Threshold quantity criteria for risk management programs: recommendations for toxic releases

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Abstract

Facilities using hazardous substances are required to comply with risk management programs that aim to reduce the frequency of chemical accidents and the severity of consequences in the event of an accident. Both the European Union and the United States use chemical-specific weight thresholds for toxic substances to determine those facilities and processes that must comply with such programs. This study evaluates whether the establishment and use of these 'threshold quantities' is consistent and protective of public health. The chemical footprint or hazard zone length is calculated using current threshold quantities and 'level of concern' (LOC) concentrations for 77 toxic chemicals in the US regulations. Using the worst-case scenario and the recommended procedure involving the Risk Management Program (RMP)*Comp, footprint lengths range up to 40 km. However, the RMP*Comp program provides inconsistent results. Threshold quantities are then calculated using an atmospheric dispersion model and several meteorological and land-use scenarios. In the base scenario (winds at 4.3 m/s, neutral stability, urban conditions, and distances of 100, 250, and 1000 m), distance-based weight thresholds are considerably smaller than current listings for most toxic substances. Distance-based and current thresholds have low correlation (e.g. $r = 0.34$) and large discrepancies (e.g. differences up to three orders of magnitude). Alternative scenarios evaluated for distance-based threshold quantities, which used using stable atmospheres and rural settings further reduce the distance-based weight thresholds and increase discrepancies. Linear relationships are shown between threshold quantities and level of concerns for each scenario and dispersion mode (neutral or dense) that allow simple calculation of threshold quantities. The current thresholds may exclude facilities that could pose significant off-site risks, and the thresholds are inconsistent with the off-site consequence analysis (OCA). Recommendations include revising the threshold quantities that determine covered facilities/processes; modifying RMP*Comp to eliminate errors; establishing threshold quantities using a more rational approach, e.g. based on hazard zones or distances using

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credible scenarios; and using the same health-based level of concern in both initial screening and subsequent off-site consequence analyses.

1. Introduction

Over the past several decades, a series of regulations and directives have evolved that are aimed at decreasing the frequency and severity of chemical accidents. Spurred on by the 1974 explosion in Flixborough, England and the 1976 release of 2,3,7,8-TCDD in Seveso, Italy, the European Union (EU) adopted the Seveso Directives in 1982 (revised in 1996) [1–3]. The 1988 United Nations' Awareness and Preparedness Emergencies at the Local Level (APELL) program explicitly called for the reduction of accidents rates and the preparation of response plans [4]. The 1993 directives by the International Labour Organization (ILO) addressed risk identification, emergency planning, emergency preparedness, and information dissemination [5]. Due to concerns about large-scale chemical accidents, including the Seveso and Flixborough accidents as well as the 1984 methyl isocyanate release in Bhopal, India, the US incorporated the Risk Management Program (RMP) into the 1990 Clean Air Act Amendments, and issued final rules in 1996. The US efforts built on earlier programs including the 1986 Emergency Planning and Community Right-to-Know Act, the 1986 Accidental Release Information Program, and the 1988 Chemical Safety Audit Program [6–8].

The risk management programs across the world have much in common. For example, both US and EU programs require that large industrial facilities develop risk management plans that incorporate training, response, mitigation, and other emergency preparedness steps. Covered facilities must assess 'off-site consequences' that could result from explosions and the release of toxic chemicals. 'Hazard zones' representing areas in which an accident could cause injury or death must be delineated. For the release of toxic chemicals, hazard zones may be defined by the length, size (area), or population that might experience exposures exceeding a health-based concentration, the 'level of concern'(LOC). Hazard zones are also defined by an overpressure limit for explosive substances and a radiant energy limit for flammable substances.

Not all facilities handling hazardous substances are required to develop comprehensive risk management plans. In general, these plans must be developed only for those facilities or processes that store, transfer, or utilize a quantity of specified chemicals over specified weight thresholds. Thus, these programs apply to only those facilities that have the greatest potential risk, or perhaps viewed more correctly, the programs are designed to exclude facilities that should pose small risks. In US, threshold quantities for 77 toxic substances listed range from 227 to 9072 kg, while threshold quantities for 63 flammable substances are uniformly set at 4536 kg [9,10] (threshold quantities apply to individual processes, not the facility as a whole). Approximately 66,000 US facilities are covered by RMP rules [8]. Threshold quantities are developed using methods that consider the toxicity, reactivity, volatility, dispersion, combustibility, the amount of the chemical known or predicted to cause adverse health effects, injury or death, and other factors (described below) [11].

Currently, the basis of threshold quantities for toxic substances is a simple ranking system; for flammable substances, the basis is historical data indicating that a vapor cloud explosion is unlikely with quantities smaller than 4536 kg [11].

The focus of this study is to determine whether existing policies provide a rational and protective approach for selecting those facilities that might pose risks of toxic exposure in the event of a chemical release. Given that risk management programs are designed to evaluate and limit off-site consequences, threshold quantities based on hazard zone lengths or areas should provide a more consistent and rational approach to protecting public health. The basis of existing thresholds is reviewed, and hazard zone lengths implied in the US RMP program are calculated. Using a number of scenarios, distance-based threshold quantities are derived for these chemicals and compared to existing thresholds. Sensitivity analyses using alternative scenarios are used to evaluate meteorological conditions and other factors. The results have important implications for risk management programs.

1.1. Determination of threshold quantities

One ranking and five distance-based dispersion modeling methodologies were considered in developing the US Risk Management Program (Table 1). The ranking methodology was taken from the Extremely Hazardous Substances Threshold Planning Quantity (EHS TPQ) in the Emergency Planning and Community Right-to-Know Act [11,12] that considers a chemical's potential to become airborne and disperse and its toxicological properties. Distance is not considered. The distance-based methodologies included those used by the states of Delaware and New Jersey, the federal OSHA Process Management Safety (PMS) guidelines, the OSHA Organization Resources Counselors (ORC) methodology, and an in-house method [11,13–15]. Similar to Delaware's and OSHA's PMS guidelines, the in-house method determined the emission quantity necessary to reach a specified concentration 100 m from the release point using a dispersion model and assuming a 10 mph (4.5 m/s) wind speed, atmospheric stability class D, urban conditions, and a 30 min release duration. Threshold quantities ranged from 227 to 4536 kg [13].

