International Journal of Plant and Environment
Vol. 4, No. 2 (July, 2018), 14-26

A Review on Volatile Organic Compounds (VOCs) as Environmental Pollutants: Fate and Distribution

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Publication Info

Article history:
Received: 31.10.2017
Accepted: 31.07.2018
DOI: 10.18811/ ijpen.v4i02.2

Key words:
Air stripping
Bioremediation
Groundwater
Volatile organic compounds

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Abstract

VOCs include a variety of organic chemicals emitted as gases from certain solids and liquids. The nature and extent of these health effects depend on the concentration levels of these VOCs and the duration of their exposure and pose adverse health effects to humans. Although VOCs are found in a variety of industrial, commercial and household products; it is their concentration in wells and groundwater that has gained attention in recent years. When VOCs are spilled or improperly disposed of, a portion of it after evaporation are soaked on the ground, which eventually reaches wells and groundwater. Drinking of inadequately treated VOCs contaminated groundwater is potentially harmful to human beings. Trichloroethylene and vinyl chloride are most toxic and carcinogenic among all VOCs. The present paper reviews the sources, health risks, transport and fate of these VOCs in groundwater. Besides, analytical methods for the detection of VOCs in groundwater and techniques for mitigation of VOCs from groundwater have also been discussed.

1. Introduction

Volatile organic compound (VOC) is a large group of the organic chemical compounds found in many products that vaporise easily and enter the environment under normal condition. VOCs possess high volatility, mobility and strong resistance to degradation that allows them to be transported over long distances in the environmental medium once released (ATSDR, 2005). The most frequently found VOCs are the aromatic hydrocarbons (benzene, toluene, ethyl benzene and xylene) and halogenated hydrocarbon like chloroethylene and trichloroethylene. Cancerous volatile organic compounds (cVOCs) are a subset of VOCs that can cause cancer in human beings. The most important exposure pathways for VOCs contaminated water for both non-cancer and cancer risks are identified as drinking, swimming, bathing, food, showering and laundries (Sexton *et al*., 1995; Chowdhury and Champagne, 2009). However, the cancer risks due to the VOCs contaminated groundwater are found to be hundred times higher than the general risk guidance values.

The source of VOCs may be natural or anthropogenic. Natural sources of VOCs include emissions from trees and vegetation, forest fires produced by natural causes and anaerobic marshy bog processes. VOCs generated by anthropogenic activities from both domestic and industrial processes include metal surface degreasing, textile cleaning, food extraction, fertilizers and pesticide application, septic system, chlorination, fumigation, traffic, hydrocarbon fuel evaporation, petroleum storage, distribution and storage, landfill, printing, building materials and pharmaceutical industries. The agricultural sources of VOCs such as the use of fuels in agricultural implements, burning of agricultural waste and the use of VOCs as inert ingredients in pesticide formulation have resulted in their extensive distribution in the environment (USEPA, 1994; Moran *et al*., 2004; Liang and Liao, 2007; Liu *et al*., 2013; Abdullahi *et al*., 2014). Spengler and Chen (2000) reported VOCs as indoor air pollutants and described the model for assessing their indoor emission sources. These sources are perfumes, tobacco smoke, chlorinated water, paint removers, insulation foam, adhesives, carpets, new clothing, plastic, paints and kerosene heaters. Composting is a major source of VOCs generated in the aerobic process and emitted in the initial phase of the process (Komilis *et al*., 2004). Ionic liquids as solvents also produce VOCs (Santa *et al*., 2000; Escudero *et al*., 2013). LaKind *et al*. (2004) also detected VOCs in human milk due to the inhalation of chemicals in the dry cleaning process as well as nicotine from cigarette smoke. Diduch *et al*. (2011) reported the presence of VOCs in bottled water. USEPA has identified about 189 air pollutants among which 97 are VOCs. Nearly all plants possess the ability to emit VOCs from various organs including fruits, flowers, leaves, stem and roots. Fischer and Dott (2003) reported microbial volatile organic compounds (mVOC) which are generated from airborne microbial metabolites or spore of fungus.

The environmental and epidemiological problems caused by emissions of VOCs are adverse effect on human health such as renal, haematological, neurological, hepatic alterations and mucosal irritation; and reduction of stratospheric ozone, photochemical formation of ozone at terrestrial level (Domingo and Nadal, 2009). VOCs also increase the effect of global warming because these gases effectively absorb infra-red energy radiated from the earth and increase their concentration within earth's atmosphere (Hester *et al*., 1995; Change, 2006; Murrells and Derwent, 2007). Many plants emit VOCs in response to environmental changes such as light, temperature, flooding and drought. Apart from these, VOCs play a significant role in plant physiological and ecological functions including plant defense mechanisms against insects, pollinators attraction, plant-plant communication and plant pathogen interactions (Zhu *et al*., 2013). mVOCs can affect human health by causing lethargy and irritation in mucus membranes of nose, throat and eyes. The presence of VOCs at a concentration below the maximum concentration level (MCL) may cause negative long-term and synergistic effect on human health such as spontaneous abortion, low birth weight and birth defects due to chloroform exposure (Thomas, 1990; Lappe, 1991; Colborn *et al*., 1996; Squillace *et al*., 2002; Thiriat *et al*., 2009; Zeng *et al*., 2013). Several VOCs are currently federally regulated with maximum contamination levels set as 0.002 to 0.005 mg L^{-1} (USEPA, 2002). The EPA announced a plan to develop one national primary drinking water regulation (NPDWR) covering up to 16 cVOCs which are given in Table 1 (Roth *et al*., 2012).

