Module Five: Cyanide & Fumigants

Paul Wax, MD, FACMT
American College of Medical Toxicology
Course Overview

1. Introduction / Principles of Medical Toxicology
2. Why Toxic Industrial Chemicals as Terrorist Weapons?
3. Inhalation of Toxic Industrial Gases
4. Agricultural Chemicals of Concern
5. Cyanide and Fumigants
6. Psychological Consequences of Mass Chemical Exposure
7. Risk Communication
8. Neurotoxins
9. Water, Food & Medication as Vectors
10. Delayed-Onset Toxins
11. Post-Event Medical Monitoring
12. Tabletop Exercise
Please help us improve this course by filling out the module evaluation.

You will receive an email with instructions following the conclusion of this presentation.
Faculty Disclosure

• Faculty: Paul Wax, MD, FACMT
  – Relationships with commercial interests: none
  – Speakers Bureau/Honoraria: none
  – Consulting Fees: none
  – Other: none
Participant Question:

- How many people are in attendance at your site (including yourself)?
Learning Objectives

• Indicate the sources and uses of cyanide and fumigants
• Describe therapies used to treat cyanide poisoning
• List the three most common fumigant gases
• Describe the clinical effects of exposure to these gases
• Explain how to treat victims exposed to these gases
Cyanide & Fumigants

• Cyanide
  – Salts (solids)
  – Gas

• Fumigant gases
  – Vikane (sulfuryl fluoride)
  – Methyl bromide
  – Phosphine
Cyanide

- Notoriety well deserved
- Historical relevance
  - Mass poisoning
- Pharmaceutical terrorism
- Weapon of Mass Destruction
Cyanide (CN): Properties

- Small molecule (26 Dalton)
- Boiling Point 27.7°C
- Colorless
- Bitter Almonds? Myth
- Water soluble
Cyanide: Two Common Forms

Hydrogen Cyanide Gas

Toxic when Inhaled

Solid Cyanide Salts (sodium cyanide, potassium cyanide, calcium cyanide)

Toxic when Ingested
Generating HCN Gas from Salts

Solid Cyanide Salt (X-CN) + Acid (H-X) → Hydrogen Cyanide Gas (HCN)
Audience Response

Which of the following best describes the uses of cyanide?

a. Chemical Warfare Agent
b. Electroplating agent
c. Brick cleaning agent
d. 1&2
e. 1,2 &3
Cyanide

- Sources of cyanide (solid)
  - Industrial applications (electroplating, hardening steel, mining, fumigation, …)
  - Sodium, potassium and calcium cyanide are all readily purchased on the internet

- Other sources
  - Cyanogen chloride
  - Acetonitrile, acrylonitrile
  - Natural occurring cyanogens (laetrile)
Amazon.com, Penn sued by family of student who killed herself

Robert Moran, Inquirer Staff Writer
LAST UPDATED: Friday, September 4, 2015, 1:10 AM
POSTED: Thursday, September 3, 2015, 8:16 PM

The University of Pennsylvania and Amazon.com are being sued by the mother of a student who killed herself in 2013 with cyanide she allegedly purchased through the online retailer.

Arya Singh, 20, a junior in the School of Nursing, died Feb. 8, 2013, after ingesting soluble cyanide crystals in her dorm room.

Singh's life began to unravel after an alleged sexual assault in 2011 by a male student that she reported to authorities, the suit says. No charges were filed against the student, and he remained on campus.

In the two years that followed, Singh increasingly failed to show up for classes. On one occasion, she was arrested and hospitalized for alcohol intoxication. She was subject to multiple academic and misconduct investigations.
Chemical Agents of Opportunity for Terrorism: TICs & TIMs

Module Five – Cyanide and Fumigants

SIGMA-ALDRICH

USA Home  207810 - Potassium cyanide

207810 SIGMA-ALDRICH
Potassium cyanide
ACS reagent, ≥96.0%

CAS Number: 151-50-8  Linear Formula: KCN  Molecular Weight: 65.12
Belletstein Registry Number: 3593645  EC Number: 205-792-3
MDL number: MFCD00011397  PubChem Substance ID: 24852474

