



# Hazmat Safety & Emergency Response Vinyl Chloride



**2017 TRANSCAER® Tour**



**THE CHLORINE INSTITUTE**

# Vinyl Chloride Production

*Ethylene + Chlorine*  $\longrightarrow$  *Ethylene Dichloride*



or

*Ethylene + Hydrogen Chloride + Oxygen*  $\longrightarrow$  *Ethylene Dichloride + Water*



then, heat EDC to 500°C @ 15-30 atm

*Ethylene Dichloride*  $\longrightarrow$  *Vinyl Chloride + Anhydrous Hydrogen Chloride*



# Uses of VCM

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- Vinyl chloride or vinyl chloride monomer (VCM) is a chemical intermediate – it is not a final product - used for resin polymerization, intermediate for refrigerants and intermediate for amines
- Essentially all VCM is used to make polyvinyl chloride, which is used to make a variety of plastic & vinyl products including pipes, wire & cable coatings & packaging materials

# Vinyl Chloride Basics

NFPA Diamond



UN Placard





# Physical & Chemical Properties



# Vinyl Chloride Properties (liquid)

- Clear, colorless
- Lighter than water (liquid density @ 50° F = 0.93 g/ml)
- Becomes a solid at -245° F (freezing point)
- Becomes a gas at 7.9° F (boiling point)
- Autoignition temperature is 882° F
- High coefficient of expansion; 1 volume of liquid expands to approx. 344 volumes in gas phase
- Has a vapor pressure at temperatures above its boiling point, which increases rapidly with increasing temperature
- Liquid VCM at atmospheric pressure is very, very cold -- due to auto-refrigeration

# Vinyl Chloride Properties (gas)

- Colorless gas with a faintly sweet odor
- 2.15 times heavier than air
- Will settle & concentrate in low places & inside of buildings
- Gas pressure of vinyl chloride inside a container is directly proportional to the temperature of the gas:

<u>Temperature, °F</u>	<u>Vapor Pressure, psig</u>
25	7
50	21
75	41
100	68

# Vinyl Chloride Reactivity

AVOID	REACTION
Iron & steel	Generally not reactive in the presence of moisture
Presence of hydrogen chloride	Corrosive
Copper Copper-bearing alloys Aluminum Aluminum-bearing alloys	May cause slight corrosion or discoloration over extended use
Flames Sparks Other sources of ignition	Burns readily. Behavior in Fire: Container may explode in fire. Gas is heavier than air and may travel considerable distance to a source of ignition and flash back.
Electrostatic charges may build up during handling	May ignite vapor-air mixtures in storage containers
Air	Forms explosive polymeric peroxides in contact with air (in the presence of any of a variety of catalysts)
Oxygen, especially when water, acid, iron salts or certain organic impurities are present	Formation of unstable peroxides can occur and can detonate upon heating or under friction and can initiate polymerization under some conditions

# Fire & Explosion Hazards

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- Fire & explosion are the greatest hazards in handling VCM
- Vapors are flammable & explosive over a wide range of concentrations in air:
  - Lower flammability limit = 3.6%
  - Upper flammability limit = 33%
- Vapors may ignite at distant ignition sources & flash back
- Vapor cloud explosion yield: 24,305 lbs VCM = 1 ton TNT
- Adding water to a pool of liquid VCM will promote vaporization & increase the potential for a vapor cloud explosion

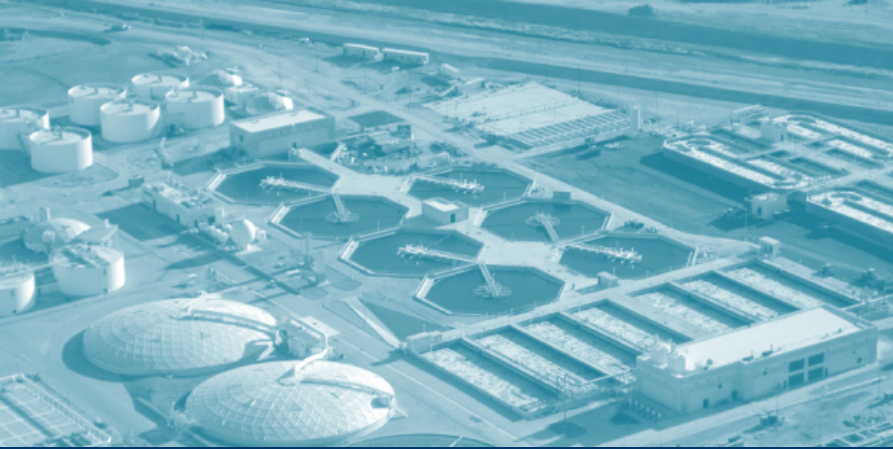
# Fire & Explosion Hazards (cont'd)

