Transport Modelling of Copper Contamination in Groundwater Caused by a Wood Preservation Plant

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Contaminants can adhere to soil and subsequent rainfall can leach the adhered contaminant into groundwater. Transport models can determine the main features of contaminant and carrier transport in groundwater systems, and therefore determine potential risks for public health and ecosystems.

In this study, the effect of copper contamination caused by a wood preservation plant near Eskisühir, Turkey, on the possible pollution of drinking water supply wells was investigated with two different models. The first model, which deals with the movement of contaminants to groundwater, is a numerical model known as Flonet/Trans (Waterloo Hydrogeologic 1997). It has been used to investigate the change in contaminants from the source with respect to time and distance. The second model, which measures contaminant movement with respect to time and distance through simulations, is an analytical model known as Multi-Flow. It was used for verification of the first model. Both numerical and analytical models have been successfully applied at the work area for investigation of the effects of copper contamination in groundwater. Using the numerical model, the copper concentration in the first observation well was found to be 1.59 mg L⁻¹, and using the analytical model, the copper concentration was found to be 1.35 mg L⁻¹ after 550 days. The measured quantity was 2.11 mg L⁻¹, thus the analytical model is best used for verification of results obtained by simulations of the numerical model.

Key words: groundwater, contaminant transport, wood preservation, transportation model, copper contamination

Introduction

Groundwater contamination is considered to be one of the most significant ecological and health problems. It greatly affects the general environmental features of large regions and drinking water supply conditions in many countries (U.S. Environmental Protection Agency 1987).

The protection of public water supplies is of paramount importance. Groundwater, the main source of drinking water for about 50% of the world’s total population, is said to be contaminated if some hazardous compounds in the water meet or exceed U.S. EPA standards (Pye and Kelly 1984). These compounds may become part of an aquifer through natural mineralization and leaching, or from waste disposal practices. Contamination resulting from human activities includes the following: industrial wastewater impoundments; land disposal sites for solid wastes; waste disposal trough wells; collection, treatment and disposal plants for municipal wastewater; disposal of mine wastes; accidental spills and leaks; septic tanks; agricultural activities; land spreading of sludge; highway de-icing salts, etc. (Javandel et al. 1984).

About 70% of industrial wastewater impoundments do not have impermeable liners (Josephson 1982). These impoundments are ponds used for the disposal of an industry’s liquid wastes. Landfill disposal of municipal, hazardous or mining wastes has resulted in considerable groundwater contamination. This occurs mainly in areas where rainfall and subsequent leaching of water trough landfills are prevalent (Pye and Kelly 1984).

One of the most dangerous known sources of groundwater contamination is wood preservation plants (Bhattacharya et al. 2002). The use of CCA (chromate, copper, arsenate) and other As-based chemicals as wood preservatives in Sweden (Bhattacharya et al. 2002) have caused widespread metal contamination in soil around the wood preservation sites due to raw material handling, spills, deposition of sludge and dripping from freshly impregnated wood or due to leaching from the piles of impregnated wood at these sites by rain water especially under low pH conditions (Lund and Fobian 1991; Warner and Solomon 1990; Andersen et al. 1996; Bhattacharya et al. 1996). Copper originating at the wood preservation plant leaches to the groundwater by infiltrating rainwater. Moreover, leakage of process liquors including very high concentrations of copper from wood preservation plant products contributes to rainwater leaching.

In this study, the effect of copper pollution caused by a wood preservation plant near Eskisühir, Turkey, on the possible pollution of drinking water supply wells was investigated using two different models. These models are the Flonet/Trans (Waterloo Hydrogeologic 1997) and Multi-Flow (Walton 1989) computer programs. Using our experience from a recent study, where we investi-
gated the movement of the total nitrogen contamination caused by the sugar factory located in Eskişehir region (Tombul and Koparal 2003), our goal in this study was the prediction of transient contaminant concentrations in a two-dimensional groundwater system given contaminant inputs at the surface of an aquifer that vary in time and space. The effects of induced gradients in the groundwater due to mounding of infiltrated rainwater are also considered. Rainfall, occurring in random amounts and times throughout the year, influences the flow of the contaminants from the soil into and within the aquifer system. Rainfall collects, or ponds, in low areas of the land. The amount of collected rainwater in these low areas is dependent on the ground surface characteristics.

