Mobility of major ions and nutrients in the unsaturated zone during paddy cultivation: a field study and solute transport modelling approach

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Abstract:
Study of the movement of water and solute within soil profiles is important for a number of reasons. Accumulation of prominent contaminants from agricultural chemicals in the unsaturated zone over the years is a major concern in many parts of the world. As a result, the unsaturated zone has been a subject of great research interest during the past decade. Hence, an intensive field study was conducted in a part of Palar and Cheyyar river basins to understand the variation of major ions and nutrients in the soil zone during paddy cultivation. The chloride and nitrate data were used to model the movement of these chemicals in the unsaturated zone using the HYDRUS-2D model. The field study shows that fertilizer application and irrigation return flow increases the major ions and nutrients concentration in the unsaturated zone. Further, the nutrient concentrations are regulated by plant uptake, fertilizer application and infiltration rate. Additionally, denitrification and soil mineralization processes also regulate the nitrogen concentration in the unsaturated zone. The solute transport modelling study concluded that the simulated results match reasonably with the observed trends. Simulated concentrations of chloride and nitrate for a 5-year period indicate that the concentrations of these ions fluctuate in a cyclic manner (from 60 to 68 mg l⁻¹ and from 3-4 to 3-5 mg l⁻¹ respectively in groundwater) with no upward and downward trend. The influence of excessive fertilizer application on groundwater was also modelled. The model predicts an increase of about 17 mg l⁻¹ of chloride and 2.3 mg l⁻¹ of nitrogen in the groundwater of this area when the application of fertilizers is doubled. The model indicates that the present level of use of agrochemicals is no threat to the groundwater quality. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS unsaturated zone; groundwater; field study; solute transport modelling; HYDRUS 2D; major ions; nutrients; Palar and Cheyyar basins; south India

INTRODUCTION
Application of agricultural chemicals and dumping of industrial and domestic wastes at the land surface or within the unsaturated zone may have considerable impact on the quality of groundwater. Among these, agricultural chemicals are generally the most significant anthropogenic source of groundwater contamination. Understanding the fate of dissolved chemicals within the unsaturated zone can greatly aid in the prediction of chemistry of water that reaches the aquifers. Investigation of water movement within the soil zone is essential for understanding the factors controlling recharge and groundwater quality. Persistence of applied fertilizers in soil depends on their solubility and adsorption capability and their rate of degradation during recharge. Adsorption of fertilizers in the soil, as well as their persistence and mobility, determines the degree to which the quality of groundwater is affected. Accumulation of prominent contaminants from agricultural chemicals in the unsaturated zone over the years is a major concern in many parts of the world. As a result, the unsaturated zone has been a subject of greater research interest during the past decade. Rice et al. (1989) studied the ionic composition of vadose zone water in an arid region and reported that irrigation activity increased the ionic concentration in soil water in the irrigated area. Oren et al. (2004) reported that Cl⁻, SO₄²⁻, sodium and calcium mainly increased in the groundwater by circulation of irrigation water, and nitrate and potassium by fertilizer application. Pratt (1978) studied the leaching of cations and Cl⁻ in the unsaturated zone from manure applied during irrigation. Tindall et al. (1995) studied the nitrate transport and transformation processes in unsaturated porous media and concluded that they are affected by small, localized variations in the soil moisture content and the diffusion of the gases through the soil solution. Munoz-Carpena et al. (2002) conducted a detailed field study to track nitrogen degradation and transport through a banana plantation soil into the aquifer and reported that high water fluxes and nitrate concentration at the bottom of the soil profile produce a yearly loss of 48–52% of the total nitrogen applied (202–218 kg ha⁻¹ year⁻¹). Costa et al. (2002) reported that high nitrate concentration in the soil profile occurred under irrigated corn where excessive nitrogen was applied. Further, they reported that high fertilization...
rates and irrigation lead to increased hazards of groundwater pollution. The use of mathematical models in assessing the possible environmental consequences of land-use change, relative to the fate of introduced chemicals, is well established in the hydrogeologic community. Growing interest to know the fate of surface-applied chemicals resulted in the development of various models of solute transport. The impacts of non-point sources, such as regional pesticide applications (Loague, 1991), on groundwater quality have been investigated by many research groups. The major processes that control the fate of near-surface applied chemicals under field conditions include transport, transformation, retention, plant uptake, and volatilization. Pang et al. (2000) used the HYDRUS-2D model for the simulation of picloram, atrazine, and simazine leaching through two New Zealand soils and into groundwater. Tim and Mostaghimi (1989) developed a mathematical model to predict the fate of pesticides and their metabolites in the unsaturated zone of the soil, for a better understanding and estimation of different mechanisms affecting their transport. Boateng and Cawlfield (1999) developed a two-dimensional probabilistic transport model by coupling a reliability algorithm to a two-dimensional unsaturated flow and transport model to determine the significance of the uncertainty of each variable to the probability outcome. Further, they noted that molecular diffusion and van Genuchten model parameters are significant in fine-grained soils and also at locations far from the contaminated source area. Wierenga and van Genuchten (1989) conducted an experiment for solute transport in the unsaturated zone using several small and large columns packed with sandy soil material. They reported that there was no clear evidence of an increase in the dispersion coefficient with depth in the large column. Stagnitti et al. (1999) has modelled the extent of solute and water flux in multiple sample percolation experiments. Even though lots of studies have been carried out previously in the unsaturated zone, this study has substantial differences from the other studies. In this study, the unsaturated zone is linked with groundwater, whereas earlier studies deal with the unsaturated zone only.

