The Cyanic Threat to Potable Water

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Overview

- Related events
- Uses of cyanide in society
- Exposure to cyanide
- Cyanide in water
  - Regulated levels
  - Chemistry
  - Detection
  - Removal techniques
- The USACHPPM field exercise

USACHPPM Media Survey

- Unofficial survey from Nov 01 - Mar 03
  - Searched newspapers, TV broadcasts, and internet news sites
  - Identified 39 documented threats and discussions about attacking water supplies
    - 51% involved cyanic compounds (20)
    - 13% involved anthrax (5)
    - Other contaminants included rat poison, botulinum toxin, pesticides, mercury, solvents, vandalism, trespassing, and shootings

Related Reports (1/2)

Date	Title	Location
Feb 02	***4 Terror Suspects Arrested in Italy***	***Italy***
Mar 02	Australian Cyanide Threat Sparks Terrorist Fears	Australia
May 02	Could Terrorists Poison Aquifer with Cyanide, Probably not?	Texas, USA
May 02	***Truck Stolen Containing Cyanide***	***Mexico***
Jun 02	On High Alert, City Water Boss Hops into Action	New York, USA
Jun 02	***'Dr. Chaos' Indicted in Subway Cyanide Case***	***Illinois, USA***

Related Reports (2/2)

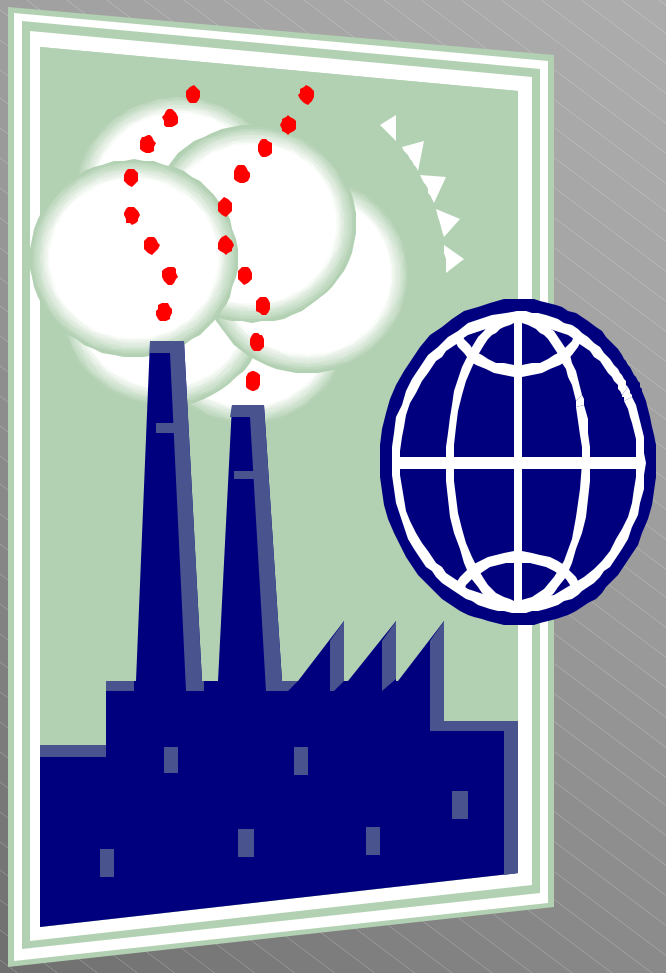
Date	Title	Location
Dec 02	***USEPA to Assess Cyanide Detection Technologies***	***Washington, D.C., USA***
Jan 03	***18 Year Old Maryland Senior Poisons Friend***	***Maryland, USA***
Feb 03	Nation put on High Alert	Washington, D.C., USA
Feb 03	***Dr. Sanjay Gupta: Cyanide Poison Hard to Detect***	***Georgia, USA***
Feb 03	Man who Threatened Melbourne Water Supply Bailed	Australia
Mar 03	New Cyanide Terror Letter Threat Sent to Newspaper	New Zealand

Related Events Prior 2001

- Ancient Romans used cyanide to poison their enemies
- 1978 Tylenol cyanide poisonings
- 1983 Anonymous threats of cyanide contamination of water systems in Louisiana
- 1986 FBI uncovered supremacist group with 30 gallons of KCN to poison urban water

