Diazinon and Chlorpyrifos as Urban Stormwater Runoff Associated Pollutants

G. Fred Lee, PhD, PE, DEE and Anne Jones-Lee, PhD
G. Fred Lee & Associates
El Macero, CA 95618
916-753-9630
www.gfredlee.com

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Review Water Quality Issues Associated with Urban Use of the Organophosphate Pesticides, Diazinon and Chlorpyrifos, That Leads to Urban Stormwater Runoff's Toxicity

Based on "Aquatic Life Toxicity in Stormwater Runoff to Upper Newport Bay, Orange County, California: Initial Results," Report G. Fred Lee & Associates, June 1997.

Urban Stormwater Runoff Toxicity

Urban Stormwater Runoff in Several Areas of California, Texas and Other Areas Has Been Found to Be Toxic to Some Zooplankton Such as Ceriodaphnia

Toxicity Due in Part to Diazinon and Chlorpyrifos
- Under-Regulated Chemicals in Stormwater Runoff
  - Diazinon - No US EPA Water Quality Criterion
  - Chlorpyrifos - US EPA Water Quality Criterion - Not Enforced

US EPA FIFRA (Federal Insecticide, Fungicide, and Rodenticide Act) Registration of Diazinon Has Not Properly Evaluated Stormwater Runoff Water Quality Impacts

Examples of Urban Stormwater Runoff Toxicity

Orange County, California:
- San Diego Creek as It Enters Upper Newport Bay Had 8 to 10 Units of Ceriodaphnia Toxicity Associated with Stormwater Runoff in October-November 1996
  - 50% of Toxicity Due to Diazinon and Chlorpyrifos
  - Other 50% Due to Unknown Causes

San Francisco Bay Region: Urban Creeks Contain Ceriodaphnia Toxicity Due to Diazinon
- Some Street Gutters in Alameda County, California Residential Areas Contain >2,000 ng/L Diazinon

Central Valley, California: Stormwater Runoff from Urban Areas Is Toxic to Ceriodaphnia Due to Diazinon and Chlorpyrifos

Fort Worth, Texas: Urban Stormwater Runoff Toxic to Ceriodaphnia Due to Diazinon

Diazinon and Chlorpyrifos Toxicity

		Cal Fish and Game-Recommended Water Quality Criteria	
	***Ceriodaphnia* LC50**	**4-day Average**	**1-hr Average**
Diazinon	500 ng/L	40 ng/L (freshwater)	80 ng/L
Chlorpyrifos	100 ng/L	20 ng/L (freshwater)	10 ng/L (saltwater)

Highly Toxic to Some Zooplankton Such as Daphnids and Benthic Organisms Such as Amphipods

Not Highly Toxic to Fish and Many Other Forms of Aquatic Life

Diazinon and Chlorpyrifos Use

Diazinon and Chlorpyrifos Widely Used by Commercial Applicators and Homeowners/Renters to Control Structural and Landscape Pests Including Termites, Ants, Fleas, Grubs, Beetles, Spiders, Chiggers, Earwigs, Silverfish, Cockroaches, Grasshoppers, Etc.

Orange County, California: 100,000 Pounds of Chlorpyrifos and Diazinon Used in Urban Areas in 1995

About 2 lb/yr in Stormwater Runoff Causes Ceriodaphnia Toxicity

Santa Clara County, California: 123,000 lb Chlorpyrifos and Diazinon Used in 1994

Persistence of Diazinon and Chlorpyrifos

In Soil:

Diazinon - “40 Days”
Chlorpyrifos - “30 Days”
Malathion - “1 Day”

Persistence Sufficient to Cause Ceriodaphnia Toxicity Associated with Urban Stormwater Runoff

- Site-Specific Evaluation for Soil, Water, and Sediments Needed to Evaluate Persistence at a Particular Location
    - Dependent upon pH, Temperature, Moisture, Formulation, Other Factors

Sediment Quality Issues

Chlorpyrifos Tends to Sorb to Organic Carbon in Sediments

- Water Solubility 0.4 mg/L
- Found in Upper Bay Sediments of Upper Newport Bay, California near Where San Diego Creek Enters the Bay
    - Toxicity in Sediments Unknown

Diazinon Reported to Not Sorb to Sediments - Water Solubility 60 mg/L

- Found in Urban Creek Sediments in San Francisco Bay Area
    - Sorbed? Toxic? - Sediments as a Buffer Source of Diazinon to Creek After Stormwater Runoff Event?