In the present study, an intensive field study was conducted in the Palar and Cheyyar river basins, Tamil Nadu, India, to understand the variation of major ions and nutrients in the unsaturated zone and groundwater during paddy cultivation. In the study region, there has been no systematic study carried out to understand the movement of chemicals in the unsaturated zone by field and modelling techniques. Rajmohan et al. (2000) studied the major ion chemistry of groundwater in part of the Palar and Cheyyar basins and concluded that silicate weathering is the probable source of sodium, calcium and magnesium in groundwater in this region.

EXPERIMENTAL SITE

The study area (Figure 1) is situated in Kancheepuram District of Tamil Nadu State, India. It forms a part of the Palar and Cheyyar river basins, and is located 70 km west of Chennai city. The study area has dry climatic conditions with a maximum temperature of 37 °C during the months of April–May, and a minimum air temperature of 21 °C during the months of November–December. It receives an average annual rainfall of 1113 mm, of which 60% is contributed by the northeast monsoon from October to December; the rest is during the southwest monsoon, i.e. from June to September. Alluvium is the most important formation, occurring on both the sides of the river. The alluvium is essentially composed of sand with intercalated clay. In these formations, wells have been dug to a depth of 23 m. Most of these are bore and dug cum borewells. The water level in these wells fluctuates between 1 and 20 m below the ground level.

The experiment was conducted at an agricultural land located in the village of Ilayanurvellur (dug well, no. 18; Figure 1). This site covers an area of 4049 m² and is located in an alluvial formation. The irrigation need for this agricultural land is met by pumping groundwater from this dug well (well no. 18). The water table in this well fluctuates between 1.8 and 7.7 m below the ground level. Rainfall is the principal source of groundwater recharge in this area, which is evident from the relation between the seasonal rainfall and water level data (Figure 2). However, the groundwater level also rises when there is flow in Cheyyar River.

Irrigation practices

This field is intensively cultivated, usually with three crops in a year. Mostly, paddy (rice crop) is cultivated. Sometimes sugarcane is cultivated, which is a 12-month crop. The main cropping season is from September to January, The second crop season is from February to May and the third from May to August. These crops are mainly dependent on groundwater and rainfall, as surface water supply is not available at this site. In the present study, soil core sampling was carried out during the third crop season, i.e. from May to August, and groundwater was used for irrigation. During this study period, paddy is cultivated. The most commonly used fertilizers for paddy are urea, complex fertilizers and muriate potash. As per the local agricultural office, the recommended rate of nitrogen fertilizer application is 120 kg ha⁻¹ for paddy, 160 kg ha⁻¹ for sugarcane (per year) and 40–100 kg ha⁻¹ for other crops. However, the actual rate of application varies depending upon the farmer’s interest. Thus, during this study, the farmer of the experimental site applied only 113 kg ha⁻¹ of diammonium phosphate (DAP), 113 kg ha⁻¹ of urea and 23 kg ha⁻¹ of zinc sulphate as basal application just before transplantation (Table I). After transplantation, on day 17, 113 kg ha⁻¹ of urea, 113 kg
ha$^{-1}$ of potash and 23 kg ha$^{-1}$ of neem cake were applied.

