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MODELING THE FATE OF TOLUENE AND BENZENE AT THE TANJERO WASTE DUMP SITE, SULAIMANIA, NORTH IRAQ

Aras Kareem | Institute of Geology
Rudy Abo | Technische Universität Bergakademie Freiberg
Broder Merkel | Freiberg, Germany

The urban landfill site of the Tanjero industrial area contains organic waste from both domestic sources and the oil industry. It contains the waste of some unlicensed petroleum refineries of the Tanjero area. The local authorities plan to discontinue the waste dumping process because considerable concentrations of organic components are detected in water samples taken from wells in the vicinity of the dump site. In this study, the focus is on BTEX components and their natural attenuation. The benzene and toluene concentrations in the sampled waters are considerably higher than those of ethylbenzene and xylenes. Therefore, only benzene and toluene were considered in the modeling part of this study. In order to estimate the recharge rate through the soil column, the software HELP3 was used. The fate of the two volatile organic contaminants in the unsaturated zone over a period of 25 years was simulated using VLEACH. It was assumed that no clean-up will take place at the surface of the dump site. The software VLEACH considers water advection, solid-phase sorption, vapor-phase diffusion, and three-phase equilibration. According to the simulation toluene is attenuated in the contaminated zone in the pore water of the topsoil from 32 ppb to 4.5 ppb after 25 years. The benzene concentration after the same time period is attenuated from 49.5 ppb to close to zero. The toluene concentration is attenuated from 2 ppb to 0.1 ppb after 25 years at the depth of groundwater, while the benzene concentration is attenuated from 0.1 ppb to below the detection limit (< 0.013 ppb) after the same period.

INTRODUCTION

Toluene (C_7H_8) and benzene (C_6H_6) are two components that together with ethylbenzene and three xylenes compose the acronym BTEX. Among the physical processes leading to the natural attenuation of BTEX components in the environment are microbial catalyzed decomposition, volatilization, dispersion, dilution, sorption, and diffusion (Newell and Connor 1998).

In general, the soil properties (porosity, organic carbon content, and mineral surface area) have significant consequences on the bioavailability and leachability of hydrocarbon components (Huesemann et al. 2005). Processes in soil such as sorption, diffusion, degradation, and volatilization of hydrocarbon contaminants depend on several factors (temperature, moisture and soil texture). The soil's composition determines its capacity to sorb hydrocarbons. A clayey soil can bind six times more BTEX than a coarse sandy soil. Thus the relationship between soil contaminant concentration and soil texture can be useful for calculating the amount of hydrocarbons sorbed on a soil and for predicting the vulnerability of this soil (Falciglia et al. 2011). While the partitioning coefficients between water and BTEX components as phase decrease according to the order of m-xylene and p-xylene ≈ ethylbenzene > o-xylene > toluene > benzene, the diffusion coefficients follow the order of benzene > toluene > ethylbenzene > m-xylene and p-xylene ≈ o-xylene. Commonly equilibrium sorption decreases with increasing temperature. However, the opposite and no temperature effects have been found as well (Hulscher and Cornelissen 1996). For gas diffusion it can be assumed that diffusion increases with increasing temperature (Nafikov and Usmanov 1969). Volatilization can significantly contribute to the attenuation of volatile organic contaminants in the subsurface, groundwater, and vadose zone. The dumped petroleum products can show high rates of volatilization from both pure phase or if dissolved in water. Henry's law defines the equilibrium between water and gas for given boundary conditions. Assuming equilibrium the rate of volatilization from water to gas can thus be calculated. Volatilization decreases as the age of the dump increases.

Region of interest (ROI)

Every day the Tanjero landfill site (Kurdistan region, northern Iraq) receives more than 1000 tons of domestic waste and industrial waste from unlicensed oil refineries. The waste is dumped in a fenced but non-constructed landfill area of 50 hectares size (Rashid 2010). The local authorities have plans to stop the dumping of waste and to establish a recycling factory instead.

The climate in Kurdistan region is characterized by cold and snow-rich winters and long and warm dry summers whilst autumn and spring are short. The air temperature may reach 45°C during summer while precipitation is more or less absent. The rainy season starts in mid-October and ends in the beginning of May. The month with the highest precipitation in the whole region is January (Stevanovic and Markovic 2004). The region of interest consists of clastic rocks such as claystone, siltstone, and sandstone and it is called Tanjero formation (Budy et al. 1980) with a thickness of approximately 140 m and clastic alluvium sediments that contain gravel, sand, and clay (Ali 2007).

