

# Mixtures in the soil environment

(seen in the context of any EU soil directive)

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# THE SOIL FRAMEWORK DIRECTIVE



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Perhaps not such  
a mythical beast

It is real

It is in (slow)  
progress



COUNCIL OF  
THE EUROPEAN UNION

Brussels, 4 March 2010

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Interinstitutional File:  
2006/0086 (COD)

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6124/1/10  
REV 1

LIMITE

ENV 64  
AGRI 35  
DEVGEN 42  
FORETS 19  
FSTR 5  
RECH 40  
REGIO 5  
TRANS 27  
CODEC 89

## REVISED NOTE

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from : General Secretariat  
to : Committee of the Permanent Representatives  
No. prev. doc. : 5772/10 ENV 44 AGRI 28 DEVGEN 37 FORETS 15 FSTR 2 RECH 23  
REGIO 2 TRANS 18 CODEC 61  
No. Cion prop. : 13388/06 ENV 495 AGRI 305 DEVGEN 232 FORETS 32 FSTR 64 RECH 242  
REGIO 53 TRANS 246 CODEC 1012 - COM(2006) 232 final  
Subject : **PREPARATION OF THE COUNCIL (ENVIRONMENT) MEETING ON  
15 MARCH 2010**  
Proposal for a Directive of the European Parliament and of the Council  
establishing a framework for the protection of soil  
- Progress report

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## I. INTRODUCTION

1. The Commission submitted its proposals for a Thematic Strategy for soil protection and a Proposal for a Directive establishing a framework for the protection of soil to the Council on 25 September 2006. The proposal for a Directive is based on Article 192(1) of the Treaty on the Functioning of the European Union.

# DEFINING SOIL ECOSYSTEM SERVICES

- food and other biomass production
- storing, filtering and transforming nutrients, substances and water
- basis for life and biodiversity, such as habitats, species and genes
- physical and cultural environment
- source of raw materials and products
- acting as carbon reservoir
- archive of geological and archaeological heritage

# DEFINING SOIL ECOSYSTEM SERVICES

- food and other biomass production
- storing, filtering and transforming substances and water
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- physical and chemical processes
- carbon and products
- reservoir
- geological and archaeological heritage

Soil is really pretty important stuff

# THREATS TO SOIL SERVICES

## Soil Degradation

- erosion by water or wind
- organic matter decline
- compaction
- salinisation
- landslides
- acidification

**Contamination (treated as a separate issue)**

# SFD AND CONTAMINATED SITES

## *Article 10 : Identification and inventory of contaminated sites*

A flexible procedure for identification of contaminated sites

- through identifying potentially soil-contaminating activities
- by following a Member States prioritisation procedure
- states can set a deadline for finalisation of the contaminated sites inventory

Strong concerns in relation to the provisions on the risk assessment methodology for identifying contaminated sites - SFD states this can be left to Member States to determine.

# SFD AND MIXTURES

**BRGM (Bureau de Recherches Géologiques et Minières) advice :**

**“Mixtures is considered as a technical issues, and not policy one.” and therefore is not covered in the current SFD proposal.**

**Member states could suggest the inclusion of Mixtures in national legal & technical frameworks, but such details would be likely to become problematic for any harmonization at European level (e.g. how to define acceptable risks for mixtures? Which mixtures?)**

## **Summary of current policy position**

**Better to have a framework directive on soil (as is available now for water) instead of nothing**

# COUNTRY SPECIFIC POLICIES

## Many countries have policies and guidance

- human health
- ecological risk assessment
- integrated approaches (ecosystem services)