Chemical endpoints or 'levels of concern' are critical parameters for both ranking and distance-based methods. After examining the toxicity, physical state, vapor pressure, production volume, likelihood of release, and accident history, the US Environmental Protection Agency (EPA) selected the Immediately Dangerous to Life and Health (IDLH) air concentration values as the LOC for determining threshold quantities [13]. The IDLH values were originally formulated in the mid-1970s for 387 chemicals by the National Institute for Occupational Safety and Health for use as respirator selection criteria, based on the effects that might occur from a 30 min exposure [16]. Later, the US Occupational Safety and Health Administration (OSHA) defined IDLH values in emergency response regulations as "an atmospheric concentration of any toxic, corrosive or asphyxiant substance that poses an immediate threat to life or would cause irreversible or delayed adverse health effects or would interfere with an individual's ability to escape from a dangerous atmosphere [17]. No specific exposure duration was given. The IDLH values were revised most recently in 1994 [18]. EPA used IDLH values to set threshold quantities in the ranking procedure for most (53 of 77 or 56%) of the listed toxic RMP chemicals [13]. If IDLH values were unavailable, acute toxicity criteria were used: inhalation $LC_{50} \geq 0.5$ mg/l air (for exposures

Table 1
Summary of methods in federal and state chemical lists reviewed by the EPA [14]

	Delaware method	New Jersey method	OSHA methodology for toxic substances	ORC methodology for toxic substances	EHS TPQ
Dispersion modeling	Yes	Yes	Yes	Yes	No
Model parameters and/or assumptions	4.3 m/s wind speed Stability class D All vapor release, no pooling Release at ambient temperature No momentum effects Ground level release and receptors Neutrally buoyant cloud Urban dispersion coefficients No mitigating design or operation features	2 m/s wind speed Stability class F Urban conditions Substances that are liquids at 20 °C were assumed to evaporate from a 2 mm deep pool Average population density for urban New Jersey counties	4.3 m/s wind speed D stability class All vapor release, no pooling Release at ambient temperature No momentum effects Ground level release and receptors Neutrally buoyant cloud Urban dispersion coefficients No mitigating design or operation features	4.3 m/s wind speed D stability class All vapor release, no pooling Release at ambient temperature No momentum effects Ground level release and receptors Neutrally buoyant cloud Urban dispersion coefficients No mitigating design or operation features	1 cm depth for liquid pools Liquids released at their boiling point Liquids have the same density as water
Level of concern	ERPG-3 The New Jersey acute toxicity concentration	*Acute toxicity concentration*: >TLV or short term exposure limit and equal to the lowest of one-tenth LC_{50}, the LC_{LO} or the IDLH		ERPG-3 10 times the LOC for EHSs The New Jersey acute toxicity concentration	IDLH values IDLH equivalent values: $LC_{50} \times 0.1$
Ranking factor	No	No	No	No	Yes, IDLH/V, where $V = \dfrac{1.6 \times MW^{0.67}}{T + 273}$
Duration of exposure/release	Steady-state release for the period of 1 h	1 h	Steady state release for the period of 1 h	Steady state release for the period of 1 h	30 min
Distance parameter	Yes, 100 m	Yes, one fatality in a location with 10,000 people per square mile	On-site	Yes, 100 m from point of release	No

greater than 8 h); dermal $LD_{50} \geq 50$ mg/kg; oral $LD_{50} \geq 25$ mg/kg; a vapor pressure of 0.5 mmHg for all toxic liquids (29 of 77 or 38%); or Threshold Limit Values (TLVs) (4 of 77 or 5%) [13]. Chronic (long-term) exposure was not considered.

Ultimately, EPA selected a relative ranking system similar to EHS TPQ with several changes: threshold quantities were increased to reflect "a level where the hazard should be considered for planning purposes"; the physical state and volatility of a substance were combined into an overall "ranking factor"; and a larger quantity was allowed for ammonia as a common agricultural chemical under the "Agricultural Nutrients Exemption" [11]. EHS TPQ-derived quantities were lower than OSHA's PMS thresholds for 15 substances, i.e. anhydrous ammonia, ammonia (aqueous solution >44% concentration), boron dichloride, bromine, chlorine, chlorine dioxide, fluorine, formaldehyde, hydrogen chloride (anhydrous), hydrogen cyanide (anhydrous), hydrogen fluoride, hydrogen peroxide ($\geq 52\%$ concentration), hydrogen sulfide, methyl chloride, and methyl mercaptan. For these chemicals, EPA followed OSHA's rule making and increased thresholds [11,13]. Six threshold quantities (226.8, 453.6, 2268, 4536, 6804, and 9072 kg) were specified for toxic chemicals (Table 2) [9,10]. Distance-based methodologies were not considered to be feasible for generic or national application due to the need for an "excess" number of chemical, site, and accident-specific parameters, e.g. wind speed, topography, and distance to receptor or fence line. Further, the (30 min) release assumption was not considered to be reflective of all accident situations.

It is important to recognize that a second set of concentration endpoints is used in the off-site consequence analysis (OCA) specified by US EPA for covered processes [19]. In the OCA, hazard zones are identified using LOCs derived from several sources: (1) Emergency Response Planning Guidelines (ERPG-2) values, defined as "the maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to 1 h without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action" [20,21], were used for 32 chemicals (42% of 77 chemicals in RMP). These values are published annually in a peer-reviewed process [25]. (2) One-tenth of the IDLH values were used for 22 chemicals (29%) where ERPGs were unavailable. (3) Acute toxicity criteria (described above) were used for 21 chemicals (27%). (4) TLVs were used for two chemicals (3%) [19]. TLVs are advisory exposure guidelines developed by the ACGIH using industrial experience, animal studies or human studies designed to represent conditions under nearly all workers may be exposed day after day (8 h workday), 7 days a week for 20–30 years with no adverse effect [20,22]. Differences between these endpoints have been discussed elsewhere [23–25]. Overall, most IDLH values significantly exceed ERPG and TLV values [23].

1.2. Selection of covered facilities

Threshold quantities based on ranking methodologies have several flaws with respect to the protection of public health. First, they do not directly account for the size of the hazard zone or the population that might experience adverse effects. Second, the level of protection (or risk averseness) is inconsistent, i.e. a release at the threshold quantity for some chemicals may adversely affect a large area and many people, while releases