Cyanides in Society

- Manmade and naturally occurring
- Industry use
  - Gold and silver extraction, electroplating, metal treatment, processing of plastics, fumigants
- Illegal fishing
- Present in cigarettes
  - Non-smoker blood 0.06 µg/L
  - Smoker blood 0.17 µg/L
- Present in fruit pits
  - Apples, apricots, and peaches
- Chemical warfare
  - World War I, France
  - World War II, Germany
  - Iraq 1980s
- Synthesized by some bacteria



Cyanic Compounds

- Simple cyanides
  - HCN, KCN, NaCN, and CNCl
- Complex cyanides (metal complexes)
  - $K_3Fe(CN)_6$
    Potassium ferriccyanide
  - CuCN
    Copper (+1) cyanide
  - AgCN
    Silver (+1) cyanide

Simple Cyanides

- Salts dissolve in water
- Form is pH dependant: $CN^- + H^+ \leftrightarrow HCN$
- CNCl formed: $CN^- + HOCl \rightarrow CNCl + OH^-$
- HCN and CNCl both highly volatile

HCN
Liquid < 25 ˚C ≤ Volatile

CNCl
Liquid < 12 ˚C ≤ Volatile

Complex Cyanides

- Less toxic than simple cyanides
- Limited solubility
- Usually particulate in form
- pH dependence greatly decreased
- Very low volatility
- Removed by
  - Sedimentation and filtration

We will focus on simple cyanides

Exposure to Cyanide

- Poisoning is an acute effect
  - Dissolves into the blood
  - Binds with enzyme
  - Does not allow utilization of oxygen
  - Symptoms can occur within minutes and can be fatal
- Exposure routes using water
  - Inhalation
  - Dermal absorption
  - Ingestion ← Most significant

