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A SYSTEMS APPROACH TO NITRATE REMOVAL FROM GROUNDWATER SUPPLIES

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ABSTRACT

Nitrate concentrations in groundwater supplies in many areas have steadily increased past the standard established by the Safe Drinking Water Act. Nitrate contamination is linked to infant methemoglobinemia as well as the formation of n-nitroso compounds which are etiologic agents for gastric cancer in humans. This article discusses the feasibility of removing nitrates from groundwater supplies. Systems analysis is used to determine the best (i.e., optimal) scenarios under which one, or a combination, of several available processes can be applied. A systems methodology for selecting cost-effective nitrate treatment strategies is outlined. Nitrate removal relationships and cost of treatment functions are developed. The systems methodology is illustrated for a typical midwestern community facing nitrate contamination problems.

Nitrate concentrations in groundwater supplies throughout many areas in the United States, particularly in the Midwest, have steadily increased well past the Maximum Contaminant Limit (MCL) established by the Safe Drinking Water Act of 1974 and its amendments of 1986. The concern over nitrate contamination stems from the fact that these salts have been linked to infant methemoglobinemia [1]. Nitrates also have been linked to the formation of n-nitroso compounds which are etiologic agents for gastric cancer in humans [2].

The methods by which nitrates can be removed from groundwater supplies are basically limited to three processes that show some potential for full-scale application. These processes are ion exchange, reverse osmosis, and biodenitrification [3-5]. There are other methods that can be used to at least

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partially reduce nitrate concentrations. These methods include electrodialysis, distillation, and to a very limited degree, chemical precipitation. Available data indicate that both electrodialysis and distillation are not likely to be cost effective when applied on a large scale basis because of the excessive energy required to operate these systems [5]. These systems might be useful for limited scale applications where the cost of energy may be considered of secondary importance. Electrodialysis may become more attractive if nitrate specific membranes are developed. Currently, available electrodialysis membranes tend to favor divalent ions such as calcium, magnesium, and sulfates over monovalent ions such as nitrates [6, 7]. Chemical precipitation is associated with excessive sludge production as well as the need for a copper catalyst to drive the reaction forward. These two disadvantages seem to make this process of very limited utility at the present time [5].

This article discusses the economic feasibility of removing nitrates from groundwater supplies. Systems analysis is used to develop a methodology by which optimal scenarios for treatment using each, or a combination, of the available treatment processes. In each situation, an account of systems elements such as input, state, and output is made to allow for an evaluation of each of the available treatment methods. Inputs include the concentration of nitrates in the available water supply, the required degree of treatment, the availability of capital, the cost of labor, and the availability and cost of alternate (uncontaminated) water supplies. It is to be expected that, as an example, bio-denitrification may be advantageous at some location for a given treatment system size and nitrate concentration whereas ion exchange is not. The reverse may be true under different conditions. It is also to be expected that under some circumstances, neither bio-denitrification nor ion exchange may be acceptable and reverse osmosis might be the best available solution. The decision-making process clearly is not simple and a basic knowledge of the local conditions that necessitate treatment is needed in addition to knowledge of the required treatment process. The peculiarities of each situation can be incorporated into a dynamic model that would allow for an informed decision to be made. An informed decision should clearly recognize the costs as well as the consequence of the basic alternative of doing nothing.

In general, three categories of nitrate pollution control strategies can be identified [5]:

a. reduce or eliminate nitrate at the source by reducing or ending the use of substances which produce nitrates—also by managing the industrial, urban, and agricultural systems that contribute nitrates efficiently;
b. provide alternative water supplies either for direct consumption or for mixing with the contaminated water—the introduction of bottled water is an example of this approach; and
c. reduce the nitrate content or eliminate nitrates altogether by treatment of contaminated water.

Category "a" is often difficult to implement since it may be economically and politically infeasible to enforce stringent enough fertilizer control actions that would reduce or eliminate nitrate contamination. In addition, it would also require a very long period of time to detect measurable results. Consequently, only alternatives "b" and "c" are considered in this article. However, the systems methodology discussed below can be extended to cover the first alternative also.

THE SYSTEMS APPROACH

A systems approach will be used to select viable nitrate treatment alternatives under typical midwest conditions. A systems approach may contribute to reducing the cost of treatment while also reducing the effects of secondary attributes such as the need to dispose of waste brine from a reverse osmosis process. The basic steps involved in using the system approach might be summarized as follows [8-16]:

1. definition of relevant systems and their objectives;
2. generation and evaluation of available alternatives for meeting the stated objectives; and
3. selection of the "best" available alternative.

