IWMI-TATA WATER POLICY RESEARCH PROGRAM

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Groundwater Pollution through Agricultural Practices and Agro Industries in India

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Abstract

The increasing trend in fertilizer and pesticide use in the agricultural production system and percolation of industrial effluent including municipal sewage, are the reasons of contamination by different harmful elements and compounds to the ground water which is the main source of drinking and irrigation water in most part of the country. The problem may take the devastating shape if appropriate preventive and remedial measures are not taken in time. Among various contaminants, nitrate pollution is considered to be most dangerous which causes various harmful effects on the health of human and animals if used for drinking purposes. In order to assess the level of ground water contamination, appropriate mathematical model (developed on the basis of pilot studies conducted on small scale) may be used and accordingly plans and strategies may be formulated to combat the menace. The paper discusses the types and sources of contaminants and status of ground water pollution in the country, philosophy of mathematical modeling, and remedial and preventive measures for ground water contamination, on the basis of research conducted under All India Coordinated Research Project on Optimization of Ground Water Utilization through Wells & Pumps and other related studies conducted in the country and abroad.

Introduction

Ground water has become major source of water in the country to meet the agricultural, animal, industry and domestic (including drinking) needs. The National water policy drawn up in 1987, and presently under revision, has already accorded the highest allocative priority to drinking water needs of the household sector (Dhawan, 2001). More than 50% of the total area under irrigation is fed by ground water resources. However, the quality of the ground water available is a concern for its sustainable and effective use. During the last few decades, disposal of effluents from industries and municipal sewage and their percolation to ground water, adversely affected the quality of the ground water. The rate generation of wastewaters in India during 1981 was estimated to be 74,529 million L/day i.e. about 27 km^3 annually. The increased use of chemical fertilizers and pesticides further aggravates the condition. All these pollutions are creating health problems, as the ground water is the major and easily available source for drinking purposes in most of the villages and urban areas. In the late 1990s, India's Central Pollution Control Board found that groundwater was unfit for drinking in all 22 major industrial zones it surveyed.

In view of the alarming conditions of ground water pollution in some regions of the country, efforts have been made under the All India Coordinated Research Project on “Optimization of Ground Water Utilization through Wells and Pumps” and other related projects, to assess the ground water quality deterioration due to fertilizers and pesticides application, and percolation of effluents from agro-based industries, and devising methods to overcome the problems.

Karanth (1990) defined the ground water pollution as “the process of induction to ground water of objectionable matter or property, arising from human activity, and thereby so changing its physical, chemical or other property as to render it unfit or less fit for drinking, agricultural or other use, is called ground water pollution. From the hydrodynamic point of view, the sources of ground water pollution can be classified according to their geometry (Gupta, 1998) as:

1. Point source (non-penetrating injection wells, leakage from tanks, etc.)
2. Line source (saltwater intrusion, seepage from canals carrying wastewater, etc.)
3. Plan or diffuse source (agricultural waste).
4. Based on characteristics of constituents, the pollution can be categorised into four groups:
5. Physical (heat, suspended solids, etc.)
6. Chemical (inorganic chemical contaminations, brines, acid, NO_3-N, sulphate, petroleum products, etc.)
7. Biological (bacteria, virus, and protozoa derived mainly from sewage and decomposable materials)
8. Nuclear (radioactive materials)
9. In the present paper, the discussion will be limited to the ground water pollution due to agricultural and agro-based industrial activities only.

1. Pollution from Agricultural Activities

In order to improve the production and quality of produce, various types of fertilisers, pesticides are applied to the agricultural fields. Some times, poor quality of irrigation water is also applied. For livestock production, feeds and animal wastes are stocked in the open area. The rainfall or irrigation water dissolves some of the constituents of these materials, percolates through the root zones, and contaminates ground water. Although, there are many harmful contaminants are added to ground water, but nitrate pollution has drawn lot of attention due to its severity for health hazards.

1.1 Nitrate pollution

Higher nitrate concentration in drinking water has drawn a lot of attention due to its harmful biological effects on health. It has been established that indigestion of water containing higher nitrate concentrations causes methemoglobinemia (i.e. infant cyanosis or blue-baby syndrome). It also affects the blood in such a way as to reduce its oxygen carrying capacity (OECD, 1988). However, it also has the risk of gastric and intestinal cancer. The functioning of central nervous system and cardiovascular system may also be affected adversely by nitrate rich water (Agrawal, *et al.*, 1999). The World Health Organisation has recommended the permissible limit of 10 mg/L nitrate nitrogen (NO_3-N) or equivalent to 45 mg/L of NO_3, which is also accepted by Indian Council of Medical Research.

The nitrate contamination to ground water may be through natural or anthropogenic sources. However, the anthropogenic sources are most often causes the amount of nitrate to rise to a dangerous level. Disposal of human waste through garbage piling, septic tanks, etc., disposal of industrial waste through liquid storage in lagoons, spreading on surface, solids dumped in landfills or garbage piling, burial in excavated pits, are some of the non-agricultural sources ground water contamination including nitrate pollution. Use of chemical fertilisers (nitrogeneous), some pesticides, field application and storage (in pits or piles) of animal wastes, are the important agricultural sources.

As per the studies of CGWB referred by Agrawal *et al.* (1999), the incidence of high nitrate in well waters was conjunctured to be due to pollution of some sort, either from human or animal sources or from irrigation return flows from agricultural fields dressed with chemical fertilisers. In the past 50 years, the use of N-fertilisers was increased tremendously in the country, from 58,700 tonnes in 1951-52 to 11,592,700 tonnes in 1999-2000, while the use of other fertilisers (P and K) was relatively less (Fig.1). Even in last two decades (1980-2000), the consumption of N was increased by three folds. The N-consumption per ha of the major states is shown in Fig.2. Punjab and Haryana are the states consuming more than 100 kg/ha of N fertilisers which is the major reason for highest nitrate pollution of well waters (Agrawal *et al.*, 1999) of the two states. However, the nitrate pollution level above the WHO permissible limits was also reported from Gujarat, Maharashtra, and Ganjam district of Orissa (Handa, 1986). There are 773 nitrate-affected villages in Gujarat (Durgaprasad, 2000). If we observe the trend in fertiliser consumption, the nitrate pollution is also likely to become a menace in Madhya Pradesh, Andhra Pradesh, West Bengal, Karnataka, etc. However, the nitrate contamination in industrial advanced states has significant contribution due to effluent percolation in addition to agricultural fertiliser use.

