Trans. Nat. Acad. Sci. & Tech. (Phils.)
1985. 7:259-267

A PREDICTIVE MODEL FOR CADMIUM CONCENTRATIONS IN WATER RESERVOIRS

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ABSTRACT

A simple mathematical model to predict cadmium concentrations in water reservoirs and lakes is developed and presented. The model is applied to the proposed San Roque Multipurpose Hydroelectric and Irrigation Project. The reservoir will receive mine tailings containing varying levels of cadmium. Based on certain assumptions made regarding the boundary conditions, input-output rates, mixing and sedimentation characteristics, and distribution coefficient, the model predicts that the cadmium level in the water released for irrigation will remain within the allowable limits for at least ten years from the start of operation.

Introduction

This paper is concerned with the development of a simple solution to the general advection-diffusion equation, otherwise known as the general transport model. This parabolic equation describes transport of any scalar quantity in a continuum. In vector invariant from the general transport model is given by

$$\frac{\partial c}{\partial t} + \nabla \cdot (\underset{\sim}{v} c) = \nabla \cdot (D \nabla c) + P \qquad (1)$$

where c is the concentration of the scalar quantity, $\underset{\sim}{v}$ is the velocity vector. D is a tensor, commonly of diagonal form, containing the turbulent and molecular diffusion coefficients, and P represents the loss and production terms of the scalar quantity. In a bounded region of a continuum, appropriate initial and boundary conditions are needed to solve equation (1).

In its generalized form the advection-diffusion equation cannot be solved and some simplifying assumptions are needed. For instance, in aquatic environments, as rivers, lakes, estuaries, and coastal seas, the characteristic length in the vertical direction is usually much smaller than the horizontal ones so that equation (1) may be averaged over the depth. For rivers, equation (1) may be further averaged over the cross-section. In addition, the molecular and turbulent diffusion coefficients may be neglected since they are at least an order of magnitude smaller than the dispersion coefficients (Fisher, 1973). Numerical solutions to equation (1) are possible with the aforementioned simplifying assumptions but explicit solutions are still not possible to obtain (Daily and Harleman, 1972).

In this paper, an explicit equation will be derived from equation (1) to predict the concentration of cadmium in the water that is released from a reservoir. This concentration, which may vary with time, will be compared with the water quality standard for cadmium. The procedure for determining the values of the different parameters in the model will be discussed and comparable published data will be presented. A simple, predictive mathematical model like this is useful in making first order estimates of pollutant concentrations needed for environment impact assessment studies.

Cadmium: As a Pollutant

Large water resources development projects, such as the construction of multi-purpose water reservoirs, produce considerable impacts on the environment. These multi-purpose water reservoirs are normally used for hydroelectric power production, fishing, recreation, irrigation, and other special purposes like impoundment of mine tailings. When the water is intended to be used for irrigation and the reservoir will receive mine tailings, or if in its watershed there will be point or non-point sources of persistent pollutants, then it is important to predict the probable levels of these pollutants in the water. One of the most pernicious pollutants is cadmium.

Cadmium pollution resulting in the "Itai-itai" disease in the human population has been documented (Yamagata and Shigematusu, 1970). Itai-itai, a very painful disease caused by chronic cadmium poisoning, was first reported during the 17th Meeting of the Clinical Surgery Association of Japan in October 1955. A number of people living in the Jintsu River basin in Toyama Prefecture became afflicted by a strange disease of unknown cause. It is now established that the strange disease was caused by cadmium and that the effluent of the Kamioka Refinery of Mitsui Mining and Smelting Co. Ltd. was the only possible source of cadmium. The disease causes kidney malfunction and brings about osteomalacia and calcium deficiency. A total of 94 persons have died in Japan from Itai-itai, 50 persons have been officially certified as Itai-itai victims and 93 have been classified as "suspected patients".

Cadmium is an extremely dangerous cumulative poison. In mammals (Nilsson, 1970), fish (Eaton, 1971) and probably other animals, there is insidious, progressive, chronic poisoning because the metal is not excreted. *Daphnia magna* appear to be very sensitive to cadmium. Concentrations of 0.0005 mg/1 were found to reduce reproduction in one-generation exposure lasting three weeks (Biesinger and Christensen, 1971). The National Pollution Control Commission has set a maximum allowable level of 0.01 mg/1 for cadmium for class C and D waters.

