Valutazione del rischio chimico

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Valutazione del rischio chimico

Processo chimico

(Emissioni)

(Dispersione
Trasferimenti di fase
trasformazioni ambientali)

Esposizione */ PEC*

Valutazione del rischio

*Valutazione degli **effetti** dell'esposizione a sostanze singole e a miscele / NOAEC /tossicologia*

Valutazione delle relazioni tra dose e risposta

Valutazione delle relazioni tra dose e risposta per effetti con soglia: l'approccio NOAEL

L'obiettivo è determinare una "dose" per cui non ci siano effetti significativamente rilevant

NOAEL = Not observable effect level
LOAEL = Lowest observable effect level
dipendono fortemente da progettazione del test (n° animali, dosi somministrate …)

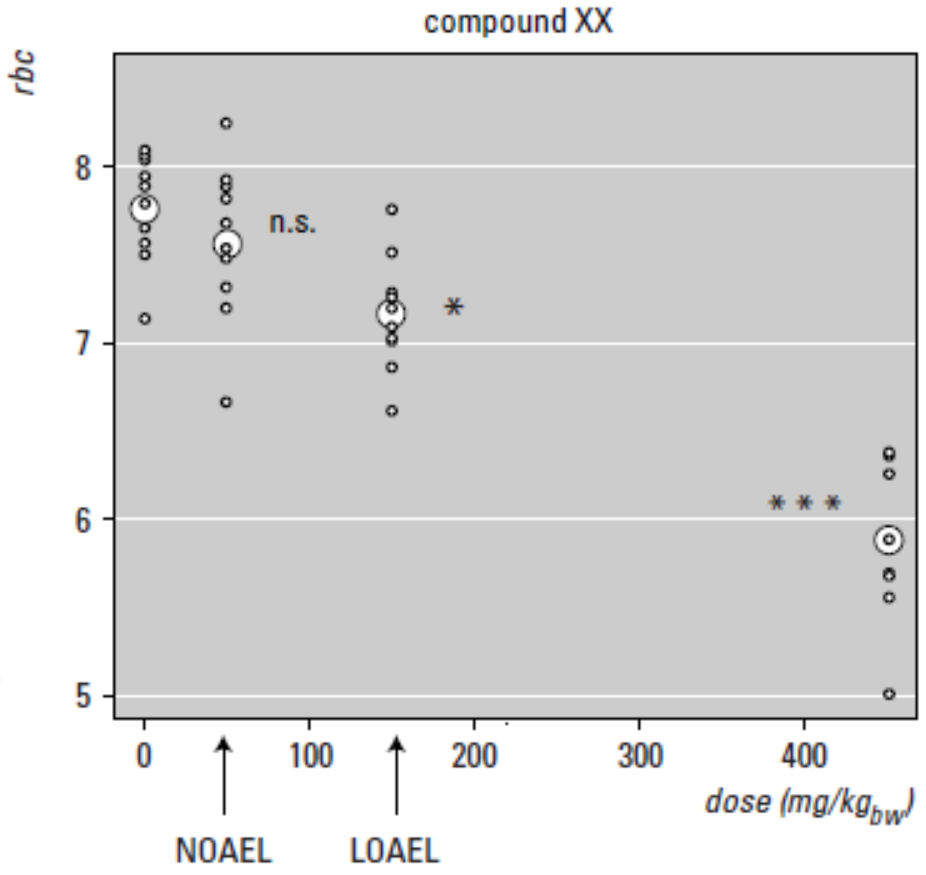


Figure 6.9. Illustration of the LOAEL and NOAEL for a decrease in red blood cell counts observed in an OECD toxicity study. The small marks indicate the observations in individual animals, the larger marks indicate the group means.
n.s.: not significantly different from the controls.
*: significantly different from the controls.
***: highly significantly different from the controls.

Valutazione delle relazioni tra dose e risposta

Valutazione delle relazioni tra dose e risposta per **effetti senza soglia**

Per le sostanze cancerogene, «anche singola molecola» ha piccola probabilità di generare un addotto con il DNA, e addotto ha piccola probabilità di causare una mutazione, in un gene potenzialmente correlato a un processo di carcinogenesi, aumentando la probabilità di generare una cellula maligna. Cancerogenesi è complessa, ma l'attivazione dei tumori sembra essere stocastica.

Diminuire le "dosi" porta sempre a diminuire la probabilità di tumori in una popolazione.

Manca quindi una soglia per le dosi d'esposizione → NOAEL non va bene

Una valutazione dei dati sull'incidenza dei tumori, può solo determinare una dose per la quale il rischio sia accettabilmente piccolo: **rischio *de minimis, es.* 10^{-6}, in una vita**

Nelle valutazioni sperimentali

Studi su animali effettuati su 50-100 individui per dose. Un rischio osservabile prevederebbe 1 caso su 10 (10^{-1}), quindi ci si trova in *condizioni di estrapolazione per basse dosi* o, meglio, *per bassi rischi*.

Alcune nazioni evitano valutazioni quantitative su dati di incidenza di tumori.

Altri applicano il principio *As Low as Reasonably Achievable (ALARA)* per cancerogeni genotossici. È approccio debole, tratta tutti i cancerogeni in modo eguale.

La tendenza attuale è verso l'**approccio BMD (*benchmark dose*)**

L'approccio BMD (*benchmark dose*)

Si costruisce/fitta un modello dose-risposta per i dati di incidenza dei tumori, e il modello è usato per stimare una dose che è associata con un livello di rischio che sta nell'intervallo osservabile (tipicamente il rischio del 10% = BMD_{10}, termine basso di confidenza è $BMDL_{10}$)).

Questo rischio di cancerogenesi non è accettabile, ed è considerato come punto di riferimento (RP) per successive valutazioni, come

Estrapolazione lineare

Margine di esposizione (l'esposizione stimata è divisa per il RP (=$BMDL_{10}$), e il rapporto risultante è l'intervallo tra l'esposizione umana e la dose con livello di rischio noto (EFSA: MOE>10000 basso livello di preoccupazione, non vi è consenso sul tema)

ROAC II ed. (2007)

