Mobilization of Heavy metals from Mineral phase and the Speciation in Potable Aquifers due to Saline Intrusion

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ABSTRACT

In order to assess if there is a potential of solubilizing trace metals from minerals by saline intrusion in costal aquifers, a series of simulations were conducted. Numerical simulations were conducted for a series of saline intrusion scenarios and different aquifer geochemical conditions like; in presence of *dolomite, qurtz and pyrites*. The effect of saline intrusion induced trace metal solubilisation was assessed using a PHREQCI hydro geochemical model incorporated with *minteq.v4* thermodynamic database. For simulation the physicochemical parameters of groundwater (*which contains lead and copper in trace level*) of the costal aquifer of Mumbai, India was taken in input file. Results show that *Cerrusite* and *Cuprite* are the predominant mineral phases in equilibrium with groundwater for Pb and Cu respectively. Further simulations at different rate of saline intrusion revealed that Pb and Cu mobilization increases with the increase in saline intrusion and exceeds their maximum contamination levels (MCL). The involved mechanism in mobilization of metal ion is nothing but the desorption of the metal ions from mineral surface by competitive positive ions Ca^{2+}, Mg^{2+}, Na^+, K^+ and subsequent formation of soluble complexes by counter ions like Cl^-, SO_4^{2-} and CO_3^{2-}.The study revealed that the presence of dolomite in the aquifer accelerate the desorption of the Pb and Cu from mineral.

Introduction

The mobility and bioavailability of metal in the environment depends not only on their total concentration but also on their association with the solid phase to which they are bound (*Ure and Davidson, 2001*). These associations are governed by a range of different physical–chemical processes such as: sorption/ desorption and precipitation/dissolution (*Tack and Verloo, 1995; Almås et al., 2006; Skrbic and Djurisic-Mladenovic, 2010*). These processes are governed by pH, ionic strength (salt content) of the solid-liquid system and cation exchange capacity of the soild phase. The metal mobilization through dissolution in runoff or lixiviation water poses a direct risk of groundwater contamination. The dissolution of soil minerals is mainly salinity/salinization is one of the important reasons for metal mobility as it affects the distribution coefficientof the metal.However, not much is yet known about the influence of salinity on heavy metal mobility. If salinization results in increased mobility of heavy metals in soil-water system, this would be an important additional adverse phenomenon. It should then be taken into account when evaluating the effects of salinization of costal aquifer as well arid zones aquifers in the context of environmental risk assessments. Increase of ground water salinity not only the case of costal aquifers it also happened to most arid and semiarid zone aquifer due to fall of ground water table and connate ascension.

About two thirds of the world's population lives within 400 km of the ocean shoreline; just over half live within 200 km, an area only taking up 10% of the earth's surface (*Hinrichsen, 2007*) and most of these regions depend upon groundwater as their main source of fresh water for domestic, industrial and agricultural purposes. As world's population continues to grow at an alarming rate, fresh water supplies as well as potential are constantly being depleted, bringing with it issues such as saltwater intrusion. This increases the importance of groundwater monitoring, management, and conservation. Considering the saline intrusion scenario, a series of simulation study was conducted using PHREQCI (*Parkhurst and Appelo 1999*) hydro-geochemical model and *minteq.v4*.database (*Allison et al 1990*).The objectives of this study were to assess the potential that saline intrusion into potable aquifers might solubilize trace metals of concern to drinking water quality and to determine what processes affect these changes. A secondary goal was to investigate the speciation of the metal. Based on simulation results, we also explored role of geochemical characteristics in overlaying aquifers in mobilization of metal w.r.t saline intrusion to aquifer.

Modelling approach

The simulation was used to investigate digenetic reactions that may occur in zones where seawater mixes with ground water in equilibrium with various minerals with special emphasis on the minerals of lead and copper. Simulations were conducted for a saturated and homogenous aquifer assuming that dissolution of minerals is the only source of trace metal species in the aquifer, and that the dissolution process is solely controlled by the change in the physico-chemical change in the aqueous phase due to mixing of sea water and ground water. As per Ghyben-Herzberg relation how deep the sea water intrudes towards the land depends on the pheretic surface ascending from sea level. If the sea water density is 1.025g/cc and fresh water density is 1.0 g/cc according to relation if the water table in an unconfined aquifer lowered by 1m, the salt water interface rise about 40 m (*Bear 1999*). With increase in intrusion the salt water- fresh water interface shift more towards the land and

convert fresh water to brackish and finally to saline. For the simulation input file was prepared taking physico-chemical parameters of sea water of Arabian Sea and ground water of coastal region of Mumbai. The values of different parameters are presented in table 1. The simulation was carried out at two phase ; a) simulation to identify the species of heavy metals and the possible mineral, b) study of change in concentration and speciation of heavy metals due to interaction of minerals with the ground water contaminated with sea water with different mixing ratio.

