Department of Pesticide Regulation Environmental Monitoring Branch

David Duncan
Department of Pesticide Regulation

DPR Mandates & Authorities

California's **Food and Agricultural Code Section 11501** sets forth the general provisions of the legal code that fundamentally authorizes the State's pesticide regulatory program

- To provide for the proper, safe and efficient use of pesticides to protect public health and safety
- To protect the environment from environmentally harmful pesticides
- To assure agricultural and pest control workers safe working conditions
- To permit agricultural pest control by competent and responsible licensees and permittees
- To assure consumers that pesticides are properly labeled and appropriate for the use designated by the label
- To encourage the development and implementation of reduced-risk pest management systems

DPR
Environmental Monitoring Branch

General branch mandate: FAC 12824 requires

cdpr.ca.gov/docs/dept/factshts/regprocess.pdf

DPR
Environmental Monitoring Branch

General branch mandate: FAC 12824 requires

- Continuous evaluation of registered pesticides

cdpr.ca.gov/docs/dept/factshts/regprocess.pdf

DPR
Environmental Monitoring Branch

General branch mandate: FAC 12824 requires

- Continuous evaluation of registered pesticides
- Evaluation of substances before registration

cdpr.ca.gov/docs/dept/factshts/regprocess.pdf

Environmental Monitoring Branch 3 Programs

- Air
- Surface Water
- Ground Water

cdpr.ca.gov/docs/emon/ehap.htm

Environmental Monitoring Branch

- Branch surface water and ground water monitoring programs and their activities

Environmental Monitoring Branch

- Branch surface water and ground water monitoring programs, requirements, activities
- Analytical quality control

Environmental Monitoring Branch

- Branch surface water and ground water monitoring programs and their activities
- Analytical quality control
- Surface water and ground water databases

Environmental Monitoring Branch
Topics to Cover

- Branch surface water and ground water monitoring programs and their activities
- Analytical quality control
- Surface water and ground water databases
- Evaluation of new active ingredients or changes to pesticide registrations

Surface Water Program

Surface Water Program
Monitoring

- Surface water, sediment, aquatic toxicity
- USEPA Benchmarks used as threshold indicators for most sensitive invertebrate and vertebrate species
- Agricultural and urban settings
- Sites in 3 urban and 2 to 3 ag areas

Surface Water Program
Mitigation

Preventing pesticide runoff to surface water

- Constructed wetlands, vegetated ditches
- Orchard cover crops
- Degradation enzymes
- Holding ponds, irrigation return systems
- Reduce or limit use

Surface Water Program
Regulation

- Pyrethroid use requirements for urban areas now in effect
- Dormant spray regulations for agriculture since the 1990s
- Reevaluation
  - Pyrethroids for sediment toxicity in urban creeks
  - Chlorpyrifos and diazinon for agricultural runoff.
- Regulations may be statewide, applied regionally, or permit conditions

Ground Water Program

Ground Water

Pesticide Contamination Prevention Act (PCPA)

- Enacted in 1985
- Prevent further pollution of ground water due to agricultural use of pesticides

Agricultural Use in California

PCPA Requires DPR to:

Call in environmental fate data for ag use pesticides

(Registration Branch)

Environmental Fate Data

Measures of mobility

- Water solubility
- Soil adsorption coefficient (Koc)

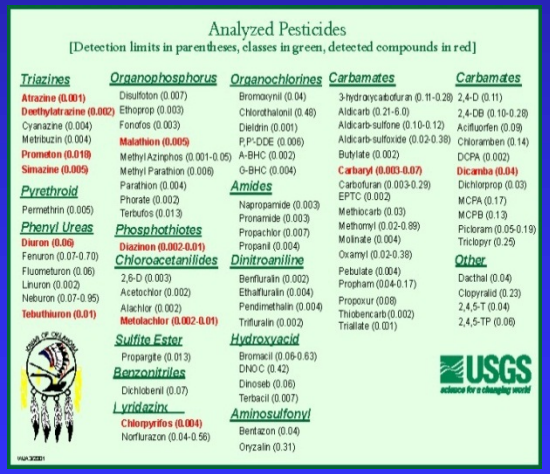
Environmental Fate Data

Measures of persistence

- Hydrolysis half-life
- Aerobic soil metabolism half-life
- Anaerobic soil metabolism half-life
- Field dissipation half-life

PCPA Requires DPR to:

Use those
data to identify pesticides
with the potential to
pollute GW



Analyzed Pesticides

[Detection limits in parentheses, classes in green, detected compounds in red]

Triazines
Atrazine (0.001)
Deethylatrazine (0.002)
Cyanazine (0.004)
Metribuzin (0.004)
Prometon (0.018)
Simazine (0.005)

Pyrethroid
Permethrin (0.005)

Phenyl Ureas
Diuron (0.06)
Fenuron (0.07-0.70)
Fluometuron (0.06)
Linuron (0.002)
Neburon (0.07-0.95)
Tebuthiuron (0.01)