using science to create a better place



An ecological risk assessment framework for contaminants in soil

Science report SC070009/SR1

# TYPICAL RISK ASSESSMENT STRUCTURE

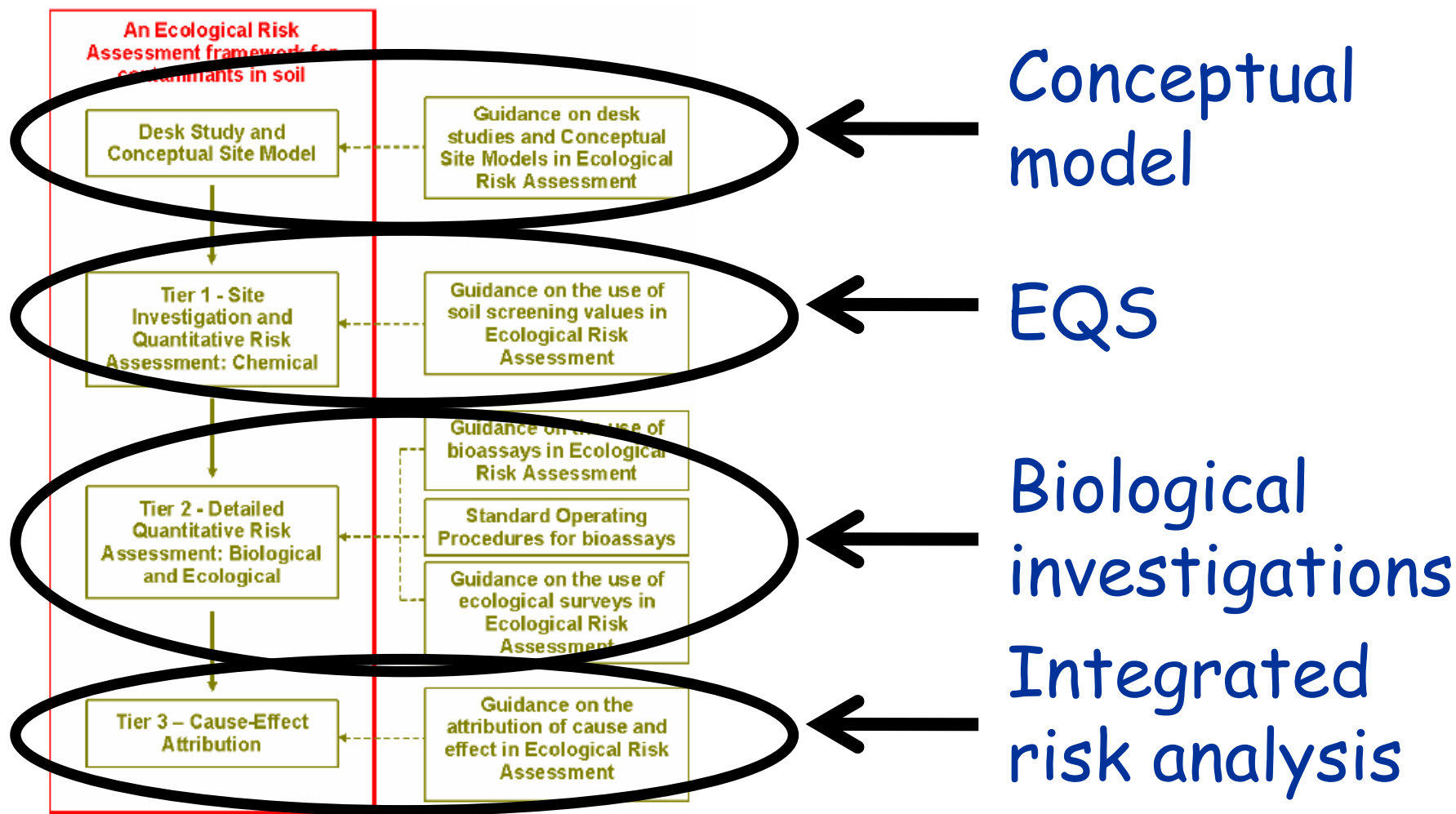


Figure 1.1 Position of this document within the overall ERA framework

# TYPICAL RISK ASSESSMENT STRUCTURE

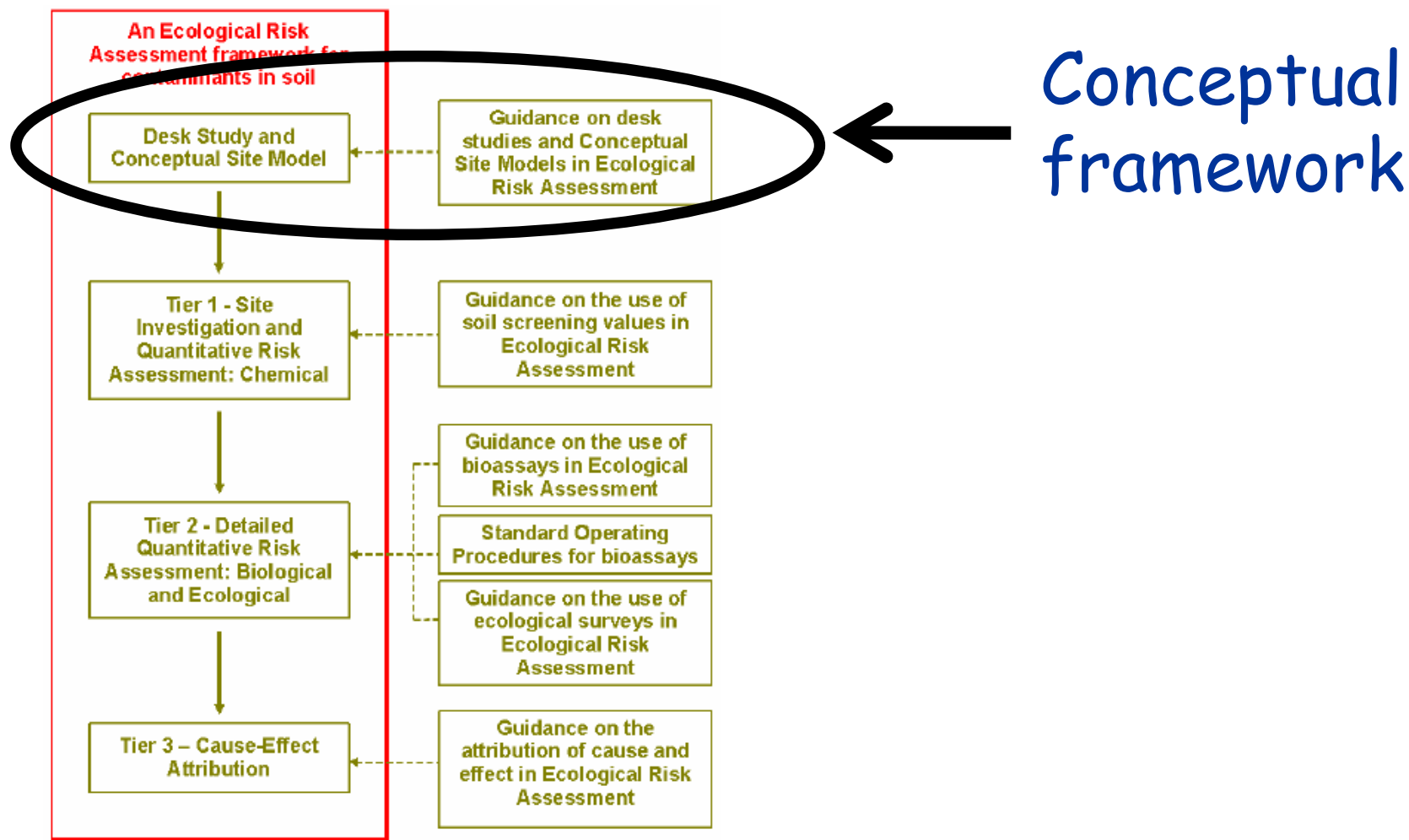


Figure 1.1 Position of this document within the overall ERA framework

# ESTABLISH SOURCES



# TYPICAL RISK ASSESSMENT STRUCTURE

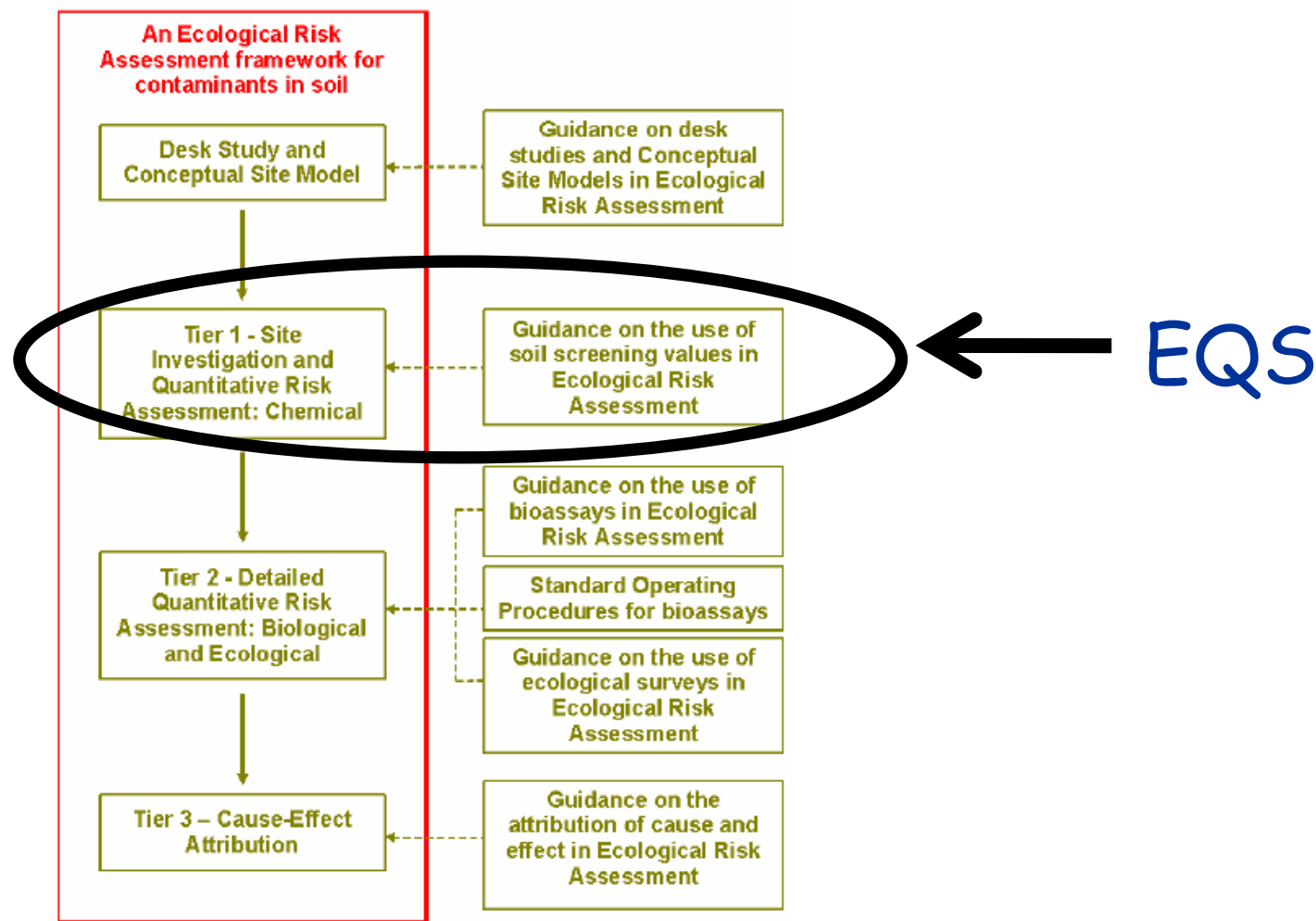
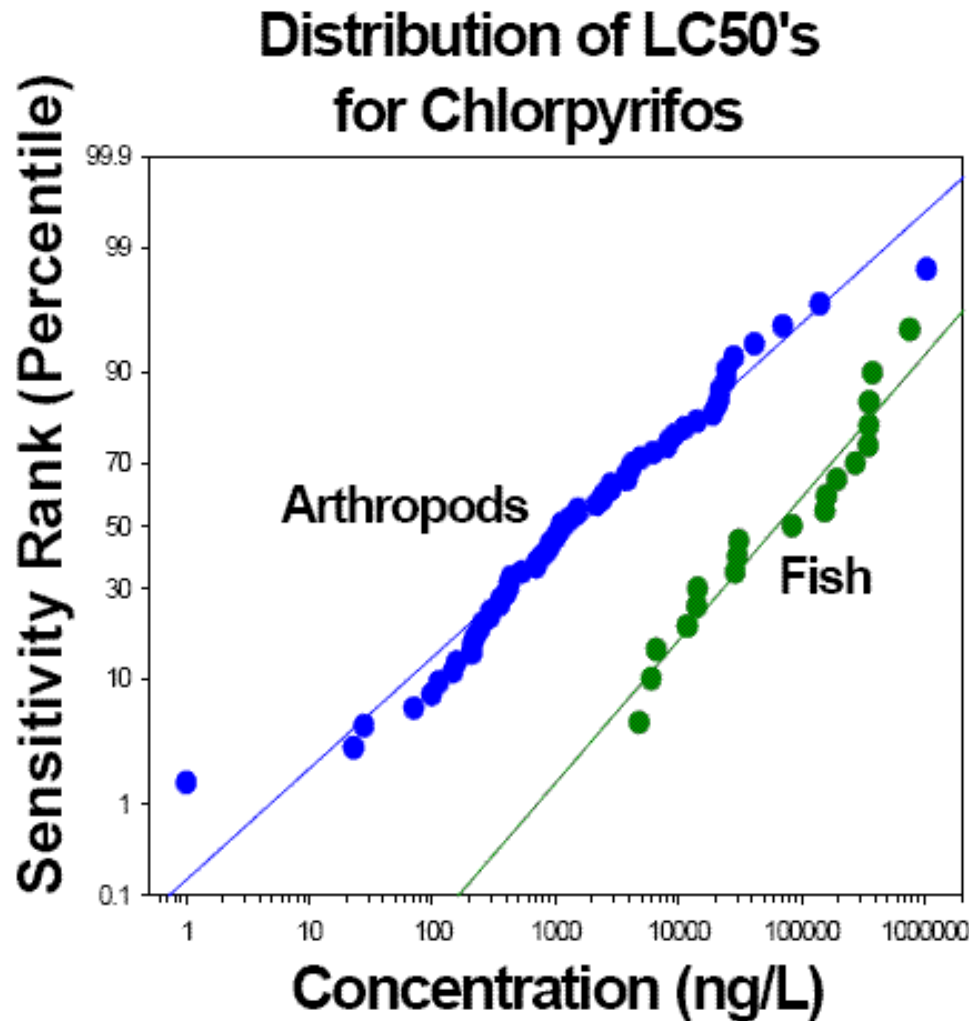


Figure 1.1 Position of this document within the overall ERA framework

# DERIVING EQS VALUES

## By species sensitivity distribution



- Order species by sensitivity to chemical
- Use of define level that would protect a certain percentage of species (e.g. 95%)
- Use as a protection value in policy

# PRIORITY CONTAMINANTS

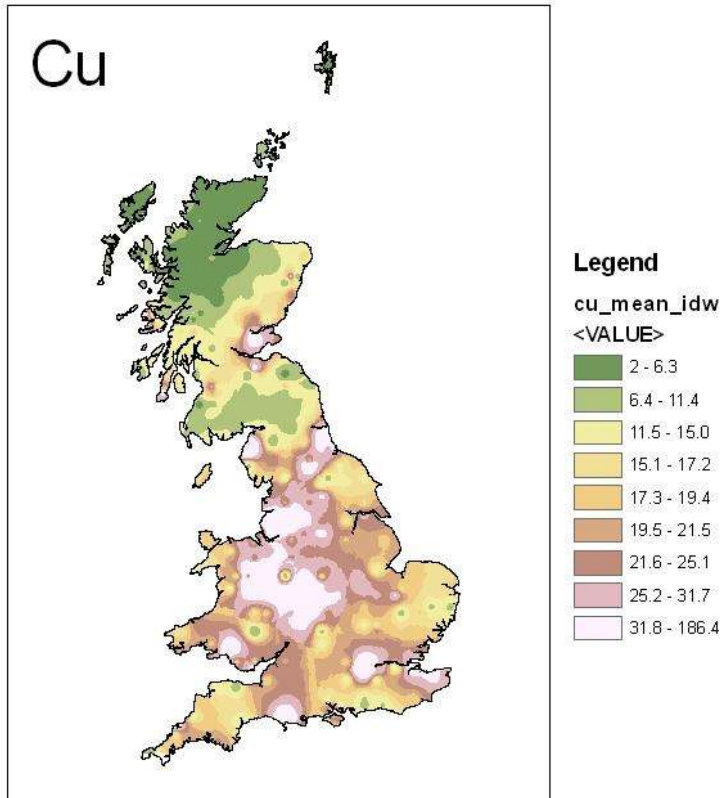
## Focus on the “usual suspects”

- metal processing
- oil and coal gas processing
- legacy pesticides and POPs
- chlorinated solvents

Metals	Arsenic	Polycyclic aromatic hydrocarbons (PAHs)	Polycyclic aromatic hydrocarbons (PAHs)
	Beryllium		Benzo(a)pyrene
Organometals	Cadmium	Chlorinated hydrocarbons	Anthracene
	Copper		Naphthalene
	Lead		1,2,4-trichlorobenzene
	Mercury		Tetrachlorobenzene
	Nickel		Pentachlorobenzene
	Selenium		1,2-Dichloroethane
	Zinc		1,1,1,-Trichloroethane
Inorganics	Organolead compounds	Trichloroethene	
	Organotin compounds, e.g. tributyltin	Tetrachloroethene	
Aromatics	Cyanides	Pentachlorophenol	
	Total petroleum hydrocarbons (TPH)	Chlorotoluenes	
	Benzene	Vinyl chloride	
	Toluene	Chloroform	
	Ethylbenzene	Hexachlorobuta-1,3-diene	
	Xylene(s)	Polychlorinated biphenyls (total)	
Pesticides	Phenol	Dioxins and furans	
	Dieldrin		
	DDT (total)		
	HCH (total)		

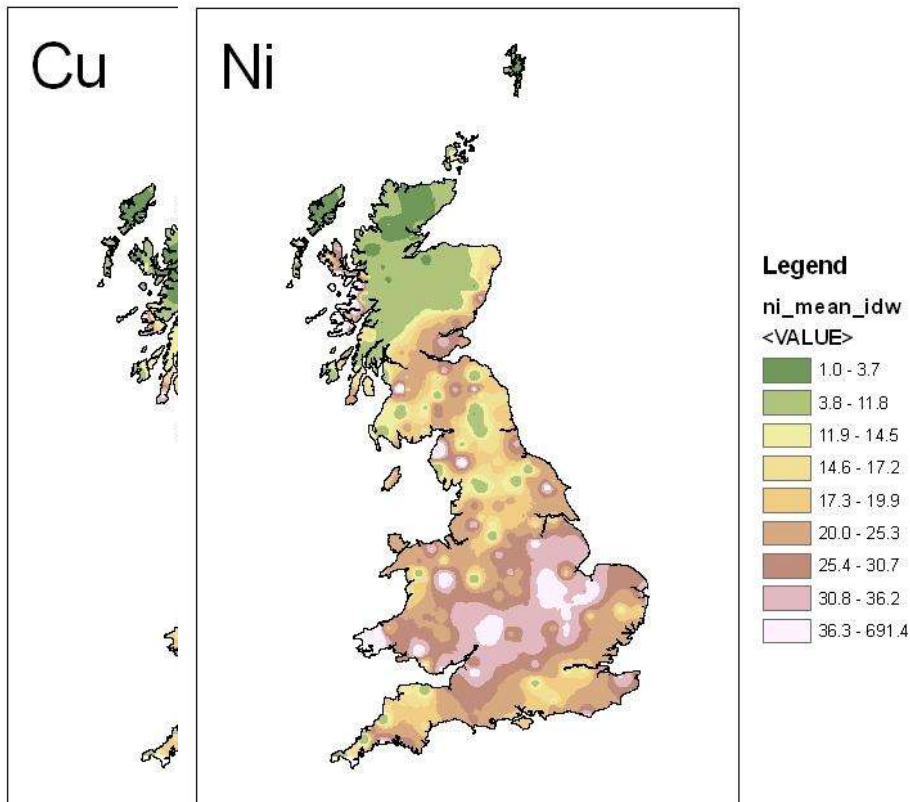
# MIXTURES

Universal (near) truth - Pollutants do not occur in isolation



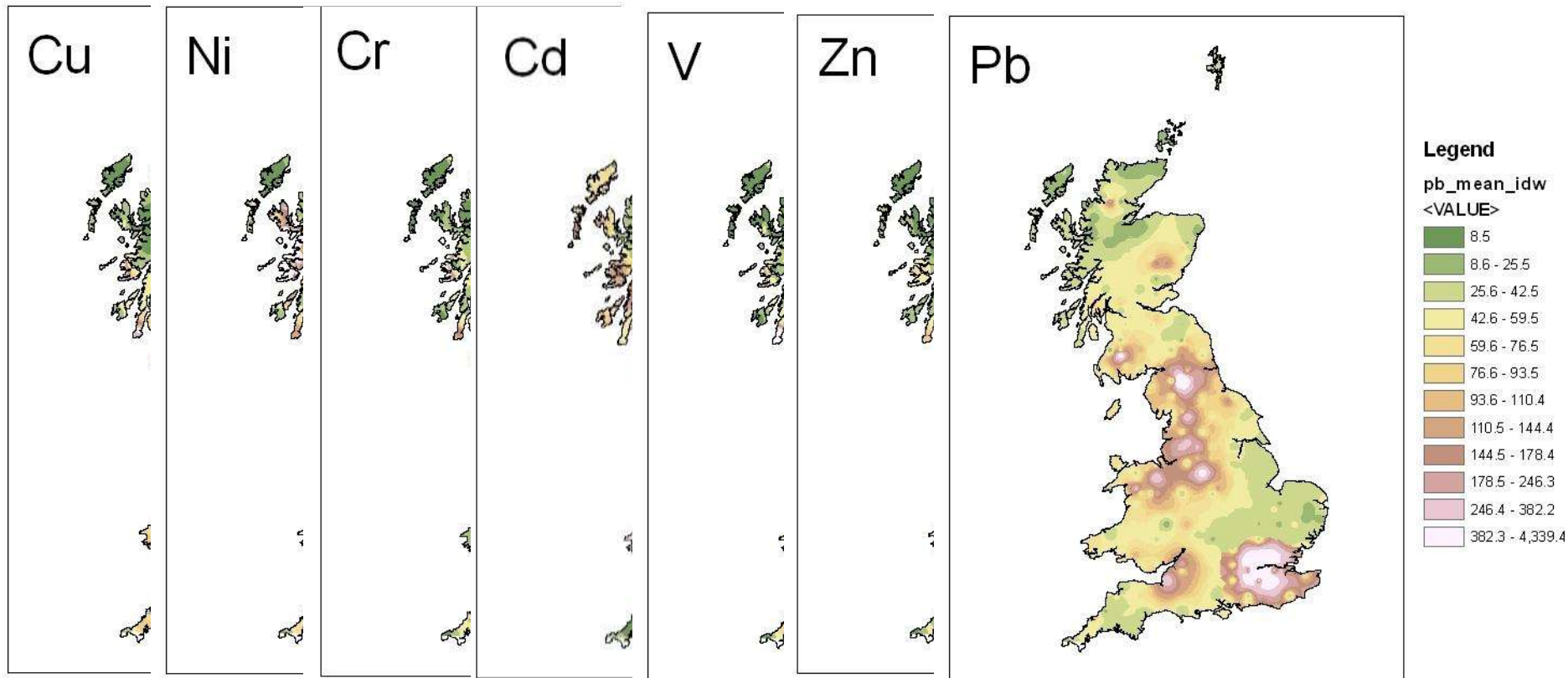
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# MIXTURES

