Transport of solutes under transient flow conditions – A case study – Yamuna river sub basin (Kosi Kalan to Agra)

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Abstract
The imbalance between incoming and outgoing salt causes salinization of soils and sub-soils that result in increasing the salinity of stream-flows and agriculture land. This salinization is a serious environmental hazard particularly in semi-arid and arid lands. In order to estimate the magnitude of the hazard posed by salinity, it is important to understand and identify the processes that control salt movement from the soil surface through the root zone to the ground water and stream flows. In the present study, Yamuna sub-basin (both sides of Gokul dam site) has been selected which has two distinct climatic zones, sub-humid (upstream of Mathura) and semi-arid region (downstream of Mathura). In the upstream, both surface and ground waters are used for irrigation, whereas in the downstream mostly groundwater is used. Both soils and ground waters are more saline in downstream parts of the study area. In this study we characterized the soil salinity and groundwater quality in both areas. An attempt is also made to model the distribution of potassium concentration in the soil profile in response to varying irrigation conditions using the Soil-Water Infiltration and Movement (SWIM) model. Fair agreement was obtained between predicted and measured results indicating the applicability of the model.

Keywords: SWIM; Disc permeameter; Guelph permeameter; Hydrolysis; Soil moisture

1. Introduction
In arid and semi-arid regions the imbalance between incoming and outgoing salt has resulted in accumulation of salts in the irrigated soils. Since, the salt tolerance of crops is often based on the concentration of salts in the saturated extracts; it would be useful to have a method to predict the salt concentration throughout the soil profile under field conditions. In order to estimate the magnitude of the hazard posed by salinity, it is important to understand and identify the processes that control salt movement from the soil surface through the root zone to the ground waters and stream flows.

Modeling and monitoring transport of water and solutes is further complicated owing to temporal variation resulting from chemical non-equilibrium and the structure of the soil. The most challenging problem confronting mathematical modeling of solute transport in field soils is how to effectively characterize and quantify the geometric, hydraulic, and chemical properties of porous media. The process can be explained through several mathematical
models based on Convective Diffusion Equations, Soil Water Infiltration and Movement (SWIM) etc. (De Rooij & Stagnitti, 2000; Evans & Stagnitti, 1996; Rajmohan & Elango, 2001; Srivastava & Brusseau, 1996; Stagnitti & Li, 1999, 2001; Valocchi, 1985; Xu & Brusseau, 1996).

The impact of agricultural activities on ground water is closely related to the quality of water from precipitation and irrigation. Soil-water systems in the unsaturated zone are highly complex. Firstly, it is seldom in stable equilibrium and is in constant flux. The degree of saturation of soil-water ($\theta$) varies both in time and space. This in turn affects flow parameters namely the suction head $h(\theta)$ and the hydraulic conductivity $K(\theta)$, which are not unique functions of $\theta$ but exhibits hysteresis.

Water quality issues originated through leaching of water soluble contaminants stems from the lack of understanding related to soil transport phenomenon, as an example fertilizer application in an agricultural field results in leaching of fertilizer ions in ground water unplanned during irrigation. Thus it is important to understand and develop a suitable transport model addressing simultaneous transport phenomenon of soil water and dissolved salts.

Fig. 1. Index map of the study area (Yamuna sub-basin) with groundwater sampling.
In this study, the solute transport process in two agricultural zones representing sub-humid (Mathura to Kosi) and semi-arid (Mathura to Agra) conditions in Yamuna sub-basin has been modeled using the Soil-Water-Infiltration-Movement (SWIM) model (Ross, 1990). Saturated hydraulic conductivity was measured in the field using a Guelph permeameter and soil sampling was done before and after application of fertilizer (N–P–K). Soil moisture retention characteristics were obtained in the laboratory using the Pressure Plate Apparatus.

2. Study area

The study area extends between 74°20 and 75°E longitude and 15°20 and 15°40 N latitude in the Mathura district of Uttar Pradesh (Fig. 1). To harness the waters of the Yamuna River, a dam has been constructed at Gokul, Mathura district to impound 1377 million cubic meter of water. There are three seasons prevailing in the catchment, the summer from March to May, the monsoon from June to November, and the winter from December to February. The Yamuna river sub basin has two distinct rainfall regimes, i.e., the area upstream of Mathura to Kosi has an annual average rainfall of 1200 mm, whereas downstream of Mathura to Agra, the average rainfall is 700 mm. The major soil groups in the catchment are clay loam soil (Ultisols), black soil (vertisols) in upstream and sandy loam soils (mainly Alisols), black soil in downstream. The land use pattern of the Yamuna sub-basin shows that 15.4% is covered by forests, 10.5% shrub, 7.9% waste land, 38.1% cropped area, 24.2% fallow land, and the remaining 4.0% is occupied by water bodies.

