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Application of Risk Assessment Study at Petro-Processors of Louisiana, Inc. (PPI) Site

Seçil TUTAR ÖKSÜZ *1 

Abstract

Petro-Processors of Louisiana, Inc. (PPI) site, located North of the city of Baton Rouge Parish, used two sites as depositories for various petrochemical wastes from mainly the 1960s until the 1980s. The main problem was the potential for leachate migration and for exposure of toxic materials, which had been released into local waterways. Therefore, the site is considered a public health hazard area because of risks to human health from past, present, and future exposure to hazardous substances. This study focuses on investigating selected chlorinated organic liquids, which are the predominant contaminants among all wastes: Hexachlorobenzene (HCB) and Hexachlorobutadiene (HCBd) with possible health effects using a risk assessment study. The results show that even though the petrochemical waste disposal has completely shut down since 1980, it will still take an average of the HCB and HCBd to reach the domestic well with groundwater is 68 years and 57 years, respectively via slow migration, which will increase the cancer risks for the people who live near PPI site. Our results indicated that the cancer risks of exposure to HCB and HCBd are 4.6×10^{-6} and 2.6×10^{-3} , respectively, which are more than the 10^{-6} goal. In addition, this study can be used at similar sites and for different compounds to investigate the potential impacts of pollutants on human health.

Keywords: Petro-Processors of Louisiana, chlorinated hydrocarbons, risk assessment

1. INTRODUCTION

The increase of the human population The world's population has exponentially increased during the last century bringing environmental problems with it [1, 2]. Even though reducing or eliminating the sources of pollution and protecting aquifers has become one of the major challenges in this century, inadequate or uncontrolled solid and liquid municipal or industrial waste disposal has

resulted in contaminated soil and groundwater resources [3, 4]. The disposal sites are generally operated illegally without environmental permits since the decision makers failed to take action to provide proper operation [5]. The level of environmental pollution depends on different factors such as the type and quantity of the contaminants, the operation period, soil type, groundwater level, distance from agricultural lands and residential areas [6, 7]. Several studies have been established on different disposal sites to

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investigate groundwater pollution by various pollutants with environmental impacts worldwide [8-11]. Petro-Processors of Louisiana, Inc. (PPI) site is one of the disposal sites in the U.S. that hasn't been investigated in detail. The site locates North of the city of Baton Rouge that covers about 97 acres, with two former petrochemical disposal areas situated 1.5 miles apart near Scotlandville, East Baton Rouge Parish, Louisiana [12]. The first petrochemical disposal area is called Scenic Highway, which is 17 acres, and was used as a depository from 1961 to 1974. After the Scenic highway site was full of waste, the Brooklawn, which is 80 acres, was started to use as a waste disposal area until 1980 (Figure 1) [13, 14].

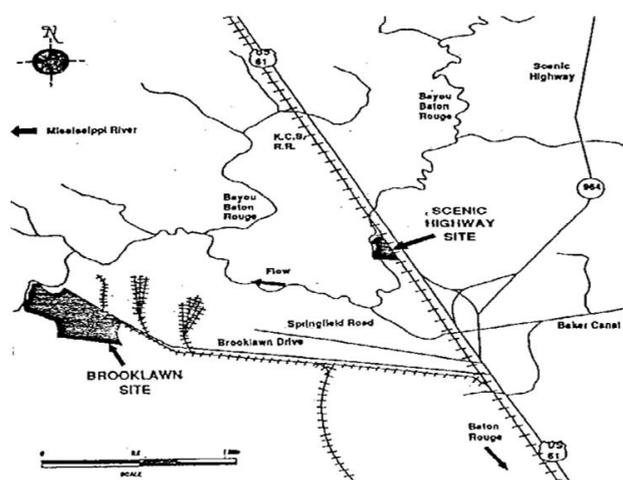


Figure 1 Site location map

Various petrochemical waste products including Hexachlorobenzene (HCB), Hexachlorobutadiene (HCBd), 1,1,2,2-Tetrachloroethane (TeCA), 1,1,2-Trichloroethane (TCE), 1,2-Dichloroethane (DCA), Tetrachloroethane (PCE), Trichloroethane (TCE), trans-1,2-Dichloroethane (trans-DCE), CIS-1,2-Dichloroethane (CIS-DCE) and Vinyl Chloride (VC) were deposited in both sites from the 1960s until the 1980s and approximately 320,000 tons of waste disposed of these areas [12, 15]. Following the disposal of wastes, the investigations have detected chlorinated aromatic and nonaromatic hydrocarbons in samples from the soil, groundwater, and air at both disposal sites and surface water samples at the Brooklawn site.

