

# Environmental Chemicals IV

Principles of Environmental Toxicology Instructor: Gregory Möller, Ph.D. University of Idaho

### Thirdpies of Environmental Tox

# Learning Objectives

- Explore the environmental challenges of the Rocky Mountain Arsenal in Colorado as it transitions to a National Wildlife Refuge.
- Study the environmental effects, chemical fate and transport, receptors and remedial controls of the Chem-Dyne site in Hamilton, OH.
- Explore the environmental clean-up and transition of Midway Island from a Naval Air Station to a sanctuary for over 2,000,000 nesting birds.

### Rocky Mountain Arsenal, CO

- Rocky Mountain Arsenal (RMA) is located approximately 10 miles NE of downtown Denver, CO.
- In 1942, at the height of World War II, the U.S. Army purchased the 17,000 acres of land on which to manufacture chemical weapons, such as mustard gas, white phosphorus and napalm.





### RMA

- Between December 1942 and the end of the war in 1945, the Arsenal made 155,000 tons of chlorine, mustard gas and arsenic trioxide, as well as 87,000 tons of chemical products.
- Private industry was encouraged to lease facilities at RMA after the war.
  - Julius Hyman and Company (JHC) began producing pesticides in 1946.
  - In 1952, Shell Chemical Company acquired JHC and continued to produce agricultural pesticides on-site until 1982.

# RMA

• Shell Chemical made pesticides, insecticides and herbicides at the Arsenal until 1982. In the meantime, the Army produced nerve agent at the site from 1953 to 1957.



One ton canisters of CB gas (PMRMA).

PMRMA

EPA

# RMA – Basin F

- The Army and private chemical manufacturers disposed of liquid wastes in numerous unlined waste-disposal basins and trenches, which allowed the waste to reach the ground water.
- By 1955, nearby residents noticed crop damage and voiced concern about contaminated ground water.
- As a result, a lined basin,
   Basin F, was built in 1956 to contain future wastes.
  - The liner in this basin failed immediately, and wastes from the basin continued to reach the ground water.

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# Site Contamination

 Possibly, the first of its kind in the country, the 93-acre, asphalt-lined pond was capable of holding 243 million gallons of contaminated liquid.



# Pollution Control and Clean-up

- The Army and Shell began a systematic investigation into the contamination problems resulting in the Army's Installation Restoration Program.
- Beginning in 1974, Interim Response Actions (IRA) were designed to protect off-site human health and environment from RMA pollution.
  - Included in the 14 IRAs was the construction and operation of four boundary and on-site groundwater treatment systems
    - Over 1 billion gallons of groundwater treated each year.

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# **Chemical Risks**

- · Ground water contaminants.
  - Diisopropyl-methylphosphonate (DIMP, byproduct of nerve gas production), pesticides, solvents, arsenic, fluoride and chloride.
- Most of the health risks posed by the site can be tied to four chemicals.
  - Aldrin, dieldrin,
     dibromochloro-propane
     (DBCP), and arsenic.

# RMA -COPCs

- SVOCs (semivolatile organic compounds)

   chloroacetic acid, dicyclopentadiene, and
  - hexachlorocyclopentadiene
- VOCs (volatile organic compounds)
  - benzene, carbon tetrachloride, chloroform, chlorobenzene, dibromochloropropane (DBCP), 1,2-dichloroethane, 1,1dichloroethene, methylene chloride, 1,1,2,2tetrachloroethane, tetrachloroethene, toluene, and trichloroethene

### Metals

- As, Cd, Cr, Pb, Hg
- Pesticides
  - Aldrin, chlordane, DDE, DDT,
- dieldrin. endrin. and isodrin

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# Pollution Control and Clean-up

- Currently there are no chemicals or chemical weapons produced or stored at RMA.
- High level contamination of environmental media and arsenal "remnants" exist throughout the site.



Nerve gas plant (PMRMA).



# RMA - Remediation



Building 412, the Arsenal's former World War II mustard agent manufacturing and filling facility, was demolished in 1995 during a South Plants pilot demolition project (PMRMA).





# Prairie Ecology USFWS involvement at RMA began in 1986 when a winter communal roost of bald eagles, then an endangered species, was discovered on-site. It was soon discovered that close to 300 wildlife species inhabit the RMA including deer, coyotes and owls.

Colorado prairie before RMA

# National Wildlife Refuge

• The 1992 Rocky Mountain Arsenal National Wildlife Refuge Act designates most of the Arsenal to become a National Wildlife Refuge once cleanup is completed.



# Case Presentation

• Rocky Mountain Arsenal, Eye on Progress; video.

# Chem-Dyne, Hamilton, OH

- The ten-acre Chem-Dyne site operated as an industrial chemical waste transfer, disposal, and storage facility located in the city of Hamilton, OH.
  - Population of approximately 87,000.
  - A residential area is located less than 1,000 feet from the site.
  - Other adjacent land uses include a recreational park and industrial facilities.

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# Chem-Dyne, Hamilton, OH

### Chemical waste processing plant.

- 250 chemical waste generators disposed of drummed or <sup>EPA</sup> bulk waste.
- Operational lifetime, 1974-1980.
- 50,000 drums on site at height of operations.
- Poor waste handling practices.
- Purposeful on-site spillage of various chemicals.
- Direct discharge of liquid wastes into storm drains.
- · Mixing incompatible wastes.

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# Chem-Dyne

- Chemical wastes may have been trucked to the site beginning in 1974.
- Wastes that were unsuitable for recycling were stored in drums and tanks on the site or shipped to other disposal sites.
- More than 30,000 drums of waste and 300,000 gallons of bulk waste materials were left on site when operations ended in 1980.

