



Chemical Agents of Opportunity for Terrorism: TICs & TIMs

Toxic Industrial Gases as Terrorist Threats

Training Support Package

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Chemical Agents of Opportunity for Terrorism:  
TICs & TIMs

### Learning Objectives

- Review history of industrial gas exposures and regulatory response
- Identify major compounds of interest
- Understand the varying clinical picture created by the gases, based on their physical properties and toxicity
- Address methods to decrease likelihood of exposure and illness

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Chemical Agents of Opportunity for Terrorism:  
TICs & TIMs

### Key Learning Points

- Legislation to regulate TICs/TIMs was generated by concerns regarding toxic gases
- Releases of large volumes of compressed gas is the most likely TIC/TIM scenario
- Toxicity of a gas is determined by
  - Dose
  - Inherent toxicity
  - Volatility
  - Water solubility
  - Warning properties
  - pH

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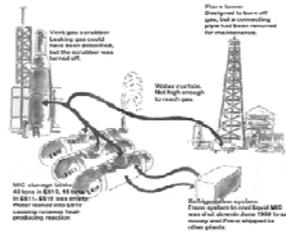
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## The Bhopal Disaster (1984)

- Methyl isocyanate (MIC) release  
Union Carbide plant in Bhopal,  
India (December 3, 1984)



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## Bhopal Disaster

- Water entered tank containing 57,000 L MIC
  - ?sabotage
- Exothermic reaction
- Release of >40 tons MIC over 2 hrs
- Multiple safety system failures
  - unreliable pressure gauges
  - nonfunctional refrigeration unit
  - inoperable gas scrubber
  - alarm failure
  - Inadequate spray “knock-down”

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## Bhopal Disaster

- Gas plume drifted over shantytown exposing 250,000 people
- Temperature inversion reduced plume dilution
- Extent of risk:
  - Modeled mean MIC ambient concentration: 27 ppm (range 0.12 -85.6 ppm)
  - Median MIC concentration: 1.8 ppm
  - 30 minute Acute Emergency Guideline Level-3 (AEG3) 0.40 ppm



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## Bhopal Disaster

- 2500 fatalities within 1 week
- Long term mortality estimated  $\geq$  6000
- Chronic disability for > 100,000 (?)
  - chronic pulmonary complaints
  - ocular inflammation



Dhara et al, Arch Environ Health 2002; 57:391-404

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## Methyl Isocyanate (MIC): $\text{H}_3\text{C}-\text{N}=\text{C}=\text{O}$

- Used as a chemical intermediary for many products, including carbamate insecticides, polyurethane foam and a variety of plastics
- Usually produced by reacting methylamine and phosgene with release of hydrochloric acid
- A high production volume chemical, as are its reagents
- Combustion products from MIC may include cyanide and carbon monoxide

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## Methyl Isocyanate: Physical Properties

- Colorless, flammable liquid at room temperature, but easily vaporizes
  - Vapor pressure 348 mm Hg
  - Boiling point 39.5 °C
- Has a pungent odor; inadequate warning
- Water soluble, but with exothermic reaction
- Vapor density: 1.4

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## Methyl Isocyanate: Clinical Effects

- Dermal/ocular
  - Irritation and ulceration
- Respiratory
  - Mucosal irritation of upper and lower respiratory tract
  - Life-threatening pulmonary edema
  - Residual chronic lung disease
- Reactive Airways Dysfunction Syndrome (RADS)

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## Reactive Airways Dysfunction Syndrome (RADS)

- Non-immunologic asthmatic condition following large exposure to certain irritants
- Syndrome diagnosis requiring:
  - No prior chronic respiratory illness (including asthma)
  - Documented exposure to chemical irritant in significant amount
  - Onset of symptoms (cough, dyspnea, wheezing) within 24 hours and persistence for >3 months
  - Demonstrated airway obstruction and bronchial hyper-responsiveness by pulmonary function testing
  - Lack of other competing pulmonary diagnosis

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## SARA

- Emergency Planning and Community Right-to-Know Act of 1986 (SARA Title III)
- State Emergency Response Commissions
- Local Emergency Planning Committees
- Chemical facilities submit annual inventory reports about hazardous chemicals

[http://www.access.gpo.gov/nara/cfr/waisidx\\_04/40cfr372\\_04.html](http://www.access.gpo.gov/nara/cfr/waisidx_04/40cfr372_04.html)

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### Clean Air Act Amendments of 1990: Risk Management Plans (RMP)

- Businesses required to prepare RMP if greater than threshold amount present of any of 77 toxic or 63 flammable substances
- EPA reviews for completeness, NOT accuracy
- RMP must include
  - Identity of type and amounts of hazardous materials
  - Accident history during past 5 years
  - Hazards associated with chemical processes
  - Process controls, mitigation systems, detection systems
- Off-site consequence analysis (OCA)
- No information on site security is included

