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Research Paper

Groundwater phosphorus contamination caused by cultural activities (case study: Babol City)

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Abstract

Background: By economic development of societies and population growth there is an immense need for more food resources. Therefore, artificial fertilizers are a necessity to enhance agricultural productions. Fertilizers could leach into groundwater by man's cultural activities and contaminate soil and groundwater.
Objectives: The main objective in this research is to evaluate the ability of LEACHN model to simulate the phosphorus movement in soil medium causing groundwater contamination.
Methods: LEACHN model was used to simulate. The required data to operation of the model are given from the Haraz Extension and Technology Development Center in Mazandaran, Iran.
Results: The model was tested in order to verify its prediction value; with a correlation coefficient of 92.3% accuracy. The mean bias error of modeling was equal to -0.087. A sensitivity analysis indicated that the phosphorus concentration in the soil was slightly sensitive to soil saturated hydraulic conductivity changes, but was highly sensitive to changes in soil bulk density.
Conclusions: The results showed that the model can accurately simulate phosphorus concentration in soil profile. The result of scenario modeling showed that the amount of phosphorus leakage was directly proportional to precipitation changes and soil permeability.

Keywords: *Groundwater; Pollution; Phosphorus; LEACHN; Modeling.*

1. Introduction

In recent decades, much attention has been devoted to the groundwater pollution. Human cultural activities have augmented the charge of nutrients in groundwater that cause serious problems on their ecological quality [1]. Nutrient such as phosphate, phosphorus, nitrate, nitrite etc. have adverse effect on groundwater quality and also on human health [2], [3]. Phosphorus is one of the vital nutrients for growth of living organisms. This nutrient has both natural and anthropogenic sources. Natural sources of phosphorus in groundwater include weathering of soluble inorganic materials, decaying biomass, infiltration, seepage and sedimentation. Anthropogenic sources include use of fertilizers for agriculture, detergents, industrial and municipal wastewater [4], [5]. The EPA water quality criteria state that phosphates should not exceed 0.025 mg/l within a lake or reservoir [6]. Phosphorus is a limiting nutrient. Furthermore the exceeding of phosphorus amount in water area can cause eutrophication. The augmentation of eutrophication in many water areas in the world is greatly driven by nonpoint source phosphorus pollution from agriculture region [7]. High rates of photosynthesis associated with eutrophication can deplete dissolved inorganic carbon and raise pH to extreme levels during the day [8]. Eutrophication can release algal growth, which in turn lead to depletion of oxygen by their decomposition. Anoxic areas have caused adverse effects on aquatic organisms and human health [9]. Inorganic phosphate is not considered harmful for human consumption. In fact, it is added to drinking water in some places to lower its pH and prevent corrosion in pipelines. However, too much phosphate in the body can cause health problems,

such as kidney damage and osteoporosis. Organophosphates that are frequently used in pesticides are powerful nerve agents that disrupt the action of the acetyl cholinesterase enzymes that allow neurotransmitters to function. Exposure to organophosphate nerve agents causes pupil contraction, salivation, lacrimation, involuntary urination and defecation, vomiting, convulsions, and eventually death by asphyxiation as control is lost over respiratory muscles [10].
Computer simulation models have become a helpful and powerful tool to evaluate the water and solute movement from one point to other points and also they show transportation of nutrients in soils and groundwater [11]. Models can be useful to assess and control of nutrient losses by providing estimates of leaching. The Leaching Estimation and Chemistry Model (LEACHM)is a deterministic model that includes different process in solute movement and have been used to evaluate the fate of contaminations in agricultural soils since more than 20 years ago [12]. There are many studies focusing on nutrient leaches in soils and groundwater [13-17]. The most studies have been used of LEACHN model for simulation of nitrogen; however in this paper the main objective was to evaluate the ability of LEACHN model to simulate the movement of phosphorus in groundwater.

