



## Review

# Chlorinated volatile organic compounds (Cl-VOCs) in environment – sources, potential human health impacts, and current remediation technologies

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## ARTICLE INFO

## Article history:

Received 30 October 2013

Accepted 24 June 2014

Available online xxxx

## Keywords:

Chlorinated volatile organic compounds

(Cl-VOCs)

Sources

Health impacts

Carcinogenicity

Remediation technologies

## ABSTRACT

Chlorinated volatile organic compounds (Cl-VOCs), including polychloromethanes, polychloroethanes and polychloroethylenes, are widely used as solvents, degreasing agents and a variety of commercial products. These compounds belong to a group of ubiquitous contaminants that can be found in contaminated soil, air and any kind of fluvial mediums such as groundwater, rivers and lakes. This review presents a summary of the research concerning the production levels and sources of Cl-VOCs, their potential impacts on human health as well as state-of-the-art remediation technologies. Important sources of Cl-VOCs principally include the emissions from industrial processes, the consumption of Cl-VOC-containing products, the disinfection process, as well as improper storage and disposal methods. Human exposure to Cl-VOCs can occur through different routes, including ingestion, inhalation and dermal contact. The toxicological impacts of these compounds have been carefully assessed, and the results demonstrate the potential associations of cancer incidence with exposure to Cl-VOCs. Most Cl-VOCs thus have been listed as priority pollutants by the Ministry of Environmental Protection (MEP) of China, Environmental Protection Agency of the U.S. (U.S. EPA) and European Commission (EC), and are under close monitor and strict control. Yet, more efforts will be put into the epidemiological studies for the risk of human exposure to Cl-VOCs and the exposure level measurements in contaminated sites in the future. State-of-the-art remediation technologies for Cl-VOCs employ non-destructive methods and destructive methods (e.g. thermal incineration, phytoremediation, biodegradation, advanced oxidation processes (AOPs) and reductive dechlorination), whose advantages, drawbacks and future developments are thoroughly discussed in the later sections.

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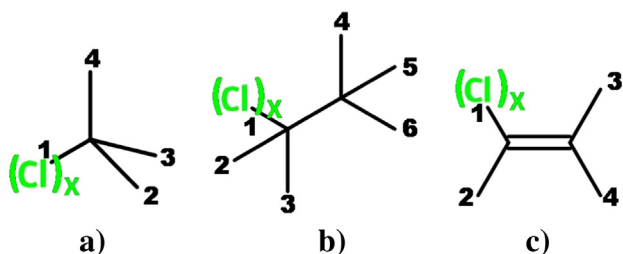
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## 1. Introduction

Chlorinated volatile organic compounds (Cl-VOCs, as shown in Fig. 1), including polychloromethanes (PCMs), polychloroethanes (PCAs) and polychloroethylenes (PCEs), are a group of ubiquitous contaminants that have been widely detected in environment media in recent years (Justicia-Leon et al., 2014; Krol et al., 2003; Li et al., 2013; Moran et al., 2007; Pecoraino et al., 2008; Siegrist et al., 2001). These compounds possess high volatility and strong recalcitrance to degradation, for instance, the atmosphere lifetime of carbon tetrachloride (CTC) and 1,1,1-trichloroethane (1,1,1-TCA) could reach as high as 100 and 6 years, respectively (ATSDR, 2005), allowing them to be transported over long distances in different environment media once released, as shown in Fig. 2. Most Cl-VOCs are colorless liquids with a special sweet smell at room temperature, while some are gas (chloromethane, chloroethane and chloroethylene) and solid (hexachloroethane), as shown in Table 1.

Cl-VOCs have been introduced into environment media due to human activities since the beginning of 20th century. They have been widely used as solvents for processes such as metal degreasing and dry cleaning, and for the production of pharmaceuticals, pesticides, adhesives and refrigerants, thus playing an essential role in the industrial development and daily life of individuals over the past several decades (Doherty, 2000a,b; U.S. EPA, 1980).

Inadvertent releases of Cl-VOCs into environment often occur during the production, consumption of Cl-VOCs-containing products and improper disposal methods over the past decades, resulting in their wide distribution in the environment (Beamer et al., 2012; Hunkeler et al., 2012; Moran et al., 2007; Scheutz et al., 2011; Siegrist et al., 2001).



**Fig. 1.** Chemical structures of Cl-VOCs (a) PCMs ( $\text{CH}_{4-x}\text{Cl}_x$ ;  $x = 1-4$ ); (b) PCAs ( $\text{C}_2\text{H}_{6-x}\text{Cl}_x$ ;  $x = 1-6$ ); (c) PCEs ( $\text{C}_2\text{H}_{4-x}\text{Cl}_x$ ;  $x = 1-4$ ). **Acronyms:** PCMs, polychloromethanes; PCAs, polychloroethanes; PCEs, polychloroethylenes; CM, chloromethane; DCM, dichloromethane; CF, chloroform; CTC, carbon tetrachloride; CA, chloroethane; 1,1-DCA, 1,1-dichloroethane; 1,2-DCA, 1,2-dichloroethane; 1,1,1-TCA, 1,1,1-trichloroethane; 1,1,2-TCA, 1,1,2-trichloroethane; 1,1,1,2-TeCA, 1,1,1,2-tetrachloroethane; 1,1,2,2-TeCA, 1,1,2,2-tetrachloroethane; PCA, pentachloroethane; HCA, hexachloroethane; CE, chloroethylene; 1,1-DCE, 1,1-dichloroethylene; 1,2-DCE, 1,2-dichloroethylene; TCE, trichloroethylene; PCE, perchloroethylene.

Another cause of Cl-VOCs contamination is chlorination, one of the most prevalent methods for water disinfection. Chlorine reacts with natural organic matters in water to form large amounts of disinfection by-products (DBPs), among which, chlorinated methanes like chloroform (CF) are the most abundant (U.S. EPA, 2005; Hunkeler et al., 2012; Lourencetti et al., 2012; Zeng et al., 2013). All these factors thus have made Cl-VOCs the ubiquitous contaminants subsisted in soil, air and any kind of fluvial mediums, such as groundwater, rivers, and lakes (Krol et al., 2003; Moran et al., 2007; Pecoraino et al., 2008). For instance, there are thousands of sites contaminated by chlorinated organic solvents throughout the U.S. (Moran et al., 2007). In China, Cl-VOCs are found to be one of the most frequently detected volatile pollutants in soil, atmosphere, and groundwater of Beijing–Tianjin–Tangshan area, Yangtze River Delta area and Pearl River Delta area (He et al., 2013; Kranzioch et al., 2013; Shao et al., 2011; Song et al., 2012; Zhang et al., 2014).

Due to the presence of Cl-VOCs in many consumer products, human exposure to Cl-VOCs may be frequent via different routes. People are exposed to Cl-VOCs-contaminated water through drinking, swimming, bathing, showering, food or laundering. The high volatility of Cl-VOCs makes inhalation an easy way to enter the human body. Yet, the relative importance of ingestion, dermal absorption as well as inhalation has not been clearly classified (Thiriat et al., 2009). There are already epidemiologic studies showing the association between CF exposure and the elevated risk of cancers such as bladder, rectum and colon cancer (Lourencetti et al., 2012; Thiriat et al., 2009). Recent epidemiologic studies have also suggested the link between adverse reproductive outcomes (e.g. spontaneous abortion, low birth weight and birth defects) and CF exposure (Yang et al., 2007; Zeng et al., 2013). Furthermore, some epidemiological evidences confirmed the link between increased rates of esophageal cancer, cervical cancer and non-Hodgkin's lymphoma and tetrachloroethylene (PCE) exposure; the link between liver cancer, biliary cancer and non-Hodgkin's lymphoma and trichloroethylene (TCE) exposure; and the link between lymphohematopoietic malignancies and carbon tetrachloride (CTC) exposure (Lyng et al., 1997; Malaguarnera et al., 2012; Scott and Jinot, 2011). Due to their potential carcinogenic effects on people, some of Cl-VOCs have thus been listed as priority pollutants by the Ministry of Environmental Protection (MEP) of China, Environment Protection Agency of the U.S. (U.S. EPA) and European Commission (EC), and are under strict monitor and control (European Commission, 2008; MEP of China, 2009c; U.S. EPA, 1981). Therefore, the development of effective technologies for the removal of Cl-VOCs from contaminated sites has attracted tremendous attention worldwide in recent years.

Different remediation approaches, including thermal incineration (Lin et al., 2003; Tseng et al., 2003), biodegradation (Gander et al., 2002; Grostern and Edwards, 2006), phytoremediation (Wang et al., 2004; Aken, 2008), physical adsorption (Wei and Seo, 2010; Yang

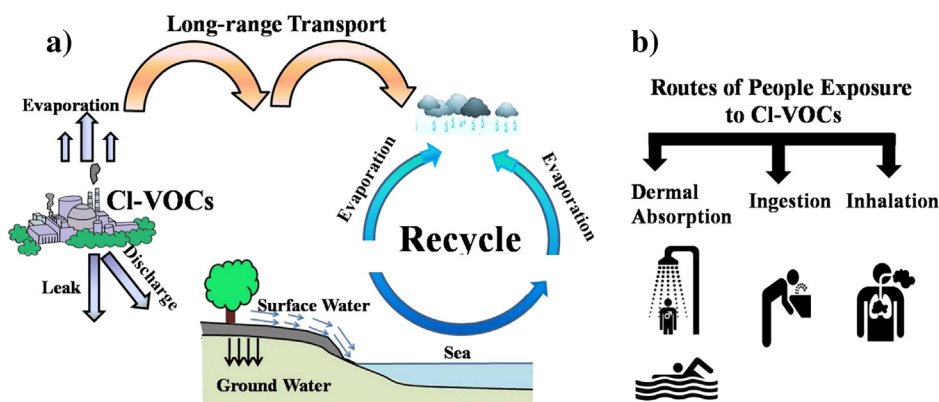


Fig. 2. A schematic representation of the fate for CI-VOCs releasing into environment (a); and the primary routes of human exposure to CI-VOCs (b).

et al., 2007), thermal incineration (Lin et al., 2003; Tseng et al., 2003), advanced oxidation processes (AOPs) like photocatalytic oxidation (Borisch et al., 2004; Zuo et al., 2006), Fenton oxidation methods (Tsai et al., 2010; Vilve et al., 2010), and reductive dechlorination methods, such as zero valent reduction (He et al., 2010; Zhang et al., 2011), catalytic dehydrochlorination (McNab and Ruiz, 2000; Orbay et al., 2008) as well as electrochemical dechlorination method (Huang et al., 2012; Li and Farrell, 2001), have been explored for the removal of CI-VOCs from contaminated sites. Although these methods are effective for CI-VOCs degradation, each has its advantages and limitations, which will be covered in the later sections.

While the previous studies (Bukowski, 2011; Cappelletti et al., 2012; Doherty, 2000a,b; Green, 1990; McCulloch, 2003; Suttinun et al., 2013) have provided a wealth of data on the production levels, sources, human health impacts, and remediation methods toward CI-VOCs, an integrated knowledge from individual researches is still missing. A literature review on CI-VOCs will be beneficial to help environmental research and regulatory bodies to have better understanding of the issues. Furthermore, it may further attract researchers' attention and motivate them to conduct studies on the impacts of CI-VOCs on environment and human health, as well as the remediation technologies. The objectives of this review are to consider chloromethanes, chloroethanes, and chloroethylenes as a whole and to summarize the results regarding the production levels, important sources and their potential human health impacts as well as state-of-the-art current remediation approaches of CI-VOCs, so as to provide a comprehensive review of CI-VOC contaminations in China, U.S. and Europe.

## 2. Properties, sources and health impacts to human

CI-VOCs are a group of volatile compounds widely used in human activities and have strong resistance to biodegradation, as a result, they are frequently detected in the environment. Their physicochemical properties are shown in Table 1. The main sources of CI-VOCs contamination are the emissions from the manufacture of CI-VOCs-containing products, the uses of such products, the disinfection process as well as the improper storage and disposal methods, which result in CI-VOCs being discharged into the environment, as shown in Fig. 3. The relative importance of contributors to environment contamination is mainly determined by the geographical distributions of source types, source strengths, local productions and degradations, and seasonality of CI-VOCs. Human exposure to CI-VOCs may occur through different routes, such as the inhalation of ambient air, ingestion of drinking water or food, dermal absorption during bathing or swimming. A schematic presentation of the fate for these compounds and their principally routes of human exposure is displayed in Fig. 2. The toxicological impacts of CI-VOCs demonstrate that they are potential human carcinogens; some of CI-VOCs thus have been listed as priority pollutants by MEP of China, U.S. EPA and EC, and are under strict monitor and control.

### 2.1. Chlorinated methanes

Polychloromethanes or chlorinated methanes (PCMs), are a group of analogous compounds where at least one hydrogen atom in methane is substituted by chlorine, as shown in Fig. 1(a). Except for CM which is a gas at room temperature, other PCMs are colorless volatile liquids with very poor water solubility. They share the common properties of high stability, high volatility, low flammability and high solvent capacity, and thus are widely used in the chemical industry as solvents, dry cleaners, degreasing agents, adhesive components, intermediates in the synthetic industry, etc. (Martin-Martinez et al., 2013). More physicochemical properties of PCMs are given in Table 1.

Large amounts of PCMs are released into the environment through either water discharges or evaporation into atmosphere (Hunkeler et al., 2012). Besides their contributions to global warming, depletion of ozone layer and formation of photochemical smog, PCMs are found to possess high toxicity and carcinogenic characteristic towards human (Martin-Martinez et al., 2013). Therefore, PCMs are classified among the most hazardous atmospheric pollutants nowadays (Álvarez-Montero et al., 2010). In particular, dichloromethane (DCM) and CF are included in the list of 17 highly dangerous chemicals targeted in the emissions reduction effort (33/50 program) of the U.S. EPA (Álvarez-Montero et al., 2011; U.S. EPA, 1999a). Due to their potential detrimental effects on both environment and human health, DCM, CF and CTC have been listed as priority pollutants by U.S. EPA (U.S. EPA, 1981), appear in the blacklist of pollutants in water by MEP of China (MEP of China, 2009c), and are among the 33 priority substances issued by EC except CTC, but the environmental quality standard for CTC is also included in the Environmental Quality Standards Directive 2008/105/EC (European Commission, 2008).