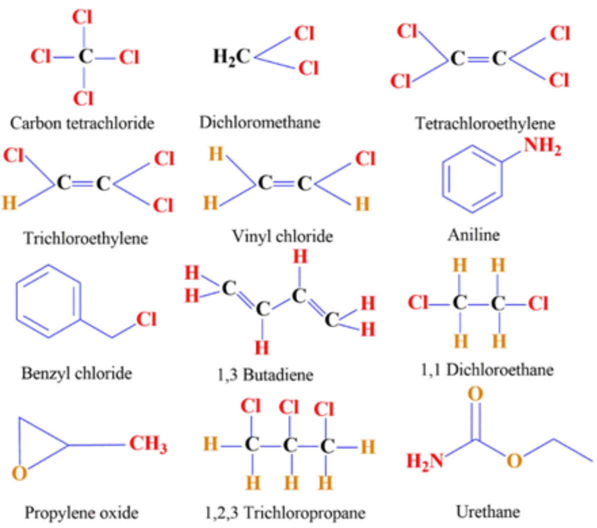

Fig. 1: Structure of carcinogenic VOCs.

Table 1: List of cVOCs for potential grouping by USEPA (Mandona, 2015).CASRN=Chemical Abstracts Service Registry Number.

S.N.	Compound name	CASRN	Carcinogenicity
1.	Benzene	71-43-2	Group 1
2.	Carbon tetrachloride	56-23-5	Group 2B
3.	1,2-Dichloroethane	107-06-2	Group 2B
4.	1,2-Dichloropropane	78-87-5	Group 1
5.	Dichloromethane	75-09-2	Group 2A
6.	Tetrachloroethylene (PCE)	127-18-4	Group 2A
7.	Trichloroethylene (TCE)	79-01-6	Group 2A
8.	Vinyl chloride	75-01-4	Group 1
9.	Aniline	62-53-3	Group 3
10.	Benzyl chloride	100-44-7	Group 2A
11.	1,3-Butadiene	106-99-0	Group 1
12.	1,1-Dichloroethane	75-34-3	Group 2B
13.	Nitrobenzene	98-95-3	Group 2B
14.	Propylene oxide	75-56-9	Group 2B
15.	1,2,3-Trichloropropane	96-18-4	Group 2A
16.	Urethane	51-79-6	Group 2A

In a national survey of VOCs conducted by the United States Geological Survey, cVOCs such as trichloroethylene, tetrachloroethylene and carbon tetrachloride were frequently detected in US groundwater and drinking water supply wells of United States (Moran *et al*., 2006). Trichloroethylene causes liver cancer, biliary cancer and non-Hodgkin's lymphoma; while tetrachloroethylene causes an elevated risk of cancers such as the bladder, oesophageal, cervical, rectum and colon cancer and non-Hodgkin's lymphoma; carbon tetrachloride exposure causes lymphohematopoietic malignancies (Siegel and Jinot, 2011; Malaguarnera *et al*., 2012). Environmental Protection Agency of U.S. (USEPA) and European Commission (EC) set these VOCs as priority pollutant due to their adverse epidemiological effect on the human beings. The structures of carcinogenic VOC species which require human monitoring are shown in Figure 1.

Groundwater is the largest source of drinking water for virtually all the people (USEPA, 2000). It contains up to 95% of the available freshwater of the world (Barbash and Roberts, 1986). India is the largest consumer of the groundwater in the world; about 60% of agricultural irrigation and 85% of drinking water supply depends on groundwater because it is pure and safer than surface water due to earth covering (Suhag, 2016).

However, contamination of groundwater with organic compounds has been encountered with greater frequency in recent years. Besides, land use pattern in urban areas such as leaking underground storage tanks (USTs), above ground storage tanks (ASTs) septic tanks, landfills, waste disposal and detention basins are the point source of VOCs in groundwater (Baehr *et al*., 1999). USTs and ASTs are used for storage of heating oil, gasoline or diesel fuel for domestic or agricultural purposes. Leakage from these residential USTs and ASTs is a significant source of VOCs contamination in groundwater

