Environment and Climate Change Canada
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Canada

Perspectives and Issues on Health and Safety at Non-conventional (Diluted Bitumen) Crude Oil Incidents

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Environment and Climate Change Canada

Introduction

- Environment and Climate Change (ECCC) has an on-site operational role at spills
- Health and safety (H&S) is important to all responders
- ECCC personnel and others are typically well trained, equipped and experienced with on-site response to conventional oil spills
- Lac Mégantic, QC (Shale) and Marshall. MI (Dilbit) incidents highlighted H&S knowledge gap with nonconventional oil spills

Lac Mégantic, Quebec Incident , July 2013

Photo: Michael Forlan, Twitter

AP Photo: The Canadian Press, Paul Chiasson

Objective

- To present information from a project on:
  - Health and safety concerns, chemical properties of two diluted bitumen crude oils and the implications for H&S;
  - The development of a H&S "toolkit" including procedures and training material specific to Dilbit/Synbit spill for ECCC Personnel; and,
  - A study comparing different laboratory methods used to classify dangerous goods.

Historical Perspective on ESTS's H&S Program

- For approximately 40 years ESTS has delivered an oil and chemical spill R&D program
  - 1977 Arctic and Marine Oilspill Program (AMOP)
  - Chemical Hazardous Emergency Countermeasures (CHEC) program -1980
- Research and Development (R&D) by ESTS to support all aspects of the Environmental Emergencies Program (EEP) including H&S and to develop "tools"
- Elements include:
  - R&D
  - Training courses
  - Technical guidebooks
  - Reach-back and on-site support

Project Rationale and Overview

- H&S programs should be reviewed and evolve over time

- Industry predicts continued increases in oil production over next 20 years (ref. *Crude Oil*, CAPP 2016, www.capp.ca)
  - >4.0 million b/d in 2015
  - Major supply source is oil sands heavy as Dilbit, Synbit
  - Railbit is also produced from the oil sands but volumes less than above
  - Shale is a primary non-conventional crude oil in the U.S. production

- Oil spills account for 50% of reported spills in Canada (ref. *Summary of Spill Events in Canada*, EC, www.publications.gc.ca)