2.1. Materials and methods

Ground water samples were collected from selected wells (locations are shown in Fig. 1) during pre-monsoon and post-monsoon seasons and analysed for various chemical parameters such as, electrical conductivity ($EC_e$), total alkalinity (Carbonate $CO_3$ and bicarbonate $HCO_3$), total dissolved solids (TDS), chloride (Cl), sulfate ($SO_4$), sodium (Na), potassium (K), calcium (Ca) and magnesium (Mg) using APHA methods (Carter, 1993). Soil samples were collected from agriculture fields located at Mathura to Kosi (upstream) and also from Mathura to Agra (downstream). Soil extracts were prepared by stirring 20gm of soil sample into 50 ml water, and analysed for chemical parameters.

The cation exchange capacity (CEC) of a soil is the total negative charge of the soil measured under specific conditions. Its determination involves the saturation or all the charges by one cation. Conventionally, for soils with less than 7.0 pH. Ammonium (NH$_4$) is the cation of choice, and the determination is done at pH 7.0 by leaching the soil with NH$_4$OAc solution buffered at that pH. Kjeldahl distillation apparatus was used for the estimation of calcium and magnesium. Sodium and potassium were determined by analyzing the ammonium acetate extract directly for sodium and potassium using Flame photometer.

2.2. Estimation of soil hydraulic properties

Saturated hydraulic conductivity was determined by using a disc permeameter and a Guelph permeameter. Saturated moisture content was estimated by the gravimetric method (Hillel, 2012). Soil moisture retention characteristics were determined by using pressure plate apparatus. Detailed methodology is given below.

2.2.1. Disc permeameter

The disc permeameter (Perroux & White, 1988) was used for the determination of soil hydraulic conductivity at the surface. The instrument allows a constant supply potential, either positive or negative, in a manner analogous to ponded ring devices. Based on the expression developed by Wooding (1968), for three dimensional flow from a circular disc, the steady state infiltration ($q_\infty$) is expressed as Eq. (1)

$$q_\infty = K + \frac{4b(S_0)^2}{(\theta_0 - \theta_n)\pi r^2}$$

(1)

where $b$ is a constant taken as 0.75 (Smettem, Parlange, Ross, & Haverkamp, 1994), $\theta_0$ is the saturated moisture content and $\theta_n$ is the in situ moisture content, $r$ is the radius of the disc (0.1 m). When the disc permeameter test is run, data are collected to obtain cumulative infiltration at various times after the start of the test. $S_0$ can be found from the slope of early-time plot of $q_\infty$ vs. $St^{1/2}$ and $q_\infty$ from the slope of the late time plot of $q_\infty$ vs. $t$. The water content
is measured before and after the experiment (by taking soil samples for gravimetric water content multiplied by dried bulk density determinations) to obtain the saturated moisture content ($\theta_0$) and in situ moisture content ($\theta_n$). Thus $K$ can then be calculated from Eq. (1). The disc permeameter is portable and can be used for the measurement of infiltration, hydraulic conductivity, and pore characteristics, although only the hydraulic conductivity is reported here.

2.2.2. Guelph permeameter

The Guelph permeameter (Reynolds & Elrick, 1985) was used to determine the depth-wise field saturated hydraulic conductivity. The method involves measuring the steady state rate of water recharge into unsaturated soil from a cylindrical well hole, in which a constant depth (head) of water is maintained. Constant head level in the well hole is established and maintained by regulating the level of the bottom of the air tube which is located in the center of the permeameter. As the water level in the reservoir falls, a vacuum is created in the air space above the water. The vacuum can only be relieved when air, which enters at the top of the air tube, bubbles out of the air inlet tip and rises to the top of the reservoir. Whenever the water level in the well begins to drop below the air inlet tip, air bubbles emerge from the tip and rise into reservoir air space. The vacuum is then partially relieved and water from the reservoir replenishes the water in the well. The size of opening and geometry of the air inlet tip is designed to control the size of air bubbles in order to prevent the well water level from fluctuating.

The steady state discharge from a cylindrical well in unsaturated soil, as measured by the Guelph permeameter technique accounts for all the forces that contribute to three dimensional flow of water into soils, the hydraulic push of water into soil, the gravitational pull of liquid out through bottom of the well, and the capillary pull of water out of the well into the surrounding soil. The Richard analysis is the basis for the calculation of field saturated hydraulic conductivity (Carter, 1993).
3. Soil Water Infiltration and Movement (SWIM) model

Ross (1990) proposed the SWIM model which is based on a numerical solution of the Richards equation and the advection–dispersion equation. In the present study, the model has been applied to simulate the movement of solute in the unsaturated zone. The physical system and the associated flows addressed by the model are shown schematically in Fig. 2. Soil water and solute transport properties, initial conditions, and time dependent boundary conditions (e.g., precipitation, evaporative demand, solute input) were provided in order to run the model (Verburg, Ross, & Bristow, 1996).