(Council, 1988). The septic tank is the second largest potential source of groundwater pollution in the vicinity of the system if the organic matter of the effluent of these tanks does not get completely degraded. These are several studies which explain the presence of VOCs in the fluid of septic tank or in groundwater where these tanks are situated (DeWalle *et al*., 1985 a,b; Viraraghavan and Hashem, 1986). Worldwide contamination of VOCs in groundwater was detected in the middle of 1970s (Zoeteman *et al*., 1981; Gardini *et al*., 1982; Westrick *et al*., 1984). Leakages and emissions of these compounds due to inadequate treatment and improper disposal of industrial waste are potentially disastrous to human health and the natural environment (Guo *et al*., 2004; Malherbe and Mandin, 2007). The pathways by which atmospheric deposited VOCs can enter in groundwater are precipitation, recharge, and diffusive transport through the unsaturated zone. So, the atmosphere is the potential non-point source of low-level concentrations of VOCs in groundwater. VOCs are transported to relatively long distances in groundwater, because of their relatively weak sorption affinity and resistance to degradation (Barbash and Roberts, 1986). VOCs are the most common contaminant of groundwater in comparison to surface water, because of their high volatility. Very high tetrachloroethylene (PCE), trichloroethylene (TCE), dichloroethylene (DCE) and vinyl chloride were detected in the groundwater aquifers (Golfinopoulos *et al*., 2001; Nikolaou and Tsaousis, 2002). There are several studies which indicate the contamination of VOCs in groundwater (Westrick, 1990; Baehr *et al*., 1999; Squillace *et al*., 1999, 2002; Vroblesky and Campbell, 2001; Moran *et al*., 2002, 2007; Rowe, 2004; Shapiro *et al*., 2004). Fan *et al*. (2009) reported the risk assessment of VOCs in groundwater in Taiwan using Multimedia Environment Pollutant Assessment System (MEPAS) model for specific non-cancer and cancer risk at an exposure level of 1 µg L^{-1} of each VOC.

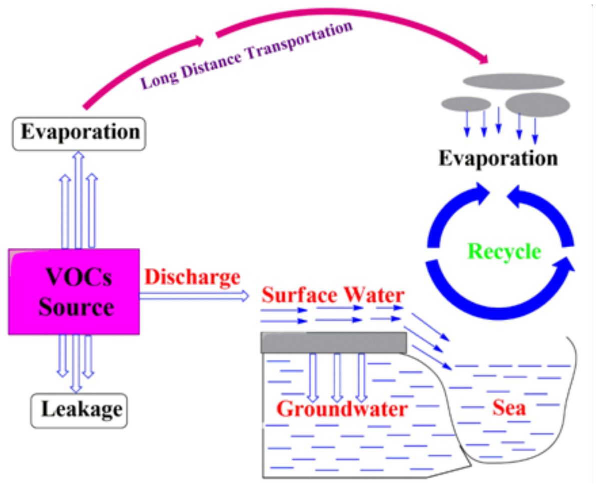

Fig. 2: Process of VOCs transportation (Huang *et al*., 2014).

The current criteria for VOCs might not be capable of ensuring public safety when groundwater is used as the primary source of drinking water. VOCs themselves, their reactive intermediates and decomposition products, are proven human carcinogen, mutagen and teratogen that create an apparent threat to public health (Belpomme *et al*., 2007; Claxton and Woodall, 2007). Physiologically Based Pharmacokinetic modeling (PBPK) permit the simulation of the internal dose of chemicals associated with multiple exposure routes (Krishnan and Carrier, 2008; Valcke and Krishnan, 2014). The health risk assessment process for drinking water contamination is considered as the only oral route of exposure. Some studies of past several years have shown that the dose received by other routes of exposure such as dermal exposure and inhalation might be just as important as the oral route and in some cases may be more important than the oral route.

1.1. Processes of groundwater contamination by VOCs

VOCs pass into liquid phase after their hazardous discharge from different sources of the land surface (Fig. 2). The VOCs containing materials fall to the bottom of groundwater due to their higher density than water at the concentration above residual saturation.

VOCs concentration is low in downstream areas due to low groundwater flow velocity and large scale of contact surfaces in groundwater body. Hence, the further movement of dissolved VOCs is influenced by convection, hydrodynamic dispersion, sub-stream dependent absorption and the transformation processes (Wiedemeier, 1999). Natural and anthropogenic factors that affect the source, transport and fate of VOCs in groundwater are given in Table 2.

