



## Transport Modeling and Leaching Kinetics in Groundwater of Shiwashok Oil field, Kurdistan Region, Iraq

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### ABSTRACT

Groundwater is one of the most important sources of water supply. Drinking safe water is vital for the health and well being of the community. To do this research, eight groundwater samples were collected from different sampling stations during the three sampling periods (January, May and July). The detected predominant cations are calcium and magnesium along with sulfate from the anions in most of the samples. Mean total dissolved solid of Darbasar Bchuk shows exceptionally high concentration levels compared to the other sampling sites, which is equal to 1193.3 mg/L. Due to concerns about the effects of oil production activities on groundwater quality in Shiwashok oil field, a one-dimensional transport modeling was simulated. The simulated data shows that the contaminants that reach the water wells have a high concentration compared to the detected concentrations of the contaminants in the wells. More time scale is required for the contaminant to reach the steady state or decrease to be lower than the permissible level. The O<sub>2</sub> and NO<sub>3</sub><sup>-</sup> reduction rates are slow as compared with the downward rate of water transport. CEC and organic matter in the groundwater are the main factors that govern the fate of transport of the contaminants.

### 1. Introduction

The Shiwashok oil field was discovered in 1930. The first well was drilled in 1960 and the second drilled in 1978, but due to political circumstances, oil was not extracted until 1994 where the production was 44,027 barrels/day in that year. Then production reached 140,000 barrels a day by 2016 [1]. A total of 35 wells have been drilled and currently more wells are being drilled. However, the field has rarely been studied scientifically, especially regarding its ecological aspects [2]. Assessment of the environmental impact of contaminants represents the first scenario implying contact with water which is the main activity for industrials, scientists, and stake holders because of the risk of contaminant release by leaching and generation of significant environmental problems. The leaching behavior of a given contaminant depends on the chemical nature of the material and its

morphology on both the leachant composition and the specific solid/liquid contact conditions, i.e. mass transfer properties [3]. The geochemical computer code PHREEQC can be used to model solute transport in different aquifers because it simulates solute water-rock chemical reactions involving natural or contaminated groundwater, and it also includes a dual-porosity transport model that can simulate solute diffusion in the bedrock matrix [4]. Within PHREEQC one-dimensional (1D) transport model can be simulated through two options with constant velocity. Using the ADVECTION, simple simulations can be carried out by a mixing cell approach. Using the keyword TRANSPORT, dispersion, diffusion and dual porosity can be taken into account [5]. 1D solute transport occurs in the bedrock fractures (mobile zone) via advection,

dispersion, diffusion, and solute water-matrix interactions. Only diffusive and reactive solute transport occurs in the bedrock matrix (immobile zone), where groundwater is assumed to be stagnant. Mixed factors are used to approximate the diffusive transport of solutes between the bedrock fractures and the rock matrix, and within the bedrock matrix [4].

In this research, 1D transport modeling will be made for eight locations regarding the contaminants released from the produced water of Shiwashok oilfield. Many of the chosen contaminants demonstrated high detection frequencies in the groundwater samples. Only those substances were included that might show concentrations higher than the permissible levels. The chosen study area characterized by the influence of an urban area with oil produced water from the Shiwashok oilfield, manure, and waste disposals as by surrounding agricultural uses. Consequently, a high yield of contaminants with different applications was expected, more than in sparsely populated areas.

Villagers around the oilfield area believed that their water wells have been recently polluted with hydrocarbon products; therefore, this paper is trying to evaluate the statement of the villagers regarding the water contamination level in the area.

## 2. Materials and Methods

### 2.1. Study Area

The study area located between (E 44°24'47" - 44°38'18") and (N 35° 56'36" - 36° 05'47"); the area covers about 342 km<sup>2</sup> and the elevation is in the range of 335 to 750 m above sea-level. The area is a part of Koysinjaq-Surdash Basin. The area lies within the foothill zone [6], characterizing by a semi-arid climate (cold, rainy winter, and hot, dry summer). The area bounded by Lesser Zab River at the southern part, Koya river at the eastern part and Shiwashok anticline at the northwestern part (Figure 1). The exposed Pre-Quaternary sediments which consist of the main aquifer in the study area are represented by clastic sediments of Bai Hassan and Muqdadeya Formations (Pliocene); impermeable sediments of Fatha and Injana

Formations (Miocene); carbonate rocks of Kolosh, Sinjar, Khormala, Gercus, and Pila Spi Formations (Paleocene and Eocene); and cretaceous carbonate rocks of Balambo, Qamchugha, Dokan, Kometan, Akra-Bekhme, Shiranish, and Tanjero Formations (Figure 2). Porous aquifer of Bai Hassan and Muqdadeya formations are the main source of groundwater in the area.