Materials and Methods

Study Site

The study site is situated northwest of the middle of the Anadolu basin, between 39°56' altitude and 30°45' longitude. The drainage area is 1225 km² (Fig. 1). Annual average precipitation is 358.8 mm (Kacaroglu 1991). The following geologic layers are found in the study site: schist, flysch, konglomera, tuffite, basalt and alluvium. The most productive aquifers in the plain are old and new alluviums. Recharge and discharge values for alluvium aquifers are given in Table 1. Thickness of alluvium in Eskişehir plain varies from 5 to 95 m (D.S.I. 1975). In the models, the aquifer has been taken to have an average thickness of 30 m. The aquifer begins at 5 m below the surface and extends to a depth of 95 m. Alluvium is composed of gravel, sand and sandy clay and the study site also has the same soil structure. The mean transmissivity coefficient of the alluvium in Eskişehir plain is 100 m³d⁻¹m⁻¹ (D.S.I. 1975).

In this study, we used the parameters associated with the alluvium aquifer which carries the groundwater for the study site. The thickness of the considered saturated aquifer is 30 m, and has a hydraulic gradient of 0.0667 (Tombul and Koparal 2003). Other input values for the models are given in Table 2.

Copper in the Soil

Copper is present with a valence state of II. It is possible for copper to be adsorbed by the soil (Appelo and Posma 2000). In case the soil contains lime and organic materials, copper can be adsorbed by the soil, and additionally by the surface minerals. The effect of mineral surfaces on the adsorption of copper in the soil is smaller compared to lime and organic materials (Benedetti et al. 1995). In our case, since the soil in the study area contains small amounts of lime and organic materials, the possibility of adsorption of the copper by the soil has to be considered. Thus, to take possible adsorption of copper in the soil into account, the retardation factor was set to be R = 1.8 (de Matos et al. 2001) in both models.

Groundwater Flow and Contaminant Transport Models

Groundwater flow models are used to calculate the rate and direction of movement of groundwater through aquifers and confining units in the subsurface. Fate and transport models estimate the concentration of a chemical in groundwater starting at the chemical’s point of introduction to the environment, and moving to locations down the gradient of the source.

Models are conceptual descriptions or approximations that describe physical systems using mathematical equations; they are not exact descriptions of physical systems or processes. The mathematical equations that describe the groundwater flow and transport processes may be solved using different types of models. Some models (e.g., analytical models) may be exact solutions to equations that describe very simple flow or transport conditions, and others (such as numerical models) may be approximations of equations that describe very complex conditions. Because of the simplifications inherent in analytical models, it is not possible to account for field conditions that change with time or space.

Analytical models are best used for checking results of numerical model simulations, or where field conditions support the simplifying assumptions embedded in the analytical models (Mandle 2002). Numerical models are capable of solving more complex equations that describe groundwater flow and solute transport. These equations generally describe
multi-dimensional groundwater flow, solute transport and chemical reactions.

Model Description

Over the last two decades, the environmental industry has seen a dramatic increase in the application, understanding and acceptance of numerical modelling techniques for simulating groundwater flow and contaminant transport. This industry has witnessed some incredible advances in the development and application of groundwater models, from water resources protection and management to groundwater remediation system evaluation and optimization.

In this study, the following assumptions were made to idealize aquifer conditions which carry the groundwater in the study site:

- The movement of pollutants in the groundwater is the same as that of the groundwater.
- The differences in density and viscosity between contaminant and groundwater have been ignored.
- The flow velocity of groundwater is uniform and is in one direction.
- The dispersion properties are independent of time and distance.
- The movement in a horizontal direction is much higher than the movement in a vertical direction.
- The movement field is two-dimensional—vertical and horizontal.
- The porous environment is homogenous and isotropic, and is saturated with water.
- There are plenty of analytical expressions to develop mathematical modelling of contaminant movement (Hunt 1983; Keinzelbach 1986).