2. Study area

Babol is located in Mazandaran province. This area encompasses 14301 km2 which is about 5.94 percent of the Mazandaran province, is located between 36° 05' and 36° 35' latitude, and 52° 30' and 52° 45' longitude. City of Babol is situated 210km northeast of Tehran and it is surrounded by Babolsar at north, Alborz Mountains at south, Amol city at west and Ghaemshahr and Savadkooh at east. Location of the area is shown in Fig. 1. In this area main source for drinking water supply are shallow wells. The maximum water table depth is at 5.5 m level in southern part of plain, and the minimum is at the level of ground surface; however, the average depth is 2.5 m. The observed data shows groundwater hydraulic gradient and flow directions are from the east to the west of the region. About 60% of this area (809 km2) is under cultivation of rice, citrus, fresh vegetables, melons, cereal and other produce which are shown in table 1.

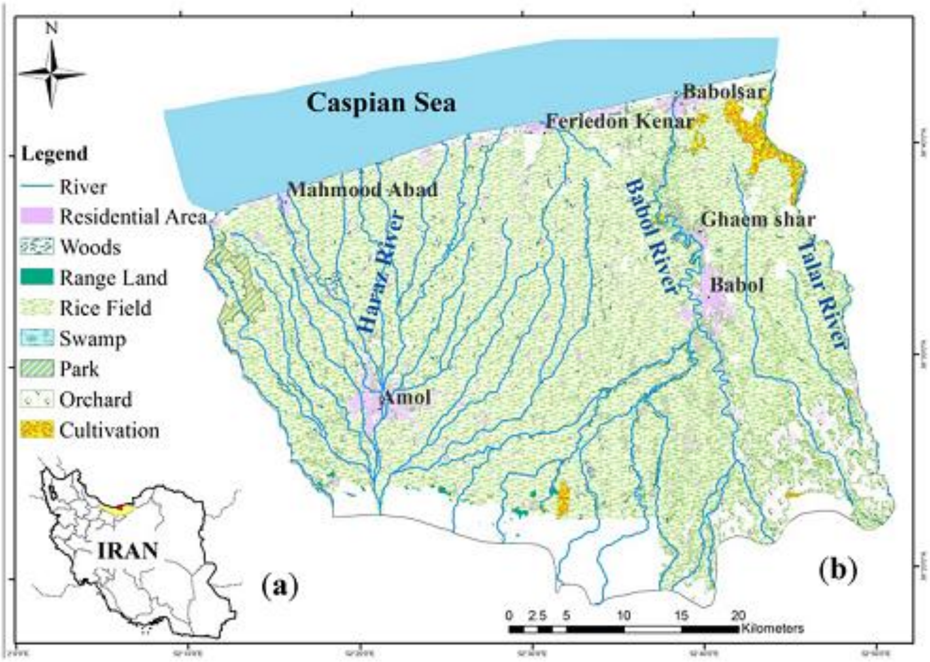

Fig. 1: Babol Location

Table 1: Different Type of Crops and Area under Cultivation (Ha)

Type of cultivation	Rice	Citrus	Summer Crops	Cereal	Other
Extent (Ha)	50000	11000	6500	400	13000

The main fertilizer used in this region is Urea and phosphate fertilizer which are used in amount of 13000 tons and 4000 tons, respectively. Annual average amount of Phosphate fertilizers used for different crops are shown in table 2.

Table 2: Annual Amount of Phosphate Fertilizer Used in Different Cultivation Babol City

Type of cultivation	Phosphate Fertilizer (Kg/Ha)
Rice	50
Citrus	50
Summer Crops	Nil
Cereal	50
Other	50

Table 3 shows the properties of three most dominant soil types in study area in different layers. Soil samples, evapotranspiration and precipitation data are provided by Mazandaran Water Organization and they are used as input data for LEACHN model.