High Toxicity to Amphipods - May Be Cause of Unexplained Sediment Toxicity

- Issue Needs to Be Examined for Water Quality Significance

Agricultural Use As a Source of Diazinon for Urban Area Stormwater Runoff

Application of Diazinon as an Orchard Dormant Spray in the Sacramento and San Joaquin Valleys, CA Causes Rainfall and Fogfall to Be Toxic to Ceriodaphnia in Many Areas at Considerable Distances from Application

- Airborne Transport
    - Rainfall in Central Valley, CA after Dormant Spray Application Can Contain over 5,000 ng/L Diazinon - Toxic Level 500 ng/L
- Toxic Pulses of Diazinon Lasting Several Weeks Pass through San Joaquin and Sacramento Rivers and Delta into Upper San Francisco Bay Each Winter
    - Likely Adverse to River and Delta Aquatic Life-Related Beneficial Uses
    - Due to Toxicity Magnitude and Persistence
- Agricultural Use of Diazinon as Dormant Spray Also Causes Urban Areas and Highway Stormwater Runoff to Be Toxic to Ceriodaphnia

Alameda County, CA Found Local Airborne Transport as Part of Home Use

Regulatory Requirements for Control of Diazinon and Chlorpyrifos Toxicity

POTW's and Industrial Wastewater Discharge

- No Acute Toxicity in Discharge/Mixing Zone
- No Chronic Toxicity at Edge of Mixing Zone

NPDES Permitted Urban Area Stormwater Runoff Dischargers

- Control Pollution of Receiving Waters for Stormwater Runoff to Maximum Extent Practicable Using Best Management Practices

- Pollution Defined as Impairment of Designated Beneficial Uses
    - Could Require Protection of All Desirable Forms of Fish and Aquatic Life
- Agriculture - No NPDES Permit Required
    - General Requirement of No Ambient Water Toxicity - Not Enforced

Control of Diazinon and Chlorpyrifos Toxicity

Small Amounts of Diazinon and Chlorpyrifos Use Responsible for Stormwater Runoff Toxicity

- Orange County, California: about 2 lbs Out of the Estimated 20,000 lbs Used Annually Caused Toxicity in San Diego Creek
    - Toxicity Likely Difficult to Control

Need Detailed Forensic Studies of Sources of Toxicity and Toxic Components in Urban Area Stormwater Runoff

When Sources of Toxicity and Toxic Components Known, Examine Uses That Lead to Stormwater Runoff Caused Toxicity

- Forensic Studies Should Be Funded by Pesticide Manufacturers, Formulators, Commercial Applicators, and Users

Development of Diazinon and Chlorpyrifos Toxicity Control Strategy: Issues

If Diazinon and Chlorpyrifos Causes Toxicity to or Impacts Several Types of Zooplankton and/or Fish Larvae, Require Control of Toxic Constituents to Eliminate Toxicity

Diazinon and Chlorpyrifos Apparently Toxic to Limited Number of Types of Zooplankton and Benthic Organisms

- Additional Study Needed to Determine Water Quality Significance of Toxicity to Fisheries-Related Beneficial Uses of Concern to Public
- Diazinon and Chlorpyrifos Are of Significant Value to Public for Pest Control

Determine Water Quality Significance of Toxicity

- Urban Streams - Cannot Assume Toxicity Significant to Water Quality
- Receiving Waters for Urban Streams and Stormwater Runoff
    - Rivers, Bays, Lakes, Ponds, Wetlands, Estuaries and Ocean
- Assess Whether Toxicity Significantly Adversely Impacts Numbers, Types, or Characteristics of Desirable Forms of Aquatic Life
- Determine Significance of Toxicity through Use of Best Professional Judgement, Non-Numeric Weight-of-Evidence Evaluation Based on:
    - Magnitude, Fate/Persistence, Duration of Aquatic Life Exposure, Transport Time in Creek, River and Bay/Lake Plumes, Type of Organisms Impacted, Importance of Organisms as Component of Food Web for Higher Trophic Level Organisms, Duration of Impact, etc.