3.1. Theoretical development

Assuming a homogeneous and isotropic porous medium, the one-dimensional partial differential equation describing the transport of an interacting, degrading solute can be written as

$$\frac{\partial \theta C_i}{\partial t} + \frac{\partial (\rho \phi_i)}{\partial t} = D \left\{ \frac{\partial ^2 \theta C_i}{\partial z^2} \right\} - q \left\{ \frac{\partial C_i}{\partial z} \right\} \pm \phi_i$$

(2)

where $C_i$ is concentration of solute (parent material or metabolite, $i$), in the solution phase; $s_i$ is concentration of species $i$ in the adsorbed phase; $\theta$ is volumetric water content; $q$ is Darcy’s flux; $\phi$ source-sink term denoting the rate of species $i$ transformation in the degradation pathway; $D$ is apparent dispersion coefficient dependent on $\theta$ and $q$; $\rho$ is soil bulk density; $z$ is vertical coordinate measured vertically downward and $t$ is time.

The apparent dispersion coefficient represents the combined effects of molecular diffusion and mechanical dispersion (velocity-dependent). This combined expression can be written as

$$D = D_m + \alpha |V|$$

(3)

where $D_m$ is molecular diffusion coefficient dependent on the moisture content $\theta$; $V = q/\theta$ is effective pore-water velocity; and $\alpha$ is dispersivity. In laboratory experiments using relatively homogeneous porous media, values of dispersivity $\alpha$, determined from breakthrough curves of conservative non interacting solutes such as chloride, are known to be of order of 0.01–1.0 cm. In contrast, field modeling studies use values of the dispersivity in the range of 10–100 m, which are three to six orders of magnitude larger than typical laboratory studies. This wide difference in field and laboratory dispersivity estimates may be due to the non-homogeneous and anisotropic nature of the field flow system compared to homogeneous, isotropic conditions of laboratory tests (Reddell & Sunada, 1970).

Given that Eq. (3) is valid for defining the apparent dispersion coefficient for saturated and partially saturated flow conditions and that the mechanical dispersion term is analogous to molecular diffusion in effect, but not in mechanism, assumption of steady flow ($\partial \theta/\partial t = 0$) reduces Eq. (2) to

$$\frac{\partial C_i}{\partial t} + \rho \frac{\partial S_i}{\partial t} = D \frac{\partial ^2 C_i}{\partial z^2} - V \frac{\partial C_i}{\partial z} \pm \frac{1}{\theta} \phi_i$$

(4)

Eq. (3) is a generalized expression representing transport, adsorption, and transformation of a single solute species $i$. The source-sink term $\phi_i$ in Eq. (4) represents the sequential steps in the degradation pathway from the parent material to the first-step product, from the first-step product to the second-step, and so on to the end of the $n$th product. The term $\phi_i$ does not reflect either adsorption to the soil matrix of a degradable chemical or its metabolites, nor plant uptake and volatilization. The term $S_i$ represents the amount of parent material or metabolite adsorbed to the soil. If, for simplicity, one assumes an existence of a local equilibrium and linear adsorption isotherm solution and adsorbed phases, then

$$S_i = K_{pi} C_i \quad (i = 1, 2, \ldots, N)$$

(5)

where $K_{pi}$ is the distribution or partition coefficient for the solute species $i$. Taking the derivative of Eq. (4) with respect to time, $t$, yields

$$\frac{\partial S_i}{\partial t} = K_{pi} \left( \frac{\partial C_i}{\partial t} \right)$$

(6)
Transformation process determines the fate and persistence of chemicals in the unsaturated and saturated zones. Principal among these processes are microbiological degradation (biodegradation), hydrolysis (chemical degradation) and volatilization. The driving force behind these reactions is the microorganism’s need for energy, carbon, and other essential nutrients. Thus, the rate of biodegradation depends on both the concentration of the chemical and the size of the microbial population. Hydrolysis is a transformation process that changes the chemical speciation of an organic contaminant. It is the reaction of the chemical with water resulting in an exchange of some functional group from the organic molecules with a hydroxyl (OH⁻) group. Like bio degradation, the extent of contaminant attenuation depends on both the chemical properties of the contaminant and the aqueous medium. Both transformation processes can be mathematically represented by first-order kinetic reactions (Smith & Johnson, 1988). In this study the degradation pathway of the solute can be represented in a manner similar to Wagenet and Hutson (1986) as

\[ C_i \rightarrow C_{i+1} \rightarrow C_{i+2} \]

\[ k_i' \rightarrow k_2' \rightarrow k_3' \]

where \( k_i (i = 1, 2, 3) \) denotes the first-order rate constants of the \( i \)th degradation step; and \( k_i' (i = 1, 2) \) denotes the rate of constants for hydrolysis. Based on Eq. (7) and assuming that hydrolysis processes produce innocuous products which can be neglected in the analysis, the sequential transformations for the parent material and its two metabolites can be expressed as

\[ \phi_1 = \left\{ \frac{\partial C_1}{\partial t} \right\} = -(k_1 + k_1')\theta C_1 \]  