**METHODOLOGY**

**Soil core sampling and analysis**

Soil core samples were collected at different times (Table I). The first core sample was collected 3 days before transplantation and fertilizer application. In order to derive a representative value, three core samples were collected during each sampling event and an arithmetic mean was used. Soil core samples were collected by coring up to 1 m depth and subsamples were collected at every 10 cm interval. Care was taken by collecting the subsamples from the centre of the core and neglecting the outer portions. The soil samples were placed in a plastic container at 4°C in the field itself. The collected samples were divided into two portions in the laboratory: one portion was used to determine the concentration of N-NO$_3$ and soil moisture and the other portion was air-dried and used for the analysis of pH, electrical conductivity (EC), major ions, nutrients, organic carbon and grain size analysis. Grain size analysis was by the pipette method (Krumbein and Pettijohn, 1938) using 20 g samples. Soil moisture was measured from weight loss of a sample oven-dried at 105°C. EC and pH were measured using digital meters from a 1:5 soil solution prepared from the air-dried soil sample.

The major anions, such as Cl$^-$, HCO$_3^-$ and SO$_4^{2-}$, were measured from 1:5 soil solutions. Cl$^-$ and HCO$_3^-$
Figure 2. Major ion and nutrient variations in groundwater at experimental site

Groundwater sampling and analysis

During this study, groundwater samples were collected once in a month from the experimental site for 18 months. Additionally, groundwater samples were also collected during the soil-core sampling period. Water samples were collected in clean polythene bottles. All sampling bottles were soaked with 1:1 HNO₃ and washed using double-distilled water. At the time of sampling, sampling bottles were thoroughly rinsed two to three times using the groundwater to be sampled. EC, pH and temperature of groundwater samples were measured in the field immediately after sample collection using
portable digital meters. Water level was recorded using a water level recorder. Samples collected were transported to the laboratory on the same day and they were filtered using 0.45 μm Millipore filter paper and acidified with HNO₃ (Ultra pure, Merck). For nutrient and anion analyses, these samples were stored below 4 °C. The samples were analysed for major ions (Na⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, SO₄²⁻, HCO₃⁻) and nutrients (Si-H₂SiO₄, N-NO₃ and P-PO₄) as per the procedures given in (APHA, 1995). The analytical precision for the measurements of ions was determined by calculating the ion balance error, which is generally within 5%.

Solute transport modelling

A variety of analytical and numerical models are available to predict water and solute transport processes between the ground surface and the groundwater table. The most popular models use the Richards equation for variably saturated flow and the Fickian-based convection-dispersion equation for solute transport. Deterministic solutions of these classical equations have been used for predicting water and solute movement in the vadose zone. Several analytical solutions have been published for simplified transport systems involving consecutive decay reactions (van Genuchten, 1985). In the present study, the HYDRUS-2D model developed by the International Groundwater Modelling Centre, USA, is used (Simunek et al., 1999). It is a Microsoft Windows-based model for the analysis of water flow and solute transport in variably saturated porous media. This model numerically solves the Richards equation for saturated–unsaturated water flow and convection–dispersion-type equations for solute transport. The water flow part of the model can deal with prescribed head and flow boundaries, boundaries controlled by atmospheric conditions. The governing flow and transport equations are solved numerically using Galerkin-type linear finite-element schemes (Neuman, 1975). In this method, the solution for water flow is obtained by an iterative process using Gaussian elimination. Similarly, the same Galerkin finite-element method is also used to solve the solute transport equation. To obtain a numerical solution of the solute transport process, first, an iterative procedure is used to obtain the solution of the Richards equation (Simunek et al., 1999). In this study, modelling of solute transport for the experimental site located near dug well no. 18 was carried out for the unsaturated zone of 5 m thickness, as the water table occurs at this depth. As irrigation return is the major source of flow in the unsaturated zone, one-dimensional vertical flow was assumed in a column of unit width and a length of 5 m. Further, among the fertilizers used in this area (Table I), Cl⁻ and nitrate are the major pollutants that reach the groundwater due to their high mobility. Hence, these two ions were considered for modelling in the movement of these chemicals in the unsaturated zone.