<http://www.epa.gov/fedrgsr/EPA-AIR/2004/April/Day-09/a7777.htm>

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### DHS Chemical Facility Antiterrorism Standard (Interim Final Rule 2007)

- Risk-based focus on facility security and improvements
- Security Vulnerability Assessments and Site Security Plans
- Mandates audits and inspections
- Penalties for non-compliance
- Confidential information – preventing “inappropriate public disclosure”

<http://a257.g.akamaitech.net/7/257/2422/01jan20071800/edocket.access.gpo.gov/2007/E7-6363.htm>

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### Chemical Accidents in US Industry RMP for 1994-1999

#1	Anhydrous Ammonia	656
#2	Chlorine	518
#3	Hydrogen Fluoride	101
#4	Flammable Mixture	99
#5	Chlorine Dioxide	55
#6	Propane	54
#7	Sulfur Dioxide	48
#8	Ammonia (>20%)	43
#9	Hydrogen Chloride	32
#19	Phosgene	12

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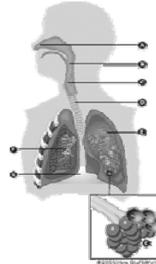
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### Inhalational Exposure: Determinants of Toxicity

- Individual exposed
  - Health
  - Respiratory rate x tidal volume
- Exposure circumstances
  - Concentration
  - Duration
- Properties of Agent
  - Water solubility
  - pH
  - Volatility/Vapor density
  - Mixtures and particle size of possible carriers




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### Clinical Effects Based on Properties of Agent

	High Solubility	Low Solubility
Onset of Symptoms	Rapid	Delayed
Warning Properties	Good	Poor
Airway Injury	Upper with irritation	Lower with lung injury

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### Comparative Toxicity Of Likely Terrorist Industrial Gases

- Irritancy

**Ammonia > Phosgene**

- Danger/Lethality

**Phosgene > Ammonia**

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## Railway Accident: Minot, ND 2002

- Derailment of 31 cars
- Immediate release of ~150,000 gallons of anhydrous ammonia from 5 of 15 cars
- One car airborne ¼ mile striking a house
- Plume 300 feet high spreading 5 miles downwind



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## Response and Outcomes

- Shelter-in-place order
- Difficulty with communication
- Exposed population: 11,600
  - Minor symptoms: 322
  - Serious symptoms: 11
  - Fatal: 1

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## Anhydrous Ammonia (NH<sub>3</sub>)

- Used mainly in manufacture of fertilizer as nitrogen source (>80%)
- Other uses include plastics, fibers and resins, explosives, cleaning disinfectants, refrigeration
- Third highest production volume chemical in U.S.
  - ~9 million metric tons
- Transported as liquefied gas under pressure via pipeline, railcar, tanker truck, and refrigerated barge

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## Ammonia: Physical Properties

- Colorless gas with pungent odor
- Low odor threshold; good warning properties
- Highly water soluble
- Boiling point – 33°C
- Vapor density 0.6 (lighter than air)
- Combustible in narrow range
- Highly reactive gas



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## Clinical Effects

- Damage from alkali burn and thermal reaction
- $$\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{OH}$$
- Low concentration: irritant to nose, throat, upper respiratory tract
  - Higher concentrations or more prolonged contact
    - Skin burns: 30% of admitted chemical burns attributed to ammonia (variable by extent of clandestine drug labs)
    - Lower airway inflammation with pneumonitis and pulmonary edema

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## Anhydrous Ammonia

- Concentration and duration of exposure determines clinical effect
  - From minor irritation to blindness with extensive scar formation
- Center picture shows fluorescein uptake indicating diffuse corneal injury



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## Next Gas: Homemade WWI Warfare Agent

- 29 yr old man with acute respiratory distress after cleaning toilet
- RR 36/min, HR 128/min, BP 148/76
- Lip and throat swelling
- Diffuse wheezing
- Required intubation ventilation
- Hypoxia with CXR



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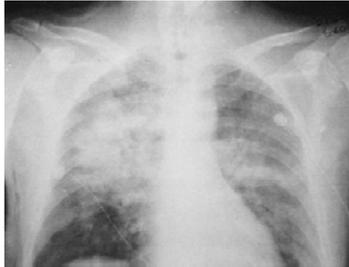
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## What Toxic Gas Did He Inhale?



**Chlorine**

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## Audience Response

Mixing together which of the following is most likely to form chlorine gas?

1. Ammonia and acidic toilet bowl cleaner
2. Bleach and acidic toilet bowl cleaner
3. Cyanide and bleach
4. Acidic toilet bowl cleaner and a dirty toilet
5. Unable to make chlorine gas in the house

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Mixing together which of the following is most likely to form chlorine gas?