Project Rationale and Overview

- A H&S project over 3 years

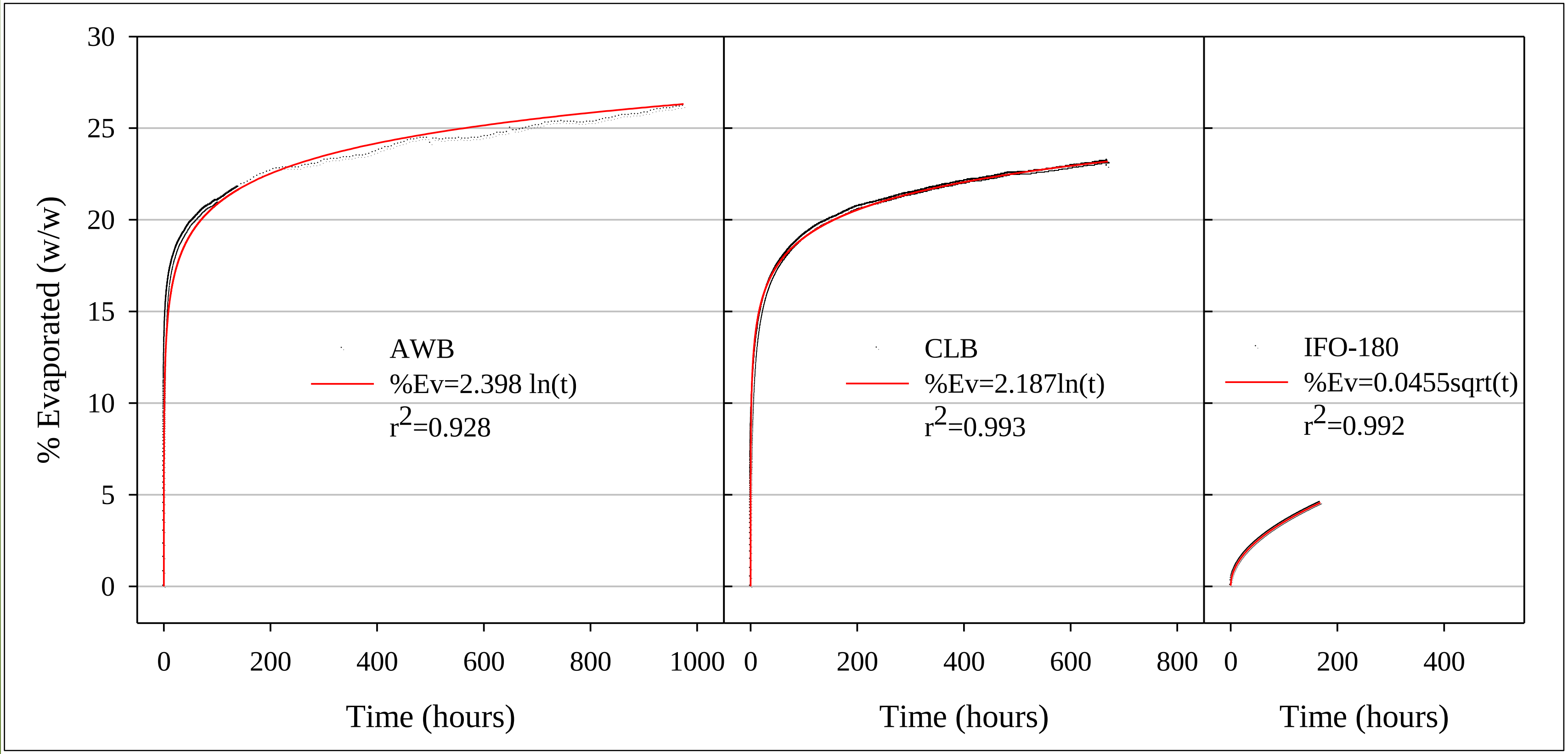
- Year 1 – Literature Review and Scoping Study:
  - To identify and characterize potential hazards, exposure and risks;
  - Review current work practices and safety procedures; and,
  - Provide recommendations for any additional precautions and control measures

- Year 2 – H&S Procedures and Training “Tool Box”:
  - Prepare a critical task inventory and task hazard assessment (Compliant with Part 19 of Canada Occupational Health and Safety Regulations);
  - Prepare H&S procedures;
  - Develop an Awareness level training course; and
  - To develop an Introduction level training course.

