GREEN PROCESS DESIGN, GREEN ENERGY, AND SUSTAINABILITY: A SYSTEMS ANALYSIS PERSPECTIVE

Urmila M. Diwekar* and Yogendra N. Shastri
Center for Uncertain Systems: Tools for Optimization & Management
Viswamitra Research Institute
Clarendon Hills, IL 60514

Abstract

This paper presents a systems analysis perspective that extends the traditional process design framework to green process design, green energy and industrial ecology leading to sustainability. For green process design this involves starting the design decisions as early as chemical and material selection stage on one end, and managing and planning decisions at the other end. However, uncertainties and multiple and conflicting objectives are inherent in such a design process. Uncertainties increase further in industrial ecology. The concept of overall sustainability goes beyond industrial ecology and brings in time dependent nature of the ecosystem and multi-disciplinary decision making. Optimal control methods and theories from financial literature can be useful in handling the time dependent uncertainties in this problem. Decision making at various stages starting from green process design, green energy, to industrial ecology, and sustainability is illustrated for the mercury cycling. Power plant sector is a major source of mercury pollution. In order to circumvent the persistent, bioaccumulative effect of mercury, one has to take decisions at various levels of the cycle starting with greener power systems, industrial symbiosis through trading, and controlling the toxic methyl mercury formation in water bodies and accumulation in aquatic biota.

Keywords

Green Process Design, Green Energy, Sustainability.

Introduction

Chemical process simulation tools and models allow engineers to design, simulate and optimize a process. Steady state simulators like PRO-II and ASPEN Plus are well known in this area and are extensively used for simulation of continuous processes. In recent years, chemical process industries have become aware of the importance of waste reduction and environmental consciousness demanded an effort extending far beyond the capability of existing process simulation to model processes with environmental control options. For tracking trace components non-equilibrium based models are implemented. Packages like Waste Reduction Algorithm (WAR) (EPA, 2002) provide data related to various environmental impacts like toxicity and exposure data. Designing green processes with "process integration" which takes into consideration the entire process is now possible with the new tools. However, there is still a long way to attain the goal of sustainability. Unlike traditional

* To whom all correspondence should be addressed

design where engineers are looking for low cost options, environmental considerations include objectives like the long term and short term environmental impacts. Green process design and green energy involves not only extending the design framework to include process integration, environmental control technologies, starting as early as the material selection stage, and going beyond just green energy, green processing, and green management but to look industrial sector level management through industrial ecology as shown in Figure 1. In industrial ecology, this decision making changes from the small scale of a single unit operation or industrial production plant to the larger scales of integrated industrial park, community, firm or sector. Uncertainties increase as one goes from traditional process design to green design and to industrial ecology. The concept of overall sustainability goes beyond industrial ecology and brings in time dependent nature of ecosystem. Decisions regarding regulations, human interactions with ecosystem come in picture. It involves dealing with various time scales and time dependent uncertainties. This work presents a systems analysis approach to various steps involved from green process design to sustainability.

Mercury has been recognized as a global threat to our ecosystem, and is fast becoming a major concern to the environmentalist and policy makers. Mercury is a major pollutant from power plants. The task of mercury pollution management is arduous due to complex environmental cycling of mercury compounds. Successful handling of the issues calls for a sustainability based approach. This work presents the systems analysis approach to sustainability with the case study of mercury.

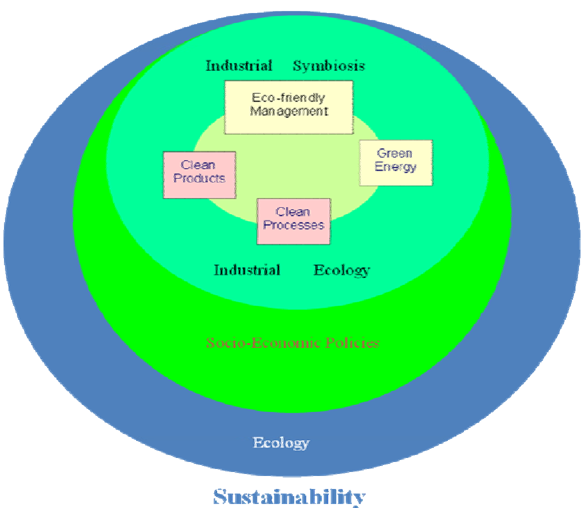

Figure 1: Green Design to Industrial Ecology to Sustainability.