Headaches

Weakness

Apprehension

Rashes

Gasping

Rapid breathing

Poisoning

Seizures

Tremors

Convulsions

Irregular heartbeat

Symptoms

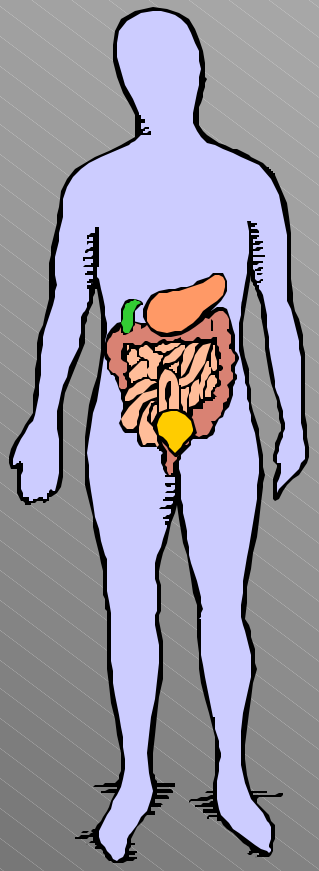
Vomiting

Loss of consciousness

Hyperventilation

Cyanide Detoxification

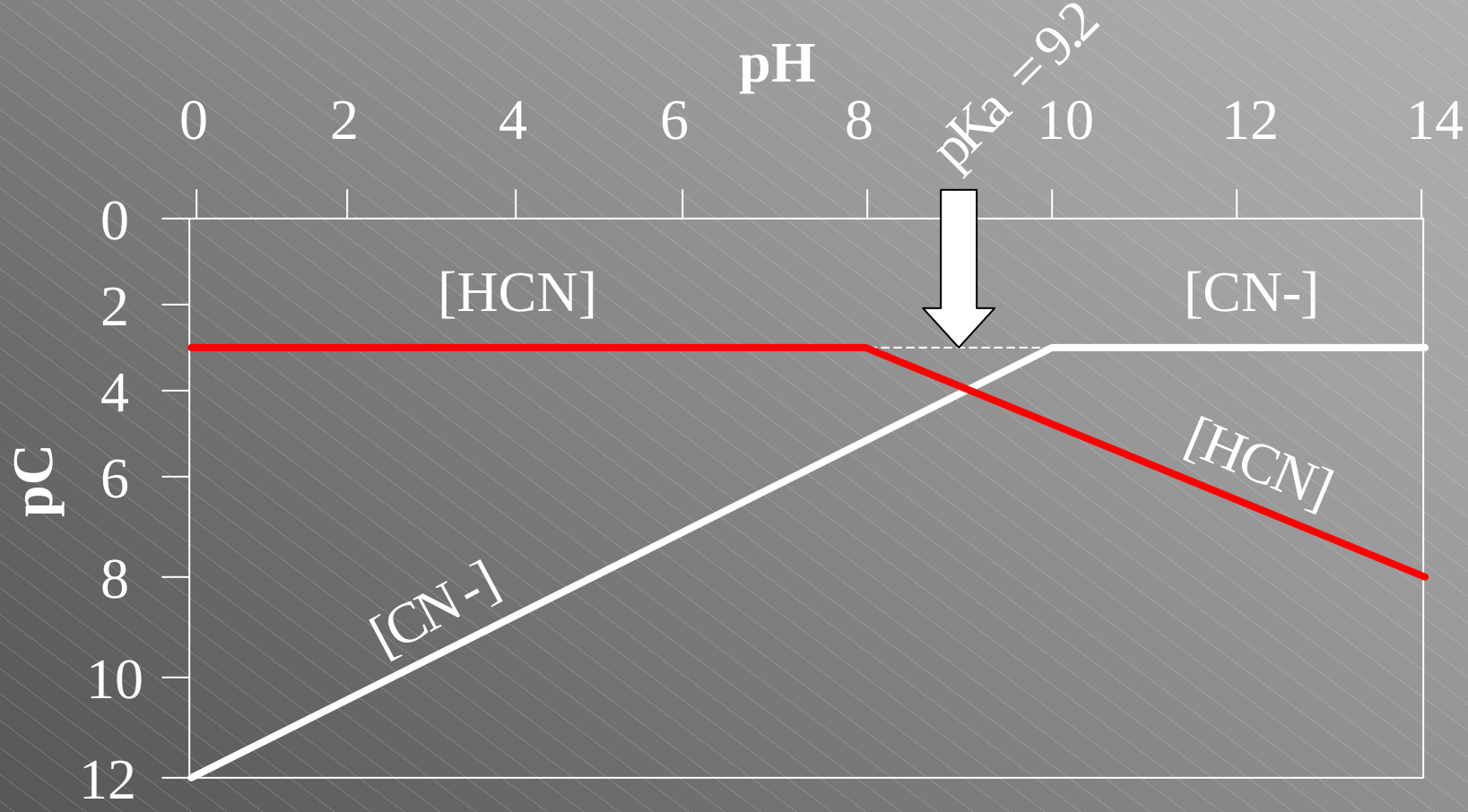
- Human body has a natural defense
  - Breaks down cyanide
- Cyanide is excreted in urine as SCN^-
- Antidotes are available
- 4-8 hours blood levels return to normal



Cyanide in Water

- Water sources
  - 1970 water supply survey
    - Avg. 0.09 µg/L
    - Max. 8 µg/L
  - Contam. GW 411 µg/L
- Regulations
  - EPA
    - MCL 0.2 mg CN^-/L
    - Child 1 and 10-day HA 0.2 mg CN^-/L
  - U.S. Army field standards
    - 6.0 mg/L for 5L/day
    - 2.0 mg/L for 15L/day

Free Cyanide Water Chemistry



…… Most cyanide as CN^- above 9.2 (Soluble)

…… Most cyanide as HCN below 9.2 (Volatile)

Detection by Water Utilities

- Source water
  - Fish/aquatic life kill
- At the plant
  - FAC decrease
  - Operator observed
    - Illness symptoms
    - Metallic taste
    - Odors (Almond, peach kernels, pepperish odors)
- Distribution system
  - FAC level decrease
  - Consumer complaints
    - Illness, taste, odors

USACHPPM Water Supply Management Program

Aqueous Detection Equipment

Ion chromatography

Color Strips

On-line Monitor

Colorimeters

Detecting Cyanide using Equipment

- The USACHPPM evaluation
- HACH company; Loveland, CO
  - Color disk kit (0-0.3 mg/L)
  - Portable colorimeters (0-0.24 mg/L)
- EM Science; Gibbstown, NJ
  - 10044 EM Quant Cyanide Test
    - Semiquantitative 0, 1, 3, 10, 30 mg/L
- CHEMetrics, Inc.; Calverton, VA
  - Test strips (0.005-1.0 mg/L)