Table 3: Soil Analysis of Three Most Dominant Soil Types in Study Area

soil name	Horizon	Depth (m)	Organic Carbon (%)	Bulk Density (g/cm3)	Volumetric Water Content (%)		Saturation (%)
					at- 0.1 Mpa	at -15	
Babol	1	0.15	2.4	1.35	40	12	46
	2	0.45	1.44	1.35	40	12	50
	3	0.8	0.86	1.35	40	12	50
	4	1.3	0.6	1.4	40	10	50
Darzikola	1	0.15	1.9	1.35	40	12	50
	2	0.65	0.87	1.2	40	14	50
	3	0.95	0.9	1.2	40	14	50
	4	1.2	0.7	1.35	40	10	50
	5	1.5	0.3	1.35	40	10	50
Haraz	1	0.22	0.74	1.3	35	15	44
	2	0.64	0.62	1.35	35	15	44
	3	1.12	0.35	1.35	35	15	44
	4	1.5	0.32	1.3	35	15	44

Table 4: Average Three Years Hydrological Data of the Study Area

Month	2009		2010		2011	
	P (mm)	ET (mm)	P(mm)	ET(mm)	P(mm)	ET(mm)
1	38.9	30.2	1.1	34.4	22.6	24.7
2	24.8	42.4	2.6	48.6	13.5	39.1
3	196.3	17.1	40.3	19.1	117.4	18.3
4	204.4	76.1	281.3	80.9	241.3	73.6
5	181.1	162.6	197.8	173.4	200.7	181.4
6	270.5	239.2	280.5	248.8	306	220.8
7	193.7	89.2	187.8	88	132	82.5
8	4.4	23.1	8.2	23.5	38.9	22.4
9	74.1	16.2	39.6	16.7	42.4	15.2
10	23	10.7	80.1	9.4	30.2	9.1
11	11	46.5	9.1	49.4	25.3	38.6
12	17	37.2	18	33.4	18.5	22.4

3. Methods

3.1. LEACHN model

LEACHN is one of the five sub-models of LEACHM. This model is a one-dimensional model that can be used to simulate nutrients transportation and movement in the unsaturated zone of the soil profile and leaching to groundwater.

Fig.2 shows P pools and pathways included in LEACHN that simulates flows between these pools in each soil segment [18].

The inorganic P model was based on concepts defined by Shavivand Shachar (1989) [19]. In that model the strongly bound P pool was considered to be a precipitated form of P with a very low solubility; in our model this pool can be assumed to be a precipitate or to follow a sorption isotherm. The labile pool is always in local equilibrium, but sorption to or desorption from the bound pool is kinetic.

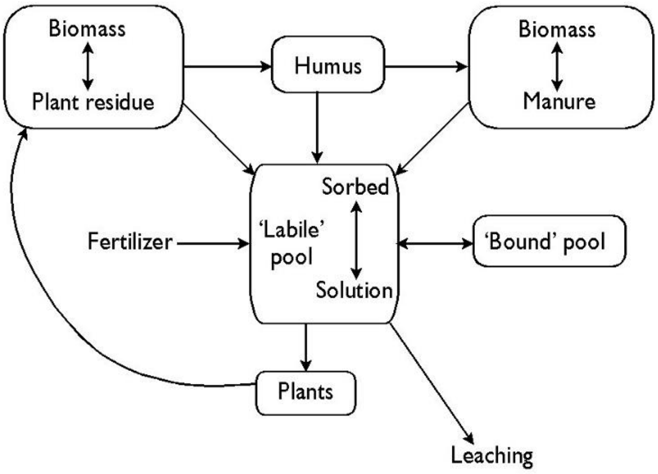

Fig. 2: Phosphorus Cycling in LEACHN

Main input data are needed for LEACHN model operations include: (i) Soil data for the different layers (water potential, hydrological constants, initial inorganic nitrogen or phosphorus content); (ii) Soil surface boundary conditions (irrigation and rainfall amounts and rate of application, mineral nitrogen or phosphorus fertilizer application rates and dates, mean temperature and diurnal amplitude, weekly totals of pan evaporation); (iii) Crop data (time of planting, root and crop maturity and harvest data, parameters of root and ground cover growth, pan factor for converting pan evaporation to potential crop evapotranspiration, lower soil and plant water potential for water extraction by plants); (iv) Other constants needed include diffusion coefficients, maximum value for time step, dispersion coefficient, rate constants for the nitrogen or phosphorus transformations, the adsorption coefficient[20].In this research calculating of all these functions followed the manual discipline as proposed by Hutson (2011) [18].