POPULAR DOCUMENTS: SPECIFICATION SHEET (PDF)

Properties

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<th>Related Categories</th>
<th>Essential Chemicals, Potassium Salts, Research Essentials, Salts</th>
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<td>ACS reagent</td>
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<td></td>
<td>≥96.0%</td>
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<td>assay</td>
<td></td>
</tr>
<tr>
<td>mp</td>
<td>634 °C (lit.)</td>
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<tr>
<td>anion traces</td>
<td>≤0.005%</td>
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<td>SCN⁻ passes test</td>
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<td>chloride (Cl⁻)</td>
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<tr>
<td>phosphate (PO₄³⁻)</td>
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Price and Availability

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Ultra-high Purity Salts

High-purity is crucial for some applications. We offer a range of 5N and 6N salts, metals and oxides.

Did you use this product in your Paper? If so click here.
Buy pure POTASSIUM CYANIDE both pills and powder

Our laboratory manufactures and distributes the best quality potassium, which is a colorless crystalline compound. Our potassium cyanide is known by jewelry dealers for its extreme and exceptional high-quality chemical gilding and buffing properties. Our gold mining, organic synthesis, and electroplating customers have never looked anywhere ever since they tested our potassium cyanide. Potassium cyanide is offered in powder or cylindrical tablet each tablets weighing 100 grams. It is an inorganic compound with the formula KCN. This colorless crystalline compound, similar in appearance to sugar, is highly soluble in water. Most KCN is used in gold mining, organic synthesis, committing suicide and electroplating.

Contact us directly through our email at.. tradelink.research@gmail.com

skype us at: tradelinks.chem
Cyanide: Mechanism of Action

- Readily enters cells
- Inhibits mitochondrial respiration
Cyanide

Other Cytochrome Oxidase Inhibitors:

- Hydrogen sulfide
  - “sewer gas”
- Sodium azide
  - Component of airbags
- Carbon monoxide
  - Minor mechanism
Cyanide: Toxic Quantities

- Cyanide salts
  - Lethal dose: 200-300 mg (3 mg/kg)

- Hydrogen Cyanide (HCN) gas
  - Lethal dose: 50-100 mg
    - 10 ppm for 2-hours = headache
    - 100-200 ppm = death in 1-hour
    - 200-300 ppm = death in several minutes
Cyanide: Clinical Manifestations

• “Gasp poison”

• Central Nervous System
  – Headache, confusion, agitation, syncope, convulsions, coma, death

• Cardiovascular
  – Tachycardia, hypertension
  – Bradycardia, hypotension
  – Cardiac arrest

• GI
  – nausea, vomiting, abdominal pain
Chemical Agents of Opportunity for Terrorism: TICs & TIMs

Knock-Down Gases

Some possible suspects:

- Hydrogen cyanide
- Hydrogen sulfide
- Carbon monoxide
- Oxygen-deficient air
Cyanide: Onset of Symptoms

Time to Onset of Symptoms

- Cyanide salt and cyanide gas (HCN)
  - Minutes
  - Inhalation of gas >> ingestion >> dermal
  - Survival > 10 minutes, most likely will survive
    - All or Nothing

- Aliphatic cyanogens & Natural cyanogens
  - Hours – must be metabolized
Cyanide: Diagnostic Testing

- **ABG**
  - Anion gap metabolic acidosis
- **VBG**
  - “Arteriolization” of venous blood gas
- **Lactate**
  - Elevated
- **Blood cyanide levels**
  - Whole blood or serum
  - 2-3 day turn around time
Cyanide: Real World Scenarios

- Battlefield
- Mass Murder
- Mass Suicide
- Homicide
- Pharmaceutical Terrorism
- Environmental Terrorism
- Economic Terrorism
Cyanide: Battlefield

- WMD
  - Researched as a weapon in WW I
  - Used in concentration camps in WW II and in caves (Adjimushkaiskye)
    - Zyklon B
Cyanide: Mass Murder

Nazi Death Camps

- Millions of Jews, gypsies, and others died in CN gas chambers
- Gas chambers disguised as communal showers
- Some suffering more than 20 min before death
Execution by Cyanide Gas Chamber