Mercury Cycle

Mercury can cycle in the environment in all media as part of both natural and anthropogenic activities (USEPA, 2000). Majority of mercury is emitted in air in elemental or inorganic form, mainly by coal fired power plants, waste incinerators, industrial and domestic utility boilers, and chloro-alkali plants. However, most of the mercury in air is deposited into various water bodies such as lakes, rivers and oceans through 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, and agricultural runoffs. Once present in water, mercury is highly dangerous not only to the aquatic communities but also to humans through direct and indirect effects. Methylation of inorganic mercury leads to the formation of methyl mercury which accumulates up the aquatic food chains, so that organisms in higher trophic levels have higher mercury concentrations (Jensen and Jarnelov, 1969; Desimone et al., 1973). 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. The work proposes sustainable management strategies at various levels of mercury cycle.

- Industry level environmental control technologies selection and design.
- Industrial sector (inter-industry) level symbiosis through trading. Combined with industry level management resulting in mixed integer nonlinear programming (MINLP) and stochastic mixed integer nonlinear programming (SMINLP) problems.
- Ecosystem level management: Effective control strategies of mercury bioaccumulation in water bodies. These strategies are given below.
    - Lake pH control to manage methyl mercury formation.
    - Manipulation of the regimes of species population by controlling Fisher information variation.

  Optimal control and stochastic optimal control methods are used for these strategies.

The following section presents the algorithmic framework for this work.

Algorithmic Framework

The algorithmic framework is shown in Figure 2. The optimization framework is used for green process design and industrial ecology, while stochastic optimal control is used for time dependent decisions under uncertainty.

Level 1: is the inner most level and corresponds to models for processes. For ecological level management, at this level optimal control and stochastic optimal control problems are formulated. Optimal control problems in engineering have received considerable attention in the literature. In general, solutions to these problems involve finding the time-dependent profiles of the decision (control) variables so as to optimize a particular

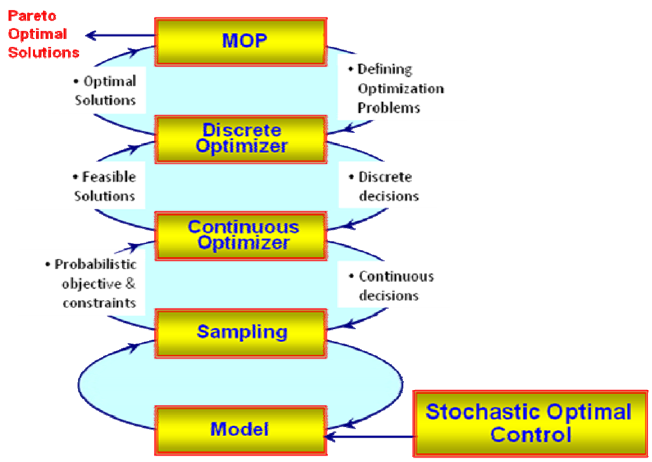

Figure 2: Algorithmic Framework

performance index. The dynamic nature of the decision variables makes these problems much more difficult to solve compared to normal optimization where the decision variables are scalar. In general mathematical methods to solve these problems involve calculus of variations, the maximum principle and the dynamic programming technique. Nonlinear Programming (NLP) techniques can also be used to solve this problem provided all the system of differential equations is converted to nonlinear algebraic equations. For details of these methods, please see Diwekar (2008). In the maximum principle, the objective function is reformulated as a linear function in terms of final values of state variables and the values of a vector of constants resulting in ordinary differential algebraic equation that are easier to solve as compared to calculus of variations or dynamic programming. However, this maximum principle formulation needs to include additional variables and additional equations. We use the maximum principle and the stochastic maximum principle formulation (with sampling) (Rico-Ramirez and Diwekar, 2003) along with NLP optimization technique to obtain the control profiles.