Need to Develop Technical Guidance on How to Determine if Toxicity in Specific Waterbody Is Significant to Water Quality

If "Ceriodaphnia" Toxicity Judged Significant - Determine Cause of Toxicity

- Use Guided TIEs, PBO Dilution Series Toxicity Tests, ELISA Analyses, etc.
- Assess Amount of Toxicity Due to Diazinon and Chlorpyrifos
    - Use TIEs to Identify Cause of Non-Diazinon and Non-Chlorpyrifos Ceriodaphnia Toxicity
    - Potential Role of Chromium VI - Toxic to Daphnia at <0.5 µg/L

Through Forensic Studies Using Specific Toxic Chemical and Toxicity Measurements at Various Locations in Watershed, Determine Source of Toxicity

- Examine Use/Activity Leading to Toxicity in Runoff Waters from Specific Area

Develop Toxicity and Specific Chemical Control Programs to Reduce and, Where Possible, Eliminate Stormwater Runoff-Associated Toxicity That Is Significantly Adverse to Beneficial Uses of Receiving Waters for Runoff; Options:

- Educate Users on Types and Manner of Use That Lead to Stormwater Runoff-Associated Toxicity
    - Need Studies to Define These Conditions
- Restrict Certain Types of Uses That Lead to Urban Area Stormwater Runoff Toxicity
- Reformulate Diazinon and Chlorpyrifos so Their Use Does Not Lead to Significant Stormwater Runoff-Associated Toxicity
- Ban Use of Chlorpyrifos and Diazinon in Areas Where Stormwater Runoff -Associated Toxicity Is Judged to Be Significantly Adverse to Receiving Water Beneficial Uses

Assessment of an Urban Stormwater Runoff Aquatic Life Toxicity Water Quality Problem

Potential Water Quality Problems Associated with Laboratory-Measured Aquatic Life Toxicity Occur Where the Toxicity Impacts the Numbers, Types and Characteristics of Desirable Forms of Aquatic Life of Concern to the Public

Regulatory Requirements on Urban Area Street Stormwater Runoff Toxicity Not Definitively Defined

Control Pollution (Use-Impairment) to Maximum Extent Practicable Using Best Management Practices

Water Quality Problem Cannot Be Evaluated Solely by Measurement of the Concentration of a Pesticide Such as Diazinon or Ceriodaphnia Toxicity in Standard Toxicity Test

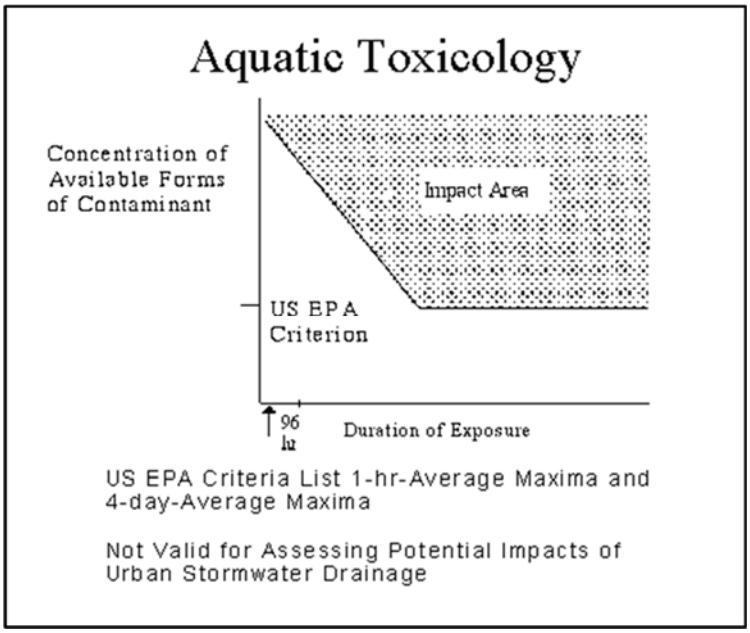
Assessment of an Urban Stormwater Runoff-Caused
Significant Aquatic Life Toxicity Water Quality Problem

Toxicity Impacts Based on a Measured Level of Toxicity for a Sufficient Duration of Exposure to Be Adverse to an Organism

Toxic Conditions Defined by Toxicity - Duration of Exposure Relationship

Each Organism Type, e.g., *Ceriodaphnia*, Has a Certain Toxic Response - Duration of Exposure Relationship for a Particular Chemical