- Study comparing different laboratory methods used to classify dangerous goods

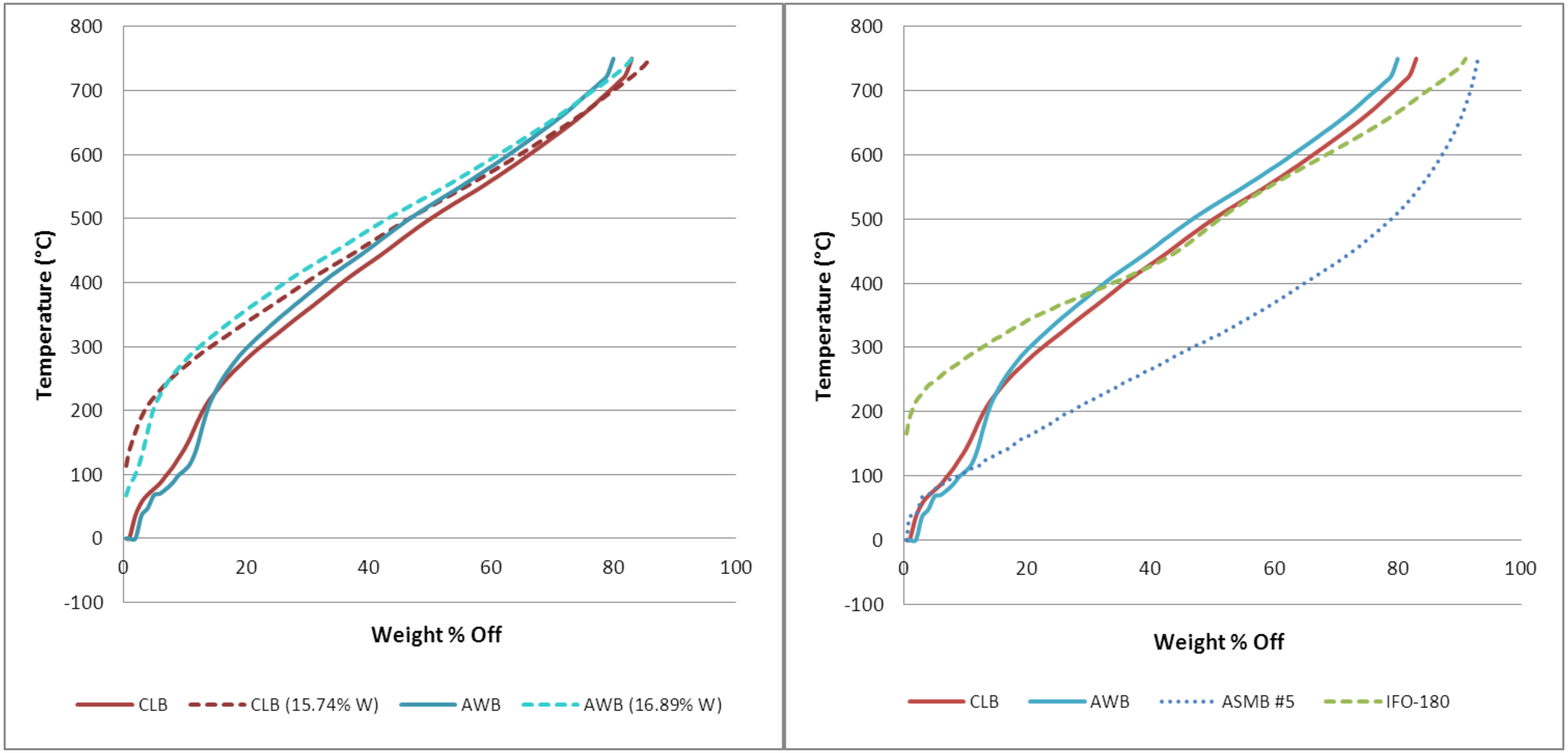
Health and Safety Concerns

- Pan evaporation of Access Western Blend, Cold Lake Bitumen and IFO 180



Health and Safety Concerns

- Simulated Distillation of Diluted Bitumens, ASMB and IFO 180



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Health and Safety Concerns

Chemical Composition of Diluted Bitumen

- A comprehensive chemical composition and distribution of the saturated petroleum hydrocarbon, petrogenic biomarkers and PAHs was undertaken

- Findings
  - There is an abundance of n-alkanes in the AWB and CLB
  - The concentration of alkanes n-C_9 to n-C_{14} initially decreased slowly with increased weathering but a marked decrease in abundance following the W2 (17%)
  - Almost a complete loss of n-alkanes up to C_{13} in the W4 (26%) AWB
  - Indicating a significant VOC presence and therefore potential loss to evaporation as AWB weathers

Health and Safety Concerns

- Selected physical properties of Access Western Blend (Environment Canada 2013)

		Fresh AWB 0%	W1 AWB 8.5%	W2 AWB 17%	W3 AWB 25%	W4 AWB 27%
Sulphur (%w/w)		3.0	4.1	4.5	4.9	4.8
Flash Point (°C)		<-5	<-5	29	159	173
Pour Point (°C)		<-25	<-25	-6	24	33
Density (g/mL)	0 °C 15 °C 20 °C	0.9399 0.9253 0.9148	0.9646 0.9531 0.9547	0.9949 0.9846	1.0214 1.0127	1.0211 1.0140
Viscosity (mPa-s)	0 °C 15 °C 40 °C	1.30E+03 347 59.8	9.82E+03 1.72E+03 348	2.04E+05 2.97E+04	9.35E+07 2.52E+05	>1.00E+08 7.91E+06

Hazard Assessment and Safe Work Procedures

- Critical Task Inventory
  - To consider deployment to a rail or pipeline or marine spill of dilbit/synbit
  - The deployment job safety analysis was broken down into a number (33) of travel and on-site tasks such as:
    - Travel by vehicle, boat, helicopter, ATV, snowmobile; and
    - On-site may require climbing structures, entering the hold of a ship, work near water or ice, work near spilled and/or burning chemicals/fuel etc.