Organophosphorus
Disulfoton (0.007)
Ethoprop (0.003)
Fonofos (0.003)
Malathion (0.005)
Methyl Azinphos (0.001-0.05)
Methyl Parathion (0.006)
Parathion (0.004)
Phorate (0.002)
Terbufos (0.013)

Phosphothiotes
Diazinon (0.002-0.01)

Chloroacetanilides
2,6-D (0.003)
Acetochlor (0.002)
Alachlor (0.002)
Metolachlor (0.002-0.01)

Sulfite Ester
Propargite (0.013)

Benzonitriles
Dichlobenil (0.07)

Lyridazin
Chlorpyrifos (0.004)
Norflurazon (0.04-0.56)

Organochlorines
Bromacynil (0.04)
Chlorothalonil (0.48)
Dieldrin (0.001)
P,P'-DDE (0.006)
A-BHC (0.002)
G-BHC (0.004)

Amides
Napropamide (0.003)
Pronamide (0.003)
Propachlor (0.007)
Propanil (0.004)

Dinitroaniline
Benfluralin (0.002)
Ethalfluralin (0.004)
Pendimethalin (0.004)
Trifluralin (0.002)

Hydroxyacid
Bromacil (0.06-0.63)
DNOC (0.42)
Dinoseb (0.06)
Terbacil (0.007)

Aminosulfonyl
Bentazon (0.04)
Oryzalin (0.31)

Carbamates
3-hydroxycarbofuran (0.11-0.28)
Aldicarb (0.21-6.0)
Aldicarb-sulfone (0.10-0.12)
Aldicarb-sulfoxide (0.02-0.38)
Butylate (0.002)
Carbaryl (0.003-0.07)
Carbofuran (0.003-0.29)
EPTC (0.002)
Methiocarb (0.03)
Methomyl (0.02-0.89)
Molinate (0.004)
Oxamyl (0.02-0.38)
Pebulate (0.004)
Propham (0.004-0.17)
Propoxur (0.08)
Thiobencarb (0.002)
Triallate (0.001)

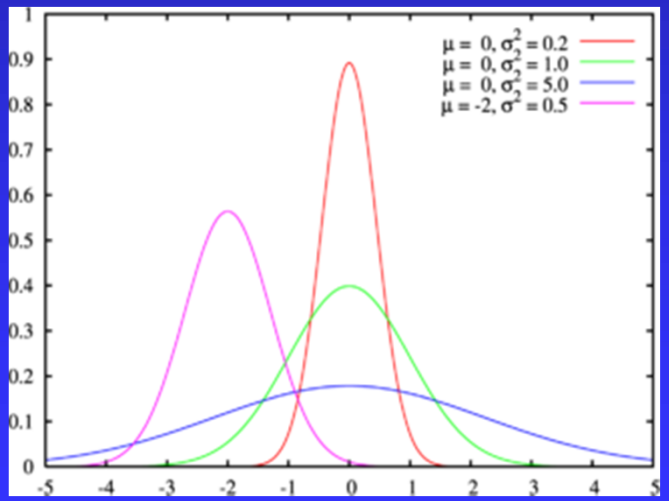
Carbamates
2,4-D (0.11)
2,4-DB (0.10-0.28)
Acifluorfen (0.09)
Chloramben (0.14)
DCPA (0.002)
Dicamba (0.04)
Dichlorprop (0.03)
MCPA (0.17)
MCPB (0.13)
Picloram (0.05-0.19)
Triclopyr (0.25)

Other
Dacthal (0.04)
Clopyralid (0.23)
2,4,5-T (0.04)
2,4,5-TP (0.06)

USGS science for a changing world

PCPA Requires DPR to:

Establish specific numerical values (SNVs) for mobility and persistence data types to distinguish leachers from nonleachers (EM Branch)



Pollution Potential

- Is it mobile?
- Is it persistent?

	Not Mobile	Mobile
Not persistent	Breaks down and doesn't move	
Persistent		

	Not Mobile	Mobile
Not persistent	Breaks down and doesn't move	Breaks down before moves to GW
Persistent		

	Not Mobile	Mobile
Not persistent	Breaks down and doesn't move	Breaks down before moves to GW
Persistent	Persists but doesn't move	

	Not Mobile	Mobile
Not persistent	Breaks down and doesn't move	Breaks down before moves to GW
Persistent	Persists but doesn't move	Can move to GW

PCPA Requires DPR to:

Annually list the pesticides that exceed at least one mobility SNV and at least one persistence SNV on the DPR Web site

GWPL

- 108 of ~300 agricultural pesticide active ingredients

PCPA Requires

All state and local agencies to submit results of all well sampling for pesticides to DPR

PCPA Requires DPR to:

Maintain a database of well sampling results

PCPA Requires

Annually on the DPR Web site:

- DPR to
  - summarize the latest sampling results
  - determine the possible sources
  - describe actions taken to prevent nonpoint source movement to GW
- SWRCB to describe actions taken to prevent point source movement to GW

PCPA Requires DPR to:

Monitor ground water and determine if detected pesticides are due to legal agricultural use

Ground Water Protection List (GWPL)

- 108 of ~300 agricultural pesticide active ingredients
- 7 AIs found in ground water due to agricultural use
- 101 AIs listed because they exceed the SNVs and include certain label language, including application to soil