#### 2.1.1. Chloroform

CF is a heavy volatile liquid that slightly dissolves in water. It is a common solvent because of its relatively unreactive nature and miscibility with most organic solvents. For example, CF was once widely used as a surgical anesthetic and in cough syrups as well as in toothpastes (Cappelletti et al., 2012). Its use in consumer products was banned in 1976 by the U.S. Food and Drug Administration (FDA) as CF was found to be carcinogenic in animal tests (Cappelletti et al., 2012; Rosenthal, 1987). Nowadays, CF is primarily used as a solvent in pharmaceutical industry and as an important raw material for producing dyes, pesticides, chlorodifluoromethane (HCFC-22) (Cappelletti et al., 2012). CF also serves as a source of producing dichlorocarbene applied in organic synthesis industry. In addition, it is also added in pesticide formulations, as a solvent for fats, oils, rubber, alkaloids, waxes, gutta-percha, and resins as a cleansing agent, in fire extinguishers, as well as in the rubber industry (Cappelletti et al., 2012). CF was mainly produced in U.S., European Union and Japan, and the total global annual

**Table 1**  
Physicochemical properties of Cl-VOCs and their toxicological clarifications.<sup>a</sup>

Substrate	Abbreviation	Molecular Formula	CAS Number	Appearance	Density (g/cm <sup>3</sup> )	Melting Point (°C)	Boiling Point (°C)	Solubility in water (g/L)	<i>n</i> -Octanol–water partition coefficient (log <i>P</i> <sub>ow</sub> )	Vapor Pressure at 20 °C (kPa)	Occupational exposure limits <sup>b</sup>	Carcinogenicity <sup>d</sup>	Priority Pollutant <sup>e</sup>
<b>Polychloromethanes</b>	<b>PCMs</b>												
chloromethane	CM	CH <sub>3</sub> Cl	74-87-3	Colorless gas	2.306 (0 °C)	−97.4	−23.8	5.325 (25 °C)	0.91	506.09	50 ppm	Group 3	N
dichloromethane	DCM	CH <sub>2</sub> Cl <sub>2</sub>	75-09-2	Colorless liquid	1.322 (20 °C)	−96.7	39.6	13.0 (20 °C)	1.25	47.0	50 ppm	Group 2B	Y (U.S. EPA, MEP of China, EC)
chloroform	CF	CHCl <sub>3</sub>	67-66-3	Colorless liquid	1.483 (20 °C)	−63.5	61.2	8.0 (20 °C)	1.97	21.0861	10 ppm	Group 2B	Y (U.S. EPA, MEP of China, EC)
carbon tetrachloride	CTC	CCl <sub>4</sub>	56-23-5	Colorless liquid	1.5867 (20 °C)	−22.92	76.72	0.785 (25 °C)	2.64	11.94	5 ppm	Group 2B	Y (U.S. EPA, MEP of China)
<b>Polychloroethanes</b>	<b>PCAs</b>												
chloroethane	CA	C <sub>2</sub> H <sub>5</sub> Cl	75-00-3	Colorless gas	0.906 (12.2 °C)	−139.0	12.3	5.74 (20 °C)	1.54	133.3	100 ppm	Group 3	N
1,1-dichloroethane	1,1-DCA	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	75-34-3	Colorless liquid	1.174 (20 °C)	−97	57.2	6.0 (20 °C)	1.8	24.0	100 ppm	N	Y (U.S. EPA)
1,2-dichloroethane	1,2-DCA	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	107-06-2	Colorless liquid	1.253 (20 °C)	−35.0	84.0	8.7 (20 °C)	1.48	8.7	10 ppm	Group 2B	Y (U.S. EPA, MEP of China, EC)
1,1,1-trichloroethane	1,1,1-TCA	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	71-55-6	Colorless liquid	1.31 (20 °C)	−33.0	74.0	<1 (20 °C)	2.49	13.3	350 ppm	Group 3	Y (U.S. EPA, MEP of China)
1,1,2-trichloroethane	1,1,2-TCA	C <sub>2</sub> H <sub>3</sub> Cl <sub>3</sub>	79-00-5	Colorless liquid	1.435 (20 °C)	−37.0	114.0	4.5 (20 °C)	2.35	2.5	10 ppm	Group 3	Y (U.S. EPA, MEP of China)
1,1,1,2-tetrachloroethane	1,1,1,2-TeCA	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	630-20-6	Colorless liquid	1.5406 (20 °C)	−70.2	130.5	1.1 (25 °C)	2.66	1.9	NOT ESTABLISHED	Group 2B	N
1,1,2,2-tetrachloroethane	1,1,2,2-TeCA	C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub>	79-34-5	Colorless liquid	1.595 (20 °C)	−44.0	146.5	2.857 (20 °C)	2.39	0.647	1 ppm	Group 3	Y (U.S. EPA, MEP of China)
pentachloroethane	PCA	C <sub>2</sub> HCl <sub>5</sub>	76-01-7	Colorless liquid	1.6728 (25 °C)	−29.0	162.0	<0.1 (25 °C)	3.67	0.453	MAK <sup>f</sup> : 5 ppm	Group 3	N
hexachloroethane	HCA	C <sub>2</sub> Cl <sub>6</sub>	67-72-1	Crystal solid	2.091 (20 °C)	183–185	186.78	<1.0 (21 °C)	3.9	0.053	1 ppm	Group 2B	Y (U.S. EPA)
<b>Polychloroethylenes</b>	<b>PCEs</b>												
chloroethylene	CE	C <sub>2</sub> H <sub>3</sub> Cl	75-01-4	Colorless gas	0.969 (−13 °C)	−153.8	−13.4	Slightly soluble (25 °C)	0.6	516.95	1 ppm	Group 1	Y (U.S. EPA)
1,1-dichloroethylene	1,1-DCE	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	75-35-4	Colorless liquid	1.213 (20 °C)	−122.0	32.0	2.5 (25 °C)	1.32	66.5	5 ppm	N	N
1,2-dichloroethylene	1,2-DCE	C <sub>2</sub> H <sub>2</sub> Cl <sub>2</sub>	156-59-2 (Z) 156-60-5 (E)	Colorless liquid	Z <sup>f</sup> : 1.28 (20 °C) E <sup>f</sup> : 1.26 (25 °C)	Z: −81.47 E: −49.44	Z: 60.2 E: 48.5	1–5 (16 °C) <1.0 (17.8 °C)	Z: 2.0 E: 2.09	Z: 26.66 (25 °C) E: 53.33 (30.78 °C)	200 ppm	N	N
trichloroethylene	TCE	C <sub>2</sub> HCl <sub>3</sub>	79-01-6	Colorless liquid	1.46 (20 °C)	−73.0	87.2	1.280 (20 °C)	2.42	7.8	50 ppm	Group 2A	Y (U.S. EPA, MEP of China)
tetrachloroethylene	PCE	C <sub>2</sub> Cl <sub>4</sub>	127-18-4	Colorless liquid	1.63 (20 °C)	−19.0	121.1	0.15 (20 °C)	2.9	1.9	25 ppm	Group 2A	Y (U.S. EPA, MEP of China)

Notes:

<sup>a</sup> Data from the International Programme On Chemical Safety (IPCS), the CAMEO chemicals (CAMEO chemicals) and the IARC monographs.

<sup>b</sup> Threshold limit value-time weighted average (TLV-TWA) is based on ACGIH.

<sup>c</sup> Germany Maximum workplace Concentration.

<sup>d</sup> Based on the IARC, five groups have been classified according to the carcinogenicity of chemicals to humans. Group 1 represents those chemicals that are carcinogenic to humans; Group 2A is probably carcinogenic to humans; Group 2B stands for possibly carcinogenic to humans; while Group 3 and Group 4 are not classifiable as to its carcinogenicity to humans, and probably not carcinogenic to humans, respectively.

<sup>e</sup> “Y” represents yes, “N” stands for no.

<sup>f</sup> “Z” and “E” correspond to cis and trans, respectively.



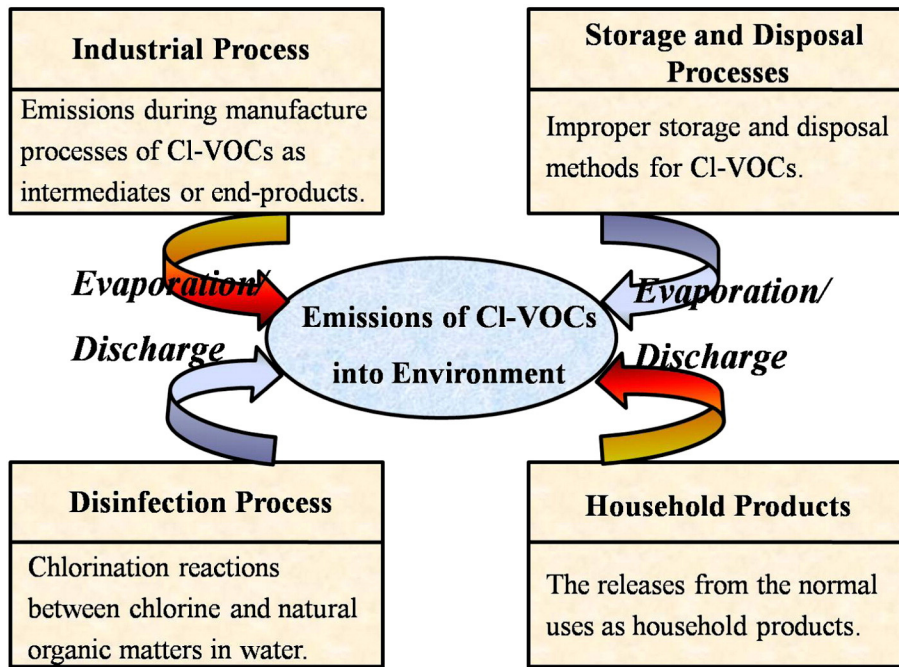


Fig. 3. Principal sources of CI-VOCs in environment. References from U.S. EPA, 1985; ATSDR, 2005; Siegrist et al., 2001; IPCS, 2002a; U.S. EPA., 2003b; Moran, et al., 2007; WHO, 2010; Scheutz et al., 2011; Hunkeler et al., 2012; Beamer et al., 2012; Lourencetti et al., 2012; Zeng et al., 2013.

production capability was 520,000 tonnes in the late 1990s (McCulloch, 2003). The production of CF was 216,000 tonnes in U.S. at 1993, and 316,000 tonnes in European Union at 1997 (International Programme on Chemical Safety (IPCS), chloroform, 2004). CF was once mainly used in the production of HCFC-22, which accounted for around 90%–95% of its total use in the European Union (IPCS, chloroform, 2004). After the signing of Montreal Protocol, its use for the production of HCFC-22 has been gradually phased out (Ozone Secretariat United Nations Environment Programme, 1987). In China, CF production has

steeply increased since the late 1990s, and the annual production capacity is estimated to be 500,000 tonnes in recent years (Chemsino Weekly, 2011; DRC, 2006). The production rates of CF for U.S., Europe and China are shown in Fig. 4.

CF is principally emitted to environment as exhaust gas and wastewater. Besides the releases of CF during its manufacture and use processes, as aforementioned, disinfection by-products (DBPs) during water disinfection are another big source for CF (Lourencetti et al., 2012; Zeng et al., 2013). Main anthropogenic CF sources include but

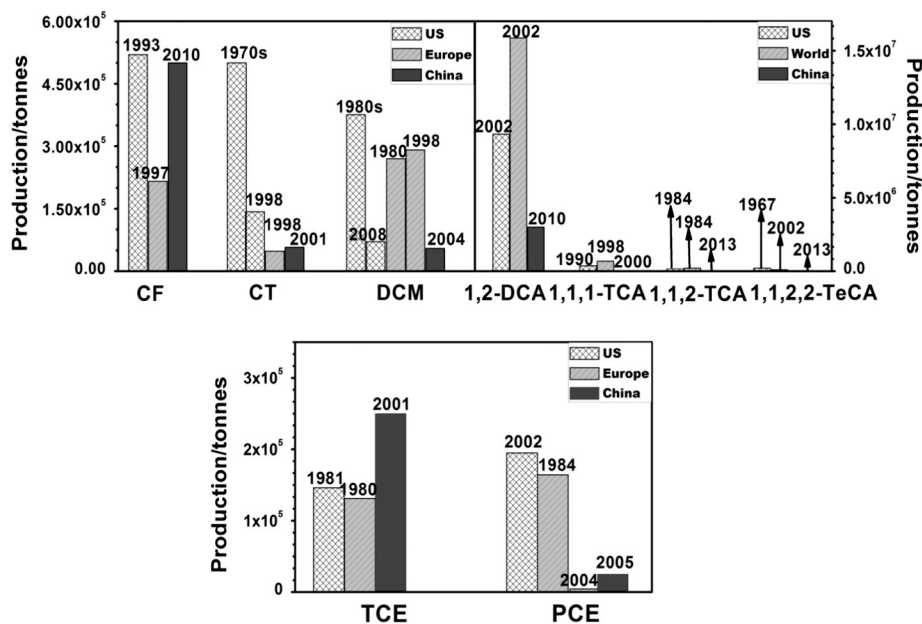


Fig. 4. The production rates of some CI-VOCs in different regions. References from McCulloch, 2003; IPCS, chloroform, 2004; DRC, 2006; Chemsino Weekly, 2011; Chemical and Engineering News, 1991, 1992; IPCS, Carbon tetrachloride, 1998; Rossberg et al., 2006; Wang and Tang, 2003; DRC, 2004; National Toxicology Program, 2011a; Cooper et al., 2011; DRC, 2004; Field and Sierra-Alvarez, 2004; DRC, 2011; Chinabaogao, 2012; IPCS, 1,1,1-Trichloroethane, 1990; De Rooij et al., 2004; Lu et al., 2008; IARC, 1999h; IPCS, 1,1,2-Trichloroethane, 2000; ATSDR, 2008; Research Center of Shuoxun Chemical Industry, 2014a; 2014b; U.S. EPA, 2007; DRC, 2012; Lash and Parker, 2001; National Toxicology Program, 2011b; DRC, 2005; Field and Sierra-Alvarez, 2004.

are not limited to, pulp and paper mills, water treatment plants, chemical manufacture plants, and waste incinerators (Cappelletti et al., 2012; McCulloch, 2003). Besides human activities, CF is also emitted from natural sources like volcanic emissions and marine algae. Moreover, CF can be generated naturally due to the chlorination reaction between the organic matters subsisted in water and soil and naturally formed hypochlorous acid (Cappelletti et al., 2012; Hoekstra et al., 1998). Studies have shown that CF is frequently found in both ground and surface water sources. A general survey of environmental quality throughout China, including the Beijing–Tianjin area, Yangtze delta area and Pearl River delta area, shows that volatile organic compounds, in particular, CF, CTC, PCE and TCE, are among the most frequently detected contaminants (He et al., 2013; Kranzioch et al., 2013; Shao et al., 2011; Song et al., 2012; Zhang et al., 2014). In addition, CF is a common contaminant that can be detected in over 50% of U.S. EPA's National Priority List (NPL) sites, and it is also the most frequently detected pollutant according to the U.S. Geological Survey (Carter et al., 2012; Chan et al., 2012; Grady, 2003; Squillace et al., 1999; U.S. EPA, NPL, 2013).

