Environmental Chemicals II

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

Learning Objectives

- Examine the cause and effects of the release of an industrial cyanide/heavy metals impoundment into a major European river system.
- Examine the heavy metals release from a tailings dam failure in Southwestern Spain.
- Describe the science and toxicological impacts of ionizing radiation resulting from radionuclides.

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Learning Objectives

- Understand the science and issues surrounding mixed waste management in the US.
- Examine the technological difficulties associated with subsurface radionuclide plumes of the Hanford Reservation migrating towards the Columbia River.

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Baia Mare, Romania

- Cyanide leak from a gold smelter pollutes a major European river system, January 2000.
- A cyanide-containing slurry overflowed over a 25 m length of a tailings dam.
  - 100,000 cubic meters of waste into the Tisza and Danube river system, Europe's largest waterway.
- The accident wiped out fish stocks and threatened water supplies in several countries downstream from the spill.

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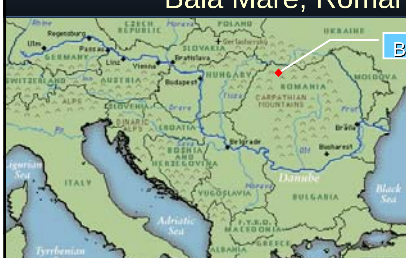
Baia Mare, Romania



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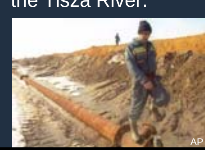
Cyanide Waste Water

- Heavy snows caused an overflow of a tailings dam wall.
- Waste water containing cyanide flowed into the adjacent Lapus River, then entered the Somes River, and crossed the border into Hungary, before reaching the Tisza River.



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Waste Material

- 100 thousand cubic meters liquid waste entered the water with 7800 mg/L cyanide concentration
  - Hungarian authorities - conservative estimate.
  - 100 tons cyanide.

Acute, Chronic, Sub-lethal Toxicity

Ingles

Fish

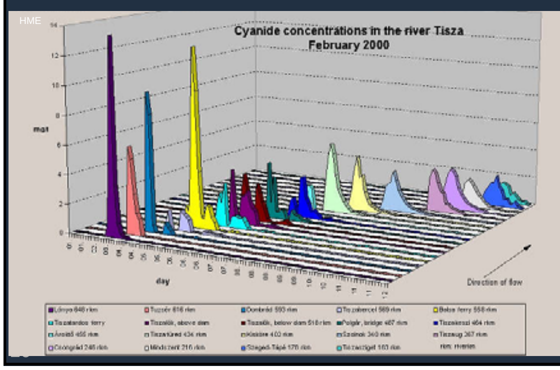
LETHAL EFFECTS		SUBLETHAL EFFECTS		
ACUTE (Dynamic LC_{50} - 96 h) mg/L CN	**CHRONIC** (Juniors/ Adults) mg/L CN	Activity or Organ Affected	Nature of Effect at mg/L	CN^-
0.05 - 0.2	0.0019 - 0.07	Spawning Egg Production Egg Viability Spermatogenesis Abnormal embryonic development Hatching Swimming	-completely inhibited -reduced by 42% -eggs infertile -permanent reduction -severe deformities -up to 40% failure -reduced 90% at 6°C	0.005 0.01 0.065 0.02 0.07 0.01-0.1 0.015

Scope of Contamination

Location	Date	Concentration
Spring Lonya (Romania)		CN 800 times higher than allowed concentration
Szamos at Csenger (Hungary)	2/1/00	CN 32.6 mg/l, Zn 540 ug/l, Cu 12000 ug/l
Tisza at Lónya (Hungary)	2/3/00	CN 13.5 mg/l, Zn 190 ug/l, Cu 7400 ug/l
Under Bodrog: Tiszalök (Hungary)	2/5/00	CN 3.7 mg/l
Before Kisköre (Lake Tisza, Hungary)	2/8/00	CN 3.8 mg/l, Cu 2.4 ug/l
Szolnok(water works closed-120 thousand people)	2/9/00	CN 3.2 mg/l, Cu 0.2 ug/l
before Maros, at Szeged (Tape, Hungary)	2/11/00	CN 2.2 mg/l
Below Szeged (Tiszasziget, Hungary)	2/11/00	CN 1.49 mg/l
Danube at Beograd (Yugoslavia)	2/13/00	CN 0.6 mg/l