- CN salts dropped into sulfuric acid → HCN
- Few states now use it
- 1930 to 1980 (11 states):
  - 945 men
  - 7 women
- 1960 Caryl Chessman told reporters he would nod his head if it hurt. He nodded his head for several minutes before he died.
Cyanide: Other Sources

The most common source of cyanide exposure is incomplete combustion of:

- Wood
- Plastic
- Rubber
- Polyurethane
- Wool
- Silk
Cyanide: Incomplete Combustion

Happy Land Social Club Fire Bronx 1990: 87 deaths
Cyanide: Incomplete Combustion

The Station Nightclub Fire Providence 2003: 100 deaths
Cyanide: Homicide

Teen charged with poisoning friend

Friday, January 10, 2003 Posted: 1:50 PM EST (1850 GMT)

ELLIOTT CITY, Maryland (AP) — A teenager was charged Thursday with first-degree murder for allegedly killing a romantic rival by spiking his soda with cyanide.

Police said Ryan Furlough, 18, laced his friend's drink with the poison as they played video games in Furlough's basement in Ellicot City in suburban Baltimore.

Benjamin Vassiliev, 17, went into respiratory arrest last Friday after drinking the soda and died Wednesday.
Cyanide: Homicide

Timeline:

• 17 yr old male drinks KCN spiked soda
• Feels unwell and goes to the bathroom
• Emerges from the bathroom and collapses
• EMS intubate for apnea. Vital signs present.
• Cardiac arrest in hospital. ACLS and recovery.
• Transfer to tertiary care center.
• Dx made. Steps 2 & 3 of antidote kit administered.
• No neurologic recovery.
Cyanide: Suicide

- 55 yr old male ingests KCN tablets at sentencing hearing.
- Subject tells lawyer who tells judge
- In minutes: lethargy > collapse > shock
- No antidote kit at scene
- Subject received antidote kit at hospital (~15 min post-ingestion)
- No neurological recovery.
Cyanide: Suicide

• The following video is taken from courtroom footage of a sentencing hearing in Phoenix in 2012
• It demonstrates the delay to onset, initial symptoms and rapidity of progression of a suicidal ingestion of cyanide
Cyanide: Mass Murder

The Jonestown Massacre
- Jonestown, Guyana (1978)
- CN-laced Kool-Aid
- 913 Deaths
Cyanide: Drug Tampering

- Pharmaceutical Terrorism
  - 1982 – Acetaminophen
  - 1991 – Pseudoephedrine
Cyanide: Copycat Events

- Cyanide has been implicated or suspected in a number of medication and food supply tampering or terrorist events.
- These will be discussed in more detail in the “Water/Food/Medication as a Vehicle for Terrorism Module” (Module 9).
- This next video clip provides an example of the potential impact of a single tampering event.
Chemical Agents of Opportunity for Terrorism: TICs & TIMs
Cyanide: Terrorism

Appearance at incidents:

- **NY WTC (1993)**
  - Ingredients for HCN in the truck
- **Tokyo Subway (1995)**
  - Sarin
  - Ingredients for HCN in bathroom
Improvised Cyanide-Producing Devices

- Potential use of a “mubtakar” device
Cyanide: Environmental Terrorism?

- Cyanide spill into Tisza River, Romania (2000)
- 100,000 cubic meters of cyanide containing water released when a gold mine dam overflowed
- All river life killed for miles downriver
Cyanide: Economic Terrorism

- Hoax - 1989
- Chilean Grapes Imported into the US Alleged to Contain Cyanide

- 15-gallon drum of sodium cyanide was lost from a delivery truck
- Located after 1-week search in N. Dakota
  - Was being hauled for delivery to beekeepers
  - Used to fumigate and kill excess bees
  - Not legally registered for this use
- Became a multi-state investigation
Module Five – Cyanide and Fumigants

Chemical Agents of Opportunity for Terrorism: TICs & TIMs

Audience Response

Which of the following is least helpful in the treatment of cyanide poisoning?

a. Hydroxocobalamin
b. Oxygen
c. Sodium Nitrite
d. Sodium Thiosulfate
Cyanide: Treatment