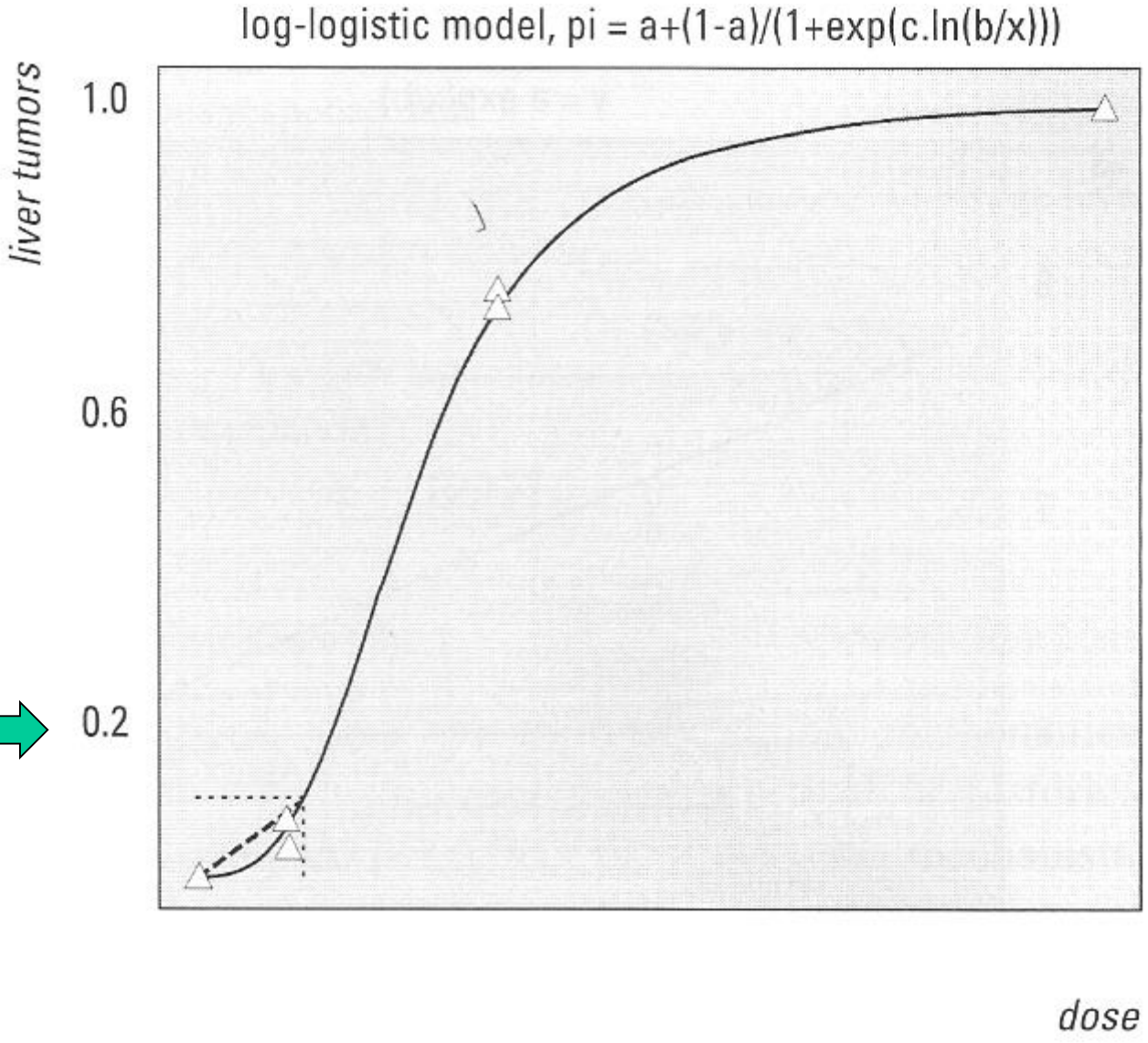


Figure 6.10. Sigmoidal dose-response relationship. Linear extrapolation from the BMD10 overestimates the risk.

Per sostanze con effetto di soglia

Dividiamo i NOAEL per fattori di valutazione (vedi lezione precedente) per arrivare ad Derived No Effect Level (DNEL) - Acceptable Daily Intake (ADI) ponderato/cautelativo

DNEL *derived no effect level* che tengano conto di:

- Differenze interspecie
- Differenze intraspecie
- Differenze nella durata dell’esposizione
- Aspetti associati alla dose-risposta
- Qualità della base di dati

Tossicologia umana

Dagli studi di laboratorio alla definizioni di massimo rischio accettabile (MPR) o dosi giornaliere accettabili (ADI/TDI/RfD) o esposizione

Table 5.11. Estimated conversion factors between an LD50, the NOEL of a subchronic or chronic study and the acceptable daily intake (ADI)

LD50	NOEL subchronic	NOEL chronic	ADI
100,000 - 5,000,000	300 - 1000	100	1

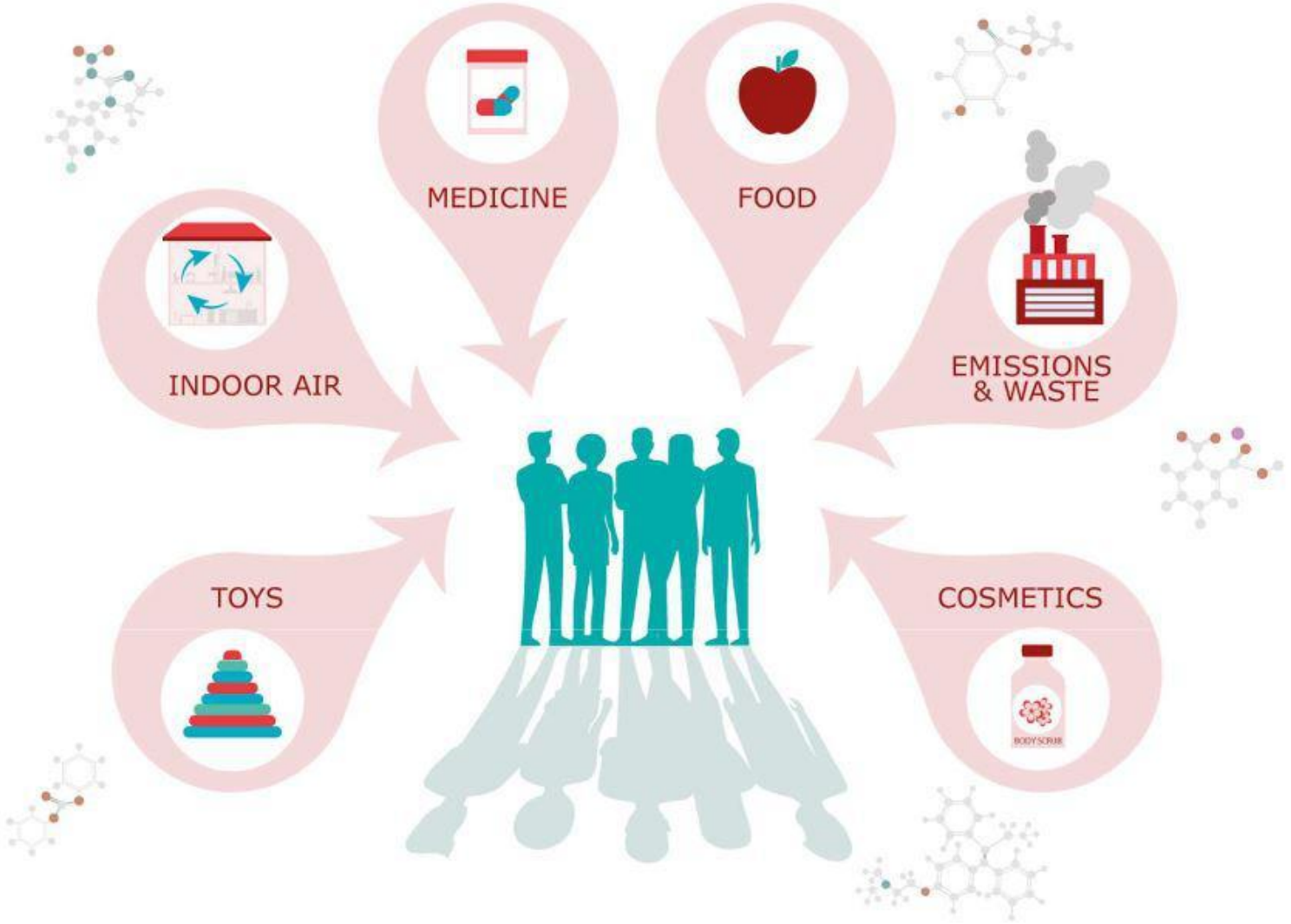
RAoC, 2007
Van Leeuwen, Vermeire

Box 6.4. Maximum Permissible Risk level

Examples of oral MPRs for non-carcinogenic substances are the ADI (acceptable daily intake, for substances deliberately added to food items) and TDI (tolerable daily intake, for substances unintentionally present in food items), both are expressed in mg/kg bw/day and defined as the daily intake of a chemical which, during the entire lifetime, appears to be without appreciable risk on the basis of all known facts at the time. The RfD (Reference Dose) is similar to the ADI/TDI, but is more strictly defined. Inhalation MPRs are defined in a similar way and expressed as concentrations in air. An example of another health-based limit value is the AOEL (acceptable operator exposure level): the level that has no harmful effects on the health of operators (people working with the substance).

MPRs for carcinogenic substances are usually defined as the daily dose, taken during the entire lifetime that will cause $1{:}10^4$, $1{:}10^5$ or $1{:}10^6$ additional cancer cases during the entire lifetime.