Table 2
The 77 toxic compounds in US RMP Program

Chemical Name	CAS number	Molecular weight (amu)	Threshold (kg)	Level of concern			Hazard zone (km)
				Concentration (mg/m3)	Concentration (ppm)	Basis	
1,1-Dimethylhydrazine	57-14-7	60.1	6804	12	5.0	IDLH/l0	19.2
Acrolein	107-02-8	56.06	2268	1.1	0.5	ERPG-2	40.3
Acrylonitrile	107-13-1	53.06	9072	76	35.0	ERPG-2	6.4
Acrylyl chloride	814-68-6	90.51	2268	0.9	0.2	Tox/10[a]	40.3
Allyl alcohol	107-18-6	58.08	6804	36	15.0	IDLH/10	4.8
Allylamine	107-11-9	57.1	4536	3.2	1.0	Tox/10[a]	40.3
Ammonia (anhydrous)	7664-41-7	17.03	4536	140	200.0	ERPG-2	3.2
Ammonia (conc. 20% or greater)	7664-41-7	17.03	9072	140	200.0	ERPG-2	1.6
Arsenous trichloride	7784-34-1	181.28	6804	10	1.0	Tox/10[a]	3.2
Arsine	7784-42-1	77.95	453.6	1.9	0.6	IDLH/10	13.9
Boron trichloride	10294-34-5	117.17	2268	10	2.0	Tox/10[a]	13.9
Boron trifluoride	7637-07-02	67.81	2268	28	10.0	IDLH/10	7.5
Boron trifluoride compound w/methyl ether (1:1)	353-42-4	113.89	6804	23	10.0	IDLH/10	4.6
Bromine	7726-95-6	159.81	4536	6.5	1.0	ERPG-2	17.6
Carbon disulfide	75-15-0	76.14	9072	160	50.0	ERPG-2	9.8
Chlorine	7782-50-5	70.91	1134	20	3.0	ERPG-2	5.4
Chlorine dioxide	10049-04-4	67.45	453.6	2.8	1.0	IDLH/10[b]	10.9
Chloroform	67-66-3	119.38	9072	490	100.0	IDLH/10	2.9
Chloromethyl ether	542-88-1	114.96	453.6	0.25	0.1	IDLH/10	13.9
Chloromethyl methyl ether	107-30-2	80.51	2268	1.8	0.6	Tox/10[a]	35.2
Crotonaldehyde	4170-30-3	70.09	9072	29	10.0	ERPG-2	6.4
Crotonaldehyde, (E)-	123-73-9	70.09	9072	29	10.0	ERPG-2	6.4
Cyanogen chloride	506-77-4	61.47	4536	30	12.0	Tox/10[c]	9.9
Cyclohexylamine	108-91-8	99.18	6804	160	39.0	Tox/10[a]	1.6
Diborane	19287-45-7	27.67	1134	1.1	1.0	ERPG-2	35.2
Dimethyldichlorosilane	75-78-5	129.06	2268	26	5.0	ERPG-2	10.9

Epichlorohydrin	106-89-8	92.53	9072	76	20.0	ERPG-2	2.7
Ethylene oxide	75-21-8	44.05	4536	90	50.0	ERPG-2	5.8
Ethylenediamine	107-15-3	60.1	9072	490	200.0	IDLH/10	0.5
Ethyleneimine	151-56-4	43.07	4536	18	10.0	IDLH/10	13.9
Fluorine	7782-41-4	38	453.6	3.9	2.5	IDLH/l0	10.9
Formaldehyde (solution)	50-00-0	30.03	6804	12	10.0	ERPG-2	0.6
Furan	110-00-9	68.08	2268	1.2	0.4	Tox/10[a]	40.0
Hydrazine	302-01-2	32.05	6804	11	8.0	IDLH/10	2.2
Hydrochloric acid (conc. >30%)	7647-01-0	36.46	6804	30	20.0	ERPG-2	2.7
Hydrocyanic acid	74-90-8	27.03	1134	11	10.0	ERPG-2	8.6
Hydrogen chloride (anhydrous)	7647-01-0	36.46	2268	30	20.0	ERPG-2	7.5
Hydrogen fluoride/hydrofluoric acid (conc. >50%)	7664-39-3	20.01	453.6	16	20.0	ERPG-2	4.8
Hydrogen selenide	7783-07-5	80.98	226.8	0.66	0.2	IDLH	17.6
Hydrogen sulfide	7783-06-4	34.08	4536	42	30.0	ERPG-2	9.9
Iron, pentacarbonyl-	13463-40-6	195.9	1134	0.44	0.1	Tox/10[a]	19.2
Isobutyronitrile	78-82-0	69.11	9072	140	50.0	ERPG-2	3.4
Isopropyl chloroformate	108-23-6	122.55	6804	100	20.0	Tox/10[a]	3.4
Methacrylonitrile	126-98-7	67.09	4536	2.7	1.0	TLV[d]	28.8
Methyl chloride	74-87-3	50.49	4536	820	400.0	ERPG-2	1.8
Methyl chloroformate	79-22-1	94.5	2268	1.9	0.5	Tox/10[a]	19.2
Methyl hydrazine	60-34-4	46.07	6804	9.4	5.0	IDLH/10	11.8
Methyl isocyanate	624-83-9	57.05	4536	1.2	0.5	ERPG-2	40.3
Methyl mercaptan	74-93-1	48.11	4536	49	25.0	ERPG-2	8.3
Methyl thiocyanate	556-64-9	73.12	9072	85	29.0	Tox/10[a]	1.9
Methyltrichlorosilane	75-79-6	149.48	2268	18	3.0	ERPG-2	10.9
Nickel carbonyl	13463-39-3	170.73	453.6	0.67	0.1	Tox/10[a]	33.6
Nitric acid (conc. 80% or greater)	7697-37-2	63.01	6804	26	10.0	Tox/10[a]	1.6
Nitric oxide	10102-43-9	30.01	4536	31	25.0	TLV[d]	9.9
Oleum (fuming sulfuric acid)	8014-95-7	80.06	4536	0.01	3.0	ERPG-2	1.0
Peracetic acid	79-21-0	76.05	4536	4.5	1.5	Tox/10[a]	5.3
Perchloromethylmercaptan	594-42-3	185.87	4536	7.6	1.0	IDLH/10	4.3
Phosgene	75-44-5	98.92	226.8	0.81	0.2	ERPG-2	17.6

Table 2 (*Continued*)

Chemical Name	CAS number	Molecular weight (amu)	Threshold (kg)	Level of concern			Hazard zone (km)
				Concentration (mg/m3)	Concentration (ppm)	Basis	
Phosphine	7803-51-2	34	2268	3.5	2.5	ERPG-2	22.4
Phosphorus oxychloride	10025-87-3	153.33	2268	3	0.5	Tox/10[a]	11.8
Phosphorus trichloride	7719-12-2	137.33	6804	28	5.0	IDLH/10	9.9
Piperidine	110-89-4	85.15	6804	22	6.0	Tox/10[a]	8.8
Propionitrile	107-12-0	55.08	4536	3.7	1.6	Tox/10[a]	14.9
Propyl chloroformate	109-61-5	122.56	6804	10	2.0	Tox/10[a]	8.6
Propylene oxide	75-56-9	58.08	4536	590	250.0	ERPG-2	3.5
Propyleneimine	75-55-8	57.1	4536	120	50.0	IDLH/10	5.6
Sulfur dioxide (anhydrous)	7446-09-5	64.07	2268	7.8	3.0	ERPG-2	8.3
Sulfur tetrafluoride	7783-60-0	108.06	1134	9.2	2.0	Tox/10[a]	9.9
Sulfur trioxide	7446-11-9	80.06	4536	10	3.0	ERPG-2	19.2
Tetramelhyllead	75-74-1	267.33	4536	4	0.4	IDLH/10	11.8
Tetranitromethane	509-14-8	196.04	4536	4	0.5	IDLH/10	6.4
Titanium tetrachloride	7550-45-0	189.69	1134	20	2.6	ERPG-2	1.4
Toluene 2,4-diisocyanate	584-84-9	174.16	4536	7	1.0	IDLH/10	0.2
Toluene 2,6-diiaocyanate	91-08-7	174.16	4536	7	1.0	IDLH/10	0.3
Toluene diisocyanate (unspecified isomer)	26471-62-5	174.16	4536	7	1.0	IDLH/l0	0.2
Trimethylchlorosilane	75-77-4	108.64	4536	50	11.0	Tox/10[a]	11.8
Vinyl acetate monomer	108-05-4	86.09	6804	260	75.0	ERPG-2	3.0

