Case Report

Implications of Extended Environmental Multimedia Modeling System (EEMMS) on Water Allocation Management: Tritium Numerical Case Study

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Abstract: Tritium waste deposition in air-unsaturated groundwater zones poses great challenges to optimal water allocation. This paper reviews the research progress of air-unsaturated-groundwater interaction. Traditional interaction studies typically model the fate and migration of pollutants in different regions. This can lead to biased results and simulation errors. The development of air-unsaturated-ground integrated modeling will be a breakthrough and a hotspot in tritium management. In this paper, the fate and migration of tritium leakage is further studied using the existing extended Environment Multimedia Modeling System (EEMMS). Moreover, to better understand its distribution in three zones, using tritium as a typical pollutant, it is necessary to consider its characteristics in different zones, especially its migration from unsaturated zones to groundwater and air zones. The result shows that the tritiated water vapor transfer in unsaturated groundwater areas decreases and part of the tritiated water vapor transfers to atmospheric areas as tritiated gas vapor. Compared with the analytical test accuracy (5 pCi mL\(^{-1}\)), the accuracy of the tritium modeling using the finite element method can reach the minimum concentration limit of 0 pCi mL\(^{-1}\). The study of its distribution in air-unsaturated-groundwater zones can provide reference for other similar tritium management or NAPLs distribution across multimedia area.

Keywords: multimedia; air-unsaturated-groundwater zones; water allocation; finite element method

1. Introduction

Once a contaminant is released into environment from a pollution source, such as trim spill or a solid waste disposal site, it has a potential to migrate into all connected environmental media (air, unsaturated, and groundwater media); subsequently, humans may eventually be affected by the contaminant [1,2]. In the air-unsaturated-groundwater zones, hydrological interactions between atmospheric processes, soil, and groundwater dynamics need to be considered, and this depends largely on the characteristics of the air, unsaturated, and groundwater zones [3]. Globally, water management has traditionally treated groundwater and unsaturated zones as separate entities [4,5]. Research on unsaturated zones mainly focuses on the application of empirical equations, which usually adopt a small time step and small, medium, and large spaces [6]. The establishment of the model based on water balance principle usually uses a large time step and a medium to large space scale [7]. As there is interaction among air-unsaturated-groundwater zones in different geographical locations, their storage and transportation role cannot be ignored [8]. Therefore, it is incorrect to study air, unsaturated zones, and groundwater separately. Their interactions are particularly important. Groundwater and unsaturated water interact with each other in different environments and have different degrees of correlation [9]. For
instance, the flow direction between unsaturated water and groundwater can be constant, or it can change according to environmental conditions such as precipitation, evaporation, and transpiration [10]. Groundwater interacts with rivers in three ways: through the inflow of the riverbed to acquire groundwater, through the outflow of the riverbed to lose water to groundwater, or through the loss and combination of groundwater losses. In order to discharge groundwater into a river, the water table near the river must be higher than the surface of the river. The opposite is true of groundwater, which draws water from rivers [11]. Lakes and wetlands, such as streams and rivers, interact with groundwater in three ways: to obtain it, to drain it to saturated areas, or to obtain it in some areas and to lose it in others [12]. Losing streams can be connected to the groundwater system by either a continuous saturated zone, or they can be disconnected from the groundwater system by an unsaturated zone [13].

In addition, the flow of unsaturated zones caused by natural forces plays an important role in many environmental and engineering fields, such as environmental remediation and groundwater recharge, coastal soil ventilation, mine and tunnel ventilation, and gas exchange between soil and air. Balugani et al. found that in late autumn, winter, and early spring, evaporation dominated the unsaturated zone, while in dry summer, the correlation of groundwater evaporation increased, reaching 1/3 of the total loss of soil water evapotranspiration, although the wrong ending point in the water balance was still a potential underestimate [14]. Moreover, the relationship between air, unsaturated, and groundwater zones are studied theoretically. Evan et al. concluded that limiting the flux from the contaminated unsaturated zone is the key to the protection of groundwater resources, while the deep trap zone is not necessarily the resource to be recovered [15].