Tossicità di miscele



https://ec.europa.eu/jrc/en/news/chemical-mixtures-safety

Tossicità di miscele

In generale l'informazione disponibile per sostanze testate
•in condizioni di laboratorio
•in studi di campo
si riferisce a singole sostanze

Ecosistemi terrestri e acquatici «raramente» (mai) inquinati da una singola sostanza

Necessario considerare possibili **interazioni tra specie chimiche** e **interazioni tra i loro effetti** sugli organismi.

E' importante considerare i "**modi di azione"** delle sostanze:
"A mode of action (MoA) describes a functional or anatomical change, at the cellular level, resulting from the exposure of a living organism to a substance."

Quattro tipi di azioni congiunte di specie chimiche secondo Plackett e Hewlett (J. Roy. Stat. Soc. B, **14**, 141 –163 (1952))

	Similar joint action	Dissimilar jont action
Interaction absent	simple similar action (concentration-addition)	independent action (response-addition)
Interaction present	complex similar action	dependent action

L'**azione congiunta** è definita
simile o **diversa** a seconda che i siti di azione primaria delle due specie chimiche considerate siano gli stessi o diversi,
interattiva o **non interattiva** a seconda che una specie chimica influenzi o meno l'azione biologica dell'altra

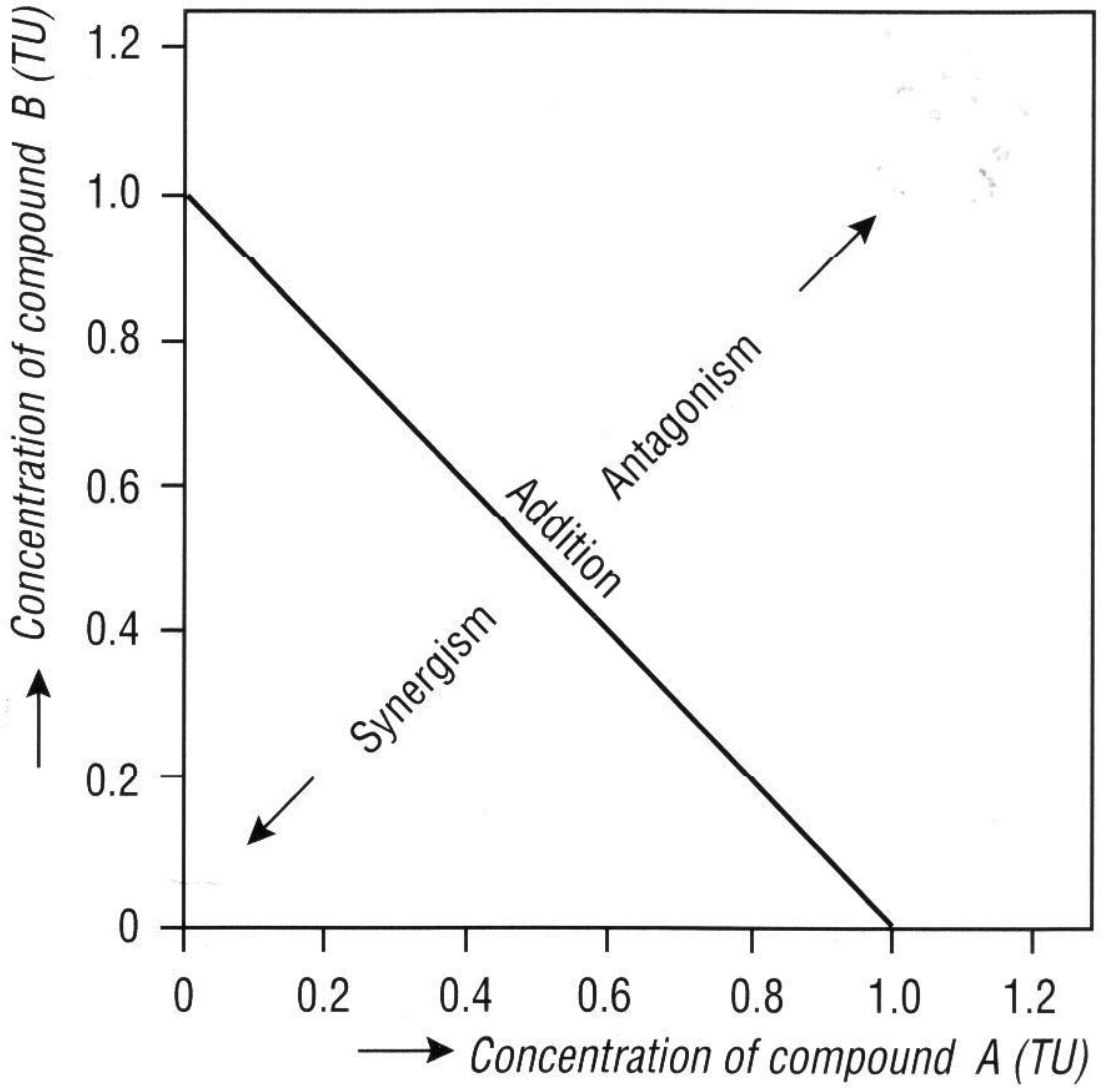


Figure 6.33. Possible toxicological interactions in a mixture of two chemicals.

https://ec.europa.eu/jrc/en/news/chemical-mixtures-safety

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Chemical mixtures: How to address the safety of combined exposures to multiple chemicals for people and the environment

JUN 28 2018

Every day we are exposed to low levels of hundreds of different manmade chemicals present for example in our food, consumer products and the air we breathe.

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Our environment too is exposed to a near-infinite number of chemical mixtures derived from numerous sources.

However, current safety assessment practice is primarily based on understanding the potential risk posed by single substances rather than their "real life" combinations, thus potential combination effects might be overlooked.

The JRC is investigating recent progress in considering combined exposures to multiple chemicals to help translate best science into best assessment practice. The latest policy brief, Something from nothing? Ensuring the safety of chemical mixtures, puts together issues around the topic, including the specific challenges that will further inform discussions of the working group of Commission services and EU agencies on the combination effects of chemicals.

Related Content

JRC policy brief: Something from nothing? Ensuring the safety of chemical mixtures

News: Towards improved safety assessment of combined exposure to chemicals

Report: Assessment of Mixtures - Review of Regulatory Requirements and Guidance

Report: Scientific methodologies for the assessment of combined effects of chemicals - a survey and literature review

Report: Review of case studies on the human and environmental risk assessment of chemical mixtures

Article: Mixtures of chemical pollutants at European legislation safety concentrations: how safe are they?

Article: Regulatory assessment of chemical mixtures: Requirements, current approaches and future perspectives

Tool: IPCHEM

https://ec.europa.eu/jrc/en/news/chemical-mixtures-safety

Per la descrizione matematica della tossicità congiunta di una miscela di n composti ($n \geq 2$), è (possibile in pochi casi in cui l'assenza di interazione sembra essere un prerequisito.) difficile.

http://ec.europa.eu/environment/chemicals/effects/effects_en.htm (2017)

http://ec.europa.eu/environment/chemicals/effects/pdf/report_mixture_toxicity.pdf (2009)

Relativamente a miscele di composti, gli effetti per esperimenti per valutare LC50 possono essere predetti per composti con azione simile semplice (addizione delle concentrazioni)

Azione simile semplice

Sostanze chimiche nella miscela agiscono nello stesso modo, attraverso gli stessi meccanismi, con diverse potenze. L'effetto additivo può essere descritto con la somma delle dosi di ciascun componente individuale, dopo la correzione per la differenza nelle potenze:

Fattori di tossicità equivalente (TEF) e equivalenti di tossicità (TEQs) si definiscono per diossine, furani, PCB *dioxin-like*, e altri per IPA

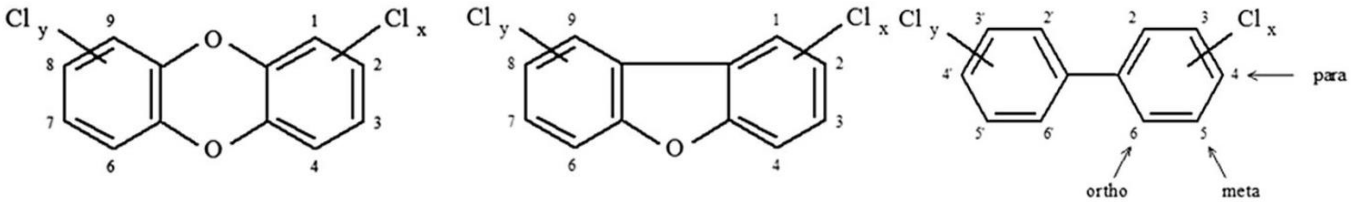
PCDXs & DL-PCBs: What are TEFs and TEQs?