Before the remediation movement was started for the PPI sites, several actions have been considered. First, the U.S. Justice Department, the State of Louisiana, the City of Baton Rouge, and the Parish of East Baton Rouge jointly filed a lawsuit against PPIs and industry defendants who dumped wastes at the sites in 1980. According to the consent decree, the defendants had to design and perform a remedial action for the sites. Therefore, a remedial action work plan was submitted and the Middle District of Louisiana (Federal Court) issued an order approving the CD (NPC 1984a) for the remedial action at the PPI site in 1984. In this context, the remedial program was designed by the Industry Defendants and NPC Services, Inc. (NPC) to carry out these remediation activities. However, airborne volatile organic wastes at the sites were detected depending on the remedial activities. That's why hydraulic containment, recovery, and treatment were selected as the primary remedial activities for the sites in 1988. Later, the United States Environmental Protection Agency (EPA) approved an Interim Remedial Action for the Scenic OU in November 2001 (NPC 2001c) and for the Brooklawn OU in July 2003 (NPC 2003a). A Preliminary Close Out Report was also approved in July 2003 (NPC 2003b) [13, 15].

The limited work has been done on the disposal sites in the literature, and most of them were about the degradation processes of the waste products [16]. The first study was published by Constant and his research group in 1995. The main objective was to investigate the biodegradation of chlorinated organics. The authors found that a high concentration of chlorinated organics is toxic to microorganisms and has inhibitory effects on biodegradation [15]. In the following study, Zhang and colleagues [17] investigated how to enhance the biodegradability of chlorinated organics by adding nutrients and surfactants. The authors suggested that biodegradation of wastewater containing high chlorinated organics was significantly enhanced by amended mineral nutrients (such as N and P)

and carbon sources (such as Witconol). Following studies mostly focused on the degradation of desorption-resistant organic chemicals with mineralization and plant uptake [18-22]. Lee and colleagues (2003) [18] studied the mineralization of 1,4-dichlorobenzene at the site. They found that aged compounds result in slow diffusion in soil samples, which decreases the overall mineralization rate. In another study, Gomez (2002) [19] studied plant-based remediation of the disposal sites investigating how wetland plants take up organic chemicals and transport them to other parts of the plants. The author indicated that desorption-resistance and aged chlorobenzene slow the plant uptake, and it is not easy to develop a mathematical model.

Even though few works have been published on degradation of organics in the disposal sites, no study has been conducted on risk assessment of the contaminated sites. This study focuses on Hexachlorobenzene (HCB) and Hexachlorobutadiene (HCBD) as model pollutants since they are reported as the principal contaminants among all wastes at both sites. The main problem was the potential leachate migration and exposure to toxic materials into local waterways. Therefore, in addition to finding a suitable treatment method, it is necessary to evaluate the risk of exposure since the adverse effects can emerge after decades, even after hundred years. The aim of this work is to investigate the possible pathways of the contaminants and find the average travel times for both contaminants from the source area to the closest water well. Then, a risk assessment study was conducted to evaluate the potential health risk of exposing HCB and HCBD.

2. METHODOLOGY

2.1. Transport of the Contaminants

This paper has investigated the transport of the chlorinated organic liquids (HCB and HCBD) in the different phases to calculate average travel time and then conducted a risk assessment study to evaluate the risk for the

people who live near the PPI site. Since the environmental fate and transport of the pollutants depend on their concentration in the environment, which controls the rate of chemical reactions and pollutant effects (such as toxicity), the mass-based concentration is calculated using the ideal gas law (Eq. 1) [23]. Chemical and physical properties of these chemicals are listed in Table 1.