FIELD STUDIES

Major ions

The concentrations of HCO₃⁻, Cl⁻ and SO₄²⁻ in the unsaturated zone were studied in order to understand the effect of fertilizers application and irrigation practice. The concentration of Cl⁻ and SO₄²⁻ is regulated by fertilizers application and irrigation return flow. The concentration of HCO₃⁻ is expected to indicate the effect of dissolution of soil CO₂. Figure 3 shows both the vertical and the temporal variation of HCO₃⁻ in the soil zone. It shows that HCO₃⁻ concentration is significantly higher than the background value at all depths on days 22 and 28 (Figure 3). However, vertical variation shows that it is almost constant up to 1 m of the soil zone. The inferences on days 22 and 28 seem to be related to root respiration, which produces CO₂ in the soil zone. Further, flow of irrigation water in the unsaturated zone is likely to be another reason for the higher concentration on day 22, which may probably be preferential flow rather than normal infiltration. Later, the concentration of HCO₃⁻ reduces to the level measured before irrigation started (Figure 3). In the case of Cl⁻ and SO₄²⁻, vertical variations indicate that the concentrations of these ions are high in the top 15 cm of the soil core compared with the background value (Figure 3). Like HCO₃⁻, both Cl⁻ and SO₄²⁻ concentrations are significantly higher than the background value during day 22 after transplantation (Figure 3). The increase in Cl⁻ concentration is quite reasonable due to fertilizer application (muriate of potash; KCl) on 17 day after transplantation. Among the fertilizers applied, Cl⁻ is highly water soluble and has minimal adsorption and precipitation tendencies under normal field conditions. Further, evaporated irrigation water may also increase the Cl⁻ concentration. However, the significant increase in SO₄²⁻ concentration on day 22 is not due to the fertilizer application; it may be due to evaporated irrigation water, because ZnSO₄ was applied only during the transplantation (0 days; Figure 3). Except for the top layers (up to 15 cm), both Cl⁻ and SO₄²⁻ are almost constant throughout the depth of 1 m. Figure 3 shows that both these ions reach the background value after 43 days from transplantation. Thus, the concentration of these ions fluctuates during cultivation due to fertilizers application and recharge of evaporated irrigation water. After harvest (Table I), on day 98, the concentrations of all ions reduce to levels observed before irrigation.

Nutrients

The important nutrients considered for this study are potassium, phosphorus and nitrogen, as they are commonly used in this area (Table I). The vertical and temporal variations of potassium concentration are given in Figure 4. This shows that the variations in concentrations of potassium are not uniform and fluctuated greatly throughout the depth. This variation is not only due to fertilizer application and plant uptake, but also due to other factors such as adsorption, soil
MOBILITY OF MAJOR IONS AND NUTRIENTS IN THE UNSATURATED ZONE

Figure 3. Vertical variation of \( \text{HCO}_3^- \), \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) at different times from the date of transplantation

Texture and recharge. Further, temporal variation indicates that a slightly higher concentration is observed below 15 cm on day 96 (after harvest; Figure 4), which may be derived from crop residues after harvest. The vertical and temporal variations of AP are given in Figure 4. This shows that, except for days 16 and 22, the concentration of AP is constant through out the 1 m depth (Figure 4). The fluctuation in the concentration of AP on day 16 is understandable and due to fertilizer application. The phosphate fertilizer (DAP) was applied only at the time of transplantation (0 days; Table I). However, the high concentration within 15 cm on day 22 is likely due to irrigation water return flow.

