Environment and Climate Change Canada / Environnement et Changement climatique Canada

Substance Risk Evaluation for Determining Environmental Emergency Planning Under the *Environmental Emergency Regulations* Set Under the *Canadian Environmental Protection Act, 1999* (CEPA 1999)

16 Petroleum Substances including:

Diesel Fuel (4 substances)
Heavy Crude Oil (2 substances)
Aviation Fuels (3 substances)
Heavy Fuel Oils (3 substances)
Light Fuel Oils (1 substance)
Natural Gas Condensates (3 substances)

Risk Evaluation Conclusion:

- **There are 16 petroleum substances described herein that are candidates for the *Environmental Emergency Regulations* due to their potential to cause pool fires and/or vapour cloud explosions. Refer to table 1 for Chemical Abstract Registry Numbers (CAS Nos.).**

1.0 INTRODUCTION

The *Environmental Emergency Regulations*, developed under Part 8 of the *Canadian Environmental Protection Act (CEPA), 1999* (Government of Canada, 2011), establish a list of substances for which fixed facilities must notify Environment Canada that they store or use the substance on-site, by providing notices to Environment Canada, reporting when the substance is released into the environment, and developing an environmental emergency plan (E2 plan) for each substance stored or used at the facility at or above specified threshold quantities.

To determine if a substance is a candidate to be added to the *Environmental Emergency Regulations*, Environment Canada has developed a risk evaluation methodology based on the following hazard categories:

- Physical: flammable and combustible or oxidizing substances, or those having a potential to cause vapour cloud explosions or pool fires.
- Human Health: substances that are toxic by inhalation, are carcinogenic, or are corrosive.
- Environmental Health: substances that are: corrosive, persistent, bioaccumulative, or aquatically toxic.

Canada

Thresholds for substance quantities stored or used on site for the criteria inhalation toxicity, aquatic toxicity, carcinogenicity to humans and corrosiveness are based on typical container sizes normally found at facilities. For example, 0.22 tonnes is representative of drum-size containers, 1.13 tonnes is typical of typical tanker trucks, and up to a maximum of 9.1 tonnes is typical for larger typical handling quantities. For flammable substances, the threshold has been set at 4.5 tonnes, which represents the average quantity that could cause harm at a distance of 100 metres (m) from the source. Thresholds for oxidizers, combustible substances and those causing pool fires were set individually because the quantity that could cause harm at 100 m varied considerably and could not be averaged. Overall, the lower the threshold for maximum expected quantity and container size, the higher the risk to humans and/or the environment; conversely, the higher the threshold for maximum expected quantity and container size, the lower the risk to humans and/or the environment.

This methodology developed under Part 8 of CEPA 1999 differs from the methodology used to identify substances that meet the criteria under section 64 of the Act. Although the definitions within Part 3, section 64, and Part 8, section 200, are similar, the definitions for this regulation are interpreted according to what causes immediate harmful effects (section 200) versus long-term toxicity (section 64).

The petroleum substances listed under Table 1 were selected for evaluation because they are substances under the Government of Canada’s Chemicals Management Plan (CMP) in the Petroleum Sector Stream Approach (PSSA)[a] that, if spilled, could be immediately harmful to humans and/or the environment. These substances have been grouped together into 6 categories according to the chemical and physical properties; however, properties can still vary with a given category. For example, the Fuel Oil No.6 has a boiling point[b] ranging from 212 to 588°C.

Due to the varying composition of each petroleum substance, representative substances with similar physical and chemical properties were selected for the purpose of modelling fire pools and vapour cloud explosions to determine threshold quantities (Table 1). This approach of using representative substances is consistent with assessments under the CMP. Once the decision to add these substances to the E2 Regulations has been accepted, the 16 substances will be listed within Schedule 1 of the E2 Regulations according to their respective CAS No. and there will be no reference made to the categories or representative substances that are listed within this report.