Table 1 Physical and chemical properties of HCB and HCBD

	HCB	HCBD
Chemical Formula	C ₆ Cl ₆	C ₄ Cl ₆
Molecular Weight (g/mol)	284.76	260.76
Vapour Pressure (atm) ^a	1.72x10 ⁻⁵	0.22
Density (g/m ³)	2.04	1.66
Kow	6.18	4.78
Henry's constant (L atm mol ⁻¹) ¹	3.3x10 ⁻²	2.3x10 ⁻³
Boiling Point (°K) ^b	612	419
Melting Point (°K)	441	-6

^aVapor pressures at 25 °C

^bBoiling points at 1 atm

$$C_g = \frac{x P_{vp} MW}{R T} \quad (1)$$

Where C_g is concentration in gas (mg/L), x is mole fraction (equal mole fractions which is 0.5), P_{vp} is vapour pressure (atm), MW is molecular weight (g/mol), R is the universal gas constant (0.0821 L-atm/°K-mole) and T is the temperature (298 °K) [24, 25].

To calculate the retardation factors for HCB and HCBD, first, we calculated the soil-water partition coefficient, K_d (L/kg). This partition coefficient is dependent on the fraction of organic matter (f_{oc}), which is 0.39%, present in the soil and also on the octanol-water partition coefficient (K_{ow}), as given in Equation 2 [26].

$$K_d = 10^{0.81} K_{ow} f_{oc} \quad (2)$$

Using K_d values, we calculated the retardation factors (R), which is that a chemical is held back by the soil in comparison to the groundwater velocity [Eq.3] [27].

$$R = 1 + \frac{\rho_b}{n} K_d \quad (3)$$

Where ρ_b is the bulk density (g/cm^3), and n is the porosity [24, 25, 28]. Based on this information, the estimated average travel time of the HCB and HCBd will be calculated.

2.2. The Risk Assessment Framework

The risk is an inherent property of everyday human existence, so a key factor in all decision making [29]. Risk assessment can be defined as the process of estimating both the probability that an event will occur, and the probable magnitude of its adverse effects such as economic, health-related, or ecological from a chemical or stressors over a specified time period [30, 31]. A formal risk assessment has four steps: hazard identification, exposure assessment, dose-response assessment, and risk characterization as shown in Figure 2 [31].

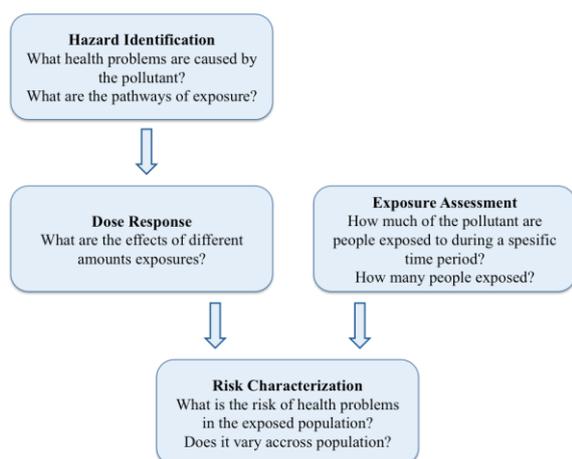


Figure 2 The process of risk assessment

Definition of the hazard is the potential for harm or an adverse effect on humans; for example, identifying chemical contaminants such as, a heavy metal, and documenting its toxic effects on humans. For HCB and HCBd, the substances can be absorbed through the skin as well as inhaled. Chronic oral exposure to HCB in humans can result in a liver disease with associated skin lesions. In addition, HCBd can irritate the nose, eyes, and throat besides damage the lung, liver, and kidneys [32-34].

Calculation exposure requires information on the concentrations of contaminants and the

timeframe over which exposure occurs in target organisms [30]. For example, finding the concentration of mercury in canned tuna products and determining the dose an “average” person would receive. In this study, for exposed of HCB and HCBd, the reported intake/contact rate (CR) is 2 L/day; exposure frequency (EF) is 350 days/year; exposure duration (ED) is 1 year [31].