1.2. Retention of VOCs in soil

VOCs enter soil surface from the atmosphere as vapors, liquids and aqueous solution. Then, move throughout the soil profile due to diffusion, convection and advection under the effect of gravity (Breus and Mishchenko, 2006). Once a leakage has happened in storage tank or storage area and landfill leachate, VOCs are transported in unsaturated zone due to gravity from the leakage area. Then, some of the VOCs get adsorbed on the surface of the soil particles and some spread horizontally due to capillary forces (Rivett *et al*., 2011). The amount of VOCs adsorbed on the surface of soil particles depends on the nature of soil that includes permeability, porosity, surface area and inorganic and organic contents of soil; but the presence of water may actively reduce the adsorption capacities (Delle Site, 2001). The soil having higher organic content will tend to adsorb higher amount of VOCs on their surface (English and Loehr, 1989). With continued downward movement, the VOCs eventually reach the top of the water table as a result of which the water is initially pushed downward until the hydrostatic pressure stops the downward movement of the VOCs. At this point, the VOCs that are denser than groundwater continue moving downward through the water and the lighter VOCs begin to spread horizontally over the groundwater surface. A small quantity of the VOCs also dissolves in the groundwater. Singh (1989), Vroblesky *et al*. (1996) detected VOC in fractured rock aquifer at the groundwater-surface water interface using passive vapour collectors in the central piedmont of South Carolina. The result showed higher concentration of VOCs was found in an area where VOCs were known to get discharged from groundwater to surface water. The data revealed that this area was a site where very low frequency electromagnetic anomalies intersected the creek. Singh and Niven (2013) reported non-aqueous phase liquids (NAPLs) create serious risk of soil and groundwater pollution in cold region due to their slow dissolution in groundwater over decades. They also reported the fate and transport of NAPLs contamination in freezing-thawing and frozen soils. Various studies have occurred on the transport of VOCs through leakage which is given in Table 3.

Moran *et al*. (2004) reported the presence of VOCs in untreated groundwater of United State as given in Table 4. Among these detected VOCs, the concentration of 1,1-Dichloroethene, 1,2-Dichloropropane, Trichloroethylene and Tetrachloroethene were greater than their maximum contamination level which was harmful to the human health. Baehr *et al*. (1999) reported that atmosphere served as a source of VOCs in shallow groundwater over an area in Southern New Jersey. The result showed that Chloroform, methyl tert-butyl ether (MTBE), 1,1,1-trichloroethane, tetrachloroethylene (PCE) were detected at low-level concentration in a network of shallow wells in the surficial Kirkwood Cohansey aquifer system. Squillace *et al*. (2002) analysed samples of untreated groundwater from 1255 domestic drinking water wells and 242 public supply wells as part of the National Water Quality Assessment Program of U.S. Geological Survey between 1992 and 1999. They analysed as many as 60 VOCs for each sample. Phillips *et al*. (2007) studied the fate and transport of VOCs in groundwater at an industrial site, Belfast in Northern Ireland. They reported that trichloroethane (TCE) was the most prominently occurring VOC in groundwater of this area with concentration range of 2400 to 39990 µg L^{-1}.

1.3. Factor that influences contamination of groundwater by VOCs

The factors that influence the contamination of groundwater by VOCs includes proximity of the well to the source of contamination, the amount of VOCs that are spilled or discharged, depth of well (shallow well is affected by the surface spills more quickly and more severely than deep well) and time (groundwater moves slowly, so it can take months or years after a spill before contamination reaches wells).

The potential of VOCs to cause pollution of groundwater quality in concern of public health is significant in areas where groundwater is used as a primary source of drinking water (Exner *et al*., 2007; Hohener *et al*., 2003). The USEPA has established the maximum permissible level of VOCs in drinking water that is of concern to human health as given in Table 5.

2. Methods and Models of Analysis of VOCs

In the last few decades, the detection of VOCs in water samples is one of the most important tasks in environmental monitoring. There are various technologies that have been developed for the detection and analysis of VOCs. USEPA Method 524.2 uses purge and trap extraction system followed by gas chromatography/mass spectrometry (GC/MS) (Eichelberger *et al*., 1989) for the analysis of VOCs in water. Besides, other techniques that have been used for analysis of VOCs are gas chromatography (GC), mass spectroscopy, head space-solid phase micro extraction followed by gas chromatography (SPME/GC/HS) quantification (Mieure, 1980; Wylie, 1988), the surface acoustic wave (SAW), ion mobility spectrometry (IMS), photo-ionization detector (PID) (Ho *et al*., 2001). GC and GC/MS have greater sensitivity and detection limit (ppb) compared to other techniques for VOCs (Archbold, 2005; Schellin and Popp, 2006). The process of collecting groundwater sample is time-consuming and labour intensive and off-site laboratory analysis of samples is the major limitation of these techniques. However, advanced technologies do not require sample collection and off-site laboratory analysis which reduces the analysis errors. Apart from these, graphene sensor is used to analyze the nature and content of VOCs released by packaged food (Sundramoorthy and Gunasekaran, 2014). The sensors and automated systems for sampling and

Table 2: Factors associated with VOCs in groundwater (Moran *et al*., 2006).