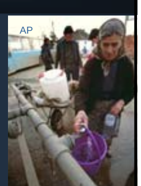
HME

Plume: Spatial-Temporal

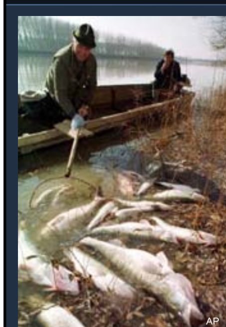


Mobility and Impact

- The polluted waters moved downstream to the Danube, which forms Romania's border with Bulgaria over more than 500 miles.
- Countries banned water intake and Danube fishing as the spill moved downriver towards the Black Sea,
  - Black Sea Delta rich in wildlife.



Environmental Impact



- Spill eradicated life for approximately 250 miles of the river.
- The accident killed thousands of fish in neighboring Hungary and Yugoslavia.

Fish Mortality

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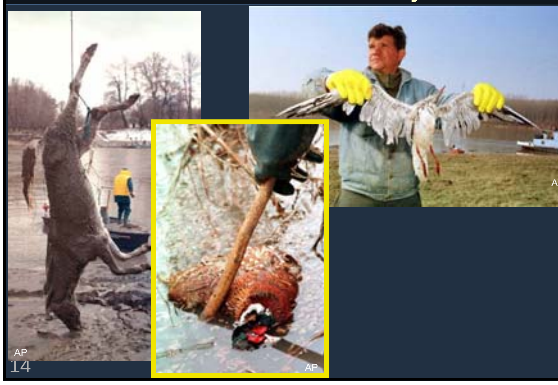
Terrestrial Mortality



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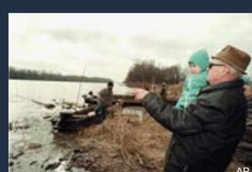
Public Health – Env. Quality



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Aznalcóllar, Spain

- On April 25, 1998, a tailings dam failure of the Los Frailes lead-zinc mine at Aznalcóllar near Seville, Spain, released 4-5 million cubic meters of toxic tailings slurries and liquid into nearby Río Agrio, a tributary to Río Guadiamar.
- The slurry wave covered 5,000 hectares of farmlands, including parts of the Doñana protected area.
  - One of the largest protected areas in the EU and it is a World Heritage Site.

Fernandez Delgado

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Aznalcóllar, Spain

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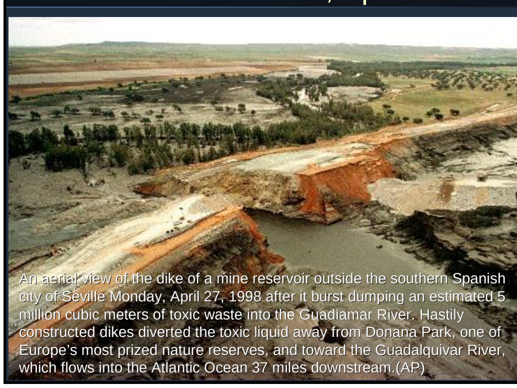
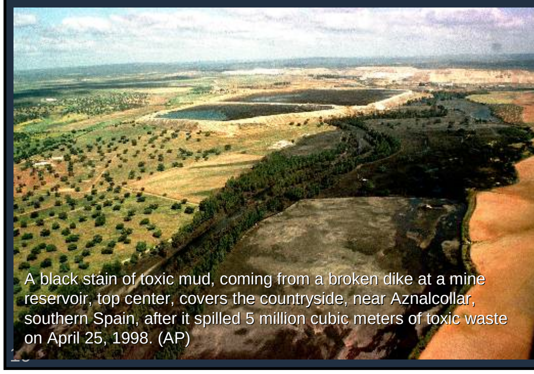
Aznalcóllar, Spain



