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Hazardous Organic Compounds in Groundwater Near Tehran Automobile Industry

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Abstract Potential of groundwater contamination by trichloroethylene (TCE) and other volatile organic compounds VOCs near car industry was conducted in this study. TCE, PCE, toluene, xylene, dichloromethane, cyclohexane, n-hexane and n-pentane were detected in all groundwaters. Mean TCE levels in groundwater ranged from 124.37 to 1,035.9 μg L^{-1} with maximum level of 1,345.7 μg L^{-1}. Due to the data obtained from conventional wastewater treatment in car factory the TCE removal efficiency was only 24 percent which necessitates the TCE removal by advanced treatment processes before the use of well water.

Keywords Trichloroethylene · Organic matter · Wells · Car industry

Groundwater contamination can be originated from different categories: natural processes, man disposal practices and industrial activities. The presence of hazardous chemicals which may leak out of industrial wastewater areas to the groundwater resources is responsible for subsurface water contamination. This accident especially happens by the industries contributory negligence. Presence of VOCs in water is an important concern to all who use groundwater as a source for different uses. These materials such as chlorinated aliphatic hydrocarbons (CAHs) can enter the groundwater and endanger human health in a direct or indirect manner through the contamination of ground waters bodies. One of these CAHs that has been mainly used as a degreaser is TCE (An et al. 2004). TCE is a non-flammable, volatile and colorless liquid. The summary of TCE physical properties are presented in Table 1 (Gist and Burg 1995). Electronic and electrical, fabricated metal products and transport equipments are the main industries that use TCE in cold or vapor degreasing operations. TCE has many different uses such as extraction solvent, chemical intermediate and as a component in paints and coating, varnishes, paint strippers, adhesives, pesticide, lubricants and metal cleaners (ATSDR 1995).

TCE is considered as probable Carcinogenic chemical to human based on limited evidence from studies in human and sufficient evidence in experimental animals (Wartenberg et al. 2000) and as well as many other adverse effects on human and animals (Gist and Burg 1995; Wartenberg et al. 2000; Michihiro et al. 2007; Windemuller and Ettema 1978). Water bodies also may be contaminated to TCE by different routes, and the main source of TCE release into water bodies is discharge of industrial wastewaters (Henschler et al. 1980).

Both surface water and groundwater sources may be contaminated with TCE. Most conventional treatment processes such as coagulation, sedimentation, precipitative softening, filtration, and chlorination are not efficient in removal of TCE and possibility of groundwater contamination to TCE with regard to such industrial wastewater discharges are possible (Russell et al. 1992). In addition, due to health effects of TCE and lack of TCE groundwater contamination monitoring in Iran, the purpose of this study is the detection of trichloroethylene along with the existence of other VOCs in groundwater. The field of

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Table 1 TCE physical properties (Gist and Burg 1995)

Molecular weight	Density at 20°C (g mL^{-1})	Solubility** at 20°C (g L^{-1})	Melting point (°C)	Boiling point (°C)	Henry's law constant*
131.4	1.465	1.07	−87.1	86.7	0.020

* At 20°C (atm-m^3 mol^{-1})

** Solubility in water

research was near the car industry wastewater treatment plant which discharges its treated effluent into groundwater source.

Materials and Methods

The car factory is located in the Tehran- Karaj highway, West of Tehran. There are four groundwater wells in the factory site which all of them were selected as sampling points. The sampling was done in 6 months from July through December 2009. From each groundwater well four samples were taken during the study, a sample in each 45 days. 40 mL vials equipped with a screw cap with Teflon (TFE)-faced silicon septum were used for sampling. Samples were stored in chilled condition (at 4°C) and analyzed immediately after delivery to laboratory (APHA 2005).

Organic compounds in the groundwater samples were identified as below:

GC/MS analysis with an Agilent (Agilent Technologies, Palo Alto, CA, USA) 6890 plus gas chromatograph equipped with a 5973 mass selective detector quadruple mass spectrometer was used. The gas chromatograph was fitted with a DB-1 capillary column (60 m, 0.25 mm id, 0.25 μm film thickness). The instrument temperatures were as following: injector temperature 150°C, initial oven temperature 40°C (held for 3 min), increased to 100°C at a rate of 10°C min^{-1}, held for 1 min then increased to 130°C at a rate of 30°C min^{-1}, held for 1 min. The inlet was operated in splitless mode. Helium (99.999%) was used as carrier gas at 1.5 mL min^{-1}. The electronic beam energy of the mass spectrometer was set at 79 eV and the mass selective detector was operated in scan mode.