3.1.1. Soil water

a) Water retention and hydraulic conductivity

The water retention function in LEACHN model is based on Campbell equation, as nonhomogeneous and layered soils can be simulated by altering the values of two water retention constants, bulk density and saturated hydraulic conductivity [21].

Campbell's water retention equation is:

$$h = a(\theta/\theta_s)^{-b} \tag{1}$$

Where: (h) = pressure potential,
(θ) = volumetric water content,
(θ_s) = volumetric water content at saturation and a and b are constants.
This equation have a sharp discontinuity at $h = a$ and $\theta/\theta_s = 1$.

Hutson and Cass (1987) modified equation (1) by describing a parabolic section expressed in terms of the constants a and b [22]. For pressure potential between zero and h_c:

$$h = [a(1 - \theta/\theta_s)^{1/2}(\theta_c/\theta_s)^{-b}]/(1 - \theta_c/\theta_s)^{1/2} \tag{2}$$

Where:(h_c, θ_c) = the intersection of the exponential and parabolic curves. This point is given by:

$$h_c = a[2b/(1 + 2b)]^{-b} \tag{3}$$

$$\theta_c = 2b\theta_s/(1 + 2b) \tag{4}$$

Campbell's hydraulic conductivity equation is:

$$K(\theta) = K_s(\theta/\theta_s)^{2b+2+p} \tag{5}$$

Where: $K(\theta)$= hydraulic conductivity (mm/d) at water content θ,
K_s = hydraulic conductivity saturation θ_s,
p = a pore interaction parameter [18].

b) Water flow

LEACHN model operates numerical solution a technique is based on solution on Richard's equation by using a mobile/immobile region capacity model, and, for laboratory column studies, by considering steady-state water flow. In Richard's equation, solute transport is assumed to follow the convection-dispersion equation. WATFLO is used during time step when considering the Richards water flow option to solve the Richard's equation. It is not used when considering the steady-state water flow option, because water fluxes and contents are described in the input data. It is a mean of predicting water contents, fluxes and potentials.

Richard's equation for transient vertical flow derived from Darcy's law and the equation of continuity is:

$$\frac{\partial\theta}{\partial t} = C(\theta)\frac{\partial h}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\frac{\partial H}{\partial z}\right] - U(z,t) \qquad (6)$$

Where: θ = volumetric water content [m3/m3],
$C(\theta)$ = differential water capacity,
h = soil water pressure head,
H = hydraulic head [mm],
K = hydraulic conductivity [mm/d],
t = time [d],
z = depth [mm]
U = a sink term showing water lost by transpiration [d-1].

This model uses a center differential implicit method to solve the equations at all nodes [23].

3.1.2. Solute Transport Modeling

Solute transport like water flow is determined by a numerical solution to the diffusion-convection equation with the subroutine WATFLO. The general movement equation is:

$$\frac{\partial(\theta+\rho k_d+\varepsilon K_H^*)c}{\partial t} = \frac{\partial}{\partial z}\left[\theta D(\theta,q)\frac{\partial c}{\partial z} - qc\right] \pm \emptyset \qquad (7)$$

Where: c = phosphorus concentration of the particular solute [mg/l],
ρ = soil bulk density [kg/l],
K_d = the solute partition coefficient between the liquid and solid phases [l/kg],
ε = the soil porosity,
K_H^* = a modified Henry's law constant, q is the water flux [mm/day],
$D(\theta,q)$ = the obvious diffusion coefficient [mm2/day],
z = the soil depth [mm],
$\emptyset$ = sources and/or sinks of phosphorus [mg/l/day].

3.2. Input data

The required data to operation of the model such as soil moisture content, water retentivity curves and hydraulic conductivity measurements are given from the Haraz Extension and Technology Development Center in Mazandaran, Iran. In order to calculate the parameters a and b needed by the model, log $|h|$ was plotted against $\log\theta$. The spots corresponding to low water followed nearly a straight line. Then a and b were estimated by linear regression. The complete retentivity curve was obtained by using eqs. (1) to (4).Table 5shows the soil hydraulic parameters used in the simulations. The initial concentration of phosphorus in different layers of soil is shown in table 6.