Gao et al. proposed a new method that combines the Finite Element Method (FEM) and the Finite Difference Method (FDM) to simulate unsaturated water flow to solve the mass balance problem [16]. Arrey et al. estimated the moisture flux in the unsaturated zone to determine whether the applied agricultural fertilizers would reach the groundwater [17]. Rodriguez-Iturbe et al.’s quantitative description of artificial groundwater provides some challenging characteristics because it needs to be correlated with the interwoven random fluctuations of groundwater tables and soil moisture in unsaturated zones [18]. A very promising study shows that groundwater and surface water interact in most landscapes and that disturbances from one resource often directly affect the quantity or quality of the other. Therefore, to understand how groundwater and surface water interact as an integrated resource, which is the basis for effective water resource management, mass balance through those three media needs to be considered. Numerical models, such as EEMMS model combined with the mass balance theory, are used to simulate tritium migration and assess its potential impact in air-unsaturated-groundwater zones. Yuan et al. proposed an Extended Environmental Multimedia Modeling System (EEMMS) in air-unsaturated-groundwater zones [1,19]. A multi-phase and multi-component case study of Light Non-Aqueous Phase Liquid (LNAPL), for example, benzene, has been successfully validated in the former EEMMS numerical modeling [20,21]. DNAPLs is an immiscible organic liquid that is denser than water. This case proves that NAPLs can reach the saturated zone through the whole unsaturated zone and will also partially remain in the unsaturated zone during migration. Therefore, in order to better study the air-unsaturated-groundwater interaction, mass balance theory should be considered [8]. Furthermore, the typical characteristics of the pollutants themselves should also be considered. In this case report, tritium is a radioactive isotope of hydrogen, and its migration in air-unsaturated-groundwater zones is not only affected by the above interactions among different zones, but is also affected by its unique characteristics, especially its short half-life [22]. Tritium has a radioactive half-life of approximately 12.3 years, leading to its natural decay into helium-3 over time. This decay process influences the decrease in tritium concentrations over successive half-lives [23]. In conclusion, with increasing water scarcity worldwide, water management strategies that combine unsaturated and groundwater zones in all regions need to be considered in order to better allocate water resources [24]. The comprehensive
utilization of mass balance theory is one of the water resources management strategies that must be considered in order to optimize water distribution management and water conservation.

In this case report, the characteristics of tritium pollutants in the multi-phase, contaminant transport, and transformation processes are studied by combining the former EEMMS and the mass balance theory, and the distribution of 2-D adapted case study of Tritium Spill in the multimedia area is determined. The characteristics of this spill’s emission sources are extremely complex, considering the migration range, fate, and behavior of pollutants in multimedia environments such as water, air, and sediment [25]. In this study, the focus is on examining the connection between the air-saturated groundwater zones and using mass balance to optimize the water distribution in three different zones. For example, the application of the model, COMSOL Multiphysics, is a large-scale advanced numerical simulation software using Finite Element Method (FEM).

2. Methodology

Figure 1 shows details of flows affecting air, soil, and groundwater in air-unsaturated groundwater zones. It is important to note that the flow induced by topographic effects has been least studied. However, it has important applications in unsaturated zones and air transport. Groundwater is constantly flowing, but at a much slower rate than unsaturated water. It can take days, weeks, centuries, or even longer for groundwater to flow from one area to another. Groundwater flow depends on several factors. It moves from high altitude to low altitude. Groundwater flows from high-pressure areas to low-pressure areas, from high-permeability areas to arid areas [26]. In addition, groundwater flows from the recharge area to the discharge area. Groundwater discharges can occur in springs, streams, and other surface waters.

![Diagram showing flows affecting air, soil, and groundwater](image)

**Figure 1.** Air-unsaturated-groundwater zones fluctuations.

Furthermore, multimedia dissemination of pollutants depends not only on advection and transformation but also on non-diffusion and diffusion transfer, carbon sink, adsorption, radioactive decay, and biodegradation. Taking tritium as an example, key fate characteristics include its dispersion, decay, sorption, and evaporation. Tritium can disperse horizontally and vertically in the unsaturated zone due to the variability in hydraulic conductivity and preferential flow paths. Tritium has a radioactive half-life of
approximately 12.3 years, leading to its natural decay into helium-3 over time. Tritium can be adsorbed or desorbed onto soil particles, affecting its mobility and transport in the multimedia zones. A fraction of tritium can evaporate into the atmosphere if the water table is shallow, leading to a gaseous phase. Due to its typical fate characteristics, the most common methods for tritium measurement limited among Accelerator Mass Spectrometry (AMS), Liquid Scintillation Counting (LSC), and Liquid Scintillation Counting (LSC) (converted into tritiated methane gas and measured) [22,23].