Level 2: Sampling loop: It is a common practice to use probability distribution functions like normal, lognormal, uniform distributions, to model uncertainties as stated above. However, these distributions are used for scalar parameter uncertainties. Modeling dynamic or time-dependent uncertainties is a difficult task. Recently, Diwekar (2003, 2008) presented basic concepts for modeling time dependent uncertainties. These concepts are derived from the financial and economics literature where time dependent uncertainties dominate. The following paragraphs present these concepts briefly.

A Wiener process can be used as a building block to model an extremely broad range of variables that vary continuously and stochastically through time. A Wiener process has three important properties:

1. It satisfies the Markov property. The probability distribution for all future values of the process depends only on its current value.
2. It has independent increments. The probability distribution for the change in the process over any time interval is independent of any other time interval (non-overlapping).
3. Changes in the process over any finite interval of time are normally distributed, with a variance that increases linearly with the time interval.

Stochastic processes like Weiner processes do not have time derivatives in the conventional sense and, as a result, they cannot be manipulated using the ordinary rules of calculus as needed to solve the stochastic optimal control problems. Ito provided a way around this by defining a particular kind of uncertainty representation based on the Wiener process.

An Ito process is a stochastic process *x(t)* on which its increment *dx* is represented by the equation:

$$dx = a(x,t)\,dt \;+ b(x,t)\,dz \qquad (1)$$

where *dz* is the increment of a Wiener process ($dz = \varepsilon\sqrt{dt}$), and *a(x, t)* and *b(x, t)* are known functions. ε is a unit normal distribution.

Once probability distributions are assigned to the uncertain parameters, the next step is to perform a sampling operation from the multi- variable uncertain parameter domain. Hammersley Sequence Sampling (HSS) provides an efficient method for handling uncertainties in real world (Kalagnanam and Diwekar, 1997; Diwekar, 2008) and is used here.

Level 3: Continuous optimizer: This step involves continuous decisions like design and operating conditions for a process. Derivative based quasi-Newton methods are used for this step.

Level 4: Discrete optimizer: This involves dealing with discrete decisions such as various point sources and environmental control options. Decomposition strategies are used for MINLP problems.

Level 5: Multi-Objective Programming, MOP):This represents the outermost loop in Figure 2. There are a large array of analytical techniques to solve this MOP problem; however, the MOP methods are generally divided into two basic types: preference-based methods and generating methods. Preference-based methods like goal programming attempt to quantify the decision-maker's preference, and with this information, the solution that best satisfies the decision-maker's preference is then identified. Generating methods, such as the weighting method and the constraint method, have been developed to find the exact Pareto set or an approximation of it. A new variant of constraint method that MInimizes the Number of Single Objective Optimization Problems (MINSOOP) (Fu and Diwekar, 2004) to be solved which is based on the HSS method can be used for this framework. HSS method can be combined with the weighting method also.

Industrial Level and Industrial Sector Level Mercury Management

In the wake of increasingly stringent discharge regulations on mercury, efficient management at the individual level is not sufficient. Innovative methods are required that will analyze the problem from industrial sector level achieving simultaneous economic and ecological sustainability.