Hazard Assessment and Safe Work Procedures

- A Hazard Assessment Matrix was created listing control measures
  - Steps to minimize or eliminate hazards at the source
- Control measures were categorized into three groups
  - Personal protective equipment (e.g. respiratory protection, High visibility, etc.)
  - Safety devices and supplies (e.g. GPS, gas detectors, bear deterrent, etc.)
  - Personnel emergency equipment (e.g. 1st aid, survival kits, etc.)
- General observations include:
  - Did <u>not</u> notice a significant difference in the process from conventional spills
  - Implying critical task inventory/hazard assessment process sufficiently flexible to deal with new or evolving tasks
  - Rail, pipeline or marine scenario resulted in a few variations to the relative hazards
  - Overall the effort was valuable to ESTS as a opportunity to re-assess the risk associated with on-site support at a dilbit/synbit incident.
    - Probability of a fire or chemical exposure is greater than most conventional crude oil spills

Hazard Assessment and Safe Work Procedures

- Safe Work Procedures were developed for each of the 33 tasks
- Example for “working near spilled chemicals or fuel at a rail setting”

Potential Hazard	Recommended Protective Measures	
	Type	Control
Chemical exposures – ambient atmosphere	Personal Protective Equipment Safety Devices and Supplies	Respiratory protection Gas (VOC, benzene) detector
Chemical exposures - contents	Personal Protective Equipment	Chemical protective gloves Field safety boots Chemical boots or covers Protective eyewear Face shield Chemical impervious coveralls Respiratory protection
	Safety Devices and Supplies	Sanitizing wipes Gas (VOC, benzene) detector
Fire or explosion	Personal Emergency Equipment	Portable fire extinguisher
	Personal Protective Equipment	Respiratory protection Chemical protective gloves Field safety boots Nomex clothing Chemical impervious coveralls
	Safety Devices and Supplies	Gas (VOC, benzene) detector
Item	Additional Information	

Training Courses

- Two courses developed to meet Risk Analysis and Hazard Prevention Directive.

1. Awareness level
   - 1 hour in length, no pre-requisite, lecture style format
   - Basic information, abridged from the Introduction course
   - Covers a comparison of the H&S risk assessment between non-conventional vs. conventional crude oil
   - Target audience is either people with existing knowledge of dilbit / synbit and H&S or those whose job/task requires some awareness of non-conventional crude oils

Training Courses

2. Introduction course
   - 4-8 hours in length, no pre-requisite
   - Stand alone course but prefer to host in conjunction with other H&S training
   - 12 modules and an exam
   - Target audience is all ECCC first responders and those who may work in close proximity to the oil
   - Includes table-top and practical exercises with hands-on demonstration of these crudes
   - At the end of the day, participants should be able to create their own site safety plan

Training Courses

2. Introduction course lecture modules

    1. Conventional vs. Nonconventional Oils
    2. Oil Sands and Bitumen
    3. Chemical Composition of Dilbit and Synbit
    4. Effect of Dilbit/Synbit Chemical Composition on Spill Behaviour
    5. Effect of Dilbit/Synbit Chemical Composition on Fire and Explosion Risk
    6. Effect of Dilbit/Synbit Chemical Composition on Health Risk
    7. Health-Based Exposure Limits for Air Contaminants
    8. Air Contaminant Concentrations at nonconventional Oils Spills
    9. Health and Safety Protective Measures at nonconventional Oils Spills
    10. Respiratory Protection at nonconventional Oils Spills
    11. Basics of Self-Contained Breathing Apparatus
    12. Hazard Assessment and Safety Procedures Documents