The nitrogen applied through fertilisers or manure is converted to plant-available nitrate by bacteria living in the soil. The growing plants and the bacteria consume part of these nitrates. When sufficient decomposable organic matter is present, soil bacteria can remove a significant amount of NO_3-N through a process called immobilization. NO_3-N becomes a part of soil organic matter through this process of immobilization. Another group of bacteria use nitrates as a substitute for oxygen when oxygen is limited. These bacteria convert NO_3-N to gases such as nitrogen, nitrous oxide, and nitrogen dioxide, through the process of denitrification. The excess NO_3-N left out after crop and bacterial consumption, immobilization, and denitrification can leach out of the root zone and possibly end up in groundwater. In addition to the source, nitrate may be added to ground water through percolation of industrial effluents or sewage water.

In order to assess the nitrate pollution from different sources, studies were conducted at GBPUAT, Pantnagar; PAU, Ludhiana (Sharma, 1996); and IHH, Poondi (Tamil Nadu) under the aegis of AICRP on Ground water. At Pantnagar, the NO_3 pollution was observed to be higher (2.3 mg/L) for water samples from the wells located near Century Paper and Pulp mills, Lalkuan (Uttarakhand) which were closely followed by agricultural fields (2.05 mg/L) located in Crop Research Centre, Pantnagar. However, it certainly depends upon the level and mode of fertilizer application and use of industrially polluted water for irrigation. The NO_3 level in well water samples from the long term fertility trials (1.2 mg/L) was relatively less than those from the fields in which short term fertility studies (1.7 mg/L) were carried out. However, the nitrate pollution near Rudrabilas Sugar factory (0.75 mg/L), Rudrapur (Uttarakhand), and from domestic and municipal sewage (0.71 mg/L) was observed to be quite less. Although, the observed concentration of nitrogen contamination in ground water was below the permissible limit of 45 mg/L (recommended by WHO), it draws attention due to its increasing trend and irreversible nature of such pollution in short or medium term.

The nitrate concentration in well water samples collected from 113 village located on/adjacent to the intersection of a grid of 6.0 x 6.0 km in Ludhiana district of Punjab were collected and analysed. Initial analysis showed that the concentration of NO_3-N in the samples were in the range of 5.5 to 26.3 mg/L with an average of 12.2 mg/L. Around 68% samples were found to have concentration above 10 mg/L (WHO permissible limit). In post monsoon samples, 84% of the samples had NO_3-N concentration higher than 10-mg/L limit. This indicates that the nitrate pollution in the study area has already reached to its hazardous level and needs special attention to control its further growth.

In a laboratory study conducted with a soil column (diameter 10 cm) consisting of 100 cm depth of clay loam and 70 cm of sandy loam, leachate received at bottom of the column were analysed. Under the wetland conditions (fertilised with 341.5 mg urea, 490.0 mg SSP, 130.9 mg MOP and 785.0 mg $ZnSO_4$), the results showed that the NO_3-N concentration were gradually reduced from 80.0 mg/L for the leachate collected on 11th day to 36.8 mg/L for 66-75 days (Fig.4). The total leaching losses were found to be 36.48%, however, the higher value may be attributed to mineralisation of organic matter and high initial mineralised N in the soil (PAU, 1999). The results clearly point out the possible growth of nitrate level in the ground water in future, if the present trend of fertiliser consumption is continued without effective measures.

1.2 Other contaminations

In addition to nitrate pollution, the quantity and style of chemical fertilisers, organic fertilisers, pesticides, poor quality of water, storage of animal waste and feedlots, etc. are the sources of other chemical / biological contaminants which is extremely harmful, if crosses the permissible limits. There are reports from different parts of the World, of increasing pesticides penetration into various aquifers used for potable water. Some cases at concentrations giving serious concern for human health (Lowrence and Foster, 1987). The pesticides such as aldicarb, DBCP, EDB (soil insecticides), Atrazin, MPCC, 2-4-D (a herbicide), are more mobile and most readily leached from cultivated soils, although losses of not more 5% is involved.

Normally phosphate is not transported to ground water since it is rarely leached through the soil but eroded from the surface. The only exceptions are the case of soil with seasonally high water tables and those where phosphate saturation is reached (OECD, 1988).

The ground water sample from long term fertility trials at CRC farm, Pantnagar, had higher value of total alkalinity, chloride, and total Ca and Mg hardness. This shows that the use of fertiliser lead to infiltration of nutrients like Ca and Mg to ground water that changed the chemical characteristics of water. In study conducted in Ikkadu block of Tiruvallur district of Tamilnadu, the wells samples also show increasing trend of many chemical constituents (Ca, Mg, Cl, SO_4, Hardness, Na, K, HCO_3, TDS, etc.) during post cultivation period as compared to pre cultivation.

The organic fertilisers (compost) is mostly applied in the form of solids or slurry. They are the possible sources of pathogens in ground water (OECD, 1988).

2. Contamination from Agro-Based Industries

The methods of disposal of industrial effluents include diversion to surface water sources (rivers, lakes, canals, etc.), stored in lagoons or ponds for percolation, or spreading or spraying onto the ground surface. The effluents may be treated, partly treated or untreated. The polluted water percolates either directly from the surface water bodies or from agricultural fields (when such water is used for irrigation), and pollutes the ground water. In addition to the nitrates, the pollutants includes significant amount of heavy metals, toxic elements, bacteria, virus, etc. that make the ground water unfit for every use (drinking, agricultural or industrial). Hence, serious attention needs to given for minimising such pollution. The permissible limits for drinking purposes for various constituents of ground water pollution are given in Table 1.

The upper limits of total dissolved solids concentration for livestock use are: 2860 mg/L for poultry, 7150 mg/L for calttle (dairy), 10,100 for cattle for beef and 12,900 mg/L for sheep (adult). However, selenium is known to be highly toxic for animals and it should be within the non-toxic limits of 0.4-0.5 mg/L in water. For irrigation use, electrical conductivity (EC), sodium absorption ration, boron concentration (depending upon tolerance of plants), and residual sodium carbonate (RSC<1.25 epm safe; 1.25-2.5 marginally safe; and >2.5 unsafe) are the major chemical constituents affecting quality of water.