Water Quality Model

For incompressible fluids where the divergence of the velocity vector is equal to zero, i.e., $\nabla . \underset{\sim}{v} = 0$, and for aquatic systems where the molecular and turbulent diffusion coefficients are at least an order of magnitude smaller than dispersion coefficients, equation (1) simplifies into

$$\frac{\partial c}{\partial t} + \underset{\sim}{v} . \nabla c = D \nabla^2 c + \Sigma S - \Sigma R \qquad (2)$$

where,

c = concentration of the pollutant
t = time
$\underset{\sim}{v}$ = fluid velocity vector
D = dispersion coefficient of the pollutant in water
ΣS = summation of the sources of pollutant
ΣR = summation of the sinks of pollutant

In rectangular coordinate system, equation (2) is expressed as follows:

$$\begin{aligned} & \frac{\partial c}{\partial t} + \mu \frac{\partial c}{\partial x} + \underset{\sim}{v} \frac{\partial c}{\partial y} + \omega \frac{\partial c}{\partial z} \\ = \quad & D\{ \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}] + \Sigma S - \Sigma R \end{aligned} \qquad (3)$$

where u, v, and ω are the velocity components in the x, y and z axes.

Since the main concern is to develop a model that will predict the concentration of cadmium in the irrigation water released from the reservoir and then compare the predicted concentration with the existing water quality standard for cadmium, then the spatial distribution of cadmium may be neglected. Instead, an annual average cadmium concentration will be calculated. Under these conditions,

$$\frac{\partial c}{\partial x} = \frac{\partial c}{\partial y} = \frac{\partial c}{\partial z} = 0$$

$$\frac{\partial^2 c}{\partial x^2} = \frac{\partial^2 c}{\partial y^2} = \frac{\partial^2 c}{\partial z^2} = 0$$

and equation (3) reduces to

$$\frac{\partial c}{\partial t} = \Sigma S - \Sigma R \tag{4}$$

If we define I as the total cadmium input rate at a given time t, in ng/y (nanogram per year), then

$$S = I/V \tag{5}$$

where V is the volume of water in the reservoir.

It is expected that the removal processes for cadmium will consist mainly of outflow and sedimentation. Removal by chemical reaction in the aqueous-layer and losses by volatilization are minimal and insignificant compared to the first two processes.

Trace elements are known to concentrate in sediments of natural aquatic systems (Turekian, 1971; Gibbs, 1973; Bryan, 1976); in particular, trace cadmium has been found to be extensively absorbed by river sediments at a pH of 7.5 (McDuffie *et al.*, 1976). Sediments have aptly been called "trace element traps" because they eventually receive almost all the trace metals which are introduced into the aquatic environment (Chester and Stoner, 1975). It has also been determined that the metal enrichment of sediment is related to the removal of metals from solution by terrestrial organic matter which eventually becomes incorporated with the sediment (Lorne, 1978).

If we define R_s as the total rate of sediment accumulation in the reservoir (ng/y), K_s as the distribution coefficient for cadmium between surficial sediment and the reservoir water (1/ng), and R_o as the volume of water outflow from the reservoir, then

$$\Sigma R = \frac{R_o c}{V} + \frac{R_s K_s c}{V} \tag{6}$$

Substituting equations (5) and (6) into equation (4) results in:

$$\frac{\partial c}{\partial t} = \frac{I}{V} - \frac{R_o c}{V} - \frac{R_s K_s c}{V}$$

or (7)

$$V\frac{\partial c}{\partial t} = I - (R_o + R_s K_s)\, c$$

Equation (7) describes the variation in the average concentration of cadmium in the reservoir as a function of time. To obtain an explicit solution, it is assumed that the volume of water in the reservoir and the inflow and outflow rates are both constant and that there is thermodynamic equilibrium between the cadmium concentration in the water and the sediment phases, i.e., K_s is constant. With these assumptions, the solution to equation (7) is:

$$c = (c_o - \beta/\alpha)\, e^{-\alpha t} + \beta/\alpha \tag{8}$$

where

C_o = the initial concentration of cadmium at $t = 0$
β = I/V
α = $(R_o + R_s K_s)/V$

Evaluation of Parameters

To predict the cadmium concentration in the water discharged from the reservoir as a function of time, data on the initial concentration of cadmium (C_o), total input rate of cadmium (1), total rate of sediment accumulation (R_s), and the cadmium distribution coefficient (K_s) are needed. The values of V and R_o are known from the design of the reservoir.

