MODELING GROUNDWATER POLLUTION DUE TO FLUORIDE CONTAMINATED IRRIGATION WATER

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ABSTRACT

Out of many natural geochemical substances contaminating ground water, fluoride is the major one. It invokes considerable interest due to its unique character as regards to its impact on physiological system of living beings. A very low dose (<0.6 ppm) of fluoride promotes decay of teeth, whereas when consumed in the ranges greater than 1.5 ppm it causes fluorosis and related diseases. Fluoride contaminated water when used for irrigation, percolates down and contaminates the soil and ground water. The movement of fluoride in the vadose zone is a complex phenomenon and is largely affected by water movement. In this study, an attempt has been made to study the water and fluoride movement in the vadose zone. An experimental soil column of height 1m and diameter 20 cm was used. The movement of fluoride was studied by collecting the leachate from 90 cm depth at definite intervals of time. CHEMFLO model was used in the study for describing leachate movement. It is based on the convection-dispersion equation for water and chemical movement in vadose zone. Reasonably good correlation was noticed between observed and model predicted results. The results obtained from the study revealed that for shallow ground water table conditions, fluoride contaminated irrigation water of concentration 15 ppm produces leachate percolating the root zone, which exceeds the acceptable limit (1.5 mg/l) for drinking purpose and thereby will pollute the ground water. Under similar topsoil conditions, it was also found that the optimum number of irrigation cycles for ground water table depths of 2m, 5m and 10m are to be restricted to 2, 5 and 9 to prevent contamination of ground water.

1.0 INTRODUCTION

With fast growing population, the need of protecting the sources of water from pollution is ever increasing. Groundwater, which is the main source of water for human consumption, irrigation as well as industrial use, needs special attention. The over exploitation of groundwater resources induces degradation of groundwater quality as well as the discharge of untreated effluents, adding contaminants to the groundwater system. The pollution of groundwater regime is not only due to subsurface waste disposal, but is also attributable to the seepage of contaminants from rivers and lakes, indiscriminate spraying of insecticides, pesticides and excessive use of chemical fertilizers. Chemical composition of groundwater is related to the soluble products of rock weathering and decomposition, which changes with respect to time and space.

Of many contaminants in groundwater from natural geological sources, fluoride is one of the most hazardous, if found in excess. It invokes considerable interest due to its unique character as regards to its impact on physiological system of living beings. A very low dose 0.6-ppm promotes decay of teeth, whereas when consumed in the ranges greater than 1.5-ppm causes fluorosis and related diseases (Wodeyar and Sreenivasan, 1996). Potable drinking water is considered as the main source of fluoride, however food born fluorosis is not ruled out (Moore, 1974). High degree of weathering and easy accessibility of circulating waters to the weathered rocks due to intensive and long time irrigation are responsible for the leaching of fluoride from their parent minerals present in soil and rocks. During weathering and circulation of water in rocks and soils, fluorine is leached out and gets dissolved in groundwater (Wodeyar and Sreenivasan, 1996). The degree of manifestation of fluorosis has been related to the concentration of fluoride in drinking water and the period of consumption.

Of the 29 countries known to have excess fluoride in their drinking water, India has the highest number of people suffering from fluorosis. A recent survey conducted in 1999 by the Fluorosis Research and Rural Development Foundation, Delhi (FRRDF), concluded that about 62 million people in India including six million children are affected with dental, skeletal and non-skeletal forms of fluorosis and associated health complaints.

The movement of water in the soil is the principal mechanism for the transfer of pollutants to surface and groundwater. Water is a solvent capable of carrying significant quantities of dissolved material. Understanding the movement of water and chemicals into and through soils is of great importance in managing, utilizing and protecting our natural resources. These processes are dynamic, changing dramatically over time and space. Properties of soils and chemicals interact with the rate of application of chemical in complex ways within the soil system to determine the direction and rate of movement of these materials.

To determine the movement of water and chemicals in the vadose zone, various mathematical models have been developed by many researchers. Chemicals move in soil generally by the process of molecular diffusion and convection along with the moving water. When water moves through soil, another process called hydrodynamic dispersion also affect the movement of solutes. However, the net movement of solutes in the soil is a result of all the three processes mainly diffusion, convection and hydrodynamic dispersion. Though movement of water takes place both in horizontal and vertical direction, while considering the leaching effect only vertical movement of water is taken into account. In saturated as well as unsaturated condition this movement can be monitored by different mathematical equations. When certain chemical are added with water on soil surface, chemicals move along with water. Thus the concentration of chemicals in water varies with respect to depth and time, which ultimately hampers the groundwater quality.