Prehospital Care

- Safely remove victims from source
- Restore or maintain airway patency
- Maximize oxygenation
  - 100% NRBM or BVM
- Cardiopulmonary support to maintain VS
  - IVF and/or dopamine, norepinephrine
- Decontamination
Cyanide Antidote Kit (CAK)

- 3-steps
  - Amyl nitrite
  - Sodium nitrite
  - Sodium thiosulfate
- Converts cyanide to thiocyanate
- One kit treats two people
2011 FDA Approval of Sodium Nitrite and Sodium Thiosulfate
Cyanide: Sodium Nitrite and Sodium Thiosulfate Rx

Sodium nitrite (3% solution)
- Adults → 300 mg (10 ml) IV over 15-20 min
- Peds → Hgb based

• Sodium thiosulfate (50 ml 25% solution)
  - Adults → 12.5 g (50 ml) IV
  - Peds → 1.65 ml/kg IV

• May repeat if large cyanide exposure
Cyanide: CAK

• Effective
• Safe
• Side Effects
  – Nitrite
    • Hypotension
    • MetHb
  – Sodium Thiosulfate
    • vomiting
Cyanide: Cyanokit™

Cyanokit
• Hydroxocobalamin
• Converts cyanide to cyanocobalamin (vitamin B12)

Dosing
• 5g IV
• 10g IV in cardiac arrest
Cyanide: Treatment

Treatment: Cyanokit

- Effective
- Safe
- Adverse Effects
  - Red urine
  - Red skin
  - Interferes with cooximetry measurements because of its intense red color
Cyanide as a Weapon

An Ideal Terrorist Weapon

• Plentiful
• Readily available
• Special knowledge not required
• Capable of causing mass casualties
• Capable of causing social disruption
• Requires large quantities of resources to combat its effects
Any terrorist attack that involves explosions or fire will likely result in HCN release.
Sudden Illness at the Sandwich Shop

- 5 middle age people visit a sandwich shop for a bite to eat over the course of an afternoon
- All 5 take ill and are seen in the ED
- Illness is characterized by syncope soon after eating.
- When paramedics arrive – all are hypotensive with BP 70-80/p
- With fluid resuscitation and supportive care all get better within hours of becoming ill
Further Information

• An Epi Investigation determines that all had ingested ice tea while at the sandwich shop
• There was no other common food or beverage ingestion
• Further questioning reveals that these restaurant patrons noticed a bitter taste to the tea and did not consume more than 1-2 swallows
• They all became ill within 1-2 minutes of drinking the tea
Chemical Agents of Opportunity for Terrorism: TICs & TIMs

Module Five – Cyanide and Fumigants
### Selected Clinical Syndromes (Toxidromes) and Potential Chemical Etiologies

<table>
<thead>
<tr>
<th>Category</th>
<th>Clinical Syndrome</th>
<th>Potential Chemical Etiology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Severe gastroenteritis</td>
<td>Abdominal pain, emesis profuse diarrhea, shock</td>
<td>Arsenic, Ricin, Colchicine</td>
</tr>
<tr>
<td>Cholinergic crisis</td>
<td>SLUDGE symptoms, Fasciculations, weakness</td>
<td>OP insecticides, nicotine</td>
</tr>
<tr>
<td>Cellular hypoxia</td>
<td>N/V, headache, AMS, shock, seizures, dec pH</td>
<td>CN, SMFA, CO, Azide</td>
</tr>
<tr>
<td>Peripheral neuropathy</td>
<td>Muscle weakness, sensory loss</td>
<td>Hg, As, Thallium, Lead,</td>
</tr>
<tr>
<td>Mouth pain / ulcerations</td>
<td>Lip / mouth / pharyngeal ulcerations; burning pain</td>
<td>Paraquat / diquat; caustics, Hg</td>
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</table>

MMWR 10/3/03
Initial Lab Evaluation

ANALYSIS REQUESTED:
Alcohol and Acetone Screen, Drug Screen, Cannabinoid Screen, Heavy Metals Screen, Cyanide Screen and Gammahydroxybutyric Acid Analysis

FL# 10H0100A (Pot #1) - RESULTS:
Alcohol and Acetone Screen (liquid): negative
Drug Screen (liquid): caffeine detected
Cannabinoid Screen (liquid): negative
Arsenic Screen (liquid): negative
Cyanide Screen (liquid): negative
Gammahydroxybutyric Acid Screen (liquid): negative
Results of Examinations:

Azide and hydrazoic acid were identified in the specimen Q1-Q3 tea samples. Azide and hydrazoic acid were not identified in the specimen K1 tea sample that was submitted as a negative control. Additionally, caffeine was identified in specimens Q1-Q3 and K1. No other chemicals were identified in specimens Q1-Q3 or K1.