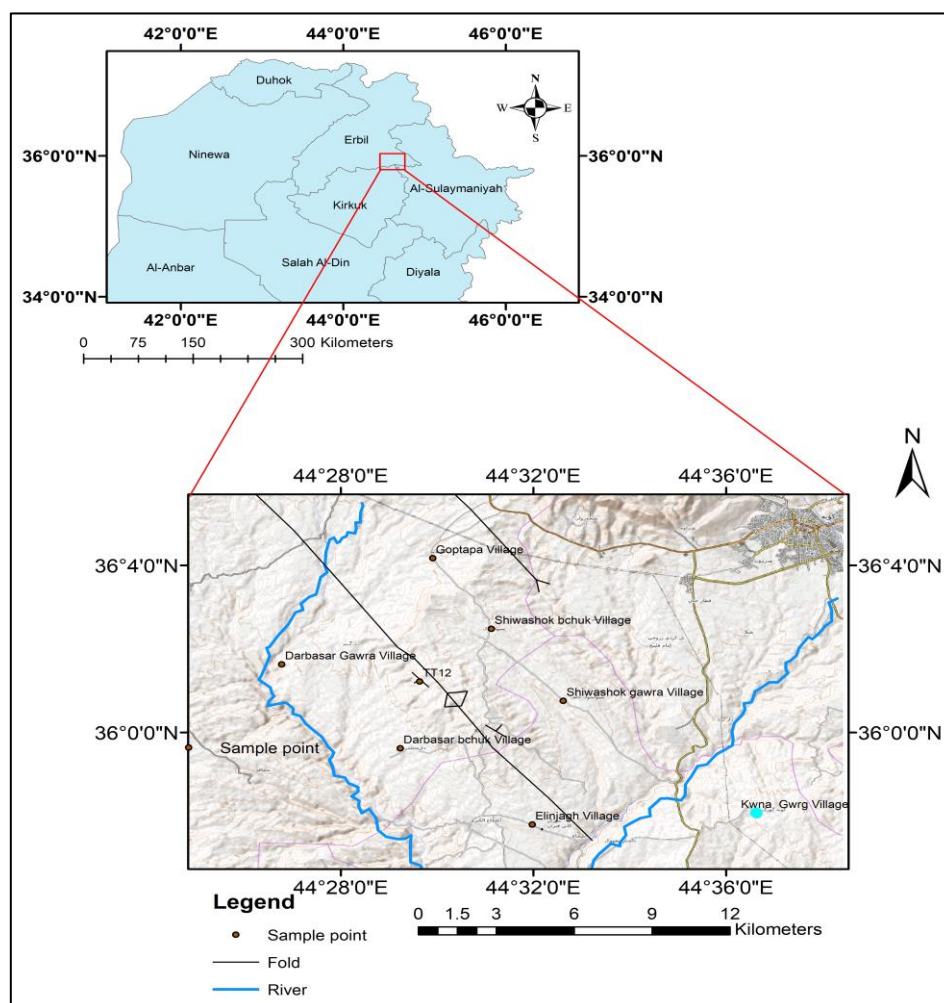


Fig. 1: Location of the study area

## 2.2. Sampling

The results from three water sampling campaigns during 2018 are presented. Samples were taken from 8 sampling points consisting of monitoring and abstraction wells (Figure 2). Groundwater samples were taken in January, May, and July representing high and low groundwater flow periods respectively. The description of sampling points is displayed in Table 1. Between winter and summer groundwater

levels decline by 2–4m. Wells for regular groundwater abstraction were sampled directly from the rising main during their continuous production. In observation wells, a submerged pump was installed for well purging purposes and the sample was taken immediately. The samples were transported in 1L glass bottles to the laboratory in a dark, cooled box and analyzed immediately after sampling.

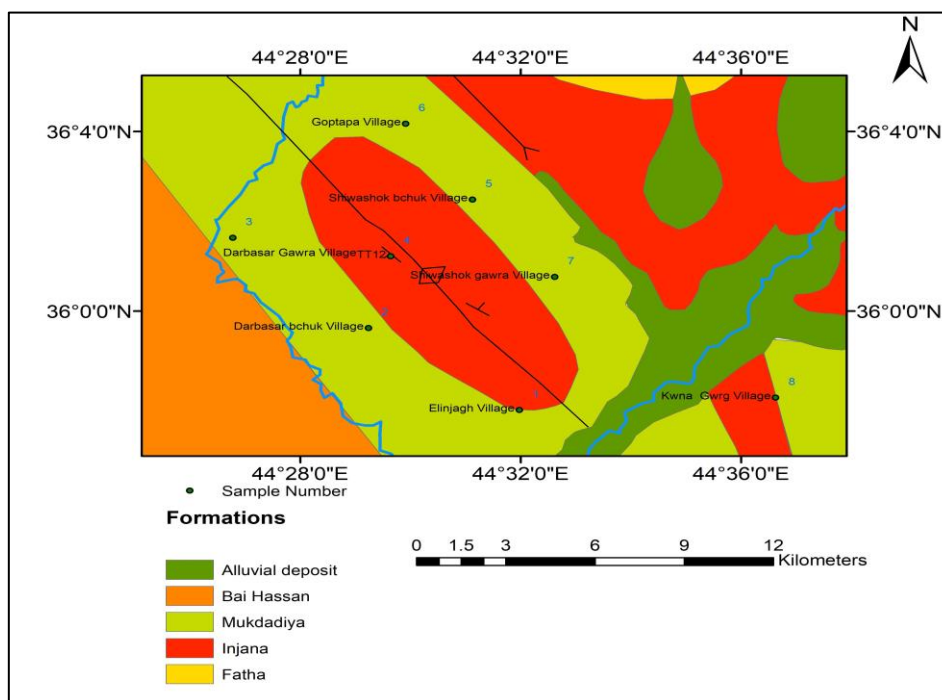


Figure 2: Sampling points on the geological map of the study area (adapted from FAO, 2003) [7]

Table 1: Description of Sampling points

| No. | Site Name               | Northing    | Easting     | S.W.L (a.m.s.l)<br>m | Depth to groundwater<br>(m) |
|-----|-------------------------|-------------|-------------|----------------------|-----------------------------|
| 1   | Elinjagh Village        | 35°57'47.8" | 44°31'58.5" | 434.47               | 36                          |
| 2   | Darbasar bchuk Village  | 35°59'37.2" | 44°29'14.3" | 463.2                | 7.4                         |
| 3   | Darbasar Gawra Village  | 36°1'38"    | 44°26'46.4" | 447.35               | 33.65                       |
| 4   | TT12                    | 36°1'13.3"  | 44°29'38.3" | 506                  | 60                          |
| 5   | Shiwashok bchuk Village | 36°2'29"    | 44°31'7.5"  | 577.78               | 8                           |
| 6   | Goptapa Village         | 36°4'10.5"  | 44°29'54.7" | N/A                  | N/A                         |
| 7   | Shiwashok gawra Village | 36°0'45.6"  | 44°32'37"   | 503.73               | 7                           |
| 8   | Kwna Gwrg Village       | 35°58'4.3"  | 44°36'37.6" | 490.77               | 14.3                        |
|     | N/A = Not available     |             |             |                      |                             |

## 2.3. Field Measurement

Field parameters (pH, electrical conductivity, dissolved oxygen (DO), water temperature and turbidity) were measured on-site using versatile devices (WTW and HACH multi-meter). After sampling, ultra-pure HNO<sub>3</sub> (30%) acid was added to those samples for ICP–MS determination of trace elements.