An aerial view of the dike of a mine reservoir outside the southern Spanish city of Seville Monday, April 27, 1998 after it burst dumping an estimated 5 million cubic meters of toxic waste into the Guadiamar River. Hastily constructed dikes diverted the toxic liquid away from Donana Park, one of Europe's most prized nature reserves, and toward the Guadalquivir River, which flows into the Atlantic Ocean 37 miles downstream.(AP)

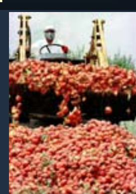
Aznalcóllar, Spain



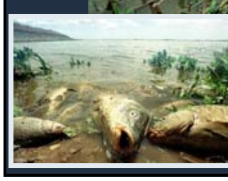
A black stain of toxic mud, coming from a broken dike at a mine reservoir, top center, covers the countryside, near Aznalcollar, southern Spain, after it spilled 5 million cubic meters of toxic waste on April 25, 1998. (AP)

Dam Failure

Impacted Farmland



Impacted Aquatic Habitat



About 60 km of the Guadiamar principal river bed was absolutely destroyed.

--Fernandez-Delgado
Universidad de Córdoba

Ionizing Radiation

- Ionizing radiation (X-rays, alpha particles), cause chemicals reactions and alterations of chemicals in tissues.
  - Can be toxic or fatal.
- Much of the reactivity in organisms is with water.
- Produces:
  - Superoxide radical (O_2• -),
    Hydroxyl radical (HO•),
    Hydroperoxyl radical (HOO•),
    and hydrogen peroxide.

Ionizing Radiation

- Oxidative stress
  - Recall endpoints: lipid peroxidation, DNA strand breaks, enzyme inactivation, covalent binding to nucleic acids, covalent binding to proteins.
- Direct ionization of organic molecules can yield carbonium ions CH_3^+.
  - Can alkalyate DNA.
- Example: Radon, a noble gas that emits alpha particles.
  - Results from the decay of U and Ra in naturally occurring minerals.
  - Presents the most risk of any element to humans.

Manahan

Radiation Sickness

- Illness caused by the effects of radiation on body tissues.
  - May be acute, delayed, or chronic.
  - May occur as a result of cumulative exposure to small doses of radiation; high exposure to solar radiation; or exposure to a nuclear event.
  - Symptoms may be mild and transitory, or severe, depending on the type of radiation, the dose, and the rate at which exposure is experienced.
    - Symptoms: weakness, loss of appetite, vomiting, diarrhea, a tendency to bleed, increased susceptibility to infection, and-in severe cases-brain damage and death, possible long-term genetic effects and increased cancer rates.

NC-DRP

Alpha Particle

- A positively charged particle ejected spontaneously from the nuclei of some radioactive elements.
  - Low penetrating power and a short range.
- The most energetic alpha particle will generally fail to penetrate the dead layers of cells covering the skin.
- Alphas are hazardous when an alpha-emitting isotope is inside the body.

NC-DRP

Beta Particle

- A charged particle emitted from a nucleus during radioactive decay.
  - Mass equal to 1/1837 that of a proton.
  - A negatively charged beta particle is identical to an electron; a positively charged beta particle is called a positron.
- Large amounts of beta radiation may cause skin burns, and beta emitters are harmful if they enter the body.
- Beta particles may be stopped by thin sheets of metal or plastic.

NC-DRP

Gamma Ray

- High-energy, short wavelength, electromagnetic radiation (a packet of energy) emitted from the nucleus.
  - Gamma radiation frequently accompanies alpha and beta emissions and always accompanies fission.
- Gamma rays are very penetrating and are best stopped or shielded by dense materials, such as lead or uranium.
- Gamma rays are similar to X-rays.

NC-DRP

Half-life

- The time in which one half of the atoms of a particular radioactive substance disintegrates into another nuclear form.
  - Measured half-lives vary from millionths of a second to billions of years.