Source type	Geology	Thickness of unsaturated zone	Reference
Landfill leachate and gas flume	Fine to medium coastal sand	10-40	Barber *et al*. (1992)
Landfill leachate and gas plume	Sand and gravel	10	Ward *et al*. (1996)
Crude oil LNAPL releases	Glacial outwash	6	Molins *et al*. (2010)
CAH chemical waste disposed to quarry pit	Triassic sandstone	75	Lawrence *et al*. (2006)
Chemical waste landfill incl. VOCs (TCE)	Alluvial sediments	150	Peterson *et al*. (2000)
CT/CAHs wastewater and DNAPL releases	Gravel, sand, silt and carbonate	Up to >100	Oostrom *et al*. (2007)
CT/CAHs wastewater and DNAPL releases	Sand, silty sand, thin clay	10	Kirtland *et al*. (2003)
TCE wastewater pond and DNAPL releases	Sand and gravel	2-4	Choi *et al*. (2002)
Petrol-injected LNAPL	Coastal sands	10	Barber and Davis (1991)
BTEX aqueous-phase infiltration	Fine-medium sand	3-4	O'Leary *et al*. (1995)
T,X aqueous-phase infiltration	Fine, coarse sands	3.5	Søvik *et al*. (2002)
Jet fuel-emplaced LNAPL	Sand	3	Christophersen *et al*. (2005)
Kerosene-injected LNAPL	Sandy loam	> 1	Dror *et al*. (2001)
TCE emplaced DNAPL	Fine-medium sand	3-4	Conant *et al*. (1996)
TCE emplaced DNAPL	Sand and pea gravel	4.5	Johnson *et al*. (1992)
TCE/PCE emplaced DNAPL	Sand	2	Jellali *et al*. (2003)

Table 3: Transport of VOCs in the unsaturated zone (Rivett *et al*., 2011).

Source factors	Transport factors	Fate factors	Indeterminate
Septic system	Climatic condition	Dissolve oxygen concentration ($\leq$ 5 mg L^{-1})	Type of well
Urban land	Depth to top of well screen	-	-
RCRA hazardous waste facilities	Hydric (anoxic) soils	-	-
Gasoline underground storage tank	-	-	-
Leaking underground storage tank sites	-	-	-

Table 4: VOCs detected in groundwater (Moran *et al.*, 2004). MCL=Maximum Contamination Level; HC=Hydrocarbon.

VOCs	Predominant use	Detected concentrations (µg L^{-1})		MCL (µg L^{-1})
		Minimum	Maximum	
1,2-Dibromoethane	Fumigant	0.3	1.1	0.05
1,4-Dichlorobenzene	Fumigant	1.2	1.2	75
Benzene	Gasoline HC	0.2	4.4	5.0
Ethylbenzene	Gasoline HC	0.2	5.4	700
Naphthalene	Gasoline HC	1.8	2.5	20
1,2,4-Trimethylbenzene	Gasoline HC	0.2	12	-
Chloroethene	Organic Synthesis	0.4	0.4	2.0
(1-Methylethyl) benzene	Organic Synthesis	0.4	0.8	23.3
Chloromethane	Solvent	1.1	2.5	3.0
Trichlorofluoromethane	Refrigerant	0.2	1.9	2000
Chlorobenzene	Solvent	3.5	3.5	100
Chloroethane	Solvent	0.3	0.7	-
1,1-Dichloroethane	Solvent	0.2	1.7	-
1,2-Dichloroethane	Solvent	0.2	2.9	5.0
Cis-1,2-Dichloroethene	Solvent	3.0	4.4	70
Trans-1,2-Dichloroethene	Solvent	0.4	0.4	100
Dichloromethane	Solvent	0.2	4.0	5.0
1,2-Dichloropropane	Fumigant	0.2	19	5.0
Tetrachloromethane	Solvent	0.2	0.6	5.0
Trichloroethene (TCE)	Solvent	0.2	25	5.0
1,2,3-Trichloropropane	Fumigant	0.2	2.1	40
Bromodichloromethane	Trihalomethane	0.2	7.0	80
Chlorobromomethane	Trihalomethane	0.3	11	80
Tribromomethane	Trihalomethane	0.3	8.2	80
1,2-Dibromo-3-chloropropane	Fumigant	0.2	3.2	0.2
Methylbenzene (toluene)	Gasoline HC	0.2	12	1000
Dichlorodifluromethane	Refrigerant	0.2	2.0	1000
Tetrachloroethene (PCE)	Solvent	0.2	29	5.0
1,1,1-Trichloroethane	Solvent	0.2	120	200
Chloroform	Trihalomethane	0.2	74	80

analysis of VOCs in groundwater are given in Table 6.

Mechanistic models for prediction of VOCs emissions from various sources have been reported in various studies as given in Table 7.

3. Microbial Decomposition of VOCs

In groundwater flow system (aquifer), VOCs are mobile and do not quickly get degraded (Jeffers *et al*., 1989; McNab and Narasimhan, 1994). However, degradation of VOCs parent compounds into various daughter compounds is common in highly contaminated groundwater system (Barrio-Lage *et al*., 1986; Gupta *et al*., 1996; Dinicola *et al*., 2000; Davis *et al*., 2009; Adhikari *et al*., 2012).