Effects on Health Risk
Spill-Only Scenario

BITUMEN

ALKANES

Formula		Name	
CH_4	CH_4	methane	
C_2H_6	CH_3CH_3	ethane	gases
C_3H_8	$CH_3CH_2CH_3$	propane	
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane	
C_5H_{12}	$CH_3(CH_2)_3CH_3$	pentane	
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane	
C_7H_{16}	$CH_3(CH_2)_5CH_3$	heptane	
C_8H_{18}	$CH_3(CH_2)_6CH_3$	octane	
C_9H_{20}	$CH_3(CH_2)_7CH_3$	nonane	
$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	decane	
$C_{11}H_{24}$	$CH_3(CH_2)_9CH_3$	undecane	liquids
$C_{12}H_{26}$	$CH_3(CH_2)_{10}CH_3$	dodecane	
$C_{13}H_{28}$	$CH_3(CH_2)_{11}CH_3$	tridecane	
$C_{14}H_{30}$	$CH_3(CH_2)_{12}CH_3$	tetradecane	
$C_{15}H_{32}$	$CH_3(CH_2)_{13}CH_3$	pentadecane	
$C_{16}H_{34}$	$CH_3(CH_2)_{14}CH_3$	hexadecane	
$C_{17}H_{36}$	$CH_3(CH_2)_{15}CH_3$	heptadecane	
$C_{18}H_{38}$	$CH_3(CH_2)_{16}CH_3$	octadecane	
$C_{19}H_{40}$	$CH_3(CH_2)_{17}CH_3$	nonadecane	solids
$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$	eicosane	

Evaporation of aliphatic and aromatic hydrocarbons

DILUENT

Percentage (by Volume) of Low-Molecular-Weight Hydrocarbons in Selected Diluted Bitumen Blends and Other Canadian Crude Oils								
Alkane Content	Access Western Blend (Diluted Bitumen)	Wabasca Heavy (Diluted Bitumen)	Borealis Heavy Blend (Diluted Bitumen)	Koch Alberta (Light Crude Oil)	Light Sour Blend (Light Crude Oil)	Sour High Edmonton (Medium Crude Oil)	Smiley-Coleville (Heavy Crude Oil)	Loyd Kerrobert (Heavy Crude Oil)
Butanes	0.72	1.93	0.38	4.50	2.43	2.43	0.54	2.04
Pentanes	8.53	1.92	4.01	2.39	3.25	2.56	4.88	6.00
Hexanes	7.06	3.00	5.75	4.54	6.13	4.59	3.95	3.96
Heptanes	4.73	3.47	4.57	5.61	7.44	5.31	2.7	2.12
Octanes	2.74	3.53	5.28	6.09	8.72	5.58	2.12	1.38
Nonanes	1.43	2.64	4.04	4.97	7.18	4.60	2.05	1.36
Decanes	0.70	1.21	1.49	2.49	3.46	2.46	1.10	0.81
Total	25.91	17.7	25.52	30.59	38.61	27.53	17.34	17.67
Mass Recovered	Distillation Temperature °C							
5%	38	93	64	45	69	64	6	51
10%	70	152	93	92	87	93	114	136

Evaporation of aliphatic and aromatic hydrocarbons

TRACE COMPOUNDS

Sulphur, Metals

Possibly minor evolution of hydrogen sulphide

Effects on Health Risk
Add Fire Scenario

BITUMEN

ALKANES

Formula		Name	
CH_4	CH_4	methane	gases
C_2H_6	CH_3CH_3	ethane	
C_3H_8	$CH_3CH_2CH_3$	propane	
C_4H_{10}	$CH_3CH_2CH_2CH_3$	butane	
C_5H_{12}	$CH_3(CH_2)_3CH_3$	pentane	liquids
C_6H_{14}	$CH_3(CH_2)_4CH_3$	hexane	
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Carbon dioxide, carbon monoxide, partially oxidized hydrocarbons, polyaromatic hydrocarbons, soot particulate, oil mists and atmospheric condensates