USACHPPM Report, Evaluation of Interim Field Water Test Kits for Chemical and Microbiological Analysis, Project No. 31-EC-4974-01

Detecting Cyanide using Equipment

- Tested and verified by EPA ETV
  - AQUAfast© IV (Thermo Orion)
  - 1919 SMART 2 (LaMotte Co.)
  - Mini-Analyst Model 942-032 (Orbeco-Hellige)
  - VVR V-1000 Multi-Analyte Photometer with V-3803 (CHEMetrics, Inc.)
  - Cyanide electrode CN 501 (WTW Measurement)
  - Model 9606 Cyanide Electrode (Thermo Orion)

http://www.epa.gov/etv

Free Cyanide Removal Techniques

- Effective
  - Alkaline chlorination
  - Ozonation
  - Reverse osmosis
  - Ion exchange
  - Aeration/Boiling

pH and water temperature must be controlled

- Not effective
  - Coagulation/ flocculation
  - Sedimentation
  - Rapid and slow sand filtration
  - Ultrafiltration, microfiltration, nanofiltration
  - Activated carbon

Field Exercise Overview

- Date
  - 21-22 May 03
- Location
  - WTP outside Maryland
- Personnel
  - USACHPPM WSMP engineer and microbiologist
  - On-site actors for the FBI, WTP, media, and local community officials
- Role of the USACHPPM
  - Represent Army on response and recovery

Cyanide Field Exercise Previsit Briefing

- Approx. 2200, 21 May 03
  - Terrorist dropped and ruptured two 100 lb. cylinders into a water system clearwell
  - System serves a US Army post and surrounding community (~20,000 people)
- 0600, 22 May 03
  - Access discovered, plant and pumps shutdown, population warned do not drink but can bathe, water tests initiated, valves closed
- 0630
  - HAZMAT team arrives onsite, conducts sampling, then leaves for a higher priority mission
- 0700-0900
  - The USACHPPM is contacted for technical support, arrives onsite

Questions We Asked Upon Arrival

What is the contaminant(s)?

What are the types of consumer complaints received?

What are the symptoms received in emergency rooms?

Where are the complainants located?

Where is the contaminated water?

Where is the emergency response plan?

What is the water pH?

What are the disinfectant residual concentrations?

What is the residual disinfectant?

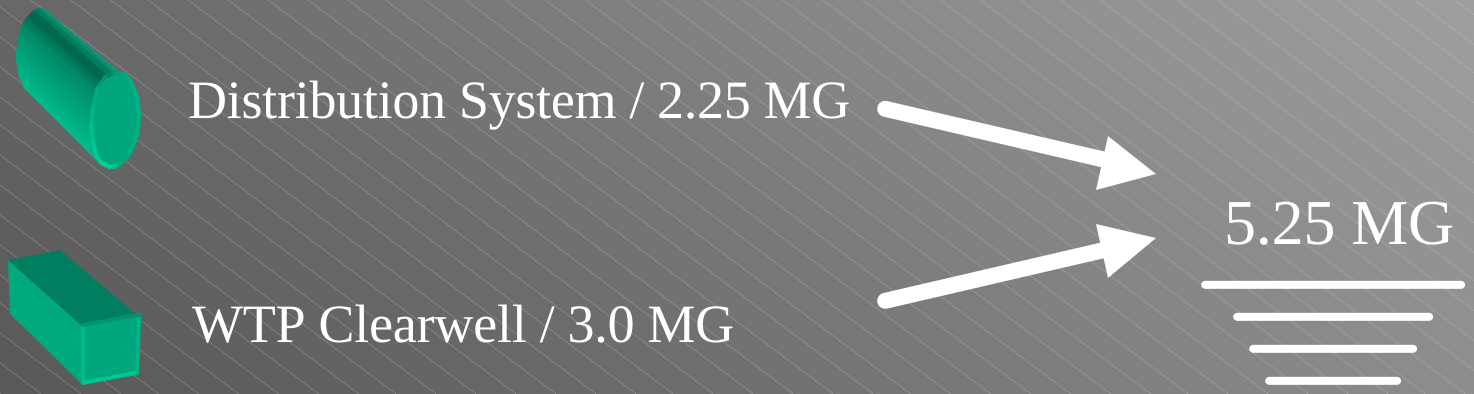
Where are sensitive populations located? (I.e., daycares, schools, nursing homes)

Where is the map of the distribution system?