[a] http://www. chemicalsubstanceschimiques.gc.ca/petrole/index-eng.php
[b] http://www. cameochemicals. noaa.gov/chris/OSX.pdf

Table 1: Petroleum Substances and their Threshold Quantities

#	CMP Category ("Representative Substance")[3]	CAS No.	Name of Petroleum Substance	Recommended Threshold Quantity (tonnes) and Associated Hazard	Other Emergency Hazards[4]
1	Diesel Fuel (Sample Diesel Fuel)	68476-34-6	Fuels, diesel, No. 2	2,500 pool fire	-
2		68334-30-5	Fuels, diesel		
3		64742-80-9	Distillates, petroleum, hydrodesulphurized middle		
4		101316-57-8	Distillates, petroleum, hydrodesulphurized full-range middle		
5	Heavy Crude Oil (Sample Heavy Crude)	8002-05-9	Petroleum crude oil	2,500 pool fire	10,600 vapour cloud explosion
6		128683-25-0	Crude oil, oil sand		
7	Aviation Fuels (Sample Kerosene)	64741-86-2	Distillates, petroleum, sweetened middle	2,500 pool fire	-
8	Aviation Fuels (Sample Naphtha)	64741-87-3	Naphtha, petroleum, sweetened	4.5 (if boiling point < 35°C) 80 (if boiling point ≥ 35°C) vapour cloud explosion	2,500 pool fire
9		68527-27-5	Naphtha, petroleum, full-range alkylate, butane containing	80 vapour cloud explosion	2,500 pool fire
10	Light Fuel Oil (Sample Diesel Fuel)	68476-30-2	Fuel Oil No. 2	2,500 pool fire	-
11	Heavy Fuel Oils	68476-31-3	Fuel Oil No. 4	2,500	-

[3] Representative substances are included in the PHAST software.
[4] These Emergency Hazards are for additional information only and will not be incorporated into the E2 Regulations.

#	CMP Category ("Representative Substance")[3]	CAS No.	Name of Petroleum Substance	Recommended Threshold Quantity (tonnes) and Associated Hazard	Other Emergency Hazards[4]
12	(Sample Heavy Distillate)	68553-00-4	Fuel Oil No. 6	pool fire	
13		68476-33-5	Fuel Oil, Residual		
14	Natural Gas Condensates	64741-47-5[5]	Natural gas condensates, petroleum	340 Vapour Cloud Explosion	-
15		64741-48-6[6]	Natural gas, petroleum, raw liquid mix	4.5 Vapour Cloud Explosion	-
16		68919-39-1[7]	Natural gas condensates	45 Vapour Cloud Explosion	-

[5] Representative substance based on a compilation of 40% n-octane and 60% n-heptane (Trican Production Services,Calgary, Alberta, Canada, MSDS, 2001)

[6] Representative substance based on a compilation of 26% ethane, 26% propane, 15% n-butane, 13% isobutene, 20% hexane (Oneok, MSDS, Tulsa, Ok, USA, 2009)

[7] Representative substance based on a compilation 62.5% n-heptane, 10% n-nonane, 15% n-hexane, 7% isopentane, 3.5% n-pentane, 2% butane (Marathon, MSDS, Findlay, OH, USA, 2011)

2.0 SUMMARY OF THE RISK EVALUATION

2.1 Flammable, Combustible, Oxidizers and Pool Fires

Methodology

The methodology used to determine the flammability threshold of a substance is based on the approach developed by the United States Environmental Protection Agency (U.S. EPA) (U.S. EPA, 1994). A vapour cloud explosion could occur if the flash point for a substance is less than 23°C and the boiling point is less than 35°C. If a substance meets both criteria, the substance is considered to be flammable and the threshold is set at 4.5 tonnes. For these substances that meet only one of the criteria, the substance is considered to be combustible and the threshold is higher. In order for a vapour cloud explosion to occur, the overpressure resulting from an explosion of a flammable or combustible quantity is 3 psi (approximately 166 km/hr wind speed) at 100 meters (Ketcheson, 2012).

The methodology used to identify oxidizers for the E2 Regulations was adopted from the methodology used by CRAIM. Oxidizers act as explosives when they are heated in confined spaces. These substances could explode and also produce a pressure wave of 3 psi at 100 meters.