## 2.4. Laboratory Analysis

The analysis of significant cations, anions, and trace elements was performed in the laboratories of the Koya University. Trace elements were analyzed by ICP–MS X-Series (Thermo Scientific). Cations (Ca<sup>2+</sup>,

Mg<sup>2+</sup>, Na<sup>+</sup>, and K<sup>+</sup>) and anions (SO<sub>4</sub><sup>2-</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>) and minor elements such as (NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and F<sup>-</sup>) were measured by ion chromatography. Hydrogen-carbonate (HCO<sub>3</sub><sup>-</sup>) was determined immediately after sampling by means titration according to APHA [8]. The total reproducibility of the IC and ICP–MS determinations was around 2 and 10%, respectively. BTEX components' concentrations were analyzed by a headspace technique with gas chromatography, and detection was made by mass spectrometry (Thermo Scientific GC-MS) [9]. The following (table 2) represents setup

parameters of 1D model in PHREEQC that is crucial to create the geochemical model.

**Table 2: Setup parameters of 1D model in PHREEQC**

| Parameter             | Value     | Unit  |
|-----------------------|-----------|-------|
| Cell No.              | 10        |       |
| Length                | 10        | m     |
| Shifts                | 100-1160  |       |
| Time steps            | 10        | m/day |
| Flow direction        | Forward   |       |
| Boundary condition    | Flux      |       |
| Diffusion coefficient | 1.056e-10 |       |
| Dispersivity          | 2         | m     |

### 3. Results and Discussion

#### 3.1 BTEX in Groundwater:

The measurements of volatile compounds of benzene, toluene, ethyl benzene, and xylene (BTEX) in groundwater samples show concentrations under detection limit and the results are not listed in this paper. Degradation of BTEX compounds under natural aerobic condition could be the reason for under estimation of these compounds [10].

#### 3.2 Hydrochemistry:

Results of some measured parameters in the studied samples are listed in Table 3. The hydrochemical data were assessed by PHREEQC. The relative analytical error (E%) was assessed by PHREEQC and most samples were within an acceptable range of  $5\pm$ .

The results of physiochemical parameters are presented in Table 3. The sample Darbasar Bchuk indicates exceptionally high concentration levels compared to the other sampling sites and the mean TDS value of this site is 1193.3 mg/L. The data indicated that  $\text{Ca}^{2+}$  is the dominant cation in all of the samples followed by  $\text{Mg}^{2+}$  whereas  $\text{SO}_4^{2-}$  is the most abundant anion in all samples. The mean concentrations of  $\text{Ca}^{2+}$  range between 12 mg/L to 164 mg/L and for  $\text{SO}_4^{2-}$  range between 59 mg/L to 790.7 mg/L. Other predominant ions are  $\text{Mg}^{2+}$ ,  $\text{Ba}^+$ ,  $\text{Cl}^-$ , and  $\text{NO}_3^-$  ions. The relatively high concentration of ( $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ) is expected to be sourced from gypsum layers of the Fatha Formation rocks.