How long have pumps been running with contaminated water?

Field Exercise Findings

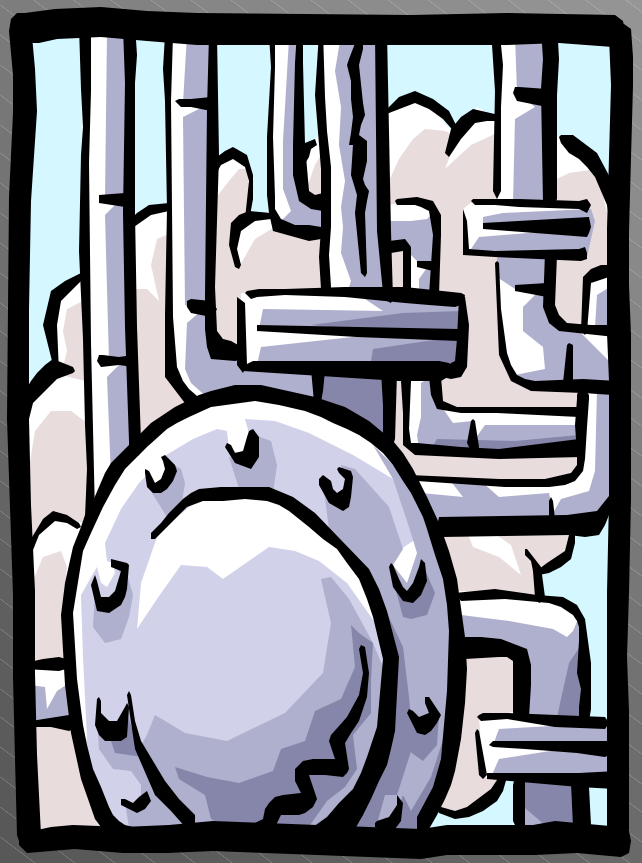
- 0930 we received water sampling results
  - 1.0 mg /L cyanide in distribution system, pH 10
  - 1.25 mg /L cyanide in clearwell, pH 10
  - All cyanide present as CN^-
- Concluded that
  - Chloramines were not effective at cyanide destruction
- Contaminated water location/volume



Field Exercise
Water Removal & Disposal

- Removal and disposal of contaminated water
  - > 75% discharge to sewer (per approval of local, state, fed regulators and WWTP)
  - Vacuum truck used to dispose of remaining volume offsite
    - $$$ and time

Field Exercise Infrastructure Decontam.



- Infrastructure decontamination
  - System wide flushing
  - Repetitive water testing
  - Use free chlorine to fully destroy cyanide in pipes for limited time
  - Require consumers to flush taps before use

Cyanide Field Exercise Learning Points

- Misinformation
  - Do not allow water use
- Response tools missing
  - No emergency response plan
  - No distribution system map
- What about FAC?
  - Some destruction, but not enough

- Response difficulties
  - Removal and disposal of contaminated water
  - Cleanup of household contaminated piping
  - Public/risk communication

Overall Conclusions

- Cyanic compounds are widely used
- Simple *vs.* complex cyanides
  - Simple more concerning
- Available detection equipment
- Existing effective treatment processes
- Field exercise is a good indicator of preparedness

Recommendations to Water Utilities

- Knowledge
  - Stay current on contaminant knowledge
  - Assess the effectiveness of existing treatment barriers
- Update
  - Emergency response plans
  - Distribution system map
- Readiness
  - Determine and monitor system FAC and pH
  - Be alert for complaints (illness, metallic tastes, bitter almond and pepperish odors)
  - Integrate complaints into the early-warning system

Acknowledgements

- Co-authors
  - US Army CHPPM
    - Todd Richards and Richard Valdivia
  - US Army SBCCOM
    - Janet Jensen
- Oak Ridge Institute for Science and Education (ORISE) for financial support
- U.S. Army CHPPM for resources and facilities
- Margaret Cooney for reviewing the manuscript

QUESTIONS?

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(Also see CD proceedings paper)