NC-DRP

Curie

- The special unit of radioactivity.
- One curie is equal to 3.7×10^{10} disintegrations/s.
- Replaced by the becquerel (Bq), which equates to one decay/s (1 Ci = 37 Gbq)

Radioactive Decay

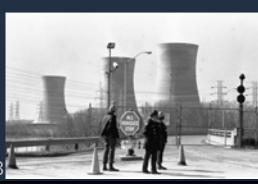
- The decrease in the amount of any radioactive material with the passage of time, due to the spontaneous emission from the atomic nuclei of either alpha or beta particles, often accompanied by gamma radiation.

Environmental Radiation Standards

- Standards issued by the U.S. Environmental Protection Agency (EPA) under the authority of the Atomic Energy Act of 1954 (42 U.S.C. 2D11 et seq;), as amended.
  - Impose limits on radiation exposures or levels, or concentrations or quantities of radioactive material, in the general environment outside the boundaries of locations under the control of persons possessing or using sources of radiation.

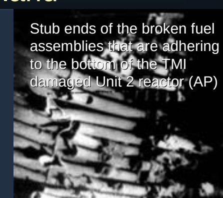
Three Mile Island

- The accident began about 4:00 a.m. on March 28, 1979, when the plant experienced a failure in the secondary, non-nuclear section of the plant: main coolant pump fails
- Back-up coolant pump valve non-reopened after a test 2-day earlier due to human error.



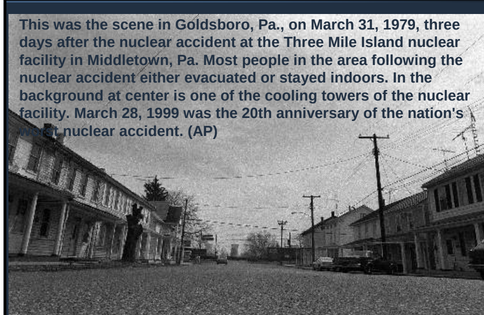
Three Mile Island

- Erroneous coolant water level readings in the reactor
  - Reading high actually low due to gas bubble voids.
  - H_2 gas buildup in the containment structure.
- Top of the fuel rods melted.
  - Radioactive water to basement.



Stub ends of the broken fuel assemblies that are adhering to the bottom of the TMI damaged Unit 2 reactor (AP)

Three Mile Island



This was the scene in Goldsboro, Pa., on March 31, 1979, three days after the nuclear accident at the Three Mile Island nuclear facility in Middletown, Pa. Most people in the area following the nuclear accident either evacuated or stayed indoors. In the background at center is one of the cooling towers of the nuclear facility. March 28, 1999 was the 20th anniversary of the nation's worst nuclear accident. (AP)

Three Mile Island

The cooling stacks for the Unit 2 reactor, foreground, at the Three Mile Island Nuclear Facility are dormant on Wednesday, March 3, 1999, in Middletown, Pa. The reactor at Unit 2 ceased operations following a partial meltdown on March 28, 1979. Only the reactor and cooling stacks at Unit 1, rear, have continued to produce power. March 28, 1999 was the 20th anniversary of the nation's worst nuclear accident. (AP)

Public Health/Env. Impacts

- Thousands of environmental samples of air, water, milk, vegetation, soil, and foodstuffs were collected.
  - Very low levels of radionuclides could be attributed to releases from the accident.
- Comprehensive investigations and assessments by several well-respected organizations have concluded that in spite of serious damage to the reactor, most of the radiation was contained and that the actual release had negligible effects on the physical health of individuals or the environment.
  - Average dose < an X-ray and << background.

37 NRC

20 Year Cancer Epidemiology

- The overall number of deaths from cancer among the "exposed" population was not significantly different from the general population.
  - Exposed = 5 mile radius.
- There was a small rise in the number of lymphatic and blood cancer deaths among women in the exposed group.