The general lithology is dominated by alluvium or alluvial deposits as typical soil type in the ROI. The soil texture is characterized by silty clayey loam based on the quantitative percentages of sand, silt and clay, which are 17.9 %, 53.3 % and 28.8 %, respectively (Najmadeen et al. 2010). These sediments stem from nearby mountains and have rapidly been transported by surface water as debris flow or as stream bed and deposits in the plain during Quaternary in the form of alluvium fans (Rashid 2010). The average depth to groundwater in the well A3 varies from 5 m to 9 m. (see Figures 1 and 2).

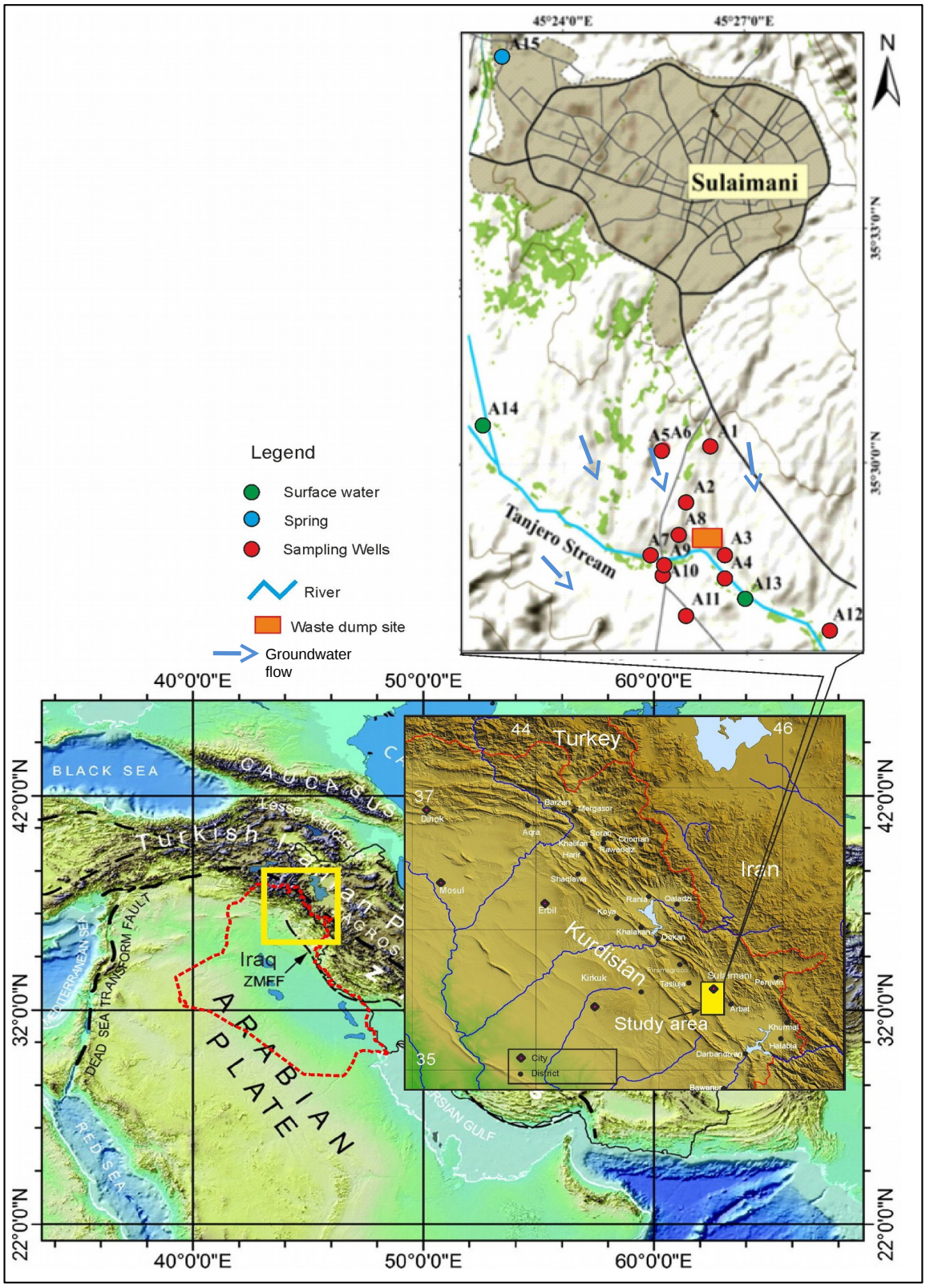

Figure 1. Location of ROI, monitoring wells, waste dump site and groundwater flow direction