PCPA Requires DPR to:

Formally review pesticides found in GW due to legal agricultural use to determine if continued use can be allowed

Formal Review

- Registrant requests a hearing and submits a specified report

Formal Review

- Registrant requests a hearing and submits a specified report
- Subcommittee of Pesticide Registration and Evaluation Committee (PREC) holds a hearing

Formal Review

- PREC Subcommittee
  - SWRCB member
  - OEHHA member
  - DPR member

Formal Review

- Subcommittee of PREC holding a hearing
- Makes 1 of 3 specified recommendations to DPR Director

Formal Review

- Subcommittee of PREC holding a hearing
- Makes 1 of 3 specified recommendations to DPR Director
- Director makes 1 of 3 findings or a contrary finding as specified

PCPA Requires DPR to:

Adopt regulations to modify use, if continued use can be allowed

California Code of Regulations

Title 3

Pesticides Regulated (Section 6800(a)) & Found in GW Due to Ag Use

- Atrazine
- Simazine - Princep®
- Bromacil – Hyvar®, Krovar®
- Diuron – Karmex®, Krovar®
- Prometon - Pramitol®
- Bentazon - Basagran®
- Norflurazon - Solicam®, Predict®, Zorial ®

Two Paths to Listing Pesticides on GWPL

- Exceed Specific Numerical Values for persistence and mobility + label language
- Found in ground water due to agricultural use

What We've Learned

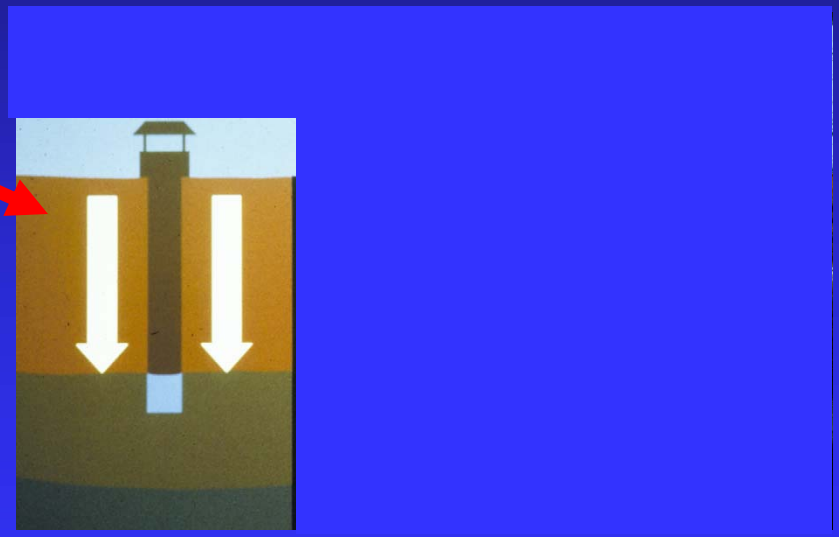
1. Pesticide detections in ground water are associated with certain soil types
   - coarse soils
   - hardpan soils
   - certain clay soils

What We've Learned

2. Pathway/mechanism of movement to ground water is different in a sandy soil vs. a hardpan and a cracking clay soil

Leaching

Downward movement of pesticides through the soil matrix, including the soil microbial zone

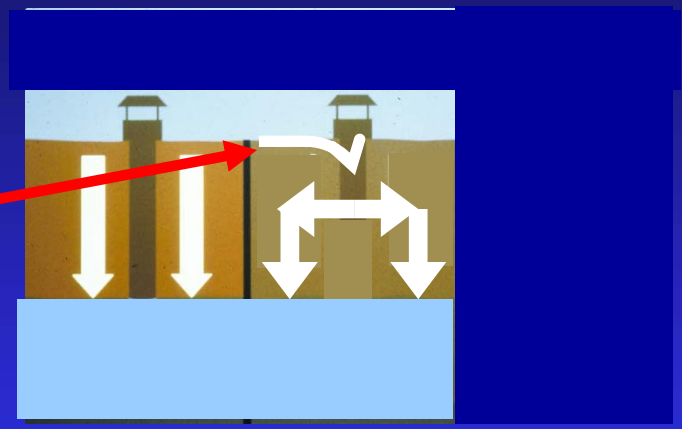


Runoff, Then Leaching

- Movement in surface water runoff to sensitive areas, such as:

Runoff, Then Leaching

- Dry wells



Runoff, Then Leaching

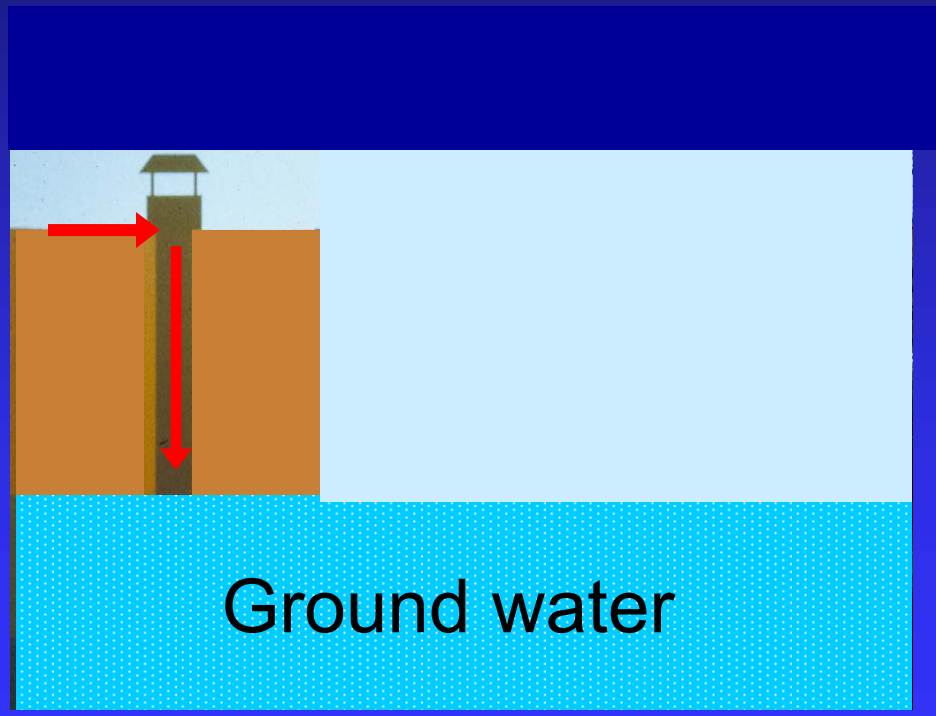
- Ditches dug below a confining soil layer

Runoff, Then Leaching

- Ponds

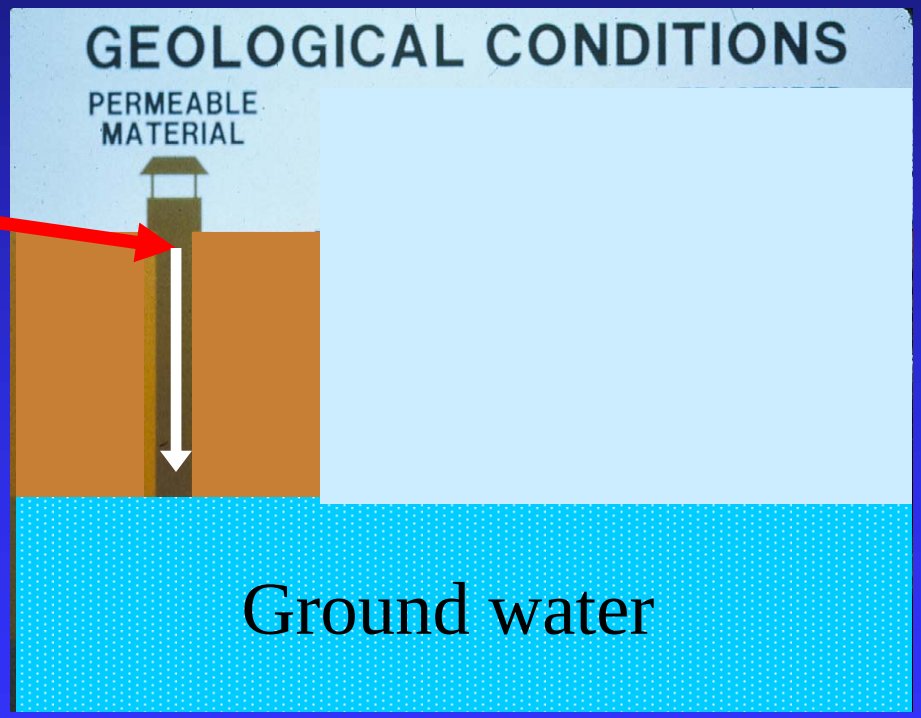
Runoff, Then Direct Movement to Ground Water

- Movement in surface water runoff to unprotected water wells



Direct Movement to Ground Water

Backflow during mixing/loading or chemigation directly into wells to ground water



What We've Learned

1. Pesticide detections in ground water are associated with certain soil types
2. Pathway/mechanism of movement to ground water varies
3. Pesticide detections in ground water are more likely at depths to ground water of 70 feet or less. (Spurlock)

What We've Learned

4. Rainfall is not significant source of water to leach pesticides to ground water in most ag areas

What We've Learned

5. Over-irrigation is the principal mechanism in leaching (coarse soil) areas

What We've learned

6. Rainfall runoff is the principal mechanism in runoff (hardpan, clay soil) areas because:
   - rainfall main source of water close to pre-emergent herbicide application
   - rainfall contacts 100% of area treated (vs. irrigation)

How Mitigate?