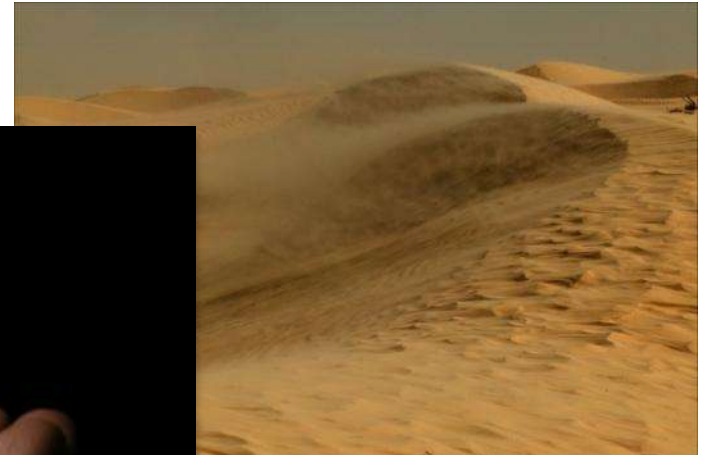
Universal (near) truth - Pollutants do not occur in isolation



Current risk assessment practice does not recognise this

# MULTIPLE STRESSORS

## Chemicals not in isolation of other stressors



# TYPICAL RISK ASSESSMENT STRUCTURE

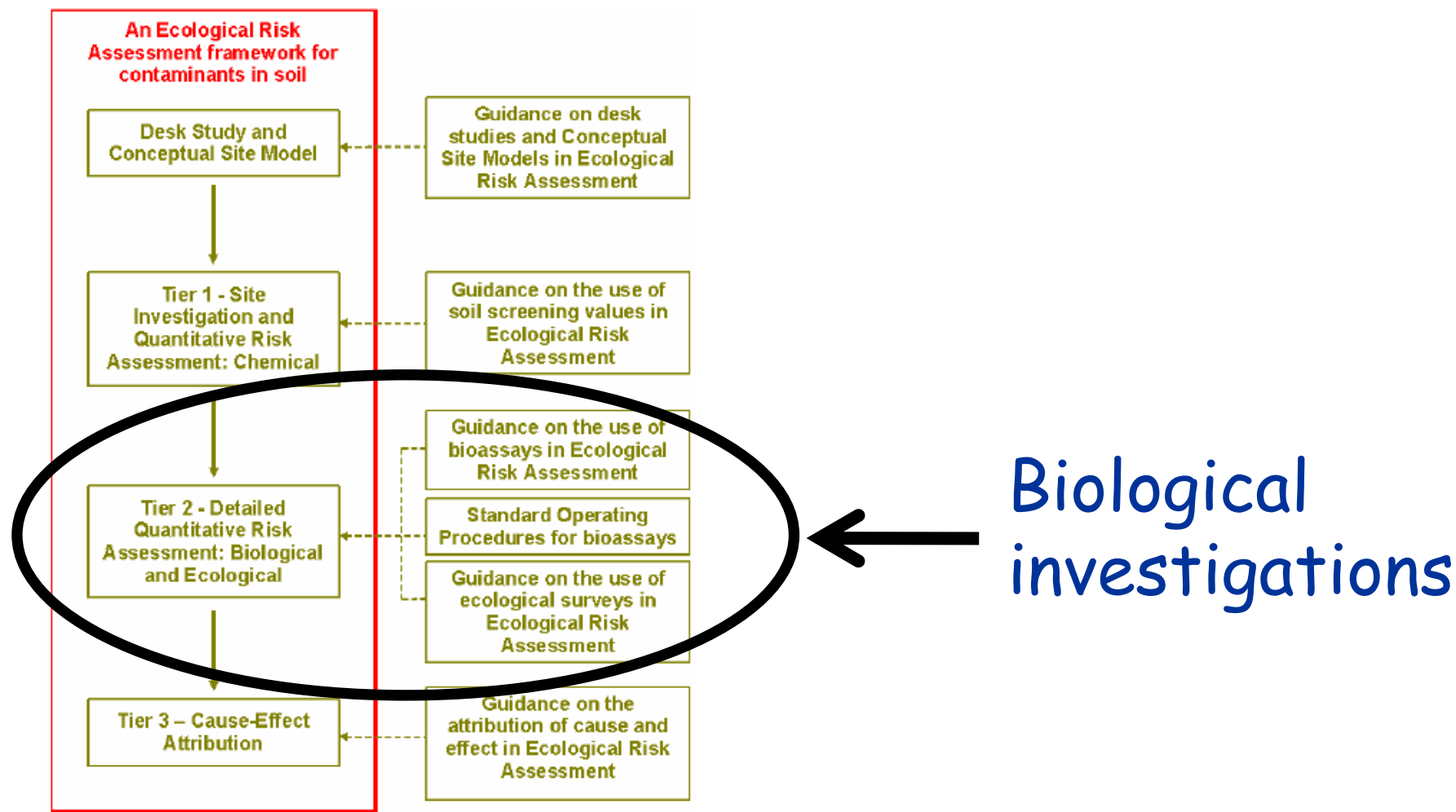


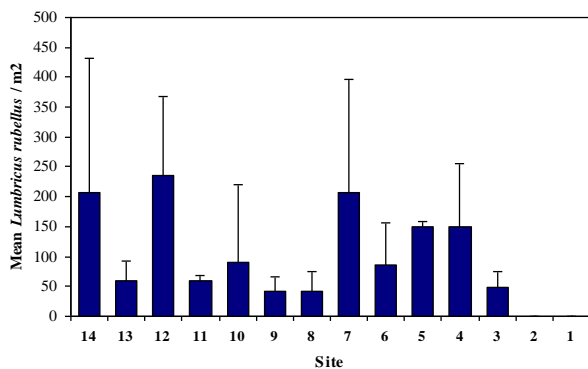
Figure 1.1 Position of this document within the overall ERA framework

# ECO-SURVEY OR BIOASSAY

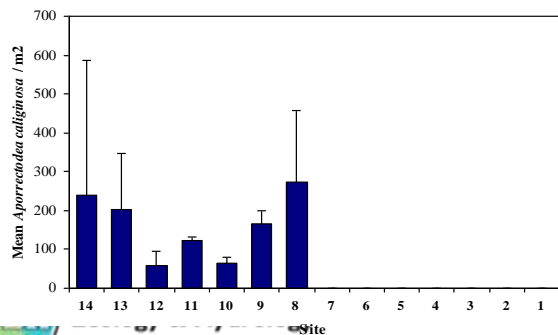
## Earthworms

### Species abundance

#### *Lumbricus rubellus*

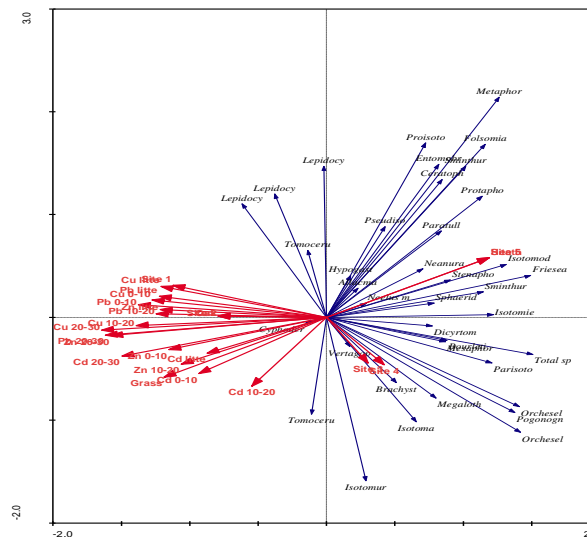


#### *Aporrectodea caliginosa*

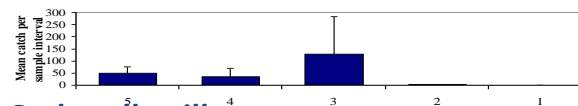


## Springtails

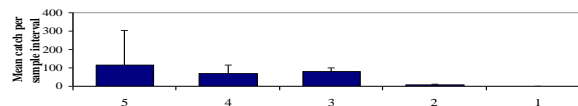
### Community composition



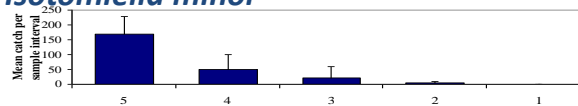
#### *Orchesella cincta*



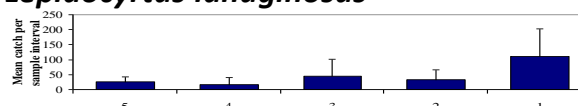
#### *Orchesella villosa*



#### *Isotomiella minor*



#### *Lepidocyrtus lanuginosus*



# TYPICAL RISK ASSESSMENT STRUCTURE

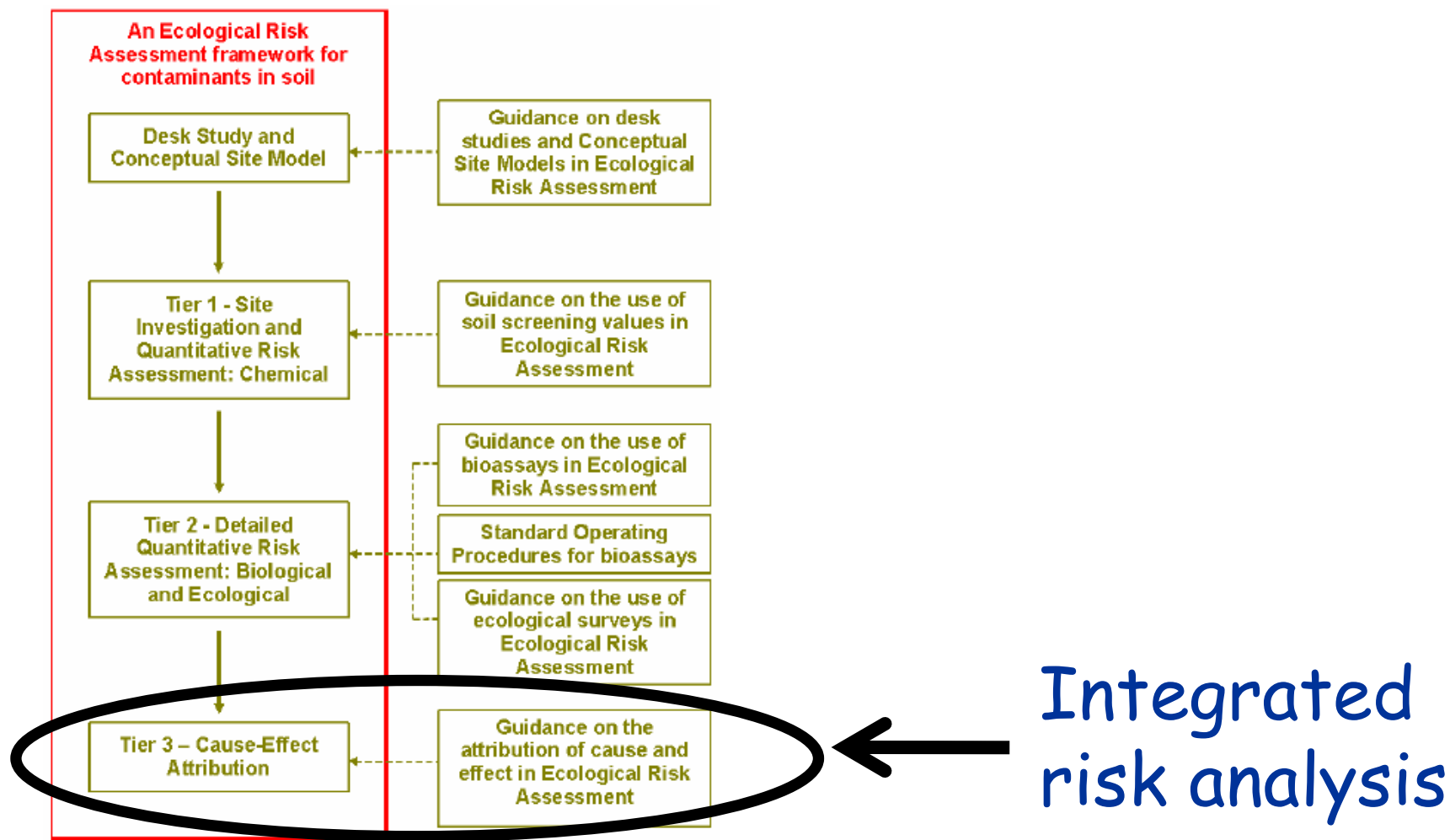


Figure 1.1 Position of this document within the overall ERA framework

Linking exposure and effects in mixtures risk assessment still remain a research question