Studies also confirm that crops grown in fluoride-contaminated soils are likely to contain traces of fluoride, which are not beneficial for human health (Dwarakanath and Subburam, 1991). Fluoride contaminated water when used for irrigation, percolates down and contaminates the soil and groundwater. Once the groundwater is polluted, it remains in that state for a prolonged period of time. Leachable fluoride absorbed in the soil and clays are the main sources of fluoride in groundwater (Sahu and Karim, 1989). Therefore, it is necessary to study the movement of fluoride in the vadose zone and in the aquifer so as to predict migration properties and chalk out some suitable remedial measures by taking various factors into consideration. Keeping the above facts in mind the current study was undertaken with the following objectives:

1. To study the vertically downward movement of fluoride in soil.
2. To calibrate and validate the CHEMFLO model using experimental results.
3. To suggest the measures for effective management of irrigation water to prevent contamination of groundwater.

2.0 CHEMFLO MODEL

CHEMFLO estimates the impact of mobilization and migration of a contaminant located in unsaturated zone on the underlying ground water resources. One dimensional water movement is governed by Richard's equation and chemical transport is based on convection-dispersion model. The initial and boundary conditions are also specified to describe the behavior of water and chemicals at the surfaces or boundaries of the soil system.

2.1 Richard's Equation for One Dimensional Water Movement

$$\mathrm{B(h)}\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(h)\left(\frac{\partial h}{\partial t} - \cos(A)\right)\right] \qquad \text{...(3.1)}$$

Where

B (h) = specific water capacity = dθ /dh.

θ = Volumetric water content.

h = h(z ,t) is the matric potential.

z = distance co-ordinate parallel to the direction of flow time.

t = time.

cos (A) = cosine of the angle A between the direction of flow vertical downward direction.

K (h) = hydraulic conductivity as a function of matric potential.

Movement and degradation of chemicals in this model is described by convection-dispersion equation.

$$\frac{\partial}{\partial t}(\theta_c+\rho s) = \frac{\partial}{\partial z}\left(\theta D\left(\frac{\partial c}{\partial z}\right) - qc\right) - \alpha\theta_c - \beta\,\rho\,s + \gamma\theta \qquad \text{...(3.2)}$$

Where,

c = concentration of chemicals in liquid phase.

s = concentrations of chemicals in solid phase.

D = dispersion coefficient.

θ = Volumetric water content.

q = flux of water.

ρ = Soil bulk density.

α = First order degradation rate constant in the liquid phase.

β = First order degradation rate constant in solid phase.

γ = Zero order rate constant in the liquid phase.

If concentration of the chemical adsorbed on the solid phase is assumed to be directly proportional to the concentration in the liquid phase, then

$$S = Kc \qquad \text{...(3.2a)}$$

Where,

K = partition coefficient.

Therefore, equation 3.2 becomes

$$\frac{\partial}{\partial t}(\theta Rc) = \frac{\partial}{\partial z}\left(\theta D\left(\frac{\partial c}{\partial z}\right) - qc\right) - (\alpha\theta + \beta\rho K)c + \gamma\theta \qquad \text{...(3.3)}$$

Where

R= retardation factor for chemical in the soil.

$$R = 1+\rho K\theta \qquad \text{...(3.3a)}$$

In the model, the concentration of chemicals in the liquid phase at any location and time is determined by solving equation 3.3 coupled with equation 3.1 for water movement, (Values of θ (z, t) and q(z,t) from the solution of equation 3.1 can be used in equation 3.3). Equation 3.2 can be used to determine the concentration adsorbed on the solid phase.

3.0 MATERIALS AND METHODS

To evaluate the influence of fluoride contamination on groundwater quality, monitoring of the soil moisture distribution pattern is needed. The concentration of chemical at different depths varies with respect to time. The soil type and the rate of chemical application with water influence the horizontal and vertical moisture distribution in the soil. For efficient irrigation management the application rate of contaminated water plays an important role.

3.1 Study Area

The study was undertaken in Singpur, a small village under Bhapur, a sub-block of Nayagarh District of Orissa. Water samples from 4 different sources, 3 from open wells and 1 from a tube well were collected. Water and soil samples were also collected from the adjoining villages to study the extent of fluoride contamination. The fluoride content of water and soil samples was measured using the ion-meter with an Ion Selective electrode.