Table 3: Statistics of some measured parameters

| Parameter                     | Units                   | Statistics | TT12  | Elimjagh | Darbasar<br>Gawra | Darbasar<br>Bchuk | Shiwashok<br>Bchuk | Kwna Gwrg | Goptapa | Shiwashok<br>Gawra |
|-------------------------------|-------------------------|------------|-------|----------|-------------------|-------------------|--------------------|-----------|---------|--------------------|
| pH                            |                         | Mean       | 7.9   | 7.5      | 8.5               | 7.7               | 8.2                | 7.3       | 7.8     | 7.4                |
|                               |                         | Min        | 7.8   | 7.4      | 8.4               | 7.7               | 8                  | 7.2       | 7.1     | 7.1                |
|                               |                         | Max        | 8.1   | 7.7      | 8.6               | 7.8               | 8.4                | 7.3       | 8.4     | 7.9                |
| TDS                           | mg/l                    | Mean       | 1143  | 636.7    | 610               | 1193.3            | 500                | 900       | 590     | 773.3              |
|                               |                         | Min        | 450   | 500      | 560               | 580               | 430                | 770       | 470     | 710                |
|                               |                         | Max        | 2400  | 720      | 660               | 1700              | 570                | 1100      | 660     | 870                |
| Turbidity                     | NTU                     | Mean       | 32.5  | 0.6      | 2.2               | 3.8               | 1.3                | 1.9       | 5.9     | 3.6                |
|                               |                         | Min        | 5.8   | 0.3      | 0.6               | 0.4               | 1                  | 0.6       | 0.6     | 0.9                |
|                               |                         | Max        | 77    | 1        | 3                 | 9                 | 1.6                | 4         | 16.1    | 5                  |
| T.H                           | mg/l Ca CO <sub>3</sub> | Mean       | 274   | 313      | 56.3              | 533               | 60.3               | 530.7     | 298     | 433.7              |
|                               |                         | Min        | 140   | 295      | 36                | 451               | 47                 | 429       | 218     | 396                |
|                               |                         | Max        | 437   | 329      | 71                | 663               | 74                 | 708       | 349     | 482                |
| Color                         | Hazen                   | Mean       | 17    | 8        | 17                | 10                | 4                  | 16        | 6       | 7                  |
|                               |                         | Min        | 17    | 8        | 17                | 10                | 4                  | 3         | 6       | 1                  |
|                               |                         | Max        | 17    | 8        | 17                | 10                | 4                  | 29        | 6       | 13                 |
| COD                           | mg/l                    | Mean       | 9     | 29       | 25                | 30                | 0                  | 14.3      | 0       | 13                 |
|                               |                         | Min        | 8     | 29       | 25                | 11                | 0                  | 8         | 0       | 13                 |
|                               |                         | Max        | 10    | 29       | 25                | 49                | 0                  | 26        | 0       | 13                 |
| Ca <sup>2+</sup>              | mg/l                    | Mean       | 58    | 75.3     | 11.7              | 164               | 12                 | 84.3      | 61      | 112.3              |
|                               |                         | Min        | 23    | 73       | 8                 | 139               | 9                  | 66        | 47      | 103                |
|                               |                         | Max        | 103   | 78       | 15                | 201               | 15                 | 112       | 76      | 125                |
| Mg <sup>2+</sup>              | mg/l                    | Mean       | 31.3  | 30       | 6.3               | 30                | 7.7                | 77.7      | 35      | 37.7               |
|                               |                         | Min        | 20    | 27       | 4                 | 25                | 6                  | 64        | 24      | 34                 |
|                               |                         | Max        | 44    | 32       | 8                 | 39                | 9                  | 104       | 43      | 42                 |
| Na <sup>+</sup>               | mg/l                    | Mean       | 155   | 52.26    | 25.73             | 320.2             | 119.12             | 116.94    | 85.06   | 65                 |
|                               |                         | Min        | 121   | 41.52    | 14                | 265.3             | 70.15              | 83.44     | 53.1    | 42                 |
|                               |                         | Max        | 189   | 63       | 37.46             | 375.1             | 168.09             | 149.5     | 117.02  | 88                 |
| K <sup>+</sup>                | mg/l                    | Mean       | 19.2  | 2.14     | 1.22              | 2.94              | 3.84               | 4.33      | 2.22    | 5.19               |
|                               |                         | Min        | 11.3  | 1.08     | 0.9               | 1.3               | 3.1                | 2.2       | 0.8     | 3.5                |
|                               |                         | Max        | 27.1  | 3.2      | 1.54              | 4.58              | 4.58               | 6.46      | 3.64    | 6.88               |