DILUENT

Percentage (by Volume) of Low-Molecular-Weight Hydrocarbons in Selected Diluted Bitumen Blends and Other Canadian Crude Oils

Alkane Content	Access Western Blend (Diluted Bitumen)	Wabasca Heavy (Diluted Bitumen)	Borealis Heavy Blend (Diluted Bitumen)	Koch Alberta (Light Crude Oil)	Light Sour Blend (Light Crude Oil)	Sour High Edmonton (Medium Crude Oil)	Smiley-Coleville (Heavy Crude Oil)	Loyd Kerrobert (Heavy Crude Oil)
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Carbon dioxide, carbon monoxide, partially oxidized hydrocarbons

TRACE COMPOUNDS

Sulphur, Metals

Hydrogen sulphide, sulphur dioxide, metal oxides, metals in mists and particulates, acidic atmospheric condensates

Health and Safety Concerns

- **Spills without fires**
- The potential of inhalation exposure experienced by personnel working at a spill site will be highest during the first 24 hour period.
- Potential inhalation exposures will be a function of a variety of factors, including:
  - proximity to the spilled material
  - quantity of material spilled and surface area over which it is spread
  - spilled material temperature and ambient atmospheric temperature
  - atmospheric thermal gradients, wind speed and direction
  - precipitation
  - worker position relative to prevailing wind direction and spill zone
  - use of respiratory protection
  - Basic considerations lead to the conclusion that the resultant air concentrations and potential levels of inhalation exposure at the spill site could be extraordinarily high during this period of rapid volatiles evaporation.

Health and Safety Concerns

- **Spills without fires**
- In addition to inhalation exposure, there is potential for additional exposure by skin contact with bulk oil liquid.
- Some condensate species in the bulk liquid readily penetrate skin, which will contribute to body dose. These have “Skin” notations in the ACGIH TLVs.
- The condensate hydrocarbon species that will evaporate from the spilled material vary considerably in their acute and chronic toxicities:
  - Alkanes gases (e.g. methane, ethane, propane, butane) are simple asphyxiants.
  - Vapours of aliphatics and aromatics (i.e. C5 to C20) produce similar kinds of acute health effects from high level exposure. These include mucous membrane and upper respiratory tract irritation, nausea, headache, dizziness, and central nervous system depression.
  - Certain substances have unique and serious adverse chronic health effects.
    - Benzene is a proven human liver carcinogen.
    - N-hexane causes damage to peripheral nerves (typical is pain in hands and feet).

Health and Safety Concerns

- **Spills with fires**
- Air pollutants will be generated from the spill zone by combustion at a much higher rate than by evaporation under a non-fire scenario.
- Most of the airborne mass will consist of combustion products and incomplete combustion products, along with non-combusted volatiles.
- Much of the hydrogen sulphide in the bulk oil will oxidize to sulphur dioxide and react with water vapour generated by combustion to produce sulphuric acid. Hydrogen sulphide will volatilize from hot non-burning oil.

Health and Safety Concerns

- **Spills with fires**
- The potential of inhalation exposure experienced by personnel working at a spill site will be high throughout the duration of the fire.
- Local air concentrations and occupational exposure levels will be function of a variety of factors, including:
  - proximity to the spilled on-fire material
  - proximity to spilled material that has not caught fire
  - quantity of material spilled and surface area over which it is spread
  - quantity of material that is on fire
  - spilled material temperature and ambient atmospheric temperature
  - atmospheric thermal gradients, wind speed and direction
  - precipitation
  - worker position relative to prevailing wind direction and spill zone
  - use of respiratory protection