Industrial Level Management: Environmental Control Technologies

Three environmental control technologies are considered for this problem and they are available to all industries for implementation. These include: coagulation and filtration, activated carbon adsorption and ion exchange process. The capital requirement and reduction capability of any process is expected to be nonlinearly related to the capacity of the treatment plant and the form and concentration of the waste to be treated, amongst many other factors. The total plant cost is reported as a function of the waste volume (USDOI, 2001). Since waste volumes encountered in this case study are mostly greater that 1 MGD, asymptotic values reported in USDOI (2001) are used. The treatment efficiencies depend on the waste composition and concentration. In general though, a more efficient treatment is likely to be more expensive. This criterion, along with data given in USEPA (1997a), is used to decide the treatment efficiencies. Table 1 gives the technology data. The nonlinear cost functions are reported in USEPA (1997b). The models are not reproduced here for the sake of brevity and interested readers are referred to the mentioned reference.

Table 1: Data for the Various Environmental Control Technologies.

Process	Mercury Reduction Capability (ng/lit)	Capital Requirement ($/1000 gallons)
Activated carbon adsorption (A)	3.0	1.5
Coagulation and Filtration (B)	2.0	1.0
Ion exchange (C)	1.0	0.6

Industrial Sector Level Management: Pollutant Trading

Pollutant trading is a market based strategy to economically achieve environmental resource management. The goal is to attain the same or better environmental performance with respect to pollution management at a lower overall cost for the industrial sector. The concept is attributed to Crocker (1966), Dales (1968), and Mongomery (1972).

Various aspects of watershed based trading are extensively discussed in USEPA (1996) and USEPA (2003) and hence not reproduced here. To summarize the aspects relevant for this work, the state or federal authority proposes a regulation such as Total Maximum Daily Load (TMDL) which establishes the loading capacity of a defined watershed, identifies reductions or other remedial activities needed to achieve water quality standards, identifies sources, and recommends waste load allocation for point (and nonpoint) sources. To comply with the regulation, a point source (industry) in the watershed may need to reduce its discharge level. It has two options to accomplish this:(1) the point source can implement an environmental control technology, (2) the point source can trade a particular amount of pollutant to another point source in the watershed that is able to reduces its discharge more than that specified by the regulation.

Trading optimization problem formulation: The basic optimization model assumes that all information is deterministically known. Under such as assumption, the model is formulated as follows.

$$\text{Minimize} \quad \sum_{i=1}^{N}\sum_{j=1}^{M} f_j(\phi_j, D_i).b_{ij} \tag{2}$$

$$t_{ii} = 0 \qquad \forall \mathrm{i} = 1,\ldots, \mathrm{N} \tag{3}$$

$$red_i \le \sum_{\mathrm{j=1}}^{\mathrm{M}} \mathrm{q}_{\mathrm{j}}.D_i.b_{ij} + \sum_{\mathrm{k=1}}^{\mathrm{N}} \mathrm{t}_{\mathrm{ik}} \text{ - } r\sum_{k=1}^{N} t_{ki} \tag{4}$$

$$P_i \ge \sum_{\mathrm{j=1}}^{\mathrm{M}} \mathrm{b}_{\mathrm{ij}}.\, f_j\,(\phi_{\mathrm{j}}, D_i) + F(\sum_{k=1}^{N} t_{ik} - \sum_{k=1}^{N} t_{ki}) \tag{5}$$

where there are *N* point sources (*PS*) disposing pollutant containing waste water to a common water body or watershed. D_i is discharge quantity of polluted water from PS_i [volume/year]. red_i is desired pollutant quantity reduction in discharge of PS_i [mass/year]. P_i is treatment cost incurred by PS_i. There are *M* technologies available for waste reduction. f_j is the linear or nonlinear cost function for technology *j* [$]. ϕ_j is set of design variables for technology *j*. q_j is pollution reduction possible from technology *j* implementation [mass/volume]. *r* is the trading ratio and *F* is the transaction cost [$/mass]. b_{ij} are the binary variables representing point source technology correlation. The variable 1 when PS_i installs technology j. t_{ik} [mass/year] is the amount of pollutant traded by PS_i with PS_k. All parameters are on annual basis. The objective function gives the sum of technology cost for all point sources.

The proposed model is applied to the Savannah River watershed. There are 29 major polluters in this watershed including a power plant.