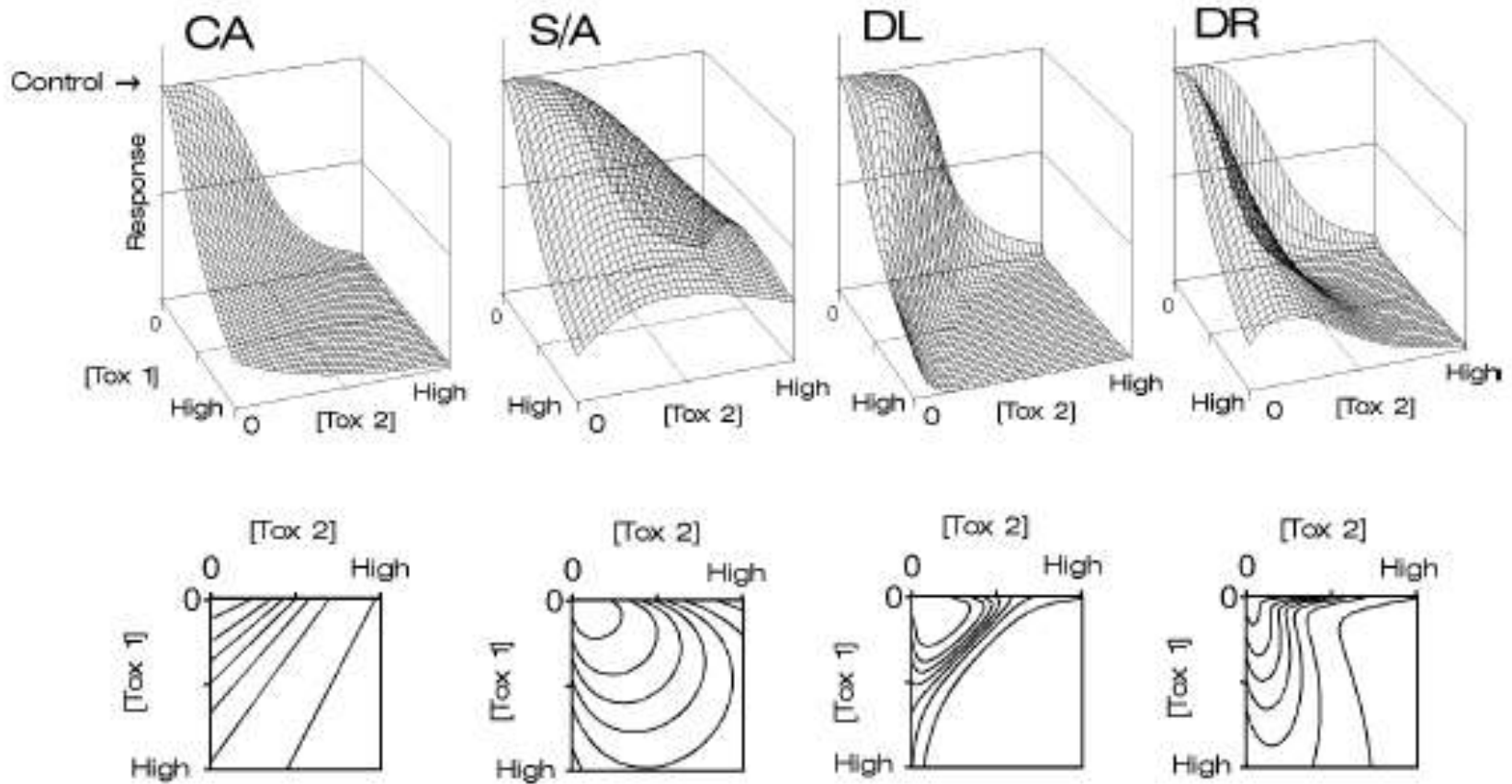
SO WHAT DOES SOME OF THE RESEARCH SAY?

# MIXTURE THEORY: THE BASICS

<i>The 4 classes of joint effect</i>	No interaction (additive)	Interaction (non-additive)
Similar action	Simple similar action	Complex similar action
Dissimilar action	Independent action	Dependent action

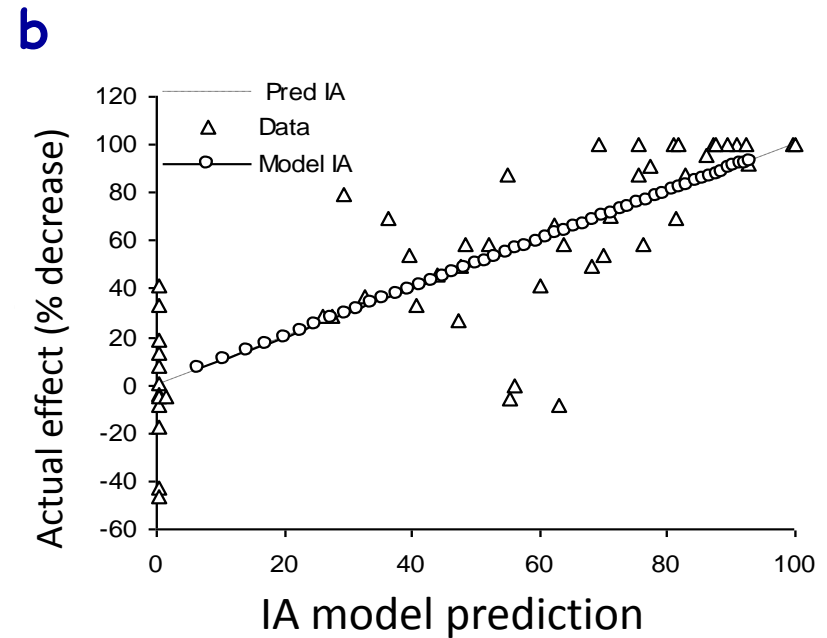
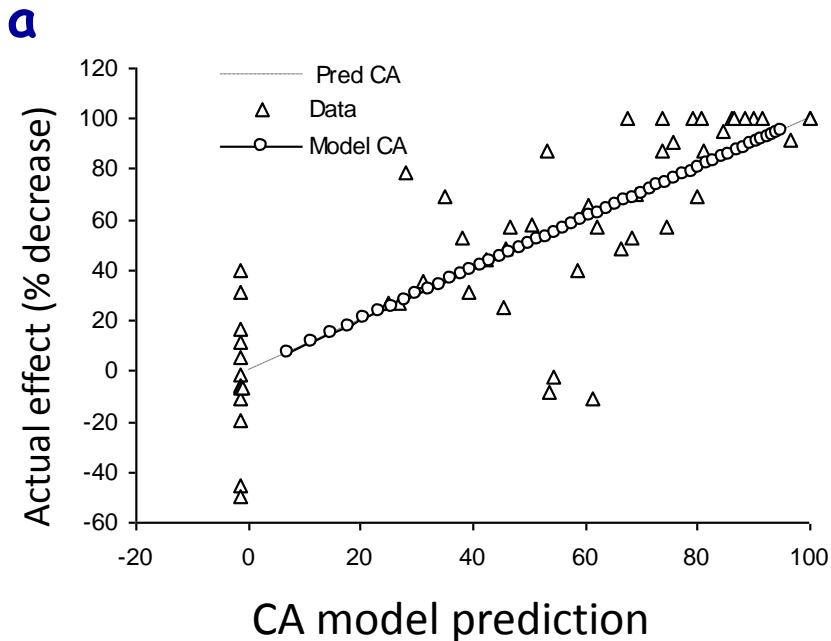
# MIXTURE ANALYSIS IN DETAIL

1) CA & IA  $\xrightarrow{\text{Add parameter "a"}}$  2) S/A  $\xrightarrow{\text{Add parameter "b"}}$  3A) DL or 3B) DR



# MIXTURES PRACTICE

- Exposed *L. rubellus* to the pesticide chlorpyrifos and metal nickel
- Exposure 28 day in natural soil
- Measured effect on cocoon production

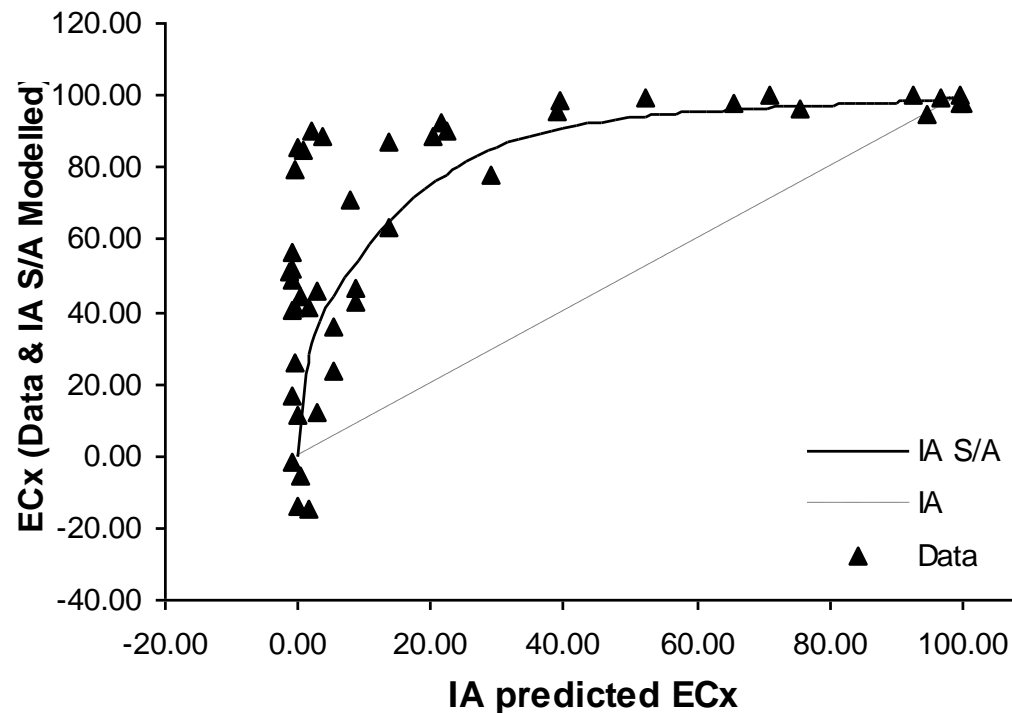


**Conclusion - This stressor mixture is additive (can't tell how)**

# MIXTURES PRACTICE

## An example: Cd + diuron in *C. elegans*

Predict EC<sub>x</sub> values by IA and S/A models and compare to data

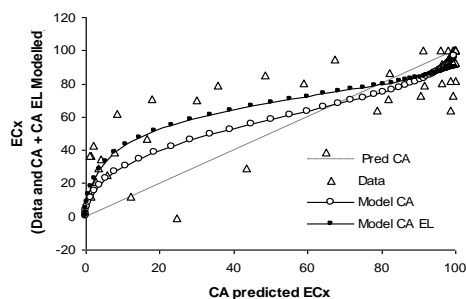


Conclusion - This binary mixture is synergistic

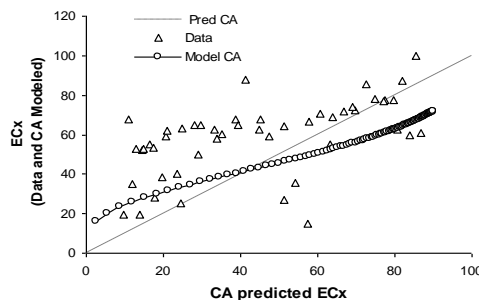
# MIXTURES – A SURVEY

Mixtures of pesticides (Organophosphates (Chlp, Diaz), pyrethroids (Perm) and neonicotinoids (Imid, Thia)).

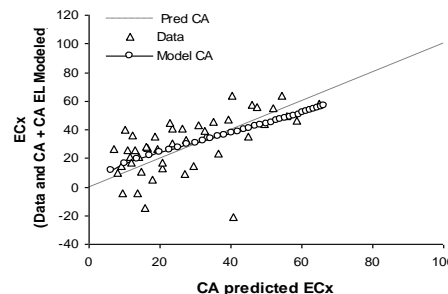
A Clp x Diaz



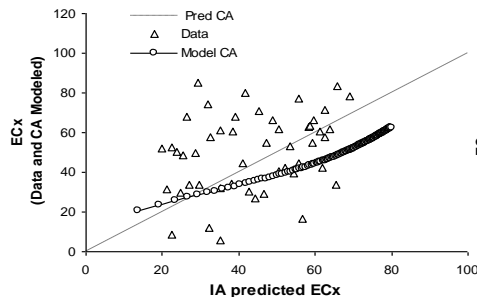
B – Imid x Thia



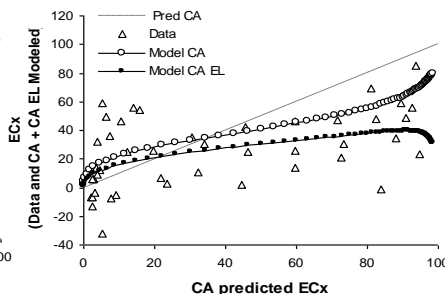
C – Perm x Imid



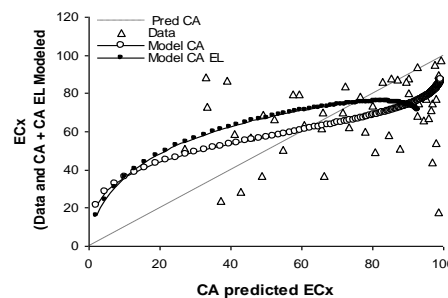
D – Perm x Thia



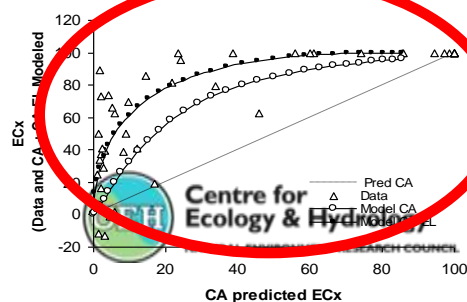
E – Perm - Clp



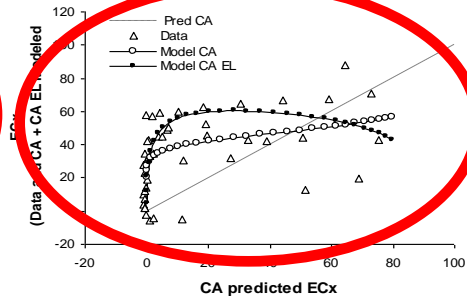
F – Perm - Diaz



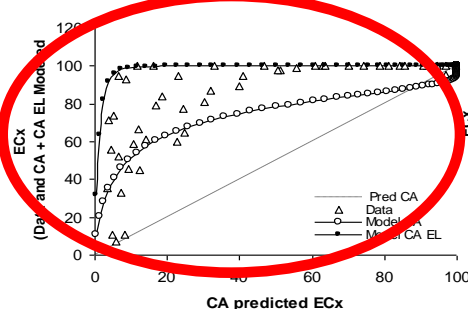
G – Clp x Imid



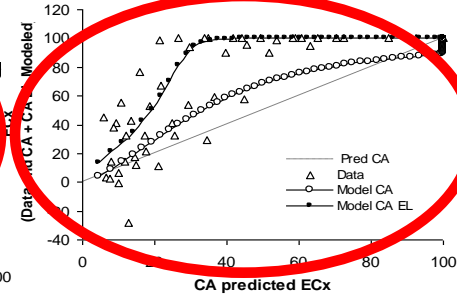
H – Clp x Thia



I – Diaz x Imid



J Diaz x Thia



# MIXTURES – A SURVEY

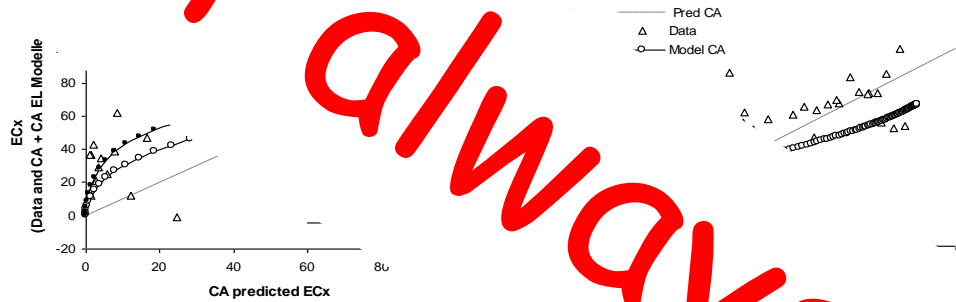
of pesticides (Organophosphates (Chlp, Diaz),  
(Perm) and neonicotinoids (Imid, Thia).