The following techniques were utilized in the analysis of specimens Q1-Q3 and K1: visual inspection, pH testing, infrared spectroscopy, gas chromatography/mass spectrometry, liquid chromatography/mass spectrometry, time-of-flight mass spectrometry, and scanning electron microscopy with energy dispersive x-ray spectrometry.

Specimens Q1-Q3 and K1 are suitable for comparison should a suspect source become available.
Poisoning at Harvard
6 lab workers sickened by coffee

By Adam Smith and O’Ryan Johnson
Sunday, October 25, 2009 - Updated 11 months ago

Harvard University Medical School is locking down its New Research Building, installing new surveillance cameras and imposing tighter security after researchers in the pathology department of the Boston building drank poisoned coffee and were hospitalized.

The six victims - a group of scientists and students at Harvard Medical School - used a communal, single-serve coffee machine on the eighth floor near their pathology lab Aug. 26, according to an internal memo. Seconds later all six reported symptoms such as dizziness and low blood pressure. One victim’s ears were ringing and another passed out.
Fumigant Gases

- Sulfuryl fluoride (Vikane 7)
- Methyl bromide
- Phosphine
Fumigants

Applications

• Insect or rodent control in grain storage
• Insect or rodent control in structures
• Eradication of soil pests in farming
Fumigant Gases

- Like HCN, could be introduced into a closed space through ventilation system or other conduits
Sulfuryl Fluoride

• Used in 85% of building fumigations
• Colorless
• Odorless
• Irritating
• 3.5 times heavier than air
• Exposure to fatal concentrations possible without warning odor
• No re-entry until air levels < 5 ppm
Sulfuryl Fluoride

• Clinical Manifestations
  – High concentrations
    • Seizures
    • Syncope / dysrhythmias
    • Respiratory arrest
  – Lower concentrations:
    • Vomiting
    • Diarrhea
    • Salivation
    • Lung injury
Sulfuryl Fluoride: Treatment

Management

- Removal from source of exposure
- Ventilation
- Oxygen
- Monitor for hypocalcemia
  - ECG (prolonged QTc)
  - Serum or ionized Ca2+
- Administer calcium as needed
Sulfuryl Fluoride

Elderly couple reenter fumigated home before Vikane had fallen to a safe levels:

• Husband:
  – Shortness of breath, seizures
  – Death 48 hrs after reentry

• Wife:
  – Weakness, nausea, vomiting
  – Death 72 hrs after reentry (lung damage)
Methyl Bromide

- Odorless, colorless gas
- Chloropicrin (lachrymator) added as warning agent
- MeBr heavier than air
- Broad spectrum of activity
  - Alkylating agent
- Penetrates rubber and neoprene
- Being phased out due to environmental concerns
Methyl Bromide: Clinical Signs

- Acute high-level exposure → rapid onset of sxs
  - CNS depression, delirium, seizures, pulmonary edema
  - Skin injury, burns, blistering reported with high-level dermal exposure
- Lower level exposure
  - Delayed onset toxicity well-documented
  - Mucosal irritation
  - Headache, dizziness, Nausea, vomiting
  - Progression (hours) to visual symptoms, ataxia, tremor, delirium, seizures
- Sxs reversible with mild intoxication
  - Permanent effects have been reported in severe cases
Methyl Bromide: Case Study

- Adult female occupying a guest house rapidly developed headache, flu-like symptoms
- Within 24 hours, found in status epilepticus
- Initial labs remarkable for severe liver, kidney injury
- Expired 19 days post-exposure
- A building next door had undergone fumigation with methyl bromide. Seven 1-2 inch underground conduits connected the buildings.
- Methyl bromide had traveled from the adjacent building into the cottage.
Phosphine (PH₃)