| SO <sub>4</sub> <sup>2-</sup> | mg/l                    | Mean       | 447.3 | 224      | 143.7             | 790.7             | 59                 | 126       | 106.3   | 133.7              |
|                               |                         | Min        | 99    | 205      | 131               | 667               | 52                 | 89        | 86      | 123                |
|                               |                         | Max        | 1140  | 245      | 168               | 950               | 67                 | 165       | 125     | 143                |
| Cl <sup>-</sup>               | mg/l                    | Mean       | 223   | 58.7     | 59.7              | 125.7             | 23.3               | 99        | 34      | 107.3              |
|                               |                         | Min        | 95    | 48       | 54                | 106               | 20                 | 69        | 29      | 84                 |
|                               |                         | Max        | 433   | 64       | 69                | 155               | 26                 | 158       | 38      | 128                |
| HCO <sub>3</sub> <sup>-</sup> | mg/l                    | Mean       | 253   | 231      | 211               | 198               | 224                | 293       | 259     | 231                |
|                               |                         | Min        | 198   | 170      | 157               | 145               | 169                | 201       | 183     | 152                |
|                               |                         | Max        | 308   | 292      | 265               | 251               | 279                | 385       | 335     | 310                |
| Al <sup>2+</sup>              | µg/l                    | Mean       | 23    | 35.5     | 0                 | 43                | 15.5               | 27        | 34.3    | 71.7               |
|                               |                         | Min        | 10    | 23       | 0                 | 19                | 13                 | 19        | 12      | 16                 |
|                               |                         | Max        | 36    | 48       | 0                 | 67                | 18                 | 35        | 46      | 166                |
| Fe <sup>2+</sup>              | µg/l                    | Mean       | 0     | 0        | 0                 | 0                 | 0                  | 0         | 0       | 236                |
|                               |                         | Min        | 0     | 0        | 0                 | 0                 | 0                  | 0         | 0       | 236                |
|                               |                         | Max        | 0     | 0        | 0                 | 0                 | 0                  | 0         | 0       | 236                |
| Ba <sup>2+</sup>              | µg/l                    | Mean       | 99    | 91.7     | 35.7              | 19.7              | 63.3               | 458.3     | 83.3    | 156.3              |
|                               |                         | Min        | 47    | 77       | 27                | 17                | 51                 | 391       | 64      | 74                 |
|                               |                         | Max        | 192   | 106      | 43                | 21                | 77                 | 559       | 108     | 201                |
| F <sup>-</sup>                | mg/l                    | Mean       | 0.3   | 0.3      | 1.3               | 0.3               | 0.4                | 0.3       | 0.6     | 0.5                |
|                               |                         | Min        | 0.2   | 0.2      | 1.2               | 0.3               | 0.3                | 0.2       | 0.5     | 0.4                |
|                               |                         | Max        | 0.3   | 0.3      | 1.4               | 0.3               | 0.4                | 0.3       | 0.7     | 0.6                |
| NO <sub>3</sub> <sup>-</sup>  | mg/l                    | Mean       | 4.6   | 21.2     | 25                | 9.1               | 38.9               | 209.3     | 34      | 52.5               |
|                               |                         | Min        | 0.5   | 9.6      | 17.8              | 1.9               | 31.5               | 132       | 15.4    | 35.3               |
|                               |                         | Max        | 8.7   | 27.3     | 39.4              | 12.9              | 44.2               | 286.9     | 61.7    | 74.7               |
| NO <sub>2</sub> <sup>-</sup>  | mg/l                    | Mean       | 0.3   | 0.2      | 0                 | 0                 | 0                  | 0         | 0       | 0                  |
|                               |                         | Min        | 0.1   | 0.2      | 0                 | 0                 | 0                  | 0         | 0       | 0                  |
|                               |                         | Max        | 0.4   | 0.2      | 0                 | 0                 | 0                  | 0         | 0       | 0                  |
| Zn <sup>2+</sup>              | µg/l                    | Mean       | 39.5  | 586      | 24                | 73                | 87                 | 2.3       | 25.7    | 5.7                |
|                               |                         | Min        | 6     | 263      | 24                | 33                | 51                 | 1         | 6       | 2                  |
|                               |                         | Max        | 73    | 767      | 24                | 100               | 123                | 4         | 45      | 12                 |
| Mn <sup>2+</sup>              | µg/l                    | Mean       | 28    | 0        | 0                 | 2                 | 0                  | 2         | 6       | 53                 |
|                               |                         | Min        | 12    | 0        | 0                 | 2                 | 0                  | 2         | 6       | 53                 |
|                               |                         | Max        | 46    | 0        | 0                 | 2                 | 0                  | 2         | 6       | 53                 |