In this study, the former EEMMS is mainly for the unsaturated landfill and groundwater case studies with an incorporation of finite element numerical analysis. The developed EEMMS includes four component modules: an air module, a landfill module, an unsaturated zone module, and a groundwater zone module. A simple mass balance box model, based on this previous development of EEMMS, is presented to describe the main transportation among air-unsaturated-groundwater zones. The chemical’s fate in space is then recalculated using the water, air, or soil mass balance equation. According to the mass balance, the flux \( F_t(M L^{-2} T^{-1}) \) is the total mass flux. The total mass flux is the sum of fluxes including the air, the unsaturated zone, and the groundwater zone, and the calculation equation is:

\[
F_t(z,t) = F_g(z,t) + F_u(z,t) + F_a(z,t)
\]

where, \( F_g \) is the flux from groundwater zone, \( F_u \) is the aqueous phase diffusive flux from unsaturated zone, and \( F_a \) is the aqueous and gaseous phase flux into air zone. In the 3D version, when the flux transferred from one zone to another, the total flux \( F_t \) (g m\(^{-2}\) d\(^{-1}\)) is the total mass flux. The total mass flux is the sum of fluxes including the air, the unsaturated zone, and the groundwater zone, and the calculation equation is:

\[
F_t(x,y,z,t) = F_{air}(x,y,z,t) + F_{leachate}(x,y,z,t)
\]

3. Case Study

Figure 2 shows a modified example of two-dimensional steady-state subsurface flow and transient solute transport along a vertical section into unsaturated and groundwater zones, with tritium selected as the primary pollutant [28]. The objective is to evaluate the effect of tritium on the surrounding soil, air, and groundwater systems. Recent case studies conducted in Pennsylvania, California, New York, and New Jersey show that elevated tritium levels in municipal solid waste leachate are common. A two-domain mass balance model was used for field data [29–31]. This region is the deformed quadrilateral region as shown in Figure 2. The length and depth of the left boundary region are 200 m and 65 m, respectively. The detailed input parameters of 2-D adapted case study using mass balance model which will be used in COMSOL are listed in Table 1.
As shown in Figure 3, the areas where pollutants enter or discharge from the unsaturated layer extending is 40 m to 80 m, and 0 in other places. After five years of clearance, the concentration of tritium was determined along the top returns to 0. The uniform porosity is 0.35, the longitudinal dispersivity is 0.1 m, the transverse dispersivity is 0.001 m, and the effective diffusion coefficient in the air domain is assumed to be isotropic. The tritium concentration of 300 pCi mL$^{-1}$ was treated with constant values [32]. In this paper, the constant values of $D_x$ and $D_y$ are assumed to be 10 m$^2$s$^{-1}$. Wind speeds are usually between 0–10 m s$^{-1}$ with p between 0% (no rain time) and 100% (rain time).

According to Equations (1)–(5), the mass balance equation of tritium was solved from top to bottom by COMSOL and the transport of tritium from top to bottom was determined. As shown in Figure 3, the areas where pollutants enter or discharge from the unsaturated layer, such as the tritium leak contraction area and the near-atmospheric surface area, have the highest grid resolution. The cylinders in Figure 3 represent the boundaries of the computational domain. Figure 3 also shows the whole geometry view of the model.