Also shown are CAS number, molecular weight, threshold quantity, level of concern, and estimated hazard zone length using threshold quantity and RMP*Comp. In part from [19].

[a] Based on IDLH-equivalent level from toxicity data.

[b] Not an EHS; LOC-equivalent value was estimated as IDLH/10.

[c] Not an EHS; LOC-equivalent value estimated as 1/10 IDLH-equivalent level estimated from toxicity data.
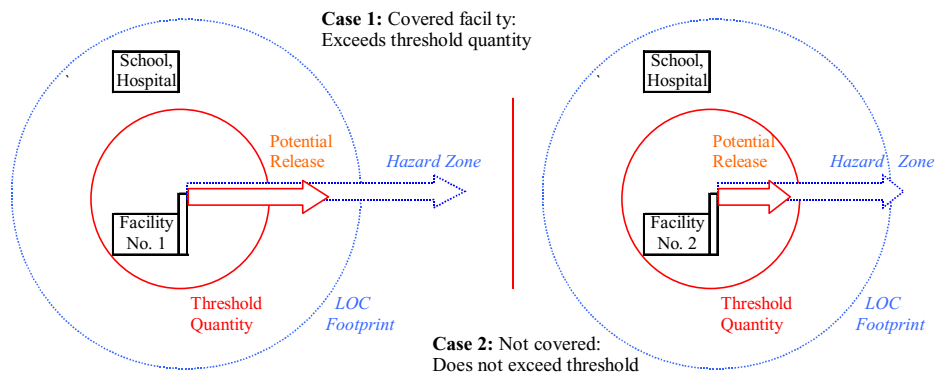
[d] LOC based on TLV.

Fig. 1. Depiction of inconsistency in facilities covered and not covered by RMP rules. This inconsistency results as the threshold quantity is based on a higher concentration endpoint that yields a smaller hazard zone (inner circle) than the off-site analysis that uses a lower concentration endpoint that gives a larger hazard zone (outer circle).

of a different chemical, again at the threshold quantity, might cause much smaller and possibly negligible impacts. Third, selecting covered facilities using a ranking procedure initially using a high LOC (e.g. IDLH) and then determining the hazard zone in subsequent off-site consequence analyses using a lower LOC (e.g. ERPG-2) is inconsistent since a facility that is not covered (because potential releases fall under threshold quantities) can still cause a hazard zone that is problematic. As Case 1 of Fig. 1 shows, potential releases from the facility exceed the threshold quantity, the facility is covered by the RMP, and the required OSA appropriately defines the hazard zone, which happens to encompass sensitive receptors (school, hospital, etc.) that would be incorporated in emergency planning activities. In Case 2, potential releases at a second facility do not exceed the threshold quantity and thus no OSA is required, but the hazard zone still encompasses the sensitive receptors. For this facility, risk planners and managers might be unaware of the hazard zone and emergency plans might not account for the associated risks to sensitive receptors.

Two step procedures are frequently and appropriately employed to prioritize the workload by eliminating analyses of facilities that pose low or 'phantom' risks and to identify situations or facilities that require further analysis. In air quality permitting, for example, simplified and rapid 'screening' analyses using 'generic' or 'worst-case' assumptions initially are used to determine whether a facility might exceed some concentration or risk criterion. If the criterion is exceeded, more detailed analyses using more likely, site-specific or historical conditions may be required. If the criterion is not exceeded, then little or no further analysis is needed since even the worst-case results are not unacceptable, and presumably risks under other conceivable scenarios would be lower. The RMP's use of high LOCs to determine covered facilities, followed by lower LOCs in the OCA does not follow this philosophy. This inconsistency can be rectified by using the same endpoints to select qualifying facilities and hazard zones, or better, using a lower threshold to select qualifying facilities to encourage awareness, management and mitigation activities among facilities using toxic materials. Additional and substantial improvements can be obtained by revisiting the

basis of the threshold quantities, in particular, utilizing distance-based criteria, as described below.

2. Methods

The 'implied' lengths of hazard zones for 77 toxic substances listed in the US RMP are calculated using existing threshold quantities and RMP*Comp, a computer program developed by US EPA as a planning tool to calculate worst-case footprints to identify high priority hazards [26] and the LOC endpoints specified in the OCA rules [19]. These implied lengths provide an idea of the size of the hazard zone, which are then compared to those derived below using a more sophisticated approach.

Distance-based threshold quantities are derived by determining the release quantity that just achieves the LOC for each of the listed chemicals at three source-to-receptor distances (100, 250, and 1000 m) under two meteorological conditions and two land use classes (rural or urban). (Oleum, a mixture, was not modeled.) The LOCs (Table 2) follow EPA's RMP OCA guidance [19]. The three distances represent, for example, the length from the source to the fence line, nearest residence, or critical neighborhood location, e.g. hospital, nursing home, stadium, etc. as well as RMP guidelines [13]. The base scenario uses typical or average dispersion conditions, specifically, wind speed: 4.3 m/s and stability class: D (neutral). The alternative scenario is a worst-case condition for ground level sources (producing maximum concentrations) that can occur during clear nights with low winds, specifically, wind speed: 1.5 m/s and stability class: F (stable). Stability class F is quite rare at most locations. These conditions respectively represent the alternative and worst-case scenarios in the RMP rules for off-site consequence analysis [27]. In both cases, temperature is 30 °C and relative humidity is 50%. Both rural and urban settings are modeled, which changes dispersion parameters and the surface roughness (from 3 to 100 cm).