- Relatively high heat of vaporization causes large spills to vaporize relatively slowly
- Low specific gravity causes VCM to float on top of water
- Large liquid spills are difficult to extinguish because VCM is not miscible with water
- Do not allow VCM to enter closed drainage or general sewer systems because explosive mixtures can be formed
- The primary products of combustion of VCM are:
  - Hydrogen chloride,
  - Carbon dioxide,
  - Carbon monoxide
  - Large quantities of black smoke

# VCM Vapor Cloud

Paulsboro, New Jersey – 11/30/2012





# Exposure & Health Effects



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# Acute Exposure to Vinyl Chloride

## Health Hazards of Vinyl Chloride

Inhalation	Anesthetic properties at 8,000 ppm & above Resulting in death after a short time at low percent levels
<i>Odor of VCM is too mild to be a good warning property. Odor threshold is about 3,000 ppm</i>	
Skin Contact	Thermal burns (frostbite) or irritation due to extreme cold temperature of liquid
Eyes	Escaping compressed gas or liquid can cause frostbite or irritation
Mucous membranes & Respiratory tract	Can cause irritation
Chronic exposure	Permanent liver injury Liver cancer Neurologic or behavioral symptoms Changes to the skin and bones of the hand.
<i>Impact of exposure is dependent on both VCM concentration and length of exposure time</i>	

# Vinyl Chloride Exposure Limits

Exposure Limits of Vinyl Chloride		
Agency	PPM	Time
ACGIH-TLV:	1 ppm	8-hr Time-Weighted Average
OSHA-PEL	1 ppm	8-hr Time-Weighted Average
OSHA-PEL	5 ppm	15 minutes

**Vinyl chloride is considered a human carcinogen by OSHA, NIOSH, NTP, IARC & EPA**

# Treatment of Exposures - Inhalation

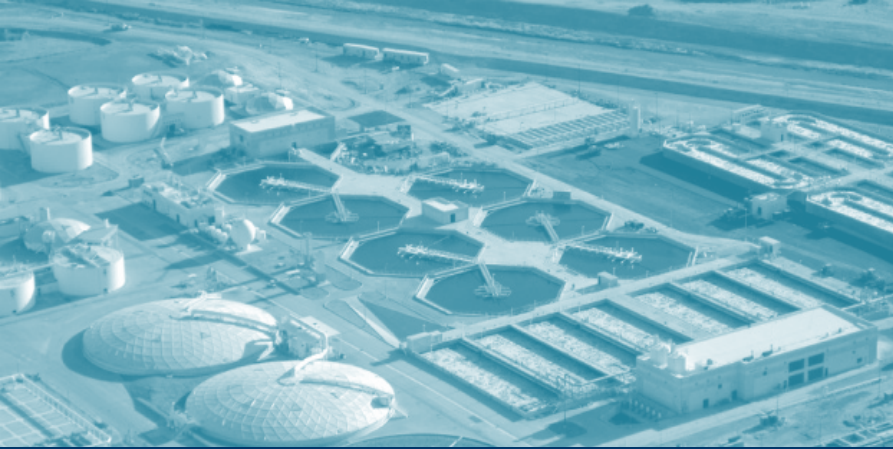
## Treatment of Exposure - Inhalation

Initial Entry	Rescuers should wear an SCBA and protective clothing
Removal of Victim	Move the victim to fresh air immediately
For minimal exposure	No specific treatment other than removal from vinyl chloride atmosphere  <i>Victims normally will be symptom free within an hour or less</i>
Severe Symptoms: <ul style="list-style-type: none"><li>• Wheezing or coughing</li><li>• Shortness of breath</li><li>• Burning in the mouth, throat or chest</li></ul>	Treat the victim with oxygen & other supportive measures
Breathing has stopped	Give artificial respiration

# Treatment of Exposures – Skin Contact

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- **Wash the skin with room temperature water for at least 15 minutes**
- **Remove contaminated clothing while under the shower & continue to wash the skin with water for at least 15 minutes**
- **If skin irritation persists after thorough washing, or if skin is broken or blistered, get medical attention promptly**



# Emergency Response



# Vinyl Chloride Shipping Containers

Tank Cars



Barges

Cylinders



Ships



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# Catastrophic Incidents Have Occurred...

