

Journal of Hazardous Materials 45 (1996) 141-147



# Health risk assessment study for a general population in case of fire of high quantities of 1,1,1-trichloroethane in urban zone

François Faucher\*, Gaétan Carrier, Jean-Claude Panisset

Département de Médecine du Travail et d'Hygiène du milieu, Université de Montréal, Case Postale 6128, Succursale Centre-Ville, Montréal, Québec, Canada H3C 3J7

Received 1 July 1994; accepted 1 June 1995

#### Abstract

A model is presented for assessing the surrounding population's health risk associated with the pollutants released in the atmosphere under the thermic degradation of 20 000 l of 1,1,1trichloroethane (TCA) in a fire assuming a temperature of 800 °C. Using literature data on the thermic degradation of that product and the Gaussian plume model, downwind outdoor and indoor concentrations at ground level of released pollutants were estimated in plume's axis up to a distance of 10 km from the source for the most frequent meteorological situation in Montreal and for a thermic inversion scenario. Results show that if such a fire should arise, the surrounding population could be exposed to levels of chlorine, hydrogen chloride and phosgene associated with mucous sensorial irritation, pulmonary inflammation, oedema and even death. Those effects could reach populations up to many kilometres from the fire and the death rate could be high for those in the toxic cloud's axis. The model suggests that, under the most frequent meteorological situation, in-place protection would be effective provided the fire does not extend one hour whereas, under thermic inversion, evacuation of persons up to 2 km from the fire should take place. Because of the various limitations of the model, these evaluations should be used with caution.

*Keywords:* 1,1,1-Trichloroethane; Thermic degradation; Atmospheric dispersion; Population's health risk; Mitigation

# 1. Introduction

1,1,1-trichloroethane (TCA) is widely used as a solvent and degreasing agent for metal and clothing [1, 2]. It has no flash point and will not support combustion in air at standard temperature [1-3]. However, according to Margossian and Limasset

<sup>\*</sup> Corresponding author. Tel.: (514) 343-6143. Fax: 343-2200.

[4], when this product is heated at temperatures over 200 °C or under UV radiations, degradation into toxic products results. Many accidents involving combustion of TCA have happened. De Nevers [5] described a fire of TCA during which a welder died and noted another case where a spark from an unknown source ignited the methyl chloroform-air mixture inside an airplane's wing in a plant in Tennessee. A case of TCA's explosion is reported by Wrightson and Santon [6] as a result of the welding of a tank. Finally, Transport Canada [7] reported a case of fire of TCA during transport in 1987 where nobody was hurt.

The thermic degradation of TCA has been the object of several studies. Margossian and Limasset [4], who studied the destruction of gaseous TCA at different temperatures, found the presence of combustion by-products including chlorine (Cl<sub>2</sub>), hydrogen chloride (HCl), phosgene (COCl<sub>2</sub>), carbon monoxide (CO) and carbon tetrachloride (CCl<sub>4</sub>). The rate of formation of these byproducts is a function of the temperature and is shown in Table 1. At a temperature of 400 °C, TCA starts breaking down into Cl<sub>2</sub>, COCl<sub>2</sub> but, above all, HCl. The rate of formation of these byproducts reaches a maximum at 800 °C when TCA is almost totally decomposed. Koshland and Thomson [8] also observed formation of 1,1-dichloroethylene, COCl<sub>2</sub> and HCl.

Because of the toxicity of the byproducts resulting from the thermal destruction of TCA, our objective is to estimate the potential health risk for the population close to storage places and transportation routes for that product, in the eventuality of a fire involving high quantity of TCA. This health risk evaluation brings one to compute effective prevention steps. This study is related to a real storage situation of 20 000 l of TCA located at a distance of 1 km from a residential area in Montreal.