The complex nature of polychlorinated dibenzo-p-dioxin (PCDD), dibenzofuran (PCDF), and biphenyl (PCB) mixtures complicates the risk evaluation for humans. For this purpose the concept of **toxic equivalency factors (TEFs) has been developed and introduced to facilitate risk assessment and regulatory control of exposure to these mixtures.**

TEF values for individual congeners in combination with their chemical concentration can be used to calculate the total TCDD toxic equivalents concentration (TEQs) contributed by all dioxin-like congeners in the mixture using the following equation which assumes dose additivity:

$$TEQ = \sum (PCDD_i \times TEF_i) + \sum (PCDF_i \times TEF_i) + \sum (PCB_i \times TEF_i) + ..$$

The majority of studies have demonstrated that the interaction does not deviate significantly from dose additivity.



Martin Van den Berg et al. 1998 “Toxic Equivalency Factors (TEFs) for PCBs, PCDDs, PCDFs for Humans and Wildlife” Environmental Health Perspectives Volume 106, 775-792,

Denison MS, Nagy SR (2003). "Activation of the aryl hydrocarbon receptor by structurally diverse exogenous and endogenous chemicals". Annual Review of Pharmacology and Toxicology. 43: 309–34.

PCBs	TEF
2,3,7,8TCDD	1
PentaCB 126	0,1
HexaCB 156	0,0005
HexaCB 157	0,0005
TetraCB 77	0,0001
PentaCB 105	0,0001
PentaCB 118	0,0001
PentaCB 123	0,0001
HeptaCB 189	0,0001
HexaCB 167	0,00001

Le 17 “pecore nere” e la loro tossicità equivalente

Tabella 1: I fattori di tossicità equivalente secondo NATO e WHO

PCDD/F	I-TEFs (NATO/CCMS[14], 1988)	WHO-TEFs (Van den Berg *et al, 1998)*
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	0,5	1
1,2,3,4,7,8-HxCDD	0,1	0,1
1,2,3,6,7,8-HxCDD	0,1	0,1
1,2,3,7,8,9-HxCDD	0,1	0,1
1,2,3,4,6,7,8-HpCDD	0,01	0,01
OCDD	0,001	0,0001
2,3,7,8-TCDF	0,1	0,1
1,2,3,7,8-PeCDF	0,05	0,05
2,3,4,7,8-PeCDF	0,5	0,5
1,2,3,4,7,8-HxCDF	0,1	0,1
1,2,3,6,7,8-HxCDF	0,1	0,1
1,2,3,7,8,9-HxCDF	0,1	0,1
2,3,4,6,7,8-HxCDF	0,1	0,1
1,2,3,4,6,7,8-HpCDF	0,01	0,01
1,2,3,4,7,8,9-HpCDF	0,01	0,01
OCDF	0,001	0,0001

(T = tetra, Pe = penta, Hx = hexa, Hp = hepta, O = octa)

I 12 PCB, "parenti" pericolosi e la loro tossicità equivalente

Tabella 8: PCB dioxin-like e relativi fattori di tossicità equivalente

PCB_a (nome IUPAC)	PCB-TEF (Ahlborg et al., 1994)	WHO-TEF (Van den Berg *et al*, 1998)
3,3',4,4'-TCB (77)	0,0005	0,0001
3,4,4',5-TCB (81)	-	0,0001
3,3',4,4',5-PeCB (126)	0,1	0,1
3,3',4,4',5,5'-HxCB (169)	0,01	0,01
2,3,3',4,4'-PeCB (105)	0,0001	0,0001
2,3,4,4',5-PeCB (114)	0,0005	0,0005
2,3',4,4',5-PeCB (118)	0,0001	0,0001
2',3,4,4',5-PeCB (123)	0,0001	0,0001
2,3,3',4,4',5-HxCB (156)	0,0005	0,0005
2,3,3',4,4',5'-HxCB (157)	0,0005	0,0005
2,3',4,4',5,5'-HxCB (167)	0,00001	0,00001
2,3,3',4,4',5,5'-HpCB (189)	0,0001	0,0001

(T = tetra, Pe = penta, Hx = hexa, Hp = hepta)

IPA
Valutazione dell'equivalente internazionale di tossicità

$$I-TEQ_{B[a]P}=\sum_i [IPA]_i \cdot TEF_i$$

Table 13. Relative potency of individual PAHs compared with B[*a*]P (TEF values), according to different authors.[a]

Compound	Chu and Chen (1984) (cit. Nisbet and LaGoy 1992)	Clement (1986) (cit. Nisbet and LaGoy 1992); Krewski et al. (1989)	Nisbet and LaGoy (1992)	The Netherlands (RIVM 1989)	CARB (1994); Collins et al. (1998)	Health Canada (Meek et al. 1994)	Ontario (Muller 1997)	Larsen and Larsen (1998)
Anthracene			0.01	0				0.0005
Phenanthrene			0.001	0.01			0.00064	0.0005
Benz[*a*]anthracene	0.013	0.145	0.1	0–0.04	0.1		0.014	0.005
Benzo[*c*]phenanthrene							0.023	0.023
Chrysene	0.001	0.0044	0.01	0.05–0.89	0.01		0.026	0.03
Fluoranthene			0.001	0–0.06				0.05
Pyrene		0.081	0.001				0	0.001
B[*a*]P	1	1	1	1	1	1	1	1
Benzo[*e*]pyrene		0.004					0	0.002
Benzo[*b*]fluoranthene	0.08	0.14	0.1		0.1	0.06	0.11	0.1
Benzo[*j*]fluoranthene		0.061			0.1	0.05	0.045	0.05
Benzo[*k*]fluoranthene	0.04	0.066	0.1	0.03–0.09	0.1	0.04	0.037	0.05
Cyclopenta[*cd*]pyrene		0.023					0.012	0.02
Dibenzo[*a,h*]anthracene	0.69	1.11	5				0.89	1.1
Anthanthrene		0.32					0.28	0.3
Benzo[*ghi*]perylene		0.022	0.01	0.01–0.03			0.012	0.02
Dibenzo[*a,e*]pyrene					1		1.0[b]	0.2
Dibenzo[*a,h*]pyrene					10		1.2	1
Dibenzo[*a,i*]pyrene					10			0.1
Dibenzo[*a,l*]pyrene					10		100[b]	1
Indeno[1,2,3-*cd*]pyrene	0.017	0.232	0.1	0–0.08	0.1	0.12	0.067	0.1

[a]See comments in the text. [b]Data from Muller et al. (1995), cited in WHO/IPCS (1998).

Miscele con diversi modi d’azione → maggior complicazione.

Gli effetti possono essere predetti se e solo se i composti nella miscela agiscono in modo diverso e indipendentemente (**azione indipendente**).