1. ammonia and acidic toilet bowl clearer
2. bleach and acidic toilet bowl clearer
3. cyanide and bleach
4. acidic toilet bowl cleaner and dirty toilet
5. unable to make chlorine in the house
- 6.
- 7.
- 8.
- 9.
- 10.

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Chemical Agents of Opportunity for Terrorism:  
TICs & TIMs

### Dangerous Mixture

$$\text{HOCl} + \text{HCl} \leftrightarrow \text{Cl}_2 (\text{gas}) + \text{H}_2\text{O}$$


[http://www.clorox.com/5img/product\\_photos/mw/white.jpg](http://www.clorox.com/5img/product_photos/mw/white.jpg) <http://www.cpsc.gov/ocps/pubs/brosp/brnclm01031102.html>

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Chemical Agents of Opportunity for Terrorism:  
TICs & TIMs

### Chlorine Gas

- Multiple Uses
  - Manufacturing of non-agricultural chemicals
  - Pulp and paper industry
  - Commercial & household bleaching agents
  - Water purification & waste treatment
- 1998 US production > 14 million tons
  - Shipped as liquefied compressed gas



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## Chlorine: Physical Properties

- Green-yellow, pungent gas
- Low odor threshold; moderate warning properties
- Intermediate water solubility
- Boiling point -31 oF
- Vapor density 2.5 (heavier than air)
- Reacts explosively with many compounds



[http://www.amazingrust.com/Experimentshow\\_to/Images/Chlorine\\_gas.jpg](http://www.amazingrust.com/Experimentshow_to/Images/Chlorine_gas.jpg)

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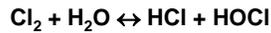
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## Chlorine: Clinical Effects

- Intermediate water-solubility
- Low concentrations:
  - irritant to eyes, nose, throat, upper respiratory tract
- Higher concentrations:
  - acute pulmonary edema, chemical pneumonitis
- Chronic sequelae:
  - RADS



<http://www.aliciapatterson.org/APF1403/Borg/Borg04.jpg>

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## Chlorine: 1st Successful Chemical Warfare Agent, WW I



Wind-borne Chlorine Attack, WWI



Chlorine Gas Respirators

[http://www.germannotes.com/hist\\_ww1\\_poison.jpg](http://www.germannotes.com/hist_ww1_poison.jpg)

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### Chlorine from Train Accident (Graniteville, SC; Jan 6, 2005 02:40)



<http://www.hazmatteam.com>

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### Consequences of Graniteville Train Accident (MMWR January 28, 2005)

- 9 deaths
  - 1 train engineer, 6 mill workers, 1 in home, 1 in truck
- 529 sought medical care
  - 69 hospitalized, 11 critical
  - 18 were treated at area physicians' offices
- 5,400 evacuated in 1 mile radius of crash
- Initial report : "sodium nitrate"
- Chlorine was not reported to ED for 1 hour

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### Chlorine Transport in the US

Rail transportation of chlorine and other toxic gases is common in highly populated cities



photo: Jim Dougherty  
July 9, 2004

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## Chlorine Gas Attack by Truck Bomber Kills Up to 30 in Iraq

BAGHDAD, April 6 (NY Times) — A suicide truck bomb loaded with chlorine gas exploded in Ramadi on Friday, killing as many as 30 people, many of them children, a security official said.



The explosion burned victims' lungs, eyes and skin. Dr. Ali Abdullah Saleh, of the main Ramadi hospital, said 30 people had been admitted with shrapnel wounds and 15 had been sent to a second hospital in the city. He said 50 people had been admitted for breathing problems.

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## Phosgene: $Cl_2C=O$

- Used in the manufacture of
  - Organic chemicals: dyestuffs, isocyanates
  - Plastics
  - Insecticides
  - Pharmaceuticals
- 80% used for isocyanate production
- US production: estimated 1 million tons/year
- Also formed as a combustion product when chlorine-containing compounds are burned

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## Phosgene: History

- Synthesized in 1812
- First used in WWI against the British at Ypres, Belgium (December 1915)



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## Phosgene: Community Threat Assessment

- 99.9% of production is "used on-site"
- Storage and transport as liquefied compressed gas



<http://www.chemicaldesign.com/Phosgene.htm>

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## Phosgene

- BASF Plant Ascension Parish, LA
  - 1981: Plant operator killed
  - 1982: 28 workers injured
  - 1986: phosgene plume over unpopulated parts of Ascension Parish



[http://commons.wikimedia.org/wiki/Image:Map\\_of\\_Louisiana\\_highlighting\\_Ascension\\_Parish.svg](http://commons.wikimedia.org/wiki/Image:Map_of_Louisiana_highlighting_Ascension_Parish.svg)