#### 2. Method

Table 1

From Margossian and Limasset's thermic degradation curves [4], the quantities of thermic degradation by-products were estimated for the scenario of a fire

T (°C)	Rate of formation (% weight)									
	Cl <sub>2</sub>	HCI	СО	CO <sub>2</sub>	COCl <sub>2</sub>	CCl <sub>4</sub>	TCA*			
500	0.73	19	1.6	2.0	1.7	N.D.	75			
600	2.9	38.5	14	4.3	17	6.2	14			
700	6.4	50	15	11	10	3.8	2.4			
800	7.0	57	11	23	7.1	1.6	0.12			
900	3.9	53	7.0	36	2.0	N.D.	N.D.			
1000	7.3	41	6.0	46	N.D.	N.D.	N.D.			

Degradation by-products of TCA and rate of formation at different temperatures (according to Margossian and Limasset [4])

TCA\*: TCA nondegraded.

N.D.: not detected.

involving 20 0001 of TCA at a temperature of 800 °C where the formation of these products is maximum. Using the Gaussian plume model suited for a residential area [9] and considering a 3 h fire, concentrations of pollutants were estimated indoor and outdoor at ground level on toxic cloud's centerline up to 10 km from the source. Indoor houses' concentrations were calculated with the Glickman and Ujihara formula [10] considering an air change rate per hour (ACH) of 1.5 commonly found in Canadian houses [11]. Modeling is performed for two atmospheric scenarios: atmospheric stability class D with 2 m/s winds and for thermic inversion (stability class F) with respect of the climatic data specific for that region [12].

The estimated concentrations of  $Cl_2$ , HCl and of COCl<sub>2</sub> inside and outside houses are divided by the mucous irritation threshold concentrations for  $Cl_2$  and HCl, and by the pulmonary inflammation and oedema threshold concentrations resulting from  $Cl_2$ , HCl and COCl<sub>2</sub> exposure [13–18]. Table 2 shows a summary of these threshold concentrations for man for a duration of exposure of 30 min. The additive effect of those pollutants is taken into account, that is to say the sum of the concentrations of each one divided by its threshold concentration for a given exposure for a toxic effect. For resulting rates higher than 1, the toxic effects reported in Tables 4 and 5 could be observed. The death rate associated with the exposure to these substances is assessed using Probit equations obtained from animal studies with responses closest to the those found for humans [19, 20]. The highest death rate resulting from exposure to  $Cl_2$ , HCl and COCl<sub>2</sub> is also computed.

#### 3. Results

Table 2

### 3.1. Concentrations of pollutants released

The data of estimated outdoor pollutants' concentrations consecutive to a 20 000 1 TCA fire, under stability class D, are presented in Table 3. This table shows that persons located up to 1 km from the fire would be exposed to the highest concentrations. Further than 1 km from the source, the concentrations of pollutants decrease

Studied health effects	Concentrations of pollutants (ppm)							
	Cl <sub>2</sub> [13, 19]	HCl [14, 20]	COCl <sub>2</sub> [15–17, 20]	CO [14, 21]	CCl <sub>4</sub> [18, 22]			
Death rate (CL 1) <sup>a</sup>	60	1300	12.8	1969	217.7			
Pulmonary oedema	23	1000	3		_			
Pulmonary inflammation	11.7	110	1.2	_				
Irritation	3.5	35	_	_	-			
Hepatic and renal necrosis		_	-	_	125			
Palpitations and headache	-	-	-	1200				

Summary of concentrations – effects data for degradation by-products from combustion of TCA for a 30 min exposure

<sup>a</sup>CL 1: concentration which produces death of 1% of the exposed human population.