(8a)

\[ \phi_2 = \left\{ \frac{\partial C_2}{\partial t} \right\} = \theta k_1 C_1 - (k_2 + k_2')\theta C_2 \]  

(8b)

\[ \phi_3 = \left\{ \frac{\partial C_3}{\partial t} \right\} = \theta k_3 C_3 - (k_3 + k_3')\theta C_3 \]  

(8c)

where the subscripts 1, 2 and 3 represent the parent material and its two metabolites, respectively. Substituting Eq. (6) and Eqs. (8a)-(8c) into Eq. (4) and upon simplification yields the following expressions for the parent material (\( i = 1 \)) and its two metabolites (\( i = 2, 3 \))

\[ R_1 \left\{ \frac{\partial C_1}{\partial t} \right\} = D \left\{ \frac{\partial^2 C_1}{\partial z^2} \right\} - V \left\{ \frac{\partial C_1}{\partial z} \right\} - (k_1 + k_1')C_1 \]  

(9a)

\[ R_2 \left\{ \frac{\partial C_2}{\partial t} \right\} = D \left\{ \frac{\partial^2 C_2}{\partial z^2} \right\} - V \left\{ \frac{\partial C_2}{\partial z} \right\} + k_1 C_1 - (k_2 + k_2')C_2 \]  

(9b)

\[ R_3 \left\{ \frac{\partial C_3}{\partial t} \right\} = D \left\{ \frac{\partial^2 C_3}{\partial z^2} \right\} - V \left\{ \frac{\partial C_3}{\partial z} \right\} - k_2 C_2 - k_3 C_3 \]  

(9c)

where \( R_1, R_2 \) and \( R_3 \) are the retardation factors for the parent material and its first and second metabolites, respectively. These retardation factors represent the extent to which the movement of the parent material or its metabolites are retarded relative to the water movement in the soil. The retardation factors \( R_1, R_2 \) and \( R_3 \) can be defined as

\[ R_1 = \left\{ 1 + \rho \frac{Kp^1}{\theta} \right\} \]  

(10a)

\[ R_2 = \left\{ 1 + \rho \frac{Kp^2}{\theta} \right\} \]  

(10b)

\[ R_3 = \left\{ 1 + \rho \frac{Kp^3}{\theta} \right\} \]  

(10c)

where \( Kp^1, Kp^2 \) and \( Kp^3 \) are the partition coefficients of the parent material, first metabolite and second metabolites,
respectively. In solving Eqs. (9a)–(9c) the initial with boundary conditions
\[
C_i = 0 \quad t = 0 \quad z \geq 0
\]  
(11a)
\[
C_i = C_i^0 \quad 0 < t \leq t_1 \quad z = 0
\]  
(11b)
\[
C_i = 0 \quad t > t_1 \quad z = 0
\]  
(11c)
\[
C_i = 0 \quad t \geq 0 \quad z = \infty
\]  
(11d)
\[
\frac{\partial C_i}{\partial z} = 0 \quad t \geq 0 \quad z = \infty
\]  
(11e)
where \( C_i^0 (i = 1, 2, 3) \) is the initial concentration of the parent material or its two metabolites and \( t_1 \) is the time for pulse application of the chemical. Rearranging Eqs. (9a), (9b) and (9c) one obtains
\[
D \left\{ \frac{\partial^2 C_1}{\partial z^2} \right\} - V \left\{ \frac{\partial C_1}{\partial z} \right\} - (k_1 + k'_1)C_1 - R_1 \frac{\partial C_1}{\partial t} = 0
\]  
(12a)
\[
D \left\{ \frac{\partial^2 C_2}{\partial z^2} \right\} - V \left\{ \frac{\partial C_2}{\partial z} \right\} + k_1 C_1 - k_2 C_2 - R_2 \frac{\partial C_2}{\partial t} = 0
\]  
(12b)
\[
D \left\{ \frac{\partial^2 C_3}{\partial z^2} \right\} - V \left\{ \frac{\partial C_3}{\partial z} \right\} + k_2 C_2 - k_3 C_3 - R_3 \frac{\partial C_3}{\partial t} = 0
\]  
(12c)
Values of the transformation rate constants \( k_i \) and \( k'_i \) \((i=1,2,3)\) given in Eqs. (12a), (12b) and (12c) are assumed to be constants, although it is well known that microbiologically mediated reactions are functions of many environmental variables (Ou & Penman, 1989). Inadequate information on the functional nature of these relationships prevents representation, at present, of \( k_i \) values as other than constants. However, the value of \( k_i \) can be changed with depth and time in a manner similar to Tilluston, Robbins, and Wagnet (1980). In obtaining closed-form analytical solutions of Eqs. (12a), (12b) and (12c) the initial and boundary conditions given by Eqs. (11d) and (11e) are modified to
\[
C_i = 0 \quad t \geq 0 \quad z = L
\]  
(13a)
and
\[
\frac{\partial C_i}{\partial t} = 0 \quad t \geq 0 \quad z = L
\]  
(13b)
\((i=1,2,3)\) so as to adequately describe the lower boundary of a finite column of soil of length \( L \).

