, 2006.

[27] Y. Shastri and U. Diwekar. Sustainable ecosystem management using optimal control theory: Part 2 (stochastic systems). *Journal of Theoretical Biology*, 241:522–532, 2006.

[28] D. Ludwig, S. Carpenter, and W. Brock. Optimal phosphorous loading for a potentially eutrophic lake. *Ecological Applications*, 13(4):1135–1152, 2003.

[29] E.N. Chukwu. *Stability and time-optimal control of hereditary systems - with applications to the economic dynamics of the U.S.*, volume 60 of *Series on advances in mathematics for applied science*. World Scientific, 2001.

[30] G.E. Kolosov. Size control of a population described by a stochastic logistic model. *Automation and Remote Control*, 58(4):678–686, 1997.

[31] D. Kirk. *Optimal Control Theory: an introduction*. Prentice-Hall, Englewood Cliffs, NJ, 1970.

[32] F. Lewis. *Optimal Control*. John Wiley & Sons, 1986.

[33] F. Ottosson and L. Håkanson. Presentation and analysis of a model simulating the pH response of lake liming. *Ecological Modelling*, 105:89–111, 1997.

[34] A.K. Dixit and R.S. Pindyck. *Investment under uncertainty*. Princeton University Press, Princeton, New Jersey, 1994.

[35] U.M. Diwekar. *Introduction to Applied Optimization*. Kluwer Academic Publishers, Dordrecht, 2003.

[36] U. Diwekar. Green process design, industrial ecology, and sustainability: A systems analysis perspective. *Resources, conservation and recycling*, 44(3):215–235, 2005.

[37] S. Ulas and U. Diwekar. Thermodynamics uncertainties in batch processing and optimal control. *Computers and Chemical Engineering*, 28:2245–2258, 2004.

[38] V. Rico-Ramirez, U. Diwekar, and B. Morel. Real option theory from finance to batch distillation. *Computers and Chemical Engineering*, 27:1867–1882, 2003.

[39] V. Rico-Ramirez and U. Diwekar. Stochastic maximum principle for optimal control under uncertainty. *Computers and Chemical Engineering*, 28:2845–2845, 2004.