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## Phosgene: Physical Properties

- Colorless gas with odor of musty hay
- Higher odor threshold; poor warning properties
- Low water solubility
- Boiling point 8.2 °C
- Vapor density 3.5 (heavier than air)

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## Phosgene

Odor threshold:  
0.5 - 1.5 ppm  
10 min AEGL-2:  
0.60 ppm  
10 min AEGL-3: 3.6  
ppm



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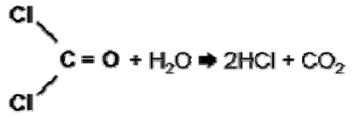
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## Phosgene: Clinical Effects

- Limited initial symptoms
  - Irritation of eyes, nose, upper airways
  - Higher concentrations cause airway spasm
- Low water solubility - slow hydrolysis to HCl



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## Phosgene: Delayed Effects

- Latent development of pulmonary edema
  - Onset 1 to 24 hours after exposure
  - Pulmonary function abnormalities
  - May be fatal
- Chronic airway disease



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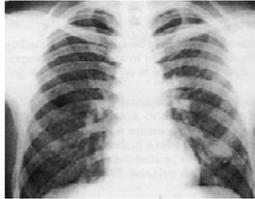
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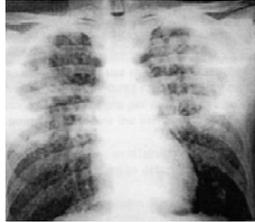
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### Phosgene: Delayed Lung Injury



6 hrs post-exposure



10 hrs post-exposure

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### Hydrofluoric Acid (HF)

- HF is used for a variety of industrial processes and consumer products (dilute), including
  - Catalyst in oil refineries
  - Manufacture of silicon semiconductor chips
  - Separating uranium isotopes
  - Etching glass or enamel
  - Cleaning brass, crystal and as a rust remover
- Production in U.S. is < 1 million tons/year
- Transported as pressurized anhydrous liquid by rail



<http://www.viewimages.com/Search.aspx?mid=130700&keyword=1&partner=Google>

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### HF: Physical Properties

- Colorless, non-flammable, fuming liquid or gas with irritating odor
- Low odor threshold; good warning property
- Highly water soluble - with release of heat
- Weak acid
  - Not highly dissociated, but penetrates tissue well
- Boiling point 20°C
- Vapor density 0.7

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## HF: Clinical Effects

- Highly corrosive depending on concentration and irritating to all tissues
- Onset of pain and skin changes may be delayed for hours with dilute (<20%) solutions
- Release of fluoride ion results in binding to calcium and magnesium, with unique and severe systemic effects
  - Tissue necrosis
  - Hypocalcemia, hypomagnesemia, hyperkalemia leading to cardiac dysrhythmia and death

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## Texas City, TX Industrial Accident Releasing HF (October 31, 1987)

- ~30,000 pounds of hydrofluoric acid leaked from an HF alkylation reactor drum when a 50 foot long convection unit was dropped on the vessel
- Vapors emitted under pressure for 2 hours
- Estimate of AEGLS 3 at ~3/4 mile away
- ~4000 residents evacuated for 3 days
- >1000 people to hospital with skin, eye, nose/throat irritation and pulmonary symptoms
- No fatalities

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### HF: Preparedness

- Community threat assessment
- Emergency response planning
- Prevention through zoning and/or substitution of less hazardous processes



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### Summary: Toxic Gas Characteristics

AGENT	PHYSICAL PROPERTIES			EXPECTED CLINICAL EFFECTS		
	H <sub>2</sub> O Solubility	Odor / Warning	Vapor Density	Mucosal / Upper Airway	Lower Airway	Systemic
MIC	High	Pungent / Inadequate	1.4	Yes	Possible	No
NH <sub>3</sub>	High	Pungent / Good	0.5	Yes	Possible	No
Cl <sub>2</sub>	Interm.	Pungent / Fair	2.5	Yes	Yes	No
COCl <sub>2</sub>	Low	Mown Hay / Inadequate	3.5	Unlikely	Yes	No
HF	High	Pungent / Good	0.7	Yes	Possible	Electrolyte & Cardiac Rhythm

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### Treatment for Irritative Gas Exposure

- Remove from exposure
- Irrigation of eyes or skin if involved
  - Extensive decontamination usually not necessary unless liquid exposure
- Oxygen
- Nebulized beta-agonists (e.g. albuterol) for wheezing or dyspnea



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### Special Considerations

- Consider adding sodium bicarbonate to nebulizer in chlorine gas exposures
- Intravenous and inhaled calcium gluconate, and continuous cardiac monitoring are important for hydrogen fluoride exposure
- Observe patients for late pulmonary effects, particularly in those with severe early symptoms

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### Questions?

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