**Figure 2.** Definition of the environmental multimedia transport problem and its boundary conditions.

**Table 1.** Input parameters of mass balance model.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Symbol (Units)</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>recharge</td>
<td>m d$^{-1}$</td>
<td>1.4 × 10$^{-4}$</td>
</tr>
<tr>
<td>Water table depth</td>
<td>$z_{wt}$ (m)</td>
<td>53.75</td>
</tr>
<tr>
<td>hydraulic conductivity of layer</td>
<td>$K$ (cm s$^{-1}$)</td>
<td>5 × 10$^{-4}$</td>
</tr>
<tr>
<td>hydraulic conductivity of layer</td>
<td>$K$ (cm s$^{-1}$)</td>
<td>1 × 10$^{-2}$</td>
</tr>
<tr>
<td>Trinitium concentration (patch of 40 m to 80 m)</td>
<td>pCi mL$^{-1}$</td>
<td>300</td>
</tr>
<tr>
<td>longitudinal dispersivity</td>
<td>$D_L$ (m)</td>
<td>0.1</td>
</tr>
<tr>
<td>transverse dispersivity</td>
<td>$D_T$ (m)</td>
<td>0.0011</td>
</tr>
<tr>
<td>effective diffusion coefficient in unsaturated zone</td>
<td>$D_x$ and $D_y$ (cm$^2$s$^{-1}$)</td>
<td>1.34 × 10$^{-5}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>$\phi$</td>
<td>0.35</td>
</tr>
<tr>
<td>effective diffusion coefficient in the air</td>
<td>$D_x$ and $D_y$ (m$^2$s$^{-1}$)</td>
<td>10</td>
</tr>
<tr>
<td>Wind speeds</td>
<td>$V$ (m s$^{-1}$)</td>
<td>0–10</td>
</tr>
</tbody>
</table>
area, have the highest grid resolution. The cylinders in Figure 3 represent the boundaries of the computational domain. Figure 3 also shows the whole geometry view of the model.

Figure 4a–d show the development of pollution plumes at 328, 1080, 1440, and 1800 days calculated using the mass balance model solution. The X-axis is the transport distance in dispersion direction, and the Y-axis is the transport distance in diffusion direction. It can be seen from Figure 4a that in the groundwater medium, the simulated tritium plume results are basically consistent with the analytical solution of Feehley and Molz at 328 days [30]. The results in Figure 4 also well reflect the interaction among air, the unsaturated zone, and the groundwater zone, indicating that the tritium plume can volatilize into air, migrate in soil column, infiltrate into groundwater, runoff into surface water, and migrate through air or other means.

Related to the accuracy evaluation, the analytical solution has a minimum concentration limit of 5 pCi mL$^{-1}$, while the finite element solution has a minimum concentration limit of 0 pCi mL$^{-1}$ (Figure 4). Moreover, Figure 4 shows that the link between surface water and groundwater is very close, as shown in Figure 4a,d, and this trend will be further strengthened as increasing groundwater resources continue to develop.

Related to the model validation, Figure 5 shows the comparison between the field mass balance model results. The flow data on Figure 5 are from Sudicky’s real experimental data [33]. A two-dimensional finite difference method (FDM) is used to obtain numerical results related to the Macrodispersion Experiment (MADE) site by Zheng and Jiao. As can be seen from Figure 5, the model results are in good agreement with the experimental data of Zheng and Jiao [34]. For example, Figure 5 estimates the water table at the left boundary to be about 6.25 m. This approximates rather than replicates the data of Sudicky, Zheng, and Jiao, as shown in Figure 5.

In addition, using Equation (2), the concentration of tritium released into the air increased as shown in Figure 6, indicating that the pollutants mainly flowed southeast. Figure 6 also shows concentrations in different years (1, 2, 3, 4, 5, 7.5, and 10). Tritium concentrations in different years were 23, 20, 15, 10, 5, 2, and 1 pCi mL$^{-1}$, respectively. For example, when the tritium concentration in leachate was about 300 pCi mL$^{-1}$, the tritium concentration in the first year was about 23 pCi mL$^{-1}$, or 7% of the total tritium concentration. After 10 years, this concentration would reach the maximum annual air exposure ($1 \times 10^6$ pCi mL$^{-1}$) recommended by the Nuclear Regulatory Commission (NRC) for the public near nuclear plants [35]. This means that only a small fraction of the pollutants are released into the air, where they are diluted over time.

![Figure 3](image-url)
According to the above characteristics, the tritium flux in leachate is discharged to the unsaturated zone at a rate of 7.7 curies per year, and part of it enters the groundwater zone. By comparison, the tritium gas produced at the site enters the air at a rate of 0.59 curies per year. As shown in Table 2, according to the flux transfer theory in Equations (3)–(5), the total flux is equal to the sum of air flux and leachate flux. Thus, the total flux of tritium is 8.3 Curie/year, and leachate accounts for 93% of the total flux. After 5 years of attenuation, the tritium flux dropped to 1.8, a 79% reduction from the original. Ten years later, the tritium flux had dropped to 0.36, a 96% reduction. The U.S. Environmental Protection Agency (USEPA) sets the maximum level of tritium contamination at 20,000 microbiocentimeters per liter (pCi L$^{-1}$) [36]. As a result, this level is equal to 1000 curies of tritium per year, and many nuclear reactors are allowed to release this amount into water bodies due to its short half-life. Therefore, if vertical migration between multimedia needs to be considered, it is important to use a mass balance model for correct mass distribution.
planning and management of risk communication. perception problems can be overcome through careful analysis of actual risks and careful planning and management of risk communication.