The extent of pollution depends upon the volume of effluents discharged per day and their characteristics. A rough estimate of discharged wastewater can be made from the volume of water required per unit of produce and the total production in a particular factory. It has been estimated that various chemical factories need water upto 1100 m^3/tonnes of produce while water to the extent of 277 to 455 m^3/tonnes by pulp and paper industry, 45 m^3 both by steel and laudering and 4 to 10 m^3/tonnes by vegetable canning, sugar refining, coal mining, milk processing and baking industry, 140 m^3/tonnes for 1000m of cotton cloth, is needed (Paliwal, 1989). This reflects that except some chemical industries, pulp and paper industry discharges maximum amount of polluted waters. Newprint and paper Mill at Nepanagar, M.P. discharges about 18 million gallons/day of effluent and about 650,000 gallons/day of water is discharged by Amul Dairy, Anand. The characteristics of some selected industrial effluent and sewage is given in Table 2.

The analysis of effluents from Pulp and Paper Mill, and Sugar factory at GBPUAT, Pantangar revealed that the effluents contain very high concentration of inorganic, organic and microbial pollutants, which severely affects the quality of surface and ground waters. The analysis of ground water samples collected from the areas subjected to effluent discharge from Pulp and Paper Mill, and Sugar factory also indicated the presence of various pollutants with concentration above tolerance limit, except acidity.

In Maharasthra, the effluents from sugar factories and associated paper mill and distilleries are poured into lagoons or diverted to nallas from which it seeps through the soil and pollutes ground water. However, the farmers of the area are bound to apply the polluted well water that deteriorates the soil properties. Studies conducted at MPKV, Rahuri revealed effluents from the industries were highly polluting as evidenced by presence of BOD, COD, various anions and cations with very high concentrations as compared to permissible limits. In the study area, about 8% and 92% of the total area was demarcated as highly polluted and medium polluted, respectively on the basis of analysis of well water and soil samples. Efforts were also made to formulate a strategy to use the polluted well water in conjunction with canal water for irrigation.

Studies made in the leather tennary affected areas around Palar river in the North-Arcot district of Tamilnadu showed that the ground water had been polluted up to a width of 2.4 km from the river bank which was found unfit both for human use and irrigation. Similarly, the ground water and soil around the sugar factories in Tamilnadu was considerably polluted.

The effects of domestic wastewaters and sewage on ground water pollution were studied at Pantnagar and found that the ground water samples were highly acidic and contains oil and grease.

3. Ground Water Pollution Modelling

Mathematical models are essential to analyse complex problems in ground water environment. Both simulation and optimisation models have been used in the analysis of ground water system dynamics. With simulation models, alternative management decisions are evaluated by recomputing the model for each alternative considered. The results of the alternative strategies are compared in terms of criteria used, and, accordingly, an appropriate decision is made. On the other hand, optimisation models use mathematically based search policy that maximizes the criteria without actually simulating the model for every possible alternative. Most groundwater simulation models developed are deterministic mathematical models that are based on conservation of mass, momentum, and energy. The models generally require solution of partial differential equations under specified boundary or initial conditions of the system.

In ground water pollution modelling, two partial difference equations are to be solved simultaneously with appropriate boundary and initial conditions. The first partial difference equation pertains to ground water flow in an saturated (or partly unsaturated if recharge from soil mass above water table is considered) porous medium, while second one pertains to solute transport. In the following text, both the processes responsible for groundwater contamination and its spread is discussed in brief.

3.1 Ground Water Flow

The basic governing equation for flow in porous medium is derived on the law of conservation of mass coupled with Darcy’s equation. Henry Darcy (1856) observed that the velocity of flow through a porous medium is proportional to the hydraulic gradient, i.e.

$$V = -K\nabla h \qquad \ldots 1$$

Combining eq(1) with the continuity equation, the equation governing the ground water flow can be derived in the form

$$\nabla V = \nabla(-K\nabla h) = -(S_s \frac{\partial h}{\partial t} \pm Q) \qquad \ldots 2$$

where V=Darcy velocity
K=hydralic conductivity, $[LT^{-1}]$;
h = hydraulic head [L];
∇= differential operator;
S_s= specific storage = S/b $[L^{-1}]$;
S = storage coefficient of aquifer [];
b = thickness of the aquifer [L];
Q= specific source (-) or sink (+) as volumetric flow rate per unit aquifer area, $[T^{-1}]$.

For saturated flow, the value of K remains constant to its maximum value known as saturated hydraulic conductivity. Under unsaturated condition, the Darcy equation (1) is modified such that the value of K becomes dependent upon soil moisture or hydraulic head (h). Combining this concept with equation (2), the S (specific storage) is replaced with C (specific capacity = dθ/dh, θ is the soil moisture).

In anisotropic flow medium eq(2) is reduced to

$$\frac{\partial}{\partial x}\left(T_x \frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(T_y \frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(T_z \frac{\partial h}{\partial z}\right)=S\frac{\partial h}{\partial t}+Q \qquad \ldots 3$$

where T = aquifer transmissivity (=Kb), the subscripts x,y,z refers to the directional component in Cartesian coordinates.

For isotropic flow medium, the governing equation is simplified to eq(4) that has been adopted under most of the model development.

$$\frac{\partial^2 h}{\partial x^2}+\frac{\partial^2 h}{\partial y^2}+\frac{\partial^2 h}{\partial z^2}=\frac{S}{T}\frac{\partial h}{\partial t}+Q \qquad \ldots 4$$

However, as the flow in vertical direction (capillary rise, etc.) is mostly ignored, the eqs (3&4) excludes terms related with z direction. The term Q includes the rainfall or irrigation recharge, or effluent flow, direct leakage between aquifers, water yielded from storage in clay layers, pumping of water, subsurface flow across boundaries. However, the sign of each component of Q must be taken i.e. positive for withdrawal and negative for addition to the system.

The governing equation is solved for ground water flow in a region that may be infinite in areal extent or bounded on one or more sides by source boundary (river, reservoir, etc.) or sink boundary (down sloping terrains, drains, etc.) or barriers (hard rocks or impermeable clay). At bottom, mostly a impermeable clay layer is assumed.