The biodegradation of VOCs can occur in aerobic or anaerobic groundwater condition. The rate of biodegradation of VOCs in aerobic condition is higher than anaerobic condition (Suarez and Rifai, 1999). The presence of dissolved oxygen can affect the occurrence and biodegradation of VOCs in groundwater because oxygen is an electron acceptor which is favoured by the microorganism in their respiration and degradation of organic compounds (Pasteris *et al*., 2002; Rockne and Reddy, 2003).

Table 5: Maximum contaminant level of VOCs in drinking water in concerns of human health (Acrylamide, 1995).

VOCs	Maximum contaminant limit (MCL) (mg L^{-1})	Health Effect	Source of contaminant in drinking water
Benzene	0.005	Anemia, decrease in blood platelets, increased risk of cancer	Discharge from factories, leaching from gas storage tanks and landfills
Carbon tetrachloride	0.005	Liver problems, increased risk of cancer	Discharge from chemical plants and other industrial activities
Chlorobenzene	0.1	Liver or kidney problems	Discharge from chemical and agricultural chemical factories
Ortho-dichlorobenzene	0.6	Liver, kidney, or circulatory system problems	Discharge from industrial chemical factories
Para-dichlorobenzene	0.075	Anemia, liver, kidney or spleen damage, changes in blood	Discharge from industrial chemical factories
1,2-Dichloroethane (1,2-DCA)	0.005	Increased risk of cancer	Discharge from industrial chemical factories
1,1-Dichloroethylene (1,1-DCE)	0.007	Liver problems	Discharge from industrial chemical factories
1,2-Dichloropropane (1,2-DCP)	0.005	Increased risk of cancer	Discharge from industrial chemical factories
Xylene	10.0	Nervous system damage	Discharge from petroleum and chemical factories
Ethylbenzene	0.7	Liver or kidneys problems	Discharge from petroleum refineries
Styrene	0.1	Liver, kidney, or circulatory system problems	Discharge from rubber and plastic factories, leaching from landfills
Tetrachloroethylene (PCE)	0.005	Liver problems, increased risk of cancer	Discharge from factories and dry cleaners
Tolune	1.0	Nervous system, kidney, or liver problems	Discharge from petroleum factories
1,2,4-Trichlorobenzene (1,2,4-TCB)	0.07	Changes in adrenal glands	Discharge from textile finishing Factories
1,1,1-Trichloroethane (1,1,1-TCA)	0.20	Liver, nervous system, or circulatory problems	Discharge from metal degreasing sites and other factories
1,1,2-Trichloroethane (1,1,2-TCE)	0.005	Liver, kidney, or immune system problems	Discharge from industrial chemical Factories
Trichloroethylene	0.005	Liver problems, increased risk of cancer	Discharge from metal degreasing sites and other factories
Vinyl chloride	10.0	Nervous system damage	Discharge from petroleum factories, discharge from chemical factories
cis-1,2-Dichloroethylene (1,2-DCE)	0.07	Liver problems	Discharge from industrial chemical factories
trans-1,2-Dichloroethylene (1,2-DCE)	0.1	Liver problems	Discharge from industrial chemical factories
Dichloromethane (DCM)	0.005	Liver problems, increased risk of cancer	Discharge from drug and chemical factories

Tetrachloroethylene is subsequently decomposed to vinyl chloride via several intermediate products in anaerobic condition as trichloroethylene cis-1,2 dichloroethylene and then these intermediate products get decomposed to ethylene (Bolesch *et al*., 1997; Distefano *et al*., 1991; Wild and Jones, 1995). Under anaerobic conditions, vinyl chloride gets biodegraded into methane and CO2 via ethylene and HCl as intermediate products (Freedman and Gossett, 1989). However, the reaction velocity of the higher chlorinated compounds such as tetrachloroethylene is faster than the reaction speed of lower chlorinated compound such as vinyl chloride in groundwater aquifer (Wittsiepe *et al*., 1993). The microbial biodegradation rate is influenced by temperature, pH, concentration and type of microorganisms in the underground and substratum level, availability of nutrients and electron acceptors (Mackay *et al*., 1985).

4. Remediation of VOCs

It is important to understand the behaviour of VOCs in the environment before effective treatment. Various remediation technologies have been used for the removal and decomposition of VOCs from contaminated water, air and soil medium over several decades including pump and treat air stripping (Gorelick and Gvirtzman, 1993; Miller, 1996; Suthersan, 1999), adsorption (Amy *et al*., 1987; Davidson and Parsons, 1996; Pankow and Cherry, 1996), in situ air stripping (Brown and Fraxedas, 1991; Johnson *et al*., 1993; Reddy *et al*., 1995; Bausmith *et al*., 1996; Suthersan, 1999), air stripping with centrifugal vapour-liquid contactor (Singh, 1989), membrane assisted solvent extraction (Hutter *et al*., 1994) and rotary air stripper (Singh *et al*., 1992). These conventional techniques have some limitations such as generation of undesirable by-product and transfer of contaminants from one phase

Table 6: In-situ sensors and automated systems for sampling and analysis of VOCs in groundwater (Ho *et al*., 2001; USEPA, 2003).