Mitigation in Leaching Areas

- Control irrigation

Mitigation in Runoff Areas

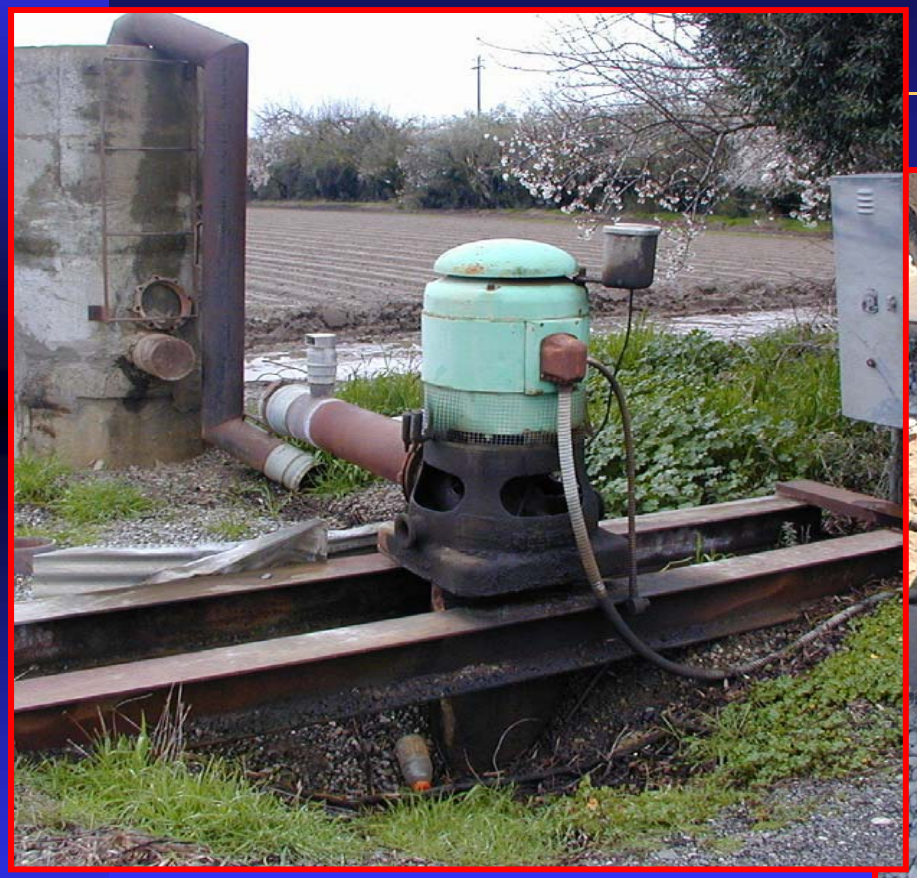
- Keep pesticide out of runoff water, or
- Manage contaminated runoff water

Ground Water Regulations

- Pesticides regulated – active ingredient
- GWPAs (1 square mile)
- Permit requirement
- Use restrictions inside GWPAs
- Statewide use restrictions (permit in GWPA)
- Wellhead protection from runoff
- Annual monitoring of 70-well network, detection level trending down

Well Sampling – The Good

Well Sampling – The Bad



Well Sampling – The WAY Bad

General Quality Control Requirements

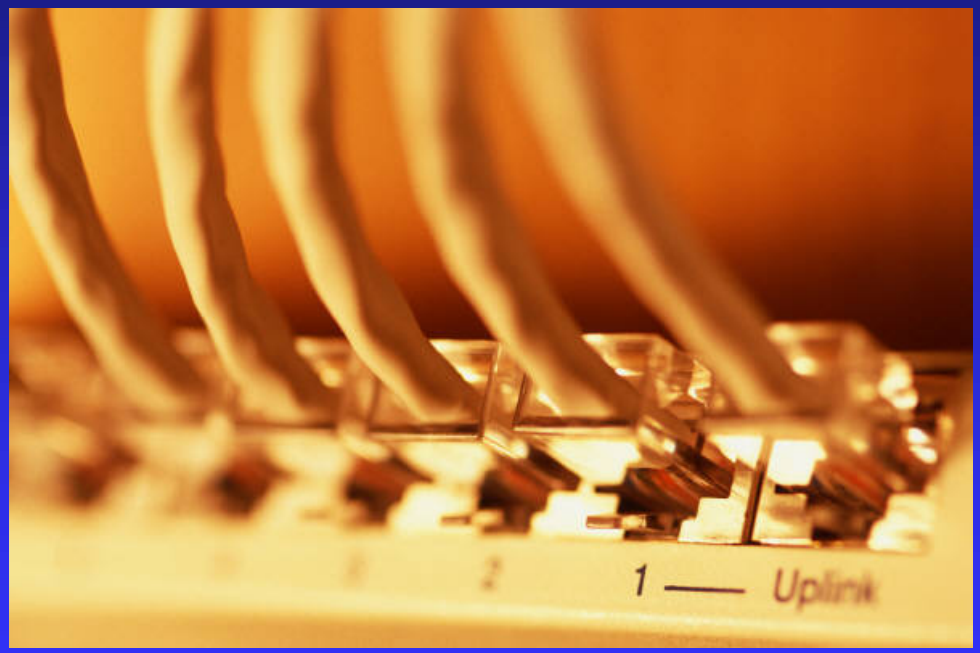
General Quality Control Requirements

- Written SOPs, lab methods, study protocols
- Method development – MDL US EPA method (40 CFR, Part 136, Appendix B)
  - RL set 1 – 5 times the MDL
  - Method Validation, Warning & Control Limits
  - Storage Stability