The ALOHA (aerial locations of hazardous atmospheres) dispersion model is used to predict concentrations. This model is among several recommended by the US EPA for the RMP OCA [19]. It simulates neutrally buoyant releases using a modified, time-dependent Gaussian equation [28–30] and heavy gas releases using the dense gas dispersion model (DEGADIS) [31] applicable to most atmospheric (e.g. stability class and wind speed) and terrain (e.g. urban, and rural) conditions [32,33]. ALOHA allows a variety of source configurations, and the placement of a receptor at a given downwind (x) and crosswind (y) distance. To determine hazard zone lengths, releases are modeled as direct sources in which the chemical immediately enters the atmosphere using a 1 h release duration, reflecting the basis of the ERPG-2 and modified IDLH values, as well as the dispersion coefficients used in the dispersion model. Releases occur at ground level without momentum effects, and emissions are not mitigated. Dense or buoyant dispersion modes are automatically selected by the ALOHA model, based on chemical properties, release rates, and prevailing meteorology. For each combination of toxic substance, source–receptor distance, meteorological condition, and land use type, the threshold quantity is determined by incrementally increasing the release quantity until the predicted concentration reaches the LOC.
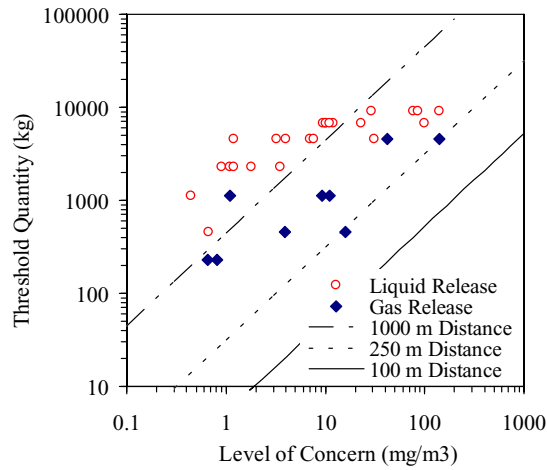
Fig. 2. Existing threshold limits for releases modeled as buoyant plumes vs. level of concern (shown as points) and distance-based limits for the base scenario (urban, day-time at three distances; shown as lines).

3. Results

3.1. Current threshold quantities and chemical toxicity

Figs. 2 and 3 plot the existing threshold quantities versus the LOC for chemicals (and quantities) dispersing in neutral (buoyant) and dense modes, respectively. If threshold quantities had been selected solely using the LOC as a measure of toxicity, then the points on the plots would lay on a straight line. The figures' log scales exaggerate agreement. For buoyant plumes (Fig. 2), the correlation coefficients are 0.66 and 0.82 for liquid and gaseous
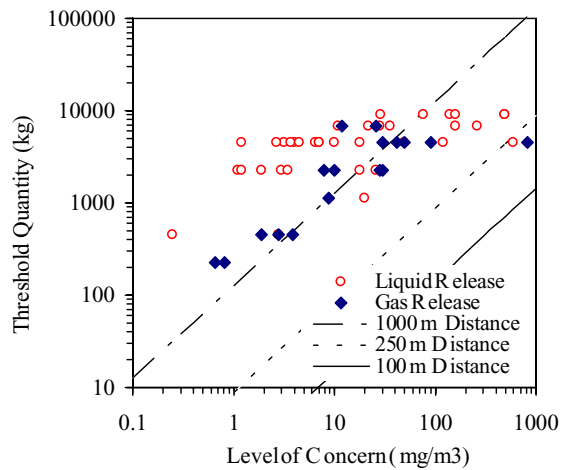

Fig. 3. Existing threshold limits for releases modeled as dense plumes vs. level of concern. Otherwise as Fig. 2.

releases, respectively, and threshold quantities tend to be smaller (more conservative) for gaseous releases. For dense plumes (Fig. 3), the correlations between threshold quantities and LOCs are only 0.46 and 0.26 for liquid and gaseous releases, respectively. For all 77 chemicals, the correlation between threshold quantity and LOC is only 0.34, indicating that only 12% of the variance is explained. The figures and correlations show that existing threshold quantities depend only weakly on the LOC.

3.2. Implied hazard zone lengths and RMP*Comp

Hazard zone lengths determined using existing threshold quantities and RMP*Comp range from 0.16 km (toluene diisocyanate, unspecified isomer) to 40 km (acrolein, acrylyl chloride, allylamine, furan, and methyl isocyanate), the maximum distance computed by RMP*Comp (Table 2). For 77 compounds, the median hazard zone length is 8.6 km (average: 11.4 km). The hazard zone length exceeds 1 km for 71 of the listed chemicals (92%), and 5 km for 51 chemicals (66%). For planning purposes, the hazard zone is generally assumed to be a circle since most any wind direction is possible at the time of an accident. Thus, the median hazard zone length (8.6 km), for example, corresponds to an area of 232 km^2. The size of the implied hazard zone is very large for nearly all of the listed chemicals. This can be explained, in part, since RMP*Comp predicts worst-case concentrations using a very short release duration (10 min) and the most stable atmospheric conditions (stability class F), assumptions that increase concentrations and the size of the hazard zone.

Surprisingly, implied hazard zone lengths and threshold quantities are negatively correlated ($r = -0.43$), e.g. chemicals with the largest threshold quantity (9072 kg) tend to have shorter hazard lengths (0.5–10 km) than chemicals with smallest threshold quantities (227 and 454 kg that give lengths from 1.4 to 35.2 km). Hazard zone lengths and LOCs are weakly, but negatively correlated ($r = -0.29$). In part, simplifications in RMP*Comp's algorithms and lookup charts cause these results [34,35]. While recommended for the OCA, RMP*Comp may inaccurately represents potential impacts of a release. For example, hazard zone lengths are limited from 0.1 and 25 miles. A release of toluene from 1 to 22,000 kg gives the same minimum (0.1 mile) footprint. While recognizing that RMP*Comp was designed as a planning tool and not as a simulation model, such approximations can distort the OCA and subsequent mitigation and response plans. RMP*Comp is not intended and should not be utilized to generate distance-based threshold quantities.

3.3. Distance-based threshold quantities

Threshold quantities derived by meeting the level of concern at distances of 100, 250, and 1000 m for the base scenario (urban, wind speed: 4.3 m/s, stability: D, urban conditions) are shown in Table 3 for the listed toxic compounds. Distance-based threshold quantities rapidly increase with the length of the hazard zone considered. For example, the median distance-based threshold quantities were 39, 224, and 2858 kg for 100, 250, and 1000 m distances, respectively. In comparison, the current median threshold quantity is 4536 kg.