Toxicity - Duration of Exposure Relationship



Duration of Exposure Issues

Necktonic Organisms

- Are Fish Attracted - Repelled by Water Containing the Toxicant(s)?
  - If Repelled - Can They Escape from Toxicant?
- Usually Larval/Sensitive Forms of Fish Are Essentially Planktonic
  - Limited Ability to Control Position

Planktonic Organisms

- Position Largely Controlled by Water Motion
- May Be Able to "Hide" in Low Velocity Areas
  - Longer Exposure to Toxic Conditions Possible
  - Those That "Hide" during Runoff Event May Be Important to Restocking Stream/Area

Additional Toxicity - Duration of Exposure Issues

Some Urban Stormwater Runoff Has Been Found to Contain Short-Term, Greatly Elevated Spikes of Toxicity in the First Flush Runoff

- Spikes of Toxicity Last Few Minutes to Few Hours - Could Readily Be Missed by Normal Sampling
- Toxicity Is Not Representative of Average Conditions During Typical First Flush Event
- Water Quality Significance of Toxicity Spikes Unknown

Latent Toxicity Found

- Organisms Exhibit Toxic Effects Several Days after Exposure to Toxic Conditions While Organism in Non-Toxic Waters
- Needs Further Investigation

Assessing Water Quality Significance of Toxicity

Normally Consider Direct Toxicity to Fish and Shellfish, Including Larval Forms, of Water Quality Significance That Requires Control

Also Consider Toxicity to Substantial Parts of Zooplankton Population of Water Quality Significance, That Requires Control

For Ceriodaphnia Toxicity Associated with Urban Area Stormwater Runoff of Short Duration

- Linkage between Water Column & Sediment Toxicity and Significant Water Quality Impacts to Higher Trophic Level Organisms Less Well-Defined

Issue That Must Be Resolved: Does Reduction in Numbers of a Certain Component of Food Web for Limited Period of Time Significantly Adversely Affect Numbers, Types or Characteristics of Desirable Forms of Aquatic Life Such as Game Fish and Shellfish

- Is There Substitute Fish Food That Can Sustain System Populations during Time of Toxic Pulse Impacts Associated with Stormwater Runoff Event?

Current Status of Diazinon/Chlorpyrifos Ceriodaphnia Toxicity in Urban Stormwater Runoff Pollution

Sufficient Concentrations of Diazinon & Chlorpyrifos Found in Stormwater Runoff to Waterbodies, Urban Creeks and Near-Shore Waters of Receiving Waters for Stormwater Runoff to Be Toxic to Ceriodaphnia under Standard Test Conditions

- Potential for Water Quality Problem Exists - Likely Potential Problem Not Confirmed
- Before Significant Efforts Are Made to Develop Use-Restrictions for Diazinon and Chlorpyrifos beyond Good Housekeeping and Conservative Use in Accord with Label, Should Evaluate Whether Critical Toxicity-Duration of Exposure Conditions Exist in Urban Creeks, Ponds, Bays, Lakes, Estuaries and Near-Shore Marine Waters to Result in Potentially Adverse Impacts on Aquatic Life-Related Beneficial Uses

Inadequate Information Available Today to Justifiably Claim That Significant Potential Water Quality Problem Exists Due to Diazinon & Chlorpyrifos in Urban Area Stormwater Runoff

- Likely Will Be Significant Water Quality Problems Due to Diazinon/ Chlorpyrifos Toxicity in Some Urban Area Stormwater Runoff Situations
    - Rare or Common?
- Must Conduct Intensive Studies to Develop Needed Information to Evaluate with Best Professional Judgement/Weight-of-Evidence Approach, Whether Significant Toxic Conditions Exist in Various Types of Urban Stormwater Runoff Situations to Confirm That There Is Significant Potential for Water Quality Use-Impairment Due to Stormwater Runoff-Associated Constituents Such as Diazinon and Chlorpyrifos
- Locations at Which Real Water Quality Problems Occur Will Likely Be Limited to Certain Types of Receiving Water Situations
    - Those Situations Should Be Defined and Receive Highest Priority for Evaluation

Diazinon & Chlorpyrifos Manufacturers, Formulators, Applicators, and Users Should Fund Independent, Peer-Reviewed Studies to Define Whether Diazinon and Chlorpyrifos Are Potentially Causing Significant Water Quality Impacts - Use-Impairments