Not

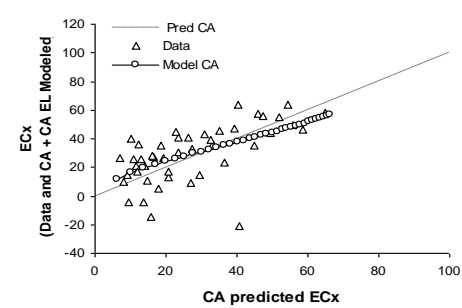
always

additive

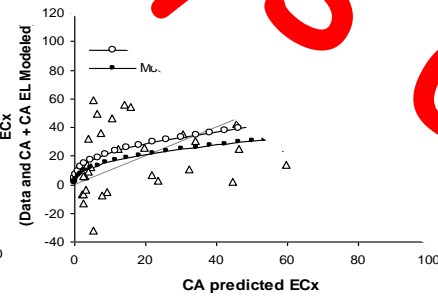
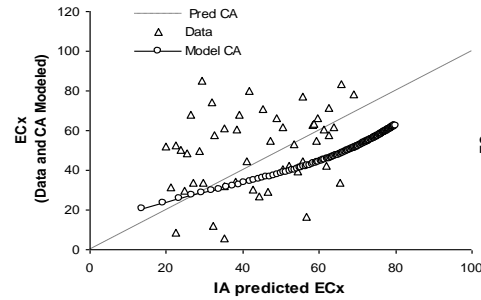
B – Imid x Thia



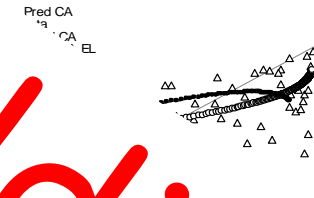
C – Perm x Imid



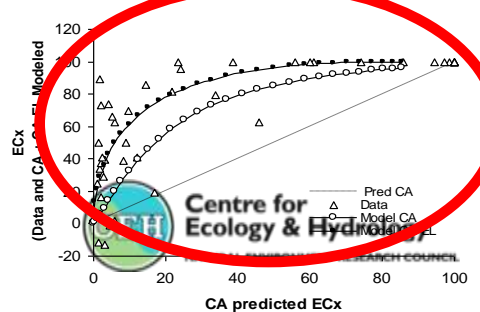
D – Perm x Thia



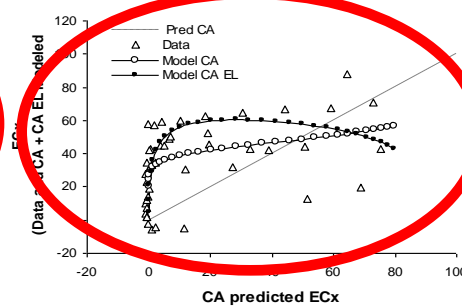
F – Perm - Diaz



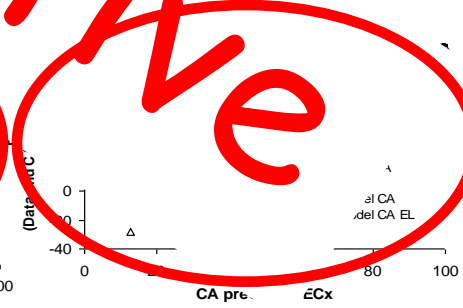
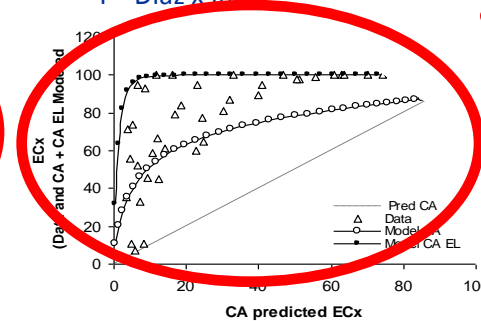
G – Clp x Imid