The ability of the flammable and combustible substances to exhibit vapour cloud explosions was assessed using computer models (PHAST software version 6.7, DNV 2013).

The methodology used to determine pool fires involves computer modeling (i.e., PHAST software, version 6.7) to evaluate the quantity threshold capable of traveling 100 m from the source and generating a heat radiation of 5 kW/m^2. This level of heat radiation is expected to produce second-degree burns over the exposed skin when exposed for 30 seconds or more (Phani, 2008).

PHAST employed typical physical properties for the following CMP categories: Diesel Fuel; Crude Oil; Aviation Fuels; Light Fuel Oil; Heavy Fuel Oils; and, Natural Gas Condensates.

Findings

The 16 petroleum substances, listed under Table 1, are modeled by their respective representative substance. The average physical properties for each representative substance are shown in Table 2.

Table 2: Physical Properties of Representative Petroleum Substances

Averaged Physical Properties	Flash Point (˚C)	Boiling Point (˚C)	Vapour pressure (kPa)	Heat of Combustion (kJ/kg)	Molecular Weight (g)	Density (kg/m^3)
Diesel Fuel (Sample Diesel Fuel)	116	254	0.002	44,018	198	759
Heavy Crude Oil (Sample Heavy Crude)	76	196	0.056	44,166	156	736
Aviation Fuels (Sample Kerosene)	44	151	0.580	44,321	128	714
Aviation Fuels (Sample Naphtha)	7	98[8]	6	44,556	100	682
Light Fuel Oil (Sample Diesel)	26	126	1.4	44,420	114	703
Heavy Fuel Oils (Sample Heavy Distillate)	116	254	0.002	44,018	198	759
NGC[9]	-62[10] -4[11] -125[12]	80[9] 106[10] -71[11]	17[9] 4.5[10] 1997[11]	43116[9] 44502[10] 46129[11]	99.4[9] 105[10] 46[11]	738[9] 669[10] 467[11]

[8] This is the average boiling point for naphtha as shown in Table 2. But, the boiling point range for naphtha provided by CMP can vary considerably. The boiling points of naphtha can range from values lower than 35˚C to values higher than 35˚C. Industry will have to know the boiling point for their naphtha at their facility to determine if their substance is capable of causing either a vapour cloud explosion (boiling point < 35˚C) or a combustible mixture (boiling point > 35˚C).

[9] Natural Gas Condensates (NGC) data estimated from PHAST software.

[10] 68919-39-1

[11] 64741-47-5

[12] 64741-48-6

Of the 16 substances modeled, the following four compounds were found to have the potential for a vapour cloud explosion based on physical property data provided by PHAST (version 6.7) and published Material Safety Data Sheets (see footnotes).

Table 3: Potential for Vapour Cloud Explosion for Representative Petroleum Substances

CAS No.	(CMP Category) PHAST 'Averaged' Sample	Threshold for Vapour Cloud (tonnes)	Emergency Hazard
8002-05-9	(Heavy Crude Oil) Sample Heavy Crude	10,600	Combustible
128683-25-0			
68527-27-5	(Aviation Fuel) Sample Naphtha	80	Combustible
64741-87-3		80 (if boiling point ≥ 35°C)	Combustible
		4.5 (if boiling point < 35°C)	Flammable

Computer modeling demonstrates that the representative substances listed in Table 1 are capable of causing pool fires at quantities ranging from 3,000 to 10,000 tonnes under a range of wind speeds and bund heights, or dike heights. A wind speed of 5 m/s and 1 meter bund height resulted in the most conservative thresholds (< 3,000 to < 4,500 tonnes; see Appendix).

2.2 Inhalation Toxicity to Humans

Methodology

The methodology used to determine the inhalation threshold of a substance is based on the approach developed by the U.S. EPA (U.S. EPA, 1994). The methodology takes into consideration the toxicity of a substance as well as its ability to become airborne and disperse in air. In order for the vapour of a substance to be released in a concentration sufficient enough to pose an inhalation toxicity risk to humans, the substance’s vapour pressure must be greater than 1.33 kPa (10 mmHg).