BBC, PDH

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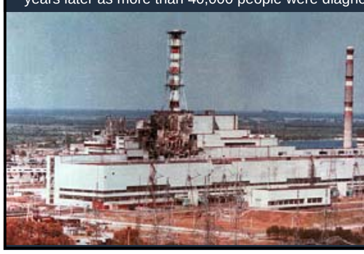
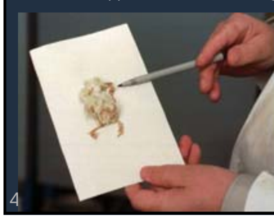
Chernobyl

An aerial view of the Chernobyl nuclear power reactor in Chernobyl, Ukraine, shows damage from an explosion and fire on April 26, 1986. The blast killed 31 people and sent large amounts of dangerous radioactive material into the atmosphere. The contamination was carried across western Europe by the wind to Sweden, Finland, the northern part of Britain, France and Italy. The ghosts of history's worst nuclear reactor accident lurked everywhere in the surrounding countryside more than ten years later as more than 40,000 people were diagnosed with cancer. (AP/Tass)



Environmental Impacts

Ukrainian Academy of Sciences member Vyacheslav Konovalov, shows a stuffed four-legged chick in his laboratory in Zhytomyr, 120 km (75 miles) west of Kiev, Ukraine, on Monday, March 11, 1996. Konovalov, who has been studying biological mutations since the the explosion in April 1986, has found dozens of new bacteria and viruses and new forms of plant and animal diseases after Chernobyl catastrophe. No one can prove that Chernobyl blast directly caused a chick born after the blast to die because it could not support its four extra wings.(AP)



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Chernobyl

This 1986 aerial view of the reactor four at the Chernobyl nuclear plant in Chernobyl, Ukraine shows damage from an explosion and fire on April 26, 1986 that sent large amounts of radioactive material into the atmosphere. Ten years after the world's worst nuclear accident, the plant was still running due to a severe shortage of energy in Ukraine. (AP)

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Long Term Effects

42 AP

US Mixed Waste Challenge

- Mixed waste: combined radioactive (LLW, HLW, TRU) and hazardous waste.
- Scale of soil contamination problem.
  - 4,000 DOE sites.
  - 7,313 DoD sites.
- Hazardous waste.
  - TCE, Cr, Pb, PHC.
- Radioactive waste.
  - 3-Hydrogen (Tritium), 14-Carbon, 99-Technetium, 129, 131-Iodine, 133-Xenon, 137-Cesium, 238-Uranium, 239-Plutonium, 241-Americium.

3-Hydrogen (Tritium)

- Half life = 12.33 y.
- Beta; 0.0186 MeV (weak).
- Highly mobile; commingle with H spontaneously
- 99% appears as tritiated water (HTO).
- Product of cosmic radiation, weapons production & reactors.
- Natural sources = 30MCi.
- 4,500 MCi from 1960's weapons tests.
- Not a major toxicological hazard.

14-Carbon

- Half life = 5730 y
- Beta; 0.156 MeV
- Carbon chemistry
- ^{14}C is virtually inseparable from ^{12}C
- At sufficiently low concentrations, ^{14}C is exempted from treatment as nuclear waste.
- No known chemical or physical process can re-concentrate the radioisotope.
- From cosmic radiation and nuclear fission.
- About 300 MCi from natural sources
- In the environment – carbonate system CO_3^{2+}, CO_2

99m/99-Technetium

- Half life - internal isomeric transition: two step decay
- 6.01h for 99m; 2.13 x 10^5 y for 99
- Gamma, 0.142 MeV for 99m and Beta, 0.293 MeV for 99 (weak Gamma also)
- ^{235}U fission ^{99}Mo decay ^{99}Tc
- Tc+7, pertechnate ion TcO_4^-
- $Tc^{+5, +4, +3}$
- TcO_4 (oxidized- soluble, slightly sorbed to minerals; TcO_2 (reduced- insoluble) are the most common forms in groundwater.
- Trace concentration, 10^{-9} M

129,131 Iodine

- Half life = 1.6 x 10^7 y for 129 and 8.04d for 131
- Beta 0.150 MeV; Gamma 0.0396 MeV and e^- for 129 and Beta 0.606 MeV; Gamma 0.364 MeV for 131
- ^{235}U fission to ^{131}I (most medical use)
- $I_2 + 2e^- = 2I^-$ E_o = 0.535 eV
- I^- can be oxidized by O_2 in solution.
- Predominantly found as iodate ion in the environment, IO_3^-

133 Xenon

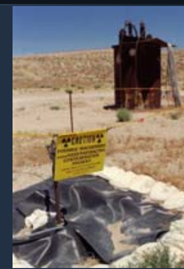
- Half life = 5.25 d.
- Energy - Beta 0.606 MeV and Gamma 0.081 MeV and e^-.
- Nobel gas and therefore inert to chemical reaction.
- Highly soluble in plastics/polymers.
- Not concentrated in living systems.