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# Chem-Dyne

- A storm sewer drained the site into the Ford Canal, which flows into the Great Miami River.
  - The Ford Canal is used only for drainage and hydroelectric power generation.
  - The Great Miami River is used for recreation.
  - Water supplies in the area rely on groundwater as their source.











# Ford Canal Sediments, 1983

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PAHs	ND	1.1-1.8
Toluene	ND	1.5
Chlordane	ND	3.8
4-methylphenol	ND	3.3
Chromium	69-83.5	8-122
Lead	71.8-111.5	5.1-991
TSDR		



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### Chem-Dyne Contamination

- Groundwater is contaminated with volatile organic compounds (VOCs) and heavy metals.
   No drinking water supplies have been affected.
- Soil was contaminated with VOCs, pesticides, other organic compounds, and heavy metals.
   Hg, As, Ni, Be.
  - пу, Аз, Ni, De.
- The on-site buildings were contaminated with PCBs.

# Groundwater VOCs, 1983



Red = 1,000 μg VOC/L Orange = 500 μg VOC/L Yellow = 100 μg VOC/L

# Chem-Dyne Clean-up

• In 1980, USEPA stabilized, removed, and disposed of 17 potentially explosive drums to a treatment facility.

 Beginning in 1982, USEPA removed another 9,000 drums and solidified and removed 200,000 gallons of liquid and solid wastes in 33 storage tanks.

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# Chem-Dyne

- In 1985, USEPA issued a Record of Decision (ROD) which required the installation of a system to extract the groundwater and treat it by air stripping.
  - Contaminants are further treated with activated carbon before being released into the air.
- Buildings were demolished, selected areas of soil were removed, and a synthetic cap with a clay layer was placed over the site.

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# Initial Site Survey

- · GW flowed to the west towards the Miami R.
  - A shallow trough flowed parallel to the river as a result of weak and temporary stream influences.
- Study concluded that contaminants already in the aquifer would be discharged into the GMR and would not need to be removed.
- Study concluded that removal of the top 3' of soil would eliminate source of contaminants.

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## Initial Site Survey-- NOT!

- Faulty soil sampling procedures.
   Not preserved in air-tight containers so VOCs leaked out.
- The oily upper surface soils showed high VOC because of co-solvation of VOCs by viscous oils and other chemicals.
  - These other chemicals did not migrate far enough to exert this effect at depths greater than a few feet.

# Additional Site Investigations

- Incorporated more detailed characterizations of fluvial sediments & the natural flow system.
  - Vertical profiles obtained from split spoon samples of subsurface solids.
- Large industrial wells caused the sub-surface water gradient to drop dramatically compared to the normal horizon.
- Plume drops under the zone of influence of the GMR.

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### Additional Site Investigations, 2

- Major pump test (14 hr) to determine hydrologic interplay of the GMR.
- Costly; 100,000 gal of contaminated water; personnel air-tanks.
- All monitoring wells were monitored for flow and level; helped explain:
  - Local hydrologic complications.
  - Unusual plume configuration
  - Design needed for pump and treat system.

# Contaminant Biotransformations

 Transformation of subsurface tetrachloroethene to less halogenated daughter products.

 Trichloroethene, dichloroethene, vinylchloride/monochloroethene



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# Chem-Dyne Treatment

- The groundwater pump and treatment system has been in operation since 1988, and may continue to operate through 2008 or longer, to meet cleanup standards.
- Approximately 3,500,000,000 gallons of groundwater have been treated and nearly 31,000 pounds of VOCs removed from the aquifer.

### Role of Modeling and Calculations

- Many contaminants followed relative rates of transport predicted by sorption principles.
   Used in estimating the capacity of the treatment system and the length of time needed.
- Prediction- pump and treat would be effective at the interior of the plume but not at the periphery – confirmed.
   Air stripping used extensively.
- Site demonstrated the importance of knowing natural process parameters!











Midway Island National Wildlife Refuge.





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# Range of Contamination

- Jet fuel leaked from underground storage tanks into the atoll's groundwater.
- · Old buildings: asbestos and lead paint
- Utility transformers: PCBs.
- DDT and other chemicals have leached into the soil.
- · Mercury from old batteries.

# Remediation

- Jet fuel, diesel and fuel oil needed to be removed from the atoll's groundwater, which lies 5 to 8 feet below the surface.
  - Island residents use catchment systems for drinking.
- Brackish groundwater is being cleaned to protect wildlife and the ocean.
- \$43M clean-up.

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# **Remediation Approach**

- Steam injection vapor extraction system

   The world's largest such system was used on Midway.
- PHC/water is extracted from 300 wells drilled around the island and run through tanks
  - Vapor is burned off and the fuel is collected.
- Purified water is returned to the ground through a series of 200 injection wells.

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## Pure Product Recovery

- More than 33,000 gallons of PHC were recovered.
  - Used to power the two 16-cylinder generators that run the system around the clock.
  - No leftover fuel had to be shipped off.



# LUST and Soil

- Crews removed more than 100
   underground jet fuel tanks.
  - Included two with a capacity of 2 million gal each.
- 7,000 yards of soil contaminated with petroleum were excavated.
- Contaminated soil (PHC, DDT, asbestos, Pb) was stabilized (cement) or used as road fill as allowed.

# **Removal Actions**

- Marine salvage removed more than 68 vehicles and 300 batteries from the lagoon.
- Navy divers detonated 23 gas cylinders in the harbor.
- Water, sediment and biota sampled.
  - Initial concerns about extensive marine pollution have not been borne out.
- Navy retiring facilities. - Historical, ecotourism facilities remain.

it was before man got here, but this is an example of humans cleaning up and giving back to the wildlife. And with the world's population expanding, there are not many places like that." (K. Niethammer, USFWS)