In general, these expressions may not represent mass transport. The interaction mixture which is at a certain distance from a point source depends on its speed, vertical dispersion constant and aquifer’s thickness (Keinzelbach 1986).

The governing equation for two-dimensional steady-state groundwater flow can be written in the dual formulation as:

\[
\text{Transport Modelling of Copper Contamination in Groundwater}
\]

TABLE 1. Groundwater recharge and discharge at the Eskişehir region (D.S.I. 1975)

<table>
<thead>
<tr>
<th>Recharge (× 10⁶ m³ y⁻¹)</th>
<th>Discharge (× 10⁶ m³ y⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infiltration from precipitation</td>
<td>17.5</td>
</tr>
<tr>
<td>Infiltration from surface runoff</td>
<td>10</td>
</tr>
<tr>
<td>Recharge from Porsuk and irrigation channels</td>
<td>81</td>
</tr>
<tr>
<td>Recharge from inflow</td>
<td>24</td>
</tr>
<tr>
<td>Total</td>
<td>132.5</td>
</tr>
<tr>
<td>Recharge from inflow</td>
<td>24</td>
</tr>
<tr>
<td>Total</td>
<td>132.5</td>
</tr>
</tbody>
</table>

TABLE 2. Data used in application of the model

<table>
<thead>
<tr>
<th>Numerical model</th>
<th>Analytical model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of grid in x-y direction</td>
<td>50 x 25</td>
</tr>
<tr>
<td>Grid space in x direction (m)</td>
<td>2</td>
</tr>
<tr>
<td>Grid space in y direction (m)</td>
<td>0.8</td>
</tr>
<tr>
<td>The length of x-y simulation region (m)</td>
<td>100–20</td>
</tr>
<tr>
<td>The porosity of aquifer</td>
<td>0.25</td>
</tr>
<tr>
<td>Longitudinal dispersivity (m)</td>
<td>10</td>
</tr>
<tr>
<td>Transverse dispersivity (m)</td>
<td>1</td>
</tr>
<tr>
<td>Diffusion coefficient (m² d⁻¹)</td>
<td>0.0001</td>
</tr>
<tr>
<td>Contaminant decay rate (1 d⁻¹)</td>
<td>0</td>
</tr>
<tr>
<td>Source decay rate (1 d⁻¹)</td>
<td>0</td>
</tr>
<tr>
<td>The number of contaminant source of contaminant</td>
<td>1</td>
</tr>
<tr>
<td>The number of contaminant source of point</td>
<td>1</td>
</tr>
<tr>
<td>Hydraulic conductivity in x and y direction (m d⁻¹)</td>
<td>1.064</td>
</tr>
<tr>
<td>Constant head segment (m)</td>
<td>20</td>
</tr>
<tr>
<td>Specific flux segment (m³ m⁻² d⁻¹)</td>
<td>0.0096</td>
</tr>
<tr>
<td>Retardation factor</td>
<td>1.8</td>
</tr>
<tr>
<td>The concentration of contaminant in source (mg L⁻¹)</td>
<td>24.9</td>
</tr>
<tr>
<td>Thickness of aquifer (m)</td>
<td>30</td>
</tr>
<tr>
<td>The amount of infiltration from contaminant source (L d⁻¹)</td>
<td>—</td>
</tr>
</tbody>
</table>
The equations are written in a form which assumes that the principal directions of hydraulic conductivity coincide with the coordinate axes.

**Advective-Dispersive Contaminant Transport**

The governing equations for two-dimensional advective-dispersive mass transport of a dilute species within a porous medium can be written as (Bear 1972):

\[
\frac{\partial}{\partial x} \left( \frac{D_{ij} \frac{\partial c}{\partial x}}{R \frac{\partial c}{\partial x}} \right) - \frac{\partial}{\partial x} \left( \frac{v_i}{R} \frac{\partial c}{\partial x} \right) - \frac{\partial}{\partial x} \left( \frac{v_i}{R} \frac{\partial c}{\partial x} \right) = \frac{\partial c}{\partial t} - \frac{\partial c}{\partial t}
\]  

where \( x \) is the spatial coordinates \((x, y)\), \( v_i \) is the average linear flow velocity \((L T^{-1})\), \( D \) is the hydraulic dispersion tensor \((L^2 T^{-1})\), \( R \) is the linear retardation factor, \( \lambda \) is the linear decay rate \((T^{-1})\), \( t \) is time \((T)\) and \( c \) is concentration \((M L^{-3})\).