- Forms
  - Gas (vapor density 1.17)
  - Aluminum and Zinc phosphide pellets
- Smells like garlic and rotten fish
- Many uses in agriculture & structural pest control
- Used in semiconductor industry
- Concentration effects
  - 400-600 ppm - severe toxicity in 30 min
  - 1000 ppm - immediate death
Generating Phosphine Gas

Solid Phosphide Pellets / Tablets + Water or Acid → Phosphine Gas
Phosphine: Treatment

Clinical

• Early/mild cases
  – Non-specific
  – GI effect, cough, chest tightness, eye irritation

• Late/serious exposure
  – Pulmonary edema, coma, seizures, death
  – Knock-down gas
    • Rapid progression and deterioration in fatal cases
Phosphine: Case Study

- 5-year-old girl suddenly develops difficulty breathing at home
- Has a cardiac arrest - Unable to resuscitate
- Family members were ill as well
  - Developed acutely after a period of heavy rainfall
  - Odor noted in basement
- Investigation: a cupful of aluminum phosphide pellets had been placed in a hole adjacent to the basement foundation
- Child’s father was a professional exterminator
Chemical Agents of Opportunity for Terrorism: TICs & TIMs

Phosphine

Inhalation of phosphine from illicit Methamphetamine production labs:

- Willers-Russo (1998)
  - 3 victims found dead in motel room
  - First responders noted significant chemical odor
  - Phosphine gas levels far greater than 0.3 ppm (TLV)

- Burgess (2001)
  - Acute symptomatic inhalation exposure in first-responder (law enforcement)
    - 2.7 ppm for 20-30 minutes
  - Persistent, objective signs of obstructive pulmonary impairment weeks after initial exposure
Treating Fumigant Poisoning

- No antidotes available
- Remove victim from source
- Thorough decontamination
- Oxygenation
- Symptomatic and supportive care as indicated
## Fumigants: Summary

<table>
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<tr>
<th>Gas</th>
<th>Properties</th>
<th>Clinical manifestations</th>
<th>Management</th>
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</thead>
<tbody>
<tr>
<td>Vikane</td>
<td>Poorly detectable (occasionally mixed with chloropicrin)</td>
<td>Neurologic, Gastrointestinal</td>
<td>Remove from exposure, Flush skin/eyes, 100% O2, Supportive care</td>
</tr>
<tr>
<td>Methyl Bromide</td>
<td>Poorly detectable (occasionally mixed with chloropicrin)</td>
<td>Potentially delayed onset, Mucous membranes irritation, Neurologic, Seizures, Lung</td>
<td>Same</td>
</tr>
<tr>
<td>Phosphine</td>
<td>Fishy / garlic odor</td>
<td>Neurologic, Cardiac, Lung</td>
<td>Same</td>
</tr>
</tbody>
</table>

Gas Properties

- Vikane: Poorly detectable (occasionally mixed with chloropicrin)
- Methyl Bromide: Poorly detectable (occasionally mixed with chloropicrin)
- Phosphine: Fishy / garlic odor
Audience Response

Which of the following is added to fumigants to make them more easily detectable?

a. Mercaptans  
b. Hydrogen sulfide  
c. Chloropicrin  
d. Organophosphates  
e. Yellow dye number 20
Summary

- Forced air ventilation systems could be used by terrorists to disperse toxic gases or aerosols.
- Cyanide gas and fumigants are easily obtained and well-suited for airborne dispersal.
- Cyanide gas exposure should be treated with oxygenation, supportive care, and antidotal therapy.
- No antidote is available for the fumigants discussed in this module. Treatment should focus on decontamination and supportive therapy.
Questions?

• Please click on the “raise your hand” icon and the host will unmute your phone line; or type your question into the “chat” box for the host to pass on to the presenter

• If you have registered for the course, you will receive an evaluation survey (SurveyMonkey) from info@acmt.net
REMINDERS

Agents of Opportunity Course LIVE – Nassau County, NY (Bethpage) Saturday, September 12, 2015

Next Webinar: October 2015 “Psychological Consequences of Mass Chemical Exposure”