3.2 Solute transfer

The solute transfer models simulate and predict the movement and concentration of various contaminants in aquifers. For pollution problems, ground water analysis is mainly concentrated on assessment of already contaminated sites and / or planning to minimise concentration hazards from future activities. Both types of conditions require the capability to predict the behaviour of chemical contaminants in flowing ground water. To accomplish this, the models incorporate mathematical approximations of the transport by means of fluid flow with chemical reactions (non-conservative models) and without chemical reactions (conservative models). The models are much more complex than flow models as they also include quality.

The governing equation for expressing the process of solute transport in a flow region is also derived using law of mass conservation of constituent contaminants. The various mass transport processes that affect the transport of contaminants in the subsurface environment include advection, molecular diffusion, mechanical dispersion, biochemical transformations, and interphase mass transfer. Considering the mathematical basis for expressing these processes and taking the mass balance of chemical constituents into account, the solute transport may be expressed by the equation (Gupta, 1998)

$$\frac{\partial}{\partial x}\left(D_x \frac{\partial C}{\partial x}\right)+\frac{\partial}{\partial y}\left(D_y \frac{\partial C}{\partial y}\right)+\frac{\partial}{\partial z}\left(D_z \frac{\partial C}{\partial z}\right)-\frac{\partial}{\partial x}(V_x C)-\frac{\partial}{\partial y}(V_y C)-\frac{\partial}{\partial z}(V_z C) = \frac{\partial C}{\partial t}+\frac{\rho_b}{\Phi}\frac{\partial S}{\partial t}+Ck_l+S\frac{k_s}{\Phi}\rho_b \qquad \ldots 5$$

where C = concentration in liquid phase (mass of contaminants/volume of solution);
S = concentration in solid phase (mass of contaminants/volume of solution);
V = seepage velocity components (predicted using flow models);
D = hydrodynamic dispersion coefficient;
ρ_b= bulk density of soil;
k_l, k_s = first order decay rate in the liquid phase and soil phase, respectively,
Φ = effective porosity;
and the subscripts x,y,z refers to the directional component in Cartesian coordinates.

For solving the dispersion equation (5) for S and C, the flow velocity component (V) has to be evaluated using the flow models (section 3.1). If a retardation factor [$R=1+\rho_b S/(C.\Phi)$] and overall first order decay rate [$k=k_l+k_s\rho_b S/(C.\Phi)$] is introduced eq(5) then the solution is to be obtained only for one dependent variable i.e. C and right hand side of the equation is simplified into two terms only.

The process of modelling nitrate dynamics from urea application under wetland conditions as developed by PAU centre, has been discussed here to demonstrate the modelling phenomenon.

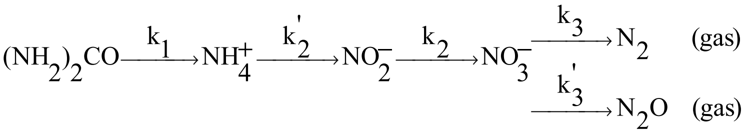
Brief Description of Nitrate Dynamics Model

Wetland moisture regime is the simulation of the moisture regime prevailing under rice crop. The general equation describing reversible ion exchange reaction and reversible microbial transformations is

$$\frac{\partial c_i}{\partial t} + \frac{\partial s_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - v \frac{\partial c_i}{\partial x} \pm \phi_i \qquad \ldots 6$$

Where c_i is the solute concentration; s_i is the quantity of absorbed solute per quantity of soil, assumed to be linearly related to solution conc. of solute; ϕ_i is the source or sink; D_i diffusion coefficient; v is the velocity of flow.

A series of transformations often encountered in soils as a result of urea applications:



$$(NH_2)_2CO \xrightarrow{k_1} NH_4^+ \xrightarrow{k_2'} NO_2^- \xrightarrow{k_2} NO_3^- \begin{cases} \xrightarrow{k_3} N_2 & \text{(gas)} \\ \xrightarrow{k_3'} N_2O & \text{(gas)} \end{cases}$$

The first order rate constants (in sec^{-1}) for the transformation processes of urea hydrolysis (k_1); nitrification (k_2, k_2') and de-nitrification (k_3,k_3'). These transformations can be represented by the following expressions

$$\frac{\partial c_1}{\partial t} = - k_1 c_1 \qquad \ldots 7$$

$$\frac{\partial c_2}{\partial t} = k_1 c_1 - k_2 c_2 \qquad \ldots 8$$

$$\frac{\partial c_2'}{\partial t} = k_2 c_2 - k_2' c_2' \qquad \ldots 9$$

$$\frac{\partial c_3}{\partial t} = k_2 c_2 - k_2' c_2' - (k_3 + k_3') c_3 \qquad \ldots 10$$

Where c_1, c_2, c_2' and c_3 are the concentration of urea, NH_4^+, NO_2^-, and NO_3^- respectively. It should be noted that because of the enzymatic hydrolysis of urea to NH_4^+, the concentration of urea is monotonically decreasing as can be seen from eq(7). For the other solutes of nitrogen, their rates of change can be either positive or negative depending upon the relative magnitudes of the terms on the right hand sides of other equations (8,9,10). The independent parameter s from the eq(6) was reduced to c using partition coefficient (R=s/c).

A known amount of solute is added or maintained at a constant value for a specified time, at the surface of soil column. Eq (6) in conjunction with eqs (7 to 10) was solved using Laplace transformation subject to the following initial and boundary conditions;

$$c_i = 0, \quad t = 0; x \geq 0 \qquad \ldots 11$$

$$c_i = c_i^0, \quad 0 < t < t_1; x = 0 \qquad \ldots 12$$

$$c_i = 0, \quad t \geq t_1; x = 0 \qquad \ldots 13$$

$$c_1 = 0, \quad t > 0; x \to \infty \qquad \ldots 14$$

where ci the concentration of urea, Ammonium and/or Nitrate fertilizer and c_i^0 the initial concentration of any or all of these three.

These equations could be solved either for steady feed or pulse feed application of urea. The computer program was written in FORTRAN 77. The model was used to predict distribution of NO_3-N as a function of depth and time.