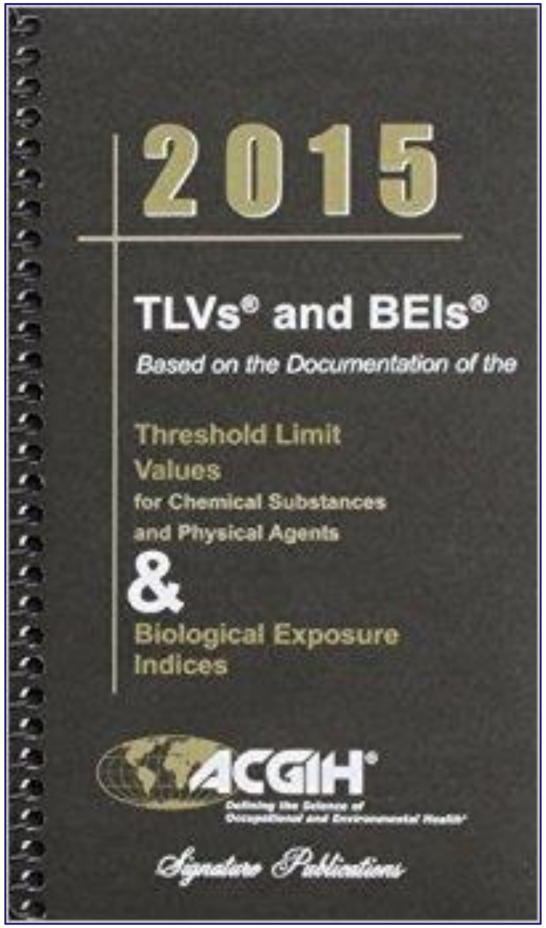
Health and Safety Concerns

- American Conference of Governmental Industrial Hygienists ("ACGIH") "Threshold Limit Values for Chemical Substances and Physical Agents, and Biological Exposure Indices"

- ACGIH limits are adopted by the *Canada Occupational Health and Safety Regulations – made under the Canada Labour Code Part II*.

- These are the exposure limits applicable to ECCC personnel at spill sites.

- Limits provided for approximately 700 chemicals and chemical mixtures.



Personal Protective Measures

Air Monitoring

- Dilbit pipeline and marine tanker spills have the potential to release significant VOCs rapidly to air.
- The importance of site safety planning is highlighted and should include air monitoring instrumentation for
  - Initial response and worker personal safety
  - Worksite safety
  - Air monitoring for the larger public safety concerns

Personal Protective Measures

Chemical Protective Clothing (CPC) and Respiratory Protection(RP)

- Based on review of chemical compounds in AWB and CLB
  - Risk of contact with unknown or skin permeating chemical decrease over time and with distance from volatile and liquid crude oil
  - Level A CPC/RP is unlikely in a Dilbit spill in the open marine environment
  - Level B CPC/RP is a consideration because of the volatile condensate fraction evaporating off during initial hours of a large spill
  - Level C and Level D CPC/RP are most probable especially later in the response and typical of the activities undertaken by EC personnel
- Ensure selection process for
  - CPC complies with U.S.EPA/OSHA guidelines
  - RP complies with Canadian Standards Assoc. and OSHA/NIOSH criteria

Study Comparing Laboratory Methods

- ECCC and Transport Canada (TC) undertook complementary but independent studies to consider crude oil sampling and analysis methods
- ECCC study objective
  - To assess the capability of contract labs to measure flashpoint and initial boiling point of crude oils (Class 3 flammable classification)
  - To compare and evaluate differ ASTM methods for initial boiling point and boiling point distribution
- TC study objective
  - More comprehensive than ECCC, 68 crude oil samples all transported by road and rail
  - To verify the applicability of the current classification requirements described in the TDGR Part 2, for Class 3 – Flammable and Class 2 - Gases and to determine other hazards that crude oil may pose during transport.
  - The final report is available on TC's website (https://www.tc.gc.ca/eng/tdg/safety-menu-1242.html) and overview paper Prefontaine, A., et al., *Crude Oil Sampling and Analysis*, AMOP 2016.