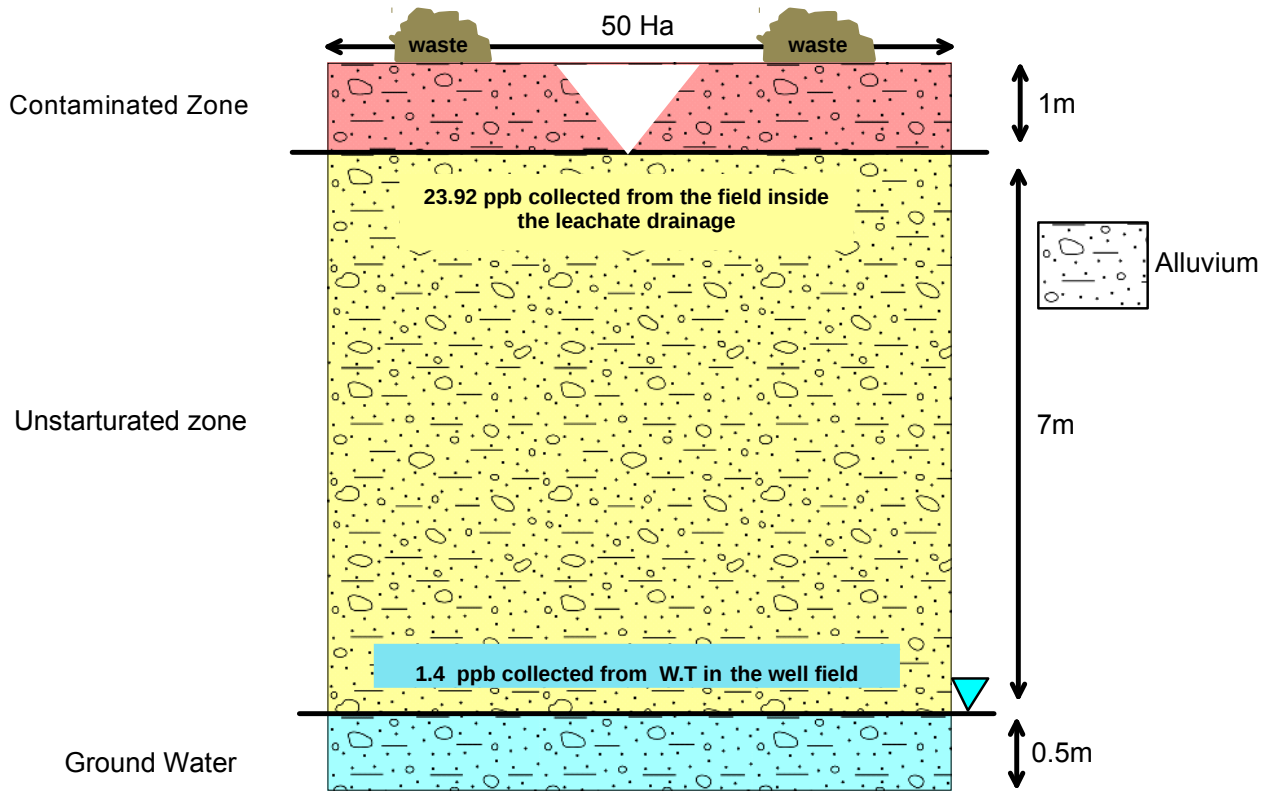

Figure 2. The conceptual profile of the unsaturated zone in the waste dump site

MATERIAL AND METHODS

Hydrochemical data of the monitoring well (A3) was used for the investigation of the BTEX leakage in the study area. The well is located at the eastern margin of the dump site, Tanjero area, and southeast of Sulaimani city. Groundwater samples were taken during summer 2013. They were analyzed using Gas Chromatography-Mass Spectrometry (Thermo-Scientific Ultra-ISQ GC-MS).