In the case of nitrate removal processes, system definition will involve an accounting of all basic systems elements and components that are required for the evaluation of each treatment alternative. A conceptual design, or a prototype, might be used as an example. The overall objectives will be the reduction of nitrates (i.e., to a concentration equal to or less than maximum contaminant level (MCL) mandated by law) while minimizing the cost of treatment so that a specific cost ceiling can be defined. The systems approach will be used in two steps:

1. a preliminary screening to select the main types of nitrate control and treatment alternatives; and
2. formulation of a dynamic systems model around the selected alternatives to design a cost-effective facility.

A systems methodology which is used as the general tool of the systems approach is presented in the following section and the process of preliminary screening is illustrated at the end of this article using a small midwestern community.

THE SYSTEMS METHODOLOGY

The system formulation is based on a definition of model elements that are relevant to the problem. It is assumed that there is a total planning horizon (T) which is made of a specific maximum period of time. This period of time can be any desired number of years (e.g., thirty five years). During this planning horizon, a number of stages (t = 1, 2, . . . , T) are assumed to take place at discrete points in time during the total planning horizon. At each of these stages a decision (or a combination of decisions) can be made regarding the nitrate treatment system. Figures 1 and 2 represent a graphical illustration of this methodology. For each of the stages defined above, the following basic elements are defined.

a. System Inputs

System inputs, I(t), are assumed to include the following parameters:

- the water supply requirements necessary to meet the demand for a given community–this requirement is denoted by Q(t);
- groundwater nitrate content or concentration, CN(t);
- the available amount of alternative water supply that can be used when needed in place of current and contaminated supplies–this input parameter is denoted by AV(t);
- actual or estimated unit costs of the different unit operations or processes for the removal of nitrates from groundwater–this parameter is denoted by C(t); and
- environmental standards or governmental regulations that must be met–these specifications include as an example the nitrate maximum contaminant limit of 10 mg/L (as N) mandated by the Safe Drinking Water Act.

b. Decision Variables

The system decision variables, D(t), include the following:

- treatment capacity expansions (or increments thereof) for each of the available treatment alternatives (i.e., bio-denitrification, reverse osmosis, and ion-exchange) denoted by: ΔBD(t), ΔRO(t), and ΔIE(t); and
- the amount of alternative water supply, ΔAV(t).

c. State Variables

The state variables, S(t), are assumed to include the following main elements:

- development state which includes the state of development of each of the three main treatment processes at each stage during the total planning horizon: at each stage the available capacity supplied by each of the nitrate removal systems is defined as BD(t), RO(t), and IE(t); for bio-denitrification, reverse osmosis, and ion-exchange, respectively–in addition the development state of the alternative water supply is assumed to be AV(t); and