Several simulations using ALOHA differed from RMP*Comp in terms of the dispersion mode (buoyant or dense gas). For example, in the base scenario at 1000 m distance, 17 substances were using a buoyant mode (Table 3). In comparison, RMP*Comp and the OCA

Table 3
Distance-based threshold quantities for the base scenario (urban, wind speed: 4.3 m/s, stability: D, urban conditions) at distances of 100, 250, and 1000 m

Class and substance	Distance based quantity			Percent current (%)
	100 m (kg)	250 m (kg)	1000 m (kg)	
All				
Median	39	224	2858	66
Minimum	0.04	0.25	3.48	0.77
Maximum	1177	7299	105400	2324
Dense toxic gases				
Ammonia (conc. 20% or greater)	730	4440	62500	689
Arsine	2[a]	15	204	45
Boron trichloride	13	74	1035	46
Boron trifluoride	36	213	3030	134
Chlorine	11	66	932	82
Chlorine dioxide	4[a]	21	296	65
Cyanogen chloride	39	231	3303	73
Ethylene oxide	118	704	9900	218
Fluorine	>	34[a]	414	91
Formaldehyde	10	83	1158	17
Hydrogen chloride (anhydrous)	43[a]	341	4819	212
Hydrogen selenide	>	6[a]	71	31
Hydrogen sulfide	>	319	4500	99
Methyl chloride	1177	7299	105400	2324
Methyl mercaptan	64	377	5350	118
Nitric oxide	45	977	13900[a]	–
Phosgene	>	6	86	38
Phosphine	18	111	>	–
Sulfur dioxide (anhydrous)	11[a]	60	844	37
Buoyant plume from a liquid substance				
1,1-Dimethylhydrazine	65	392	5500	81
Acrolein	6	35[a]	>	–
Acrylyl chloride	4	24	332	15
Allylamine	12	>	>	–
Arsenous trichloride	39	238	3336	49
Boron trifluoride compound	122	728	10379	153
Chloromethyl methyl ether	10	63	885	39
Crotonaldehyde	151	915	12850	142
Epichlorohydrin	402	2355	34090	376
Ethyleneimine	95[a]	>	>	–
Furan	6	38[a]	>	–
Hydrazine	55	334	>	–
Iron, pentacarbonyl-	2	13	180	16
Isopropyl chloroformate	525	3200	44900	660
Methacrylonitrile	14[a]	>	>	–
Methyl chloroformate	10[a]	>	>	–
Methyl hydrazine	49	301	4220	62
Methyl isocyanate	6	38[a]	>	–
Methyl thiocyanate	455	2760	38800	428
Nickel carbonyl	4	23	314	69
Nitric acid	34	199	2810	41

Table 3 (*Continued*)

Class and substance	Distance based quantity			Percent current (%)
	100 m (kg)	250 m (kg)	1000 m (kg)	
Peracetic acid	24[a]	>	>	–
Perchloromethylmercaptan	40	243	3410	75
Propyl chloroformate	53	320	4480	66
Propionitrile	20[a]	>	>	–
Tetramethyllead	23	140	1960	43
Toluene 2,6-diisocyanate	38	227	3200	71
Buoyant toxic gases				
Ammonia (anhydrous)	730	4440	62500	1378
Arsine	10[a]	<	<	–
Diborane	6	36	508	45
Fluorine	20	124[a]	<	–
Hydrocyanic acid	58	354	4950	437
Hydrogen chloride (anhydrous)	158[a]	<	<	–
Hydrogen fluoride	86	521	7325	1615
Hydrogen selenide	3	21[a]	<	–
Hydrogen sulfide	220	<	<	–
Nitric oxide	<	<	3900[a]	–
Phosgene	4	<	<	–
Phosphine	<	<	370	16
Sulfur dioxide (anhydrous)	41[a]	<	<	–
Sulfur tetrafluoride	47	282	3950	348
Dense plume from a liquid substance				
Acrolein	<	10[a]	122	5
Acrylonitrile	100	587	8340	92
Allyl alcohol	46	273	3920	58
Allylamine	<	18	250	6
Bromine	9	51	705	16
Carbondisulfide	210	1234	17850	197
Chloroform	705	4350	64450	710
Chloro methyl ether	0.04	0.3	3	1
Crotonaldehyde, (E)-	38	220	3150	35
Cyclohexylamine	222	1262	18400	270
Dimethyldichlorosilane	36	206	2905	128
Ethylenediamine	700	4151	60000	661
Ethyleneimine	26[a]	134	1900	42
Furan	<	11[a]	119	5
Hydrazine	<	<	1116	16
Isobutyronitrile	189	1118	16060	177
Methacrylonitrile	4[a]	21	294	6
Methyl chloroformate	3[a]	15	206	9
Methyl isocyanate	<	11[a]	124	3
Methyltrichlorosilane	24	145	1995	88
Peracetic acid	7[a]	36	497	11
Phosphorus oxychloride	4	24	337	15
Phosphorus trichloride	38	218	3084	45
Piperidine	28	161	2276	33
Propionitrile	5[a]	27	385	8

Table 3 (*Continued*)

Class and substance	Distance based quantity			Percent current (%)
	100 m (kg)	250 m (kg)	1000 m (kg)	
Propylene oxide	845	5141	73169	1613
Propyleneimine	154	923	13130	289
Sulfur trioxide	13	75	1055	23
Tetranitromethane	5	31	430	9
Titanium tetrachloride	27	158	2225	196
Toluene 2,4-diisocyanate	9	55	767	17
Toluene dusocyanate	9	54	766	17
Trimethylchlorosilane	65	385	5400	119
Vinyl acetate monomer	363	2200	31350	461

'Percent of current' compares 1000 m distance-based quantity to current US RMP threshold quantities. ">'' denotes modeled as a dense plume. "<'' modeled as a buoyant plume, and both modes are shown.

[a] Manual selection of dispersion mode.

guidance specify a dense gas mode as the worst-case scenario for toxic liquids (except for hydrazine and toluene isomers), although buoyant modes are used in a number of alternative scenarios [19]. For 20 chemicals, ALOHA's algorithm selected buoyant plumes for smaller releases (and smaller distances) and dense plumes for larger releases (and larger distances), which is indicated in Table 3 as a new or deleted entry. This occurred for acrolein, allylamine, arsine, chlorine dioxide, ethyleneimine, fluorine, furan, hydrazine, hydrogen chloride, hydrogen selenide, hydrogen sulfide, methacrylonitrile, methylchloroformate, methyl isocynate, nitric oxide, peracetic acid, phosgene, phosphine, propionitrile, and sulfur dioxide. Also, no unique distance-based quantity could be identified for some substances at some distances, as the switch from buoyant to dense mode with increasing emissions sometimes skipped over the distance of interest (i.e. 100, 250, or 1000 m). In this case, quantities for both buoyant and dense modes were calculated by manually selecting the dispersion mode. Table 3 shows results for each dispersion mode.