Nitrogen (both N-NO\(_3\) and available nitrogen) concentration is high in the soil zone after the application of fertilizer (Table I, Figure 5). A high concentration of nitrogen is observed on days 16, 22 and 96 after transplantation. Vertical variation indicates that, generally, the nitrogen concentration is constant throughout the depth except for days 16, 22 and 96. On day 22 after transplantation, there is an abrupt vertical variation in the nitrogen concentration. As mentioned earlier, higher concentrations of \( \text{HCO}_3^- \), \( \text{Cl}^- \), \( \text{SO}_4^{2-} \) and potassium are also observed throughout the depth on day 22. These inferences apparently show that these variations may not be due to individual ion properties, but may be due to the flow in the unsaturated zone, which is likely to be preferential flow rather than normal infiltration (Tindall et al., 1995). However, the low concentration of nitrogen in the top layers seems to be due to plant uptake as well as denitrification. Generally, plant uptake of nitrogen is influenced by numerous factors, including temperature and moisture, that affect the plant growth rate, the available nitrogen pool, the nitrogen source, rate, etc. (Petrovic, 1990). Based on a field study, Wang et al. (2001) reported that 50–60% of the applied nitrogen is consumed by rice plants. Additionally, denitrification may also regulate the nitrogen concentration in the top layers. Denitrification, the process by which the nitrate ion is reduced to nitrous oxide or nitrogen, decreases the nitrogen concentration during...
both the growing and the non-growing seasons. Tindall et al. (1995) reported that planted sand cores had large gaseous nitrogen loss owing to denitrification, as much as 17% of the N-NO₃. Further, they pointed out that denitrification is high in the planted soil cores compared with unplanted soil cores because carbon derived from exudates or sloughed off root cells provided the carbon necessary for a high rate of denitrification. Furthermore, if the plant uptake only controls the nitrogen concentration in the top layers, its concentration should increase after harvest. However, even after harvest, the nitrogen concentration is less in the top layer (Figure 5). Hence, denitrification is also an important process in addition to plant uptake for the observation of low nitrogen concentration in the top layers. Similar results were observed by Liang et al. (1991). Additionally, the high organic carbon and soil moisture observed in the top layer (Figure 6) of this area also support our argument of the promotion of denitrification (Broadbent and Clark, 1967; Trudell et al., 1986). In contrast, a slightly elevated concentration of nitrogen is observed below 30 cm on day 96 (Figure 5). This observation seems to be a mineralization process, which will increase the nitrogen concentration (Cooke, 1976; Jacks and Sharma, 1983; Flipse and Bonner, 1985). However, leaching of nitrogen from the plant residues after harvest may also contribute to the higher nitrogen content.

MODELLING STUDIES

Model input parameters

Finite-element discretization. The finite-element mesh is constructed for the 5 m column by dividing the flow region into triangular elements whose shapes are defined by the coordinate nodes that form the element corners (Neuman et al., 1974). Small finite-element mesh sizes were given at and near the soil surface, i.e. up to 10 cm, as highly variable meteorological factors can cause fast changes in the pressure head. Similarly, closer mesh intervals were given for the lower 10 cm of the column. In general, the size of the mesh along the x direction was 0.04 m and along the y direction it varied from 0.01 to 0.02 m. Thus, the column of 5 m length was divided into 250 nodes with 248 meshes.

Soil layers and properties. The number of soil materials and layers were decided based on the field data. The soil core collected from the top 1 m of the unsaturated zone and its grain size analysis indicate that there are seven different zones. As soil coring was not carried out beyond 1 m, the same soil type was considered from 1 to 5 m of the column. Thus, seven layers were considered in the 5 m column, based on the variation in soil characteristics. Analyses of the soil core for
the contents of sand, silt and clay, were used to input the soil hydraulic properties for modelling. Grain size analysis of a soil core sample shows that it is generally sandy with silt and clay. The sand percentage is between 65 and 85% (Table II). These data were used in the model for determination of the unsaturated soil hydraulic properties. The soil hydraulic properties were estimated by the van Genuchten (1980) equation in the HYDRUS model itself using neural network prediction technique developed by the US Salinity Laboratory (Simunek et al., 1999). The calculated soil hydraulic properties based on the percentage of sand, silt and clay are given in Table II.