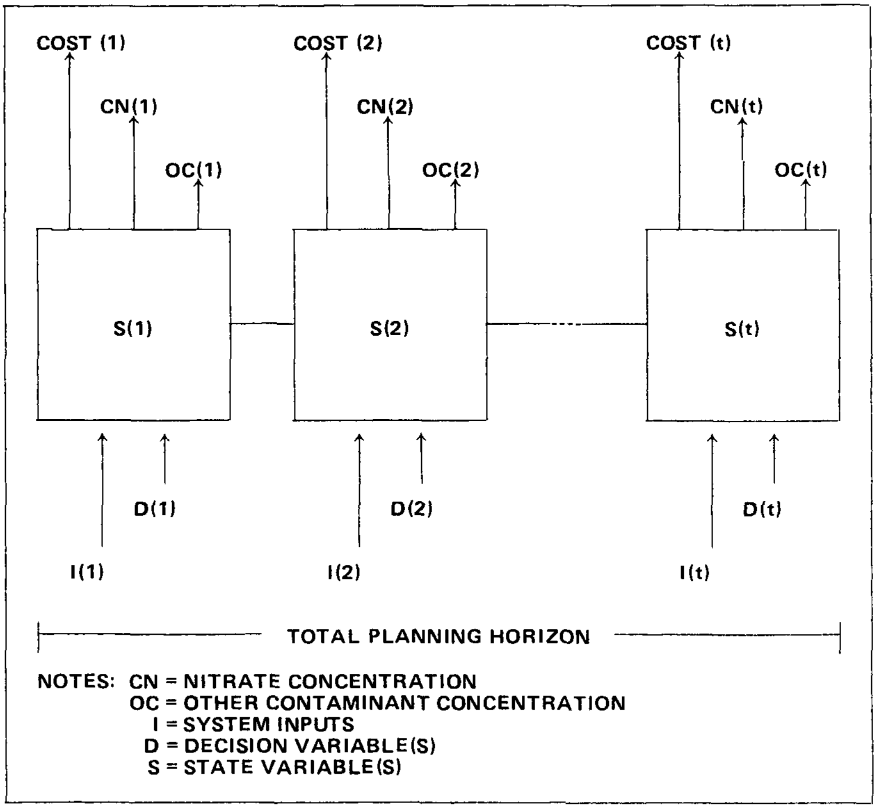

Figure 1. Illustration of the systems methodology.

- environmental state which is assumed to include the state of development of the treatment system(s) with regard to the amount of contaminants being removed at each stage during the assumed total planning horizon—this state is also assumed to account for the removal of other contaminants that might be present in the water supply such as hardness and total dissolved solids removal systems.

d. System Outputs

There are two main elements that define the system outputs, O(t), at each stage during the planning process:

- the cost, [Cost (t)], including treatment costs and costs associated with the development of alternative water supplies; and
- the efficiency which relates the nitrate level in the water supply before treatment and the nitrate levels remaining in the treated water including

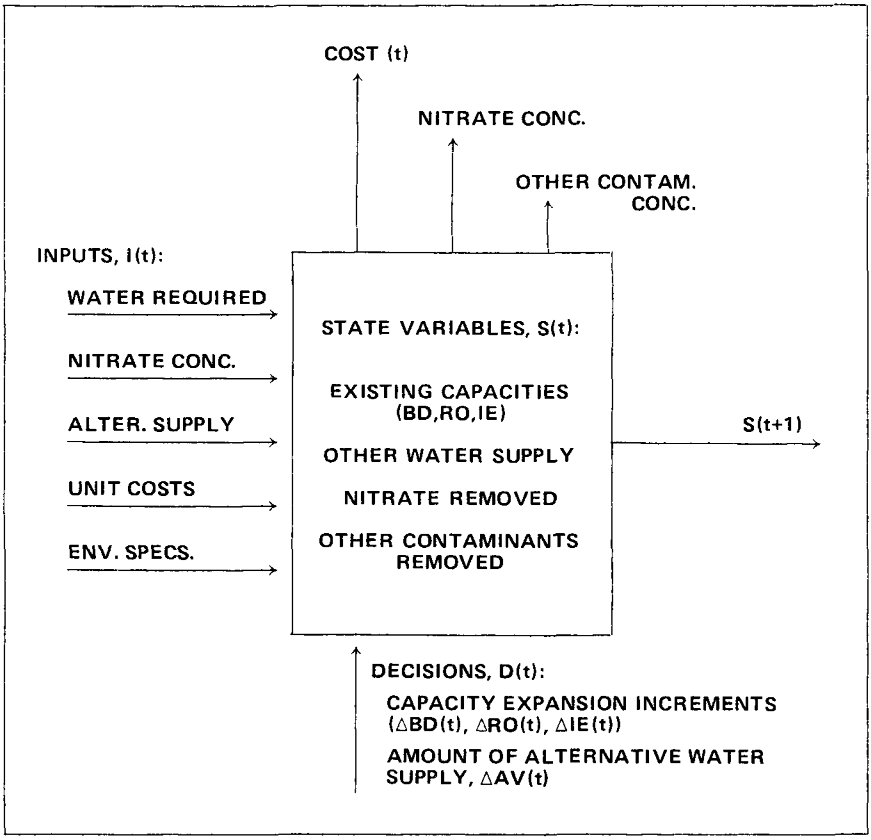

Figure 2. Elements of the system model.

that of the alternative water supply—this term may be taken to include the amounts of other chemical contaminants removed from the water supply as per design.

e. State Transition Functions

The state transition functions consist of the following relationships:

$$S(t+1) = f[I(t), D(t), S(t)] \quad (1)$$

Specifically, the following state transition functions are considered:

1. for capacity expansions:

$$BD(t+1) = BD(t) + \Delta BD(t) \quad (2)$$
$$RO(t+1) = RO(t) + \Delta RO(t) \quad (3)$$
$$IE(t+1) = IE(t) + \Delta IE(t) \quad (4)$$
$$AV(t+1) = AV(t) + \Delta AV(t) . \quad (5)$$

2. for the environmental state:

   As pointed out earlier, the environmental state refers to the amount of nitrate removal as well as the removal of other contaminating chemicals in the water supply. The amount of nitrate removed is a function of the treatment capacity, the influent nitrate concentration in the water supply, the amount of alternate water supply available, and total water requirements.

f. Output Functions

The basic output function involves the following relationship:

$$O(t) = f[\,I(t), D(t), S(t)\,]\ . \tag{6}$$

Output functions for the nitrate removal efficiency as well as the efficiencies of removal of other chemical contaminants correspond to the environmental state transition functions discussed above.

Given the main elements (a through f) above, a model describing a system for cost effective nitrate removal from groundwater supplies can be formulated. The general goal is to find strategies (expressed as decisions) such that the overall cost of treatment is minimized while maximizing the treatment efficiency. As such, the following criteria are defined:

$$\text{Min. Cost} = \sum_{t=1}^{T} \text{Cost}\,(t) \tag{7}$$

$$\text{Min. nitrate} = \sum_{t=1}^{T} N_e(t,i) \tag{8}$$

$$\text{Min. Contaminant} = \sum_{t=1}^{T} \text{Cont}(t,i) \tag{9}$$

In the above relationships, "N_e" and "Cont" denote the treated water supply nitrate concentration and the concentration of other contaminants, respectively, and "i" denotes an individual treatment process.

NITRATE REMOVAL RELATIONSHIPS

The removal relationships for nitrates are basically related to the characteristics of the removal process involved. More specifically, these relationships are controlled by the process kinetics and energetics. Therefore, for each of the nitrate removal processes discussed above (i.e., bio-denitrification, reverse osmosis, and ion-exchange), a model describing the physical operating system must be defined. For example, bio-dentitrification is a biological system in which nitrate removal follows first-order reaction kinetics such as:

$$dN/dt = -kN, \tag{10}$$

where:

N = nitrate concentration, mg/L, at any time, t; and
k = reaction rate constant. (1/time).

In a similar fashion, both ion exchange and reverse osmosis are membrane processes. Therefore, isotherms describing these processes can be defined. For example, for an ion exchange batch-type reactor, the rate of nitrate removal can be expressed as follows [6, 7]:

$$dN/dt = -k_f(a/V)(N-N_e), \tag{11}$$

where:

k_f = mass transfer coefficient;
a = effective area for mass transfer;
V = volume; and
N_e = effluent nitrate concentration.

The above equation for the ion exchange is usable if the process is of the batch reactor type. Although such systems are not common to large-scale applications, they are prevalent in small-scale applications. Similar expressions can be generated for full-scale countinuous-type reactors [6, 7].

Similar to ion exchange systems, some models depicting water permeation in reverse osmosis systems have been proposed [6, 7]. For example, the water flux across a reverse osmosis membrane is described by the following relationship [6]:

$$F_w = K(\Delta P - \Delta \pi), \tag{12}$$

where:

F_w = the water flux across the membrane, (cm/sec);
K = constant, which is dependent on membrane characteristics;
ΔP = pressure drop across the membrane (atm); and
$\Delta\pi$ = difference in osmotic pressure between the treated and untreated water.

TREATMENT COST FUNCTIONS

The cost of treatment for nitrate removal (the basic output function) for any of the processes outlined above can be described as a function of the plant (system) capacity. In fact, this is the general methodology commonly used in most environmental engineering works (i.e., Water and wastewater treatment) [17]. As an example, the capital cost function for bio-denitrification for wastewater treatment is estimated as follows:

$$Cost(BD) = a\,Q^b, \tag{13}$$

where:

Cost(BD) = the cost in millions of dollars;
Q = the plant flow rate in millions of gallons per day; and
a and b = constants which are mostly process dependent.

Similar cost functions can be developed for operating costs as well as both capital and operation costs. Functions of the same type are developed for reverse osmosis and ion exchange systems. There are, however, problems that must be overcome in developing cost functions for processes that are not as yet very common and consequently cost data are likewise very scarce.