Table 1. Model input parameters used in the simulation

Parametrs	Ground water	Sea water
Temprature	25° C	25 °C
pe	4.07	8.41
pH	7.85	8.22
Ca^{+2}	59.1 (mg/l)	412.3(mg/l)
Mg^{+2}	16.25(mg/l)	1285.8(mg/l)
Na^+	136.9(mg/l)	10625.3(mg/l)
K^+	6.4(mg/l)	354.2(mg/l)
Si	4.1(mg/l)	4.3(mg/l)
Cl-	260.8(mg/l)	19300(mg/l)
SO_4^{-2}	5.2(mg/l)	2703.5(mg/l)
Cu	5.4 (µg/l)	-
Pb	1.2(µg/l)	-
Alkalinity (as HCO_3^-)	143.8(mg/l)	141.68(mg/l)

Table 2. Key Reaction and their *log K* values

Specis	Reaction	Log k
Cerrusite Dissolution	$PbCO_3 = Pb^{+2} + CO_3^{-2}$	-13.13
Cuprite Dissolution	$Cu_2O + 2H^+ = 2Cu^+ + H_2O$	-1.406
$PbCO_3$	$Pb^{+2} + CO_3^{-2} = PbCO_3$	6.48
$Pb(CO_3)_2^{-2}$	$Pb^{+2} + 2CO_3^{-2}= Pb(CO3)_2^{-2}$	9.94
$PbCl_2$	$Pb^{+2} + 2Cl- = PbCl_2$	2.2
$PbCl_3^-$	$Pb^{+2} + 3Cl- = PbCl_3^-$	1.8
$PbCl_4^{-2}$	$Pb^{+2} + 4Cl-=PbCl_4^{-2}$	1.46
$Pb(SO4)_2^{-2}$	$Pb^{+2} + 2SO_4^{-2} = Pb(SO4)_2^{-2}$	3.47
$CuCl_2^-$	$Cu^+ + 2Cl^- = CuCl_2^-$	5.42
$CuCl_3^{-2}$	$Cu+ + 3Cl^- = CuCl_3^{-2}$	4.75

Aqueous Speciation Calculations

Chemical composition of the ground water used as input to calculate aqueous speciation, distribution of aqueous species and saturation indices of phases. First, the model describes the thermodynamic activities and mass-action equations for aqueous, exchange, and surface species followed by algebraic equations are derived for each thermodynamic activity of parameters.Then, a set of functions (*f*) are defined that must be solved simultaneously to determine equilibrium for set conditions. These functions are generally derived from mole-balance equations for each element or element valence state or from mass-action equations for pure phases. For alkalinity, activity of water, aqueous charge balance and ionic strength etc. additional functions are derived. Mole-balance equations for hydrogen and oxygen are not included, because the total masses of hydrogen and oxygen generally are not known and the mass of water is assumed to be 1.0 kg. The dissolved species in the aqueous phase are assumed to be in thermodynamic equilibrium, with one exception; in initial solution calculations, disequilibrium among valence states of redox elements is allowed. The unknowns for each aqueous species *i* are the activity, a_i, activity coefficient, $ɣ_i$, molality, m_i and moles in solution, n_i. The numerical method (*Newton-Raphson* method) reduces the number of unknowns to be a minimum number of master unknowns, and iteratively refines the values of these master unknowns until a solution to the set of algebraic

equations is found. The master unknowns for aqueous solutions are the natural log of the activities of master species, the natural log of the activity of water, a_{H2O}, the ionic strength, µ, and the mass of solvent water in an aqueous solution, W_{aq}. The following relationships apply to all aqueous species (except aqueous electrons and water itself):

$$a_i = ɣ_i m_i$$
and $$n_i = m_l W_{aq}$$

The mass action equation used to calculate equilibrium constant is expressed as;