Azione diversa semplice

(Azione semplice indipendente, azione indipendente congiunta o **addizione degli effetti** o delle risposte)

La natura, il meccanismo o il sito d'azione delle specie chimiche nella miscela sono diversi. Quindi ciascuna specie chimica esercita il suo effetto tossico individuale, e non altera l'effetto degli altri *chemicals* nella miscela.

Pericolosità di una miscela con azione diversa semplice ma correlazione positiva completa delle suscettibilità (risposte degli organismi ai tossici) è quella del componente più tossico della miscela.

Interazione

Effetti di due o più sostanze in una miscela, risultano in un effetto più forte della semplice somma di effetti delle sostanze individuali (sinergia, potenziamento, supra-additività).

Avviene per natura chimico-fisica

o nella fase tossicocinetica.

Supra-additività: possibile che

sostanze in conc. sotto livelli

di effetto avverso abbiano effetti

avversi

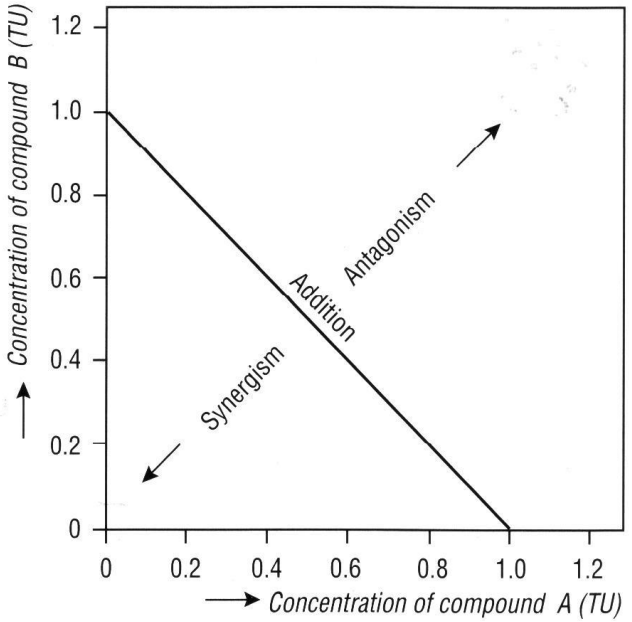


Figure 6.33. Possible toxicological interactions in a mixture of two chemicals.

Esposizione a miscele di sostanze genotossiche cancerogene

Sostanze senza soglia d'effetto: si assume additività delle risposte (nell'esprimere il rischio da sostanze cancerogene non si fa differenza tra i tipi di cancro)

$CR_{total} = \Sigma CR_i$

CR_i = rischio cancerogeno per l'i-mo componente nella miscela.

Scientific Committee on Health and Environmental Risks

Scientific Committee on Emergin and Newly Identified Health Risk

Scientific Committee on Consumer Safety

Dicembre 2011

Comunicazione EU DGA

https://ec.europa.eu/transparency/documents-register/detail?ref=COM(2012)252&lang=it

ABSTRACT

The EU Chemicals legislation is based predominantly on assessments carried out on individual substances. Since humans and their environments are exposed to a wide variety of substances, there is increasing concern in the general public about the potential adverse effects of the interactions between those substances when present simultaneously in a mixture. Based on their analysis of the available scientific literature, the non-food Scientific Committees of the European Commission reached the following conclusions:

1. Under certain conditions, chemicals will act jointly in a way that the overall level of toxicity is affected.

2. Chemicals with common modes of action will act jointly to produce combination effects that are larger than the effects of each mixture component applied singly. These effects can be described by dose/concentration addition.

3. For chemicals with different modes of action (independently acting), no robust evidence is available that exposure to a mixture of such substances is of health or environmental concern if the individual chemicals are present at or below their zero-effect levels.

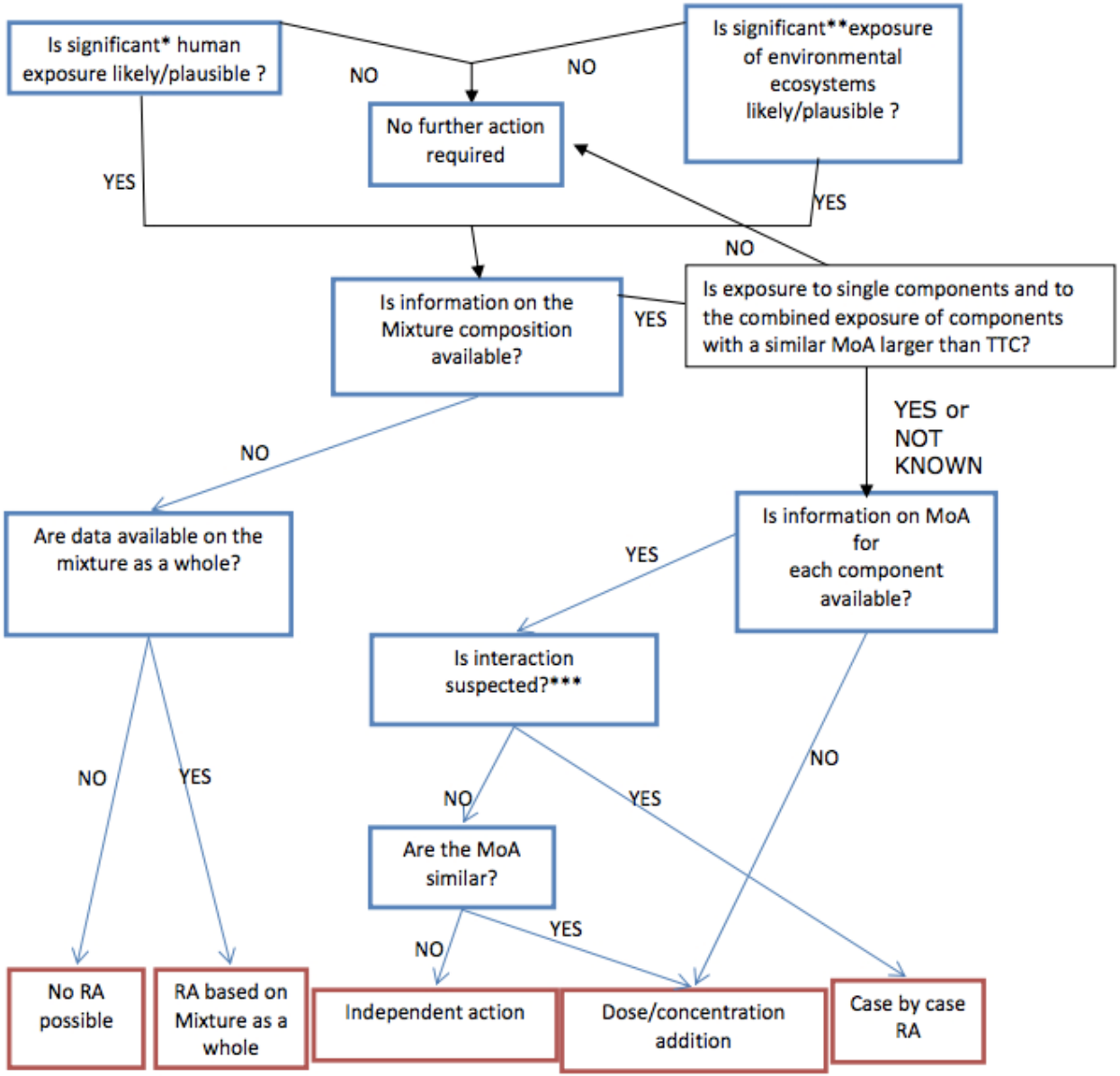
4. Interactions (including antagonism, potentiation, and synergies) usually occur at medium or high dose levels (relative to the lowest effect levels). At low exposure levels, they are either unlikely to occur or are toxicologically insignificant.

5. In view of the almost infinite number of possible combinations of chemicals to which humans and environmental species are exposed, some form of initial filter to allow a focus on mixtures of potential concern is necessary. Several criteria for such screening are offered.