To quantify the adverse effects arising from exposure to a hazard on the degree of exposure Eq. 4 is used. For average daily doses (or chronic daily intake) of HCB and HCBd is normalized as milligrams of HCB and HCBd inhaled through the skin per kilogram of body weight per day ($\text{mg kg}^{-1} \text{day}^{-1}$).

$$CDI = \frac{C \times IR \times EF \times ED}{BW \times AT} \quad (4)$$

Where CDI is chronic daily intake ($\text{mg kg}^{-1} \text{day}^{-1}$); C is concentration of chemical in each medium (e.g., mg/L for water or mg/m^3 for air); IR is intake/contact rate (L/day); EF is exposure frequency (days/year); ED is exposure duration (years); BW is body weight (kg); AT is averaging time (period over which the exposure is averaged-days). According to United States Environmental Protection Agency [35], standard default exposure factors for inhalation of contaminants: IR is 2 L/day; EF is 365 days/year; ED is 1 year; BW is 70 kg; AT is 365 days (365 days/year x 1 year).

Since the objective of the risk characterization is to summarize the outputs from the previous sections and provide an overall conclusion about the risk, Eq. 5 is used to calculate the theoretical risks of HCB and HCBd to determine if they would be carcinogenic in humans.

$$Risk = CDI \times CSF \quad (5)$$

Where CSF is cancer slope factor (also known as potency factor) and risk is a unitless probability of an individual developing cancer over the period of exposure.

3. RESULTS AND DISCUSSION

Even though various petrochemical wastes were disposed of in Brooklawn and Scenic sites, HCB and HCBd were found as predominant contaminants among all wastes. HCB (C_6Cl_6) is a persistent white crystal-looking solid, which is not naturally available in the environment but is produced as a by-product in different industries [36]. Even though there is no longer uses of HCB in the United States currently, it was widely used as a pesticide against fungus until 1965 [37]. After it is banned, the emissions of HCB has been significantly decreased but it is still found in the environment and also the food chain because of its high molecular chemical stability, low solubility, persistence and liposolubility, and may create a significant risk for groundwater [38, 39]. HCB may be released into the receiving environment during production, usage, discharged as waste, and other processes. HCB has a greater *Kd* value that indicates it is more likely to sorb to the soil compared to HCBd. On the other hand, HCBd has a greater solubility value that indicates it is more likely to dissolve to water compared to HCB. These explains why travel time of HCB to the well is longer than HCBd's. The average travel time of HCB through the groundwater was evaluated based on the concentrations in gas, which is 1×10^{-4} mg/L. According to the calculations, the estimated average travel time of the HCB to reach the domestic well with a groundwater is 68 years (Table 2).

Table 2 Estimate average travel time for the HCB and HCBd

	Cg (mg/L)	Kd (L/kg)	Reterdation Factor	Time (year)
HCB	1×10^{-4}	0.156	1.542	68
HCBd	1.17	0.120	1.41	57

Even though the main routes of human exposure to HCB are through food and water, it can also occur through the inhalation of particles and dermal absorption [40-42]. Right after HCB enters the body, it may spread to the tissues and can stay in the body for years. The health effects of HCB exposure have been

extensively studied in animal studies, and results show that relevant concentrations of HCB may cause cancer of the liver, kidney, and thyroid, and also harm immune system [32]. One of the previous studies confirmed that long-term oral exposure to HCB in humans results in skin lesions due to the consumption of bread made of HCB-contaminated grain in Turkey in the late 1950s [43, 44]. Miret and colleagues (2019) [45] conducted a study to investigate the impact of HCB on the mammary gland and breast cancer. Their findings indicated that if HCB exists and bioaccumulates in high-fat tissues, this increases a risk factor for breast tumor development in both rodent and human. Exposure to HCB during pregnancy resulted in reduced baby birth weight. In another work, Krönke and colleagues (2022) [46] reported that HCB exposure to pregnant woman cause abnormalities in thyroid hormone of both mother and the baby.