3.2 Experimental Setup

For conducting the leaching experiments, a cylindrical soil column setup of diameter 20 cm and height 100 cm was prepared with a hole at the bottom of the setup to collect the leachate. The experiments were conducted in the Research Building of the Department of Agriculture and Food Engineering, Indian Institute of Technology, Kharagpur.

The soils were collected from the experimental farm of Agriculture and Food Engineering Department. The experimental soil was analyzed by sieve analysis. The physical properties of the soil are shown in the TABLE 1

Table 1 : Physical Properties of experimental soil

Soil Depth (cm)	**Particle size distribution in %**			**Bulk density (g/cc)**	**Sat. Hydraulic Conductivity (cm/day)**
	clay	**silt**	**sand**		
0-15	14.3	26.2	59.5	1.69	9.84
15-30	21.0	19.5	59.7	1.56	6.72
30-45	27.3	20.2	52.5	1.59	0.89
45-60	28.6	19.2	52.2	1.63	0.74
60-100	29.7	24.7	45.6	1.69	0.34

pH 1:2.5 = 5.2
EC = 0.56 mmhos/cm
CEC = 6.00 meq/100g of soil
Total N = 0.03%
Available N = 0.025

3.3 Soil Water Retention Curve

To determine saturated and residual moisture content, plotting of this curve was necessary. Soil samples were screened through a 2mm-size sieve to remove the coarser substances. The sample was oven dried at 105°C for 24 hr. In this study soil water retention curve was developed by pressure plate technique with a precise control system for making measurements under water extraction condition suitable for extraction studies.

3.4 Leaching under saturated condition

The experimental soil column was filled with the soil collected from the field whose physical properties are given in Table 1. Bulk density was calculated for 0-15cm, 15-30cm, 30-45cm, 45-60cm and 60-100cm layers under the field condition. Experimental soil was compacted layer wise to maintain the same bulk density as in the field. It was then made fully saturated. Water having 15-ppm fluoride concentration was then passed through the soil column. Leachate collected at the bottom was analyzed for fluoride.

Total soluble fluoride is determined using a fluoride ion-selective electrode (ISE), in conjunction with a standard single-junction reference electrode or a fluoride combination ISE, and a pH meter with an expanded milli volt scale or an ISE meter capable of being calibrated directly in terms of fluoride concentration. The Ion Selective Electrode was calibrated using 1, 10 and 100 ppm standard solutions. After the recommended slope of -54 to -60 was achieved, the above instrument was used in the analysis of fluoride concentration in the leachate.

The soil samples were also analyzed using the ion-meter. The method applied was Sodium Hydroxide Fusion method for total fluorine. The F^- values were determined from the standard curve following the direct potentiometric method. The above method is adapted from McQuaker and Gurney (1977).

3.5 Calibration and Validation of CHEMFLO model

Model calibration includes the adjustments of coefficients required for running the model on the basis of comparison between predicted and observed results. It was done to make the model suitable for the conditions of Kharagpur region. In this there were three coefficients, which were calibrated for the solute movement in the soil of Kharagpur region (sandy loam). Those coefficients were :

1. **Diffusion coefficient of chemical in water (cm^2/hr).**

   It refers to the diffusion coefficient for the chemical in bulk water.

2. **Dispersivity (cm).**

   This is an empirical index of the magnitude of variations of the pore velocities in the soil. Soils with a small range of pore sizes have smaller values than that with a wide range in pore sizes.

3. **Water: Soil partition coefficient (cc/g soil).**

   This is the proportionality factor between the concentration of chemical in the solid and liquid phases as shown in Equation 3.2a.

The model was calibrated and validated first for coarse sand and then for sandy loam soil. It is because the calibrated coefficients obtained for sand, does not apply to the soil. The model was calibrated for 15-ppm of CaF treatment. After calibration, the model was validated for 20-ppm treatment without changing the calibrated value of the coefficients. The validated model was then used to extrapolate the results for different groundwater table depths. In the present study, depth to groundwater table of 2m, 5m and 10m were considered. The model was used to find out the optimum number of irrigation cycles for different groundwater table depths to prevent contamination of groundwater if the concentration of fluoride in the irrigation water is 15-ppm.