$$K_i = a_i \prod_m^{M_{aq}} a_m^{-C_{m,i}}$$

Where, K_i is a temperature-dependent equilibrium constant, $c_{m,i}$ is the stoichiometric coefficient of master species *m* in species *i* and M_{aq} is the total number of aqueous master species. The values of $c_{m,i}$ may be positive or negative. The total moles of the aqueous species derived from the mass action equation can be expressed as;

$$n_i = m_i W_{aq} = K_i W_{aq} \frac{\prod_m^{Maq} a_m^{C_{m,i}}}{\gamma_i}$$

The Newton-Raphson method uses the total derivative of moles with respect to the master unknowns. The total derivative is;

$$dn_i = n_i \left[d\ln(W_{aq}) + \sum_m^{M_{aq}} c_{m,i} d\ln(a_m) - \frac{\partial}{\partial\mu}\ln(\gamma_i)d\mu \right]$$

In mixing of sea water and fresh water each solution is multiplied by its mixing fraction and a new solution is calculated by summing over all of the fractional solutions. The compositions of new solution formed due to mixing, is then used for the speciation modelling as discussed above.

Mineral Dissolution and kinetics

Two possible cases have to be distinguished to study the interactions between solid and liquid phases; a) weathering of rock-forming minerals and b) the weathering of trace minerals. For the weathering of rock-forming minerals, the solution kinetics is determined by the solubility-product and transport in the vicinity of the solid water-interface (*Merkel and Friedrich 2002*). If the dissolution rate of a mineral is higher than the diffusive transport from the solid-water interface, saturation of the boundary layer and an exponential decrease with increasing distance from the boundary layer results. This kind of solution is referred to as solubility-product controlled. If the dissolution rate of the mineral is lower than diffusive transport, no saturation is attained. This process is called diffusion-controlled solution.

For the weathering of trace minerals from the solid matrix, the dissolution occurs selectively on spots where the mineral is exposed to the surface. These mineral surfaces are usually not smooth, but show dislocations (screw, jump, step dislocations) and point defects (vacant sites, interstitial sites). Dissolved ions are immediately transported from the surface into solution, so that no gradient can develop. Since the total concentrations of trace minerals in the solution are low, no equilibrium can be reached. In the following this dissolution of trace minerals is called surface-controlled.

The overall rate for a kinetic reaction of minerals and other solids can be expressed as:

$$R_k = r_k \frac{A_0}{V}\left(\frac{m_k}{m_{0k}}\right)^n$$

where r_k is the specific rate (mol/m^2/s), A_0 is the initial surface area of the solid (m^2), V is the amount of solution (kgw), m_{0k} is the initial moles of solid, m_k is the moles of solid at a given time, and (m_k / m_{0k})^n is a factor to account for changes in A_0 / V during dissolution and also for selective dissolution and aging of the solid. For uniformly dissolving spheres and cubes n = 2/3. As frequently ball the parameters are not available simple approach are useful like:

$$R_k = k_K \times (1 - SR)^\sigma$$

k_K is empiric constant and SR is the saturation rate (Ion Activity Product/Solubility Product; *IAP/K$_{SP}$*), frequently the exponent σ is equal to 1. The equation is valid for both under saturation and supper saturation. With saturation R_k become zero. R_k can also be written in terms of saturation index SI as:

$$R_k = k_K \cdot \sigma \cdot SI$$

The solubility product is depends on the mineral, the solvent, the pressure of certain gas, temperature pH, E_h and on the ions previously dissolved in the water and the to what extent they have formed complexes among themselves.

Model Application and Discussion

In the following section, the model described above was applied to two simple hypothetical scenarios in order to assess some of the possible effects of saline intrusion starting from 10% to 90% and mineral dissolution rates on the quality of ground water of potable aquifers.

Simulating to study aqueous speciation and identification of the mineral phase in equilibrium

The aqueous speciation study of the ground water of coastal regions of Mumbai was carried out taking average values of physicochemical parameters (*See Table 1*) of the ground water collected from 25 locations of costal aquifer of the Mumbai, India. Pb and Cu were detected in the ground water samples. Parameters values were taken as input file for the *PHREQCI* and simulation was carried out using *minteq.v4* thermodynamic database. The simulation identified that the *Cerrusite* and *Cuprite* are the predominant minerals of the hypothetical system for Pb and Cu.