### 3.3. 1D Transport Modeling

To show the impact of leaching of the oil produced water on the groundwater of the area, a 1D transport model was simulated with PHREEQC. The selected wells for this study were chosen based on the possible impact from the produced water depending on the groundwater direction and geological formations. The groundwater is flowing mainly in two directions, north-south and north-southeast (Figure 3). All the selected water wells were located in the route of the

groundwater flow from the site of produced water. Only Darbasur Gawra and Goptapa wells were not in the flow direction route, however, the 1D model was also run for them to include the contamination scenario of possible geologic and structural controls. The distance between the produced water site and the wells was control the time of the model simulation through length, cell and shifts (Table 2). The input data of PHREEQC was reported in Table 4.

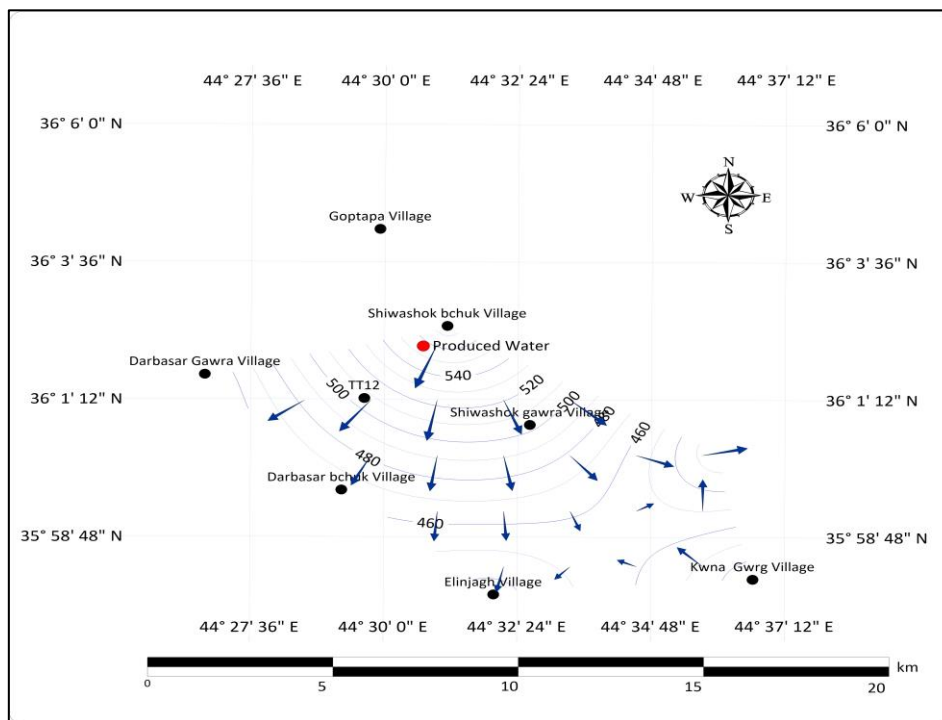


Fig. 3: Flow net map of groundwater of the study area

Table 4: Input data of groundwater in 1D model of PHREEQC

| Parameters                    | Units | TT12   | Elinjagh | Darbasur Gawra | Darbasur Bchuk | Shiwashok Bchuk | Kwna Gwrg | Goptapa  | Shiwashok Gawra | Produced Water |
|-------------------------------|-------|--------|----------|----------------|----------------|-----------------|-----------|----------|-----------------|----------------|
| Ca <sup>2+</sup>              | mg/l  | 158    | 95.3     | 117            | 164            | 12              | 84.3      | 61       | 112.3           | 1100           |
| Mg <sup>2+</sup>              | mg/l  | 41.3   | 30       | 16.3           | 30             | 7.7             | 67.7      | 35       | 37.7            | 400            |
| Na <sup>+</sup>               | mg/l  | 155    | 52.26    | 25.73          | 320.2          | 119.12          | 116.94    | 85.06    | 65              | 637            |
| K <sup>+</sup>                | mg/l  | 19.2   | 2.14     | 1.22           | 2.94           | 3.84            | 4.33      | 2.22     | 5.19            | 198            |
| SO <sub>4</sub> <sup>2-</sup> | mg/l  | 437.3  | 224      | 143.7          | 790.7          | 59              | 126       | 106.3    | 133.7           | 1650           |
| Cl <sup>-</sup>               | mg/l  | 220    | 58.7     | 59.7           | 125.7          | 23.3            | 129       | 34       | 107.3           | 3500           |
| HCO <sub>3</sub> <sup>-</sup> | mg/l  | 253    | 231      | 211            | 198            | 224             | 293       | 259      | 231             | 700            |
| Al <sup>2+</sup>              | µg/l  | 0.023  | 0.0355   | 0              | 0.043          | 0.0155          | 0.027     | 0.034333 | 0.072           | 3.1            |
| Fe <sup>2+</sup>              | µg/l  | 0.025  | 0.023    | 0.011          | 0.017          | 0.02            | 0.023     | 0.021    | 0.009           | 100            |
| F <sup>-</sup>                | mg/l  | 0.3    | 0.3      | 1.3            | 0.3            | 0.4             | 0.3       | 0.6      | 0.5             | 1              |
| NO <sub>3</sub> <sup>-</sup>  | mg/l  | 4.6    | 21.2     | 25             | 9.1            | 38.9            | 209.3     | 34       | 52.5            | 10             |
| Cu <sup>2+</sup>              | µg/l  | 0.001  | 0        | 0              | 0.001          | 0               | 0.005667  | 0        | 0.0073          | 150            |
| Li <sup>+</sup>               | µg/l  | 0.02   | 0.015    | 0.025          | 0.02           | 0.03            | 0.034     | 0.02     | 0.025           | 30             |
| Ni <sup>2+</sup>              | µg/l  | 0.001  | 0        | 0              | 0              | 0               | 0.003667  | 0.0015   | 0.003           | 170            |
| Pb <sup>2+</sup>              | µg/l  | 0.001  | 0        | 0              | 0              | 0               | 0.007333  | 0        | 0.072           | 88             |
| Zn <sup>2+</sup>              | µg/l  | 0.0015 | 0.586    | 0.024          | 0.073          | 0.087           | 0.002333  | 0.025667 | 0.0057          | 70             |
| Mn <sup>2+</sup>              | µg/l  | 0.03   | 0        | 0              | 0              | 0.002           | 0         | 0.002    | 0.006           | 175            |

Figures 4, 5, 6, 7 and 8 shows the results of the 1D transport models for several components during the different time steps. The time step of each model is different from the others and refers to the time of arrival of the contaminant in the well site. The models in the Figure 4 refers to the simulation of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . The simulated concentration of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  that reach Kuna Gurg well site is equal to 0.0162 and 0.0063 mol/l respectively, which is more than what detected in the well water. The time of arriving the contaminants in the Kuna Gurg well from the source is 1160 days (Figure 4a). Probably, more time is needed for the contaminant to reach the steady state or to be in a safe concentration (under the permissible level). In Shiwashok Bchuk the arrival time is 360

days and the simulated concentration of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  is also more than the detected values (Table 3) and it's also true for Darbasar Bchuk and Gawra wells (Figure 4b, c and d). The presence of organic matter oxidation in aquifers is related to the gradual decreases of oxygen and nitrate with depth and this indicates that  $\text{O}_2$  and  $\text{NO}_3^-$  reduction rates are slow as compared with the downward rate of water transport [11]. The same is may be true for  $\text{SO}_4^{2-}$  as it affected by oxidation in the aquifer. This could be explained by complexity of the underground conditions like: hydraulic conductivity. The hydraulic conductivity of porous media controls the displacement of liquids in the soil pores and affects the fate and transport of contaminants in the environment [12].

