No. 4 December

Environ Engg and Policy 1 (1999) 235–248 © Springer-Verlag 1999

Exposure and health risks potentially posed to petroleum storage tank cleaners by volatile organic compounds

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Abstract This study models and assesses the significance of risks to health potentially posed to individuals exposed to volatile organic compounds (VOCs) due to being occupationally engaged in cleaning petroleum storage tanks. Exposure processes include hydrocarbon vapor inhalation, ingestion via hand-to-mouth contact, and dermal exposure. Under confined space entry regulations, tank cleaners must wear protective clothing and a breathing apparatus. However, such regulations are recent and sometimes violated. Several factors were found to influence exposure of unprotected individuals cleaning tanks. One factor is climate. This paper reports on a study of tanks in south Texas, which is sunny and hot during most of the year. Solar irradiation of metal surfaces may elevate internal temperatures above ambient air temperatures. Vaporization then elevates airborne hydrocarbon concentrations, and ventilation reduces them, producing a dynamic equilibrium. Human entry, however, disturbs this equilibrium by agitating petroleum residuals. Based upon the above considerations, we have modeled petroleum fuel storage tank dynamics in a case study. We considered three cases: manways closed, manways open, and manways actively ventilated. For CASE I, the concentration of each pollutant in the vapor phase was calculated using Raoult's Law. CASE II and CASE III applied Raoult's Law and also evaluated a mass balance via a mass transfer coefficient derived using the Reynolds Number and the Schmidt Number. Based upon empirical data, the velocity of the air within the tank was assumed to be 1.6 mph. Outputs of the case study included the steady-state concentration of each constituent and time required to reach it. Health risk assessment was conducted to quantify non-cancer risks posed by individual substances (the hazard quotient, HQ) and by simultaneous and/or sequential exposure to multiple substances (the hazard index, HI). During hot months, gross exceedances of acceptability criteria for acute and chronic exposures to mixed solvent vapors occurred. The HI exceeded the acceptability criterion by more than three orders of magnitude. The HI for chronic occupational neurological risks exceeded the acceptability criterion by more than two orders of magnitude. This result is consistent with observed neurological deficits among tank cleaners, such as depression of performance on memory tests among crew members who had worked during hot months. Finally, in such instances, eight-hour time-weighted average mixed-solvent vapor concentrations can exceed half of lethal levels, suggesting that tank cleaners can potentially approach lethal exposure routinely during hot seasons.

Introduction

Purpose

Industry powered by fossil fuels has characterized much of the current millennium. A legacy of this epoch in human history has been global deployment of heating systems, engines powered by petroleum products, and industrial plants using petroleum reactants to synthesize petrochemical products, such as plastics. The global landscape, as a result, has become strewn with the relatively primitive vessels needed to contain petroleum fuels, both above ground and underground, namely, steel tanks.

Much attention has been focused in recent years upon leakage of corroded steel tanks as a source of human health risk arising from soil and groundwater contamination. In contrast, relatively little attention has been focused upon health risks posed by direct human exposure to petroleum products contained in steel tanks. To elucidate this issue, we assess the significance of risks to health potentially posed by volatile organic compounds (VOCs) to individuals occupationally engaged in cleaning and refurbishing petroleum storage tanks.

Scope

The size of tanks containing petroleum products is a critical parameter determining human exposure. The most common tanks have low volume, exemplified by automotive fuel tanks. A smaller fraction of tanks have high volume, exemplified by fuel tanks on ships, including tanks powering diesel ship engines, and tanks transporting fuels from refineries to ports where off-loading occurs. The most (in)famous example of the latter is the Exxon Valdez, which spilled its petroleum cargo in Alaska, damaging sensitive coastal ecosystems. Routinely, however, off-loading is accomplished via pipelines trans-

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Received: 27 October 1999

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porting petroleum products to coastal tank farms for storage prior to distribution, such as by truck to inland consumers. Here we focus upon tank farms, and large tanks, defined as tanks which are large relative to people.

Within the wide range of tank sizes, we differentiate simply between small and large tanks because, historically, small tanks more often have been discarded than cleaned, whereas large tanks typically are cleaned occasionally, and their cleaning has required human entry into the tanks. Human entry into large petroleum storage tanks has been necessary when tanks storing a particular product, such as crude oil, have been rededicated to storage of a different product, such as heating oil, gasoline, or jet fuel. Here we focus upon such large storage tanks, which typically are located within tank farms consisting of multiple tanks, which together are capable of storing diverse petroleum products simultaneously.