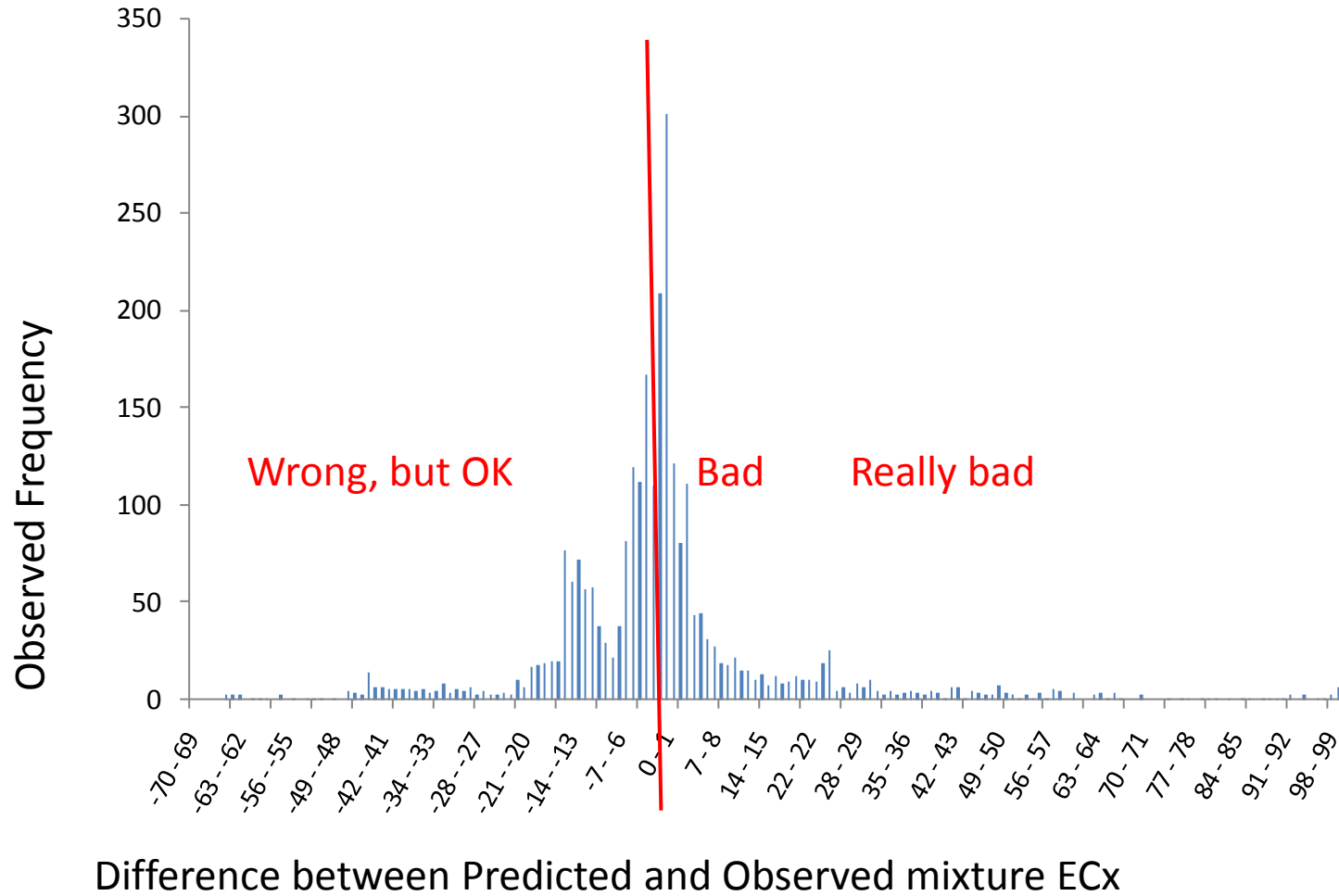
H – Clp x Thia



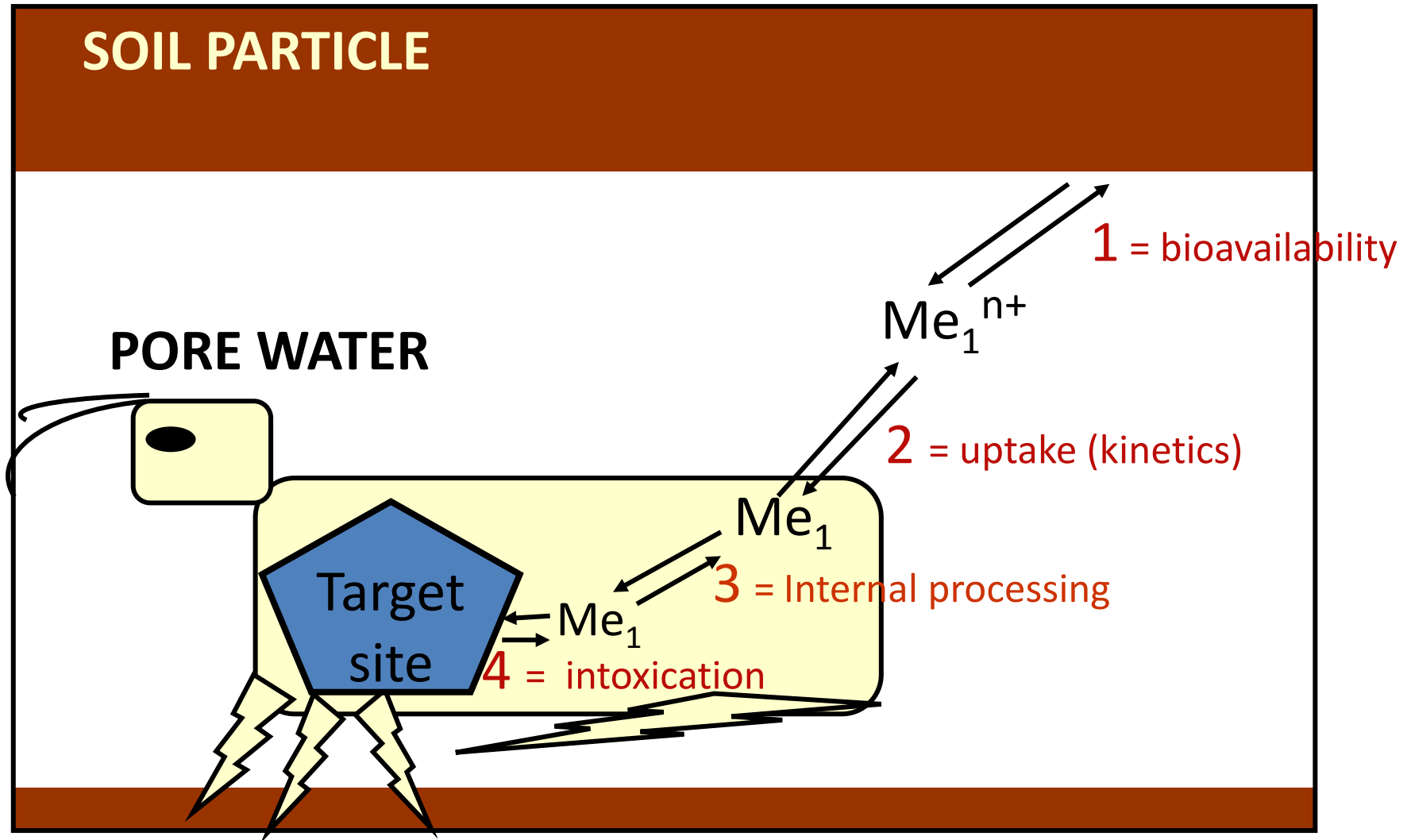
I – Diaz x Imid



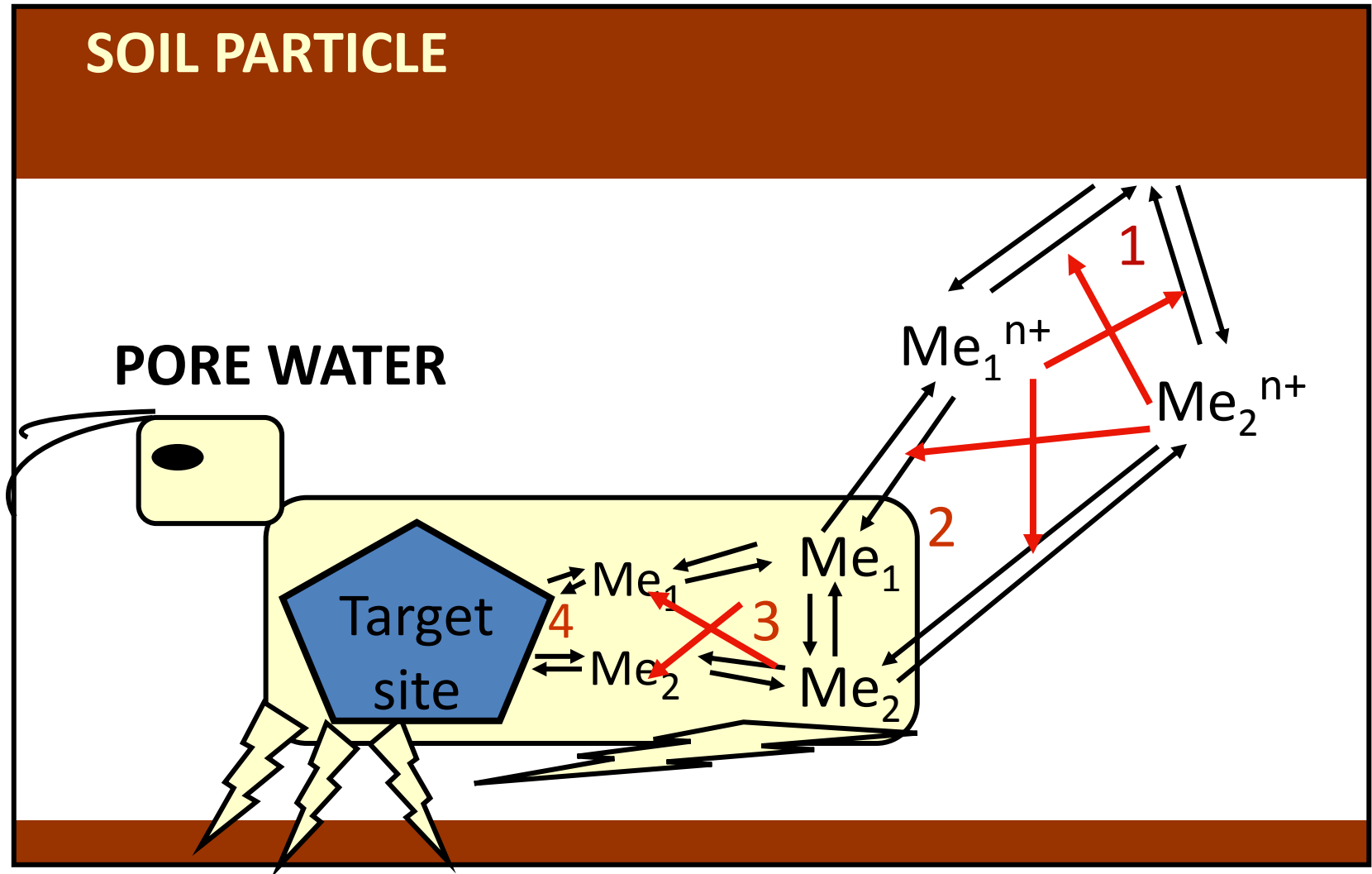
# PATTERNS OF OBSERVED EFFECTS



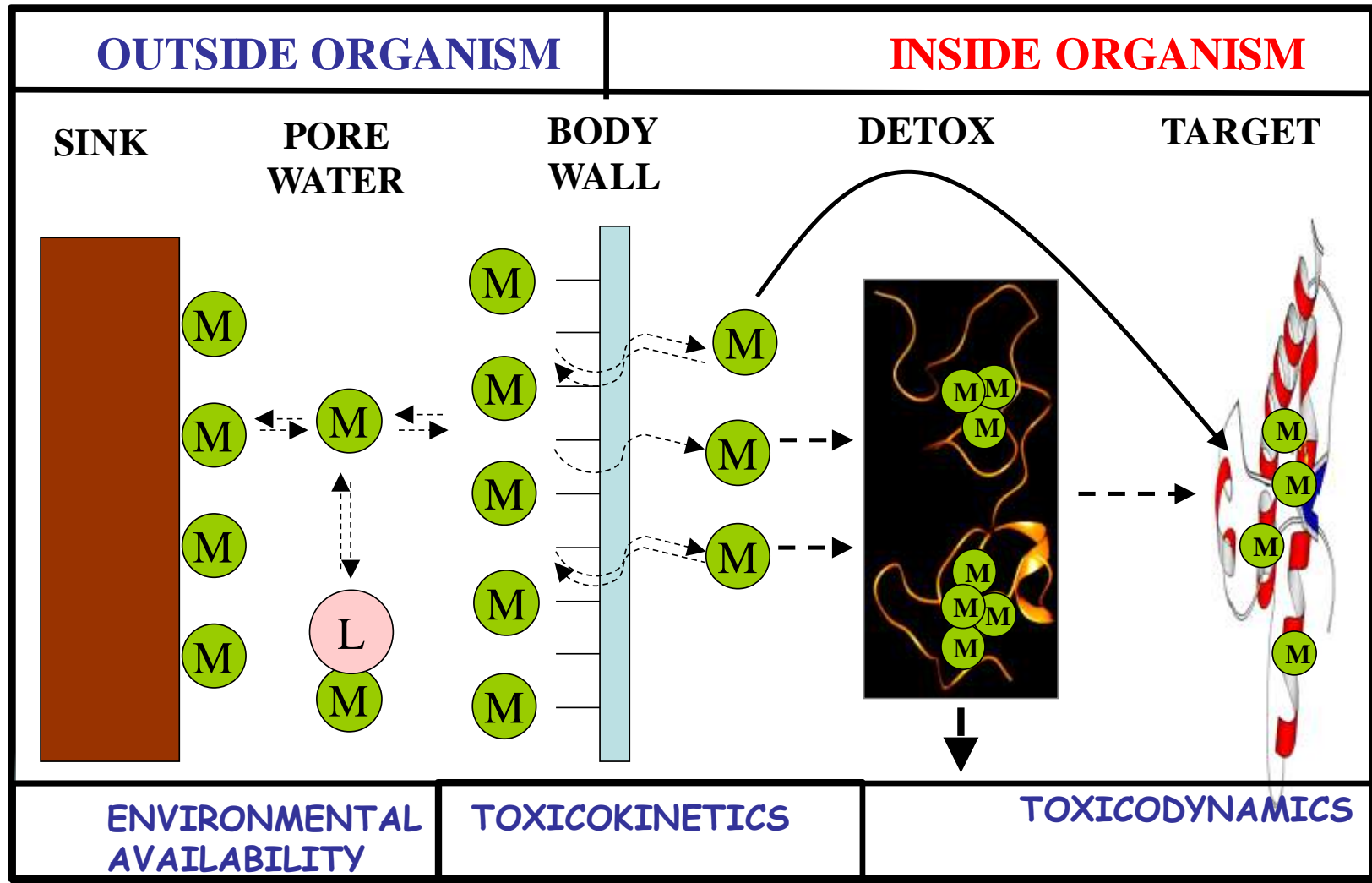
# STEPS IN UPTAKE AND INTOXICATION



# STEPS IN UPTAKE AND INTOXICATION



# A CONCEPTUAL MODEL OF INTERACTION

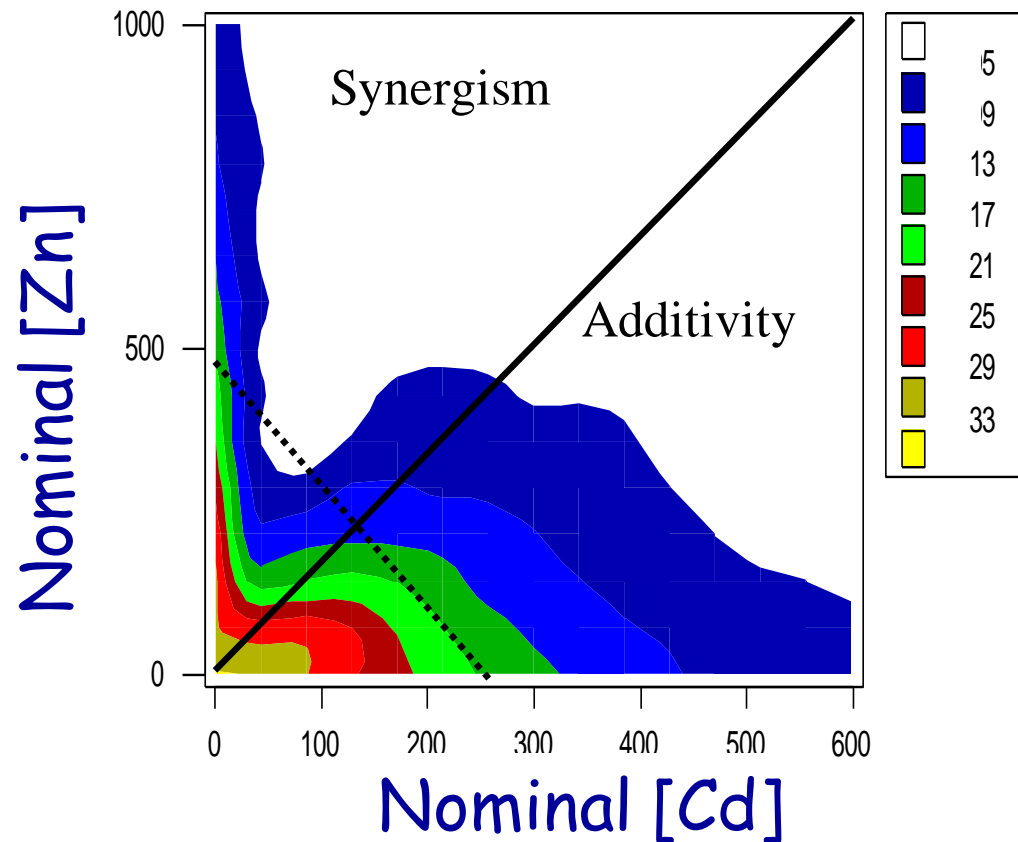


# FOUR TYPES OF INTERACTIONS

1. **Chemical and physico-chemical interactions**  
→ affecting exposure and bioavailability
2. **Physiological interactions at uptake sites**  
→ quantity taken up by organisms
3. **Physiological/biochemical interactions**  
internal processing → amount available at target
4. **Interactions at target site(s)**  
→ intoxication processes

# EXAMPLE – ENVIRONMENTAL AVAILABILITY

- Exposed *E. andrei* to Cd and Zn mixture for 28 day
- Partial factorial design (different levels and ratios)
- Measured effect on cocoon production