# Train Derailment – Tank Car Breach



**Tamaroa, Illinois**  
February 9, 2003

- **21 cars derailed:**
  - Methanol car on fire
  - Formaldehyde, phosphoric acid & hydrochloric acid cars breached
  - VCM car breached, hot tapped & transloaded
- **1,000 residents in 3 mile radius evacuated**

# Tamaroa (cont'd)



# Tamaroa (cont'd)



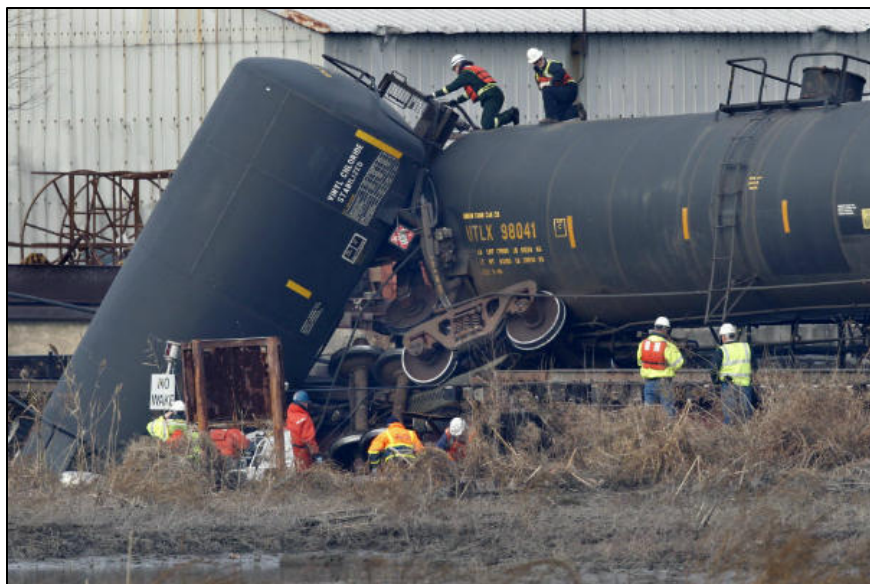
# Tamaroa (cont'd)



# Tamaroa (cont'd)



# Train Derailment – Tank Car Breach



**Paulsboro, New Jersey**  
November 30, 2012

- **5 tank cars derailed:**
  - 4 VCM cars (1 breached)
  - 1 ethanol car
- **About 3000-5000 gallons of VCM remained in the breached car**
- **Recovery operations took 2-1/2 weeks**

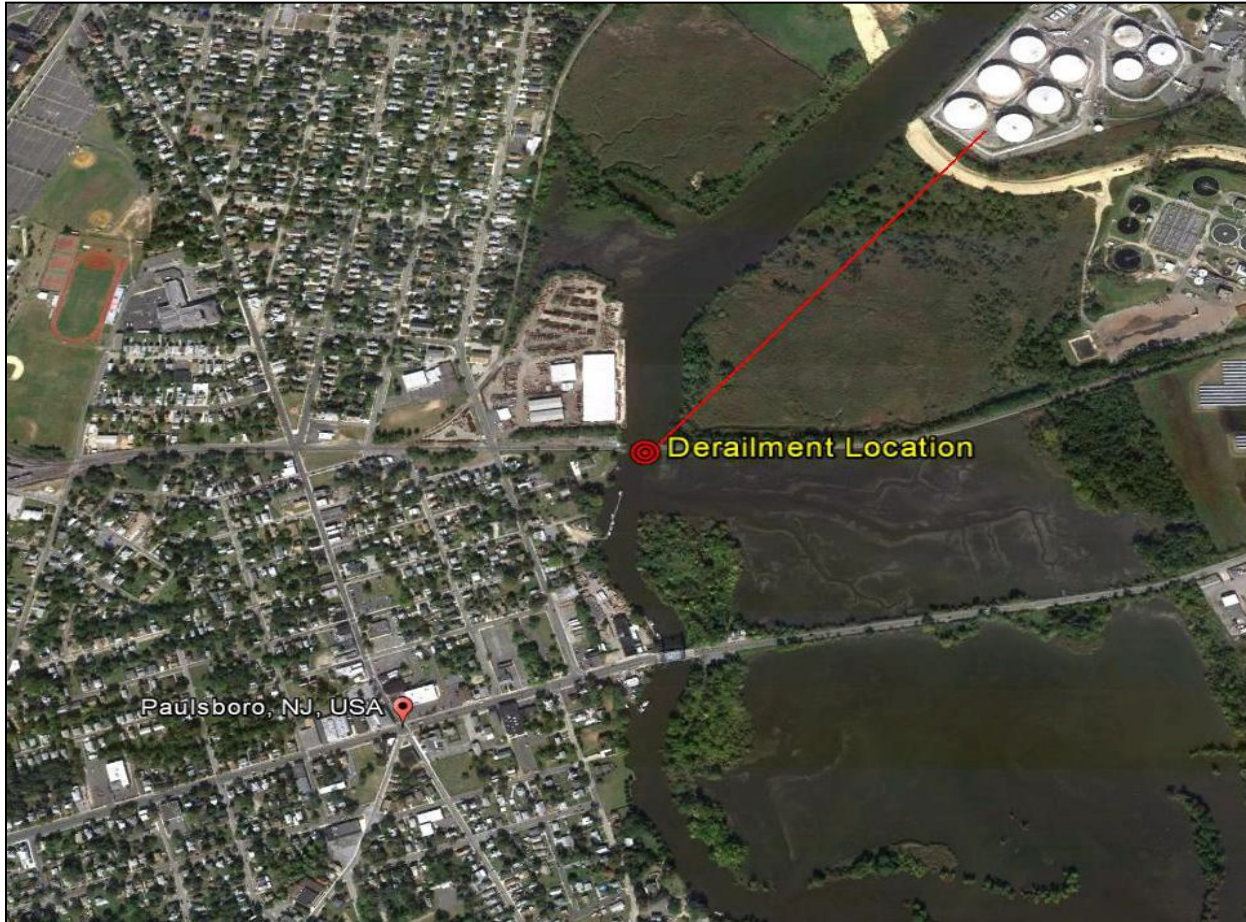
# Paulsboro (cont'd)