This study addresses the case of crude oil storage tanks normally varying in 70–200 ft. in diameter; an enclosure may be considered any area where air flow is constricted. Eight of the most volatile crude oil components are addressed. The methodology developed, however, may be applied very similarly to other situations (such as a worker's exposure to paint fumes in a paint room). More specifically, this study provides a paradigm for industries (such as crude oil storage and refining) which often must manage risk potentially posed by worker exposure to dangerous volatile organics. The tank bottom constituents were analyzed and worker exposure for various cases was studied.

Findings

The tank cleaning process

The process of cleaning large petroleum storage tanks was found to include a variety of alternative procedures, depending upon tank size and product stored (Lillienberg et al. 1992; Midzenski 1992; Powers 1990). In general, however, cleaning begins with draining and thereby reducing the depth of the residual petroleum product, and exposing deposits known as tank bottoms. Tank bottoms consist of preferentially deposited, relatively heavy constituents of the parent petroleum product(s). Petroleum product depth initially may be reduced via an external pump connected to a floor drain within the storage tank. In recent years, remotely controlled mobile skimmers also have been used to remove lighter, less viscous constituents, until a relatively solid sludge is exposed.

Eventually, human entry into tanks is necessary to complete cleaning. Teams of people equipped with squeegees push remaining liquids and viscous sludges toward the floor drain/pump intake. During this process they may be exposed to petroleum products. Exposure pathways include hydrocarbon vapor inhalation, ingestion via hand-to-mouth contact, and dermal exposure. To protect against such exposures, confined space entry regulations of the U.S. Occupational Safety and Health Administration (OSHA), and similar regulations in other nations, require tank cleaners to wear protective clothing and breathing apparatus (Lillienberg et al. 1992). However, such regulations are of relatively recent vintage, and sometimes have been violated (U.S. OSHA 1993). For most if not all of the petroleum fuel era, therefore, tank cleaners have been subject to acute and chronic risks potentially posed by exposure to VOCs in petroleum products stored in tanks.

Factors influencing exposure

Several factors have been identified which influence exposure of unprotected or inadequately protected individuals cleaning tanks from within. One factor is ambient conditions. We studied tanks located in south Texas, a region which is sunny and hot during most of the year. Ambient air temperature imposes a baseline condition on internal tank temperature, which in turn drives vaporization of hydrocarbon components of petroleum products inside the tanks. Superimposed on this baseline is the effect of solar irradiation on the metal surfaces of the tank, specifically, the roof and cylindrical walls. These structures may absorb solar energy and radiate it as heat within the tank. Consequently, internal temperatures may exceed ambient air temperatures.

Prior to human entry in the cleaning process, manways may be opened and air-driven (non-sparking) fans operated to reduce the concentrations of accumulated hydrocarbon vapors. After a period of such ventilation, perhaps one week, human entry is undertaken. Vaporization will continue to elevate airborne hydrocarbon concentrations, and ventilation will continue to reduce them, producing a dynamic equilibrium characteristic of the temperature and ventilation conditions. Once human entry occurs, however, this equilibrium is disturbed by two processes which agitate the surface of the petroleum residuals: the action of booted feet walking through the tank, and the action of squeegees further agitating the liquid hydrocarbon surface. These sources of agitation may increase the rate of hydrocarbon vaporization, whereas the ventilation rate remains constant, producing a net increase in airborne hydrocarbon concentrations.

Based upon the above considerations, we have modeled petroleum fuel storage tank dynamics in a case study. We consider three cases: manways closed, manways open, and manways actively ventilated. The case study is set forth below.

Case study: fuel storage tanks

In the crude oil storage industry, fuel tanks often vary in size. Some of the larger tanks are 250,000 barrel tanks (56 ft. in height × 180 ft. in diameter), while smaller tanks may be only 26,000 barrel tanks (40 ft. in height × 70 ft. in diameter). Most storage tanks have floating roofs that float on the liquid stored in the tank, but descend only partially towards the tank floor when the tank is emptied, allowing human entry for cleaning. For the purpose of this study, a tank diameter of 180 ft. and roof height of 7 ft. will be used. For smaller diameter tanks, pollutant concentrations would be similar to the larger diameter tanks or possibly somewhat higher due to reduced indoor air volume. The typical tank has five entrances, called manways which may either be closed or open. The center of a typical manway is located about 2.5 ft. off the ground and the diameter of the manway is about three feet.