### 3.2. Analytical solution

A finite-difference procedure for solving a solute transport equation similar to that developed in this study has been presented by Wagenet and Hutson (1986). However, the finite difference method, in general, requires extensive data input (data that may be sparse and uncertain) and detailed familiarity with the numerical code (a process that can be tedious and time consuming). Furthermore, the method is complicated by the dominating convective term \( V \frac{\partial C}{\partial z} \) which can give rise to considerable numerical oscillations or dispersion. Therefore, the closed form analytical method of solution of the solute transport equation offers a useful means for an initial estimation of order of magnitude of the extent and concentration of the contaminant. Data input is relatively simple and results compare reasonably well with those obtained numerically (Huyakom, Mercer, & Ward, 1985).

The standard Laplace transform technique is used to obtain analytical solutions of Eqs. (12a), (12b) and (12c) subject to initial and boundary conditions given in Eqs. (11a), (11b), (11c), (13a), and (13b). Because this technique has been presented in detail by several investigators (Ames, 2014; Bieniasz, 2015; Gökdoğan, Merdan, & Yıldırım, 2012), only some pertinent steps in solving are outlined in this paper. Additionally, since Eqs. (12a), (12b) and (12c) are structurally similar, only the solving procedure for Eq. (12a) is described. For the parent compound \((i=1)\), the
Laplace transformation of Eq. (12a) with its associated boundary condition given by Eq. (11a) may be written as

\[
\frac{d^2 C_1}{dz^2} - \frac{V}{D} \frac{dC_1}{dz} - \frac{1}{D} \left( (k_1 + k_1') + s \right) C_1 = 0
\]  

(14)

where

\[
\overline{C_1} = \int_0^\infty C_1 \exp(-st) dt
\]  

(15)

Using Eqs. (11a), (11b) and (11c) the solution of Eq. (14) is

\[
\overline{C_1(z,s)} = \frac{C_0}{s} \exp(r_1z)[1 - \exp(st)]
\]  

(16)

where

\[
r_1 = \frac{1}{2D} \left( V - (V^2 + 4DR_1[k_1 + k_1'])/2 \right)
\]  

(17)

Recognizing that

\[
\lambda^{-1} \exp(r_1z) = \frac{z}{(4\piDt^{3/2})} \exp\left( \frac{Vz}{2D} \right) \exp\left( \frac{V^2}{4D} + (k_1 + k_1')t - \frac{z^2}{4Dt} \right)
\]  

(18)

and applying the convolution theorem to obtain the Laplace inverse of Eq. (16) yields

\[
C_1(z,t) = H_1(z,t) \quad 0 < t \leq t_1
\]  

(19)

\[
C_1(z,t) = H_1(z,t) - H_1(z,t - t_1) \quad t > t_1
\]  

(20)

where

\[
H_1(z,t) = C_0^0[P_1(\omega)]
\]  

(21)

in which

\[
P_1(\omega) = 0.5\exp\left( \frac{z(V - \omega)}{2D} \right) \text{erfc}\left( \frac{R_1z - \omega t}{(4DR_1t)^{1/2}} \right) + 0.5\exp\left( \frac{z(V - \omega)}{2D} \right) \text{erfc}\left( \frac{R_1z - \omega t}{(4DR_1t)^{1/2}} \right)
\]  

(22)

and

\[
\omega = [V^2 + 4DR_1(k_1 + k_1')]^{1/2}
\]  

(23)

A procedure similar to that outlined above for \( C_1(z,t) \) can be adopted to obtain an analytical solution for the second metabolite denote by Eq. (12b). Thus, for a pulse application of \( C_1^0 \) at the soil surface for a duration \( t_1 \), analytical solution of Eq. (12b) yields

\[
C_2(z,t) = G_1(z,t) + G_2(z,t) \quad 0 < t < t_1
\]  

(24)

\[
C_2(z,t) = G_1(z,t) - G_1(z,t - t_1) + G_2(z,t) - G_2(z,t - t_1)t > t_1
\]  

(25)

where

\[
G_1(z,t) = \frac{k_1C_0}{k_{12}} \left\{ \exp(-k_1t)p_2(\omega_{22}) - \exp[ -(k_2 + k_2')t]p_2(\omega_{21}) \right\}
\]  

(26)

\[
G_2(z,t) = \frac{k_1C_0}{k_{12}} \left\{ R_1 \right\} \left\{ \exp(-k_1t)[P_1(\omega_{11}) - P_2(\omega_{22})] + \exp(-\beta_{12})[P_2(\omega_{23}) - P_2(\omega_{12})] \right\}
\]  