Exposure to CF may result in severe health impacts. In fact, study shows that exposure to CF is associated with hepatocellular carcinoma (U.S. Department of Health, Education, and Welfare, 1976). Although full evidence concerning the CF carcinogenicity is not available, its mutagenic effects have been confirmed in animal experiments. Previous research has shown the association of CF exposure with cytotoxicity and regeneration in kidney tubular of animals (Kasai et al., 2002; Sasso et al., 2013). Acute CF exposure would cause central nervous system depression, such as excitement, nausea, vomiting, ataxia, dizziness, and drowsiness, whereas chronic effects of CF include hepatic damage (ATSDR, 1997a; Cappelletti et al., 2012). According to the U.S. National Institute for Occupational Safety and Health, CF can pose immediate threat to human life above 500 ppm. The U.S. National Toxicology Program's twelfth report on carcinogen supposes CF to be a human carcinogen (U.S. Department of Health and Human Services, 2010), and the International Agency for Research and Cancer (IARC) classifies it under group 2B designation, which indicates its probable carcinogenic nature (IARC, 1999g). Therefore, the U.S. EPA has posed a strict control on the maximum contaminant level of CF in drinking water ( $70 \mu\text{g}\cdot\text{L}^{-1}$ ) (U.S. EPA, 2003a).

### 2.1.2. Carbon tetrachloride

CTC is a colorless volatile liquid with unique sweet smell, often found in the atmosphere in gaseous form. CTC does not burn easily, and its smell would turn unpleasant with concentration beyond 10 ppm (ATSDR, 2005). It is an excellent non-polar solvent for non-polar organic compounds in the chemical industry, such as fats, oils, lacquers, wax, rubber and resin. CTC was widely used as fire extinguisher, dry cleaner, degreaser, pesticide, and the precursor to refrigerants in the past. It was once used as pesticide to kill insects for stored grains, but its use was banned in 1970 for consumer products in U.S. (Doherty, 2000a; Malaguarnera et al., 2012). In addition, large amounts of CTC were used to produce Freon refrigerants, including R-12 (trichlorofluoromethane) and R-11 (dichlorofluoromethane) before the Montreal Protocol (Doherty, 2000a; Ozone Secretariat United Nations Environment Programme, 1987). However, these refrigerants were found to play important roles in ozone depletion, and therefore this use was also banned later (Malaguarnera et al., 2012; Ozone Secretariat United Nations Environment Programme, 1987). According to the Chemical and Engineering News (Chemical and Engineering News, 1991, 1992), CTC production peaked in 1970s at 500,000 tonnes per year in U.S., and then sharply decreased since 1980s due to environmental concerns and the declining demands for chlorofluorocarbons (CFCs). At the global level, its production amounted to 960,000 tonnes per year at 1987 (IPCS, Carbon tetrachloride, 1998) and then decreased to around 720,000 tonnes per year in 1992 (Rossberg et al., 2006). In China, the CTC annual production was only 57,600 tonnes in 2001 (DRC, 2004;

Wang and Tang, 2003), and it gradually declined till totally phased out from the market as a raw material for the CFCs in 2010 based on the Montreal Protocol (MEP of China, 2009a). The production rates of CTC for U.S., Europe and China are shown in Fig. 4.

The main sources of CTC into the environment are primarily the accidental releases from the production and use, and from its disposal in landfill where it may evaporate into the air or leach into groundwater (ATSDR, 2005). It should be noted that CTC is also a common contaminant of indoor air, while the sources appear to be building materials or products, such as cleaning agents, used in home (ATSDR, 2005). Owing to its wide uses and inappropriate disposal methods, CTC has been one of the most frequently detected volatile organic compounds in environment (Shao et al., 2011; Zhang et al., 2014). As a priority toxic contaminant, it has been found in at least 425 of 1662 most serious hazardous waste sites listed in the U.S. EPA's National Priority List (ATSDR, 2005; Lin and Liang, 2013; U.S. EPA, NPL, 2013).

CTC has been extensively studied in animal tests to explore the toxin-induced hepatic injury (Hermenean et al., 2013; Weber et al., 2003). It is demonstrated that besides liver damage, CTC exposure also causes the damage of other tissues, such as kidney (Balahoroglu et al., 2008), lung (Takemura et al., 2006), testis (Manjrekar et al., 2008), brain (Anand et al., 2011) and blood (Hermenean et al., 2013; Soliman and Fahmy, 2011). Furthermore, research also indicated that exposure to CTC has severe detrimental effects on human health, which could not only degenerate the liver and kidney, but can result into acute effects on the central nervous system, including dizziness, headache, depression, confusion and, in severe cases, even respiratory failure, coma and death (ATSDR, 2005). Limited epidemiological data have indicated a possible association between certain birth outcomes (e.g., birth weight, cleft palate) and drinking water exposure. However, as the water contained multiple chemicals, the role of CTC is unclear (ATSDR, 2005). Therefore, future epidemiological studies to explain the risk assessments of CTC are still required. Due to the potential human impact, the IARC (1999b) has classified CTC as group 2B contaminant, a probable human carcinogen.

### 2.1.3. Dichloromethane

DCM, also known as methylene chloride, is a colorless volatile organic liquid that has a moderately sweet aroma. Despite its poor solubility in water, it is miscible with many organic solvents. It is the main raw material for producing cellulose acetate film, and a common solvent in the pharmaceutical industry. In U.S., Europe and Japan, DCM is also widely used in metal degreasing, varnishing stripper, adhesives and pesticide (ATSDR, 2000). Taking U.S. as an example, DCM production and consumption peaked in 1980s, with a production capacity of 376,000 tonnes per year, decreasing to 71,100 tonnes at 2008 (Cooper et al., 2011; National Toxicology Program, 2011a). The global production of DCM was 570,000 tonnes per year in 1980, of which 270,000 tonnes was produced in Western Europe. It is estimated that the current world production of DCM is at the similar level as 1980 (WHO, 2000a), whereas its annual production capacity in China is estimated at around 55,000 tonnes (DRC, 2004). The production rates of DCM for U.S., Europe and China are shown in Fig. 4.

Most of DCM releases into the atmosphere during the production and consumption of DCM-containing products, like varnish stripper and aerosol products. According to the U.S. EPA, up to 85% production of the DCM produced in U.S. is released into the environment, of which 86% is in the gas form (IPCS, Methylene Chloride, 1996; U.S. EPA, 1985). The Toxic Chemical Release Inventory of U.S. EPA indicated that approximately 170,000 tonnes out of 230,000 tonnes (total production amount at that year in U.S.) was lost to the atmosphere in 1988; among them, 60,000 tonnes was from production emissions and the remaining 110,000 was attributed to consumer products and other sources, such as hazardous waste sites (IPCS, Methylene Chloride, 1996). Yet, during 1998–2001 total on- and off-site releases of DCM in U.S. decreased to 15,000 tonnes (Moran et al., 2007; U.S. EPA, 2003b).

The total emission of DCM to air in Western Europe was estimated at 180,000 tonnes in 1991, approximately 36% of global emissions (500,000 tonnes per year) (IPCS, *Methylene Chloride*, 1996). Moran et al. (2007) revealed that DCM was among the most frequently detected pollutants with its concentration close to or even greater than the Maximum Contaminant Levels (MCLs) in the survey of more than 5000 wells all over U.S. between 1985 and 2002 (U.S. EPA, 2004). Furthermore, DCM, PCE, and TCE are among 29 of the chemicals, metals, and other substances most frequently detected at U.S. EPA Superfund sites (Moran et al., 2007). However, no such relevant information concerning DCM is available in China.

Research has shown that occupational exposure to DCM is associated to numerous adverse health impacts on the central nervous and reproductive system, in addition to liver and kidney toxicity (Olvera-Bello et al., 2010; Starr et al., 2006). Besides, methylene chloride was found to cause the body carbon monoxide poisoning via metabolizing conversion to CO. Acute exposure by inhalation can cause optic neuropathy and hepatitis, presumably due to the formation of formaldehyde by glutathione transferases (GSTs) and carbon monoxide poisoning by cytochrome P450 (CYP) (Evans and Caldwell, 2010; Starr et al., 2006). Although a tremendous amount of evidence has supported the association of DCM exposure to the carcinogenicity in experimental animals (Evans and Caldwell, 2010; IARC, 1999i; Starr et al., 2006), evidence is still lacking for the carcinogenicity of DCM for human. Even though few epidemiological studies have indicated the slightly increased cancer mortality, but the cancer in human studies do not always manifest the same sites observed in the animal carcinogenicity studies (Starr et al., 2006). Moreover, it was demonstrated that the airborne DCM concentrations of the few epidemiology studies of DCM-exposed workers were far lower than those that caused cancer for mice (Starr et al., 2006). Therefore, future epidemiological studies still should focus on the risk-assessment of DCM exposure and potential mechanisms for cancer formation. According to the IARC, DCM has been classified as a possible carcinogenic substance to human (group 2B) (IARC, 1999a).

## 2.2. Chlorinated ethanes

Polychloroethanes or chlorinated ethanes (PCAs) are a group of chlorinated aliphatic compounds in which one to six hydrogen atoms in ethane are substituted by chlorine atoms, as shown in Fig. 1(b). PCAs are generally low boiling point liquids with poor water solubility and high volatility (Data from Table 1). In general, both solubility and volatility decrease with the increase of chlorine numbers in their molecule structures, whereas detailed physicochemical properties of PCAs are shown in Table 1.

PCAs are widely used as industrial solvents, degreasing agents and intermediates for producing plastic, textile and some other compounds in the chemical industry. According to the Organization for Economic Co-operation and Development (OECD) many of these compounds, such as chloroethane (CA), 1,1-dichloroethane (1,1-DCA), 1,2-dichloroethane (1,2-DCA), 1,1,1-trichloroethane (1,1,1-TCA), 1,1,2-trichloroethane (1,1,2-TCA) and 1,1,2,2-tetrachloroethane (1,1,2,2-TeCA), still have significant usage presently, and all of them have been listed as the most high production volume chemicals with production levels greater than 1000 metric tonnes per year (OECD, 2004). Due to large-scale production and consumption of these compounds, these chemicals enter the environment through water discharges and accidental spills becoming the frequently detected groundwater contaminants in North America and Europe (Fletcher et al., 2009; Maness et al., 2012; Siegrist et al., 2001; Wu et al., 2014). Owing to their poor biodegradability, PCAs could be persistent in groundwater under natural conditions. These compounds are shown to cause circulatory and respiratory failure, neurological disorders as well as damages to skin, liver, heart, kidney and mammalian glands in human body; some of them, such as 1,2-DCA, 1,1,1,2-TeCA and HCA, are even likely to be carcinogenic (Bajpai and Zappi, 1997; Gwinn et al., 2011; Nagano et al., 2006). In view of this, 1,2-DCA, 1,1,1-TCA, 1,1,2-

TCA, 1,1,2,2-TCA have been listed as the priority pollutants by both U.S. EPA and MEP of China, in addition, 1,1-DCA and HCA are also included in the list of U.S. EPA, while only 1,2-DCA is included in the list of priority substances by EC (European Commission, 2008; MEP of China, 2009c; U.S. EPA, 1981).

### 2.2.1. 1,2-Dichloroethane

1,2-DCA, commonly known as ethylene dichloride, is a colorless liquid with an chloroform-like odour that is slightly soluble in water. 1,2-DCA is an important bulk chemical, normally used as an intermediate in the production of vinyl chloride (CE), 1,1,1-TCA, TCE and PCE, and as industrial solvent and metal degreaser (Baran et al., 2013). Other applications include scavenging lead in gasoline, cleaning textiles and equipments, extracting solvent from seeds, processing of animal fats, pesticides and pharmaceuticals (Gwinn et al., 2011). 1,2-DCA is mainly produced by several manufacturers in Europe, U.S. and Japan, with a worldwide annual production at approximately 15,868,000 tonnes (Field and Sierra-Alvarez, 2004), which is larger than any other halogenated chemicals (Olaniran et al., 2011). It is estimated that around 3,000,000 tonnes of 1,2-DCA are consumed in China every year, of which 98.9% are used for the production of vinyl chloride (Chinabaogao, 2012; DRC, 2011). The production rates of 1,2-DCA for U.S., China and world are shown in Fig. 4.