Technology	Selectivity/Sensitivity	Current focus
Chemi resistors	TCE at 1000 ug L^{-1}	Heating element to be added reduce effect from humidity
Quartz Crystal Microbalances (QCMs)	TCE at 50 ug L^{-1}	Initial field testing
High Resolution Ion Mobility Spectrometer (IMS)	Sensitivity is expected to be sufficient to meet MCL for multiple contaminants in a single sample	Prototype development
Resonance Enhanced Multiphoton Ionization (REMPI)	BTEX at 1 ug L^{-1}	Bench testing with various lasers
Wave guides and interferometry	Sensor provides VOC detection at the 50 to 100 µg L^{-1}	Field testing
Mid-Infrared Fiberoptic Sensors	Chlorinated compounds at or below 100 µg L^{-1}	Increasing sensitivity, further miniaturizing probe and extending the lifetime of the adsorbent polymers
UV-Induced Fluorescence Spectroscopy	Unknown	Unknown
Scott Burge	TCE as low as 1 µg L^{-1}	Continue improving valves
Geoff Borton	Measures the cumulative concentration of all VOCs present to a total concentration of approximately 100 µg L^{-1} and higher	Broadening the range of detection
ChemLabTM	Detect multiple contaminants (BTEX and chlorinated solvents) in a single sample	Water analysis for municipal water supplies
Hand-Held GC	Detect multiple contaminants (BTEX and chlorinated solvents) in a single sample	Water analysis
zNoseTM	Detect multiple VOCs including BTEX and chlorinated compounds	Best suited for routine monitoring of water samples contaminated with relatively few chlorinated VOCs
HAPSITE	Detect VOCs including BTEX and chlorinated compounds	Provide useful, cost- effective data for environmental site characterization and routine monitoring under appropriate application
Type 1312 Multi-gas Monitor InnovaAirTech Instruments	Detect up to five VOCs including TCE and PCE	Provide useful, cost- effective data for groundwater monitoring when the composition of the sample is known
PhotovacVoyger	Detect multiple VOCs including TCE and PCE	Sample handling and methodologies may have adversely affected the observed precision and accuracy of the instrument

to another. Because of these limitations of the conventional process, the alternative processes for VOCs removal have to be explored that are capable of avoiding the problem of conventional processes. The conventional techniques are classified into non-destructive and destructive methods. In the non-destructive method, the nature of VOCs does not change due to use of physico-chemical properties of these compounds in their removal example- air stripping and adsorption methods (Wei and Seo, 2010). However, the nature of these compounds changes by breaking the bond between them in the destructive method. In the destructive process, VOCs can be decomposed by phytoremediation and biodegradation methods. They can also be broken down by chemical reaction such as Fenton oxidation, zero metal reaction, and by using energetic process like thermal incineration, photocatalytic oxidation and electrochemical oxidation and reduction approaches given in Table 8 (Tsai *et al*., 2009; Randazzo *et al*., 2011; Huang *et al*., 2012; Justicia-Leon *et al*., 2014).

Williams (2002) reported the phytoremediation of VOCs by using the plants and sediments of wetland. Limmer and Burken (2016) reported the phyto-volatilization of VOCs. They differentiated the direct and indirect process of phyto-volatilization and plant physiology implementing phyto-volatilization in different ecosystems. Among these techniques, air stripping is a standard method successfully employed for VOCs remediation in groundwater. Mahmud *et al*. (1998) used membrane air stripping for a broad range of VOCs from groundwater and petroleum wastewater. The advantages of membrane air stripping over other types of air stripping process include negligible loading and flooding limitations, reduction of back mixing, high surface to volume ratio and reduced scaling problem. However, adsorption process is less efficient, especially when the concentration of VOCs is greater. Treatment of large quantity of water containing VOCs via membrane technology seems to be expensive and cannot be used at a large scale. However, Lelinski and Miller (1996) while studying the removal of VOCs from contaminated water by air-sparged hydro cyclone (ASH) stripping technology suggested removal efficiency of 90%, which was more than 100 times of conventional air stripping technology. The performance of permeable reactive barrier (PRB) used in remediation of dissolved chlorinated solvent in groundwater was evaluated by Vogan *et al*. (1999). A pilot-scale permeable reactive barrier consisting of granular iron at an industrial facility in New York in 1995 was installed. It was found that the rate of degradation of VOCs was similar to those anticipated from laboratory results. Based on the performance of this pilot-scale PRB, a full-scale iron PRB was installed at that site in 1997. Activated

Table 7: Models for VOCs Emission from Different Sources.