The optimization model presented in the previous section assumes that all data is deterministically known. However, there are various possible sources of uncertainty in this framework. For example, the Mercury Study Report to Congress (USEPA, 1997b) states that uncertainty in point estimates of anthropogenic mercury emissions ranges from medium (25%) to high (50%). This results in a stochastic optimization (stochastic programming) problem.

Health care cost: The bioaccumulative nature of mercury and its slow dynamics make the long term effects of mercury exposure important. Hence, it is essential to account for such effects while quantifying health care costs. Majority of mercury accumulates in the food chain as methyl mercury. Therefore, quantification of health care costs based on methyl mercury concentration is most appropriate. Health care cost is assumed to be a function of fish consumption, safe concentration if fish, and LC50 value for mercury. Addition of health care cost in the formulation results in a multi-objective optimization problem.

Results and discussions: Fig. 3 plots the annual saving due to trading implementation for the considered TMDL range (26 Kg/year to 36 Kg/year) for three different models. It is observed that approximate linear models underestimate the annual savings. Inclusion of uncertainty in the analysis predicts even higher savings for most TMDL values. It should be noted here that trends in savings do not necessarily reflect the trends in overall cost. Thus, although nonlinear stochastic model leads to higher savings than nonlinear deterministic model, the total cost with trading for nonlinear stochastic model is not necessarily lower than the total cost with trading for nonlinear deterministic model. This is because the savings for a particular model are calculated over the technology option for the same model setting.

Fig. 4 shows the implications of nonlinearity and uncertainty inclusion on technology selection for trading option. The figure shows the number of times each technology is implemented over the complete TMDL range. It can be seen that there are definite implications on technology selection. With linear technology models, various small industries implement technologies along with large industries. However, for nonlinear model, large industries implement most of the technologies and smaller industries satisfy the regulations by trading with these large industries. Due to space limitations, multi-objective optimization results are not presented here.

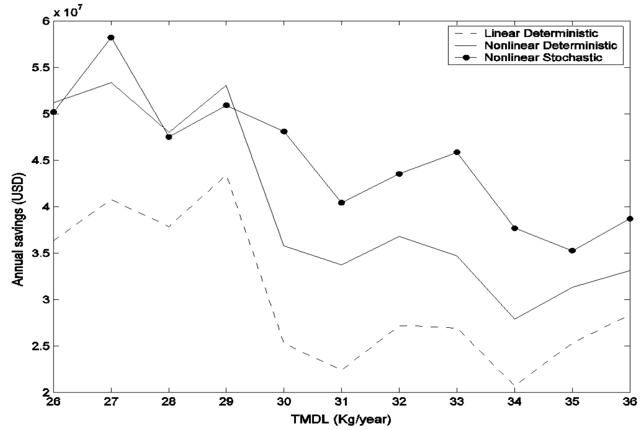

Figure 3: Effect of Nonlinearity and Uncertainty on Annual Savings due to Trading.

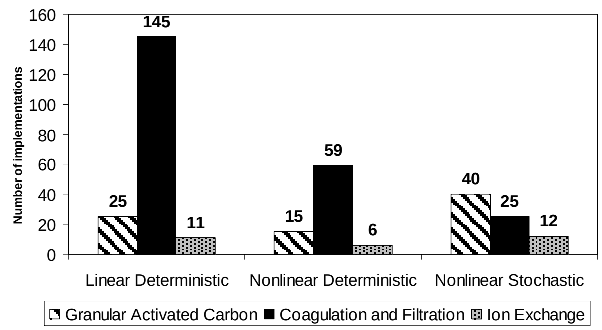

Figure 4: Technology Implementation Decisions.