Cadmium distribution coefficient (K_s)

The distribution coefficient, K_s, is defined as

$$K_s = \frac{\text{ng Cd/ng sediment}}{\text{ng Cd/1}} \tag{9}$$

If actual data are available, K_s may be estimated by dividing the average concentration of cadmium in surficial sediment by the average concentration of cadmium in water. However, since the model is normally used to predict cadmium concentrations needed for environmental impact studies on proposed projects, experimental data for the actual situation are normally not available for calculating K_s.

A variety of pathways exist for cadmium deposition to sediments. Two of the most important are precipitation and adsorption (Davis and Leckie, 1978). The relative importance of these two processes depends on the degree of supersaturation, available surface area, and the concentrations of complexing agents that are present in the water (Shuman, *et al.,* 1978). Recent studies on trace metals distribution in tropical aquatic systems show K_s values ranging from 10^{-11} to 10^{-9} 1/ng (Paul and Pillai, 1983; Reid and McDuffie, 1981).

Rate of sediment accumulation (R_s)

Sediments accumulate due to natural soil erosion (non-point source) and from point sources, such as, mine tailings and other industrial effluents. Point sources of sediment load are easily calculated from a given data but sediment load from soil erosion has to be estimated based on the area of the reservoir watershed and the soil erosion rate.

About 58.7% of Philippine terrain possesses slopes greater than 18% and are thus highly susceptible to soil erosion (NEPC, 1982). For instance, the sediment load in the Pampanga river system ranges from 182 to 2210 tonnes/km^2/y while that in Agno River averages about 4400 tonnes/Km^2/y (NEPC, 1978).

By adding all the non-point (e.g. natural soil erosion) and point (e.g. tailings) sources of sediments, R_s can be determined.

Input rate of cadmium (I)

The total input of cadmium into the reservoir is obtained by adding all the contributions from wet deposition (rain), dry deposition (dustfall), natural erosion, and industrial discharges (e.g. minetailings).

Ideally, long-term data on the contributions from non-point sources are needed to obtain representative values. In practice, these types of information are seldom available. However, published data may provide indicative values which can be used for first order approximation.

Wet deposition (rain). Published data on the concentration of cadmium in different forms of precipitation give the following information.

Rain over Lake Ontario had Cd concentration of 1000 ng/l in 1973 (Shiomi and Kuntz, 1973); rain in New Hampshire had 600 ng/l (Schlesinger *et al.*, 1974); rain from Nebraska had 260 ng/l (Struempler, 1976); a mean concentration of 600 ng/l of cadmium in bulk deposition around Lake Michigan's southern basin had also been reported (Thornton, *et al.*, 1980); 29 precipitation events occurring at the Argonne National Laboratory were sampled, and cadmium concentrations in the individual samples ranged from 70 to 1100 ng/l, with a weighted average of 320 ng/l (Hales and Dana, 1979); and 50-200 ng/l were measured from rainwater samples in Bombay, India using Differential Pulse Anodic Stripping Voltammetry (DPASV) method (Ashawa *et al.*, 1985).

Dry deposition (dustfall). Cadmium is a relatively volatile element and it is known to vaporize during combustion processes and subsequently to recondense on airbone particles. The flux of cadmium-bearing particles to the reservoir is the product of the average Cd concentration in air, the deposition velocity, and the water surface area of the reservoir.