Solute properties and boundary condition. The dispersivity and diffusion coefficient are important parameters in the solute transport process. The dispersivity for Cl~ and nitrate is considered to be same and is given in Table III. The diffusion coefficient for Cl~ in water is assumed to be 0.20 m2 day^{-1} and for N-NO3 to be 0.016 m2 day^{-1}. These values were derived from the soil characteristics of this area and from the literature (Hutson and Wagenet, 1992; De Vos et al., 2002; Paramasivam et al., 2002; Saadi and Maslouhi, 2003). In the case of nitrate, plant uptake and denitrification were considered with a degradation factor of 0.01 (Clark, 1994; Paramasivam et al., 2002). An atmospheric boundary condition

![Figure 5. Vertical variation of nitrogen and available nitrogen at different times from the date of transplantation](image)

<table>
<thead>
<tr>
<th>Layer</th>
<th>Depth (cm)</th>
<th>Before calibration</th>
<th>After calibration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \theta_r ) (cm^3 cm^{-3})</td>
<td>( \theta_s ) (cm^3 cm^{-3})</td>
<td>( \alpha )</td>
</tr>
<tr>
<td>A</td>
<td>0–10</td>
<td>0.035</td>
<td>0.385</td>
</tr>
<tr>
<td>B</td>
<td>10–20</td>
<td>0.036</td>
<td>0.391</td>
</tr>
<tr>
<td>C</td>
<td>20–30</td>
<td>0.032</td>
<td>0.385</td>
</tr>
<tr>
<td>D</td>
<td>30–60</td>
<td>0.031</td>
<td>0.389</td>
</tr>
<tr>
<td>E</td>
<td>60–80</td>
<td>0.030</td>
<td>0.395</td>
</tr>
<tr>
<td>F</td>
<td>80–90</td>
<td>0.038</td>
<td>0.385</td>
</tr>
<tr>
<td>G</td>
<td>90–500</td>
<td>0.030</td>
<td>0.391</td>
</tr>
</tbody>
</table>

\( \theta_r \): residual water content; \( \theta_s \): saturated water content; \( \alpha \): inverse of air entry value (or bubbling pressure); \( n \): pore size distribution index, \( K_s \): saturated hydraulic conductivity; \( l \): pore connective parameter.

was assumed at the top of the column and a variable head boundary condition was considered at the lower boundary. The atmospheric boundary condition varies depending upon the amount of rainfall, irrigation and evaporation. The actual variations in rainfall and water depth in the irrigated land were measured regularly in the field and used in the model. The evaporation is assumed as 40% of irrigation water. In the case Cl$^-$ and nitrogen, a third type (solute flux type) of boundary condition was applied (van Genuchten and Alves, 1982). In addition to these, a limiting value of surface pressure head is also provided. The minimum allowed pressure head at the soil surface is usually set between 100 and 150 m. In this study, it is assumed as 100m. However, variation in this value could not affect the result, and this is confirmed by test runs.

**Initial condition and model calibration**

The initial conditions were derived primarily from the field study. The initial conditions necessary for this model include pressure head and concentration. The initial concentration values used for the model simulation are given in Table III. These values were derived from the analysis of the soil cores collected 3 days before transplantation. The model was initially run with field input parameters (Tables II and III) to model the movement of Cl$^-$ in the column. The concentration computed by the model was compared with the field data. Then, the model was run by varying certain input parameters, such as evaporation, bulk density, diffusion coefficient and dispersivity. All these parameters were varied within the reasonable limit of 10% and the sensitivity of the model results to these parameters was studied. Calibration was carried out by varying these input parameters within the reasonable limit, and a comparison of the simulated Cl$^-$ concentrations with the observed field data was undertaken. The values actually used in the model after the calibration are given in Table II. After the simulation of the Cl$^-$ concentration, the model was run to simulate the concentration of nitrate. It is assumed that 6% of the applied fertilizer nitrogen becomes N-NO$_3$.