Table 5: Soil Hydraulic Parameters

Soil depth (cm)	K_s (mm/day)	θ_s (cm3/cm3)	θ_c	Campbell's parameters a (kPa)	b
0-20	540	0.41	0.37	-1.98	3.88
20-40	576	0.44	0.35	-2.48	2.16
40-60	600	0.36	0.40	-8.78	1.38
60-80	240	0.42	0.38	-1.62	3.67
80-100	432	0.54	0.41	-0.98	3.15

Table 6: The Initial Values of Phosphorus

Soil depth (cm)	Phosphorus (mg/kg)
0-20	0.35
20-40	0.16
40-60	0.16
60-80	0.12
80-100	0.08

4. Results and discussion

Phosphorus concentrations in 1th, 30th and 60th days in different depth of soil are showed in Fig.3. As seen in the figure, the changes of phosphorus concentration to the depth of 30 cm are so considerable. At the depth of 30 to 80 cm, the changes have similar trends and after 80 cm, they are relatively constant. By comparing the result of simulation and measured value can be conclude that the model predicted results with a correlation coefficient of 92.3% accuracy. By comparing the eight scenarios, it is observed that the amount of rainfall has the maximum effect on changing the leakage of phosphorus in the soil-water phase. The results show that soil type is an effective parameter on phosphorus leakage.

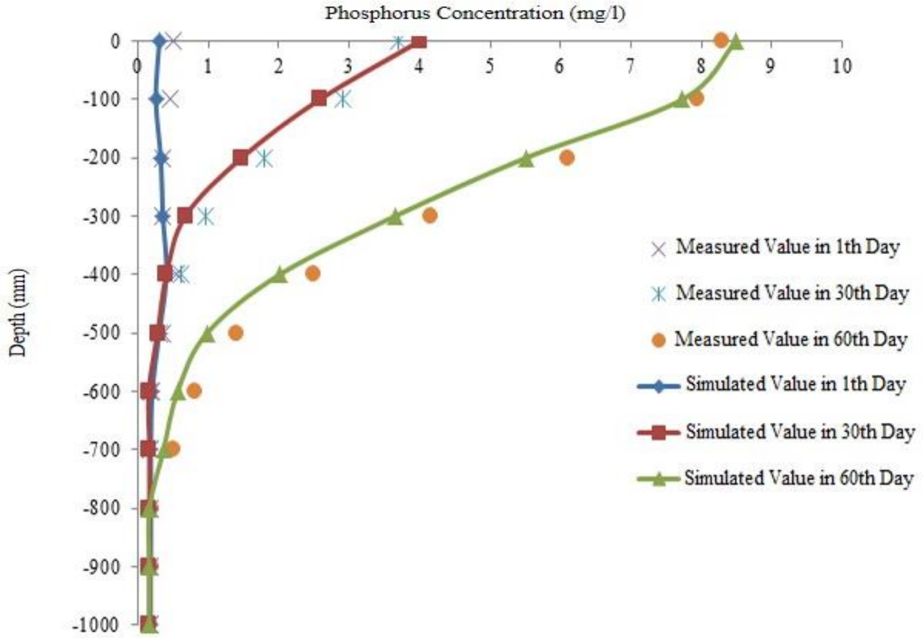

Fig. 3: Changes in Phosphorus Concentration versus Depth of Soil and Compared with Measured Values

4.1. Sensitivity analysis

Sensitivity analysis is a technique that can be used to evaluate and calibrate the model. It helps reviewers to investigate the effectiveness of the model and the actual conditions of the input data. The method used for this analysis has been proposed by Lane and Ferreira (1980) [24]. The following formula is used to assess the parameter sensitivity:

$$D_{max} = |(P_m - P_b)/P_b| \times 100 \quad (8)$$

Where: D_{max} = the maximum absolute difference,
P_m = the modified value
P_b = the base value.