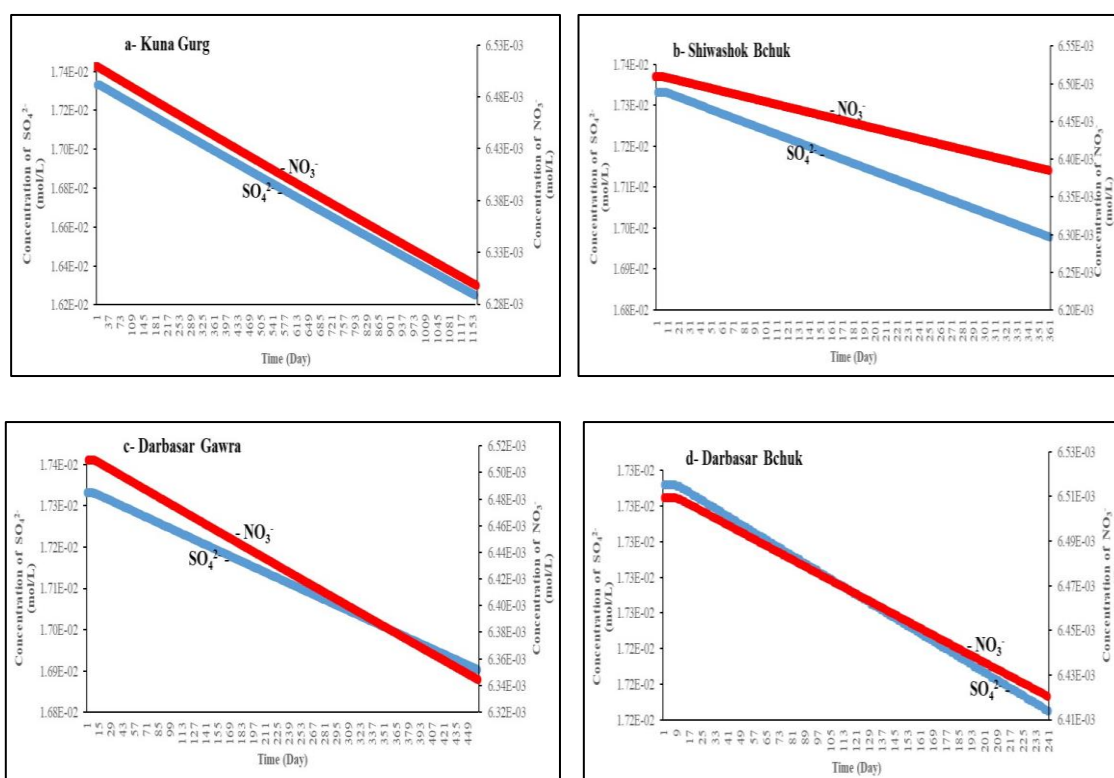
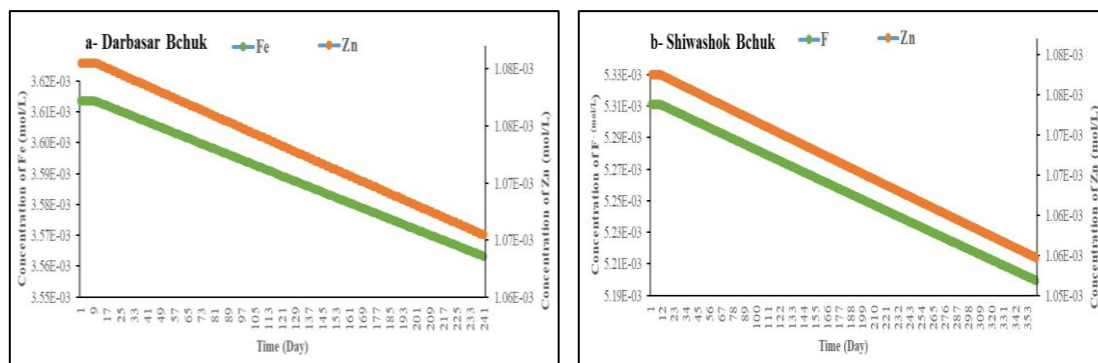
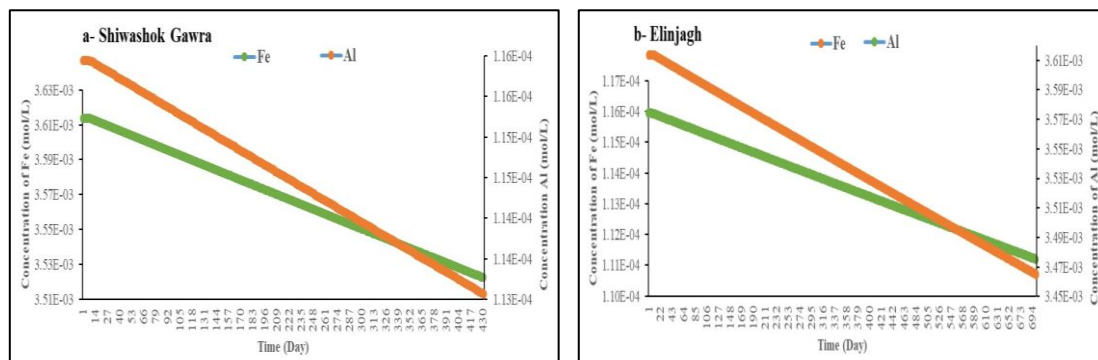
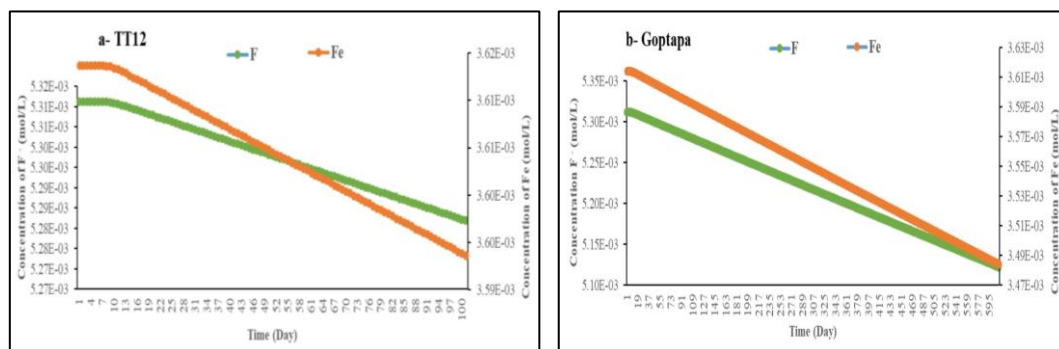


Fig. 4: 1D transport simulation of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$

The models in the Figures 5, 6 and 7 refers to the simulation of trace elements  $\text{Fe}^{2+}$ ,  $\text{Al}^{2+}$  and  $\text{Zn}^{2+}$  with fluoride ( $\text{F}^-$ ). The simulated concentration of  $\text{Zn}^{2+}$  that reach Darbasar Bchuk and Shiwashok Bchuk wells are equal 0.00106 mol/l for both, which is more than what detected in the well water and the time of arriving the contaminants from the source is 240 and 360 days respectively (Figure 5a and b). More time is needed for the contaminant to reach the steady state or to be in a safe concentration (under the permissible level) and the presence of organic matter oxidation in aquifers affect the fate of  $\text{Zn}^{2+}$  transport. The behavior and fate of trace elements is governed by different physical and chemical processes, which dictate their availability and mobility in the aquifer. The chemical form of the water phase of a metal