6. With regard to the assessment of chemical mixtures, a major knowledge gap at the present time is the lack of exposure information and the rather limited number of chemicals for which there is sufficient information on their mode of action. Currently, there is neither an agreed inventory of mode of actions, nor a defined set of criteria how to characterise or predict a mode of action for data-poor chemicals.

7. If no mode of action information is available, the dose/concentration addition method should be preferred over the independent action approach. Prediction of possible interaction requires expert judgement and hence needs to be considered on a case-by-case basis.

Based upon these conclusions, a decision tree for evaluating the risk of chemical mixtures is proposed.


Is significant* human exposure likely/plausible ?
NO
NO
Is significant**exposure of environmental ecosystems likely/plausible ?
No further action required
YES
YES
NO
Is information on the Mixture composition available?
YES
Is exposure to single components and to the combined exposure of components with a similar MoA larger than TTC?
YES or NOT KNOWN
NO
Are data available on the mixture as a whole?
YES
Is information on MoA for each component available?
Is interaction suspected?***
NO
YES
NO
YES
NO
Are the MoA similar?
YES
NO
No RA possible
RA based on Mixture as a whole
Independent action
Dose/concentration addition
Case by case RA

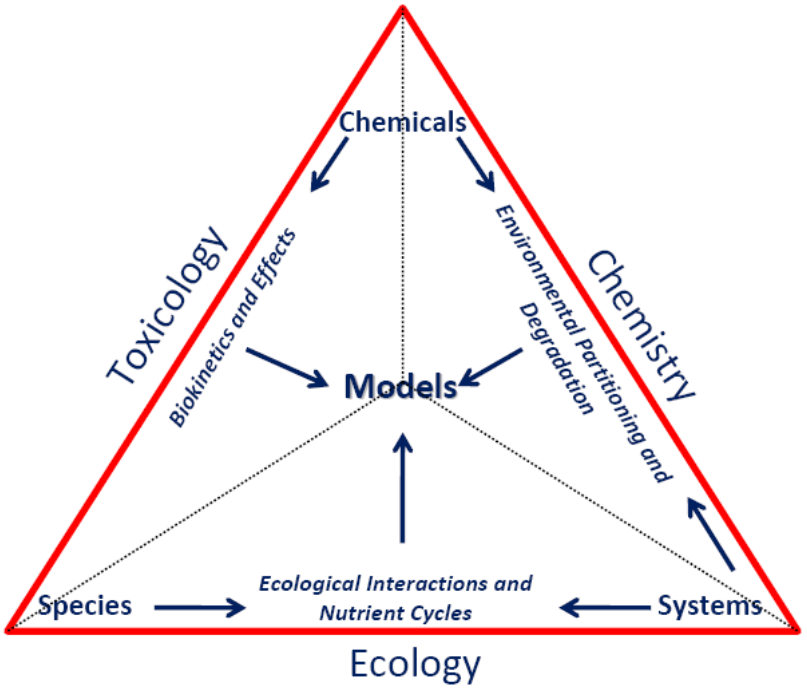
Tossicologia ambientale

Identificazione e quantificazione dei ***danni sui sistemi biologici (diversi dalla specie umana)*** a diverso livello di organizzazione, prodotto dall'esposizione ai contaminanti ambientali

Ecotossicologia

Studio del destino e degli effetti dei contaminanti nell'ambiente

Ecotossicologia: scienza delle tre S



Redrawn from Figure 7.1 of van Leeuwen and Vermeire (2007)

Table 6.1. "Disciplines" of ecotoxicology and some of their research topics

Chemistry	Toxicology	Ecology	Mathematics
Exposure assessment	effects assessment	community structure	environmental fate models
Transport	modes of toxic action	community functions	pharmacokinetic models
Partitioning	bioaccumulation	population dynamics	LC50 and NOEC statistics
Transformation	biotransformation	nutrient/energy cycling	species-species extrapolation
SARs/QSARs	extrapolation	various interactions	population and ecosystem models

Differences between HRA and ERA

1) Taxonomic diversity
2) Toxicological endpoints
3) Spatial scales
4) Temporal scales
5) Complexity of exposure

Table 6.2. Numbers of classified species of some large taxonomic groups of the plant and animal kingdom [6]

Regnum vegetabile		Regnum animalia	
Algae	20,000	Protozoa	46,000
Lichens	20,000	Porifera	5,000
Fungi	100,000	Coelenterata	10,000
Bryophyta	23,000	Plathyhelminthes	12,000
Pterydophyta	11,000	Nematoda	10,000
Spermatophyta	250,000	Mollusca	120,000
		Annelida	8,000
		Arachnida	30,000
		Crustacea	35,000
		Insecta	750,000
		Diplopoda	7,200
		Echinodermata	5,000
		Chordata	45,000

Biodiversity (macrofauna) in soil

1) DIVERSITA' TASSONOMICA

2) Endpoints tossicologici

Sono le **risposte avverse che vengono misurate**, sono i criteri per valutare gli effetti.

Cambiano con il livello di organizzazione biologica considerato (***marker biochimici***, ***attività enzimatiche - tassi di sopravvivenza, crescita, riproduzione - produzione primaria, cambiamenti nella struttura e nelle funzioni nella comunità biologica considerata***)

Criteria for Selecting Ecological Endpoints

- Societal relevance
- Biological relevance
- Unambiguous operational definition
- Accessibility to prediction and measurement
- Susceptibility to the hazardous agent

(Produzione primaria: produzione di composti organici dalla CO_2 presente nell'atmosfera o in acqua che avviene principalmente mediante processi fotosintetici o, in misura minore, chemosintetici)

Effetti inaccettabili

Riduzione nella sopravvivenza inaccettabile

Riduzione nella crescita inaccettabile

Riduzione nella riproduzione inaccettabile

Livello di *avoidance* inaccettabile

Percentuale di **deformità o tumori visibili** inaccettabile

Concentrazione inaccettabile di **residui tossici nei tessuti (edibili)**

Odore/sapore inaccettabile nei tessuti (edibili)

Selecting Ecotoxicological Endpoints in Practice

"Which species and functions of ecosystems are to be protected, and at what levels?" are largely political questions.

To what extent should ecosystems be protected?

- In ERA, clear choices for the protection of species, ecosystems, ecosystem functions or processes are normally not made.
- Many ecological effects assessments have an undefined or vaguely defined goal (Suter, 1993).

Morìa di api a Udine, il gip sequestra i terreni: “Non piantate mais conciato”

5 marzo 2019 Guido Minciotti Senza categoria

AGGIORNAMENTO DEL 25 APRILE 2019 – LA PROCURA DI UDINE RICORRE IN CASSAZIONE

Meno di un arnia

Dominella Trunfio INFORMARSI ANIMALI 03-05-2019

Strage di api in Veneto: morte in 10mila per colpa dei pesticidi

Diecimila api sono morte a Musile, tra i fiumi veneti Piave e Sile. Gli insetti sono stati trovati sulla riva e per gli apicoltori, la colpa sarebbe dell’uso sconsiderato di diserbanti.

ilfattoquotidiano.it/2020/01/26/api-fitofarmaci-per-concia-del-mais-causano-danni-anche-allambiente-lir

Flowers www.labsolutions.c... Posta in arrivo (19.7... Empire Posta in arrivo (16.4...