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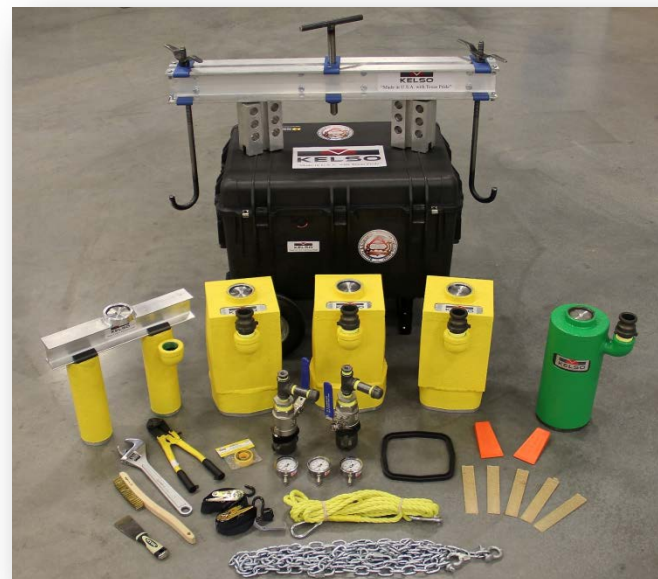
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## **... But Most Incidents Involve Small Valve & Fitting Leaks**

# Midland & Kelso Emergency Response Kits



Midland ERK



Kelso ERK

# Personal Protective Equipment

- **Self-Contained Breathing Apparatus (SCBA), positive pressure**
- **Structural firefighters protective equipment**



# Emergency Response Considerations

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- Focus on containment
- WATER + VCM Leak = this could make the incident worse:
  - Water on the vessel could raise the temperature of vinyl chloride, which will increase pressure & the vaporization rate
  - In a fire situation, water may be useful to cool equipment, but it is not an effective fire control medium for VCM
  - Spray water from a protected location or maximum distance possible – stay away from the ends of tanks
- Do not extinguish a VCM fire until the leak has been controlled
- Withdraw immediately if rising sound from venting PRD or discoloration of tank due to fire

# Emergency Response Considerations (cont'd)

- Flashback from re-ignition at hot surfaces is a real danger at the fire scene
  - Very probable that if a vapor cloud is allowed to escape it will find a source of ignition, which could result in major damage from an explosion
- Hazards presented by other containers or vehicles involved in the accident can be of great significance
- Concealed damage may be a problem not recognized at once, e.g. a damaged or overturned car may have its relief valve blocked so that it no longer is capable of relieving pressure adequately
- OSHA forbids entry into areas with concentrations over 36,000 ppm (3.6% is the lower explosive limit) except for rescue, even with full protective gear

# Public Protective Actions

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- **Consideration should be given to warning or evacuating a ¼ to ½ mile radius around a leaking VCM tank car to avoid injury from flying fragments in case of an explosion.**
- **Geographic, weather or other site-specific conditions may suggest other distances as more desirable.**



Thank You!



  
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