(27)

In which

\[
K_{12} = (k_2 + k_2') - k_1
\]  

(28)

\[
\beta_{12} = \frac{k_1R_1 - (k_2 + k_2')R_2}{R_1 - R_2}
\]  

(29)
where \( i=1, 2; j=1, 2, 3 \)

\[
\begin{align*}
\omega_{11} &= \omega_{21} = V \\
\omega_{12} &= \left( V^2 + 4DR_1[k_1 - (k_2 + k'_2)] \right)^{1/2} \\
\omega_{22} &= \left( V^2 + 4DR_2[(k_2 + k'_2) - k_1] \right)^{1/2} \\
\omega_{23} &= \left( V^2 + 4DR_3[(k_2 + k'_2) - k_1] \right)^{1/2}
\end{align*}
\]

A similar analytical procedure to that outlined above for \( C_2(z, t) \) can be adopted to obtain the solution of Eq. (12c). Solutions of \( C_1(z, t) \) and \( C_2(z, t) \) for application of \( C^0_1 \) at the soil surface for a duration of \( t_1 \) were obtained using the superposition principle for \( t > t_1 \) as given by Eqs. (20) and (25). From Eqs. (20) and (25), it can be easily verified that \( C_1(z, t) \rightarrow 0 \) as \( z \rightarrow 0 \) and/or \( t \rightarrow \infty \) for small values of \( t_1 \). Also, for continuous application of \( C^0_1 \) at the soil surface, a steady-state concentration distribution can be obtained for given \( z \) values and \( t \rightarrow \infty \). A FORTRAN computer program was used to evaluate the solutions for \( C_1(z, t) \) and \( C_2(z, t) \) and all computations were carried out in double precision.

### 3.3. Model conceptualization

The SWIM model was applied to the Yamuna sub-basin to understand the solute transport characteristics that pass through the unsaturated zone. This solute enters the soil profile with the irrigation water. Therefore, to account for the spatial variation of saturated hydraulic conductivity, twelve in situ field experiments were conducted on the soil surface (top layer) and also at the bottom layer (45–60 cm depth) at different locations with different soil types. Logarithmic mean value was considered as the model input parameter. The model was run under two conditions, one in the clay loam soil area (Mathura to Kosi) with single vegetation (Jowar) and the second run is for the downstream area, dominated by medium to sandy loam soil (Mathura to Agra), where wheat is the type of vegetation. Solute was included in the simulation through application of fertilizer (N–P–K) at the surface. The model was simulated for 30 days comprising two irrigations of 6 cm each on 3rd and 20th day and one initial application of fertilizer (solute). Exponential root growth with depth and linear interpolation with time was considered. The profile is 150 cm deep with surface at 0 cm and bottom boundary condition applying at 150 cm. There is also some solute present initially. Solute production and first order decay processes are active. In the model, solute production/uptake and first order decay processes are expressed in terms of source or sink terms. There was no solute exclusion from plant water uptake, i.e., all solute dissolved in the uptake water was also taken up by the plant. Plant uptake of solute is assumed to take place only by mass flow. In this case, vapor conductivity is not taken into account nor is the effect of osmotic potential. There are two hydraulic property sets (for upper and lower soil layers) that are applied at 16 depth nodes of the 150 cm deep profile. Initially, there is no water ponded on the surface. Runoff is governed by a simple power law function. A matric potential gradient of 0, i.e., ‘unit gradient’, has been applied as a bottom boundary condition throughout the simulation. Runoff in SWIMv2.1 is based on the assumption that the soil has a certain surface roughness, which can detain water and prevent it from running off.

### 3.3.1. Data acquisition

#### 3.3.1.1. Rainfall

Daily rainfall data for the period 1995–2005 were collected from the statistical department (Uttar Pradesh State) for rain gauges located within the catchment of Yamuna sub-basin.

#### 3.3.1.2. Evaporation

Daily evaporation data of Mathura to Kosi and Gokul dam site (1995–2003) were obtained from the Uttar Pradesh State Irrigation Department.

#### 3.3.1.3. Saturated hydraulic conductivity

Saturated hydraulic conductivity was measured at 9 stations using disc permeameter and Guelph permeameter. The saturated hydraulic conductivity near Mathura to Kosi is taken as...
2.1 cm/h (surface) and at a depth of 45–60 cm, it is 0.9 cm/h. In areas, dominated by clay loam soil, the values considered are 0.6 cm/h at the surface and 0.01 cm/h at the bottom layer.

3.3.1.4. Van Genuchten parameters. Soil samples were analyzed in the laboratory for soil moisture retention characteristics by using pressure plate apparatus. The averaged van Genuchten parameters for the soil layer were obtained by non-linear regression analysis. The van Genuchten parameter $\alpha_v$ varies between 0.0083 cm$^{-1}$ and 0.0560 cm$^{-1}$ and the $n$ parameter varies between 1.4046 and 1.5037.