SOSTIENICI

il Fatto Quotidiano.it

Api, “fitofarmaci per concia del mais cau danni anche all’ambiente”. L’indagine de procura di Udine si allarga

4) Scale temporali

Generation Times for Some Taxa

• Bacteria	~0.1 day
• Green algae	~1 day
• Waterfleas	~10 days
• Snails	~100 days
• Rats	~1 year
• Politicians	~4 years
• Humans	~25 years

← crostacei branchiopodi. Costituiscono una componente principale del plancton d'acqua dolce

5) Complessità dell'esposizione nel ERA

- Niche-partitioning
- Abiotic factors
- Surface Area/Volume
- Life-history
- Behaviour
- Exposure time
- Non-linearity
- Consumption patterns
- Feeding and growth rates
- Biotransformation

Complessità dell'esposizione

Table 6.8. The relationship between surface area and volume of species. For the sake of simplicity, the shape of species is taken to be cubic

Edge (mm)	Surface area (mm^2)	Volume (mm^3)	Surface/ Volume ratio	Examples
0.001	$6x10^{-6}$	10^{-9}	6000	cells/bacteria
0.01	$6x10^{-4}$	10^{-6}	600	algae (*Chlorella* sp.) and fungi (*Penicillium* sp.)
0.1	$6x10^{-2}$	10^{-3}	60	protozoans (*Paramecium* sp.)
1	6	1	6	nematodes and crustaceans (e.g. *Ceriodaphnia dubia*)
10	$6x10^{2}$	10^{3}	0.6	earthworms/small fish (e.g. guppy)
100	$6x10^{4}$	10^{6}	0.06	rainbow trout/pigeon
1000	$6x10^{6}$	10^{9}	0.006	sharks/cows

Complessità dell'esposizione

Fase del ciclo vitale in cui avviene l'esposizione

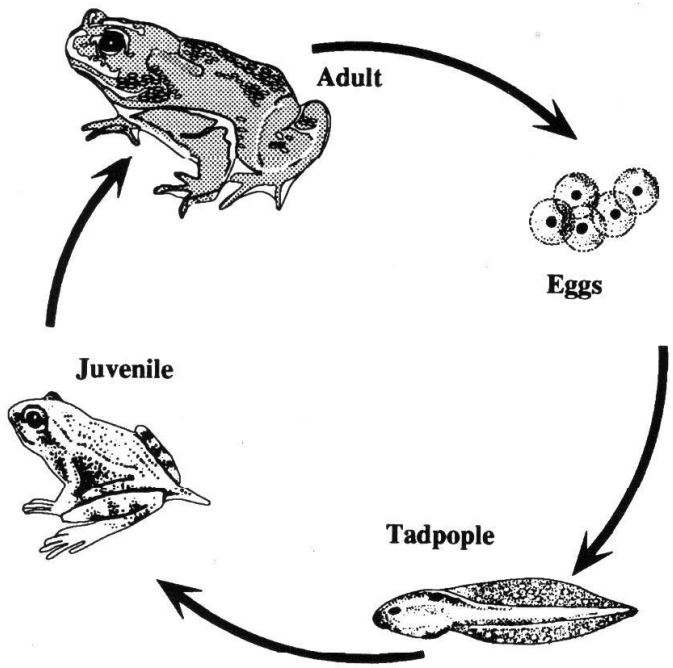


Figure 6.8. Life cycles of an insect and amphibian species with concomitant changes in exposure patterns.

Complessità dell'esposizione - *consumption pattern*

Table 6.9. Fish consumption patterns and daily intakes of hexachlorobenzene (HCB) in The Netherlands (NL), Japan and in the cormorant *(Phalacrocorax carbo)*

	NL	Japan	Cormorant	
			male	female
Body weight (kg)	70	70	2	3
Fish consumption (kg_{wwt}/d)	0.01	0.1	0.5	0.5
Fish consumption (70 kg_{bw})[a]	0.01	0.1	17.5	11.6
Intake of HCB[b] ($\mu g/kg_{bw}$·d)	0.03	0.3	50	33.3

[a] Fish consumption expressed in terms of the body weight of man (70 kg).
[b] The Swedish product standard for HCB in fish (200 μg/kg fish) was used for the calculations

0,01*200/70 =	0,028571	ug/kgbw d

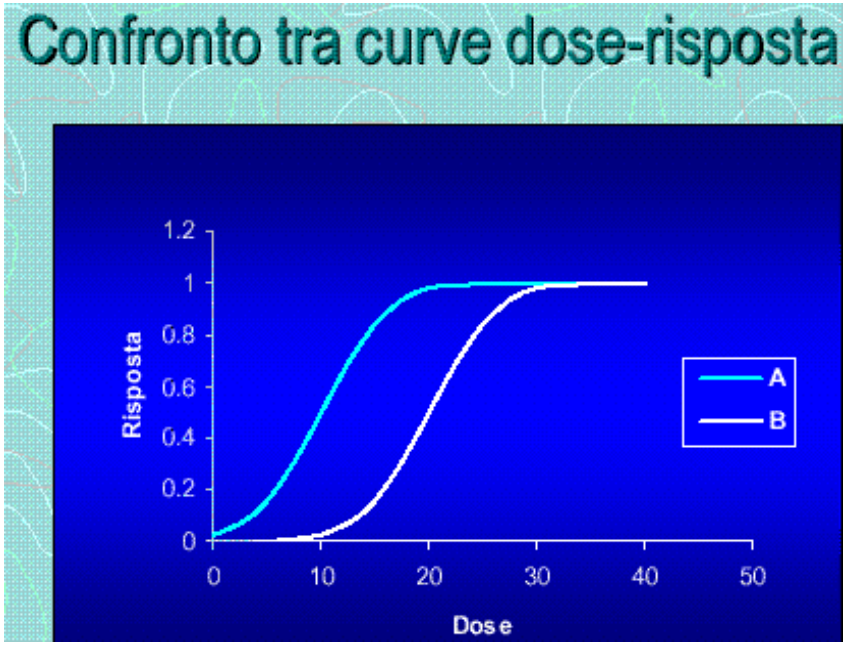
0,5*200/2 =	50	ug/kgbw d

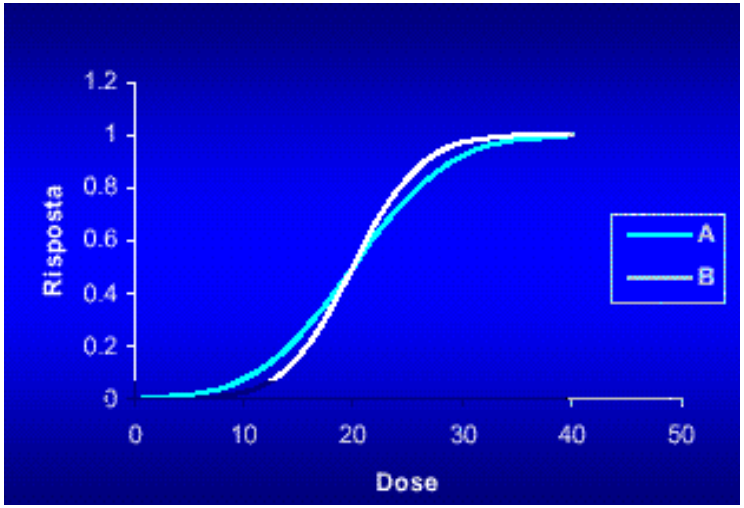
Inadeguatezza dell'approccio "sanitario"

Figure 6.7. A food specialist: the cormorant (*Phalacrocorax carbo*). From A. Belfroid, Utrecht, The Netherlands. With permission.