Distance from fire (km)	Concentration of pollutants (ppm)							
	Cl <sub>2</sub>	HCl	СО	COCl <sub>2</sub>	CCl <sub>4</sub>			
0.5	5.09	82.5	33.8	3.72	0.77			
	(28.6)	(463)	(189.8)	(20.9)	(4.31)			
1	1.60	25.9	10.6	1.17	0.24			
	(10.1)	(163)	(66.8)	(7.36)	(1.52)			
2	0.51	8.22	3.37	0.37	0.089			
	(3.50)	(56.7)	(23.2)	(2.56)	(0.53)			
4	0.16	2.59	1.06	0.12	0.02			
	(1.22)	(19.8)	(8.09)	(0.89)	(0.18)			
6	0.08	1.32	0.54	0.06	0.01			
	(0.66)	(10.6)	(4.35)	(0.48)	(0.10)			
8	0.05	0.82	0.33	0.04	0.008			
	(0.42)	(6.82)	(2.79)	(0.31)	(0.06)			
10	0.03	0.56	0.23	0.03	0.005			
	(0.30)	(4.84)	(1.98)	(0.22)	(0.05)			

Estimated concentrations of air pollutants in plume centerline from a 20000 l TCA fire under D stability class and thermic inversion (calculated according to the method described in [9])

rapidly. Using the same method, estimation of released pollutants under thermic inversion scenario shows that these concentrations would be, in average, about seven times higher than that under the D class regardless of the distance.

# 3.2. Estimation of risk for outdoor populations

Table 4 shows the estimated health effects for outdoor exposed persons to a 20 0001 TCA fire under the most frequent meteorological conditions for the region of Montreal (D stability class). In this table, one can see that, after 30 min exposure, some of the people located within 1 km from the fire could present symptoms of mucous irritation while some, at 0.5 km and less from the source, could suffer from pulmonary inflammation and oedema because of  $Cl_2$ , HCl and  $COCl_2$  in the air. Using the Probit equations for  $Cl_2$ , HCl and  $COCl_2$ , a 30% death rate was calculated for a population at 0.5 km exposed for 2 h. Under thermic inversion conditions, the model shows that, after 30 min exposure, persons up to 2 km from source on plume's centerline could be affected by mucous sensorial irritation while persons up to 1.5 km could suffer from pulmonary oedema. The death rate could be close to 100% for population within 1 km distance from the fire after 1 h and more of exposure.

# 3.3. Estimation of risk for indoor populations

Table 5 presents possible health effects for people inside houses located on the toxic cloud centerline in the eventuality of a 20 0001 TCA fire under the most frequent atmospheric conditions observed in Montreal. This table shows that the indoor population at 0.5 km from a 20 0001 TCA fire could risk a sensorial irritation as much as a pulmonary inflammation and/or oedema after a 1 h exposure. A death

Table 3

Table 4

Estimated	toxic healt	h effects or	n humans ii	n relatior	1 with	distance	of emission	and	exposure to	Cl <sub>2</sub> ,	HCl
and to CO	$OCl_2$ for a 2	0 000 I TC	A fire und	er D stab	oility c	lass					

Distance of fire (km)	Toxic-effects – exposure-time relation						
	30 m	1 h	2 h	3 h			
0.5	A, B	A, B, 0.8% <sup>a</sup>	A, B, 30% <sup>a</sup>	A, B, 75% <sup>a</sup>			
1.0	A	A, B	A, B	<b>A</b> , <b>B</b> , $03\%^{a}$			
1.5	_	Α	А	А, В			
2	_	~	А	Α			
4–10	-	-	-	-			

A: mucous irritation.

B: pulmonary inflammation and oedema.

<sup>a</sup> death rate.

-: no effect.

#### Table 5

Estimated toxic health effects on humans in relation with distance and exposure time to  $Cl_2$ , HCl and to  $COCl_2$  for in-place populations for a 20 000 l TCA fire

Distance from fire (km)	Toxic-effects – exposure-time relation						
	30 m	1 h	2 h	3 h			
0.5	_	A, B	A, B	A, B, 11% <sup>a</sup>			
1		_	A, B	A, B			
1.5	_	-	Α	A, B			
2	-	_	-	Α			
4-10	-	_	_	_			

A: mucous irritation.

B: pulmonary inflammation and oedema.

<sup>a</sup> death rate.