3.3.1.5. Vegetation. Two types of vegetation (Jowar/Gram) showing exponential root growth with depth and sigmoid with time were assumed for the study. Data pertaining to vegetation type was not available; therefore, it is adopted from the study carried out by Kumar and Shilpa (2002) for the Dharwad district.

<table>
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<th>Jowar</th>
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<td>Root radius (rad)</td>
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<tr>
<td>Root conductance (groot)</td>
<td>$1.2 \times 10^{-7}$</td>
</tr>
<tr>
<td>Minimum xylem potential ($psi_{min}$)</td>
<td>$-15,000$ cm</td>
</tr>
<tr>
<td>Root depth constant ($x_c$)</td>
<td>30 cm</td>
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</table>

Maximum root length density ($rld_{max}$) 4 cm/cm$^3$
Root radius (rad) 0.12 cm
Root conductance (groot) $1.0 \times 10^{-7}$
Minimum xylem potential ($psi_{min}$) $-15,000$ cm
Root depth constant ($x_c$) 20 cm
Maximum root length density ($rld_{max}$) 3 cm/cm$^3$

4. Results and discussion

4.1. Soil salinity

Soil salinization has been observed in the downstream part of the Yamuna sub-basin. Presently, it is noticed that only about 15–20% of the study area (out of the total irrigated land) are salt affected (i.e., $EC_e > 4$ ds/m). Although soil salinity was generally low, it tended to increase with depth, due to the accumulation of salt in the deeper layer which could be attributed to the presence of higher clay content and low permeability as observed in the soil profile.

Thus, the percentage of the irrigated area with $EC_e$ values higher than 4 ds/m was 6.8% for the 0–30 cm soil depth and increased to 15.7% for the 60–90 cm soil depth. The $EC_e$ values being greater than 4 ds/m in the soil horizons of downstream region indicate a high level of salinity particularly in deep to medium black soils from Mathura to Agra. Calcium is the dominant base on exchange complex with Ca/Mg ranging from 3.2 to 3.6 for black soils and for red soil it varies between 1.83 and 3.57.

4.2. Hydrochemistry of anions and cations

Acid-base reactions are important in groundwater because of their influence on pH and the ion chemistry. A pH value of 7.5–8.0 usually indicates the presence of carbonates of calcium and magnesium, and a pH value of 8.5 or above shows appreciable exchangeable sodium. The results of the present study (Tables 1 and 2) show clearly the dominance of bicarbonate, sodium and chloride towards down-stream as compared to upstream.

The total concentration of soluble salts expressed as electrical conductivity in ground water of Yamuna sub-basin varied from 0.36 to 29.6 ds/m. However, it is observed that in most of the cases (42%), the $EC_e$ was more than 4 ds/m, and 28% of the samples had $EC_e$ less than 2.5 ds/m, thereby indicating that salinity is more prevalent than sodicity.
in the study area. Studies carried out by Jain, Bhatia, Kumar, and Purandara (2001) also reported a similar trend in the area. ECe was found to be highly correlated with Na ($r = 0.88$), Cl ($r = 0.96$) and also with sulfate ($r = 0.71$). The soluble carbonates and bicarbonates in the water samples analyzed varied from 1.04 to 8.1 me L$^{-1}$ during pre-monsoon and 0.58 to 12.53 me L$^{-1}$ during post-monsoon. The concentrations of carbonate and bicarbonate are important because these affect the precipitation of calcium and thereby result in excessive saturation in soil. The Residual Sodium Carbonate (RSC) of waters indicates that about 71% samples had RSC between 2.5 me L$^{-1}$ and 5 me L$^{-1}$. The results indicated that the continuous and indiscriminate use of these ground waters is expected to build up excessive sodium in the soil solution and exchange complex and will also clog the soil pores which may lead to drainage problems (Sood, Verma, Thomas, Sharma, & Brar, 1998). Soluble sodium is the dominant cation varying in concentration from 0.39 to 17.5 me L$^{-1}$ in these waters. However, the Sodium Adsorption Ratios (SAR) values of all samples are less than 10. It was observed that waters of high ECe values are predominant with sodium and chloride ions. Further it was observed that saline waters also have relatively high calcium, magnesium and bicarbonate ions. This was observed specially at downstream (Runakta). Potassium and carbonate ions, if present, are mostly confined up to a range of 5% of the total salt concentration. It is quite difficult to draw a general conclusion on the ionic composition of the water in relation to geographical conditions. In general, waters in areas of high rainfall, i.e., above 1000 mm per annum and with good drainage are of good quality. It is clear from the present study that, in the upstream where there is more rainfall (above 1000–3000 mm) the quality of water is good whereas in the

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downstream area, various water quality parameters exceed the acceptable limits (Adhikary, Dash, Kumar, & Chandrasekharan, 2014; Phocaides, 2000).