- Burden of Proof Should Be on Those Who Wish to Profit from the Use of These Chemicals, Not on Non-Using Public or Environment
- Failure to Adequately Fund Needed Studies Should Result in Use Restrictions

Definition of Significant Water Quality Problem

If Unlimited Funds Were Available to Address Readily Discernable Water Quality Problems, Potential Water Quality Problems, and Other Social Problems, Then Society Could Possibly Determine That Diazinon & Chlorpyrifos Use Should Be Restricted to Control Toxicity in Urban Stormwater Runoff

However, Funds Available for Control of Readily Discernable Water Quality Problems and to Investigate Potential Problems Are Limited, and Diazinon & Chlorpyrifos Are Useful Chemicals to Large Part of Urban Population

Must Evaluate Whether Restricting Use of Diazinon & Chlorpyrifos Is Justified Based on Their Causing Significant Water Quality Problems/Use-Impairments in Receiving Waters for Urban Area Stormwater Runoff

A Determination of Significant Water Quality Problems/Use-Impairment Should Involve Adverse Impacts on the Numbers, Types, and Characteristics of Desirable Forms of Aquatic Life of Concern to Public

- Social Decision - Public Needs to Better Understand Potential Magnitude of Problem to Aquatic Resources of Interest to It
- Diazinon and Chlorpyrifos Have Existed in Urban Area Stormwater Runoff and Receiving Water for Many Years
    - Therefore, If Problem Is, in Fact, Real for Particular Runoff Situation, Those Receiving Waters Where Problem Could Be Occurring Are Already Degraded

- Issue Becomes - What Will the Improvement Be in Beneficial Uses of Receiving Water if Significant Restrictions Are Placed on Use of Diazinon & Chlorpyrifos in Urban Areas?
    - Important to Assess Whether Diazinon & Chlorpyrifos Are the Only Toxicants in Stormwater Runoff That Potentially Impact Ceriodaphnia-like Populations
        - In San Diego Creek Entering Upper Newport Bay Only about Half of Toxicity to Ceriodaphnia Found in Fall 1996 Was Due to Diazinon & Chlorpyrifos, Remainder of Unknown Cause
    - Could Control Diazinon & Chlorpyrifos Toxicity but Not Significantly Improve Receiving Water Beneficial Uses because of:
        - Limited Significance of Diazinon & Chlorpyrifos Toxicity to Beneficial Uses
        - Residual Toxicity Due to Other Constituents
    - Should Always Measure Level of Total Toxicity and Define, as Well as Possible, Its Cause through Appropriate TIEs and, Its Source(s) through Forensic Studies

Issues in Regulation of Diazinon and Chlorpyrifos

Should Use Pesticide in Accord with Label - Conservative Use, Proper Management of Residues

- Need Education on Appropriate Use

Need for Immediate Control of Present Pesticide Use because of Imminent Hazard of Adverse Impacts of Toxicity?

- No. Damage Already Done - New Significant Adverse Impacts Unlikely
- Control New Uses and New Areas of Application Which Could Result in Runoff to Ecologically Sensitive Systems
- Organophosphate Pesticide Toxicity Long-Standing Problem if Real, Significant Problem Exists
- Recommendation: Practice Good Housekeeping and Conservative Use
    - Determine if Water Quality Problems/Use-Impairment of Concern to Public Is Occurring That Could be Controlled if Use Restrictions of Urban Pesticides Were Implemented

Ecological Versus Water Quality Impacts

Ecosystems Resilient to Perturbations

- Some Societally Important Organisms, Such as Fish, May Able to Be Eliminated without Altering Functioning of Ecosystem

Water Quality Related to Beneficial Uses

- Numbers, Types, and Characteristics of Desirable Forms of Aquatic Life
    - Includes Adequate Functioning of Ecosystem and Protection of Specific Types of Organisms Such as Game Fish, Endangered Species, etc.