4. Discussion

The EEMMS model is used to analyze a typical two-dimensional pollution transport problem for air-unsaturated-groundwater zones. The COMSOL numerical method was...
used to solve the mass balance equation and the results are compared with literature data. The application of mass balance theory in air-unsaturated formation is proved by example analysis. It is necessary to prove the water distribution between the air and unsaturated zones and the groundwater zone to study the interaction among air, unsaturated water, and groundwater, especially the interaction between low concentration of tritium radioactive pollutants. Therefore, in order to meet water demand and protect the water environment, a number of water distribution schemes should be implemented [37,38], including subdivisions and their tributaries, natural surface water, and groundwater, which has direct links to surface water and air. In addition, the plan should include an overall allocation target for the entire air unsaturated area.

Finally, case studies show that the short half-life of tritium indeed results in relatively rapid reduction in its concentration over time. As mentioned earlier, after approximately 12.3 years, half of the initial tritium concentration will decay into helium 3. This exponential decay continues over successive half-lives, leading to a substantial decrease in tritium concentrations within a few decades [23,39]. Even at low concentrations, the increase of tritium in the gas will lead to a decrease in leachate, and the total mass remains balanced. Tritium is also predictably present at the MADE site in the form of tritiated water vapor and tritiated gas, in which model results are consistent with experimental data. Nevertheless, further research on this issue seems warranted, as public concerns about exposure to radiation agents are well discussed. Although the data are extremely limited, we need to correctly calculate fluxes in the entire air-unsaturated-groundwater zones using the mass balance theory, especially to consider the tritium release to the air, which makes the site potentially dangerous under certain circumstances. If tritium is released or leaked into the environment, its radioactivity diminishes relatively quickly. However, it is important to note that even though tritium's radioactivity decreases rapidly, its migration in the unsaturated groundwater zone and its potential impact on water quality and biota should still be carefully monitored and managed, especially in the vicinity of potential receptors such as drinking water wells or sensitive ecosystems [40]. In addition, perceptions of its risk may still pose problems for many facilities at an early stage.

5. Conclusions

In the context of global warming, population growth and, increasing demand for better water allocation management, the relationship between the air, unsaturated zones, and groundwater zones is studied. How to make better use of the mass balance model for tritium deposition will be one of the important directions for comprehensive simulation of its emission to air-unsaturated-groundwater zones. The mass balance theory is essential for understanding the conservation of tritium mass during migration. Modeling the migration of tritium in the air-unsaturated-groundwater zones requires the integration of hydrological, geochemical, fate characteristics, and mass balance equations to represent the complex interactions between tritium and the surrounding environment. It involves accounting for the sources, sinks, and decay of tritium in the air-unsaturated-groundwater zones and is the foundation for developing model tools to predict tritium transport. This paper applies the mass balance theory to the developed EEMMS model solving a 2-D adapted case study of Tritium Spill’ fate and migration in a multimedia environment. The theory can predict the spatial and temporal concentration distribution of pollutants in different environmental media in complex environments, and synthesize air, unsaturated, and saturated groundwater zones based on mass conservation, mass flux, and transient non-uniform initial and boundary conditions.

With the rapid development and application of numerical models (such as COMSOL finite element solver), multi-factor solving has become easier. The case study shows that the relationship between gas and tritium in leachate is based on the mass balance theory, and there is a mass balance among the gas-unsaturated zone and the groundwater zone. The accuracy of the finite element solution can reach the minimum concentration limit of 0 pCi mL$^{-1}$. However, the analytical test accuracy is on only 5 pCi mL$^{-1}$. The case
study also shows that optimal allocation of water resources is possible and necessary. For example, excessive exploitation of groundwater will change the pattern of water cycle and lead to unsaturated recharge of groundwater resources according to mass balance theory.

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