Findings

Two of the representative petroleum substances have a vapour pressure above 1.33 kPa (Table 2). However, there were no toxicity data from the official websites for Immediately Dangerous to Life and Health (IDLH) (NIOSH, 1995), final Acute Exposure Guideline Levels (AEGL) (USEPA, 2005a) or mammalian data (RTECS, 2012) to support any toxicity effects. Thus, the substances listed in Table 1 do not constitute an inhalation danger.

Therefore, no quantity threshold is set for the inhalation toxicity to humans because there are no data available to adequately assess these substances.

2.3 Aquatic Toxicity

Methodology

The methodology used to determine the aquatic toxicity threshold of a substance was developed by Environment Canada. For this category, the evaluation of risk to the environment is based on the persistence of the substance in the environment, bioaccumulation and aquatic toxicity of the substance. Thresholds are first set relative to aquatic toxicity, then there are default settings for persistence and bioaccumulation. The threshold quantity ranges were adopted from the Risk Management Plan (RMP) of the United States (RMP, 1993) and the classification of aquatic toxicity for LC50 at 96 hours duration were taken from the Organisation for Economic and Co-operation and Development (OECD) (OECD, 2001a). The persistence and bioaccumulation levels for the High rating were taken from the *Persistence and Bioaccumulation Regulations* under CEPA, 1999 (Environment Canada, 1995).

Findings

At this time, a methodology for determining aquatic toxicity for petroleum mixtures in the context of environmental emergencies is not available. The current methodology is designed for single substances only and is not intended to apply to mixtures. The toxic potential of these mixtures is difficult to evaluate, in part, because fate and behaviour of the individual constituents varies; for example, components within the mixture may float, sink, and/or evaporate. Environment Canada will consider means of determining threshold quantities based on aquatic toxicity of petroleum mixtures in the future.

Therefore, no threshold is set for the aquatic toxicity at this time because no data are available, measured or modeled, to adequately assess these substances.

2.4 Carcinogenicity to Humans

Methodology

A substance classified as carcinogenic or probably carcinogenic to humans by the International Agency for Research on Cancer (IARC, 2014) or by U.S. EPA (U.S. EPA, 2005b) and having a half-life in any medium of at least five years is automatically assigned a high-risk threshold of 0.22 tonnes. The precautionary principle is implemented in this case to establish a timeline of five years in regards to those substances that may be carcinogenic in humans, specifically children. “These empirical results are consistent with current understanding of the biological processes involved in carcinogenesis, which leads to a reasonable expectation that children can be more susceptible to many carcinogenic agents.” (U.S. EPA, 2005).

Findings

Because the petroleum substances listed in Table 1 are not classified by IARC or the U.S. EPA in any group, no threshold has been set for the carcinogenicity of these substances.

2.5 Corrosive Substances

Methodology

Substances that are classified as strong acids or strong bases exhibit a pH solution equal to or less than 2, or equal to or greater than 11.5, respectively. The OECD (OECD, 2001) classifies these substances as corrosive, and they are expected to produce significant effects on the skin and eyes. Extreme pHs are also harmful to aquatic life (Environment Canada, 2007, 2011).

Findings

These substances listed in Table 1 are not considered to be corrosive and therefore no associated threshold is assigned.

2.6 Assigned Threshold

Methodology

Following the risk evaluation methodology developed under section 200 of CEPA 1999, the hazard category (flammable, combustible, oxidizer, inhalation toxicity, aquatic toxicity, carcinogenicity, corrosiveness, or pool fires) that has the lowest threshold quantity will be assigned to the substance. For more information regarding the determination of thresholds, please refer to the *Implementation Guidelines for the Environmental Emergency Regulations 2011* (Government of Canada, 2011).

Policy Considerations

The European SEVESO Directive grouped all the petroleum derived products (gasoline and naphtha, kerosene, jet fuels, gas oils including diesels fuels, home heating oils, heavy fuels and gas oil blending streams) under one category called Qualifying Quantity. The latest version of the Directive 2012/18/UE (OECD, 2012) of the European Parliament and the Council gives the following thresholds: 2,500 tonnes (lower-tier requirements) and 25,000 tonnes (upper-tier requirements). The lower-tier requirements are mandated to develop a Major Accident Prevention Policy, which is proportionate to the hazards and risks for land-use planning, but there is no requirement for a safety report or a safety management system. The upper-tier requirements must establish a safety report, a safety management system and an emergency plan (SEVESO, 2011). The thresholds for the SEVESO Directive are for the total quantity of the dangerous substance present at a site.