![Graph showing vertical variation of organic carbon and soil moisture at different times from the date of transplantation](image)

**Figure 6.** Vertical variation of organic carbon and soil moisture at different times from the date of transplantation.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Soil texture (%)</th>
<th>Longitudinal dispersivity (m)</th>
<th>Initial condition (mg kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Clay</td>
<td>Silt</td>
<td>Sand</td>
</tr>
<tr>
<td>A</td>
<td>2-08</td>
<td>10-6</td>
<td>87-3</td>
</tr>
<tr>
<td>B</td>
<td>2-40</td>
<td>18-0</td>
<td>79-6</td>
</tr>
<tr>
<td>C</td>
<td>2-48</td>
<td>18-1</td>
<td>79-4</td>
</tr>
<tr>
<td>D</td>
<td>2-77</td>
<td>12-4</td>
<td>84-8</td>
</tr>
<tr>
<td>E</td>
<td>2-90</td>
<td>13-9</td>
<td>84-1</td>
</tr>
<tr>
<td>F</td>
<td>2-72</td>
<td>17-3</td>
<td>80-0</td>
</tr>
<tr>
<td>G</td>
<td>2-96</td>
<td>23-7</td>
<td>73-4</td>
</tr>
</tbody>
</table>
Petrovic (1990) reported that 4–10% of applied nitrogen fertilizer becomes N-NO₃. Initially, all these model runs were made for one irrigation cycle. The model was run with a time step of 1 day with a time increment of 1 min.

**Model results**

After calibration and testing, the model was used to simulate the concentrations of Cl⁻ and nitrate in the soil zone. The model results were initially obtained for the study period of 100 days after transplantation, and then simulation was carried out for a period of 1 year (three crops).

**Chloride.** The simulation was carried out initially for one crop season (third crop season) and the computed results were compared with the observed field data to a depth of 1 m (Figure 7). This shows that there is an agreement between model results and the observed field data. During the irrigation practice, the concentration of Cl⁻ varies in the top 1 m. Figure 7 shows that the Cl⁻ from the irrigated field reaches the groundwater zone (500 cm) after about 45 days. Figure 8 shows that movement of mass through the unsaturated zone is controlled by the recharging water from the irrigated land. Hence, most of the fluctuation in Cl⁻ mass takes place (i.e. from 0-0173 to 0-274 g m⁻³ in the upper zone)
Figure 8. Movement of mass of Cl$^-$ and inflow solution in the unsaturated zone during the irrigation period, i.e., up to 55 days. After that (i.e., after harvest) the mass of Cl$^-$ reaches the level measured before the commencement of irrigation. The fluctuation in the mass of Cl$^-$ with respect to time in the lower layers is less significant, as inferred from the linear nature of the curve (Figure 8).

**Nitrogen.** Similar to that of Cl$^-$, the model was initially simulated for one crop period (third crop season) and compared with field data for nitrogen (Figure 9). The computed nitrogen trend in the unsaturated zone is reasonably matched with field data. The nitrogen concentration in the unsaturated zone varies significantly during the irrigation period due to intense agricultural activities. The mass of nitrogen varies from 0.0011 to 0.0109 g m$^{-3}$ in the 30–60 cm layer (Figure 10). Further, after completion of the irrigation activity (i.e., after 55 days), the mass of nitrogen remains almost constant. This is inferred from the linear nature of the curve for mass in Figure 10.
Model prediction

The model was then used to predict the concentration of Cl⁻ and nitrogen in the unsaturated zone under different irrigation practices. The model was run for a 1-year and 5-year periods with the usual and increased application of fertilizer. These model runs were made by assuming the same input parameters. The daily average rainfall and evaporation data calculated for the past 6 years were used. The model run was made for the period starting from May 1999.