If the input parameters variations have little effect on the amount of output data and also results, the measurement error of these parameters could be neglected. Conversely, if the input parameters variations high affect the results, their amounts have to be calculated with more accuracy. Otherwise, a large error is created in the results.

In this section, the thickness of layers 50%, bulk density 15% and some of the other input data 20% were less and more, and then the model was run. Based on the output values of moisture and phosphate in the soil profile, sensitivity analysis was performed.

As shown in table 7 sensitivity analysis is defined based on D_{max} and Sensitivity Index (SI).

To perform sensitivity analysis, Dmax and SI was calculated as model’s output. The result of sensitivity analysis is shown in table 8.

Table 7: The Values of D_{max} and SI in Sensitivity Analysis

Sensitivity	SI	D_{max}
Insensitive	0	0
Slightly sensitive	1	0-10
Sensitive	2	10-50
Highly sensitive	3	>50

Table 8: The D_{max} and SI Values for Sensitivity Analysis of Input Parameters

Input parameters	D_{max}	SI
Thickness of layer	1.8	1
saturated hydraulic conductivity	2.3	1
bulk density	87	3
a	12.5	2
b	53.2	3

One of the most important parameters in the numerical calculation was distance between the nodes. The results of sensitivity analysis in table 8 showed that the amount of phosphorus in the soil is slightly sensitive to this parameter. Among the physical properties of soil, saturated hydraulic conductivity and bulk density were selected for sensitivity analysis. As shown in table 8 phosphorus concentration in the soil is slightly sensitive to soil saturated hydraulic conductivity changes, but is highly sensitive to changes in soil bulk density.

The retention factor is the significant feature in evaluating the movement of water and solute transport in porous media. Since the coefficients of Campbell equation define the retention curve, these coefficients were selected in the sensitivity analysis. As seen in table 8, this model is sensitive to a coefficient of Campbell equation; however it is highly sensitive to b coefficient. So this coefficient has a significant effect on model results. The amount of soil moisture can be diminished by increasing of this coefficient [20].

Changes in soil phosphorus depend on climate factors and soil data. So as seen in table 9 distribution of phosphorus in soil and water were investigated by defining the different scenarios.

Table 9: The Different Scenarios

	Type of Soil	The Initial Concentration	Precipitation
Scenario 1	Sandy	Low	Low
Scenario 2	Sandy	Low	High
Scenario 3	Sandy	High	Low
Scenario 4	Sandy	High	High
Scenario 5	Clay	Low	Low
Scenario 6	Clay	Low	High
Scenario 7	Clay	High	Low
Scenario 8	Clay	High	High

As seen in Fig. 4, the results of eight scenarios that contain changing phosphorus concentration against time are compared with each other. The results of modeling show that the scenarios 4 and 8 have the greatest amount of phosphorus. In these scenarios, the initial concentration and rainfall are high. The maximum concentration is allocated to scenario 4 due to the sandy soil with high permeability. The scenario 5 has the lowest amount of phosphorus concentration because of clay. Other scenarios such as the effect of the soil type, the initial concentration and rainfall on the phosphorus content in the soil profile have been shown in Fig. 4.

4.2. Model assessment criteria

The model was assessed by both graphical and statistical methods. In the graphical method, the simulated and the measured values of phosphorus leaching were plotted and compared. In the statistical method, model performance was assessed using criteria described in Loague and Green (1991) [25], namely mean bias error (MBE), coefficient of variations (CV) and modeling efficiency (EF). The mathematical expressions that define these measures of analysis are:

$$MBE = \sum_{i=1}^{n} (P_i - O_i)/n \tag{9}$$

$$CV = 100\left(\sum_{i=1}^{n} (P_i - O_i)^2/n\right)^{0.5}/\bar{O} \tag{10}$$

$$EF = \left(\sum_{i=1}^{n} (O_i - \bar{O})^2 - \sum_{i=1}^{n}(P_i - O_i)^2\right)/\sum_{i=1}^{n}(O_i - \bar{O})^2 \tag{11}$$

Where: P_i = estimated value,

O_i = observed value,
$\bar{O}$ = observed average value and n is the number of points.