General Quality Control Requirements

- Required Continuing QC
  - Reagent blanks & blank-matrix spikes
    - Each extraction set
  - Analytical confirmation, split matrix samples, blind spikes
    - Based on number of samples / detections
- Optional Continuing QC -
  - Internal standard, replicate sample, replicate extract, and split extract analyses; reference material, standards exchange
    - Case by case basis, determined by project leader and lab liaison

Ground Water and Surface Water Databases



Ground Water Well Inventory Database

- Implemented in 1985
- Statewide sampling results –
  - DPR monitoring programs
  - Public agencies, including CDPH and SWRCB GAMA
- > 2 million sample results - >25,000 wells (most non-detect)
    - Mostly drinking water wells (one detection matched the MCL)
  - >360 pesticides and pesticide degradates
- Data available through annual report or custom queries and through GeoTracker GAMA
- Database managed with Oracle software
- Results incorporated into GAMA

Surface Water Database

- Implemented in 1997
- DPR Monitors in agricultural and urban areas
- Data received from many sources, most from water boards, state agencies, USGS, UC, cities, others

Surface Water Database

- Surface water database includes 375,000 records
- Plan to test Google Fusion Tables for improved data availability and manipulation
- DPR collected ~750 samples in 2011
- Data and summaries available on DPR website
- Data managed with Oracle software

Collaboration

- CCRWQCB (Region 3)
  - Mitigation project for chlorpyrifos (OP pesticide) in surface water
- CVRWQCB (Region 5)
  - Coordinating policy issues response to comments about pesticides in ground water

Collaboration

- Assistant Executive Officers of Regional Water Boards
  - Collaborating on water/pesticide issues – pyrethroid regulation effectiveness
- SWRCB
  - Management Agency Agreement – serves as mechanism for information exchange
  - Participated in GAMA interagency taskforce

Evaluation of New Substances

Evaluation of New Substances

- Air, Surface Water and Ground Water receive data packages from DPR Registration Branch

Evaluation of New Substances

- Air, Surface Water and Ground Water receive data packages from Registration
- May be new AI, change in registration, or new data submittal for evaluation

Evaluation of New Substances

- Air, Surface Water and Ground Water receive data packages from Registration
- May be new AI, change in registration, or new data submittal for evaluation
- What is the potential for future problems with the new AI, registration or site?

Evaluation of New Substances

- Each program uses computer modeling or data-driven recommendation systems

Evaluation of New Substances

- Each program uses computer modeling or data-driven decision systems
- Models use combination of variables and constants

Evaluation of New Substances

- Each program uses computer modeling or data-driven decision systems
- Models use combination of variables and constants
- Persistence, mobility, toxicity or risk

Evaluation of New Substances

- Each program uses computer modeling or data-driven decision systems
- Models use combination of variables and constants
- AI persistence, mobility, toxicity or risk
- Use patterns

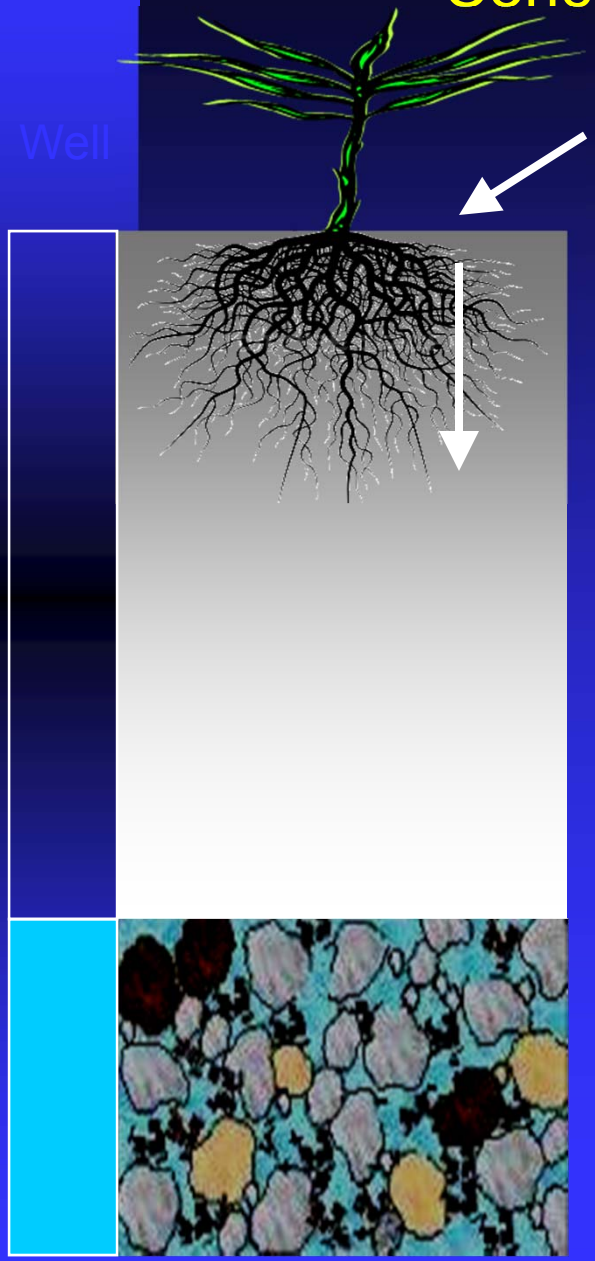
Evaluation of New Substances

- Each program uses computer modeling or data-driven decision systems
- Models use combination of variables and constants
- AI persistence, mobility, toxicity or risk
- Use patterns
- Statistical or probabilistic analysis