137 Cesium

- Half life 30.17 y
- Energy - Beta 0.512 MeV; Gamma 0.662 MeV and e^-
- Group I Alkali metal - highly soluble.
- $^{137}Cs^+$ stable aqueous environmental form.
- Strongly sorbed on common rock from dilute solutions.
  - Especially micas and clay minerals.

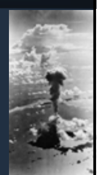
238 Uranium

- Half life = 4.468 x 10^9 y.
- Energy - Alpha 4.20 MeV.
- Valence states from 0 to IV.
- Occurs in nature as UO_2, U_3O_8, U^{4+} and UO_2^{2+} in groundwater.
- U(IV) and U(VI) oxides.
- Uranyl complexes such as carbonates soluble.
- GW/subsurface retardation varies widely.



239 Plutonium

- Half life = 2.411 x 10^4 y.
- Energy - Alpha 5.16 MeV and others.
- n activation of ^{238}U followed by beta decay to ^{239}U to ^{239}Np and then to ^{239}Pu.
- Oxidation states II through VII exist.
  - All but Pu(II) can exist in water.
- Environmental chemistry similar to uranium, PuO_2^{2+}, Pu^{3+}.
  - Can exist as a colloidal, stable hydroxide.
- Sorption on natural rocks is fairly high, however complexing by organic ligands reduces retention.



241 Americium

- Half life = 432 y
- Energy - Alpha 5.4857 MeV; Gamma 0.0595 MeV and others.
- Common alpha radiation source.
- Am (IV) forms stable, relatively soluble AmO_2.
- Am(III) stable in solution, often as $Am(OH)_3$
- Strongly sorbed by all common rocks at ambient pH.
- Complexation will reduce retention.

The Mixed Waste Challenge

- Reduce the toxicity, mobility and/or volume of the waste.
- Mixtures of organic and inorganic.
  - Requires multiple remediation approaches.
- Mixtures of heavy metals and radioactive metals.
- Approaches limited by chemistry of the metals.
  - Multiple species.
    - Actinides: M(4+); MO2(2+); M(3+); MO2(2+)
  - Complexations, sorptions.
- Box it, bag it, barrel it, store it!

Strategy

- Relative risk considerations.
  - Material (half life, energy, mobility), receptor sites, costs.
- Separations.
  - Radioactive from non radioactive.
  - Organic from inorganic.
- Can use some typical HW approaches.
- Volume reductions.
  - Vitrification.
- HLW and TRU to long term storage.
- Big "How To" questions remain!
  - Many technologies are experimental.

DOE Focus Areas

- Contaminant, plume containment and remediation.
  - Distribution and concentration?
- Containment, in-situ treatment.
- Mixed waste characterization, treatment, and disposal.
  - LLW regulations and standards?
  - Lack of accepted treatment and disposal capacity.

DOE Focus Areas

- HLW tank remediation.
  - 100's of deteriorating tanks.
- Landfill stabilization.
- Migration; *in situ* containment/treatment.
- Decontamination and decommissioning of contaminated facilities.
- Treatment considerations.
  - Special chemistry of radionuclides will require targeted approaches.

Hanford, WA

This is a World War II file photo of the historic "B Reactor" at Hanford, Wash., which was the world's first plutonium production reactor. The Hanford nuclear reservation sits along the Columbia River. (AP)

Hanford, WA

The Columbia River as it flows past the closed F Reactor on the Hanford nuclear reservation near Richland, Washington (AP).

DOE Hanford

- Case presentation:
  "Protecting the Columbia River" Video