4.0 RESULTS AND DISCUSSIONS

The water and soil samples were collected from the Balasingi and Singhpur village in Nayagarh district of Orissa and analyzed for fluoride. Water and soil samples were also collected from the adjoining villages to study the extent of fluoride contamination. It was seen that the water and soil samples of Tarabalu village are worst affected by fluoride contamination. The concentration of fluoride in the water samples of that area was as high as 15 ppm. Therefore, in this study 15 ppm was taken as standard for all simulation purposes. Soil samples of that area also had a very high percentage of fluoride concentration.

4.1 Soil physical parameters

The value of saturated water content was found to be 41 percent for coarse sand and 37.63 percent for sandy loam soil. The values of residual moisture content determined at 15 bar soil water suction was found to be 6 percent for coarse sand and 7.27 percent for sandy loam soil.

4.2 Break through curves in case of sand

The experimental column was first filled with coarse sand and two rounds of pure water followed by demonized water were passed to leach out any fluoride present in the sand. After making it fully saturated, contaminated water with a fluoride concentration of 15 ppm was passed through it. Leachate collected at definite time intervals was analyzed for fluoride. The same procedure was repeated for 20-ppm concentration of fluoride in the irrigation water.

The observed break through curves for sand, when applied with 15 ppm and 20 ppm fluoride contaminated water revealed that the concentration of fluoride in the leachate first increases and then decreases. Almost complete break through was attained in both the cases after 6 hours (Fig. 1 a and Fig. 1 b). This is mainly for the reason that flux of water in the sand decreases with respect to depth and time. Leachate was collected at 1/2 hr interval.

4.3 Calibration and validation of CHEMFLO model

The CHEMFLO model calibration includes the adjustment of different coefficients to suit the model for particular material or region. The relevant input data required for running the model were collected from the laboratory experiments conducted at IIT, Kharagpur.

The model was calibrated and validated separately for coarse sand and for sandy loam soil, since the calibrated coefficients obtained for sand did not apply to soil. The model was calibrated for 15ppm of CaF treatment for both coarse sand and sandy loam soil. The results of 20ppm CaF treatment were used for model validation both for sand and soil. Model parameter obtained after calibration were:

Diffusion coefficient of chemical in water (cm^2/hr) = 3.0E - 002
Dispersivity (cm) in case of sand = 2E + 000
Water: Soil Partition coefficient in case of sand = 0.0
Dispersivity (cm) in case of soil = 1.85E + 000
3) Water: Soil partition coefficient in case of soil = 0.135

The predicted and observed values of temporal changes in concentration of leachate obtained at 90cm depth, both for sand and soil with 15ppm of CaF treatment matched closely (Fig. 1a and 1c). Slight deviation from the predicted values was attributed to the presence of cracks in the soil and experimental error. The model coefficients determined through calibration were left unchanged and the model was validated for 20ppm of CaF treatment both for coarse sand and sandy loam soil. The validation results also reveled that the break through curves for sand and soil closely follow each other (Fig. 1 b and 1 d). However, the peak and the concentrations beyond the peak were over-predicted mainly in case of soil, though the time to peak and trend of variation closely matched with the observed values. Complete break through was not attained in case of the soil unlike the sand possibly due to the adsorption of fluoride ion in the soil matrix. Regression analysis between the observed and simulated values showed very good results. In all the cases the slope of linear regression line was close to unity and the intercept was negligible. The value of coefficient regression lied in the range of 0.92 to 0.98. After getting the model-predicted results, which matched closely with experimental results, model was used in the simulation of the other irrigation treatments.

4.4 Test of water quality in the soil column

In case of the soil column, the leachate was continuously monitored for 7 days after one pass of fluoride contaminated water of 15ppm and 20ppm. The results (Fig. 1c and Fig. 1d) indicated that the concentration of fluoride in the leachate reached its peak after 4 days in both 15 ppm and 20-ppm treatments. Again water was applied and the change in concentration was noticed. After one week (168 hr), the concentration of fluoride in the water came down to 2.59 mg/l in case of 15-ppm treatment and 3.46 mg/l in case of 20-ppm treatment. This is higher than the recommended fluoride limit in the drinking water (1.5mg/l).