Distance-based threshold quantities had little association with the current EPA threshold quantities. For the 1000 m distance-based threshold quantities, 41 of 69 (59%) quantities fell below current levels with a median difference of 34%. While the median difference is not large, discrepancies are very large for individual chemicals, as plotted in Fig. 4. For example, distance-based threshold quantities represent from 1 to 2324% of current quantities (Table 3); current and distance-based quantities had low correlation (e.g. for 1000 m distance, Pearson $r = 0.40$ and the Spearman $r = 0.62$); and for the median EPA threshold quantity (4536 kg), 1000 m distance-based quantities ranged from 124 kg (methyl isocyanate) to 105,400 kg (methyl chloride), nearly a 1000-fold range. At shorter distances, discrepancies were larger, e.g. the 100 m quantities represent an average of only less than 1% of current values and all were below current values, while the 250 m quantities represent ~5% of current values and 60 of 65 (92%) were below current values. Clearly, existing threshold quantities result in considerably larger footprints than the distance-based limits modeled here.

For each distance and dispersion mode (dense or buoyant), distance-based threshold quantities are proportional to the level of concern. Thus, distance based threshold quantities are shown as six lines in Figs. 2 and 3, representing the two dispersion modes and three
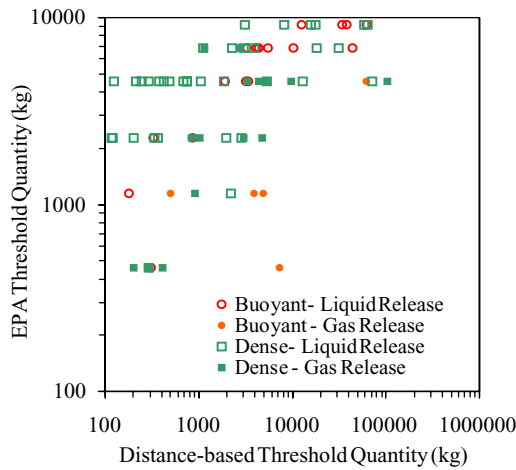
Fig. 4. Comparison of current US EPA threshold quantities and distance-based quantities for base case scenario and 1000 m distance.

distances. Distance-based threshold quantities may be expressed as:

$$TQ = f_{\text{scenario,mode,distance}} LOC \tag{1}$$

where TQ is the threshold quantity (kg), $f_{\text{scenario,mode,distance}}$ the proportionality factor (kg m^3/mg), and LOC the level of concern (mg/m^3). The proportionality factors depend on the meteorological conditions, urban/rural classification, dispersion mode (buoyant or dense gas plumes) and distance, but not whether the release occurs as a gas or liquid. Table 4 shows these factors for the base scenario (as well as alternative scenario investigated in the sensitivity analysis, described below). By comparing these constants, it is seen that a dense gas produces concentrations 3.5–3.7 times higher, depending on the distance, than the same quantity release of a buoyant gas in the base scenario. (The ratios vary for other scenarios, as discussed in Section 3.4.)

The constant and proportional relationship between threshold quantities and LOCs is an important result as it makes determination of distance-based threshold quantities very

Table 4
Proportionality constants giving inverse dispersion factor (kg/(mg/m^3)) relating threshold quantity (kg) to level of concern (mg/m^3) at indicated distance

Distance (m)	Dispersion type	Base case		Rural day		Urban night		Rural night	
		Factor	Ratio[a]	Factor	Ratio[a]	Factor	Ratio	Factor	Ratio[a]
100	Buoyant	5.26	1.00	2.13	2.47	0.70	7.56	0.19	27.54
	Dense	1.44	1.00	0.95	1.51	0.75	1.92	0.43	3.36
250	Buoyant	31.84	1.00	17.02	1.87	3.95	8.06	0.86	36.95
	Dense	8.78	1.00	5.96	1.47	4.57	1.92	2.66	3.30
1000	Buoyant	449.38	1.00	194.93	2.31	45.29	9.92	11.03	40.76
	Dense	126.77	1.00	85.45	1.48	66.97	1.89	39.14	3.24

[a] Ratio to base case (urban day).

simple. While these relationships may seem surprising and unrecognized, they follow from the fact that concentrations near a source are proportional to the emission rate. This applies for both neutral and dense gas dispersion modes, though the relationships differ for these modes. At longer distances, a proportional relationship may not hold since removal mechanisms (e.g. surface deposition, reaction, rainfall scavenging, etc.) that are pollutant-specific exert increasing influence. At short distances, however, these mechanisms have minor impacts for most chemicals, and thus they are appropriately omitted in the ALOHA and other models that focus on worst-case conditions.

3.4. Sensitivity analyses

Alternative scenarios reflecting more stable atmospheric conditions (stability class: F) and rural land use were modeled to estimate threshold quantities at the same (100, 250, and 1000 m) distances. These scenarios reduce dispersion, thus the resulting threshold quantities are decreased from the base scenario, in some cases, dramatically. Since distance-based quantities are linear with the level of concern for a given distance and scenario (except if the dispersion mode changes), it is sufficient to examine proportionality constants to interpret results. Table 4 shows the proportionality constants for the three alternative scenarios and the ratios to the base scenario:

- The rural/neutral stability (day-time) case shows the effect of smaller dispersion coefficients and surface roughness lengths, corresponding to the smoother surfaces and decreased thermal turbulence expected over vegetated landscapes. For buoyant gases, distance-based threshold quantities decrease by 1.9–2.5 times (depending on the distance) from the base scenario; for dense gases, the decrease is 1.5-fold.
- The urban/stable case (night-time) is a worst-case condition. Threshold quantities decrease from the base scenario by 7.6–9.9 times for buoyant gases (depending on the distance) and by 1.9 times for dense gases. Distance-based threshold quantities for both buoyant and dense plumes with the same level of concern are similar, i.e. under very stable conditions, buoyant and dense plumes give similar concentrations for the same emission rate. These results reflect the greater surface roughness in urban environments, which tends to dominate dispersion of both dense and buoyant plumes under extremely stable conditions. These results differ from the other scenarios in which dense plumes result in considerably smaller threshold quantities.
- The rural/stable case (night-time) is the most severe worst-case condition. Threshold quantities are decreased by 27–41 times for buoyant gases, and by 3.3 times for dense gases. This scenario has the least amount of dispersion and thus the lowest threshold quantities.

The alternative scenarios demonstrate that distance-based threshold quantities dispersing as buoyant plumes strongly depend on meteorological and land use scenario. In some scenarios, threshold quantities are unrealistically small, e.g. threshold quantities were already <10 kg for a dozen substances in the base scenario at 100 m (Table 4). The urban/rural classification makes approximately a 3-fold difference, and changes from neutral to stable conditions cause larger differences for buoyant plumes. Dense plumes are less sensitive to scenario assumptions.