Published literature on the Cd concentration in air give the following data: annual averages in 1969 ranged from 6 ng/m^3 in San Francisco, California to 36 ng/m^3 in St. Louis, Missouri in the 20 largest cities in the U.S.A. and at 29 non-urban stations the annual averages were all below 3 ng/m^3 (NASN, 1969); in Erlangan, West Germany, it was found in 1969 that Cd level in the air was

1.5 ng/m^3 while in the center of Stockholm, Sweden weekly means of 5 ng/m^3 were found in a rural area far from Cd-emitting factories, a monthly mean of 9 ng/m^3 was found (Friberg *et al.*, 1974); and high-volume air particle collections in Lake Michigan in 1978 obtained an average airborne Cd concentration of 1.9 ng/m^3 and a range of 0.43-5.0 ng/m^3 for all 28 filter samples (Muhlbaier and Tisue, 1981).

The Cd-concentration in the air multiplied by the particle deposition rate (normally about 0.1 cm/s for small particle deposition in tropical areas) and the water surface area of the reservoir gives the dry deposition rate.

Natural erosion. The natural erosion sedimentation rate (m^3/km^2/y or kg/km^2/y) multiplied by the Cd concentration in soil (mg/kg) and the total area of the reservoir's watershed gives the Cd-contribution from natural erosion.

A typical Cd concentration in soil of 0.1 mg/kg may be used as a first approximation when actual data from the site are not available. This value is based on the following published data: the average abundance of Cd in the earth's crust is given as 0.1 mg/kg (Wedepohl, 1968); as 0.2 mg/kg (Mason, 1966); and as 0.3 mg/kg (Vinogradov, 1959); and a median value of 0.13 mg/kg was found in tilled soils south of Lake Michigan (Pietz *et al.*, 1978).

Initial Cd Concentration (C_o)

Since most large water resources development projects are located in remote areas, the initial cadmium concentration in the water to be impounded in the reservoir is expected to be in the ppb (μg/l) or sub-ppb (ng/l) range. Using standard atomic absorption spectrophotometry method, cadmium concentrations of the Agno River in the Philippines showed values less than 0.01 mg/l, which is the NPCC standard for classes C and D water (TCI, 1984). The Cd levels in the water were below the instrument's (AAS) detection limit (approx. 0.001 mg/1).

By using more sophisticated analytical techniques, such as Differential Pulse Anodic Stripping Voltammetry, sub-ppb Cd levels can be detected. The order of magnitude of Cd concentrations in Lakewaters is apparent from these published data , at Lake Michigan, U.S.A. Cd concentration of about 100 ng/1 (Matson *et al.*, 1969) and 100 ng/1 (Wahlgren *et al.*, 1971) were reported; 24 samples were collected from the southern basin of Lake Michigan and half were reported to be below 100 ng/l (EPA, 1970); 16 determinations were made 16 km offshore of Chicago and 19 ng/l was found to be the average Cd concentration; and more recently, 17 samples were collected from various locations and depths in the southern basin of Lake Michigan, and the results reported a mean of 26.6 ng/l and a range of 12 to 45.6 ng/l for all 17 determinations using different analytical procedures (Muhlbaier *et al.*, 1981).

Application of the Model

The model was applied to the proposed San Roque Multi-Purpose Hydro-Electric and Irrigation Project of the National Power Corporation using different values of R_s, including the case where $K_s = 0$ (worst possible condition where all the cadmium is retained in the water phase and none is retained in the sediments), and under different operating conditions. The model predicted that for the 50-year life span of the reservoir, the cadmium level in the water released for irrigation will remain well within the current NPCC standard of 0.01 mg/l. The highest value predicted is 1440 ng/l or 0.0014 mg/l.*

Conclusion

A simple but extremely useful predictive model has been derived and the manner by which the model's various parameters can be calculated has been presented. The model is useful in making a first order of magnitude estimate of possible levels of cadmium that may be released from proposed reservoirs. Since the model gives very conservative estimates of cadmium concentrations, a prediction of a Cd level that falls within the legally allowable concentration, provides an assurance that adverse impacts are not likely to occur. If the model predicts Cd levels close to the maximum allowable concentration, there will be a need to develop a more powerful mathematical model to make certain that no negative environmental impacts will result from the proposed reservoir.

Acknowledgement

The author wishes to thank the National Power Corporation, in particular, The Environmental Management Division under Dr. Gonzalo Bantugan, which funded the project. The study on which this paper was based is a small section of the comprehensive environmental impact assessment.

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*Author's note: the details will be the subject of another paper.

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