Ecological Level Management

Mercury and its compounds exist in different segments of the water body such as water column, sediment (active and passive), and biota (fish). Mercury can undergo various transformations in a water body such as oxidation, reduction, volatilization, methylation and demethylation. All these transformations are simultaneously observed in a given water body. The relative 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, methyl mercury (MeHg) is considered to be the most dangerous due to its bioaccumulative potential. As a result, the concentration of methyl mercury in large aquatic animals (such as predatory fishes) is many times more than the water column or sediment concentration. This work explores two strategies for ecosystem mercury management: (1) the time dependent liming strategy of lakes and rivers to control water pH and (2) controlling nutrient flow to manipulate eating habits of organisms.

Liming and pH Control

Methylation of mercury to MeHg is a key step in the bioaccumulation of mercury in aquatic food chains

(Sorensen et al., 1990). The exact mechanism of the methylation reaction is however not well understood. 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 (Winfrey & Rudd, 1990; Driscoll et al., 1995). These studies have shown a strong correlation between acidic conditions (low pH values) and high mercury bioaccumulation in fish.

Although lake liming for pH control has been relatively successful in Scandinavian countries, there are various issues related to liming that need further in-depth research. These are:
(1) Liming accuracy: Currently, most of the liming decisions (liming dosage) 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. (Hakanson & Boulion, 2002). These are mostly static decisions and do not take into account the dynamic nature of the natural system. It is obvious that such heuristics based decisions do not lead to accurate liming results.
(2) Cost of liming: Liming entails considerable costs. Hence, it is essential that the liming operation is optimized 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 Hakanson (2003a) and Riely & Rockland (1988).
(3) Presence of uncertainty: Liming operation has to deal with 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. In order to make liming implementable, one needs to incorporate these uncertainties in the analysis. Due to these issues, lake liming has not been a widespread practice in North America.

To make liming more accurate, 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. The reliability of liming can be further improved if these dynamic liming decisions are based on a systematic approach rather than heuristics.

Basic liming model: The basic lake liming model is presented in Ottosson & Hakanson (1997) and further discussed in Hakanson & Boulion (2002) and Hakanson (2003b). 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 sub-models, 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.

Natural pH of a lake varies seasonally and hence constitutes an uncertain parameter. In this work, mean revering Ito process is used to model fractional variation in pH owing to its success in modeling various time dependent stochastic parameters (Diwekar, 2008; Shastri & Diwekar, 2006a,b).

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 lake liming operation is to maintain the pH value at some desired level or within a desired range. Since cost of liming is also a concern, this converts the problem into multi-objective optimal control problem.

Results and discussions: Figure 5 presents the result of deterministic and stochastic optimal control problems indicating that the targeted pH is effectively achieved. The plots also show that the stochastic optimal control leads to better pH control. Due to space limitations multi-objective optimal control results are not presented here.

Manipulation of Regime

It has been illustrated that a major portion of mercury found in the tissues of various aquatic organisms enters through food (ingestion). As a consequence, the eating habits of these organisms are expected to have a significant impact on the mercury intake by these organisms. The eating habits depend to quite an extent on the various species populations and their pattern of fluctuations at a given time in the water body. In ecological literature, these different patterns are referred to as regimes. A regime, therefore, if maintained for sufficient duration, is expected to affect the steady state mercury bioaccumulation levels in different species. As a result, manipulation of the regimes of these species populations presents a tool to control mercury bioaccumulation levels. This work performs an optimal control analysis to achieve regime shifts in a predator-prey model (Wang et al., 1998; Monson et al., 1998). The predator-prey model and the bioaccumulation model are inter-related by correlating the food intake of any particular species with the mercury intake for the bioaccumulation model. Changes in the dynamics of the Canale’s model change the instantaneous food intake for the predators and super-predators (due to changing predation rates). This affects the total mercury that is taken