The soil texture is essential for estimating the hydraulic properties of the soil column, which are needed for modeling with HELP3 and VLEACH.

Simulation of water percolation with HELP3

HELP3 was used to calculate the water percolation rate in the soil of the study area. Percolation is the vertical movement of water through the soil column (Singh 1992). It describes the infiltrated water that moves downwards to the lower boundary of the contaminated zone. HELP3 integrates meteorological data such as precipitation, solar irradiation, wind speed, and temperature. This data, together with information on slope and vegetation cover of the study site are used to estimate the actual evapotranspiration and surface runoff. Finally HEPL3 uses soil texture and hydraulic data (unsaturated hydraulic conductivity, permanent wilting point, field capacity and porosity) to estimate the soil's water balance and percolation rate through the unsaturated zone. The simulation covers a period of 100 years.

Daily climate data from the meteorological station in Sulaimani city was used. The probability of rain on a given day was estimated from the wet or dry status of the previous day. Table 1 lists the main soil input parameters in the HELP3. The calculated average annual percolation rate was then used as initial parameter in VLEACH to estimate the contaminants' flow through the soil column.

Table 1. Soil input parameters to HELP3

Parameter	Value	Unit	Source
Thickness of the polluted zone	1	meter	Field survey and assumption
Total porosity	0.478	(vol/vol)	(Najmadeen et al. 2010)
Field capacity	0.353	(vol/vol)	(Abdulla 2015)
Wilting point	18.4	%	(Abdulla 2015)
Initial moisture content	0.09	(vol/vol)	Calculated by HELP3
Saturated hydraulic conductivity	0.00019	cm/sec	(Najmadeen et al. 2010)
Surface slope	5	%	Assumption
Area from where runoff is allowed	90	%	Assumption
Vegetation class	Bare soil	-	Assumption
Evaporative zone depth	12	inch	Assumption

BTEX transport with VLEACH:

VLEACH is based on a non-linear equation of the flow in soil water. It uses the finite difference method to explain the processes involved in the transport of the contamination, namely diffusion, advection and adsorption. VLEACH simulates the flow of volatile organic carbons, which are benzene and toluene in this study. For the transport, a 9 m soil column is assumed. The upper layer is considered as the zone from which the contamination stems from. A thickness of 1 m was assumed. The average total thickness of the unsaturated zone is about 7 m. In this zone silty and clayey sand are the main soil types. The lower layer has an average thickness of 1 m and is composed of silt, clay and sand and forms the groundwater-bearing zone. The input parameters for the soil in the ROI are shown in Table 2, while the input parameters of benzene and toluene are shown in Table 3.

Table 2. The input parameters for the soil to the VLEACH model

Parameter	Value	Unit	Source
Bulk density	1.3	$(g/cm)^3$	(Rashid 2010)
Effective porosity	0.14	(vol/vol)	(Najmadeen, et al. 2010)
Water content	0.019	(vol/vol)	(Rashid 2010)
Fraction organic content	0.28	(%)	(Najmadeen, et al. 2010)

Table 3. Chemical input parameters of benzene and toluene to the VLEACH model

Parameter	Benzene	Toluene	Unit	Source
	Value			
Water solubility	1780	515	(mg/L)	Material designer (VLEACH) model of WHI UnSat Suite
Organic carbon partitioning coefficient	64.56	257.0	(mL/g)	Material designer (VLEACH) model of WHI UnSat Suite
Henry law constant	0.221	0.269	(-)	Material designer (VLEACH) model of WHI UnSat Suite
Free air diffusion coefficient	0.665	0.734	(m^2/d)	Material designer (VLEACH) model of WHI UnSat Suite

The upper boundary in the VLEACH model at the beginning of the 25 year's simulation was estimated as 27 ppb and 16.3 ppb for toluene and benzene, respectively, based on the measured leachate concentrations at the waste dump site. The leachate concentration in the vadose zone were taken from the measured concentrations as upper boundary condition and started thus with 23.93 ppb and 14.25 ppb for toluene and benzene, respectively. The measured concentrations of benzene and toluene in well A3 (0.09 ppb and 1.4 ppb, respectively) were used as lower boundary. The water table in well A3 was at a depth of 8 m during the water sample collection in summer 2013. For the upper flow boundary in the VLEACH model, the percolation values determined with the HELP3 model were used as annual percolation through the soil column for the 25 years that were simulated with VLEACH. The allowed ponding was set to 0 cm and the depth of the bottom flow boundary to 8 m (groundwater table). The thickness of the saturated zone was defined as 1 m. The lower boundary for the vapor was set to a negative value (-1 mg/L) to maintain no gas diffusion (Anderson and Woessner 2002).