4. Discussion and conclusion

The intent of risk management programs is to reduce the frequency of accidental releases and to minimize the consequences of releases that do occur. Prevention and mitigation goals are accomplished, in part, by enhanced planning, preparedness and other training, effective management and control systems, as well as increased awareness of hazards. Off-site consequence analysis plays an important role in hazard awareness. In the US, the RMP rules have been in effect since June 20 1999 [19] and as of mid-2000, 14,500 facilities had filed RMP plans in nearly 8000 communities [8]. Many of these include an off-site consequence analyses.

It is noteworthy that four of the five risk management programs reviewed by the US EPA during program development incorporated distance, although ultimately these approaches were rejected in favor of a ranking system. During rulemaking, most of the threshold quantities originally proposed underwent adjustment, and in many cases, quantities were increased by an order of magnitude. The EPA abandoned distance-based methodologies because it was felt that release assumptions would be chemical and site-specific, and the process of determining threshold quantities would be excessively complex. However, this study shows that incorporating distance is not difficult. Distance-based threshold quantities depend largely on the level of concern, which is a health-based determination on which there is reasonable agreement, land use classification, and distance or hazard zone area, which is a function of the locations of populations, sensitive receptors, and the degree of risk averseness. The linear relationship between the level of concern and the calculated quantity required to reach a specific distance makes evaluation of alternative cases very simple. Current threshold quantities do not appear to explicitly recognize these key ideas.

Four scenarios and three distances were analyzed in this study. Many other conditions might be considered. While alternatives might include other meteorology (inversions, stability class, wind speeds, etc.), the base and worst-case scenarios modeled reflect a broad range of conditions that encompass those reasonably anticipated for emergency planning purposes. Exceptions might include, for example, extremely windy sites, where dispersion would normally exceed the base case and where very stable conditions would be unlikely, and sheltered snow-covered sites, where low wind speeds predominate and very stable or inversion conditions might be very frequent. In comparison to the base case, distance-based threshold quantities would increase in the first scenario, and decrease in the second. Release conditions might be altered (e.g. shorter release periods, elevated plumes, etc.) Shorter release durations, e.g. 10 min as used in RMP*Comp, would be more conservative. However, this is somewhat problematic as most LOCs are based on a longer (1 h) exposure that are not necessarily appropriate for a 10 min exposure. Also, as the 'shelter-in-place' strategy can be effective for such short releases, thus longer releases may pose more significant response challenges. The dispersion parameters used in most Gaussian plume and puff models are based on a 1 h averaging period, and model performance generally degrades as averaging period shortens. Finally, for unpopulated areas, longer distances might be considered. For example, increasing the hazard zone length to 2 km increases the distance-based quantities for buoyant and dense gases by 3.5 and 3.2 times as compared to the base case using a 1 km distance.

The emergency response community, including first responders and organizations such as the International Association of Fire Fighters, have suggested that lower thresholds, or even the elimination of thresholds for hazardous substances, would be more useful and improve the ability to respond to chemical incidents [36]. These groups also have indicated that too much emphasis was placed on the worst-case scenario, and that probable or more likely case scenarios would be more useful. The RMP rules utilize the worst-case meteorology (stability category F) and a very short release duration (10 min). Kahn and Abbasi [37] among others have suggested the use of 'credible' scenarios in risk analysis, that is, among all possible scenarios, analysis should focus on those scenarios that have reasonable probability and that are also likely to cause significant damage. The base scenario suggested here, which uses the most common meteorological case (stability D) and a slower release (over 1 h) appears a more appropriate credible scenario than the current RMP rule.

4.1. Recommendations

The current threshold quantities in the US Risk Management Program do not reflect a consistent or protective approach to hazard assessment for several reasons. First, smaller facilities that are excluded from the program because potential emissions fall below existing threshold quantities may in fact pose greater hazards than some covered facilities. This problem results from a flawed approach in identifying facilities that should be covered by regulations since it was based on higher levels of concern than used in the subsequent off-site consequence analysis. Second, existing threshold quantities represent hazard zones that differ dramatically in size for different chemicals, implying risk averseness policies that are chemical-dependent. This results as the modified ranking factor approach used to set threshold quantities distorts the linear relationship between the LOC and the threshold quantity. In the event of a chemical release, these problems could contribute to possible loss of life and other impacts on nearby communities, impacts that might be avoided by a consistent, and rational approach to selecting facilities that must develop comprehensive risk management plans. Third, the focus on an extreme case decreases the credibility and useful of the analysis. In the absence of information that indicates that worst-case, but unlikely, assumptions are relevant, more probable scenarios should be used.

In practice, threshold quantities represent a balance between the protection of health and the environment and the reality of industrial operations. Especially in urban areas where populations near industrial facilities are large, the hazard zone length may be regarded as reflecting attitudes toward public health protection and risk aversion. Current threshold quantities tend to significantly exceed distance-based threshold quantities presented in this study. In urban areas, hazard zone lengths of 250–1000 m seem reasonable for planning purposes. Of the distances considered, the 1000 m distance gave results most similar to the current threshold quantities, although distance-based threshold quantities are smaller for most substances. Larger distances, population densities, and other variables might be incorporated into the development of threshold quantities. However, this paper shows that a very limited number of chemical and site-specific parameters are needed to estimate threshold quantities, and there is no conceptual or practical difficulty in deriving threshold

quantities that better meet the regulatory intentions, specifically the requirement "to protect human health and to safeguard the natural environment" [38].

Facility managers, the emergency response community, local planners, and state and national regulators should be able to depend on a risk management program that provides reliable and useful information regarding the nature of hazards and possible off-site impacts. Modifications to the threshold quantities used to determine covered facilities and the use of consistent levels of concern and more credible scenarios in off-site consequence analyses would increase this program's relevance to these stakeholders and would provide better protection of public health in the event of a chemical accident. Under the Clean Air Act, US EPA is required to review the listed chemicals and their thresholds at least every 5 years. Several revisions to the policies used to determine those facilities that must comply with comprehensive risk management planning activities and off-site consequence analysis are recommended. The 'screening' approach used to determine covered facilities, i.e. threshold quantities, should include facilities that might pose risks under worst-case conditions. This could be accomplished using distance-based threshold quantities employing the base or other credible scenario and an intermediate distance, e.g. 250 m. Second, site-specific off-site consequence analyses utilizing the appropriate land use classification, distances to sensitive receptors, credible worst-case scenarios, and a consistent model (not RMP*Comp) should be used to determine necessary risk management activities. Third, the same health-based levels of concern should be used in both initial screening analyses and subsequent off-site consequence analyses. These recommendations apply to both European and US approaches.

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