Indicators – Surface Water

Indicators	Input parameters	Approaches
Runoff potential	Adsorption coefficient (KOC), Field dissipation half-life, Water solubility	USDA WIN-PST model
Aquatic persistence	Half-lives in water and sediment	Critical values of 30 and 100 days of half-lives
Aquatic toxicity	Acute toxicity (LC50) for sensitive species	▪ In water: USEPA criteria ▪ In sediment: DPR criteria
Use pattern	Use pattern	High-exposure patterns identified by DPR scientists
Risk quotient	Label rate, use pattern, KOC, aerobic soil metabolism half-life, LC50	▪ USEPA PRZM, simplified ▪ USEPA Tier I Rice Model

Conceptual Modeling Process Ground Water

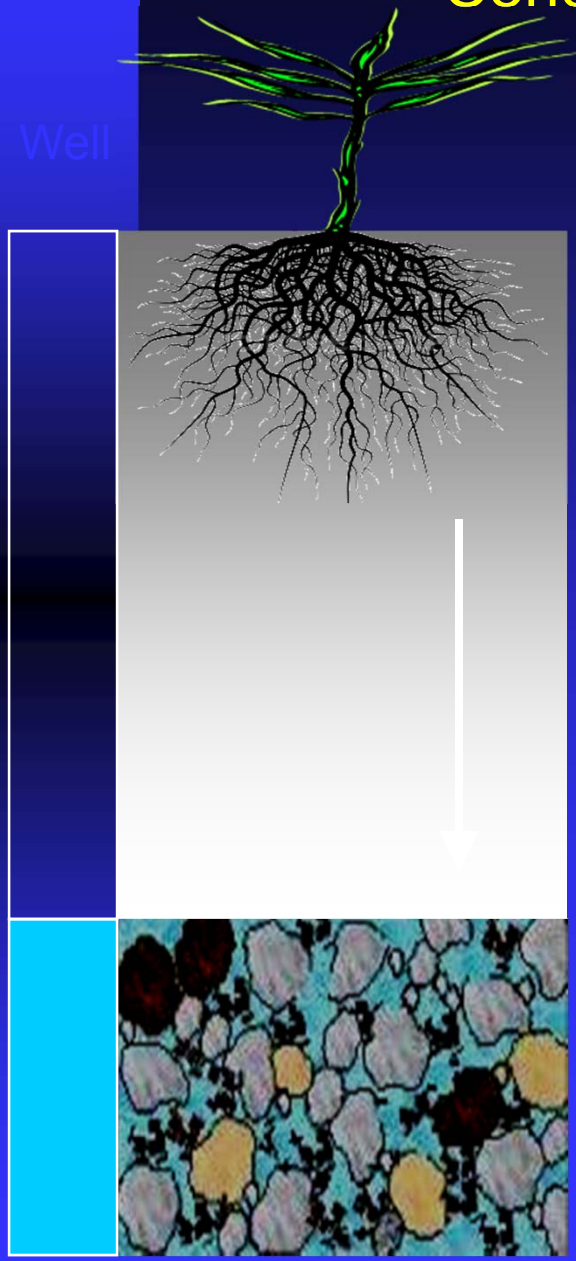


Pesticide and water inputs

Root Zone:

- LEACHM simulates pesticide and water inputs, plant growth, and pesticide soil adsorption and degradation processes.
- Estimates steady-state leaching below root zone.