The form of the dispersion tensor in equation 3 is given by Frind and Hokkanen (1987) and is dependent on the average linear flow velocities, the longitudinal \( (\alpha_L) \) and transverse \( (\alpha_T) \) dispersivities \((L)\), and on the effective molecular diffusion coefficient \( D^* \) \((L^2 T^{-1})\) according to equations:

\[
D_{xx} = \alpha_L \frac{v^2}{v} + \alpha_T \frac{v^2}{v} + D^*
\]  

and

\[
D_{yy} = \alpha_T \frac{v^2}{v} + \alpha_L \frac{v^2}{v} + D^*
\]  

\[
D_{xy} = D_{yx} = (\alpha_L - \alpha_T) \frac{v_x v_y}{v}
\]  

where

\[
v = \sqrt{v_x^2 + v_y^2}
\]

Adsorption is represented in our model as a linear equilibrium partitioning process between the dissolved and adsorbed phases, and is governed by the retardation factor, \( R \) (Freeze and Cherry 1979), and is given by:

\[
R = \left(1 + \frac{\rho_k}{\theta} K_d\right)
\]  

where \( \rho_k \) is the bulk density of the saturated porous medium \((ML^3)\), \( \theta \) is the effective porosity and \( K_d \) is the distribution coefficient that governs the partitioning of the solute into dissolved and adsorbed phases.

**Flow and Contaminant Transport Boundary Conditions**

Flow boundary conditions for the model used are specified for equation 1 only, and are required over the four boundary surfaces. The model derives the equivalent stream function boundary conditions internally, based on the solution to equation 1.

The boundary conditions for equation 1 can be one of two types. Type 1 boundaries represent a fixed head or Dricichlet condition, applicable, for example, at a river boundary, and type 2 boundaries represent a constant flux, for example, across the water table boundary. A constant flux boundary is defined by specifying a flux per unit length of boundary per unit width of aquifer \((L^3 T^{-1} L^{-1} L^{-1} = L T^{-1})\). This flow rate is multiplied in the model by the contributing length of the element. A flux boundary is most commonly applied across the water table where it represents net aquifer recharge (precipitation minus evapotranspiration and surface runoff). A zero-flux condition can be specified (i.e., left to the default value) at symmetry boundaries (such as flow divides), or along boundaries assumed to be impermeable. Because the model assumes a saturated domain, the uppermost boundary will always represent either the water table or the location of a confining layer.

Transport boundaries can be first, second or third types. At a first type boundary, the concentration is fixed, while at a second type boundary the concentration gradient is fixed, usually set to zero at a distant outflow boundary, or at a transport boundary defined as impermeable in the flow domain. The third type, or Cauchy boundary, represents continuity of mass flux across an external boundary and is written as:

\[
\frac{q_0 C_0}{\theta} = v_i c - D_{ij} \frac{\partial c}{\partial n}
\]  

where \( q_0 C_0 / \theta \) is a known mass flux term at the boundary, and \( n \) is the unit normal vector at the boundary (Frind 1982). Surface contaminant sources are most realistically represented using the Cauchy boundary condition.
**Boundary conditions.** In this study, the second type boundary condition was chosen. The problem domain contains continuous contaminant source at the left boundary. Constant head flow boundaries of 20 and 0 m are assigned at the left and right boundaries, respectively, with the top and bottom boundaries impermeable as shown in Fig. 2. A homogenous isotropic hydraulic conductivity value of $K_{xx} = K_{yy} = 1.064 \text{ m d}^{-1}$ has been assigned, and an effective porosity value of $\theta = 0.25$ has been taken.