The diffusive and convective movement of fluoride controls the depletion of fluoride following rainfall. The diffusive flux is due to concentration gradient while convective transport of fluoride is largely regulated by water pressure gradient. The temporal change of concentration gradient of fluoride in vertical direction shows that the concentration gradient is generally directed vertically upwards. Very low concentration of fluoride during the initial time period was possibly due to relatively slow movement of water in vertical direction in the soil, which has considerable amount of clay.

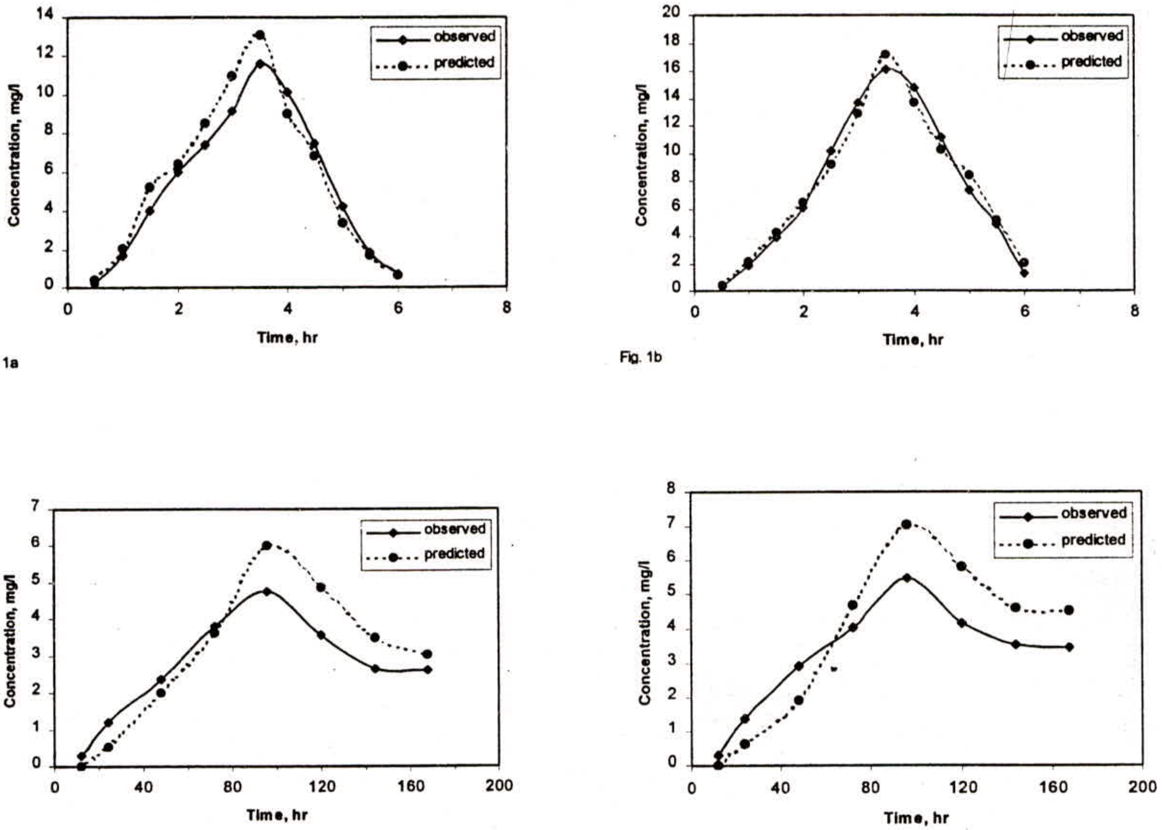
Fig. 1a

Fig. 1b

Fig. 1c

Fig. 1d

Fig. 1 Observed and predicted temporal variation of Fluoride concentration in the leachate at 90 cm depth of soil column for (a) sand with 15 ppm CaF treatment, (b) sand with 20 ppm CaF treatment, (c) soil with 15 ppm CaF treatment, (d) soil with 20ppm CaF treatment.

The CHEMFLO model was also used for extrapolating the results for different ground water table depths. In the present study depth to ground water table of 2m, 5m, and 10m were considered which could be assumed as shallow, medium and deep ground water table situations. The main objective was to find the optimum number of irrigation cycles, which will not pollute the ground water, if contaminated water with fluoride concentration of 15ppm, is used for irrigation.