Validation

The above model was validated using the data obtained in the column study as discussed in section 1 above. Using the model, depth-wise profile of NO_3-N in the column (up to 170 cm depth) was predicted for 15, 30, 45, 60 and 75 days after the application of urea. The concentration of NO_3-N in the leachates that percolated beyond 170 cm of depth was also predicted. The results were compared with the data observed in the laboratory study (Fig.3 and 4) using paired t-test analysis. The difference between the two sets of values were insignificant at 5% of probability which showed that the model predicted reasonably well the nitrate-nitrogen pattern in the soil profile and nitrate concentration in leachates, an important indicator for ground water pollution.

The above model incorporates chemical transformations of urea into different forms. The model may reasonably modified to predict the pollution from other contaminants by just modifying the mathematical expression for chemical transformation applicable to concerned contaminant. Dikshit *et al.* (2000a) presented a finite element model to predict ground water pollutant transport without chemical transformation of constituents. Dikshit *et al*. (2000b) incorporated variation of biological oxygen demand (BOD), dissolved oxygen (DO), nitrogen, phosphorous, and toxic substances in a model that simulate water quality for river system. This aspects may also be added to ground water pollution models.

4.0 Remedial Measures

There are four natural controls involved in shallow ground water contamination (Deutsch, 1965):

i) Physical and chemical characteristics of the earth materials through which the liquid wastes flow.
ii) Natural processes that tend to remove or degrade a contaminant as it flows through the subsurface from areas or points of recharge to zones or points of discharge.
iii) Hydraulics of the flow system through which the waste migrates, beginning with infiltration and ending with discharge.
iv) Nature of the contaminants.

Many chemical and biological reactions in the unsaturated zone lead to contaminant degradation, precipitation, sorption, and oxidation. The greater the thickness of the unsaturated zone, more attenuation is likely to take place. Below the water table the mineral content of the medium probably becomes more important because various clays, hydroxides, and organic matter take up some of the contaminants by exchange or sorption. Many minerals may have no effect on the contaminations with which they come into contact.

The pollutant enters the ground water in a dilute form from a dispersed, as in the case of application of pesticide in an irrigated tract, or in a concentrated form from a point source, as in the case of injecting it through a well. When applied on surface, the zone of aeration acts as an effective filtering medium so that amny undesirable properties like odour, colour and turbidity are removed and the water bacteriologically purified. Generally, filtration through 3 to 5 m of fine-grained soil removes a greater part of harmful bacteria. The horizontal path of flow of bacterial pollution, in sand from a point source such as a well used for artificial recharge, has been found to reach a maximum width of 2 m before final disappearance at about 30 m from source. Chemical pollution follows a similar but more extensive path than that of bacterial pollution (Karanth, 1990). More or less on the similar concept Soil Aquifer Treartment (SAT) has been designed that is discussed as below.

4.1 Soil Aquifer Treatment Technique

Soil Aquifer Treatment involves low wastewater treatment cost and provides greater and longer safety from pollution hazards. In this system, wastewater moves down to the ground water and is renovated by filtration through the vadose zone and subsequent movement through the aquifer. The method was tested in laboratory (in soil column of 125 cm diameters and variable heights of 75, 150, 225 cm, filled with pea gravel for bottom 10 cm and rest with loamy sand or sandy loam) as well as in field conditions at PAU, Ludhiana for its feasibility of using renovated sewage water for unrestricted irrigation. The results from a 300cm soil column established that the system is suitable for renovation of highly polluted sewage water to make it fit for irrigation as it brought most of the quality parameters within permissible limits (Table 3).

4.2 Nitrate Pollution Control and Treatment

Among the soluble contaminants, nitrate is the most important which has to be treated for providing safe drinking water. In dealing with the nitrate problem in subsurface waters, there are two options for achieving safe nitrate levels.

4.2.1 Non-treatment methods

The non-treatment processes attempt to bring the nitrate concentration down to a safer level (<10 mg/L), through blending with cleaner waters. There are four alternatives:

- Raw water source substitution: An entirely new source of drinking water is used to replace the heavily polluted water.
- Blending with low nitrate waters.
- Connection to an existing regional system: This involves using a system that is already set up to service the area, instead of drawing water from the contaminated well.
- Organizing a regional system: This is similar to the use of an existing regional system. One can "...form a new regional utility by joining with other nearby systems which may be having similar water quality problems..." (Guter, 1981).

The use of industrial effluent polluted well water in conjunction with canal water was evaluated at MPKV, Rahuri. The results shown that the mixing of medium polluted well water (EC-1.58 dS/m) may be used safely for irrigation to wheat by applying irrigation alternately with the two types of waters or blending with equal proportion (50:50) which had non-significant effect on the yield (Bhatnagar, 1999).

Greyer *et al.* (1992) observed that nitrate concentration to be high at the water table and to decrease (often to below detection level) with depth. This occurs due to natural denitrification process due to reduction in oxygen concentration with depth. Such stratification of nitrate concentration can be utilised to tap good quality ground water for domestic wells by putting well screens at a reasonable depth below water table (Ray, 2001). Mejia and Madramootoo (1998) also observed that the controlled water table management could reduce the nitrate concentration in drainage effluents and ground water pollution, and using the nitrate rich effluent taped from water table layer for irrigation, the economics of the system can be improved through fertiliser saving and enhanced crop yield.

4.2.2 Treatment Method

In this option, the treatment processes a portion of nitrates are removed (with varying efficiencies depending upon other substances present in the water) using the concepts of ion exchange, reverse osmosis, biological denitrification and chemical reduction. However, none of these methods is completely effective in removing all the nitrogen from the water.

Ion exchange: The process uses the concept that the water solution must be electronically neutral, and therefore, by inserting a negative ion, another negative ion can be removed from water. Special resins are used to substitute chloride (Cl^-) for the nitrate radical. There are four steps involved in the decontamination process: resin recharging to its maximum capacity, anion exchange in the water solution, resin become exhausted, and resin regeneration. In implementation of the method, the selection of a suitable resin for nitrate is a problem as most of the available resins are not completely nitrate selective and often remove other anions (e.g. SO_4) prior to nitrate. The disposal of spent regenerant is also a problem. The process requires huge quantity of resins, therefore, is too costly (OECD).