Findings
In accordance with the lower-tier threshold from SEVESO and supported by modeling data for pool fires (see Appendix), the quantity threshold of 2,500 tonnes is recommended for all substances in Table 1, except for the following:

- Naphtha (petroleum), sweetened (CAS No. 64741-87-3), which has the potential to cause vapour cloud explosions, has a recommended threshold quantity of 4.5 tonnes;
- Naphtha (petroleum), full-range alkylate butane-containing (CAS No. 68527-27-5) has a threshold quantity of 80 tonnes due to its potential to cause vapour cloud explosions; and,
- For the natural gas condensates, the thresholds are 340, 4.5, and 45 tonnes for 64741-47-5, 64741-48-6 and 68919-39-1, respectively, due to their potential to cause vapour cloud explosions.

A concentration at 1% has been assigned to all of the petroleum substances listed in this report to be consistent with other petroleum substances adopted from the U.S. EPA RMP regulations (RMP, 1993).

3.0 CONCLUSION

Information concerning the quantities of the 16 petroleum substances shown under Table 1 in use in Canada indicates that the substances exist in commerce. Following the risk evaluation and policy considerations of the substances listed under Table 1, and taking into consideration the quantities in use in Canada, Environment Canada recommends that these substances be proposed for addition to Schedule 1 of the E2 Regulations under CEPA 1999 at the threshold quantities shown in Table 1.

Even if the quantity of a substance in use is below the threshold quantity indicated in the *Environmental Emergency Regulations*, Environment Canada recommends that emergency planning be applied to this substance in order to minimize, or prevent, any impacts to humans or the environment in the event of a release of the substance.

4.0 APPENDIX: Modeling Pool Fires

4.1 Modeling Considerations with the PHAST Software, Version 6.7

The following conditions were used to calculate the threshold quantities for the 16 petroleum substances assess herein:

- Repeated simulations were performed with the sample petroleum mixtures, using the PHAST software version 6.7 (DNV, 2013), to find the quantity, in tonnes, necessary to yield a heat radiation of 5 kW/m^2 at 100 meters.
- Threshold volume was calculated assuming a cylindrical storage container.

- Threshold mass was found using substance liquid density from the sample petroleum mixture physical properties.
- Stability class D was used for modeling the pool fires and is defined as: “neutral - little sun and high wind or overcast/windy night”. This stability class was used because a pool fire would spread faster under these conditions.
- Simulations were performed at two different average wind speeds: 3.5 m/s; and 5.0 m/s.

4.2 Limitations Affecting Modeling Results

- Chemical Compositions: The chemical composition of each substance can vary greatly. This variability in composition would directly impact chemical properties used to calculate the flame characteristics and therefore the resulting radiation at a given point.
- Wind Speed: The radiation generated from a pool fire will vary with a given wind speed.

4.3 Results from Representative Petroleum Substances

Radiation perceived at a given point is very much dependent on wind speed. The greater the wind speed, the more tilted the flame will be, resulting in higher radiations at a given point. The potential to cause pool fires was modeled using PHAST under varying wind speeds (3.5 and 5.0 m/s) and bund heights (1 and 2 m) in order to verify that the proposed threshold of 2500 tonnes was within the predicated range. The following graphs were generated using the PHAST software data, version 6.7 (DNV, 2013).

Figure 1, below, shows that the 2,500 tonne threshold recommended by SEVESO is lower than all of the representative petroleum substances for a 3.5 m/s wind speed. Also, the quantity necessary to reach 100 meters at a heat radiaion of 5 kW/m^2 is on average 4,380 tonnes with a standard deviation of 580 tonnes for all 5 categores listed in Table 2. This graph illustrates that the irregardless of the representative petroleum substance, the quantities in tonnes do not vary considerably from the 6 categories of representative petroleum substances.