ILLUSTRATION OF METHODOLOGY

The systems methodology is demonstrated using a practical case of groundwater contamination by nitrates in the south-central Nebraska area which is heavily farmed. The city of Milford, Nebraska, is a small community with a population of 2100 people [18]. The water system in Milford is composed of four wells, ground and elevated storage, and high service pumping. The wells are fairly shallow ranging in depth from 20 to 120 feet. The nitrate concentration in all wells have steadily increased over the years with two wells exceeding the allowable limit of 10 mg/L [18]. Figure 3 indicates that if this trend is to continue, nitrate concentrations will be about twice the current standard in a few years. At the present time, careful blending of water from the various wells can lead to compliance with the standard. However, this practice may not be possible in the near future and therefore Milford will continue to face regulatory pressure to remedy the situation.

In the case of anticipated contamination requiring corrective action, the options or alternatives available to Milford are:

1. accept the existing situation with no action;
2. find an uncontaminated and treated water supply by connection to a larger nearby municipal or rural system;
3. find and utilize alternate uncontaminated water supply in sufficient quantity and quality to justify economic use—these alternate supplies can be used entirely or blended with existing supplies; and
4. employ a treatment system to reduce nitrate concentration in the existing water supply to acceptable levels.

It is clear that alternative 1 is not acceptable to the local community and the regulatory agencies and therefore can be discounted as a viable alternative. The second alternative is viable since Milford is located only twenty miles away from Lincoln which is a major city in the area. The Lincoln water system has sufficient capacity to supply a town of the size of Milford with little or no additional modification to the treatment system. However, at least twenty miles

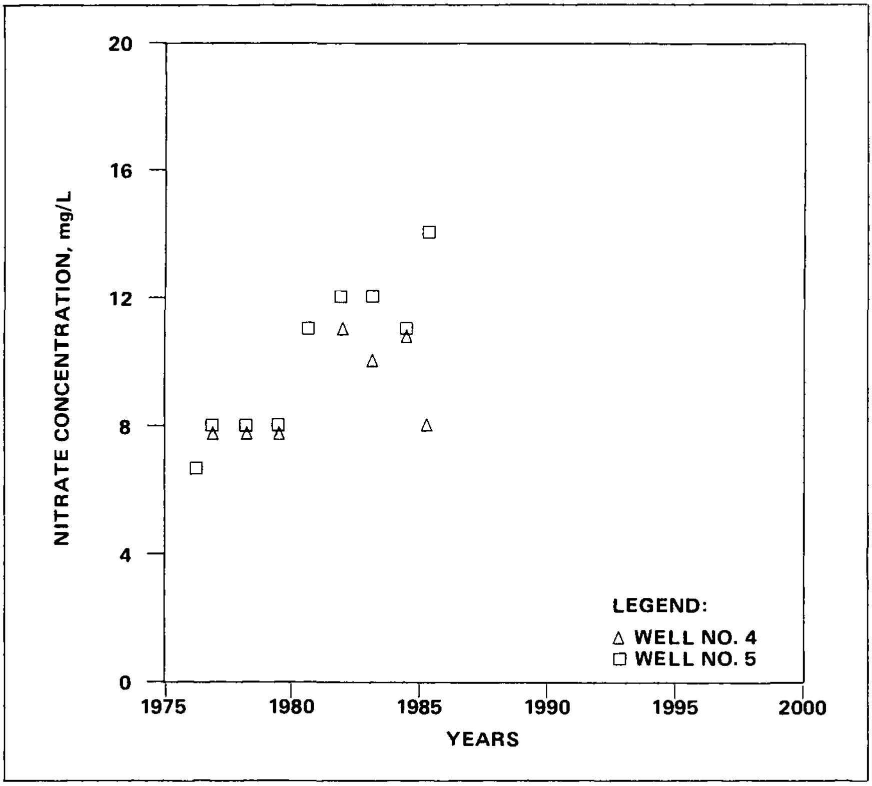

Figure 3. Nitrate concentration trend at Milford, Nebraska (based on data from [18]).

of pipeline must be constructed along with a sufficient pumping capacity to deliver the required water supply. The anticipated cost of this alternative is illustrated along with other viable alternatives in Figure 4.

A recent engineering examination of alternate water supplies in the area resulted in the finding of a possibly usable water in the vicinity of this community [18]. However, the water quality of this supply is not good due to manganese contamination at levels of about four times the recommended standard. Although manganese is not a deleterious chemical, it is a nuisance chemical that will cause staining of clothes and plumbing fixtures. In addition, the alternate water supply requires the construction of much deep wells and therefore will be expensive.