S.N.	Model	Emission source	Reference
1.	Numerical solution using Computational Fluid Dynamics (CFD) and solved by a combination	Solid	Yang *et al*. (2001a)
2.	Numerical solution using CFD	Solid and Liquid	Yang *et al*. (2001b)
3.	Fully analytical solution of C(x, t), E(t) and y(t) assuming that y is much smaller than y0 which is not always applicable	Solid	Huang and Haghighat (2002)
4.	Numerical solution using finite difference method	Solid and Liquid	Haghighat and Huang (2003)
5.	Numerical solution using CFD	Solid	Murakami *et al*. (2003)
6.	Numerical solution using single-zone method	Solid	Zhang and Niu (2004)
7.	multi-phase model	Solids	Lee *et al*. (2005)
8.	Numerical solution using implicit finite volume method	Liquid	Li *et al*. (2006)
9.	Fully analytical solution of C(x, t), E(t) and y(t)	Solid	Kumar and Little (2003)
10.	Numerical solution using CFD	Solid	Deng and Kim (2007)
11.	Numerical solution using single-zone method	Solid	Li and Niu (2007)
12.	Macro and meso two-scale model	Solid	Xiong *et al*. (2008)
13.	Vapor pressure and boundary layer (VB) model	Liquid	Tichenor *et al*. (1993)
14.	Numerical solution with high computational complexity	Liquid	Altinkaya (2009)

Table 8: Physico-chemical Techniques for Remediation of VOCs.

Methods	VOCs	Reaction Condition	Efficiency (%)	Advantage	Disadvantage	Reference
Biodegradation	CF, DCM	Anaerobic conditions	100	Low cost and in site remediation	Slow process	Justicia-Leon *et al*. (2014)
Phytoremediation	CT	Poplar	99	Economics, aesthetic and ecologic advantages	Time consuming and incomplete metabolism	Wang *et al*. (2004)
Adsorption	TCE, PCE	Granular activated carbon	90	Fast removal efficiency and recovery of pollutants	Further disposal of adsorbents	Ahmad *et al*. (2013)
Air Stripping	TCE, DCE, DCA	Packed tower	96	Fast removal efficiency	Nature of contaminants does not change	Li *et al*. (2012)
Thermal Incineration	TCE, DCM	Fixed-bed reactor	99	Efficient destruction within short time	Potential formation of highly toxic by-products	Tseng *et al*. (2003)
Photocatalytic oxidation	TCE	Gas conditions gas flow 200 mL/min	100	Fast and high efficacy	High energy consumption	Yokosuka *et al*. (2009)
Ozonation	TCE	Contaminated soil	100	Effective and fast removal of contaminants	Low solubility of ozone in water	Alcantara-Garduno *et al*. (2008)
Fenton oxidation	TCE	TCE-contaminated groundwater	87	Simplicity and efficiency;	Costly chemical addition, acidic conditions	Tsai *et al*. (2009)
Electrochemical oxidation	DCA	Sealed undivided tank	99	Environmental compatibility and high efficiency	Energy consumption	Scialdone *et al*. (2008)
Zero valent reduction	TCE	Performed in amber glass vials	44	Thermodynamically favourable	Relatively slow reaction rate	Zhang *et al*. (2011)
Catalytic hydrodechlorination	PCE	Continuous flow tubular reactor	100	Thermodynamically favorable	Catalyst passivation problems	Willinger *et al*. (2009)
Electrochemical dechlorination	PCA	Divided cell	100	Fast and high efficacy	Energy consumption	Huang *et al*. (2012)
Electrostatic precipitation	VOC	Electronic waste	95.7	Effective and fast removal of contaminants	Energy consumption	Chen *et al*. (2016)

carbon fiber for adsorption of the chlorinated VOCs from groundwater was used by Urano *et al*. (1991), Yu and Chou (2000). Groundwater samples containing activated carbon fiber were pumped through vessels and it was observed that VOCs were adsorbed on activated carbon fiber and removed from groundwater. Apart from these, various techniques like sprinkler irrigation (Richardson and Sahle-Dimessie, 1998), granular activated carbon treatment (Shih *et al*., 2003), reverse osmosis and nanofiltration have also been employed (Altalyan *et al*., 2016).

5. Conclusion

The detection and analysis of VOCs in groundwater is a challenge due to the difficulties involved in their sampling and analysis. These VOCs are transported in groundwater from leakage area and fractured rock aquifers. US-EPA method 524.2, GC/MS, IMS, PID and in-situ sensor technologies are used for the detection of VOCs in water. The biodegradation of VOCs occurs in groundwater which transforms the most toxic VOCs into their less toxic derivatives. US-EPA has reported the maximum contamination limit of VOCs in groundwater in the range of 0.005 to 10 mg L^{-1}. The presence of VOCs above their maximum contamination level causes adverse health effects on human health. The most common techniques used for the removal of VOCs from groundwater are air stripping and in-situ remediation. In the Indian context, there is a need for further research to make clear strategies for controlling the emission and health risk of VOCs from various sources as storage tanks, underground tanks, etc. The present paper has attempted to critically review the sources, health effects and mitigation strategies to safeguard humans from VOCs exposure. Screening of the exposed population for health risk should be done periodically coupled with sound medical management at different levels. Strengthening of community programs about the safe practices of waste disposal and indoor air pollution can minimize the risks of intentional and unintentional VOCs contamination.

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