RESULTS AND DISCUSSION

Hydrochemical analyses revealed BTEX concentrations to be highest at the well close to the dump site (see Figure 1 and Table 4). Toluene and benzene show significantly higher concentrations in groundwater than the other BTEX components (ethylbenzene and xylene).

Table 4. BTEX concentrations in ground and surface water in the ROI

Sample No.	Description of location	BTEX Results (ppb)				
		Benzene	Toluene	Ethylbenzene	p-xylene	m- xylene
A1	house's well near the main road	0.05	0.01	<0.13415	0.08	0.07
A2	Metal melting Factory well	0.09	0.29	<0. 13415	0.26	0.07
A3	Well No. 3 close to the waste dump site	0.09	1.40	2.25	1.72	1.72
A4	Well No. 4 close to the waste dump site	<0.013	1.15	0.94	1.00	<0.0166
A5	House's well behind the School well	<0.013	0.11	<0. 13415	0.27	<0.0166
A6	The School's well	<0.013	0.34	<0. 13415	<0.02	<0.0166
A7	The well of the Pebble factory	<0.013	0.20	<0. 13415	<0.02	<0.0166
A8	The well of the Pebble crashing Factory	<0.013	0.15	<0. 13415	0.18	<0.0166
A9	The well at the west side of Tanjero stream	<0.013	0.98	1.52	1.22	1.22
A10	The well of the oil Factory	<0.013	1.30	<0. 13415	0.44	<0.0166
A11	The well of the building material warehouse	0.25	0.19	<0. 13415	0.17	<0.0166
A12	Qaywan oil warehouse	0.37	0.39	0.54	0.44	0.44
A13	Tanjero stream south the waste site	0.38	0.16	<0. 13415	0.22	<0.0166
A14	Tanjero stream above the industry area	0.26	0.20	<0. 13415	0.21	<0.0166
A15	Sarchnar spring	<0.013	<0.0025	<0. 13415	<0.02	<0.0166

Note: the detection limits of the BTEX are: Benzene: 0.013 ppb, toluene: 0.0025 ppb, ethylbenzene: 0.13415 ppb, p-xylene: 0.02 ppb, & m-xylene: 0.0166 ppb.

The annual percolation through the model column representing the waste dump site was calculated using HELP3 and it is shown as in Figure 3. The determined total percolation was 8.2 m for 100 years. The relative standard deviation was 3.6 %. Rather significant variations in the yearly percolation from close to zero up to 1.75 m were estimated, which is mainly related to variations of the meteorological data.