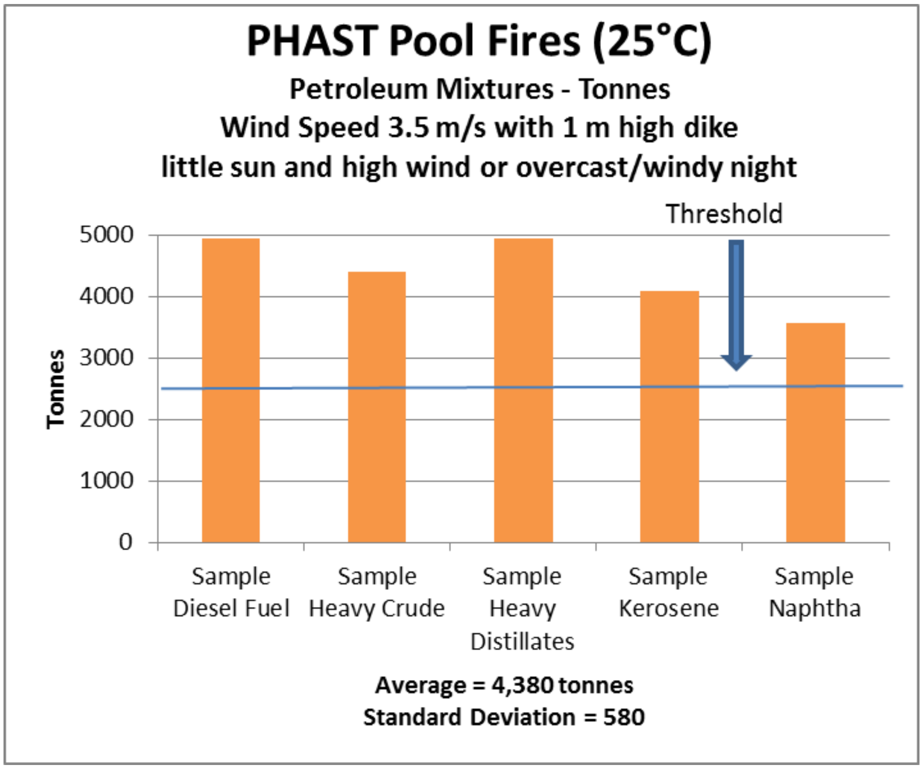

Figure 1: Pool Fire 3.5 m/s of wind with 1 meter Bund

Figure 2, demonstrates that when the bund height is increased, the quantities required to generate a pool fire are estimated to be almost double to accommodate for the higher bund height.