In optimal condition that the measured and predicted data are closer, the mean bias error and coefficient of variations are equal to zero and modeling efficiency in this case is equal to one [26], [27].

Comparing the model results with the actual observations is necessary to assessment the validity of a model. For this purpose statistical and graphical method were used. As seen in table 10, the mean bias error (MBE), coefficient of variations (CV) and modeling efficiency (EF) were determined as main criteria to understand the need of model to calibration of the parameters.

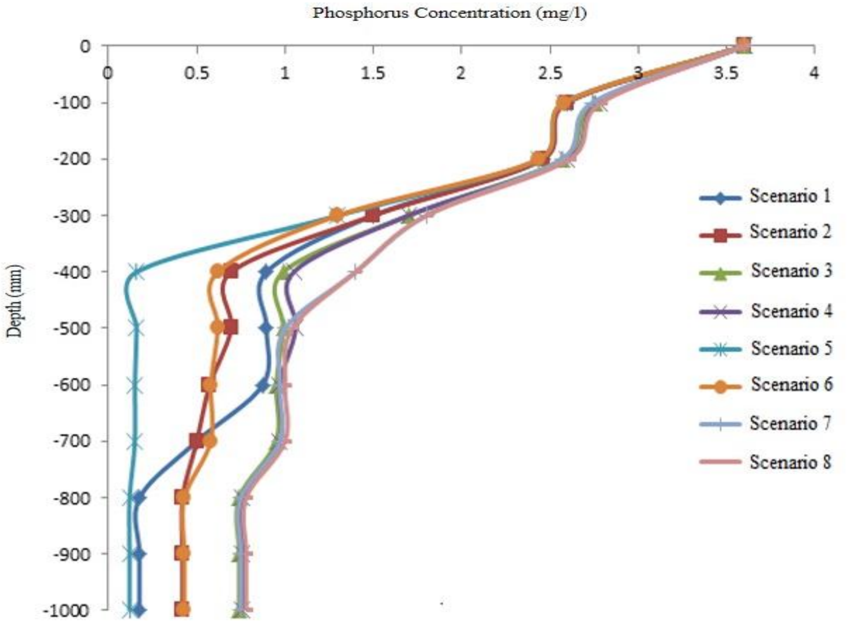

Fig. 4: Changes in Phosphorus Concentration of 8 Scenarios versus Depth for a Period of One Year

Table 10: The Values of Model Assessment Criteria

Mean Bias Error (MBE)	Coefficient of Variations (CV)	Efficiency (EF)
-0.087	0.19	-0.78

As mentioned the values of MBE and CV in optimum condition are equal to zero and the value of modeling efficiency in this condition is equal to one. The mean bias error value close to zero indicates that the estimated and measured values are similar. The negative sign of it indicates that the value model's underestimate. A negative EF value shows the average value of the measurements gives a better estimate than the simulated values (Kolahchi and Jalali, 2006).

5. Conclusion

In this research, the modeling of water and phosphorus movement in soil profile was simulated. Then the results of the modeling are compared with the actual values and it indicated that the model can measure the concentration of phosphorus, accurately. Therefore, the mean bias error value and the correlation coefficient of the modeling outputs were -0.087 and 92.3, respectively. The sensitivity analysis of output phosphorus concentration showed that the model with respect to parameters such as bulk density and soil water content is high sensitivity while there is little sensitivity to the thickness layers and saturated hydraulic conductivity. The effect of soil type and rainfall on the amount of leakage was analyzed by comparing different scenarios. Leakage of phosphorus in sandy soil is less than clay soil in shallow soil depth because of its higher permeability and leading phosphorus to leach a greater depth. Precipitation changes had the greatest effect on the leakage of phosphorus therefore; rainfall is directly proportional to the amount of leakage. According to this research findings, with applying the strategies such as proper drainage which could reduce soil moisture and thus phosphorus leakage to greater depth. Likewise, by controlling of soil clay content, implementation of appropriate water management, and improve soil properties can decrease the leakage of phosphorus into soil-water phase.

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