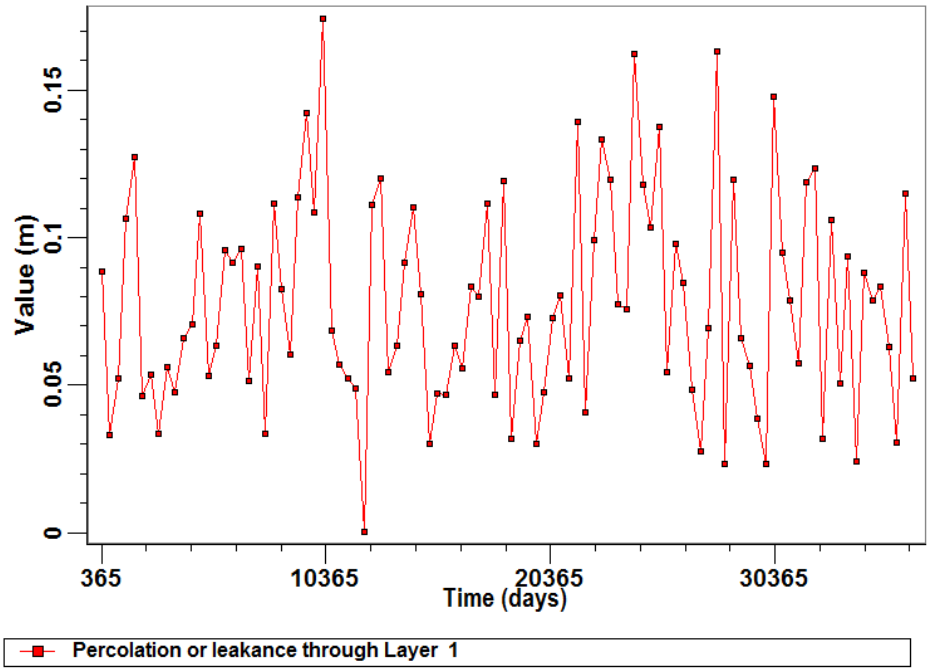

Figure 3. The annual percolation rate in meter during a period of 100 years

The results of the VLEACH model show that the toluene and benzene concentrations are more likely to be reversely with the depth during the period of simulation. The concentrations of toluene and benzene at defined depths was calculated and visualized after 1, 5, 10, 20 and 25 years. Figure 4 and 5 show significant changes that were observed within the first meter of the soil column.

Over the modeling time period of 20 and 25 years, the concentrations of toluene in the topsoil varies between 7 ppb and 4.5 ppb, respectively, and is close to 0.1 ppb at the water table's depth (Figure 4). The transport model reveals that during the last 20 to 25 years the benzene concentrations in the first meter of the soil column are lower than those of toluene. This is because benzene has a lower boiling point (80°C) than toluene (111°C). The development of the concentration gradient over time is shown in Figure 4 and 5. The concentrations in the 20 and 25 years of the benzene simulation are close to zero with values being highest at the top of the soil column and decreasing downwards (Figure 5). In the unsaturated zone the concentrations of benzene after 1, 5 and 10 years are lower and close to zero at 7.5 m depth.

The volatilization of toluene and benzene depends on temperature. Therefore, the vapor is mainly released from the contaminated zone, which is close to the surface. In this zone, especially during summer, the soil temperature can reach values of 25^0 C (Pankow und Cherry 1996).

In the unsaturated zone a significant concentration decrease can be seen. The decrease in the benzene and toluene concentrations with increasing depth may as well be a result of the decrease in the total porosity of the soil with increasing depth due to the load of the overburden (Lee 2007).

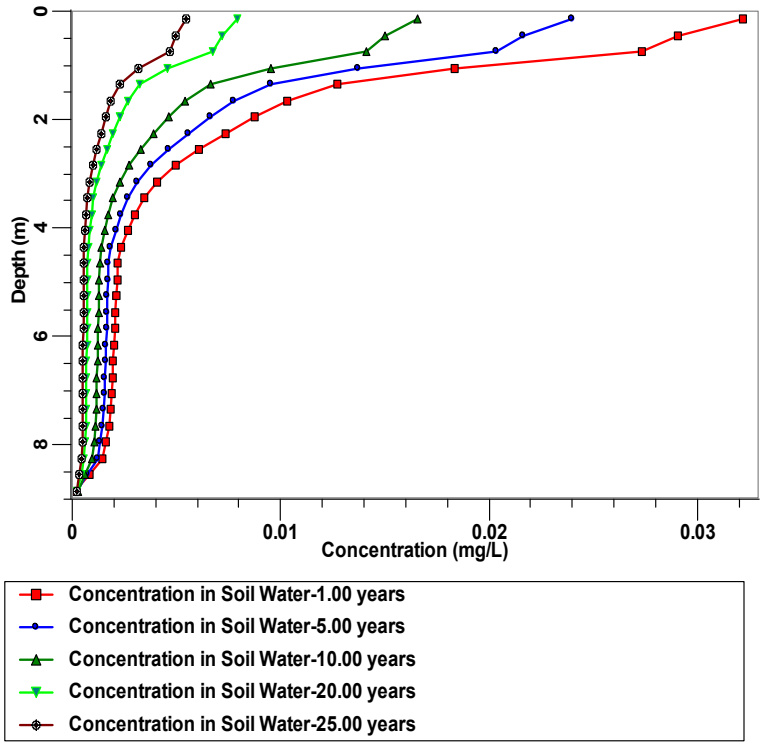

Figure 4. Toluene concentrations over depth after 1, 5, 10, 20, and 25 years in the soil modeled with VLEACH