-: no effect.

rate of 11% is estimated after 3 h exposure at the same distance. During the same time, irritation and inflammation and/or pulmonary oedema could affect people within 1.5 km from fire. Under a thermic inversion scenario, persons located up to 8 km from the fire could suffer from mucous irritation after 3 h exposure.

It is estimated that the indoor and outdoor CO and CCl<sub>4</sub> concentrations at 0.5 km from a 20 000 l TCA fire (Table 3) would be, under both atmospheric conditions scenarios, lower than the concentrations of those two substances associated with toxic effects for human [21, 22] and thus would represent a negligible risk for health.

On the basis of the results presented, it is suggested that, in the event of a 20 000 l TCA fire under the most frequent atmospheric condition for Montreal, in-place protection may be effective if such a fire is overcome in 1 h or less. Beyond that duration, people inside houses located on the toxic cloud's centerline could be exposed to a phosgene dose related to a significant risk of pulmonary inflammation and oedema. Under a thermic inversion, results obtained with the model show that indoor

population up to 2 km of emission should be evacuated because of high risk of pulmonary inflammation and oedema and also because of death risk for some persons.

# 4. Discussion

We have estimated quantities and concentrations of toxic by-products released involving a 20 000 l TCA theorical fire lasting for 3 h with a temperature of combustion of 800 °C. However, in a real fire, the temperature of combustion, as the oxygen availability, is not a constant. Thus, the quantity of by-products formed could be different from what we estimated at 800 °C. We used that temperature to estimate the worst scenario of by-products formation; as a result, our risk could be overestimated but we believe that, in public health situation, it is preferable to do so than underestimate. The use of the Gaussian plume dispersion model applied to the urban environment is recommended by EPA [23] and this model would, according to Dabbert and Brodzinski [24], predict concentrations that correlate pretty well with experience. It is generally felt that the Gaussian model approaches provide conservative risk estimates which are reasonable for planning purposes [25]. Again, it is preferable to overestimate than underestimate for public protection purpose. Nevertheless, the manner in which the dispersion of a toxic cloud is calculated depends upon the fact that the atmospheric conditions, throughout emission, stay constant and that the released toxic substances will not be eliminated by other processes.

We propose the use of many indexes like the death rate as much as the sublethal effects risk for each toxic substance studied rather than the IDLH<sup>1</sup> planned for workers. For mucous irritation due to exposure to Cl<sub>2</sub> and to HCl, and for evaluation of possible toxic effects associated with exposure to CO and CCl<sub>4</sub>, the concentrations effects data from reported studies on controled human exposures have been used. However, pulmonary inflammation and oedema health risk due to Cl<sub>2</sub>, HCl and to COCl<sub>2</sub> is based upon concentration effects data for human extrapolated from animal studies. Thus, an uncertainty factor exists. In the establishment of emergency actions, should a potential fire involving high quantities of TCA arise, criterias lower than the pulmonary oedema threshold and the IDLH should be defined. For example, considering that the odour threshold is lower than the one associated with irritation from exposure to HCl and Cl<sub>2</sub>, the measure of concentrations of these irritants at a level lower than the odour level could serve as decision criteria for mitigation. Further thought needs to be given to take into account other emergency safety standards like EEGL and SPEGL from National Academy of Sciences and ERPGS from the American Industrial Hygiene Association for similar case situation. In an emergency situation, if irritation reactions are reported, mitigation is essential.

The use of Probit equations for the death rate estimation is limited because of the differences of sensitivity within the human population itself [26, 27].

<sup>&</sup>lt;sup>1</sup>IDLH: Immediately Dangerous to Life or Health concentrations (as defined by NIOSH in 'NIOSH pocket guide to chemical hazards')

This health risk evaluation was made for a general civilian healthy population. Some people, however, are more vulnerable: these include children, pregnant women, old people and people with chronic heart and respiratory troubles. This vulnerable population is estimated to be about 25% of the general population [28]. The quantitative data presented in this study should be used above all as an evaluation guide and used with precaution in a real situation.