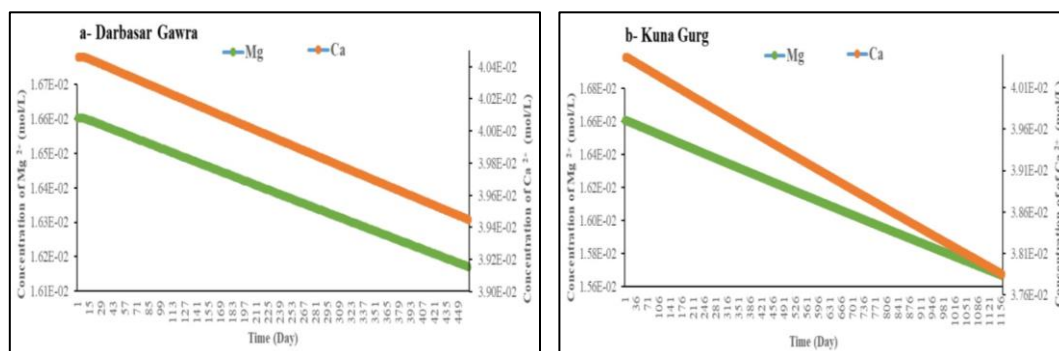
determines the biological availability and chemical reactivity (sorption/ desorption, precipitation/ dissolution) towards other components of the system [13].

Regarding the reactive transport of  $\text{F}^-$  in Darbasar Bchuk and Shiwashok Bchuk wells, the role of cationic exchange capacity (CEC) in Ca/Na exchange and calcite precipitation, works in the direction of a decrease of the  $\text{Ca}^{2+}$  activity that prevents fluorite precipitation. Iron hydroxide precipitation in the aquifer offers a not inconsiderable adsorption capacity for  $\text{F}^-$  immobilization [14]. According to what discussed by Appelo et al. [15] in their experiments, the effect of CEC on the mobilization of  $\text{Fe}^{2+}$  is concluded in case of  $\text{Fe}^{2+}$  transport in the studied area (Figure 6 and 7).

Fig. 5: 1D transport simulation of  $\text{Fe}^{2+}$ ,  $\text{F}^-$  and  $\text{Zn}^{2+}$ Fig. 6: 1D transport simulation of  $\text{Fe}^{2+}$  and  $\text{Al}^{3+}$ Fig. 7: 1D transport simulation of  $\text{Fe}^{2+}$  and  $\text{F}^-$ 

Regarding the variation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  during simulation of the model in Darbasar Gawra and Kuna Gurg wells (Figure 8), the result shows change in pH and magnesium concentration and an increase in calcium concentration, which might be illustrates

how carbonate mineral equilibria in combination with an advancing mineral dissolution front may affect the baseline concentrations on a timescale of about 1-4 years, that similarly discussed by Postma et al. [16].

Fig. 8: 1D transport simulation of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$

#### 4. Conclusions and Recommendations

The measurements of BTEX in groundwater samples show concentrations under detection limit, which can be explained by degradation of BTEX compounds under natural aerobic condition could be the reason for under estimation of these compounds. The effects of oil production activities on groundwater quality in Shiwashok oil field is clearly illustrated using 1D transport modeling. The simulated data shows that the contaminants reach the aquifer and the water wells have a high concentration compared to the detected concentrations of the contaminants especially  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ . More time scale is required for the contaminant to reach the steady state or decrease to be lower than the permissible level. The reduction rates, CEC and organic matter in the groundwater are

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- To decrease the impact of the oil production activities the main legislations listed by Sam et al. [17] have to be taken in consideration. The main cleanup activities that could help in situation of Shiwashok oil field is recommended as mentioned in Sam and Zabbey [18] and includes: dealing with raw materials, transport actions, implementation of remediation technologies and waste management.
- Remediation by silica encapsulation technique [19] is also recommended for effectiveness as a green remediation technology for the cleanup and restoration of hydrocarbons contaminated groundwater in wells of Shiwashok Bchuk, Shiwashok Gawra, Darbasar Bchuk, Darbasar Gawra, Kuna Gurg and Elinjagh.
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## نمذجة النقل وحركة الترشيح في المياه الجوفية لحقل نفط شيواشوك، إقليم كردستان، العراق

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### الملخص

تعد المياه الجوفية من أهم مصادر المياه. المياه الصالحة للشرب أمر حيوي لصحة المجتمع ورفاهيته. لإجراء هذا البحث، تم جمع ثماني عينات من المياه الجوفية من محطات مختلفة خلال فترات أخذ العينات الثلاث (يناير ومايو ويوليو). الكاتيونات السائدة المكتشفة هي الكالسيوم والمغنيسيوم مع الكبريتات من الأنيونات في معظم العينات. يظهر متوسط إجمالي المواد الصلبة الذائبة لدارباسار بتشوك مستويات تركيز عالية بشكل استثنائي مقارنة بمواقع أخذ العينات الأخرى، والتي تساوي ١٩٣.٣ مجم / لتر. بسبب المخاوف بشأن تأثيرات أنشطة إنتاج النفط على جودة المياه الجوفية في حقل نفط شيواشوك. تمت محاكاة نمذجة نقل أحادية البعد. أظهرت بيانات المحاكاة أن الملوثات التي تصل إلى آبار المياه لها تركيز عالٍ مقارنة بالتركيزات المكتشفة للملوثات في الآبار. يتطلب المزيد من المقياس الزمني حتى يصل الملوث إلى الحالة المستقرة أو ينخفض ليكون أقل من المستوى المسموح به في المياه الجوفية. معدلات تخفيض O<sub>2</sub> و NO<sub>3</sub>- بطيئة بالمقارنة مع انخفاض معدل النقل المائي تعد CEC والمواد العضوية في المياه الجوفية من العوامل الرئيسية التي تحكم مصير انتقال الملوثات.