Biochemical denitrification: This process takes advantage of naturally occurring micro-organism that reduce nitrate to nitrogen under anaerobic conditions, provided that a suitable source of carbon is added (OECD, 1988). Ethanol / methanol are the inexpensive source of carbon for the water treatment. Sometimes it is necessary to convert the nitrogen from the ammonium ion into nitrite with the use of nitrosomas (specialized bacteria) to facilitate the removal of all nitrogen from the solution. The nitrite compound is then oxidized to nitrate and eliminated. Besides bacteria, photosynthetic algae can also remove nitrates from water. However, the efficiency of the process largely depends upon other toxic chemicals and compounds present in the water that affects the biological agents. The greatest benefit of the bio-chemical denitrification is the fact that the nitrogen is completely removed in its gaseous elemental form.

Reverse osmosis: Reverse osmosis uses semi-permeable membranes and high pressures to force pure water through the membrane. The membrane rejects in organic material and allows the passage of water. The efficiency of the process depends upon the quality of the membrane and the salt rejection is anywhere from 50% to 90% (Nyer, 1987). They are expensive to run, due to high pressure required (100-250 psi).

Electrodyalysis: It is a combination of reverse osmosis and ion exchange techniques. The driving force across the membrane is provided by electric current. The ions are removed from the water and pass through the membrane, attracted by the opposite electric charge on the other side of the membrane. The advantages of the system are that the residence time controls the amount of dissolved solids removed, and that the system can be run continuously with no regeneration required. However, in the process, water must carry an electric current, and as the water is cleaner it offers more resistance to the current, that increases the cost of operation.

The process may also be applied in the soil while the movement of water solution through profile before it reaches to ground water. Eid *et al.* (1999) found that the electormigration is an effective means for concentrating and retaining nitrates close to the anode in the saturated soil at low flow rates. For a given electrical input, the effect was reduced as the hydraulic flow rate increased.

In addition to the above there are other methods for removal of dissolved salts from the water such as distillation, freeze desalinisation, liquid/liquid extraction, etc (Swarup *et al.*, 1992). The feasibility and economics in removing nitrates from the ground water should have been evaluated.

4.3 Industrial effluent and sewage treatment

It is recommended that the effluents / sewage must be treated before its disposal to surface waters or allowing it to percolate down by spilling on the soil surface. There are various mechanical, chemical or biological methods reported (Nyer, 1987) to treat the poor quality of water.

Mostly the industrial effluents and municipal sewage is treated in three stages (Swarup *et al.*, 1992). Primary treatment is a mechanical process, which simply removes solids through filtration and/or settling. It is able to remove organic material responsible for 25-30% of the BOD. Secondary treatment is essentially a biological process of decomposing organic matter by mixing bacteria and air oxygen in the wastewater. Water leaving the treatment stage is normally down to a BOD of 10% or less of the initial value; 95% of the organic bacteria is removed, along with 10% of phosphates and perhaps as much as 50% of total nitrogen. Tertiary treatment is able to remove virtually all the remaining contaminations. It includes many advanced techniques i.e. chemical coagulation and filtration, carbon adsorption, chemical oxidation, ion exchange, electrodialysis, reverse osmosis, air stripping, some advanced biological systems, etc. which may be used as per the characteristics of the contaminant or the requirement of end product quality. Air stripping is employed to remove volatile compounds from the effluents.

5. Preventive Measures

Prevention of ground water contamination to the maximum possible extent must be done, before the problem becomes menace. Many factors should be considered when determining the vulnerability of an aquifer to nitrate pollution from agricultural practices. Nitrate contamination of ground water depends upon climate, fertilizer or manure management, soil, crop, and farming systems. In order to reduce the contamination the following preventive measures may be taken up.

- ***Soil Audits and Nutrient Accounting:*** Through chemical analysis of the soil to determine natural nitrogen release, and by accounting for contributions from supplementary manure and legume crops in rotation, farmers can better estimate the amount of additional nitrogen fertilizer required to obtain the desired yield of a crop.
- ***Scheduling Fertilizing and Manure Applications*:** Nitrate losses from fertilizer use can be reduced by matching fertilizer application with nitrogen needs of a crop, using split-applications and foliar feeding. Ridge or band application of fertiliser is better.
- ***Irrigation management***: Never over-irrigate and irrigation should follow application of relatively small dose (split) of fertilisers after a reasonable period to allow percolation to take place. Fertigation with drip irrigation is useful in minimising leaching losses.

- ***Manure Capture and Management***: Storage of manure in open fields with no protection from rain, direct discharge of manure overflow water to a stream, or leaking manure lagoons can all contribute to nitrate pollution of surface and groundwater.
- ***Catch Crops***: A catch crop is a non-leguminous cover crop, densely seeded or planted shortly after main crop harvest, to absorb soluble soil nutrients (especially nitrates) to prevent their leaching. Annual grasses such as wheat, oats, rye and ryegrass during winters and forage sorghums and buckwheat during summer, are often used.
- ***Perennial Crops in Rotation***: Perennial forage crops e.g. alfalfa, white clover, bromegrass, and fescue absorb and recycle nitrates more effectively than row crops.
- ***Drainage Management***: Marginal croplands prone to flooding can be converted to wetlands as an effective means for denitrification. Various strategies to control the outflow of water from tile drains, its treatment in wetlands and reuse as irrigation water, may be worked out.

6. Conclusions and suggestions

Finally, it can be emphasised that the concern about pollution to ground water must be attended in time before it takes the shape of devastating menace. The pollution from industrial effluents/sewage has already gripped many industrially developed cities that needs special attention. However, at present the level of ground water pollution due to fertiliser use is well within the permissible limits in the country (except few patches having pollution level crossing the limits), but, ever-increasing trend of increase in fertiliser consumption in different parts of the country, certainly gives a signal for the situation that we are going to face in future. It must be considered that i) the dependence on ground water for irrigation and drinking purposes will have to increase in view of limited surface water availability and ever-increasing demand for water, ii) the pollution hazards directly affects the quality of ground water which otherwise is of high good quality (barring the natural contamination such as arsenic in West Bengal, etc.), iii) the pollution to ground water generally irreversible process especially in short and medium terms, iv) ground water pollution don’t remains localised but it has the tendency to effect the areas at very large distances and thus, it is hard to control, v) renovation of polluted ground water is highly costly affair and requires large time and huge infrastructure.