- Includes Body Burdens of Hazardous Chemicals Such as Mercury and PCBs That, While Not Necessarily Adverse to the Aquatic Ecosystem, Are of Concern to the Health of People Who Consume Them

Chemical Ecology

Important to Properly Incorporate Aqueous Environmental Chemistry Into Evaluation of the Water Quality Impacts of Chemicals

- Most Chemicals Exist in a Variety of Chemical Species, Only Some of Which Are Toxic/Available
- Chemical Species Distribution Depends on Physical, Chemical, and Biological Factors
- Many Other Factors, Such as Transport and Mixing That Impact Biological Species Also Impact Chemical Species

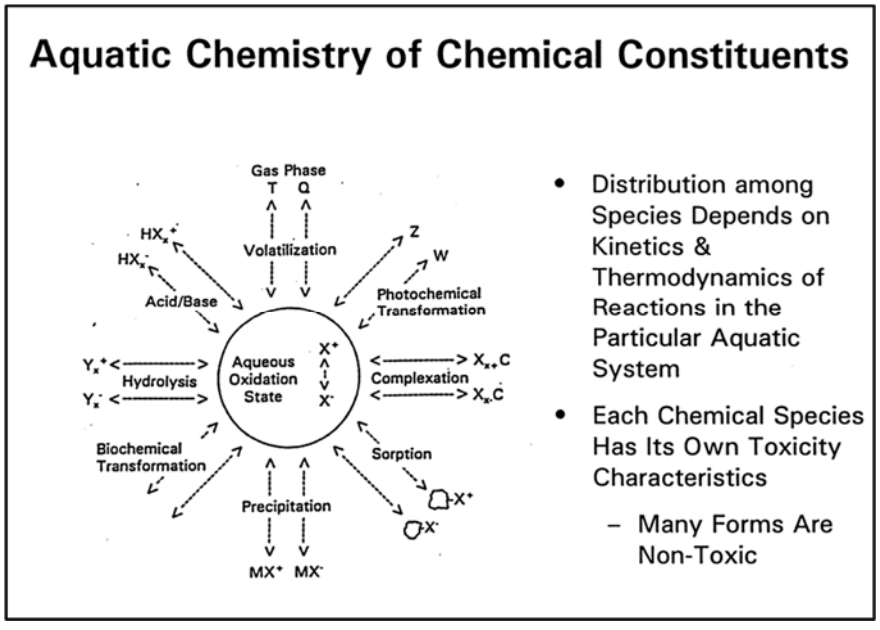
Aquatic Chemistry

Not Chemical Characteristics - Chemical Census

- Often Cannot Infer Water Quality Impacts Based on Chemical Characteristics

Chemical Reactions

- Thermodynamics (Energetics - Position of Equilibrium)
- Kinetics (Rates of Reactions)
- Transport - Advection, Mixing, Diffusion, Turbulence
    - Hydrology, Hydraulics, Hydrodynamics
- Must Consider Solution - Dissolved and Particulate Forms
    - Suspended and Bedded Sediments



Overall Assessment of
Adequacy of Current Information on
Water Quality Significance of Diazinon/Chlorpyrifos Toxicity
In Urban Stormwater Runoff

Necessary Studies Have Not Been Done to Define Whether Toxicity or Potentially Toxic Concentrations of Diazinon or Chlorpyrifos Are Present in Urban Area Stormwater Runoff to Be Potentially Significantly Adverse to Designated Beneficial Uses of Various Receiving Waters

- This Area Needs Attention

Conclusions and Recommendations

California Urban Creeks and Some Parts of Rivers, Bays, Estuaries, Ponds and Lakes Are Experiencing Aquatic Life Toxicity Due to Urban and Some Agricultural Uses of Diazinon and Chlorpyrifos

- Widespread Toxicity to Ceriodaphnia Caused by Diazinon and Chlorpyrifos Associated with Urban Area Stormwater Runoff
- Water Quality Significance of Toxicity Depends on Characteristics of Urban Creek and Receiving Waters for Stormwater Runoff and Creek Discharge
- Need Site Specific Studies to Determine Water Quality Significance of Diazinon and Chlorpyrifos Toxicity
- Need to Develop Guidance on Approach That Should be Followed to Determine, for Particular Creek or Stormwater Runoff/Receiving Water Situation, the Water Quality Significance of Diazinon and Chlorpyrifos and Other Causes of Ceriodaphnia Toxicity
- Need Forensic Studies to Determine Sources and Activities That Cause Diazinon and Chlorpyrifos Toxicity in Waters Receiving Urban Area Stormwater Runoff
- Need to Control Agricultural Use of Diazinon as Dormant Spray, to Eliminate Airborne Transport That Causes Rainfall and Stormwater Runoff to Be Toxic in Widespread Areas for Weeks at a Time

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