The release of 1,2-DCA into the environment primarily occurs during its production and disposal processes as well as during the use of products containing this substance. Additional releases may result from the use of 1,2-DCA as extraction and cleaning solvent and as lead scavenger in gasoline (IPCS, 2002a). Due to its high volatility, 1,2-DCA is mostly released into the air and, some is discharged into rivers or lakes. For instance, according to the Pollutant Release and Transfer Register Report of the Japan Ministry of Environment in 2005, around 603 tonnes and 5 tonnes of 1,2-DCA were released to the atmosphere and public waters each year, respectively (Nagano et al., 2006). In addition, the widespread uses of 1,2-DCA in a variety of products and its wide applications in different manufacturing processes make 1,2-DCA the ubiquitous pollutant that is frequently detected in sites contaminated by organic pollutants. In fact, it has appeared in at least 570 of the 1585 National Priorities List identified by U.S. EPA (ATSDR, 2001; Olaniran et al., 2011; U.S. EPA, NPL, 2013). However, no relevant data on the release and contamination level of 1,2-DCA are available in China.

Toxicity studies show that exposure to 1,2-DCA primarily affects the liver, kidney and respiratory systems. There is sufficient evidence to confirm the carcinogenicity of 1,2-DCA in experimental animal studies (IPCS, 2002a). Although epidemiological studies have been extensively carried out to assess the association of 1,2-DCA exposure with carcinogenicity in human, evidence is still inadequate to reach a conclusion. For example, five cohort studies conducted on the risk assessment of 1,2-DCA indicated no link between the excess of cancer incidence and the occupational exposure to 1,2-DCA (Nagano et al., 2006). In contrast, another three ecological studies were carried out to examine the association between cancer incidence and residential proximity to contaminated sites where 1,2-DCA was present, showing excess risks of brain, pancreatic, lymphatic, hematopoietic, and stomach cancers as a result (Gwinn et al., 2011; Morris, 2000). Although a direct link between carcinogenic effects and 1,2-DCA exposure has not been confirmed, 1,2-DCA has been characterized as a possible carcinogen to human (Group 2B) by both the IARC and the U.S. EPA (Gwinn et al., 2011; IARC, 1999c; Nagano et al., 2006; U.S. EPA, 1999b).

### 2.2.2. 1,1,1-Trichloroethane

1,1,1-TCA, also known as methyl chloroform, is a colorless sweet-smelling liquid that was produced in large quantities in the industry and used as a solvent in the past (ATSDR, 2006; Lu et al., 2008). It has low solubility in water, but dissolved readily in CF, ethanol, ethyl ester, acetone, and other organic solvents. 1,1,1-TCA is not a natural compound. It was originally produced by a replacement of other chlorinated



solvents like CTC, and once widely used in the consumer products (ATSDR, 2006; Lu et al., 2008), for instance, it was extensively used for making typewriter correction fluid, metal cleaning and a range of other applications before 1990s (Shelton, 2009). Its primary end uses included cold-cleaning, vapor degreasing and ultrasonic cleaning of metal parts for the removal of greases, oils and waxes (Doherty, 2000b). In dry-cleaning, 1,1,1-TCA was used to clean leather and suede garments (Doherty, 2000b). In addition, 1,1,1-TCA was also incorporated into aerosol products, including hair sprays, cosmetics, oven cleaners, spot removers, furniture polishes, automotive lubricants, automotive choke cleaners, water repellents, adhesives, and guitar string lubricants (Doherty, 2000b). The estimated world annual production capacity of 1,1,1-TCA was 480,000 tonnes in 1973 and 680,000 tonnes in 1988, respectively (IPCS, 1,1,1-Trichloroethane, 1990). In the past, about half of this was produced in U.S., while around 100,000 tonnes was produced in Japan, where the production of 1,1,1-TCA was more than doubled in the period of 1979–1989 (IPCS, 1,1,1-Trichloroethane, 1990). The annual production in Western Europe was 229,000 tonnes in 1990. Given its potential ozone-depleting characteristic, the production and consumption of 1,1,1-TCA had been gradually phased out since 1996 and were completely eliminated by 2005 under the Montreal Protocol (De Rooij et al., 2004; Lu et al., 2008), while it was completely phased out before 2011 in China (MEP of China, 2009b). The production rates of 1,1,1-TCA for U.S., China and world are shown in Fig. 4.

The main sources of 1,1,1-TCA are primarily the emissions from the production sites and the use as products. According to the Toxic Release Inventory of U.S. EPA, total on- and off-site releases of 1,1,1-TCA averaged approximately 226.8 tonnes during 1998–2001 (Li et al., 2013; Moran et al., 2007; U.S. EPA, 2003b). The total emissions of 1,1,1-TCA to water from production sites of Europe were 0.565 tonnes per year at 1997 (De Rooij et al., 2004). Due to its high volatility, the releases of 1,1,1-TCA may also occur during the use of metal degreasing agents, paints, glues, and cleaning products, and individuals are more likely to be exposed to 1,1,1-TCA indoors rather than outdoors because of its widespread uses in home and office products (ASTDR, 2006). Owing to its long residence time in the troposphere (around 6 years), low biodegradability as well as its widespread uses, 1,1,1-TCA has been a common groundwater contaminant that is frequently detected at or even far from industrial facility sites and waste disposal sites, including the active sites in the National Priorities List of U.S. EPA (IPCS, 1,1,1-Trichloroethane, 1990; Scheutz et al., 2011; U.S. EPA, NPL, 2013). It has been found in at least 823 of the 1662 hazardous waste sites proposed for inclusion on the National Priorities List of U.S. EPA (Lu et al., 2008; U.S. EPA, NPL, 2013). However, no relevant data on the release and distribution of 1,1,1-TCA in environment media is available in China.

People are exposed to 1,1,1-TCA principally by inhalation due to its high volatility. Exposure by dermal contact and ingestion may also occur and 1,1,1-TCA can be adsorbed quickly in lung, skin, and gastrointestinal tract. 1,1,1-TCA can be widely distributed in adipose tissue and cross the blood-brain and placental barriers (IPCS, 1,1,1-Trichloroethane, 1990; Lu et al., 2008). It has also been found in human breast milk, but is not thought to be bio-accumulatable (IPCS, 1,1,1-Trichloroethane, 1990). Although it is not as toxic as many other chlorinated compounds, inhaled or ingested 1,1,1-TCA can depress central nervous system and cause effects similar to those of ethanol intoxication, including dizziness, confusion, and under sufficiently high concentration, unconsciousness and even death (ATSDR, 2006). Cardiac sensitization and arrhythmia have been observed in dogs exposed acutely to high concentration of 1,1,1-TCA via inhalation (Lu et al., 2008). Human volunteer study indicated that acute inhalation of 1,1,1-TCA impaired performance in neurobehavioral tests (Lu et al., 2008). However, there is no adequate evidence of human carcinogenicity for 1,1,1-TCA, and it does not exhibit significant genotoxic potential (IPCS, 1,1,1-Trichloroethane, 1990). Therefore,

it has been classified as Group 3 (not classifiable based on its carcinogenicity to human) by the IARC (IARC, 1999e).

### 2.2.3. 1,1,2-Trichloroethane

1,1,2-TCA is a colorless sweet-smelling liquid that does not readily dissolve in water, but is soluble in most organic solvents. It is the isomer of 1,1,1-TCA. 1,1,2-TCA is a regulated chlorinated organic compound that has been widely used in industrial processes. It can be used as a degreasing agent, and as an intermediate in the synthesis of 1,1-DCA (ATSDR, 1989; Grostern and Edwards, 2006). It is also used in adhesives, production of Teflon tubing, in lacquer and coating formulations, and as solvent for fats and oils (ATSDR, 1989; CalEPA, 1997). Annual production of 1,1,2-TCA was estimated to be 186,000 tonnes in the early 1980s in U.S., while in Japan it was 153,000 tonnes at 1996 (IARC, 1999h; IPCS, 1,1,2-Trichloroethane, 2000). The production of 1,1,2-TCA in China was estimated to be 15,300 tonnes at 2013 (Research Center of Shuoxun Chemical Industry, 2014a). The production rates of 1,1,2-TCA for U.S., China and world are shown in Fig. 4.

1,1,2-TCA may be released into the environment media through evaporation during its use in the manufacturing of other products and as a solvent, via discharges in wastewater during production processes. In addition, because of spills and improper storage and disposal practices, 1,1,2-TCA becomes a prevalent groundwater and soil contaminant (Grostern and Edwards, 2006). Although not as common as the previous chlorinated aliphatic compounds, 1,1,2-TCA has been detected in at least 45 of 1587 National Priorities List sites according to the U.S. EPA (ATSDR, 1989; Grostern and Edwards, 2006; U.S. EPA, NPL, 2013). No similar information on 1,1,2-TCA contamination is available in China.

People exposure to 1,1,2-TCA may occur through different routes, including inhalation, ingestion and dermal contact, potentially impacting the central nervous system, liver, kidney, lung and the immune systems (ATSDR, 1989; Grostern and Edwards, 2006). Similar to 1,1,1-TCA, 1,1,2-TCA is a central nervous system depressant and the inhalation of its vapors may cause dizziness, drowsiness, headache, nausea, short of breath, unconsciousness and even death. Carcinogenicity study indicated that gavage of 1,1,2-TCA may result in hepatocellular carcinomas and pheochromocytomas in mice, but no carcinogenicity occurs in rats. Initiation/promotion screening on male rat liver demonstrated that this chemical has neither initiation nor promotion activity (IPCS, 1,1,2-Trichloroethane, 2000). No information is available on the acute, chronic, developmental, reproductive, or carcinogenic effects in human, while the only effect that has been observed in human is stinging and burning sensations of the skin upon dermal exposure (ATSDR, 1989). U.S. EPA has classified it as group C, a possible human carcinogen, because it is structurally related to 1,2-DCA, a probable human carcinogen. The IARC did not confirm 1,1,2-TCA as a human carcinogenic substance in 1991 as a result of limited evidence for the carcinogenicity in experimental animals and lack of evidence in human, so it has been classified as group 3 (IARC, 1999f).

### 2.2.4. 1,1,2,2-Tetrachloroethane

1,1,2,2-TeCA is a colorless volatile liquid with chloroform-odor. It is a synthetic chemical that is not known to occur naturally in the environment. In the past, it was widely used as an intermediate in the production of chlorinated ethylenes (e.g. PCE, TCE, and 1,2-dichloroethylene (1,2-DCE)), as an industrial solvent, extractant and as a raw material for pesticides. 1,1,2,2-TeCA is no longer used in large quantity in the U.S. due to concerns on its potential toxicity. The annual production of 1,1,2,2-TeCA reached approximately 200,000 tonnes in the U.S. at 1967, but declined drastically after late 1960s, and was ceased by early 1990s in both the U.S. and Canada (ATSDR, 2008). The production of 1,1,2,2-TeCA in China, however, has increased steadily in recent years, with the annual production reaching 21,500 tonnes at 2013 (Research Center of Shuoxun Chemical Industry, 2014b). The production rates of 1,1,2,2-TeCA for U.S., world, and China are shown in Fig. 4.



The current release of 1,1,2,2-TeCA is limited to fugitive emission or discharge during its production and use as a chemical intermediate or byproduct. It was a common solvent prior to World War II, but substantial release occurred in the recent past, resulting in its frequent presence in groundwater (Arnold et al., 2002; Chen et al., 1996). For instance, Bitterfeld, Germany, used to be a region with large chlorination chemistry industry for more than 100 years, but the contamination by 1,1,2,2-TeCA is so severe that its concentration in groundwater is still high up to date ( $80\text{--}1000\text{ mg}\cdot\text{L}^{-1}$ ) (Mackenzie et al., 2005). The total release of 1,1,2,2-TeCA in U.S. was equivalent to 30 tonnes in 1991, declining to about 1 ton in 2007 (Frascari et al., 2010). This contaminant has been detected in at least 329 of the 1699 hazardous waste sites that have been proposed for inclusion on the National Priorities List of U.S. EPA. Furthermore, it has been detected in air samples collected from 20 of these sites (ATSDR, 2008; U.S. EPA, NPL, 2013). In addition, 1,1,2,2-TeCA is also readily released into the atmosphere due to its volatility. The Toxic Release Inventory of U.S. EPA estimated that 1.44 tonnes of 1,1,2,2-TeCA was released into the atmosphere from 20 domestic manufacturing and processing facilities in 2005, accounting for about 90% of the total environment release (ATSDR, 2008), while only 0.0027 tonne of 1,1,2,2-TeCA was released into surface water, accounting for less than 1% of the total (ATSDR, 2008). The remaining 9% of the total environment release was mainly released into soil (ATSDR, 2008). No data on the release of 1,1,2,2-TeCA are available in China.

Exposure of the general population to 1,1,2,2-TeCA is expected to be very low because of the low concentration in environment media and the fact that it is no longer used as an end product. People who work or live near the facilities where this chemical is used as a chemical intermediate may be exposed to 1,1,2,2-TeCA by different routes (ATSDR, 2008; IPCS, 2002b). 1,1,2,2-TeCA can be very toxic to human if acutely exposed. It is irritating to skin and eyes. Experimental animal studies indicated that 1,1,2,2-TeCA is toxic to liver and kidney and damages the nervous and hematological systems (IPCS, 2002b). The development of a database for the toxicity of 1,1,2,2-TeCA, is still lagging behind in terms of progress, making it impossible to draw a clear conclusion on its toxicity to human based on the current research data. Further risk assessments of 1,1,2,2-TeCA on human health still need to be conducted for a better understanding of its toxicological effects. According to U.S. EPA, it has been classified as a possible human carcinogen (group C) (U.S. EPA, 1999c). In addition, the IARC has determined 1,1,2,2-TeCA cannot be classified as to its ability to cause cancer in human, so it has been classified as group 3 (IARC, 1999d).