Model results for three crops (1 year). The results of the model run for three crop periods, i.e. third crop (May–August), first crop (September–January) and second crop (February–May), show that the concentration varies significantly during the third and second cropping
Figure 10. Variation in simulated mass of nitrogen and inflow in the unsaturated zone periods (Figure 11). The first crop period, however, shows lower levels of variation in concentration due to the monsoon. This variation is also observed in groundwater (September–January, Figure 2). During this period, the unsaturated zone may be flushed by infiltrating water, thus increasing the ionic concentration in groundwater. Figure 2 apparently shows this variation, and rising groundwater level by the monsoon increases the major ion and nutrient concentrations in groundwater. However, a concentration increase in nitrogen is observed initially after that diluted by the late monsoon. Model results show that, in the groundwater zone, Cl\(^-\) varies from 60 to 68 mg l\(^{-1}\) during this 1-year simulation. In the case of nitrate, it fluctuates between 3.4 and 3.5 mg l\(^{-1}\) in the groundwater zone. The overall fluctuation during the three crops period is mainly due to variation in rainfall, fertilizer application and evaporation. The model predictions indicate that even though there is a variation in the concentration of these ions, no upward or downward trend is observed. In general, the concentrations of Cl\(^-\) and nitrate in the 40–50 cm region fluctuate between 55 and 95 mg/kg\(^{-1}\) and between 1.2 and 5.4 mg kg\(^{-1}\).
respectively (Figure 11). Similarly, in groundwater, the Cl\(^-\) varies from 60 to 65 mg l\(^{-1}\) and the nitrate varies from 3.4 to 3.5 mg l\(^{-1}\).

**Model results for 5-year period.** Assuming that the fertilizer application and other input parameters are similar, the model was run for 5 years from May 1999, considering three paddy-cropping seasons. The results indicate that the concentrations of Cl\(^-\) and nitrogen fluctuate significantly (Figure 12). Figure 12 shows that the concentrations of ions fluctuate in a cyclic trend during the simulation period. This trend is mainly because of rainfall during the monsoon and evaporation in the summer period. In the 40–50 cm layer, the concentrations of Cl\(^-\) and nitrate vary from 45 to 95 mg kg\(^{-1}\) and 1.7 and 5.3 mg kg\(^{-1}\) respectively. In the groundwater zone, the concentration of Cl\(^-\) fluctuates between 60 and 68 mg l\(^{-1}\) and nitrate between 3.4 and 3.5 mg l\(^{-1}\). Despite this cyclic trend, there are no significant overall upward or downward trends in the concentrations of ions in the unsaturated zone. It is further observed that these ions in the groundwater zone do not increase during the simulation period.

**Model results with excess fertilizer application for 5-year period.** The model was also used to predict the effect of excess fertilizer application on the unsaturated zone and groundwater. During this simulation, application of fertilizer was doubled and other model parameters were kept as in earlier predictions. The results of the 5-year run with increased fertilizer application indicate an increase in the concentration of Cl\(^-\) and nitrate in the unsaturated zone and groundwater (Figure 13). A twofold
increase in fertilizer usage results in an increase of 20 mg kg⁻¹ of Cl⁻ and 3 mg kg⁻¹ of nitrogen in the top 1 m of the unsaturated zone. Similarly, the concentrations of Cl⁻ and nitrogen in the groundwater increase by 17 mg l⁻¹ and 2.3 mg l⁻¹ respectively. However, this increase in the concentrations seems to stabilize at the end of the fifth year. The model predicts that there is no threat to the groundwater quality due to the present use of fertilizers.

CONCLUSIONS

The outcome of this study expresses that the concentrations of Cl⁻, SO₄²⁻, and HCO₃⁻ in the unsaturated zone increased during irrigation due to the application of fertilizer and due to evaporated irrigation water. The nutrient concentration is controlled by plant uptake, fertilizer application and infiltration. In the case nitrogen, denitrification and soil mineralization processes are also important factors regulating its concentration. Solute transport modelling study indicate that the simulated results match reasonably with the observed trend. Simulated concentrations of Cl⁻ and nitrate for a 5-year period indicate that the concentrations of these ions fluctuate in a cyclic manner (from 60 to 68 mg l⁻¹ for Cl⁻ and from 3.4 to 3.5 mg l⁻¹ for nitrogen in groundwater) with no upward and downward trends. The influence of excessive fertilizer application on groundwater was also modelled, and the model predicts an increase of about 17 mg l⁻¹ for Cl⁻ and 2.3 mg l⁻¹ of nitrogen in the groundwater of this area when the application of fertilizers increased twofold. Thus, the study concludes that there is no threat to the groundwater quality due to the present level of fertilizer usage.

REFERENCES