#### References

- H. Konietzko, in: J. Saxena (Ed.), Hazard Assessment of Chemicals, Vol. 3, Academic Press, Orlando FL, 1984, p. 402.
- [2] IARC (International Agency for Research on Cancer), Some Halogenated Hydrocarbons, in: Monographs on the evaluation of the carcinogenic risk of chemicals to humans, 20, Lyon, 1979.
- [3] R.J. Lewis Sr., Hazardous Chemicals Desk Reference, Van Nostrand Reinhold, New York, 2nd edn., 1991, p. 782.
- [4] N. Margossian and J.C. Limasset, Cah. Notes Doc., 67 (1972) 165.
- [5] N. de Nevers, Arch. Environ. Health, 41(5) (1986) 279.
- [6] I. Wrightson and R.C. Santon, Loss. Prev. Bull., 83 (1988) 21.
- [7] Transport Canada, Direction générale du transport des marchandises dangereuses, Accidents impliquant le trichloroéthylène, le trichloroéthane ainsi que le perchloroéthylène pour 1986–1991, Internal Report, #ASD4052-11-32, Ottawa, Ont., 1992.
- [8] C.P. Koshland and M.J. Thomson, Combust. Sci. Technol., 85 (1992) 471.
- [9] C.P.J. Van Buijtenen, Methods for the calculation of the physical effects of the escape of dangerous materials, TNO, 1979, p. 7.
- [10] T.S. Glickman and A.M. Ujihara, J. Hazard. Mater., 23 (1990) 57.
- [11] D.J. Wilson, Emerg. Preparedn. Dig., 14(1) (1987) 20.
- [12] Environnement Canada, Le climat de Montréal. Études climatologiques No. 39, le climat des villes canadiennes, No. 4, Programme climatologique canadien, Ottawa, 1987, p. 1.
- [13] R. Dandres, Le chlore hygiène et sécurité, INRS Paris, 4th edn., 1979.
- [14] G. Kimmerle, J. Fire Flammability/Combust. Toxicol. Suppl., 1 (1974) 4.
- [15] W.F. Diller and M. Habil, J. Occ. Med., 20 (1978) 189.
- [16] S.A. Cucinell and E. Arsenal, Arch. Environ. Health, 28 (1974) 272.
- [17] W.D. Currie, G.E. Hatch and M.F. Frosolono, J. Biochem. Toxicol., 2 (1987) 105.
- [18] N.I. Sax and R.J. Lewis, Dangerous Properties of Industrial Materials, Vol. 1-3, 7th edn., Van Nostrand Reinhold, New York, 1989.
- [19] R.M.J. Withers and F.P. Lees, J. Hazard. Mater., 12 (1985) 283.
- [20] C. Harris, in: J.L. Woodward (Ed.), Int. Symp. on Preventing Major Chemical Accidents, AIChE, New York, 1987.
- [21] R.D. Stewart, J. Fire Flammability/Combust. Toxicol. Suppl., 1 (1974) 167.
- [22] Agency for Toxic Substances and Disease Registry, Toxicological Profile for Carbon Tetrachloride, U.S. Public Health Services, 1988, Atlanta, GA.
- [23] EPA (Environmental Protection Agency), Standards of Performance for new stationary sources and final emission Guidelines, Federal Register (CFR) Part 60, Washington D.C., 1991.
- [24] W.F. Dabberdt and R. Brodzinsky, in: W.F. Dabberdt (Ed.), Atmospheric Dispersion of Hazardous/Toxic Materials from Transport Accidents, Elsevier, Amsterdam, 1984, p. 113.
- [25] M.P. Singh, Atm. Environ., 24A(4) (1990) 769.
- [26] V.C. Marshall, J. Hazard. Mater., 22 (1989) 13.
- [27] G.E. Hartzell, in: G.E. Hartzell (Ed.), Advances in Combustion Toxicology, Vol.1, Technomic, Lancaster, Pa, 1992, p. 19.
- [28] S. Fainhurst and R.M. Turner, J. Hazard. Mater., 33 (1993) 215.