### 2.3. Chlorinated ethylenes

Trichloroethylene (TCE) and perchloroethylene (PCE), as representatives of chloroethylenes (or polychloroethylenes, PCEs), are synthetic chlorinated hydrocarbons known for their excellent solvent properties and low fire and explosion potential. More physicochemical properties of PCEs are given in Table 1. They have been widely used as solvents for waxes, resins, fats, rubbers, oils and paint varnishes in private and public sectors, and have also been extensively used for dry cleaning and metal degreasing since 1920s (Beamer et al., 2012; CalEPA, 2009; Lash and Parker, 2001; WHO, 2010). Owing to the common occurrence of leaks and spills and their improper disposal at industrial sites, significant amounts of PCE and TCE have been introduced into the environment. In addition to their persistent nature, all of these factors have put them among the most popular groundwater contaminants. PCE and TCE have been ranked as the first and third most frequently detected VOCs in groundwater with concentration higher than the Maximum Contaminant Levels (5 ppb) all over U.S. (Moran et al., 2007; U.S. EPA, 2004). These two compounds are also among the top 33 priority hazardous substances that pose the most significant threat to human health according to the Department of Health and Human Services at the same time (ATSDR, 2011). Exposure to low levels of these substrates in drinking water may cause carcinogenic effects on human being. In fact, there

is epidemiological evidence available to relate chance of getting esophageal cancer, cervical cancer and non-Hodgkin's lymphoma with the exposure to TCE and PCE (Lyngé et al., 1997). Particularly, it should be noted that there is sufficient evidence confirming the carcinogenicity of CE to human, and it has been classified as group 1 contaminant by the IARC (IARC, 1987). Therefore, PCE and TCE have been strictly regulated in drinking water by both U.S. EPA and MEP of China (MEP of China, 2009c; U.S. EPA, 1981). Besides, CE has been listed as the priority pollutant by U.S. EPA (U.S. EPA, 1981).

#### 2.3.1. Trichloroethylene

TCE is a colorless non-flammable liquid with a sweet smell that is hardly soluble in water. It is primarily used in paint strippers, adhesive solvents, paints, and varnishes, and as metal degreaser in the manufacturing of electronics (Beamer et al., 2012; WHO, 2010; Wu and Schaum, 2000). The production volume of TCE was 146,000 tonnes at 1991 in U.S., and its annual production capacity was approximately 145,000 tonnes at that time (U.S. EPA, 2007). The annual production in Western Europe and Japan in 1990 was 131,000 and 57,000 tonnes respectively. The production volume of TCE in China was around 250,000 tonnes in 2011 and its demand has increased gradually in recent years (DRC, 2012). The production rates of TCE for U.S., Europe and China are shown in Fig. 4.

TCE can be released into the environment as vapor during degreasing operations and consumption of related products, via water discharges during production and disposal processes, and through leakages in storage process. TCE has been detected in at least 60% of the U.S. EPA's Superfund National Priorities List sites (Beamer et al., 2012; U.S. EPA, 2001), and is the most frequently reported organic contaminant in groundwater. Relative to other VOCs, TCE is also the third most frequently detected contaminant above its regulatory Maximum Contaminant Level (Moran et al., 2007; U.S. EPA, 2004). In addition, 9% to 34% water supplies in U.S. are believed to have TCE contamination problems (Beamer et al., 2012; Wu and Schaum, 2000). TCE has been identified in at least 1500 hazardous waste sites regulated under the Comprehensive Environmental Response Liability Act of 1980 (CERCLA, 1980), or the Resource Conservation and Recovery Act of 1976 (RCRA, 1976). In China, TCE has also been found to be the most commonly detected contaminant in environment (He et al., 2013; Shao et al., 2011). Generally, TCE has become one of the most prevalent contaminants subsisted in environment media (Beamer et al., 2012).

Owing to its widespread presence in environment, human exposure to TCE may occur through inhalation, ingestion and dermal contact (WHO, 2010). Exposure to TCE has been indicated to have adverse effects on the central nervous system, immune system, and endocrine (hormonal) system in adults (U.S. EPA, 2007). It is also associated with speech and hearing impairments, liver problems, skin rashes, kidney diseases, urinary tract, and blood disorders (Beamer et al., 2012; Gist and Burg, 1995). In addition, TCE exposure may also contribute to in autoimmune diseases including systemic lupus erythematosus (SLE), and is suspected to induce certain types of cancers, childhood leukemia, non-Hodgkin's lymphoma, multiple myeloma, kidney, liver, and cervical cancers (Beamer et al., 2012; Wartenberg et al., 2000). However, the interpretation of the epidemiological studies on cancer associated with TCE exposure remains a heated debate. The strongest epidemiological evidence for associations between TCE exposure and cancer was available for liver, kidney, and lymphomas, but there are different perspectives about whether human carcinogenicity of TCE can be drawn from the epidemiological database as a whole (Scott and Chiu, 2006). Besides, the human studies are limited by group and size, and dose-response assessments are still lacking. Although human studies are carried out in workplace, little information on the TCE exposure measurement is given, and the complexity of working environment always makes TCE not the only contaminant that the workers are exposed to. Therefore, future studies on the associations of TCE exposure and its toxicological effects still need to be carefully conducted. Owing

to its potential toxicity for human, TCE has been classified as group 2A by the IARC, indicating that it is probably carcinogenic to human (IARC, 1995a).

### 2.3.2. Tetrachloroethylene

Tetrachloroethylene, also known as perchloroethylene, is a colorless sweet odor liquid that is hardly soluble in water. It is widely used in dry cleaning, textile processing, and metal degreasing (ATSDR, 1997b; WHO, 2010). Over 181,000 tonnes of PCE was produced in U.S. annually (Lash and Parker, 2001). For example, the total production volume in U.S. was 195,000 tonnes in 2002 (National Toxicology Program, 2011b). Production in Europe has declined from 164,000 tonnes in 1994 to 44,000 tonnes in 2004. In contrast, the production of PCE has increased gradually over the past decades in China. The production capacity of PCE was estimated at around 25,000 tonnes in 2005 (DRC, 2005). The production rates of PCE for U.S., Europe and China are shown in Fig. 4.

PCE is widely distributed in the environment, since it is released from many industrial processes and consumer products. According to the Toxic Release Inventory of U.S. EPA, during 1998–2001 total on- and off-site releases of PCE averaged about 1800 tonnes (Moran et al., 2007; U.S. EPA, 2003b). The total environmental release of PCE has been reduced by almost 94%, from 17,000 tonnes in 1988 to 1000 tonnes in 2008 (National Toxicology Program, 2011b). PCE is readily released into the air owing to its volatile characteristic and can remain intact in the atmosphere because of its persistent property. Research demonstrated that approximately 85% of PCE consumed annually is released into the atmosphere, resulting in the concentration of PCE in air ranging from 30 ppt in rural areas to as high as 4.5 ppb in urban or industrial sites in U.S. (Lash and Parker, 2001). Using PCE as dry cleaner is commonplace in residential buildings and hence its concentration in the indoor air can reach as high as  $55,000 \mu\text{g}\cdot\text{m}^{-3}$  before the implementation of dry cleaner regulations to control PCE emission, which rarely exceeds  $5000 \mu\text{g}\cdot\text{m}^{-3}$  afterwards (Storm et al., 2013). In addition, a small portion of PCE enters wastewater and water. Therefore, PCE is a common contaminant that is frequently found in Superfund waste sites and groundwater (Lash and Parker, 2001; Moran et al., 2007). It is among 29 of the chemicals, metals, and other compounds that are most commonly detected in Superfund sites (Moran et al., 2007).

The primary routes of human exposure to PCE include inhalation, ingestion of contaminated water or food and dermal contact (Lash and Parker, 2001; WHO, 2010). Presence of PCE in ambient air results in the exposure of the general population, particularly in the urban area. Additional exposure may come from indoor air that contains PCE evaporated from dry cleaners and the use of water contaminated by PCE (WHO, 2000b). Groups with higher than average exposure level are workers in factories that manufacture or use PCE and people who live in the vicinity of these industrial sites. It is estimated that over 1.5 million workers in U.S. are exposed to this chemical every year. The mean occupational exposure levels used to be 59 ppm or even higher, but the current exposure levels have become substantially lower, presumably in the range of 1–10 ppm (Tucker et al., 2011). PCE is readily absorbed in the gastrointestinal tract and lung (WHO, 2000b). Inhalation of PCE vapors may result in acute dysfunction of central nervous system, dizziness, drowsiness and other forms of depression, while chronic over-exposure causes deficits in neurobehavioral functions (Boyes et al., 2009). According to the Occupational Safety and Health Administration, air concentration of PCE beyond 100 ppm causes neurotoxic effects on human, including changes in behavior and coordination as well as damages of the central nervous system (Tucker et al., 2011). The IARC has found sufficient evidence to prove PCE as carcinogen in experimental animals, but little evidence is available for human (IARC, 1995b; Mundt et al., 2003). Numerous studies have been conducted among people who have long term exposure to TCE (e.g. dry cleaner workers), and several cancer excesses, such as the cancer of bladder,

esophagus, large intestine, kidney and cervix, have been observed, but few consistent patterns have emerged (Mundt et al., 2003). Therefore, more epidemiological studies on the associations of PCE exposure with its toxicological effects should be conducted to gain a better understanding of its carcinogenicity and the potential carcinogenic mechanisms. Similar to TCE, PCE has been classified as a probable human carcinogen (group 2A) by the IARC (IARC, 1995b).

## 2.4. Summary

Generally, Cl-VOCs share the common characteristics of high volatility and strong persistence in environment. These compounds were once widely used as solvents, cleaning agents, degreasing agents and a variety of commercial products. The production regions are mainly in U.S., Europe, Japan and China. Owing to their widely applications in human activities, it makes Cl-VOCs become a group of ubiquitous contaminants that are frequently detected in the environment media, such as soil, air and water. The main sources of Cl-VOCs contamination are the emissions from their production processes, the consumptions of Cl-VOCs-containing products, the disinfection process as well as the improper storage and disposal processes. According to the Montreal Protocol, the uses of some Cl-VOCs are limited or even banned, besides these compounds may undergo abiotic and biotic degradation under natural conditions, thus their concentrations in ambient air, groundwater as well as other environment media are expected to be low in the future. On the other hand, owing to their persistent characteristic and strong recalcitrance to biodegradation, Cl-VOCs can still survive in the environment for a long time.

Meanwhile, human exposure to Cl-VOCs may occur through different routes such as inhalation, ingestion, and dermal contact, principally depending on their sources. In particular, inhalation of contaminated indoor air with Cl-VOC emissions from many indoor materials is an important exposure pathway for the general population (WHO, 2010). However, the relative importance of these three routes has not been clearly classified. The distribution and fate of Cl-VOCs in the environment after release as well as their exposure levels should be carefully evaluated in future work. Although a large amount of studies has been conducted to assess the potential associations of Cl-VOCs exposure to human carcinogenicity, evidence is normally inadequate. Therefore, future studies, particularly epidemiological studies, must be carried out to demonstrate the risk-assessment of each Cl-VOCs exposure and potential mechanisms for cancer formation. Owing to the widespread contamination of Cl-VOCs, some strategies should be taken, for instance, improving the production processes of Cl-VOCs to strictly control their emissions, as well as searching for appropriate remediation or disposal technologies. All of these definitely need to be carefully investigated in the future studies.

## 3. Remediation technologies

In view of their ubiquitous existences in environment and detrimental effects on human health, numerous remediation methods have been developed for the removal and decomposition of Cl-VOCs from contaminated water, air and soil media over the past decades (Alapi and Dombi, 2007; Chan et al., 2012; Justicia-Leon et al., 2014; Li et al., 2012; Meng et al., 2002; Randazzo et al., 2011; Rodríguez et al., 2005; Tsai et al., 2010; Wei and Seo, 2010; Yang et al., 2009; Yokosuka et al., 2009). Generally, these methods can be classified as non-destructive or destructive, as shown in Fig. 5. Non-destructive methods principally make use of the physicochemical properties of chlorinated compounds like high volatility and hydrophobicity to physically remove these contaminants, and the nature of these compounds normally does not change (e.g. air stripping and adsorption methods) (Li et al., 2012; Wei and Seo, 2010; Yang et al., 2009). On the other hand, destructive methods neutralize the contaminants by breaking the C-Cl bond, while the nature of these compounds changes. In the destructive methods, Cl-VOCs could be

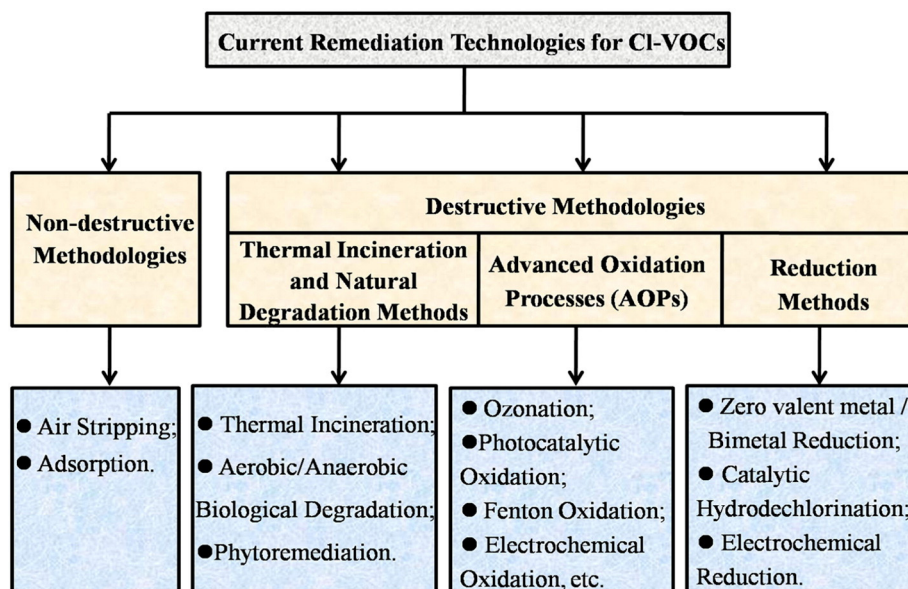


Fig. 5. Summary of current remediation technologies for Cl-VOCs.

decomposed under natural conditions by plants and microorganisms during their metabolic activities as in the phytoremediation and biodegradation approaches (Chan et al., 2012; Justicia-Leon et al., 2014). Cl-VOCs also can be broken down by chemical reactions with corresponding chemical additions, such as Fenton oxidation, zero valent metal reduction and catalytic hydrodechlorination methods (Meng et al., 2002; Randazzo et al., 2011; Tsai et al., 2010; Yokosuka et al., 2009). Cl-VOCs could also be destroyed by using energies like in thermal incineration (Lin et al., 2003; Mabrouk et al., 2012; Tseng et al., 2003), photocatalytic oxidation (Yokosuka et al., 2009; Zuo et al., 2006), electrochemical oxidation and electrochemical reduction approaches (Huang et al., 2012; Isse et al., 2009; Randazzo et al., 2011; Rondinini and Vertova, 2004; Scialdone et al., 2008). The efficacy, products, advantages and drawbacks of all the remediation methods are summarized in Table 2.