TCE concentration of samples were also determined as below:

GC-FID analysis with a VARIAN CP-3800 (Australia) was used to determine TCE concentration of samples. The GC was fitted with a CP-Sil 8 CB Capillary Column (30 m, 0. 32 mm id, 0.25 μm film thickness).

Injector temperature was 150°C, initial oven temperature was 35°C (held for 1 min) and increased to 100°C at a rate of 16°C min^{-1}, held for 5 min. The inlet was operated in 20% split mode. Helium (99.999%) was used as carrier gas at 1 mL min^{-1}.

The quality control practices including calibration, initial quality control, batch quality control (including reagent blank, laboratory-fortified blank, laboratory-fortified sample, internal and surrogate standard) were done according to standard methods (APHA 2005). The minimum detection level (MDL) for TCE analysis by GC with above method was ≤ 2 μg L^{-1} TCE/L.

Finally all groundwater samples, influent and effluent samples were analyzed for parameters including total suspended solid (TSS), total dissolved solid (TDS), electrical conductivity (EC), turbidity, pH, Ni, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, Cl^-, free chlorine, oil and alkylbenzene sulphonate (ABS) by standard methods (APHA 2005).

Results and Discussion

General characteristics of groundwater (well no. 1 to well no. 4), influent and effluent of wastewater treatment are shown in Table 2.

As can be seen in Table 3 there are different VOCs in wastewater treatment influent and effluent and also wells have some VOCs including PCE, TCE, cyclohexane, tolouene, xylene, n- pentane, n-hexance and dichloromethane.

The wastewater treatment plant in factory consists of screening, primary sedimentation, equalization tank, coagulation and flocculation, activated sludge, clarifier and chlorination. The collected wastewater from car industry process enters wastewater treatment plant in the factory.

Since there was no data on TCE monitoring in groundwater of Iran, our focus was on this kind of VOC. Table 3 shows that wastewater plant couldn't remove VOCs completely and with regard to mean TCE concentrations of influent and effluent in Table 3, conventional wastewater plant in factory had only 24 percent efficiency in TCE removal. The mean concentration of TCE in wells was found to vary widely from 124.37 to 1,035.9 μg L^{-1} and well no. 4 contained max TCE concentration with 1,345.7 μg L^{-1} level. TCE Levels in all wells exceeded the EPA TCE drinking water standard of 5 μg L^{-1} (US Environmental Protection Agency 2006).

There are several reports that list the VOCs in groundwater in different places (Wisconsin Department of Natural

Table 2 Mean analytical results of samples from groundwater wells, influent and effluent of wastewater treatment

	Influent	Effluent	Well 1	Well 2	Well 3	Well 4
Temperature (°C)	28.8	28.9	27.9	27.5	27.3	27.1
TSS (mg l^{-1})	240	40	–	–	–	–
TDS (mg l^{-1})	880	1080	371	380	365	385
EC (μs cm^{-1})	1215	1603.8	558	568	549	580
pH	7.94	7.8	7.42	7.5	7.35	7.6
Fe^{2+} (mg l^{-1})	3.4	1.02	0.00	00.0	0.00	0.00
Ni (mg l^{-1})	1.3	0.7	–	–	–	–
Ca^{2+} (mg l^{-1})	–	–	44.8	46.7	45	43.6
Mg^{+2} (mg l^{-1})	–	–	6.72	7.2	7.6	5.9
Na^{+} (mg l^{-1})	–	–	69	75	65	73
TH (mg l^{-1} $CaCo_3$)	–	–	140	146.7	144.1	133.6
NH_4^{+} (mg l^{-1})	6.33	0.09	0.00	0.09	0.00	0.00
NO_2^{-} (mg l^{-1})	0.06	0.02	0.00	0.00	0.00	0.00
NO_3^{-} (mg l^{-1})	13.29	17.94	5.89	6.01	4.95	7.15
PO_4^{3-} (mg l^{-1})	10.8	4.15	–	–	–	–
SO_4^{2-} (mg l^{-1})	134	275	66.7	70.1	64	73.2
Cl^{-} (mg l^{-1})	158	210	70	76.5	67	74
Oil (mg l^{-1})	28	2.4	–	–	–	–
ABS (mg l^{-1})	0.79	0.00	–	–	–	–

Resources 2000; Hamlin et al. 2002; Barbaro and Neupane 2001; Guertal et al. 2004; Dinicola et al. 2002; Lopes and Bender 1998). TCE, PCE, toluene and xylene were in the 10 most commonly detected VOCs in these studies that almost fitted to detect VOCs found in our study.