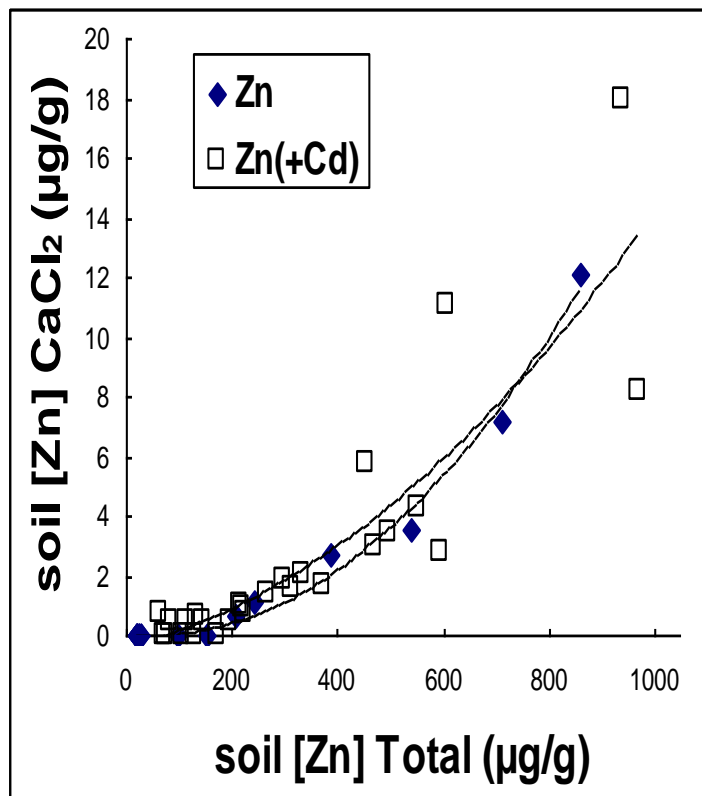


# EXAMPLE – ENVIRONMENTAL AVAILABILITY

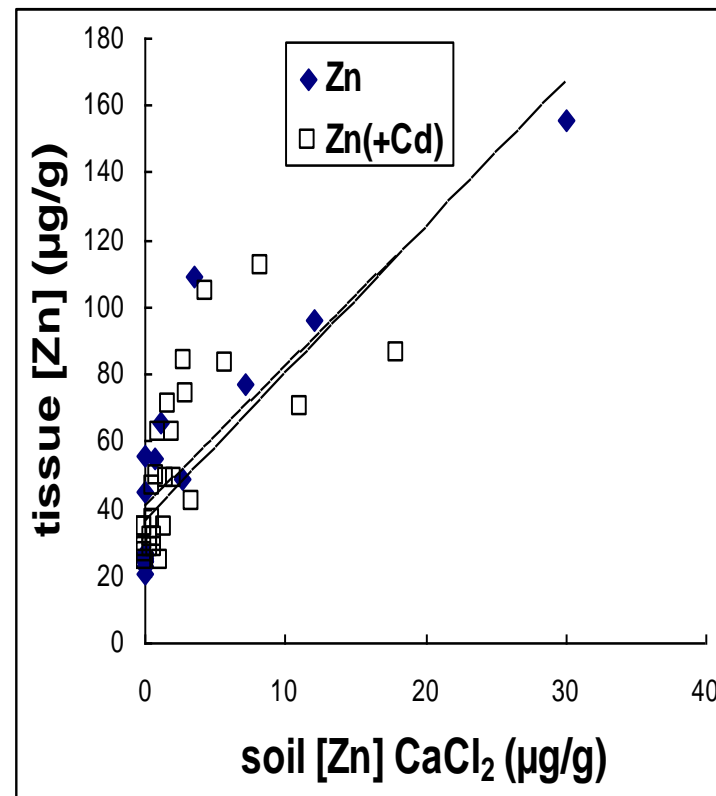
## ZN SORPTION

&

## ZN UPTAKE



No significant effects



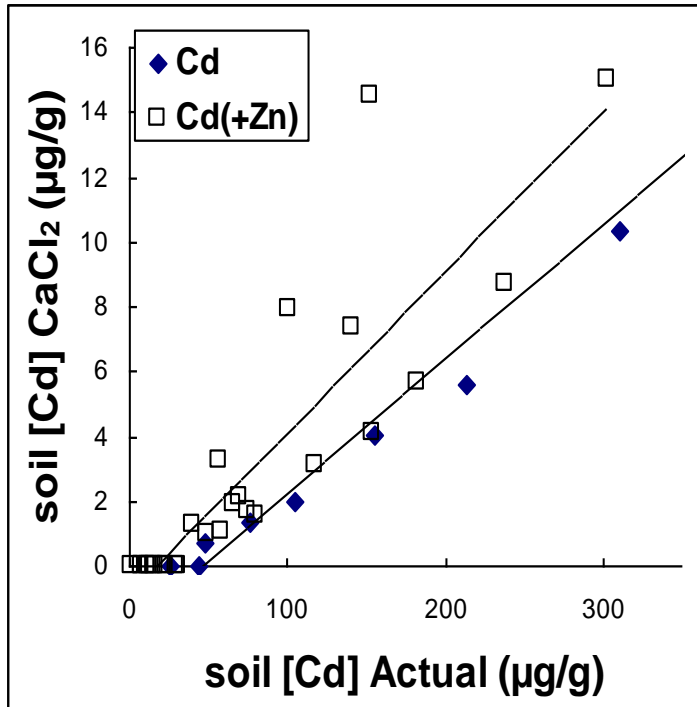
No significant effects

# EXAMPLE – ENVIRONMENTAL AVAILABILITY

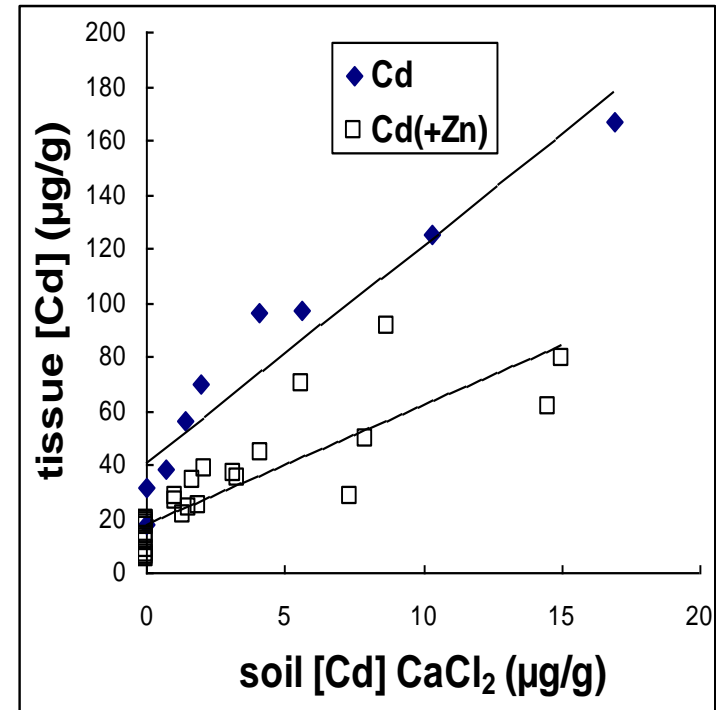
## CD SORPTION

&

## CD UPTAKE



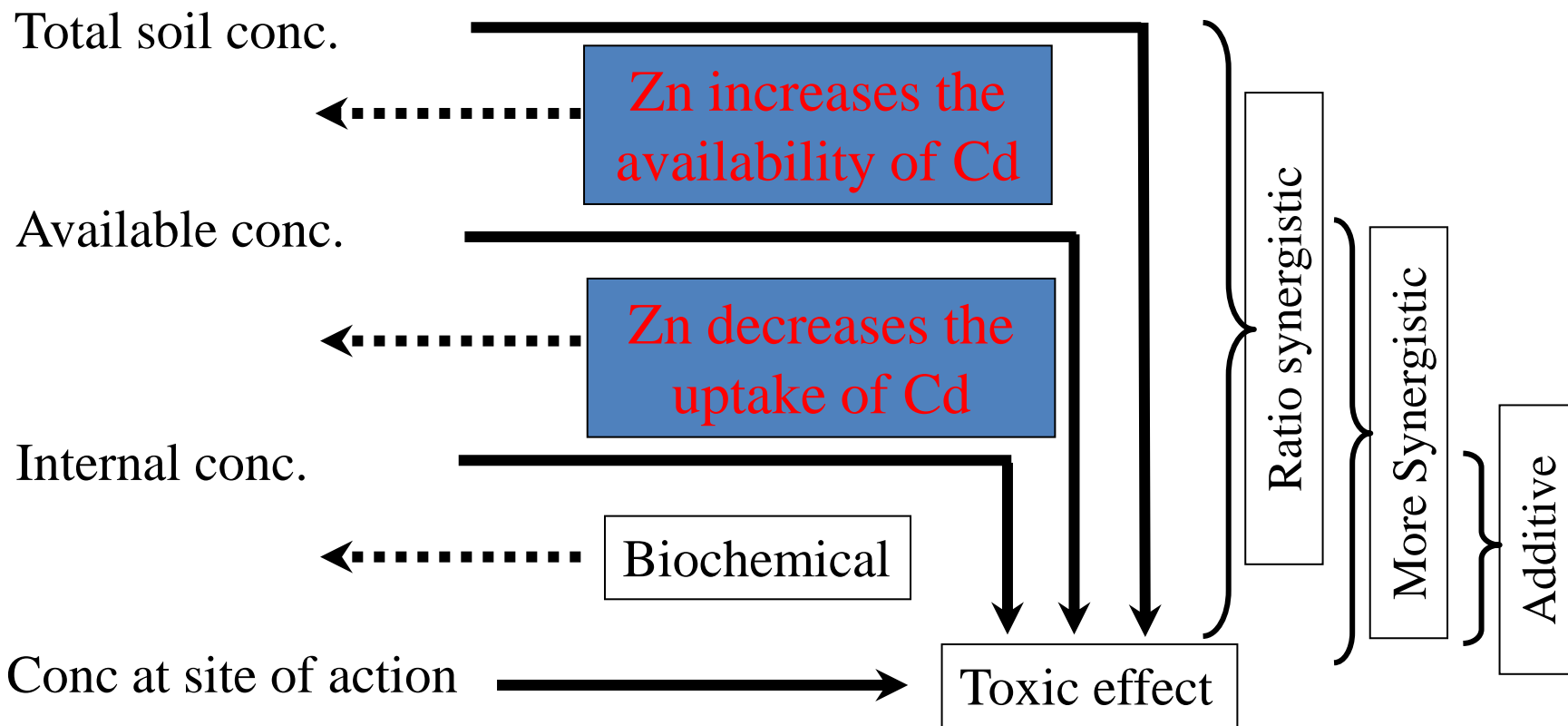
Significant effect  
(Zn makes Cd more available)



Significant effect  
(Zn lowers uptake of available Cd)

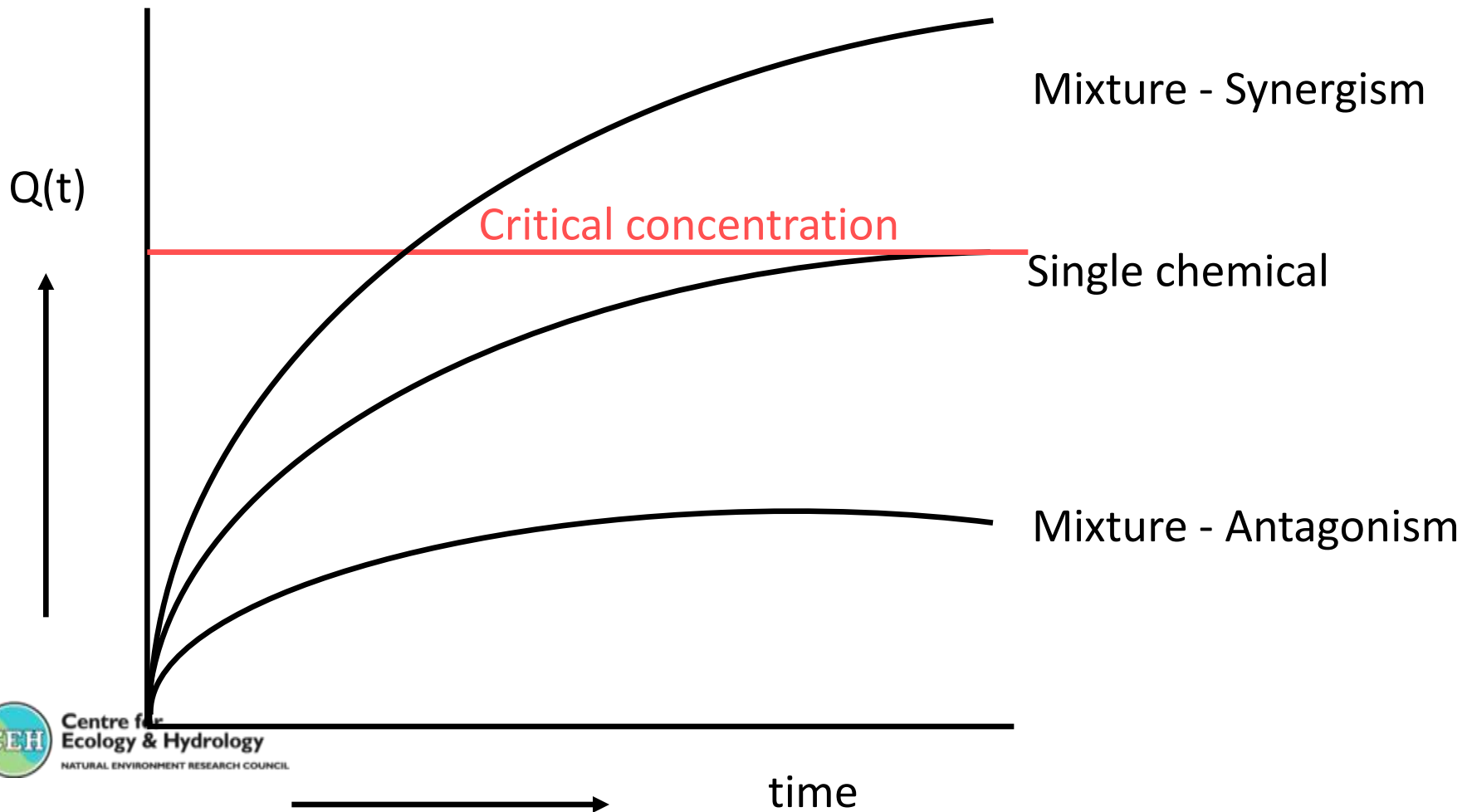
# THE TOTALITY OF INTERACTIONS

**Levels of exposure**      **Possible mixture interactions**      **Descriptive mixture models**



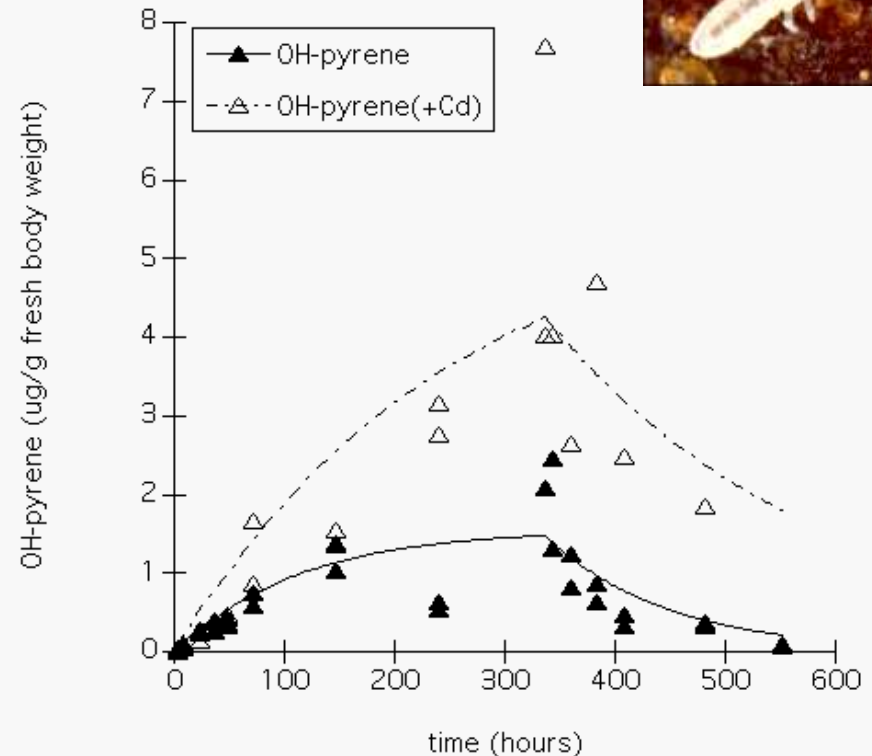
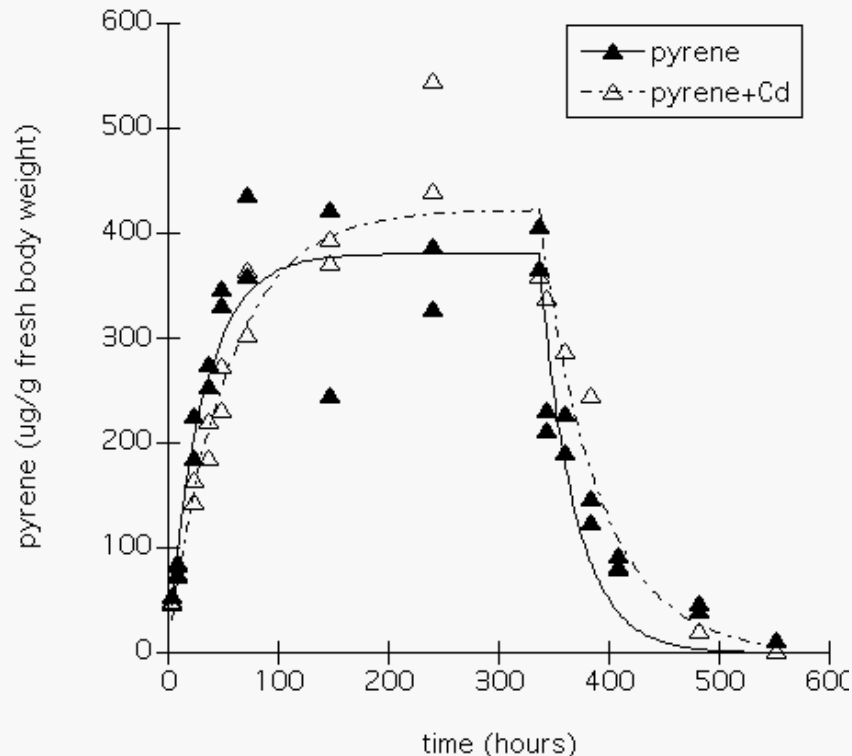
# EXAMPLE - TOXICOKINETICS