### 3.1. Non-destructive methods

Air stripping and adsorption are the most common non-destructive methods for the removal of Cl-VOCs (Li et al., 2012; Wei and Seo, 2010; Yang et al., 2009). In particular, adsorption has high reliability due to a robust operating configuration and hence is widely used for the remediation of contaminated sites. In addition, it offers the possibility of recovering the pollutants for reuse. Several adsorbents such as activated carbons (Alwary et al., 2011; Yanga et al., 2009), multi-walled carbon nanotubes (Naghizadeh et al., 2011), graphene (Åkesson et al., 2012), biochar (Ahmad et al., 2014), sol-gel substrates (Hernández et al., 2009), and organic mulch (Wei and Seo, 2010) have been developed for the removal of Cl-VOCs. Although non-destructive methods are effective for the removal of chlorinated hydrocarbons, the nature of these contaminants does not change; instead, these methods only transfer the contaminants from one phase to another, and hence additional effort must be invested into the disposal of the polluted gas and the regeneration of adsorbents (Li et al., 2012; Sonoyama and Sakata, 1999; Wang et al., 2002). Therefore, destructive methods for Cl-VOCs removal appear to be relatively more attractive in recent years.

### 3.2. Thermal incineration and natural degradation methods

#### 3.2.1. Thermal incineration method

Destructive methods for the abatement of Cl-VOCs include thermal incineration, aerobic or anaerobic biodegradation, phytoremediation,

advanced oxidation processes (AOPs) and reductive dechlorination. Thermal incineration can achieve efficient destruction of chlorinated compounds within a short time (Lin et al., 2003; Mabrouk et al., 2012; Tseng et al., 2003), but it needs an elevated temperature as high as 1000 °C to destroy these compounds due to their relatively low flammability, leading to high processing cost. Furthermore, high construction cost of incinerators and the potential emissions of highly toxic byproducts (e.g. dioxins, furans and phosgene) due to incomplete combustion have restricted the development of this technology (Martino et al., 1999).

#### 3.2.2. Biodegradation and phytoremediation methods

Aerobic and anaerobic microbial conversions of Cl-VOCs into non-toxic hydrocarbons have been studied for the potential application of in-situ treatment over the last few decades. Numerous aerobic microorganisms, including but not limited to methanotrophs, propane-oxidizers, ammonia-oxidizers and toluene-oxidizers are found to be able to co-metabolize some certain Cl-VOCs (Henry et al., 2002). Under anaerobic and sulfate-reducing conditions, both metabolic and co-metabolic microorganisms can achieve reductive dechlorination of geminal-chloroethanes (Gander et al., 2002; Grostern and Edwards, 2006). Due to high toxicity of most Cl-VOCs, few microorganisms could rely on them as the sole carbon source in the environment. Therefore, a major challenge proposed for biodegradation method is that, it often takes quite a long time for bacteria to acclimate and remove the chlorinated hydrocarbons from contaminated sites due to the inhibitive nature of these compounds (Grostern and Edwards, 2006; Justicia-Leon et al., 2014). For instance, CF is found to be toxic to microbes and inhibit microbial processes (e.g. methanogenesis) and the reductive dechlorination of other chlorinated aliphatic compounds (Chan et al., 2012; Justicia-Leon et al., 2014). It is presumed that CF may affect the dechlorinating organisms directly or indirectly by inhibiting other microorganisms (e.g. methanogenic bacteria), on which the dechlorinating organisms depended, thus limiting the dechlorination capacity and efficacy of bioremediation strategy (Chan et al., 2012; Justicia-Leon et al., 2014).

Phytoremediation has potential advantages over other remediation approaches in the economic, aesthetic and ecologic aspects, thus attracting some attention on the removal of Cl-VOCs in recent years. Wang et al. (2004) investigated the fate of CTC during phytoremediation with poplar. Results indicated that over 99% of CTC was removed, no significant amount of CTC was transpired or



**Table 2**  
The non-destructive and destructive remediation technologies for Cl-VOCs.

Remediation technology	substrate	Reaction conditions	Products	Efficacy	Advantages (Ad)/Drawbacks (Dr)	References
Air Stripping	TCE (78.6–740 mg•L <sup>-1</sup> ); 1,1,1-TCA (20–1300 mg•L <sup>-1</sup> ); 1,1-DCE (100–2400 mg•L <sup>-1</sup> ); 1,1-DCA (25–1500 mg•L <sup>-1</sup> ).	Packed tower with stainless corrugated gauze packing; temperature: 293–313 K; airflow rate, 0.5–5.0 L•min <sup>-1</sup> .	TCE; 1,1,1-TCA; 1,1-DCE; 1,1-DCA.	>96% removal efficiency at an airflow rate of 5.0 L•min <sup>-1</sup> and 298 K within couple of minutes.	Ad: Fast removal efficiency; Dr: nature of contaminants does not change; waste gas collection and further disposal;	Li et al., 2012
Adsorption	TCE (1700 mg•L <sup>-1</sup> ); PCE (1700mg•L <sup>-1</sup> ). TCE (5.0–50.0 mg•L <sup>-1</sup> ).	Fixed bed column; adsorbent, granular activated carbon (GAC); surfactant solutions; flow rate, 1 mL•min <sup>-1</sup> . Teflon-lined screw-caped glass-vials; adsorbents, pine needle biochar; solution, 1 mM phosphate buffer at pH 7.0; 50 rpm for 48 h.	TCE; PCE. TCE.	Adsorption amounts: 0.16 g TCE/g GAC and 0.24 g PCE/g GAC in triton X-100; 0.19 g TCE/g GAC and 0.35 g PCE/g GAC in triton X-165. Maximum adsorption capacity of TCE, around 100 mg TCE/g biochar within 48 h.	Ad: Fast removal efficiency; recover of pollutants; Dr: further disposal of adsorbents; desorption phenomena during adsorption process; competitive adsorption of other contaminants.	Yang et al., 2009 Ahmad et al., 2014
Thermal Incineration	TCE (100 mg•L <sup>-1</sup> ). DCM; CT (20–40 mg•m <sup>-3</sup> ).	Fixed-bed reactor; catalyst, MnOx/γ-Al <sub>2</sub> O <sub>3</sub> ; temperature, 443–873 K. Rotary kiln incinerator; temperature, ~1273 K.	CO <sub>2</sub> ; HCl; Cl <sub>2</sub> ; Trace VOC. CO <sub>2</sub> ; mono-chlorobenze; 1,2-dichlorobenze.	99% at 673–873 K >99.99% (40 min)	Ad: Efficient destruction within short time; Dr: high construction cost; potential formation of highly toxic byproducts.	Tseng et al., 2003 Lemieux et al., 1996
Biodegradation	CF; DCM (30 μmoles). 1,1,1-TCA; TCE (55 μmoles).	Anaerobic conditions; microorganisms, <i>dehalobacter</i> sp.; phosphate buffered mineral salts medium (pH = 7.2). Anaerobic conditions; microorganisms, <i>dehalobacter</i> sp. and <i>desulfobivrio</i> sp.; anaerobic mineral medium containing vitamins.	CO <sub>2</sub> ; acetate. CA; ethane; Cl <sup>-</sup> .	100% (~7 months) 100% (24 days); 100% (1,1,1-TCA + TCE, 90 days).	Ad: Low cost; in site remediation; Dr: slow kinetics; inhibitive nature for local microorganisms.	Justicia-Leon et al., 2014 Grostern and Edwards, 2006
Phytoremediation	CT (12–15 mg•L <sup>-1</sup> ).	Feeding water containing CT was added to the test beds planted with poplar; beds size, 1.5 m (depth)* 3.0 m (width)* 5.7 m (length).	CO <sub>2</sub> ; Cl <sup>-</sup> .	>99% (5 months).	Ad: Economics, aesthetic and ecologic advantages; Dr: Time consuming; incomplete metabolism and potential increase in bioavailability of contaminants.	Wang et al., 2004
Ozonation	TCE (50 mg•L <sup>-1</sup> ).	Contaminated soil; flushing solvent, acetic acid; ozone concentration, 17 ± 2 mg•L <sup>-1</sup> ; temperature, 20 ± 2°C.	CO <sub>2</sub> ; Cl <sup>-</sup> .	100% (2 h).	Ad: Effective and fast removal of contaminants; Dr: low solubility of ozone in water; ozone scavengers commonly found in environment; incomplete oxidation.	Alcantara-Garduno et al., 2008
Photocatalytic Oxidation	TCE (Absorbance, 0.042). PCMs (3.60 × 10 <sup>-5</sup> –1.75 × 10 <sup>-4</sup> M).	Gas conditions; gas flow 200 mL•min <sup>-1</sup> fir 30 min; infrared cell; UV irradiation, 150 W Xenon lamp; catalyst, N-doped TiO <sub>2</sub> . Gas conditions in O <sub>2</sub> stream; low-pressure	CO <sub>2</sub> ; CO; HCl; COCl <sub>2</sub> ; CHCl <sub>3</sub> O. CO, CO <sub>2</sub> , COCl <sub>2</sub> , HCl.	100% (5 min). 100% (1 h).	Ad: Fast and high efficacy; Dr: high energy consumption; chlorinated byproducts formation; low recovery of catalysts.	Yokosuka et al., 2009 Alapi and Dombi, 2007

(continued on next page)

Table 2 (continued)

Remediation technology	substrate	Reaction conditions	Products	Efficacy	Advantages (Ad)/Drawbacks (Dr)	References
Fenton Oxidation	1,2-DCA (120 mg·L <sup>-1</sup> ). TCE (5 mg·L <sup>-1</sup> ).	mercury vapour lamps; vacuum-ultraviolet (VUV) irradiation at 253.7 nm and 184.9 nm. Wash water of ion-exchange resin, pH 3–4; C <sub>H2O2</sub> = 1200 mg·L <sup>-1</sup> , C <sub>Fe<sup>2+</sup></sub> = 300 mg·L <sup>-1</sup> . TCE-contaminated groundwater, pH 5.4, ORP = 465 mv; 10 g·L <sup>-1</sup> basic oxygen furnace, 1.0 g·L <sup>-1</sup> of H <sub>2</sub> O <sub>2</sub> .	CO <sub>2</sub> ; Cl <sup>-</sup> ; Fe <sup>3+</sup> . CO <sub>2</sub> ; Cl <sup>-</sup> ; CE; DCE.	100% and 87% removal of 1,2-DCA and TOC in 90 min, respectively. 81% (1 h).	Ad: Simplicity and efficiency; Dr: costly chemical addition; acidic conditions; secondary pollutants formation.	Vilve et al., 2010 Tsai et al., 2010
Electrochemical Oxidation	1,2-DCA (16–20 mM). 1,2-DCA; 1,1,2,2-TeCA (4 mM).	Sealed undivided tank thermostated glass cell; aqueous solvent, pH 2, 0.035 M Na <sub>2</sub> SO <sub>4</sub> , T = 283 K; anode: Ti/IrO <sub>2</sub> -Ta <sub>2</sub> O <sub>5</sub> , PbO <sub>2</sub> , BDD etc.; under constant current conditions. Undivided, water-jacketed glass cell; aqueous solvent, pH 3, 0.035 M Na <sub>2</sub> SO <sub>4</sub> ; T = 283 K; anode: BDD; air diffusion cathode with 0.35 L min <sup>-1</sup> of compressed air feeding; under constant current conditions.	CO <sub>2</sub> ; Cl <sup>-</sup> ; 1,1,2-TCA (<1%). CO <sub>2</sub> ; Cl <sup>-</sup> ; ClO <sub>3</sub> <sup>-</sup> ; ClO <sub>4</sub> <sup>-</sup> .	>99% (COD), with current efficiency > 40% (BDD electrode). 100% (420 min).	Ad: Environmental compatibility, versatility, high efficiency, amenability of automation and mild operating conditions; Dr: energy consumption; corrosion and passivation of electrode materials.	Scialdone et al., 2008 Randazzo et al., 2011
Zero Valent Reduction	TCE (100 mg·L <sup>-1</sup> ). PCMs (DCM; CF; CT, 100 mg·L <sup>-1</sup> ).	Performed in 43 mL amber glass vials; mixed on a rotator with 50 rpm; room temperature; carboxymethyl cellulose (CMC) stabilized Fe-Pd bimetallic nanoparticles (C <sub>Fe</sub> = 0.3 g·L <sup>-1</sup> , Pd/Fe = 0.1 wt%). Serum bottles; placed on a rotary shaker (170 rpm, 22 ± 1°C); aqueous conditions, pH 7.0; 10 g·L <sup>-1</sup> Pd-Fe, Pd/Fe = 0.2 wt%. Continuous flow tubular reactor; mixed gas consisting of O <sub>2</sub> , N <sub>2</sub> , PCE and propane; catalyst, Pt/Rh (3:1, w/w); temperature: 473–873 K; residence time, 0.2–0.6 s.	Ethylene, Cl <sup>-</sup> ; DCE; CE. Dehydrogenation products; methane; Cl <sup>-</sup> .	44% and 82% of TCE sorbed in potting soil and Simith Fram soil were degraded in 30 h, respectively; 100% TCE degradation within 4 h in the absence of soil. 100% (CT, 180 min); 99% (CF, 240 min); 15% (DCM, 480 min).	Ad: Thermodynamically favorable; low-toxic or non-toxic products; Dr: relative slow reaction rate; catalyst passivation and loss problems; magnetic agglomeration problems of nanoparticles.	Zhang et al., 2011 Wang et al., 2009
Catalytic Hydrodechlorination	PCE (<600 mg·L <sup>-1</sup> ).	2-propanol as solvent; 0.03 M NaOH, 2 g·L <sup>-1</sup> Pd/Al <sub>2</sub> O <sub>3</sub> (1 wt.%); temperature: 291–348 K.	Ethylene, ethane, Cl <sup>-</sup> .	100% (0.5 s).	Ad: Thermodynamically favorable; low-toxic or non-toxic products; Dr: catalyst passivation problems; external H <sub>2</sub> addition; noble metal catalyst demands.	Willinger et al., 2009
Electrochemical Dechlorination	TCE (0.011 M). PCAs (1,1,1-TCA; 1,1,2,2-TeCA, 10 mM). CT; TCE (2–3 mM).	Divided cell; DMF as solvent, 0.1 M (C <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> NBF <sub>4</sub> as supporting electrolyte; T = 298 K; under potentiostatic conditions. Aqueous conditions, pH ~6.5, 10 mM CaSO <sub>4</sub> as electrolyte; temperature range: 275–315 K; under potentiostatic conditions.	Acetone. Ethylene, acetylene, ethane, Cl <sup>-</sup> . Methane, acetylene, ethylene, Cl <sup>-</sup> .	Turnover frequencies: 0.001 s <sup>-1</sup> in 1 h; complete conversion of TCE was not achieved. 100% (2 h). 100% (30 min).	Ad: Thermodynamically favorable; fast and high efficacy; low-toxic or non-toxic products; Dis: energy consumption; mass diffusion limitations; costly but unstable electrode materials.	Cobo et al., 2011 Huang et al., 2012 Li and Farrell, 2001