**Application of the Model**

There were three available tanks with 94.2 m$^3$ volume in the wood preservation plant used for our modelling application. Each of these tanks is capable of processing 150 trees daily. A total of 282.6 m$^3$ of water is used for 450 trees. One cubic metre of water contains 350 L of solution, which includes 14 kg of chemical with 11.8% Cu. The 450 processed trees are stocked in an open soil area of 2500 m$^2$. It was observed that the leaching rate of Cu from a preserved tree is in the range of 0.6 to 2.0 $\mu$g cm$^{-2}$ d$^{-1}$ to Hingston et al. (2001). Leaching rate depends on the pH value of the rain and also the leaching time. The rate is higher during the first 18 hours (Fahlstrom et al. 1967; Weis et al. 1991; Merkle et al. 1993). According to Hingston et al. (2001) Cu leaches at a rate of 0.8 $\mu$g cm$^{-2}$ d$^{-1}$ within the first 24 h. Moreover, in the first minutes after the storage of the products, some additional Cu leaches to the soil due to the leakage on the surface. In our study, initial concentration of Cu leaching to the groundwater by means of rain and leakage has been taken to be 24.9 mg L$^{-1}$.

The Flonet/Trans program was used to determine the polluting potential of contaminants depending on time and distance. We assume that the contaminants originate from a continuous source and mix into the groundwater by rain and leakage. As the main study area, a wood preservation plant near Eskisêhir is used, which stores its products near several groundwater wells serving as a drinking water supply to nearby residents. Our goal was then to investigate the polluting potential caused by this facility upon the groundwater wells. For this purpose three observation wells with static water levels of -5.40 m were employed and their positions and distance to the plant are depicted in Fig. 2. Water samples taken from the wells were analyzed according to standard methods (APHA 1992). The analysis has been repeated three times.

Hydraulic conductivity was determined from the study site according to ASTM D3385-75, porosity and bulk density values were determined by laboratory experimental analysis using ASTM D854-83 and ASTM D1188-83 (ASTM 1985), respectively. Groundwater velocities were calculated using experimental data in a Flonet/Trans computer program. The values for the parameters used in the models are given in Table 2.

**Results and Conclusion**

According to the results obtained with the numerical and analytical models, we have seen that the initial copper concentration (24.9 mg L$^{-1}$) from the wood preservation plant has infiltrated into groundwater eventually. According to the numerical model, at the end of 365 days, copper concentration reaching the first observation well was 0.40 mg L$^{-1}$, whereas the second observation well did not exhibit noteworthy levels of copper, and there was no contamination in the third well (Fig. 3). The concentration distribution after 550 days is shown in Fig. 4. The results obtained from the analytical model used for verification of the numerical model are given in Table 3. The results of the analytical and numerical models have been compared in Fig. 5. It can be seen in Fig. 5 that there is no difference in the solutions for the models at both 365 and 550 days. For example, the copper concentration at the first observation well was 1.59 mg L$^{-1}$ for the numerical model and 1.35 mg L$^{-1}$ for the analytical model at the end of 550 days. The measured value was 2.11 mg L$^{-1}$. Thus, the verification of the numerical model has been made using the analytical model. The results achieved by the models match very well with those found by the analysis.

It is concluded that transport of a contaminant in groundwater could be determined successfully by means of the Flonet/Trans and Multi-Flow models. Thus, possible...
Fig. 3. The distribution of concentration after 365 days.

Fig. 4. The distribution of concentration after 550 days.

Fig. 5. Comparison of numerical and analytical solutions.

<table>
<thead>
<tr>
<th>Observation well</th>
<th>Distance from contaminant source (m)</th>
<th>365 days</th>
<th>550 days</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Model output (mg L⁻¹) and model type</td>
<td>Model output (mg L⁻¹) and model type</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Observed (mg L⁻¹)</td>
<td>Numerical model</td>
</tr>
<tr>
<td>Obs-1</td>
<td>40</td>
<td>0.72</td>
<td>0.40</td>
</tr>
<tr>
<td>Obs-2</td>
<td>60</td>
<td>—</td>
<td>0.40</td>
</tr>
</tbody>
</table>

TABLE 3. Data analyzed in observation wells
effects of contaminants originating from the wood preservation facility, namely heavy metals such as copper, on the environment and groundwater sources can be determined using this method before it actually occurs. The model would then be used for future planning and management. In addition, this work would provide a literature basis for further work to be performed at the same field.

References


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