In order to make appropriate and efficient plans and strategies to combat the menace of the ground water pollution, concentrated research efforts is necessary to generate enough information on pollution status, its constituents and their behaviour. This information will certainly be specific to location, climatic pattern, geohydrological condition, and polluting source. Hence, studies must be planned for different sources (agriculture fertilisers, various types of industries), which are dominant in the region represented by the study area. As it is quite impossible to have too many field studies, representative models must have been developed or adopted from literature or other sources (internet, direct purchasing, etc.). These models has to be validated in diverse conditions under laboratory or field so that all deficiencies may be recorded which will help while extrapolating the results to other locations. However, at present, it is important to note that such information is scarcely available under the Indian context.

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Annexes

Table 1. Standards for different quality parameters for drinking waters.

Quality parameter	**WHO standards (1971)**		**Indian Standards Institution (1983)**	
	Highest desirable	**Maximum Permissible**	**Highest desirable**	**Maximum Permissible**
Physical				
Turbidity (JTU units)	5	25	10	25
Colour, Hazen-Units (on Platinum cobalt scale)	5	50	5	50
Taste and Order	Unobjectionable		Unobjectionable	
Chemical				
Ph	7.0-8.5	6.5-9.2	6.5-8.5	6.5-9.2
Total dissolved solids (mg/L)	500	1500	500	1500
Total Hardness as $CaCO_3$ (mg/L)	100	500	300	600
Calcium (mg/L)	75	200	75	200
Magnesium (mg/L)	30/150*	150	30	150
Iron as Fe (mg/L)	0.05	1.5	0.3	1.0
Manganese (mg/L)	0.1	1.0	0.1	0.5
Copper (mg/L)	0.05	1.5	0.05	1.5
Zinc (mg/L)	5.0	15.0	5.0	15.0
Chloride (mg/L)	200	600	250	1000
Sulphate (mg/L)	200	400	150	400&
Phenolic substances (as phenol) (mg/L)	0.001	0.002	0.001	0.002
Fluorides (mg/L)	0.6-0.9	0.8-1.78	0.6-1.2	1.5
Nitrates (mg/L)	-	45	45	45
Toxic constituents				
Arsenic (mg/L)	-	0.05	0.05	0.05
Mercury (mg/L)	-	0.001	0.001	0.001
Cadmium (mg/L)	-	0.01	0.01	0.01
Chromium (hexavalent) (mg/L)	-	-	0.05	0.05
Cyanide as CN (mg/L)	-	0.05	0.05	0.05
Lead (mg/L)	-	0.1	0.1	0.1
Selenium (mg/L)	-	0.01	0.01	0.01
Radioactivity				
Gross alfa-emitters (P^c_i/L)	-	3	-	-
Grass beta emitters (P^c_i/L)				

*<30 if SO_4 is 250 mg/L, upto 150 mg/L if SO_4 is less than 250 mg/L; &upto 400 if Mg does not exceed 30 mg/L

Source: Karanth (1990).

Table 2. Characteristics of selected Industrial Effluents and sewage of India.

Industry	**pH**	**SS*** **(mg/L)**	**BOD (mg/L)**	**COD (mg/L)**	**Miscellaneous Constituents**	**Pollution aspects**
Sugar Factory	7.8-8.0	1500-1832	650-820	60-98	-	Large volume; high pH, SS, Colour and toxicity
Straw Board	7.5-12.9	3000	2000	5000	-	High BOD, pH, and SS
Tannery	9.5	3200	7000	-	Chromium 15-20 mg/L	High BOD, SS, Cr and colour
Cotton textiles	8.0-11.0	30-50	200-600	-	Detergent, dyes, chromimum	Alkali, BOD, dyes and varying chemical qual ity
Distillary	4.3	4000	29000	65000	Oil & Grease	High BOD, SS, grease and ready putrescibility and low pH
Refinery	-	-	200	-	Grease, Oil and Tar NH_3/N 1000 mg/L, Phenols 1300 mg/L	Mineral oil and phenols
Fertilizer (Ammonia & Urea)	8.0	3700	30	330	NH_3/N 510 mg/L, arsenic	Toxic due to free ammonia and promotes eutrophication
Dairy	8.0	690	816	1340	Oil & grease	High BOD, SS, Grease and ready putrescibility
Sewage	7.0-8.0	200	350	500	Ammonia, Albuminod	

* Suspended solids

Source: Paliwal (1989)

Table 3: Various quality parameters of untreated and renovated sewage water using 300 cm soil column.

Parameter	**Untreated sewage**	**Renovated sewage**	
		Sandy loam	**Loamy sand**
EC (dS/m)	0.694	0.71	0.73
Turbidity (NTU)	18	0	0
Total solids	675	523.97	532.67
BOD	360	43	91
COD	583.3	70.83	145.83
Organic carbon	360	50	45
Phosphate PO_4-P	6.187	0.41	0.64
Ammonical Nitrogen	1.795	0.21	0.21
Coliform count (MPN)	1800	0	0

Unit: mg/l for all except EC, Turbidity and coliform count.

Source: Bhatnagar (2000)

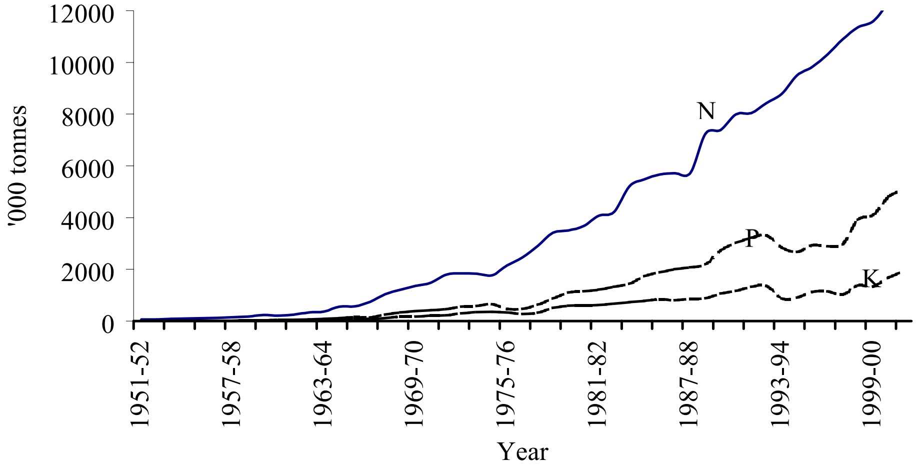

Fig. 1 Trend of fertilizer consumption in India.