Basic assumptions

In the first case considered, CASE I, the manways of the tank are closed. In addition, it is assumed that the tank is at steady state conditions. This is expected because the tank will be saturated with each of the volatile pollutants continuously as the tank is drained. Thus, by the time the tank is empty, the air above the sludge will be saturated. In the two other cases discussed, CASE II and CASE III, the manways are open providing ventilation. In addition, in CASE III the fan is on.

For all three cases, it will be assumed that the storage tank is drained of most of its oil product leaving behind only a bottom sludge about 11 inches deep. For a typical storage tank, there is often a cleaning period when unused sludge is removed and disposed of before refilling. The nature of the cleaning process may also require direct worker involvement. Thus, this situation is a good example for a human exposure study.

Typical oil tank sludge is made up of layers of hydrocarbons. In this case, the bottom three to four inches of the tank consisted of a sticky, slimy, tar-like sludge containing dirt, water and the heaviest crude components. This bottom few inches does not contribute significantly to the vapor phase concentration of the pollutants. The top six to eight inches of the sludge, however, is referred to as the "compromised product" and it does contribute significantly to volatilization into the vapor phase. This is because, although it is the heaviest of the crude that had been stored in the tank, it is still a liquid. In fact, the compromised product is refinable.

Typically, the tank has a floating roof about seven feet high when empty, so the height of the air column in the tank is simply seven feet minus the 11 inches of sludge. In addition, the air and the sludge are assumed to be completely mixed. In the compromised product, the pollutant concentrations are taken from lab test data of typical "sweet" crude oil.

Because evaporation occurs from the surface layer of the liquid, evaporation of the hydrocarbons will be controlled predominantly by the temperature of the atmosphere above the hydrocarbons, which is the temperature that will equilibrate with the atmosphere above it. The air temperature in the tank is expected to be at or above the atmospheric temperature. Thus, to be conservative, temperature ranges were chosen which would be typical for the southern United States where higher temperatures would mean more pollutant volatility. Extreme average temperatures were used in order to determine the range. The low temperature was assumed to be about 46°F (7.8 °C) which is a typical average night time temperature in January in the southern U.S. The high temperature was assumed to be about 94 F (34.6 °C) which is the average daytime temperature in July in the southern U.S. Finally, the air pressure of the tank is assumed to be at 1 atmosphere.

One of the most important assumptions is the molecular weight of the compromised product. The pollutants make up about 1–2% of the compromised product. To estimate the molecular weight, it is important to know what comprises the other 98–99%. For the purposes of this case study, it is assumed that the rest of the compromised product is straight chain hydrocarbons containing on average 40 carbons in a chain. As shown in Table 1, a conservative assumption is that the compromised product falls in the heavy gas oil category which on average contains 40 carbons per molecule.

Assuming that the compromised product is made of straight chain hydrocarbons with an average of 40 carbons (and thus 82 hydrogens), the molecular weight of the compromised product is determined to be 562 g/mol.

Basic assumptions for CASE II and III

The air is assumed to be completely mixed and initially saturated. It is expected that the air in the tank will be initially saturated because it will have been in use for a while before it had been ready to be cleaned. Thus, there was ample time for the pollutants to enter the vapor phase and saturate the tank air. Therefore, CASE II and CASE III begin with the CASE I situation (a closed tank.) At the start time ($t=0$ s) the manways are opened and in CASE III the fan is turned on. The models will show how pollutant concentrations decrease from saturation to the final steady state value.

For purposes of calculating a mass transfer coefficient, values for the density and viscosity of clean air are used. As shown in CASE I, the air in the tank contains some amount of each pollutant. However, it is expected that these small pollutant amounts in the air will have little effect on the density and viscosity of the air.

Table 1. Typical crude oil fractions (data compiled from McCain 1973)

Crude fractions	Chemical composition	Use
Hydrocarbon gases	C_1–C_4	Natural gas, bottled fuel gas
Petroleum ether	C_5–C_6	Solvent, paint thinner, cleaner
Gasoline	C_7–C_8	Motor fuel, solvent
Kerosene	C_{10}–C_{16}	Illuminating oil, diesel fuel, jet fuel, cracking stock
Light gas oil	C_{16}–C_{30}	Lubricating oil, medicinal oil, transformer oil, mineral oil, cracking stock
Heavy gas oil	C_{30}–C_{50}	Lubricating oil, bunker fuel, road oil
Residuum (residue)	C_{80+}	Tars, asphalts, bitumens, waxes, resins, pitch, mineral oil, wood preservatives, roofing compounds, road oil, paving asphalts, coke