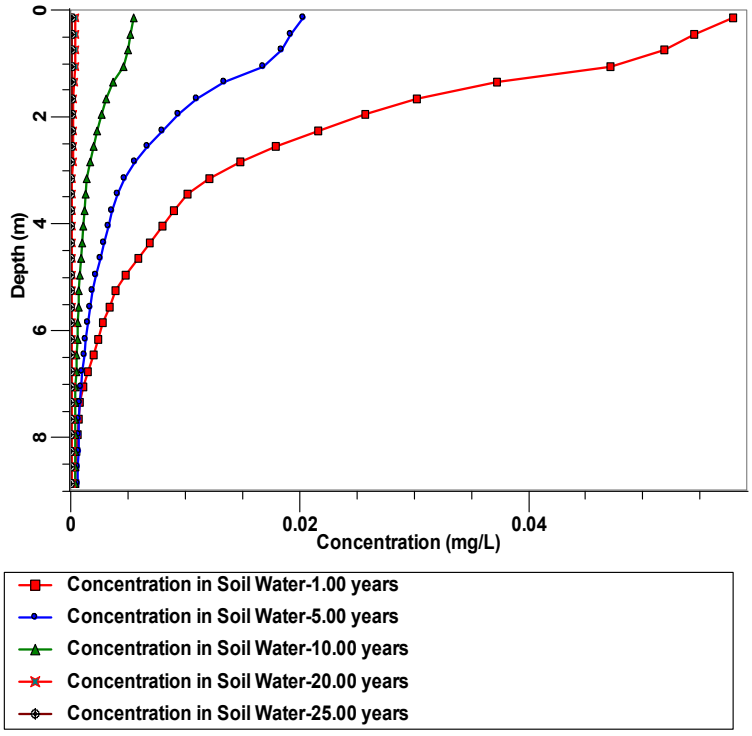

Figure 5. Benzene concentrations over depth after 1, 5, 10, 20, and 25 years in the soil determined by 1 D transport modeling with VLEACH

The downward concentration decrease in the model could be reasoned as well by several other factors and conditions, such as the presence and activity of bacteria and fungi species, environmental conditions (temperature, aquifer materials, and organic matter content) (Lawrence 2006); however, these processes are not considered by VLEACH.

The modeling results of toluene and benzene after 10 years, show that benzene is more strongly dissolved and volatized than toluene in this case study. At a depth of 8 m (depth to groundwater) there is a slight difference between the benzene concentration, which is below the detection limit (<0.013 ppb), and the toluene concentration which is higher than 0.1 ppb. The reason could be the comparatively high water solubility and low octanol–water partitioning coefficients (K_{ow}) of benzene and toluene (Table 5). Benzene dissolves more fairly in water and is evaporated into the air spaces of the soil more strongly than toluene (Charles und Asuoha 2010) and this is the reason why benzene is more mobile in the soil and groundwater environment than toluene. After 20 years the benzene concentration is below the detection limit (<0.013 ppb) at the top of the soil column, while toluene is still present at 0.0065 mg/L. That may be because of the volatility of toluene, which is lower than that of benzene because the number of carbon atoms in toluene is higher than in benzene (Ebbing and Gammon 2013).

Table 5. Physio-chemical properties of benzene and toluene

Volatile Organic Carbon	Molar weight g/mol	Density g/mL	Boiling point □C	Water solubility mg/L	Vapor pressure mmHg	Log octanol–water partitioning coefficient (K_{ow})
Benzene	78	0.88	80.1	1780	76	2.13
Toluene	92	0.87	110.8	535	22	2.69

CONCLUSIONS

In this study, the modeling results revealed that the benzene concentrations are more strongly lowered than those of toluene. After 20 years, in the unsaturated and saturated zone of the soil column of the study area there will be nearly no benzene left while toluene will still be present, yet at low concentration. Benzene will be attenuated completely before it reaches to the groundwater. Volatilization is the main process contributing to the natural attenuation of benzene and toluene. Temperature, soil moisture and soil porosity influence the extent of the natural attenuation of benzene and toluene. The difference in chemical and physical properties of benzene and toluene are the significant cause for the differences in the attenuation of benzene and toluene in the study area. This area needs more study and data on the biodegradation and long-term monitoring of the groundwater quality.

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REFERENCES

Abdulla, Z. O. 2015. Characterization and Classification of Soils and Land Use Suitability in Some Selected Areas from Iraqi Kurdistan Region. University of Sulaimani; Iraqi Kurdistan Region.