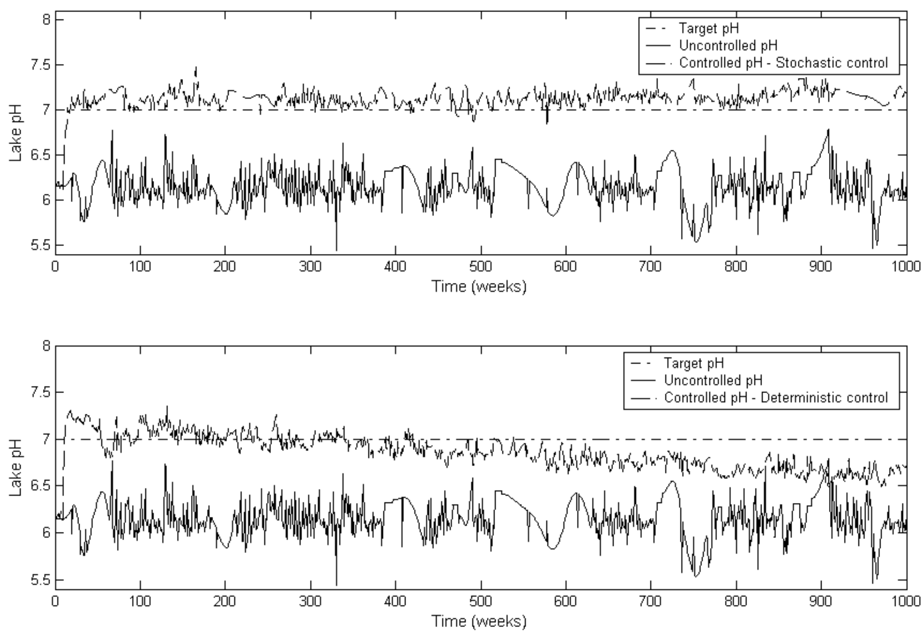

Figure 5: Liming pH Control, Deterministic and Stochastic.

by these species through food. Hence, any regime shift in the predator-prey model, which affects the predation rates, affects the mercury intake by the species. If the particular regime is maintained for a sufficient duration, the steady state mercury concentration in these species can alter. This is the basic foundation for the proposed work.

Regime change and optimal control: Optimal control theory presents an option to derive time dependent management strategies that can effectively achieve regime shifts in food chain models. Past work by the authors has illustrated the success of this approach (Shastri and Diwekar, 2006a, 06b). That work uses Fisher information based sustainability hypothesis, proposed by Cabezas and Fath (2002), to formulate time dependent objective functions for the control problem. A similar approach has been used in this work. The regime shift is to be achieved by minimizing the variation of the time averaged Fisher information around the constant Fisher information of the targeted regime. Canale's model exhibits various regimes such as cyclic low frequency, cyclic high frequency, stationary, and chaotic (Gregnani al., 1998). The idea proposed in this work is to achieve regime shift from a regime leading to high mercury bioaccumulation to a regime resulting in low mercury bioaccumulation. The control variables to achieve the regime shift are: nutrient inflow rate and nutrient input concentration.

*Results and discussion***:** Simulations for the integrated model (Canale's model and the bioaccumulation model) illustrate that there is a strong correlation between the regime and steady state mercury bioaccumulation in predator and super-predators. Hence, the objective of causing a regime change in justified. Figure 6 shows the regime shift achieved by control of nutrient flow.

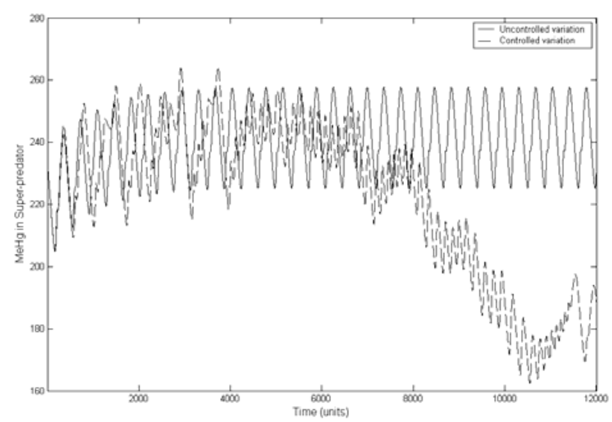

Figure 6 : Controlling Nutrient Flow

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