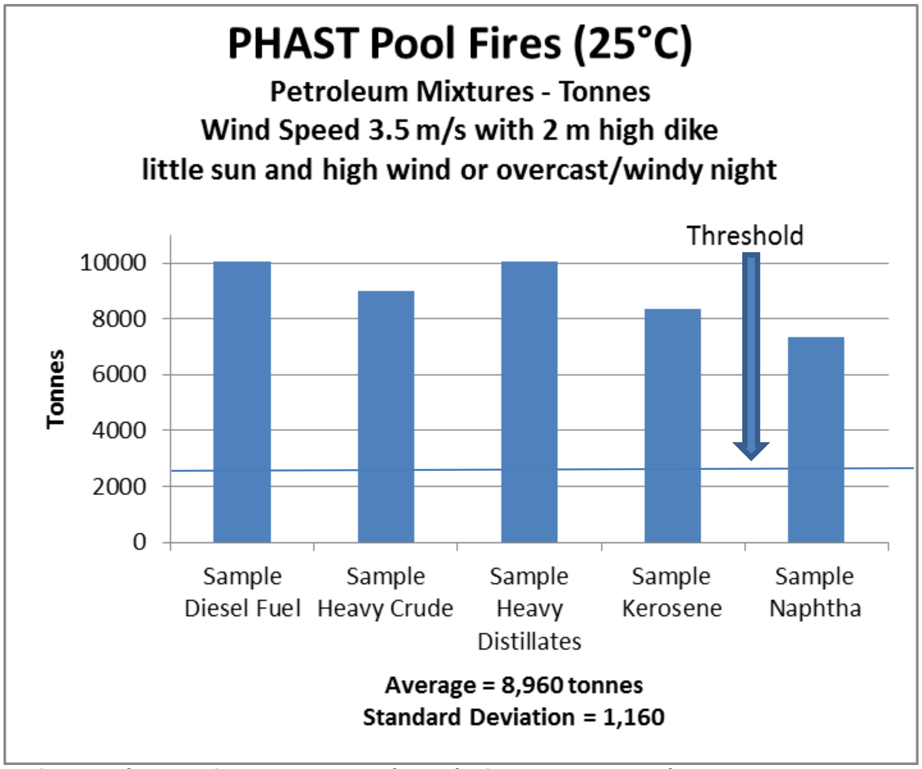

Figure 2: Pool Fire 3.5 m/s wind with 2 meter Bund

Figure 3 indicates that when the wind speed is increased to 5 m/s with a bund height of 1 meter, the quantities are lower because the wind assists in moving the substance a further distance. Therefore, less quantity is required to reach 100 meters. The quantities are higher because the bund height is now set at 2 meters, instead of the 1 meter bund used in Figure 1. The standard deviation is approximately the same ratio as in Figure 1.

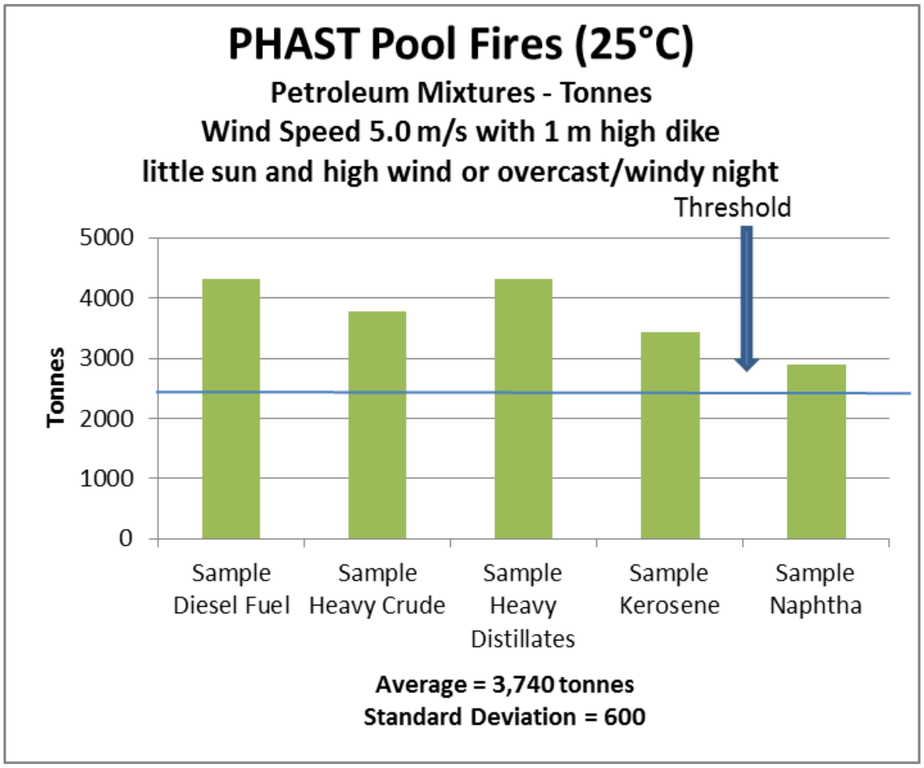

Figure 3: Pool Fire 5 m/s wind with 1 meter Bund

Figure 4 illustrates that when the bund height is doubled, the quantities necessary to reach 100 meters, also double.