The distribution of anions and cations with total ion concentration, indicate that bicarbonates and sulfate ions are the dominating anions in the upstream, whereas towards downstream, concentration of chloride increases over bicarbonates indicating salinity problems in black soil (vertisol). Similarly among cations calcium and magnesium are the predominant ones. This is attributed to rock types and clay minerals rich in potassium. In the downstream of Yamuna sub-basin (from dam site to Farah) it is expected that, the most important exchange reactions involved are the removal of Ca$^{2+}$ and Mg$^{2+}$ out of water and to replace them with Na$^+$. The main requirement for this process is a large reservoir of exchangeable Na$^+$, which is most often provided by clay minerals deposited (mostly montmorillonite and smectite group). This is evident in the present study as HCO$_3^-$ and Na$^+$ are the ions, which indicate the presence of ion-exchanged waters.

SAR of all the samples in the study area can be grouped under the low-sodium hazard zone; however, the hydraulic conductivity varies considerably from low to very high. Further, the ground water samples collected from the deep black soil areas showed a shift towards medium hazard zone due to continuous use of poor quality ground water. This indicates the future trend of soil and ground water salinization in these areas and therefore proper measures should be taken to control the possible impacts.

<table>
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<th>Stations</th>
<th>pH</th>
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<th>CO$_3$</th>
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4.3. Simulation of soil moisture

The model was calibrated by using soil moisture profiles available for the Yamuna sub-basin. In the present study, the moisture observed during the study period was compared with the simulated profile for both upstream and downstream parts of the study area (Fig. 3a and b). The profiles showed a reasonable match between the actual data and simulated results with exception at a few depths.

In the case of solute profiles (Fig. 3c and d), both observed and simulated profiles follow a similar trend of downward movement. The results indicate that in the upstream area rich in black soil, due to the very low permeability, the ions move very slowly and remain mostly in the unsaturated zone leading to water quality
problems, particularly in open wells. However, in the downstream areas covered by red loamy soils (alfsols), due to the presence of highly porous rocks and better flow conditions, ions remain in continuous movement without affecting the water quality.

Further, during the rainy season, there is an increase in water level due to which the deposited salts move in the ground water and during the sunny days the salts are accumulated in the sub-soil layers. Apart from this, in cultivated lands, plants absorb only part of each of the nutrients present in soluble forms in soils. As the concentration of the nutrients in the soil water increases, it results in greater total nutrient absorption and greater crop yields. If fertilizers are added to supplement the supplies of particular nutrients that are deficient in soils, greater residues of the nutrients remain in the soils. Part of the excess may be lost to the groundwater if it remains in soil-water. Most of the chemical ions added in fertilizers are retained to some degree by soils as a result of chemical inter-actions, and this reduces their potential for loss to groundwater. As a consequence of such a process both soil and water get contaminated. This could be the reason for accumulation of salts in the downstream area as reported by Varadarajan (2000). The present observation also indicated that there is an accumulation of salts in the top layers of black soil (vertisol), which will ultimately lead to soil and water contamination.

5. Conclusion

Ground water quality and solute transport investigations have revealed that there is deterioration in chemical quality of both soil and water at various locations of Yamuna sub-basin, particularly in the downstream region. The cause for deterioration of chemical quality is attributed to the unstable equilibrium between various ions such as carbonate, silicate and alumino-silicate minerals. These constituents will continue to dissolve in the saturated zone. The source of cations and anions may vary from place to place. However, the higher concentration of bicarbonates is attributed to the release of carbon dioxide by plant roots and the decomposing organic matter present in soils. The weathering of primary minerals can be described as a breakdown of silicate with the release of cations which will appear as bicarbonates.

Soil salinity and groundwater quality deterioration also depend on the rainfall. They increase during the summer and are considerably reduced during the monsoon due to dilution by rainwater. In the downstream area, rainfall is significantly less than in the upstream area and the climate varies from sub-humid to semi-arid, due to which there is a considerable change in ground water quality and soil salinity. Further, the variation in salinity and its ionic composition depend upon the depth of water table, infiltration capacity of the soil, and the rainfall characteristics of the area concerned. The quality of groundwater in many regions shows wide variations with depth of the aquifer.

The study revealed the fact that there are soil and water salinization problems in the study area particularly in black soils. One of the major reasons as observed that non-utilization of the available ground water due to which the salinization problem worsens further. So it is important to pump out the water regularly and conjunctive use practice of surface- and ground-water should be adopted in such areas where the soils are affected by soil salinity and the rainwater harvesting structures and sub-surface drainage should be constructed at appropriate locations. Apart from this, certain salt tolerant crops should be grown which have already given some good results in certain areas, to reduce the intensity of salinization in the study area.

References