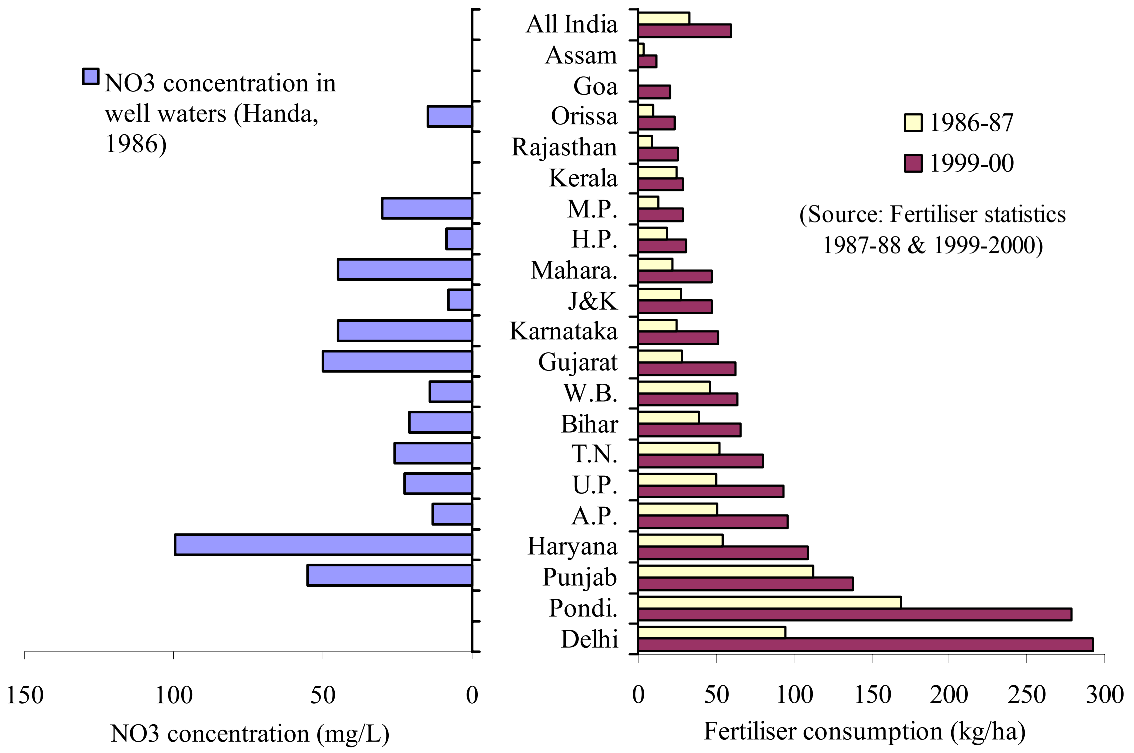

Fig.2 N-fertiliser consumption and NO_3 pollution in major states and union territories of India.

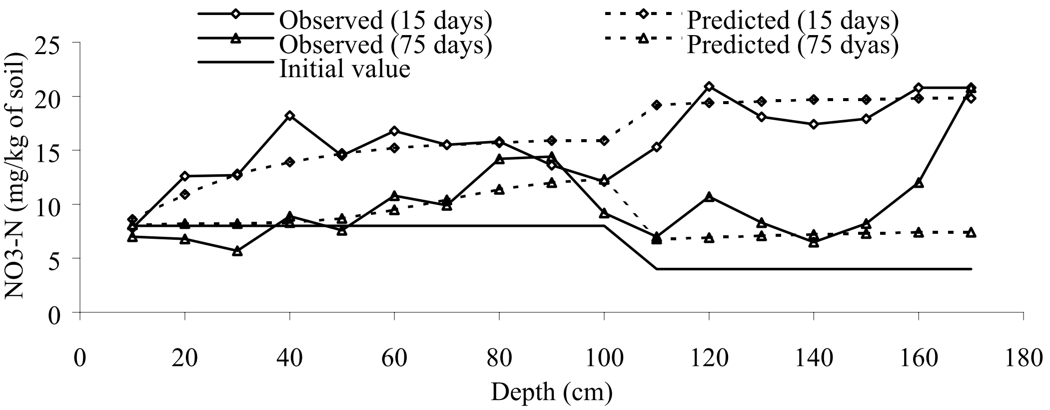

Fig.3 Observed and predicted NO_3-N profile after 15 and 75 days after urea application in the column study

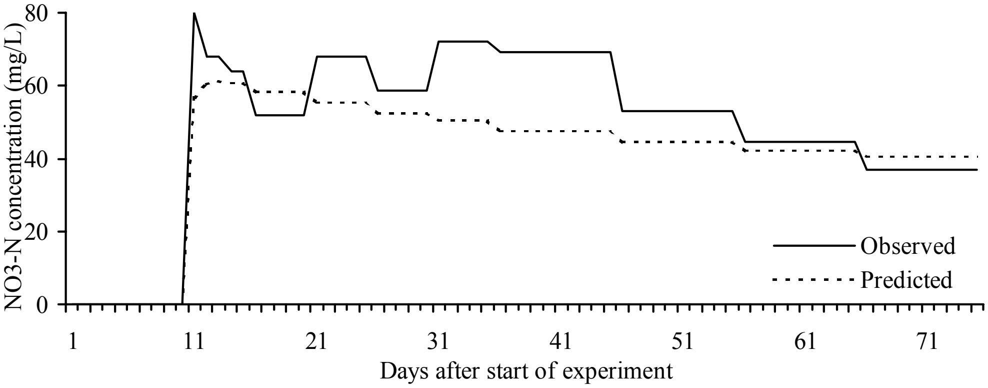

Fig.4 Observfed and predicted NO3-N concentration in the leachate in the column study.

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