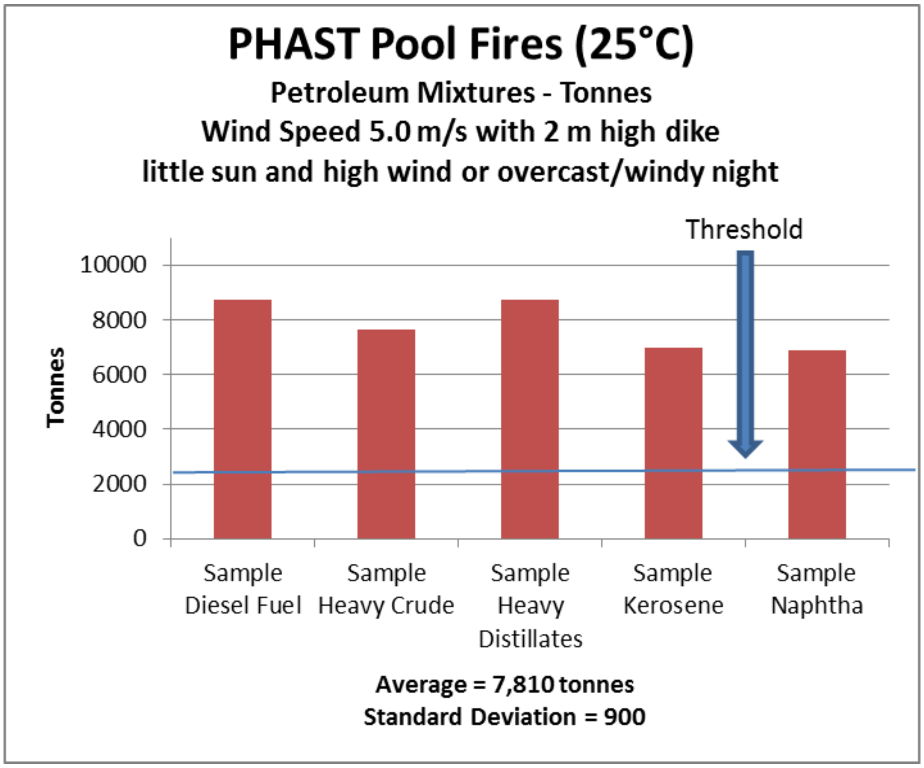

Figure 4: Pool Fire 5 m/s wind with 2 meter Bund

Figures 1 and 3 illustrate that the SEVESO threshold of 2,500 tonnes is about 50% or more of the total quantity of the highest petroleum modeled substance, when the dike height is set at 1 meter. For example, the highest thresholds for the 1 meter bund are 4,900 (figure 1) and 4,300 tonnes (figure 3). A faster wind speed will have the effect of lowering the estimated quantities because the wind will move the liquid along the ground at a faster rate. Considering that the average wind speed in Regina, where one of the oil refineries from 2007 to 2012 has been evaluated, is 5.33[13] m/s, then it is not unreasonable to select a wind speed higher than 3.5 m/s.

4.4 Effects of Wind Speed on Naphtha Pool Fires

Simulated PHAST software runs using Naphtha were performed using stronger wind speeds to assess how the increase in wind speed impacts the quantity of the substance required to reach 100 meters at a heat radiation of 5 kW/m^2. Naphtha was chosen because it has the highest burn rate of the substances listed in Table 1. The fast burn rate of Naphtha, when compared to the other substances in Table 1, results in the highest flame length of the substances thereby translating into more heat radiation at a point. Table 4 shows that higher wind speeds require less substance quantity to reach 100 meters with a heat radiation of 5 kW/m^2. The following simulation results were obtained for a

[13] http://regina.weatherstats.ca/charts/wind_speed-5years.html

constant one meter high bund, while varying the wind speed, as shown in Table 4. The SEVESO Directive of 2,500 tonnes falls between these threshold quantities. The SEVESO threshold of 2,500 tonnes is shown to be sufficiently close to the petroleum mixture with the highest burn rate (Naphtha) as indicated in Table 4.

Table 4: Simulated PHAST runs of Naphtha with Varying Wind Speeds

Wind (m/s)	Pool Fire Diameter (m)	Quantity (tonnes)
5.6	72	2,790
10	63	2,140
14	60	1,940

(JP Lacoursière Inc., 2013)

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