diffused into the air, and no significant amount of CTC-chlorine accumulated in the tree tissues. However, phytoremediation suffers from several limitations at the same time, such as slow removal rate, incomplete metabolism and potential increase in bioavailability of contaminants (Aken, 2008).

### 3.3. Advanced oxidation processes

Advanced oxidation processes (AOPs), including ozonation, Fenton oxidation, photocatalytic oxidation and electrochemical oxidation methods, among others, have been one of the most promising technologies for the abatement of Cl-VOCs recently. These methods principally take advantage of the strong oxidation capacity of hydroxyl radical ( $\cdot\text{OH}$ ) to decompose Cl-VOCs and even complete mineralize the contaminants to carbon dioxide (Meng et al., 2002; Randazzo et al., 2011; Tsai et al., 2010; Yokosuka et al., 2009). The unselective oxidation by hydroxyl radical can produce undesired chlorinated intermediates, making it necessary to use a hybrid process that consists of several AOPs to provide higher efficacy toward the degradation of Cl-VOCs (Alapi and Dombi, 2007; Rodríguez et al., 2005). It is worthwhile to point out that, although AOPs can achieve efficient removal of Cl-VOCs, these processes use costly chemicals or have high energy consumptions.

#### 3.3.1. Ozonation method

Catalytic ozonation is a promising technology for the effective removal of pollutants that are resistant to conventional treatment methods, where ozone is used as the powerful oxidizing agents ( $E^0 = 2.07\text{ V}$ ) (Ikhlaiq et al., 2013; Wu et al., 2012). It mainly involves two mechanisms in the presence of organic or inorganic compounds. One is the direct oxidation with ozone molecule, while the other is the indirect oxidation with the secondary oxidants formed upon the decomposition of ozone in water producing hydroxyl radicals (Wu et al., 2012). Ozonation of some Cl-VOCs has been studied by many researchers both under gas and water conditions with the complete removal of contaminants (Alcantara-Garduno et al., 2008; Strokova et al., 2013; Yasunaga and Hisotsuji, 2008). Alcantara-Garduno et al. (2008) used acetic acid and ozone to remove TCE from contaminated soil, where acetic acid was used as a flushing solvent. Results showed that TCE could be successfully removed from soil, and be completely decomposed by the ozone. Some researchers found that the addition of hydrogen peroxide could further improve the reaction efficiency by 40% than that of ozone treatment alone, and the ozone-hydrogen peroxide treatment was very effective on the abatement of TCE in groundwater (Yasunaga and Hisotsuji, 2008). However, the low solubility of ozone in water is the major limitation in the ozonation process, besides the ozone scavengers like humic substances and  $\text{CO}_2$  are commonly found in soil and water, thus restrict its efficacy in practical applications.

#### 3.3.2. Photocatalytic oxidation method

In photocatalytic oxidation, hydroxyl radical is generated from light irradiation of a catalyst such as titanium dioxide ( $\text{TiO}_2$ ) and zinc oxide ( $\text{ZnO}$ ) and then participates in the reaction with pollutants (Hoffmann et al., 1995; Meng et al., 2002). The destruction of Cl-VOCs by using this method could be performed under ambient temperature and pressure with significant lower cost compared to thermal treatments, when the contaminant concentration is low (Borisch et al., 2004). The general principle of photocatalytic oxidation reactions of Cl-VOCs are expressed in Eqs. (1–2). A number of photocatalytic degradation studies have been carried out for the removal of DCM (Borisch et al., 2004; Hsiao et al., 1983; Zuo et al., 2006), CF (Hsiao et al., 1983; Zuo et al., 2006), CTC (Hsiao et al., 1983; Zuo et al., 2006), and TCE (Driessen et al., 1998; Hung and Marinas, 1997; Hwang et al., 1998; Zuo et al., 2006) with remarkable results. For instance, Yokosuka et al. (2009) showed that, with N-

doped  $\text{TiO}_2$ , TCE could be decomposed rapidly under both ultraviolet (UV) and visible irradiation, producing  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{COCl}_2$  and  $\text{HCl}$  as end products. However, using photocatalytic oxidation method alone may produce chlorinated species (Borisch et al., 2004; Driessen et al., 1998), making it necessary to use a combination of ultraviolet with ozone, hydrogen peroxide, or Fenton reagent to enhance the degradation of these compounds (Alapi and Dombi, 2007; Rodríguez et al., 2005).



#### 3.3.3. Fenton oxidation method

There are two types of Fenton oxidation: one is the standard Fenton reaction with soluble ferrous ion ( $\text{Fe}^{2+}$ ) as catalyst (Eq. (3)) and the other is the so-called Fenton-like process, in which ferric ion ( $\text{Fe}^{3+}$ ) and iron oxides are utilized as catalysts (Eqs. (4–5)).

Both processes utilize strong oxidizing hydroxyl radicals generated from the reaction between  $\text{H}_2\text{O}_2$  and the catalyst to decompose recalcitrant compounds. The only difference lies in the operating pH condition: for the Fenton-like process, iron oxides can degrade organic compounds more effectively at neutral pH, whereas the standard Fenton reaction is always performed at acidic condition (Tsai et al., 2010). The Fenton oxidation process has attracted a significant amount of attention for the removal of Cl-VOCs due to its simplicity and efficiency (Chen et al., 2001; Grčić et al., 2009; Teel et al., 2001; Tsai et al., 2010; Vilve et al., 2010; Yeh et al., 2003; Yoshida et al., 2000). Vilve et al. (2010) showed that 1,2-DCA degradation and TOC (total organic carbon) removal from wash water of ion-exchange resin could reach up to 100% and 87% respectively by the standard Fenton reaction. Tsai et al. (2010) reported that around 81% of TCE could be removed by the Fenton-like reaction, in which  $1.0\text{ g}\cdot\text{L}^{-1}$  of  $\text{H}_2\text{O}_2$  and  $10\text{ g}\cdot\text{L}^{-1}$  of basic oxygen furnace slag were introduced into the system. Successful treatments of CF, TCE, PCE, and 1,2-DCA by the Fenton reagent have been reported. Taking TCE for instance (Yoshida et al., 2000), results showed that 40% of the added TCE in DNAPL (dense non-aqueous phase liquid) could be oxidized in 1 h with a single application of 3%  $\text{H}_2\text{O}_2$  to the aquifer sand containing  $2.01\text{ g}\cdot\text{kg}^{-1}$  of extractable iron, demonstrating the ability of mineral catalyzed Fenton-like reaction to directly oxidize TCE in non-aqueous liquid (Yeh et al., 2003).



#### 3.3.4. Electrochemical oxidation method

Recently, electrochemical AOPs such as anodic oxidation and electro-Fenton process have also gained much interest for the removal of chlorinated solvents due to their environmental compatibility, versatility, high efficiency, amenability of automation, and, most importantly relatively mild operating conditions. Some research showed that the electrochemical degradation of Cl-VOCs with boron-doped diamond (BDD) anode had high substrate removal and lower cost than ozonation and Fenton oxidation (Beteta et al., 2009; Cañizares et al., 2008; Cañizares et al., 2009). It was shown that the effectiveness of electrochemical oxidation of chlorinated aliphatic compounds depends mainly on the anodic materials, the best of which is high oxygen overvoltage electrodes (Bejankiwar et al., 2005; Randazzo et al., 2011; Scialdone et al., 2008). BDD electrode has much higher efficiency than stainless



steel, Pt, Au, Ebonex, Ti/IrO<sub>2</sub>-Ta<sub>2</sub>O<sub>5</sub> and PbO<sub>2</sub> anodes for the removal of dissolved organic carbon during the oxidation of 1,2-DCA (Bejankiwar et al., 2005; Scialdone et al., 2008). Almost complete conversion of 1,2-DCA was achieved at the BDD electrode with more than 40% current efficiency at proper applied current density (Scialdone et al., 2008). Chen et al. (1999) presumed that the oxidizing specie for abatement of chlorinated solvents was surface-adsorbed hydroxyl radicals resulted from oxidation of H<sub>2</sub>O and OH<sup>-</sup> at titanium oxide anode. Recently, some hybrid technologies have been developed to enhance the abatement efficiency for chlorinated aliphatic hydrocarbons. For instance, the combination of anodic oxidation and cathodic reduction gave higher removal of PCAs (1,2-DCA and 1,1,2,2-TeCA) with the same amount of electricity used in the uncoupled process (Scialdone et al., 2010).

Electro-Fenton process was carried out for the treatment of PCAs by combining a BDD anode and an air diffusion cathode to generate the H<sub>2</sub>O<sub>2</sub> in situ (Eq. (6)), which could further react with Fe<sup>2+</sup> to yield •OH (Eq. (3)). The result was almost complete mineralization of 1,2-DCA and 1,1,2,2-TeCA at 300 mA in 420 min, while treatments without Fe<sup>2+</sup> (anodic oxidation) or using Pt anode resulted in poor mineralization performance in comparative experiments (Randazzo et al., 2011). The reactions are shown in Eqs. 6–9.



In summary, although AOPs are attractive for the abatement of Cl-VOCs, certain limitations need to be overcome. For instance, ozonation is restricted by the low solubility of ozone in water and the presence of ozone scavengers in environment; the Fenton reaction is limited by the presence of dissolved oxygen, and the photocatalytic technique suffers from poor oxidation efficiency in groundwater treatment and low recovery of catalysts; the electrochemical oxidation methods face problems like high energy consumption as well as the corrosion and passivation of electrode materials. Other issues include the addition of costly chemicals, potential formation of secondary pollutants as well as rigorous reaction conditions (such as acidic pH, high temperature, etc.) (Tsai et al., 2010; Vilve et al., 2010; Yokosuka et al., 2009). All of these factors contribute to make AOPs as not devoid of drawbacks.

### 3.4. Reduction methodologies

The electronegative nature of chlorine in Cl-VOCs suggests that reductive dechlorination is thermodynamically favorable to occur. Furthermore, the corresponding end products (i.e. non-chlorinated hydrocarbons and chlorine ions) are low-toxic or non-toxic substances for environment. These advantages provide the driving force for the development of reduction methods, including zero valent metal/bimetal catalytic reduction, catalytic hydrodechlorination and electrochemical reduction. All of these methods have remarkable efficacy for the abatement of chlorinated hydrocarbons (Wang et al., 2009; Huang and Lien, 2010; Sriwatanapongse et al., 2006; Farrell et al., 2000; Li and Farrell, 2001; Rondinini and Vertova, 2004; Isse et al., 2009; Huang et al., 2012).

#### 3.4.1. Zero valent metal and bimetal reduction method

Since Gillham and O'Hannesin discovered that metallic iron fillings could be utilized in groundwater remediation (Gillham and O'Hannesin, 1992), the use of zero valent iron (ZVI) for in-situ remediation of groundwater that is contaminated by Cl-VOCs has received considerable attention worldwide (Dries et al., 2004; He et al., 2010; Kohn et al., 2005; Liu

and Lowry, 2006; Zhang et al., 2011). Iron serves as the electron donor to reductively dechlorinate Cl-VOCs to their non-chlorinated products and chlorine ions. Besides iron, other base metals, such as zinc and magnesium, are also effective for the same application (Casey et al., 2000; Patel and Suresh, 2008; Sarathy et al., 2010; Song et al., 2008). An obvious drawback of this technology is the relatively slow reaction rate as degradation of Cl-VOCs requires a couple of days to reach the desired level of completion. Another challenge to this technology is the dissolution and surface passivation problem over active metals.