Simulating the enhanced dissolution of the lead due to saline intrusion to shallow aquifer

Lead poses a significant public health threat through long term internal accumulation that can cause damages to the brain, red blood cells and kidneys, especially to young children and pregnant women. The US Environmental Protection Agency (EPA) has regulated lead in public water systems and fixed the action level at 15 µg L^{-1} (7.25×10^{-8} mol/l), and a maximum contaminant level goal (MCLG) of 0.0 µg L^{-1} has been proposed in the *lead* and *copper* rule under the Safe Drinking Water Act in 1991 (*EPA 1991*). Possible sources of lead in drinking water include corrosion of household plumbing systems and elevated levels from natural deposits. Galena and Cerussite are of the most important base minerals and are the main minerals controlling the mobility of lead in the subsurface. In our case aqueous speciation study identified cerrusite as the predominating mineral of lead of the site. Hence further simulation study was carried out taking cerrusite as the principal Pb mineral at different rate of saline intrusion from staring from 10% to 90% with an increment of 10% at each step.

As seen in Fig. 1 (and also in Fig. 2) the dissolved *Pb* concentration due to the dissolution of *Cerrusite* increases as the mixing fraction of sea water increases. The dissolution of mineral or the mobilization of Pb may be attributed due to two processes; 1) complexation capacity of salt derived anions with

lead, 2) competition of salt derived cations with positively charged heavy metal species for sorption sites on the solid phase. To identify the mechanism involved in the mobilisation of Pb from solid to liquid system, similar simulation studies were carried out at different conditions like in the presence of *Dolomite, Quartz and Pyrites*. The result is presented in Fig. 2. The simulation indicates that the dissolved lead concentration increases to two times in the case of aquifer in equilibrium with dolomite. At high intrusion level (>50%) the dissolved Pb level even increases to ten times than the aquifer is in equilibrium with/ without quartz and pyrites. This may be attributed due to increase in concentration of Ca^{2+} and Mg^{2+} as a result of dissolution of dolomite which accelerate the desorption of Pb from mineral site. At the same time the dissolution of dolomite increases the carbonate concentration in the system which form soluble complex ($PbCO_3$) readily. The speciation study presented in Fig. 3 and 4, supports the assumption; as in $PbCO_3$ was found to be predominating species followed by $PbCl^+$, $PbCl_2$, $PbSO_4$, $PbCl_3^-$ and $PbCl_4^{2-}$ etc. in the hydrogeochemical condition. At low saline intrusion rate Pb^{2+} is also exist in the system. The key reactions and the *log K for* mineral dissolution as well as different species formations is listed in Table. 2. The presence of the *pyrites* in the system has no impact on the concentration of *Pb* indicates that, *Pb* is not sorbed on pyrites in the set conditions as intrusion has no impact on the pH of the system.
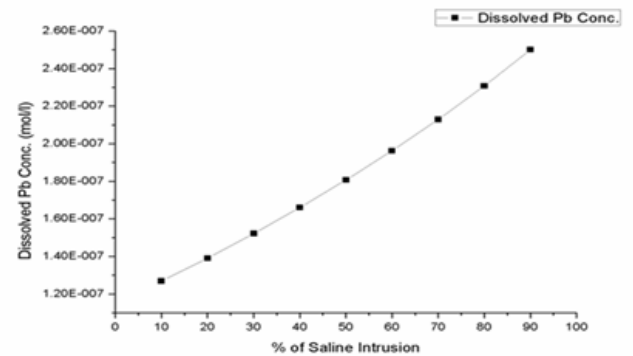

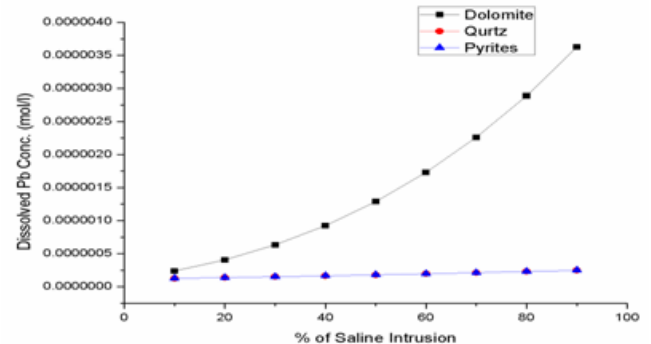**Figure 1. Dissolved "Pb" concentration w.r.t different rate of saline intrusion**

Figure 2. Dissolved "Pb" concentration w.r.t different rate of saline intrusion in different geochemical conditions (in the presence of Dolomite, Qurtz and Pyrites)

Simulating the enhanced dissolution of the copper due to saline intrusion to shallow aquifer

The MCLG for copper is 1.3 mg L^{-1} or 1.3 ppm. EPA has set this level of protection based on the best available science to prevent potential health problems. The MCL is also set close to MCLG. People who drink water containing copper in excess of the action level may, with short term exposure, experience

gastrointestinal distress, and with long-term exposure may experience liver or kidney damage. Excess copper ingestion leads to accumulation of Cu in tissues which manifests as neurological or psychiatric symptoms and liver disease and finally turns to *Wilson disease*.