Study Comparing Laboratory Methods

- Transportation of Dangerous Goods Regulations, summarized as:
  - 2.18 General Class 3, Flammable Liquids are:
    - Liquids or liquids containing solids in solution or suspension with a flash point less than or equal to 60ºC using the closed-cup test method (Chapter 2.3 of the UN Recommendations, 2015) or
    - are intended or expected to be at a temperature that is greater than or equal to their flash point at any time while the substances are in transport.
  - UN Recommendations lists four ASTM flash point methods
    - ASTM D3828-93 Standard test method for Flash Point by Small Scale Closed Tester
    - ASTM D56-05, Standard Test method for Flash Point by Tag Closed Cup Tester
    - ASTM D3278-96 (2004)e1, Standard Test Method for Flash Point of Liquids by Small Scale Closed-Cup Apparatus
    - ASTM D93-08, Standard Test Method for Flash Point by Pensky-Martens Closed Cup Tester

Study Comparing Laboratory Methods

- Transportation of Dangerous Goods Regulations, summarized as:
  - 2.19 Packing Groups Flammable liquids included in Class 3, Flammable Liquids, are:
    - (a) Packing Group I, if they have an initial boiling point of 35°C or less (at 01.3 kPa) and any flash point;
    - (b) Packing Group II, if they have an initial boiling point greater than 35°C (at 101.3 kPa) and a flash point less than 23°C; or
    - (c) Packing Group III, if the criteria for inclusion in Packing Group I or II are not met.
  - UN Recommendations lists four ASTM flash point methods
    - ASTM D86-07a, Standard Test method for Distillation of Petroleum Products at Atmospheric Pressure
    - ASTM D1078-05, Standard Test method for Distillation Range of Volatile Organic Liquids

Anton Paar Automatic Distillation Unit
Source: www.Anton Paar.com

Thermo Scientific GC/Simulated Distillation
Source: Environment Canada ESTS

Study Comparing Laboratory Methods

- ECCC study
  - IBP analysis of 12 select conventional and non-conventional petroleum samples by the following ASTM standard methods:
  - ASTM D86: Standard test method for distillation of petroleum products at atmospheric pressure
  - ASTM D7900: Standard test method for determination of light hydrocarbons in stabilized crude oils by gas chromatography
  - ASTM D6730: "Standard test method for determination of individual components in spark ignition engine fuels by 100-metre capillary (with precolumn) high-resolution gas chromatography", modified for use on liquids with a residue
  - ASTM D7169: "Standard test method for boiling point distribution of samples with residues such as crude oils and atmospheric and vacuum residues by high temperature gas chromatography"

- TC study
  - 68 crude oil samples ranging from condensate to bitumen, conventional and non-conventional, sweet and sour crude
  - Samples collected under controlled conditions with sealed pressurized vessel, eliminating loss of volatiles
  - Analysis was extensive and included flash point, initial boiling point, vapour pressure, Reid vapour pressure, chemical composition analysis by gas chromatography, gas oil ratio, vapour phase hydrogen sulphide (H2S) analysis and flammable gas testing

Study Comparing Laboratory Methods

- Guidelines for the Selection of Laboratory
  - Accredited to nation/international laboratory competency standard. (e.g. ISO 17025)
  - Personnel have appropriate education, professional certification and training
  - Use recognized and standard methods for sample handling and analysis
  - Inquire about documented QA/QC protocols including method validation and performance testing
  - Procedures are in place to handle legal samples such as chain of custody and the use of laboratory information management systems(LIMs)
  - Most common type of samples tested by laboratory, range of experience with different types of crude oils and petroleum products
  - Interview the laboratory analyst and senior scientist
  - To assess laboratory's overall understanding of the suitable application of different flash point and initial boiling point methods
  - Determine how samples are received, stored, holding time

Ongoing Work

Year 3

- To deliver at least one pilot course
- Outreach to other Federal Departments (CCG and the Boards)
- Technology transfer through joint exercises and workshops
- Revise the training package based on feedback

Conclusions

- Completing a 3 year project to update H&S procedures for ECCC personnel who may work on-site at an nonconventional crude oil incident
- Scoping study to identify potential H&S issues
  - 12 to 16% w/w loss of volatile condensate in the initial 6 hours
  - Choice of sampling method and laboratory analysis procedure may influence test results
- To undertake a critical task inventory followed by the development of necessary safe work procedures and training material
- Develop and facilitate knowledge transfer of the H&S results to ECCC, other federal agencies and the larger response community