It is clear from Fig. 2 that if the concentration of fluoride in the irrigation water is 15ppm and the ground water table is at 2m below the soil surface, then the maximum number of irrigation cycles should not be more than two, in order to avoid ground water contamination. Similarly, for

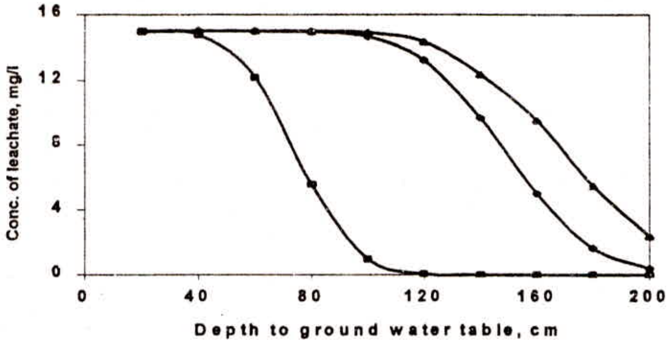

Fig 2a

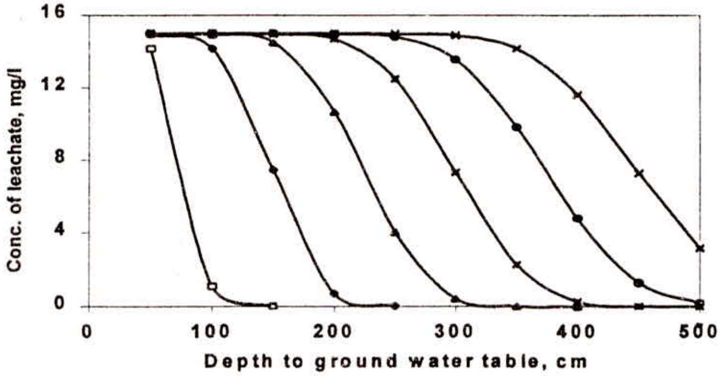

Fig 2b

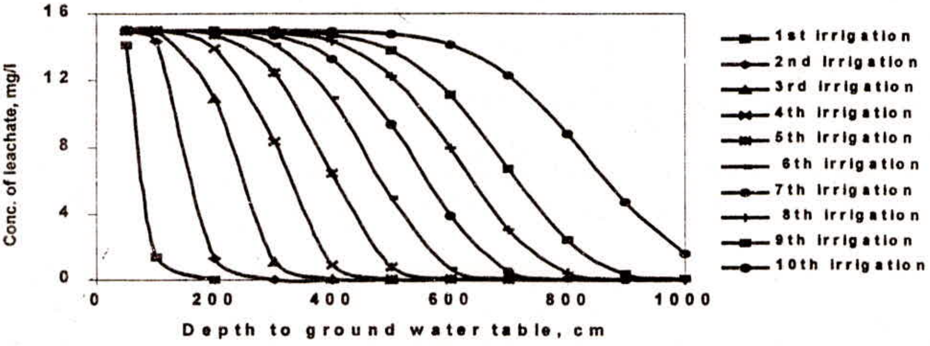

Fig 2c

Fig. 2. Fluoride concentration in leachate after 7 days of irrigation events with 15 ppm fluoride contaminated water when depth to groundwater table was (a) 2 m, (b) 5m and (c) 10m

medium ground water table depth of 5m, the number of irrigation cycles should be limited to five, and for deep ground water table (10m), the maximum number of irrigation cycles should be restricted to nine. Therefore, knowing the ground water depth and the concentration of fluoride in irrigation water, minimum number of irrigation cycles can be predicted by the CHEMFLO model, so that effective scheduling of irrigation can be done without causing ground water contamination. This will help in decisions making pertaining to effective management of contaminated irrigation water without hampering the ground water quality.

5.0 CONCLUSIONS

The following conclusions could be drawn on the basis of the results obtained from the current study :

1. The leachate percolating the root zone into a shallow ground water in case of a sandy loam soil irrigated with 15 ppm of fluoride contaminated water, exceeds the acceptable limit of 1.5 mg/l for drinking purpose and thereby will pollute the ground water.

2. A close match between observed and simulated results as indicated by the high R^2 values revealed that CHEMFLO model can successfully be used to predict the movement of water and fluoride under different irrigation scheduling and groundwater table situations.

3. Under similar topsoil and contaminated irrigation water conditions, the optimum number of irrigation cycles, for shallow (2m), medium (5m) and deep (10m) groundwater table situations, should not be more than 2, 5 and 9 respectively in order to avoid pollution of groundwater.

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