Figure 3.Speciation of Pb in ground water at the 10% level of saline intrusion

The major sources of copper in drinking water are corrosion of household plumbing systems and erosion or dissolution of the natural deposits. Copper enters the water ("leaches") through contact with the plumbing. The amount of copper in water also depends on the types and amounts of minerals in the water. In our case the simulation using PHREEQCI identified cuprite (Cu_2O) as the predominating mineral of lead of the site. Hence further simulation study was carried out taking cuprite as the principal Cu-mineral at different rate of saline intrusion from staring from 10% to 90% with an increment of 10% at each step.

Figure 4. Speciation of Pb in ground water at the 90% level of saline intrusion

Figure 5.Dissolved "Cu" concentration w.r.t different rate of saline intrusion in the presence and absence of dolomite

Fig. 5 presents the dissolved Cu concentration due to the dissolution of cuprite increase in saline water. The dissolution kinetics of mineral and mobilisation of Cu is accelerated by the processes discussed earlier i.e., complexation capacity of salt derived anions with *Cu* and competition of salt derived cations

like Ca^{2+}, Mg^{2+}, Na^+ and K^+ with positively charged heavy metal species for sorption sites on the solid phase. The mechanism involved in the mobilisation of Cu from mineral to liquid system was investigated using similar simulation studies as discussed in case of Pb.
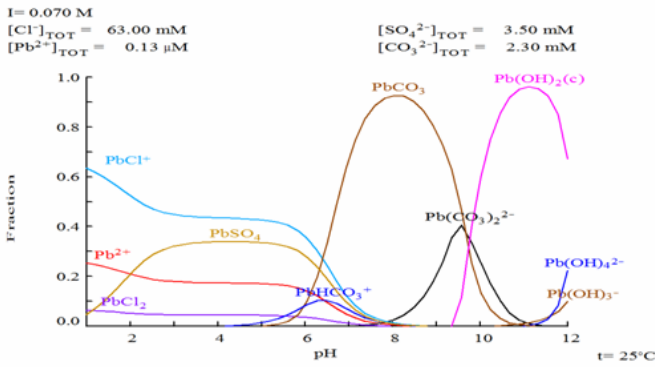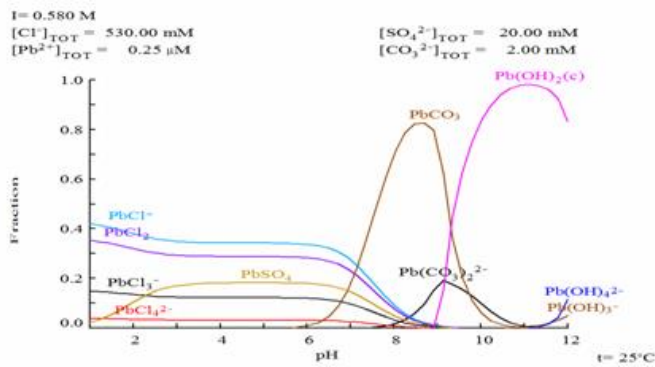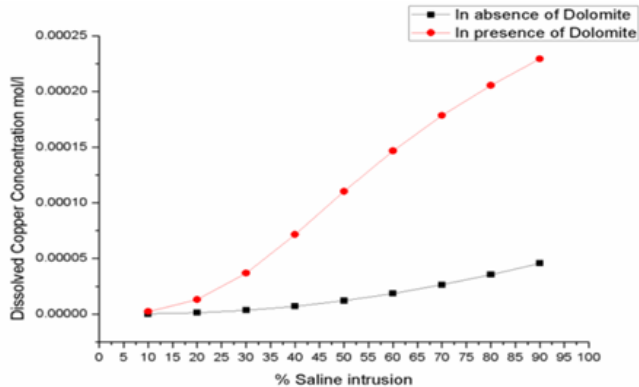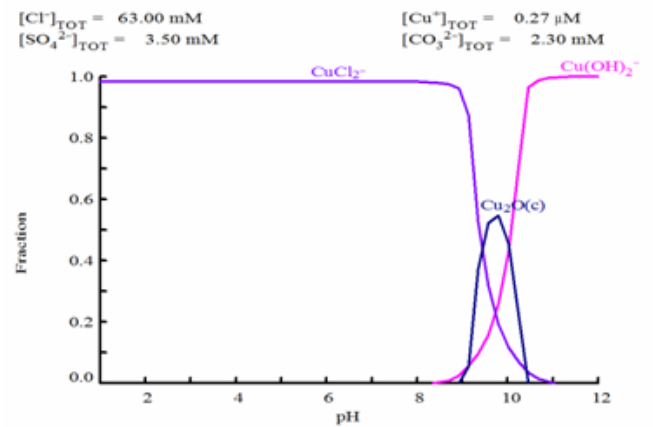