On the other hand, HCBd (C_4Cl_6) had no natural sources, and it is a man-made chlorohydrocarbon and listed in the Stockholm Convention on Persistent Organic Pollutants in 2011 [47]. HCBd is produced as a by-product during the manufacture of other chemicals (i.e. chlorinated hydrocarbons) and can be used as scrubbers for removing chlorine-containing contaminants from gas streams, hydraulic fluids, lubricants, isolation and heat-transfer liquids [48, 49]. HCBd can migrate to other places and transfer among different media through volatilization, absorption, deposition, and bioaccumulation due to its high volatility and hydrophobicity. Since volatilization is governed by a chemical's vapor pressure and the high value of *Pvp* for HCBd is an indicator of its likelihood to transfer into the gaseous phase, so we found that the concentrations in gas is 1.17 mg/L for HCBd, which is more than 10,000 times higher the concentrations in gas of HCB at the disposal sites. According to a report by Environment Canada (1999), HCBd was found to be mobile in sandy soils in a dune infiltration study [50]. Based on the concentration in gas, the estimated average

travel time of the HCBd to reach the domestic well with groundwater is 57 years (Table 2). Since HCBd has low solubility and a relatively high K_{ow} , there is a potential risk of HCBd bioaccumulation in living organisms. The previous studies show that HCBd may be absorbed by the body via inhalation, dermally or oral and may have adverse effects on human health [51]. HCBd has been demonstrated to be one of the most nephrotoxic chlorinated hydrocarbon [47, 52], and its toxicity has been extensively studied in animals [53, 54]. The animal experiments have confirmed that the primary target organ of HCBd is kidney, having caused different anomalies such as necrosis of the pars recta of the rat kidney [55], regucalcin down-regulation in rat kidney [56], and kidney injury molecule-1 in rat [57]. The transformation of highly toxic intermediates from HCBd in livers and kidneys is the key factor for HCBd nephrotoxicity [48, 58]. Literature shows that HCBd poses potentially carcinogenic toxicity to organisms. Swain and colleagues (2012) [59] observed kidney degeneration in male rats at HCBd doses of as low as 10 mg/kg. Besides, HCBd shows genetic toxicity to organisms. Brüsweiler and colleagues (2010) [60] found that HCBd can covalently bind to DNA in rats' kidney and also to mitochondrial DNA in female rats' liver and kidney.

Assess the potential human health risk that may be associated with drinking water was calculated based on chronic daily intake and potency factor. The results of risk assessments for these two pollutants showed that the cancer risks of exposure to HCBd and HCB are 2.6×10^{-3} and 4.6×10^{-6} , respectively, and both are more than the 10^{-6} goal. The carcinogenic potentials of HCB and HCBd should not be ignored. Under these conditions, it is concluded that it may be likely that HCB and HCBd will occur with a frequency or at concentrations that are of concern for public health. EPA has classified both HCB and HCBd as probable human carcinogens.

4. CONCLUSION

The Petro-Processors of Louisiana, Inc. (PPI) site used the Brooklawn and Scenic sites for waste disposal from 1960 until 1980. Mainly chlorinated hydrocarbons were disposed in significant concentration at the sites. The main problem was the potential for leachate migration, so exposing of pollutants, which had been released into local waterways. In this context, we investigated selected chlorinated organic liquids, which are two predominant pollutants: HCB and HCBd, with conducting a risk assessment study to evaluate the potential health risk that maybe associated with exposure of them. Results from this study showed that even though the petrochemical waste disposal shut down since 1980, it will still take an average of 57 years and 68 years for HCBd and HCB, respectively to reach the nearest domestic well via slow migration, which will increase the cancer risks for the people who live near PPI site. This study can provide an idea, specifically contaminated soil with hazardous matters, to the researchers about a risk assessment analysis that helps us better understand the potential impacts on human health.

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Authors' Contribution

The authors contributed equally to the study.

The Declaration of Conflict of Interest/ Common Interest

No conflict of interest or common interest has been declared by the authors.

The Declaration of Ethics Committee Approval

This study does not require ethics committee permission or any special permission.

The Declaration of Research and Publication Ethics

The authors of the paper declare that they comply with the scientific, ethical and quotation rules of SAUJS in all processes of the paper and that they do not make any falsification on the data collected. In addition, they declare that Sakarya University Journal of Science and its editorial board have no responsibility for any ethical violations that may be encountered, and that this study has not been evaluated in any academic publication environment other than Sakarya University Journal of Science.

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