Treated wastewater plant effluent is used as irrigation water for green land and plants in factory site. The main portion of treated wastewater is discharged into the absorbing wells. The groundwater in absorbing wells with higher hydraulic head moves toward wells with lower hydraulic heads. As it is seen in Table 3 wells' waters were contaminated by these contaminated groundwater flows.

Because the density of TCE is heavier than water, it is likely that TCE move downward through subsurface until lower permeability layer, a density difference of about 1% with water can mainly influence the contaminant movement in saturated and unsaturated areas (Josephson 1983).

Beside groundwater movement insoluble TCE i.e., DNAPL plumes in contaminated areas such as car factory can serve as a source for spreading of contamination spreading. As groundwater moves around these contaminated areas, equilibrium concentrations partition into the aqueous phase. Aqueous phase TCE is then spread through the aquifer by dispersion and advection activities.

Wells are located in less than 35 m from absorbing wells. The quantity (Q) of Wells' water taken in factory is about 1,40,000 m^3 $month^{-1}$ which then mixed with 1,30,000 m^3 $month^{-1}$ of Karaj reservoir and use for sanitary and industrial processes in car factory.

The use of this water can cause specific health problems especially for workers exposed occupationally.

Table 3 Mean TCE concentration in wells, influent and effluent and existence of other organic compounds

	TCE Concentration μg l^{-1}	VOC_S existence
Influent		
Mean	587.75	TCE, PCE, toluene, n-hexane, xylene, cyclohexane, tetrahaydrofuran (THF), n-pentane
Max	731.7	
Min	482.5	
(n = 4)		
Effluent		
Mean	446.52	TCE, PCE, toluene, n-hexane, xylene, cyclohexane, tetrahaydrofuran (THF), n-pentane
Max	612.7	
Min	295.6	
(n = 4)		
Well 1		
Mean	124.37	TCE, PCE, cyclohexane, n- hexane. toluene, xylene, n-pentane, dichloromethane
Max	152.6	
Min	97.7	
(n = 4)		
Well 2		
Mean	447.8	TCE, PCE, cyclohexane, n- hexane. toluene, xylene, n-pentane, dichloromethane
Max	601.2	
Min	218.3	
(n = 4)		
Well 3		
Mean	944.6	TCE, PCE, cyclohexane, n-hexane.toluene, xylene, n-pentane, dichloromethane
Max	1012.3	
Min	920.9	
(n = 4)		
Well 4		
Mean	1035.9	TCE, PCE, cyclohexane, n- hexane. toluene, xylene, n-pentane, dichloromethane
Max	1345.7	
Min	827.4	
(n = 4)		

Conclusion

The first investigation of the TCE groundwater contamination in Iran showed that these water sources have been contaminated by TCE and other VOCs, so it is recommended more monitoring of VOCs especially TCE in doubtful groundwaters near the industrial areas. The wells' water in car factory needs advanced treatment processes for

removal of TCE. In order to achieve the TCE standard it is highly recommended to pump- and – treat wells' water by proper technologies like air stripping and combined air stripping and carbon adsorption or in well aeration and bioremediation (Russell et al. 1992; Hsin and Shang 2007).

Authors' recommendations for future and related studies are as below:

1. Determination of the exact sources, vertical and lateral concentration of the TCE groundwater plume.
2. Future exposures survey of populations exposed occupationally to TCE.
3. Evaluation of the subsurface situation at the site and possible exposure pathway from groundwater to indoor air.
4. Monitoring TCE levels in groundwater and mixed water before the usage of the obtained water for industrial purpose in factory.
5. Survey of the adverse effects of TCE and other VOCs levels of wastewater plant effluent that is used for grass and plant irrigation.
6. Conduct of more studies to asses the health effects caused by exposure to TCE, features of exposure affected population and hydrogeologic condition.

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