Figure 6. Speciation of Cu in ground water at the 10% level of saline intrusion

Fig. 5 presents the simulated value of Cu concentration in ground water in equilibrium with and without dolomite at different saline water intrusion. The increased Cu concentration in the aquifer due to saline intrusion is attributed due to interaction of high ionic strength solution containing high level of competitive positive ions. The relative increase in Cu concentration in the system in equilibrium with dolomite is nothing but due to increase of divalent positive ions; Ca^{2+} and Mg^{2+} as a result of dolomite dissolution which accelerates the dissolution and /or desorption of the Cu. The speciation studies of Cu is presented in Fig. 6 and 7 (in the system of low salinity as well as high salinity) revealed that $CuCl_2^-$ is predominating species at low salinity whereas in high salinity $CuCl_2^-$ is the predominating species followed by $CuCl_3^-$ in the pH range (7.5-8.5) of the system. pH around 9 and above Cu_2O starts precipitate. The simulation also reveled that, at the 70% level of saline intrusion is the worst case, the Cu level reach MCL but in the presence of dolomite the MCL level reached at 30% level of the saline intrusion.
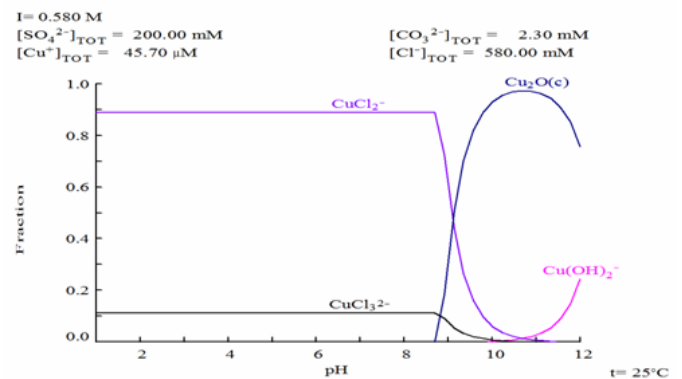

Figure 7. Speciation of Cu in ground water at the 90% level of saline intrusion

Conclusion

The simulation study for saline intrusion to costal aquifer and its effect on mobilization of heavy metals like Pb and Cu from minerals (in equilibrium with the ground water)into ground water has been presented here. Specifically, enhanced dissolution of trace metal bearing formations due to hydrochemical changes caused by the intrusion of saline water were incorporated to simulation study with equilibrium

geochemical speciation model to assess the mechanism of the mobilization of metal ion from minerals to ground water.

The model simulations clearly shows that saline intrusion into the costal aquifer may cause adverse effects on groundwater quality by enhancing mineral dissolution of trace metal species if the aquifer contains minerals containing such metals. The detrimental effect of saline intrusion is significantly increase in ionic strength of the ground water i.e., increases the ionic composition; Ca^{2+}, Mg^{2+}, Na^+, K^+, Cl^- and SO_4^{2-} etc. which alters the hydro-geochemistry of the aquifer. The simulation results also suggest that geochemical changes in shallow aquifers, such as the occurrence of trace metal species at unusually high concentrations, may serve as an indicator of saline intrusion.

It should be noted that the applicability of this model for risk analysis is limited by the incomplete characterization of mineral dissolution kinetics, which is one of the most important parameters affecting the concentration of trace metals resulting from the dissolution of a mineral phase due to saline intrusion.

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