To enhance the dechlorination activity and to prolong the active state of base metal (Fe), a second transition metal with high hydrogenation ability (e.g. Pd, Ni, Ru and Pt) is incorporated for the bimetal system (Cwiertny et al., 2006; Huang and Lien, 2010; Lien and Zhang, 2001, 2005; Tee et al., 2009; Wang et al., 2009; Zhang et al., 1998). The resulting dechlorination efficiency is higher as compared to single metals. The main mechanism is presumed to be the formation of a transition metal complex through the interactions between the empty orbital of transition metal and the p electrons of chlorines in Cl-VOCs or the π electrons from unsaturated compounds (M · · · Cl · · · R), which could lower the activation energy barrier of dechlorination reaction. The dechlorination process normally involves three reduction steps (Eqs. (10–12)) (taking Pd/Fe bimetal for example; Wang et al., 2009). H<sub>2</sub> is first generated as a result of the corrosion of base metals (Fe) under aqueous conditions (Eq. (10)); the H<sub>2</sub> then dissociates into hydrogen atoms and chemisorbs on the transition metal (Pd) surface, or even diffuses into its lattice with the formation a strong reductive substance (PdH<sub>x</sub>, Eq. (11)); eventually, reductive dechlorination reaction takes place as the hydrogen attached to the catalyst surface continuously attacks the C-Cl bond of Cl-VOCs (Eq. (12)).



Due to the remarkable properties of bimetal catalysts such as high reactivity and fast kinetics, this method has been widely applied for the remediation of CTC (Huang and Lien, 2010; Wang et al., 2009), CF (Huang and Lien, 2010; Wang et al., 2009), DCM (Huang and Lien, 2010; Wang et al., 2009), PCE (Lien and Zhang, 2001; Zhang et al., 1998), TCE (Lien and Zhang, 2001; Tee et al., 2009; Zhang et al., 1998), DCE (Lien and Zhang, 2001; Zhang et al., 1998), 1,1-DCA (Cwiertny et al., 2006), 1,1,1-TCA (Cwiertny et al., 2006; Lien and Zhang, 2005), and 1,1,2,2-TeCA (Lien and Zhang, 2005) with encouraging dechlorination efficiencies.

One particular problem associated with bimetal catalysts is the agglomeration of the fine particles because of magnetic effect, but this can be overcome by the modification of catalyst surface with polymers or surfactants (Kustov et al., 2011; Tiraferri et al., 2008). However, the excessive preparation procedures coupled with the consumption of costly noble metals limit the wide practical application of this technology.

#### 3.4.2. Catalytic hydrodechlorination method

Catalytic hydrodechlorination is another promising novel method for the treatment of hazardous chlorinated hydrocarbons and pesticides in contaminated groundwater and air (Gao et al., 2008; McNab and Ruiz, 2000; Orbay et al., 2008; Willinger et al., 2009). The equipment for catalytic hydrodechlorination comprises mainly a packed-bed catalytic reactor and a hydrogen source. Based on the reaction conditions, it can be divided into aqueous phase reaction and gas phase reaction. The influent that is saturated with hydrogen in the aqueous-phase reaction, or the hydrogen gas that is mixed with Cl-VOCs vapors in the gas phase

reaction, is fed into the reactor for the chlorinated substrates to react with hydrogen over the catalyst surface (Ordóñez et al., 2002; Sriwatanapongse, 2005; Sriwatanapongse et al., 2006). The mechanism is similar to that of bimetal reductive dechlorination, consisting of three steps: adsorption, reaction at the catalyst surface and finally desorption. Among the three steps, the adsorption between chlorinated compounds and catalyst could lower the C-Cl bond strength and promote it easier to be ruptured (Sriwatanapongse, 2005). Obviously, catalyst plays an essential role during dechlorination process. Palladium is found to be the best hydrodechlorination catalyst among other noble and transition metals, which is capable and has been widely applied for the dechlorination of various groups of chlorinated compounds, involving chlorinated methanes, ethanes, ethylenes, and chlorinated aromatics (Sriwatanapongse, 2005).

A study on the catalytic hydrodechlorination of PCE, TCE, 1,1-DCE, *cis*-DCE, and *trans*-DCE over NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst was conducted by Kim and Allen (1997). Results showed that a fast dechlorination reaction could take place even at relative lower temperature with respect to those for chlorinated aromatic compounds, while a multiple chlorines removal process rather than sequential dechlorination steps occurred during the reduction process. Another investigation of catalytic hydrodechlorination of DCM, CF and PCE on Pd/TiO<sub>2</sub> revealed that the reactivity order follow the sequence of CF > PCE > DCM, whereas significant catalyst poisoning by chlorine was observed (Gonzalez et al., 2009).

In catalytic hydrodechlorination, the catalyst is readily deactivated in both gas and aqueous phases, following a trend that drops rapidly at the beginning and then decreases gradually (Gonzalez et al., 2009). The deactivation mechanism, however, is still not very clear. One possibility is catalyst poisoning by the dechlorination products that occupy the activation sites of catalyst (Sriwatanapongse, 2005). Due to the deactivation, regeneration procedures must be taken into account. In addition, as aforementioned, external hydrogen source is required to feed into this system, coupled with noble metal demands in catalyst increase the processing cost of this method.

Similar to zero-valent metal remediation, catalytic dechlorination faces challenges such as corrosion of metals, passivation of catalyst surface, precipitation of metal hydroxides as well as slow kinetics (Álvarez-Montero et al., 2010, 2011; Gonzalez et al., 2009). One way to overcome these problems is to use these metals as cathode materials for electrochemical reduction. In contrast to the zero-valent metals, which are consumed through providing electrons for the hydrodechlorination process, the metal cathode serves as electron donor and is protected from corruptions by cathodic potential. Another advantage of electrochemical reduction is the use of electron as main reactant, a clean reagent produced by the appropriate cathode materials without additional chemicals. In addition, this technology can provide controllable reaction rate as well as cathodic protection of metals against passivation, which can further prolong the life span of cathodic materials (Durante et al., 2009; Huang et al., 2012; Li and Farrell, 2001; Liu et al., 2000). In recent years, electrochemical reductive dechlorination has attracted a huge amount of attention for the abatement of chlorinated organic compounds worldwide (Costentin et al., 2003; Farrell et al., 2000; Huang et al., 2012; Isse et al., 2009; Li and Farrell, 2001; Rondinini and Vertova, 2004; Sonoyama and Sakata, 1999).

#### 3.4.3. Electrochemical reduction method

Previous studies have shown that electrochemical dechlorination of Cl-VOCs can be performed in both aqueous (Farrell et al., 2000; Li and Farrell, 2001; Sonoyama and Sakata, 1999) and non-aqueous solutions (Costentin et al., 2003; Huang et al., 2012; Isse et al., 2009; Rondinini and Vertova, 2004). Under aqueous conditions, reductive dechlorination reactions take place on the metal electrode (Eqs. (13–14)) consisting of the formation of adsorbed atomic hydrogen from the electrolysis of water, and the hydrodechlorination reactions between adsorbed atomic hydrogen and chlorinated compounds (Li and Farrell,

2001). On the other hand, electrochemical dechlorination under non-aqueous conditions proceeds principally via dissociative electron transfer, where C-Cl bond is ruptured by accepting one electron transfer and in concomitant with dehalogenation product formation by receiving another electron transfer and proton donor, as demonstrated in Eqs. (15–16). Extensive investigations have been carried out for the dechlorination of chlorinated compounds on various electrode materials, notably, Ag, Pt, Pd and other noble metals exhibit excellent catalytic activities toward C-Cl bond dissociation (Li and Farrell, 2001; Isse et al., 2008). For instance, electrochemical dechlorination of PCE in aqueous solution at a lead cathode can achieve nearly complete degradation of PCE (lower than 7% of the initial concentration) at potentials lower than hydrogen evolution reaction onset (Sáez et al., 2009). A similar study was conducted for a porous nickel electrode, showing that TCE and *trans*-DCE were the only detectable chlorinated intermediates during electrolysis. Complete dechlorination of PCE was achieved at the end of electrolysis study with ethane, ethylene, *trans*- and *cis*-2-butene, 1-butene, propane, isobutene, and hexane as the final products (Liu et al., 2000).



Other studies show that (Durante et al., 2009, 2012, 2013; Huang et al., 2012; Isse et al., 2009, 2012), Cl-VOCs including PCMs, PCAs and PCEs can all achieve complete dechlorination with the formation of saturated or unsaturated aliphatic hydrocarbon in dimethylformamide (DMF) solution by using electrochemical reduction method at glassy carbon (GC), Ag and Cu electrode. Research also demonstrated that the mechanisms of reductive dechlorination of Cl-VOCs depend on their molecular structures regardless of cathodic materials, while the electrolytic products are determined by both the molecular structures of Cl-VOCs and solvent conditions (Durante et al., 2009; Huang et al., 2012).

Despite its remarkable dechlorination performance towards Cl-VOCs, electrochemical reduction has problems such as high energy consumption (due to low current efficiency) and costly but unstable electrode materials. Future directions on the electrochemical device construction and optimizations, such as development of dimensionally-stable and efficient cathode materials, large area flow-through cathode design, as well as assessment of the most appropriate electrolytic conditions, need to be carefully studied for a practical utilization of this approach towards the remediation of Cl-VOCs.

## 4. Conclusions

Cl-VOCs have been widely used as important solvents in both industry and laboratory, as degreasing agents and as intermediates in producing valuable commercial products. Due to their wide applications, Cl-VOCs are among the most ubiquitous environmental contaminants that are frequently detected in the contaminated soil, air and any kind of fluvial mediums, such as rivers and groundwater. In general, the releases of Cl-VOCs into the environment mainly occur during their manufacture processes (either as intermediates or end-products), the consumption of Cl-VOCs-containing products, the disinfection process as well as improper storage and disposal processes, leading to evaporation, leaks, and other pollution forms discharging into the environment media.

Owing to the persistent and recalcitrant properties of Cl-VOCs, they can remain stable in the environment for a long time, causing severe

effects on both environment and human health. Some of the Cl-VOCs released into the atmosphere may contribute to ozone depletion, further impacting on people health and other living organisms on the earth. People exposure to Cl-VOCs may occur through inhalation of vapors because of their high volatility, ingestion of contaminated food or water and dermal contact owing to their widespread presence in air and, surface and groundwater. But the relative importance of these routes has not been clearly classified, as well as the exposure levels in contaminated sites need to be carefully evaluated in the future work.

Sufficient evidence has confirmed the associations of Cl-VOCs exposure with potential toxicity to human. Most of these contaminants are suspected or even identified as being carcinogenic in experimental animals, but such evidence is lacking for human. Therefore, the epidemiological studies for the risk assessment of human exposure to Cl-VOCs and the potential mechanisms for cancer formation should be carried out in the future. Generally, some species of Cl-VOCs including DCM, CF, CTC, 1,2-DCA, 1,1,1,2-TeCA, HCA, TCE and PCE have been listed as possible human carcinogenic substances by the IARC, particularly, CE has been classified as carcinogen; some of them have also appeared in the list of priority pollutants by U.S. EPA, MEP of China and Europe Commission and are under close monitor and strict control in environment media.

The ubiquitous existence of Cl-VOCs in environment as well as their potential toxicity to human provides the driving force for the development of remediation methods. These methods generally can be classified as non-destructive and destructive. The non-destructive methods take advantage of the physicochemical properties of chlorinated compounds with fast removal efficiency. Furthermore, these methods (e.g. adsorption) provide the possibility of recovering the pollutants for reuse, as the nature of these chemicals remains.

For the phytoremediation and biodegradation methods, Cl-VOCs can be removed from the contaminated sites directly under natural conditions, but it is often time-consuming because of slow kinetics. AOPs, including ozonation, photocatalytic oxidation, Fenton oxidation and electrochemical oxidation methods, among others, can be successfully applied for the abatement of Cl-VOCs with relatively high removal efficiencies. Undesirable by-products resulted from the unselective oxidation of Cl-VOCs by radical intermediates, the addition of costly chemicals as well as high energy consumptions are some drawbacks of AOPs, which need to be overcome in the future.

Owing to the electronegative character of chlorine atoms in Cl-VOCs and the low-toxic or non-toxic nature of dechlorination products, reductive dechlorination methods, such as zero valent metal/bimetal reduction, catalytic hydrodechlorination, and electrochemical reduction, are promising abatement technologies for Cl-VOCs. The main obstacles for the first two reduction methods are catalyst passivation and poisoning as well as metal corrosion, but can be effectively overcome by cathodic protection of electrode materials. Generally, electrochemical reduction has remarkable dechlorination performance for the abatement of Cl-VOCs with the formation of dechlorinated aliphatic hydrocarbons. Further development in electrochemical reduction should focus on the construction and optimization of electrochemical device, including the development of dimensionally-stable and efficient cathode materials, large area flow-through cathode as well as the assessment of the most appropriate electrolytic conditions, in order to lower the process cost. Finally, hybrid processes that combine different methods are an interesting direction for future study as all the abatement methods for Cl-VOCs have their own advantages and limitations. The choice of remediation technologies for the contaminated sites needs a comprehensive consideration of both their applicability and the practical pollution situations.

## Acknowledgements

This work was financially supported by Hunan University (No. 531107040689), and the National Natural Science Foundation of China

(No. 21037001). The authors thank Dr. CHEN wenqian from Imperial College London for valuable suggestions.

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