Ali, S. S. 2007. Geology and hydrogeoloy of Sharzoor-Piramagroon basin-Sulaimani. Unpublished Ph.D. thesis. Belgrade Univeristy.

Berger, K. 2000. Validation of the hydrologic evaluation of landfill performance (HELP) model for simulating the water balance of cover systems. Environmental Geology, Vol. 39.

Budy, T., S. Z. Jassim, and I. I., Kassab. 1980. Regional geology of Iraq, Vol. 1, page 445.

Charles, O., and A. Asuoha. 2010. Polycyclic Aromatic Hydrocarbons (PAHs) and Benzene, Toluene, Ethylbenzene, and Xylene (BTEX) Contamination of Soils in Automobile Mechanic Workshops in Port-Harcourt Metropolis. Rivers State, Nigeria. Journal of American Science.

Ebbing, D., and S. D. Gammon. 2013. General chemistry. Cengage Learning. Wayne State University, Vol. 10 .

Falciglia, P. P., M. G. Giustra, and F. G. Vagliasindim. 2011. Low-temperature thermal desorption of diesel polluted soil: Influence of temperature and soil texture on contaminant removal kinetics. Journal of Hazardous Materials. Elsevier, Vol.185, pp. 392-400.

Huesemann, M. H., T. S. Hausmann, and T. J. Fortman. 2005. Leaching of BTEX from Aged Crude Oil Contaminated Model Soils: Experimental and Modeling Results. Soil and Sediment Contamination: an International journal, Vol. 14 (6), pp. 545–558.

Hulscher, Th., and G. Cornelissen. 1996. Effect of temperature on sorption equilibrium and sorption kinetics of organic micro pollutants. Chemosphere journal ,Vol. 32(4), pp 609–626.

Lawrence, S. J. 2006. Description, Properties, and Degradation of Selected Volatile Organic Compounds Detected in Ground Water. A Review of Selected Literature. Virginia.

Lee, S. S. 2007. Vadose-zone Leaching and Saturated-zone Mixing Model in Heterogeneous Layers. Experimental Unsaturated Soil Mechanics book. Springer Proceedings in Physics, Vol. 112, pp. 387-399.

Mulligan, C. N., and R. N. Yong. 2004. Natural attenuation of contaminated soils. Environment International journal. Elsevier, Vol. 30 (4), pp. 587–601.

Nafikov, É. M., and A. Usmanov. 1969. Temperature dependence of the diffusion coefficients of gases. Journal of engineering physics, Vol. 17(3), pp. 1158–1161.

Najmadeen, H., A. O. Mohammad, and H. Mohamed-Amin. 2010. Effects of Soil Texture on Chemical Compositions, Microbial Populations and Carbon Mineralization in Soil. The Egyptian Society of Experimental Biology journal, Vol. 6, pp. 59–64.

Newell, C. J., and J. A.Connor. 1998. Characteristics of dissolved petroleum hydrocarbon plumes results from four studies. API Soil / Groundwater Technical Task Force. American Petroleum Institute, Vol 1.1, Page 4.

Pankow, J. F., and J. A. Cherry. 1996. Dense Chlorinated Solvents and other DNAPLs in Groundwater. Waterloo Press. Oregon.

Rashid, Kh. 2010. Environmental Implication of Tanjero waste disposal site of Sulaimani. Unpublished Ph.D. Sulaimani University. Sulaimani.

Singh, V. P. 1992. Elementary hydrology. Prentice-Hall. Englewood Cliffs. New Jersey.

Stevanovic, Z., and M. Markovic. 2004. Hydrogeology of northern Iraq. Climate, Hydrology, Geomorphology, Geology. General hydrogeology and aquifer system journal. FAO. Vol. 2.

WHI. 2003. The HELP Model. Visual HELP User's Manual Waterloo, Vol.2.

Anderson M. P., and W. W. Woessner. 2002. CHAPTER 4- Boundaries. Applied Groundwater Modeling book, pp. 97–145.

ADDRESS FOR CORRESPONDENCE
Aras Kareem
Institute of Geology
Technische Universität Bergakademie Freiberg
Gustav-Zeuner Str.12
09599 Freiberg, Germany
Email: arasomer@yahoo.com