## Toxicokinetics: Conceptual model



# EXAMPLE - TOXICOKINETICS

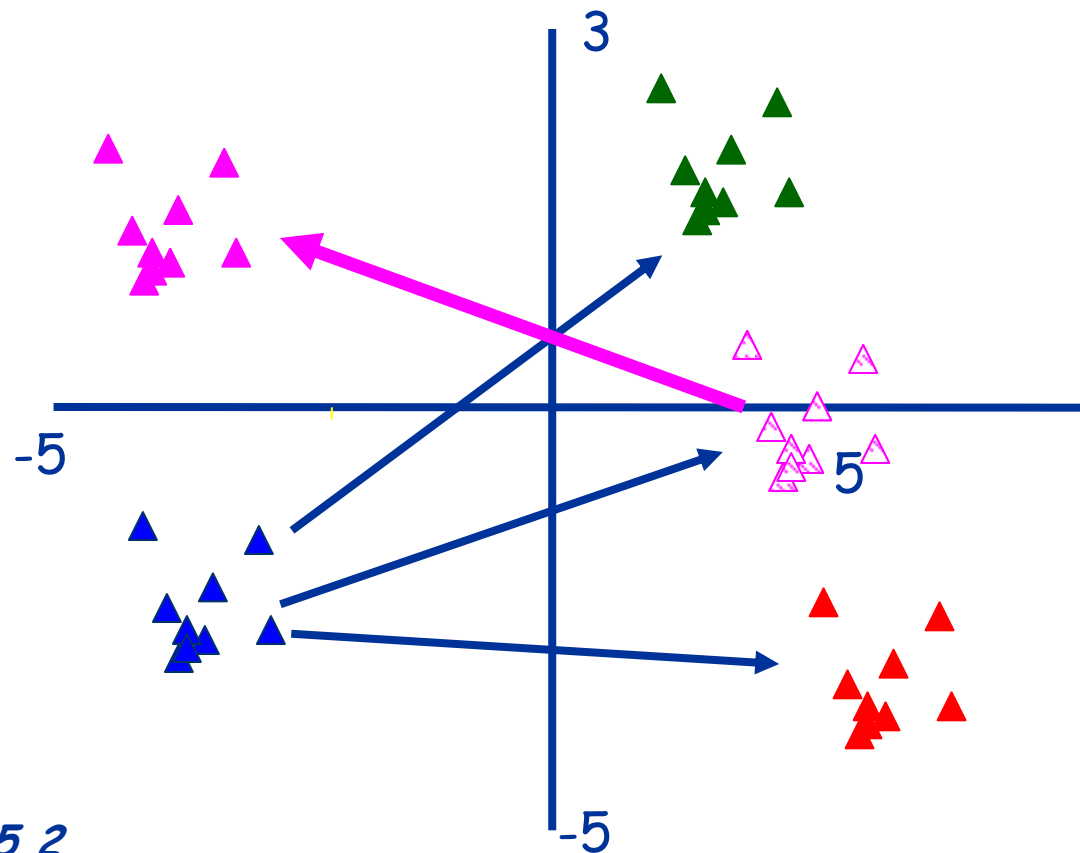
## PYRENE METABOLISM IN *F. CANDIDA* AFFECTED BY CADMIUM



→ In Cd exposed animals, pyrene metabolism inhibited - potential for synergism

# EXAMPLE - TOXICODYNAMICS

## Toxicodynamics: Conceptual model



- ▲ *Control*
- ▲ *EC50 Chem 1*
- ▲ *EC50 Chem 2*
- ▲ *EC25 1 + EC25 2*

# EXAMPLE - TOXICODYNAMICS

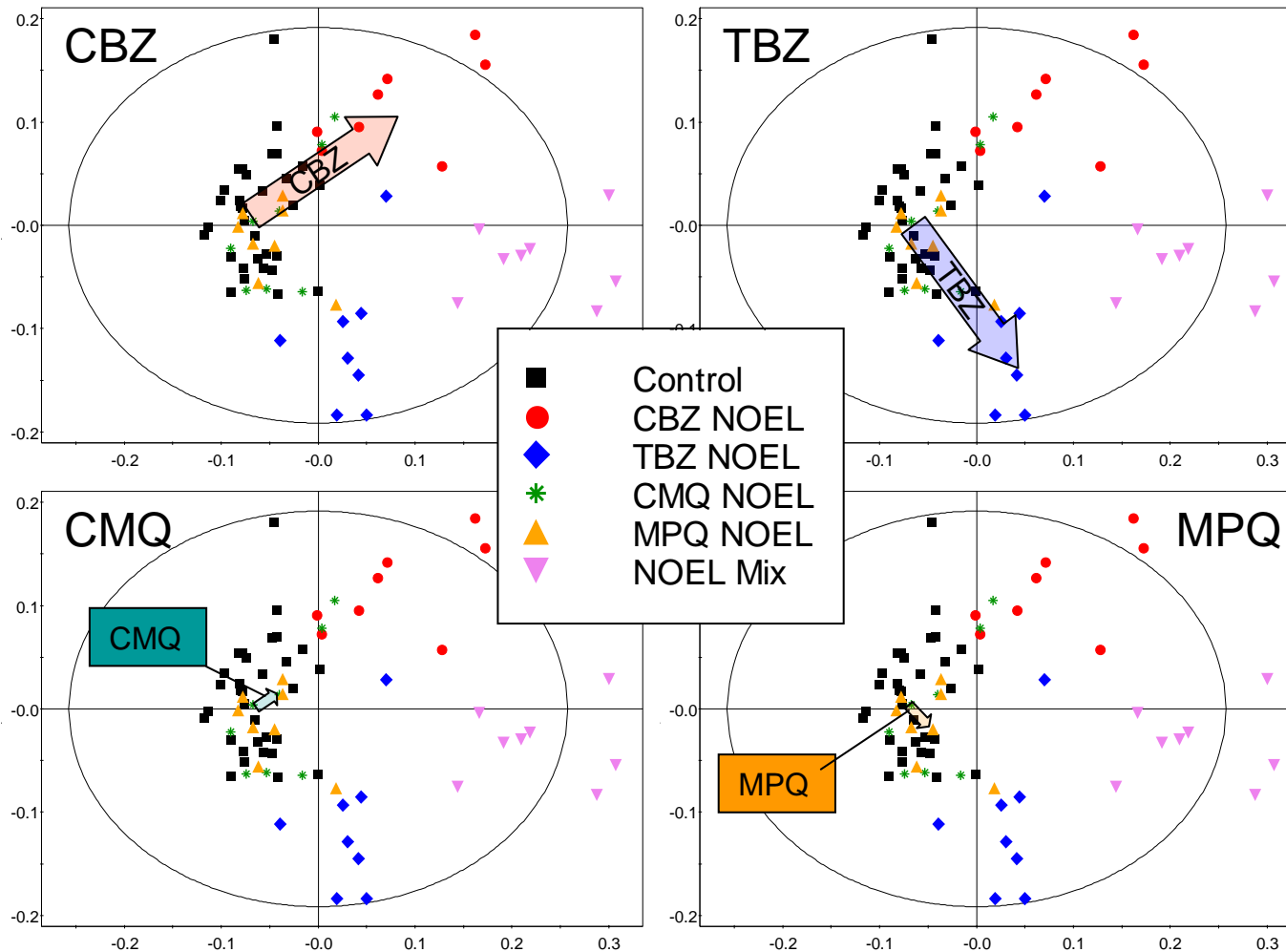
## BIOMARKERS OF MULTIPLE PESTICIDE EXPOSURE VIA FOOD

- Used pesticides that occur in food
- Four pesticides - related pairs from two groups
- Benzimidazole fungicides
  - Carbendazim (CBZ) and Thiabendazole (TBZ) (found on fruit).
- Bipyridylium herbicides
  - Chlormequat (CMQ) and Mepiquat (MPQ) (found on cereals).

# EXAMPLE - TOXICODYNAMICS

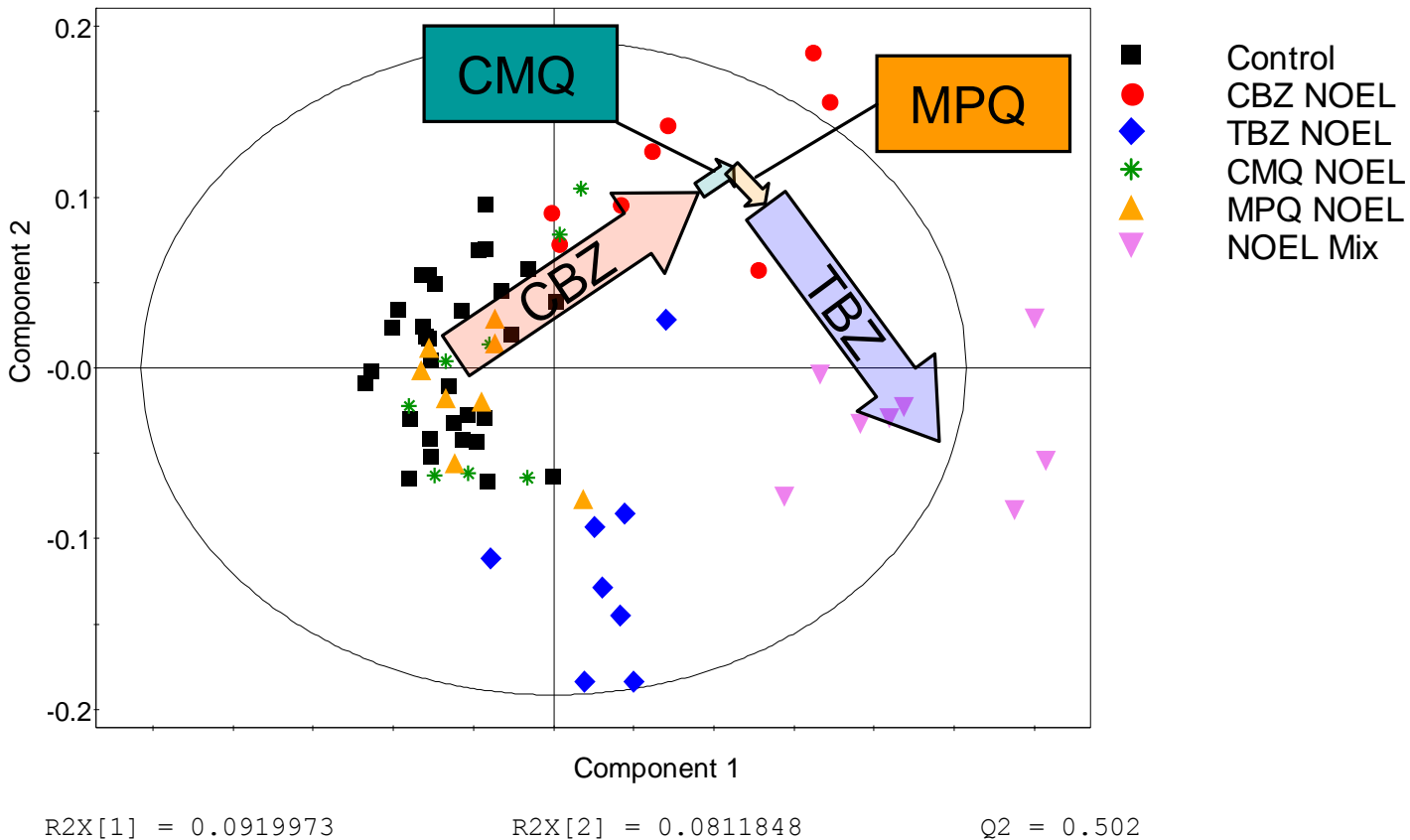
## Similar or different response?

1<sup>st</sup> class strong effects and 2<sup>nd</sup> class weak effect - all diff. directions



# EXAMPLE - TOXICODYNAMICS

## What about the mixture effect?



– Mixture effect is sum of individual effects (somehow)

# MIXTURE EFFECTS

**ADDITIVITY**  
**+**  
**UNCERTAINTY**  
**=**  
**REALITY**



It's Over