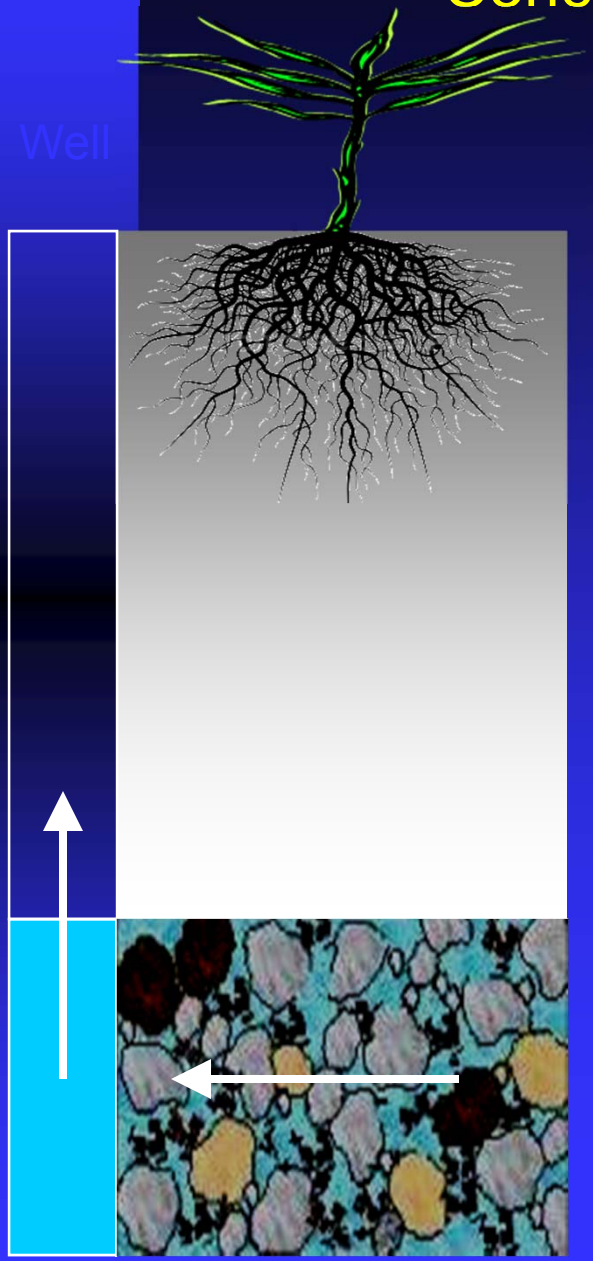
Conceptual Modeling Process Ground Water



Subsoil:

- Sorption processes assumed negligible.
- Movement of residues to 20 m modeled with velocity estimate (5 m/year).
- Residue dissipation according to longest TFD half-life rate.

Conceptual Modeling Process Ground Water



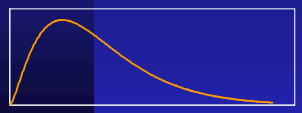
Ground water:

- Residues diluted in 0.5 m depth of annual recharge water.
- Residues aged 6 years to simulate time to reach a well.
- If hydrolysis rates unavailable, residue dissipation according to longest TFD half-life.

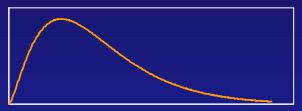
Conceptual Probabilistic Approach Ground Water

Distributional input

- Koc
- Terrestrial field dissipation rate



LEACHM predicted mass leached below root zone



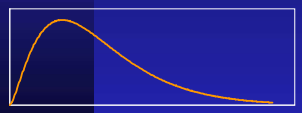
Input constants

- Chemical application
- Water applications
- Chemical properties
- Climate data
- Soils data
- Hydraulic properties

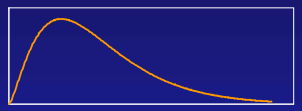
Conceptual Probabilistic Approach Ground Water

Distributional input

- Koc
- Terrestrial field dissipation rate



LEACHM predicted mass leached below root zone



Input constants

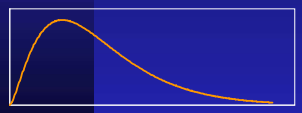
- Chemical application
- Water applications
- Chemical properties
- Climate data
- Soils data
- Hydraulic properties

Empirical-based dissipation of pesticide in vadose zone and ground water

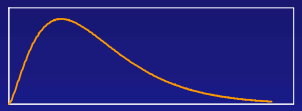
Conceptual Probabilistic Approach Ground Water

Distributional input

- Koc
- Terrestrial field dissipation rate



LEACHM predicted mass leached below root zone

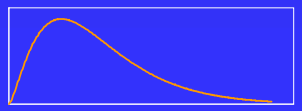


Input constants

- Chemical application
- Water applications
- Chemical properties
- Climate data
- Soils data
- Hydraulic properties

Empirical-based dissipation of pesticide in vadose zone and ground water

Distribution of well water concentrations



Probabilistic Model - Leaching To Ground Water

Distributional input

- Koc adsorption values
- Terrestrial field dissipation rate

⇒ Mass leached below root zone for 1000 model runs ⇐

Input constants

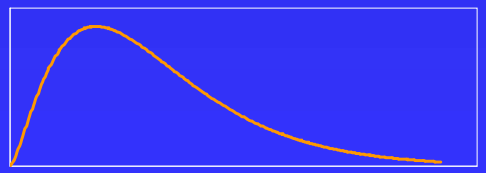
- Chemical application
- Water applications
- Chemical properties
- Climate data
- Soils data
- Hydraulic properties

⇓

Residues dissipated in vadose zone and groundwater aquifer for 10 years using longest reported TFD value

⇓

Distribution of concentration in well water from 1000 runs



⇐ 95th percentile Not above 0.05 ug/L

Not a leacher. No further action

⇒ 95th percentile above 0.05 ug/L

Potential leacher. More data required

Evaluation Results

- Registration recommendations
  - Support without condition
  - Support and request analytical methods
  - Do not support
- Watch list
  - Request analytical methods and consider for post-use monitoring
  - Flag the AI for further evaluation if a new label is associated with high-exposure use pattern