Several treatment alternatives for the existing water supply were considered. Nitrate treatment is not a proven technology at the present time. However, data from the literature indicates that for the town of Milford, ion exchange is probably the most attractive [3, 5, 17, 20]. The cost data for this alternative were based on

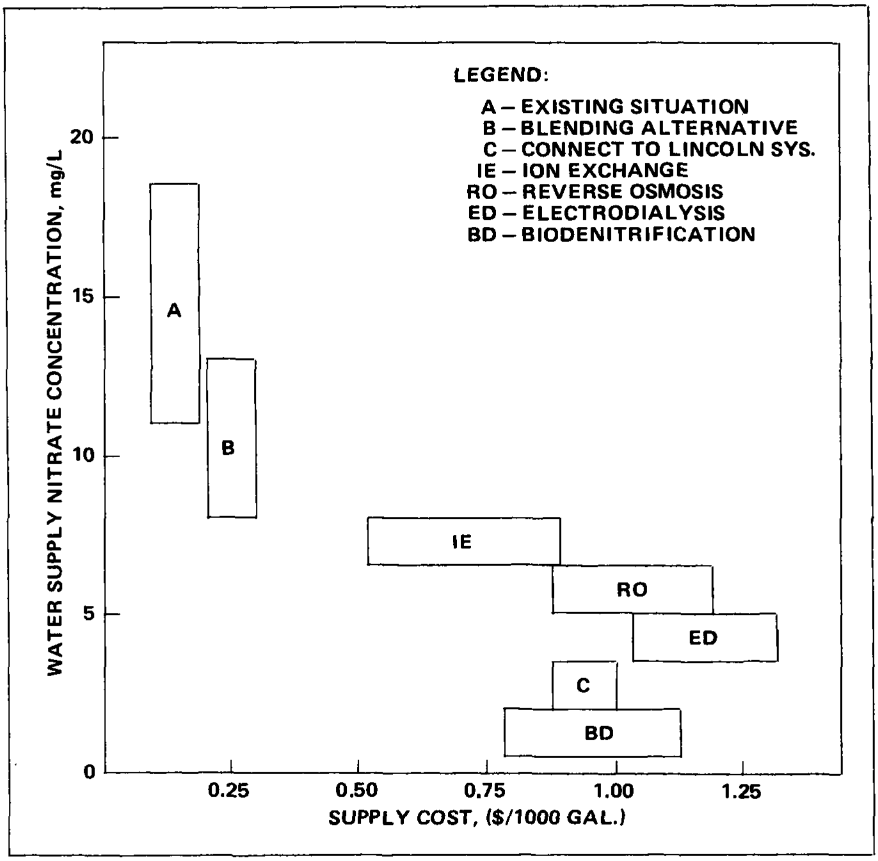

Figure 4. Trade-off between cost and nitrate levels in the water supply for control alternatives available to Milford, Nebraska.

alternative were based on the work of Clifford er al. [3], Guter [19], and Lauch and Guter [20], and were adjusted to account for disposal costs for the resultant brine and removed nitrates. Other treatment alternatives such as reverse osmosis, electrodialysis, and bio-denitrification are somewhat comparable. However, they are hampered by either excessive energy costs (i.e., for RO and ED) or by social acceptability at the present time in the case of bio-denitrification.

Based on the above analysis of treatment and supply alternatives, a preliminary conclusion was drawn regarding the situation in Milford. It is apparent from Figure 4 that the blending alternative seems to be the most acceptable under the stated conditions. This alternative will be the likely optimum solution as long as the new water supply remain free of contamination. The next available viable alternative is to consider actual treatment using an ion exchange.

CONCLUSIONS

The discussion presented in this article supports the following conclusions:

1. Although several methods can be used in the removal of nitrates from groundwater supplies, all of these processes are either unproven technologically or quite costly and thus making process selection or evaluation difficult.
2. The task of selecting the preferred solution to nitrate control problems can be facilitated by the use of the systems approach presented above. The systems methodology (which is a tool of this approach) consists of two steps: a preliminary screening of control alternatives and the formulation of a dynamic model.
3. The preliminary screening step is illustrated through the use of a typical small midwestern community and results in a trade-off analysis between the cost of nitrate control and removal efficiency for the defined alternatives.
4. The dynamic system formulation helps in arriving at cost-effective design of the alternative selected as a result of the preliminary screening.

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