FOCALIZZIAMO L'ATTENZIONE SULLE RISPOSTE DI ORGANISMI DIVERSI ALLO STESSO INQUINANTE

A e B organismi (specie) testati diversi

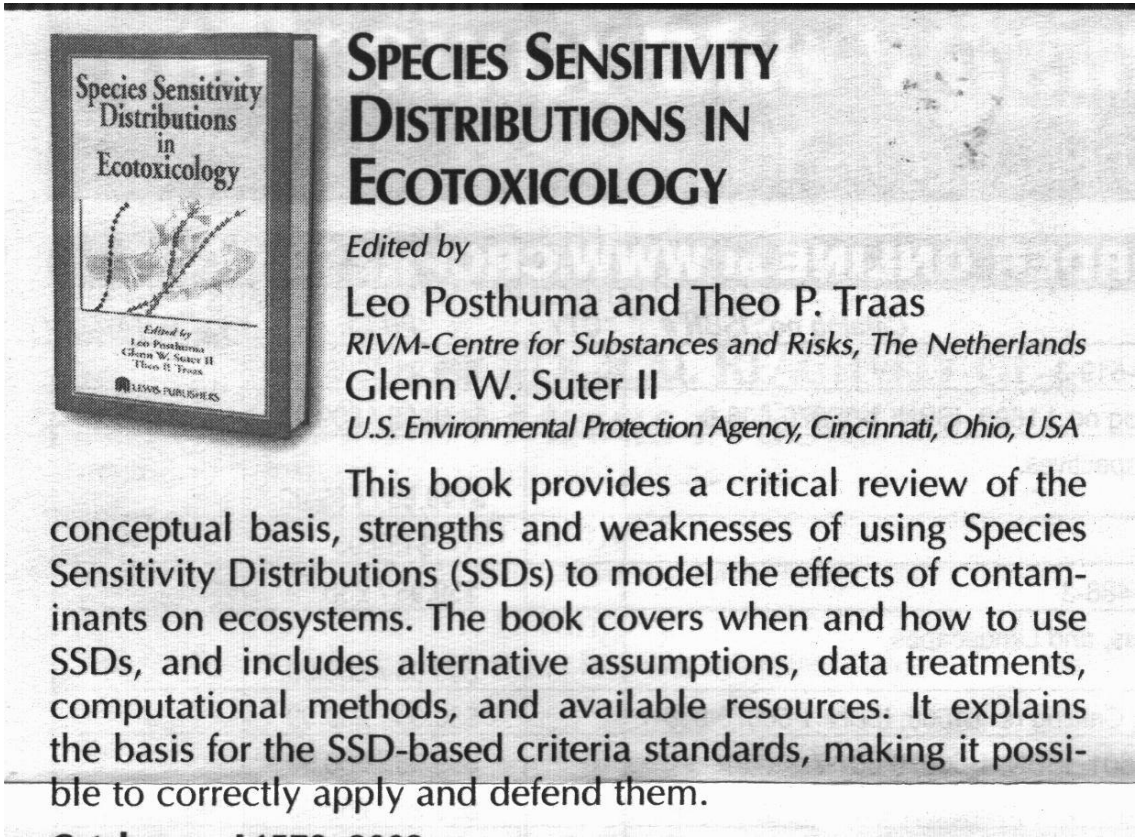




TOSSICITÀ SELETTIVA

- Risposte multiple allo stesso composto tossico principalmente dovute a
  - Differenze nella superficie di esposizione
  - Differenze nell'accumulo
  - Tassi di trasformazione ("biotransformazione")
  - Differenze nei percorsi biochimici

Si possono definire ***distribuzioni di sensibilità delle specie*** *(organismi su cui sono effettuati i test tossicologici)*



Valutazione del Rischio
Approccio Deterministico

Toxicity 

Exposure 

TER 

Valutazioni sulla tossicità

- **A livello di Specie**
  - Laboratory toxicity experiments
  - Greenhouse studies
  - Field studies
- **A livello di Ecosistema**
  - Most sensitive species
  - Mesocosm studies
  - Species Sensitivity Distribution

Species Level Assessment: NOEC (aka NOAEL) and ECx

- **LOEC = lowest tested conc at which a statistically significant adverse effect is observed**
- **NOEC = highest tested conc < LOEC**
  - **LOEC, NOEC depend on experimental design & statistical test**
- **ECx = conc producing x% effect**
  - **ECx depends on experimental design and model and choice of x**

Ecosystem level assessment

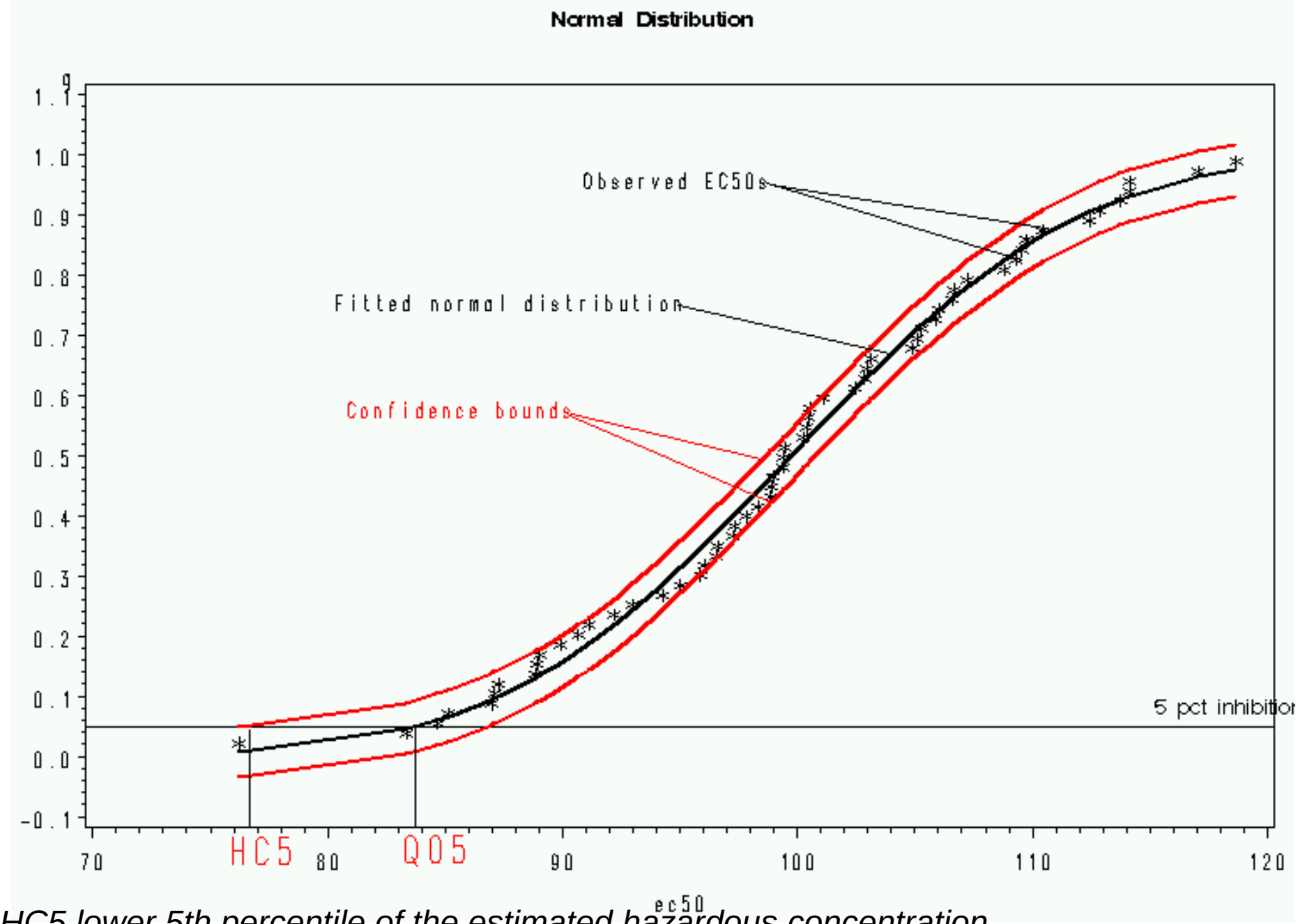
Current Method

- **Determine the NOEC (or EC50) for each species representing an ecosystem**
- **Find the smallest NOEC (or EC50)**
- **Divide it by 10, 100, or 1000 (uncertainty factor)**
- **Regulate from this value**
  - **or argue against it**

Ecosystem level assessment

Probabilistic Approach

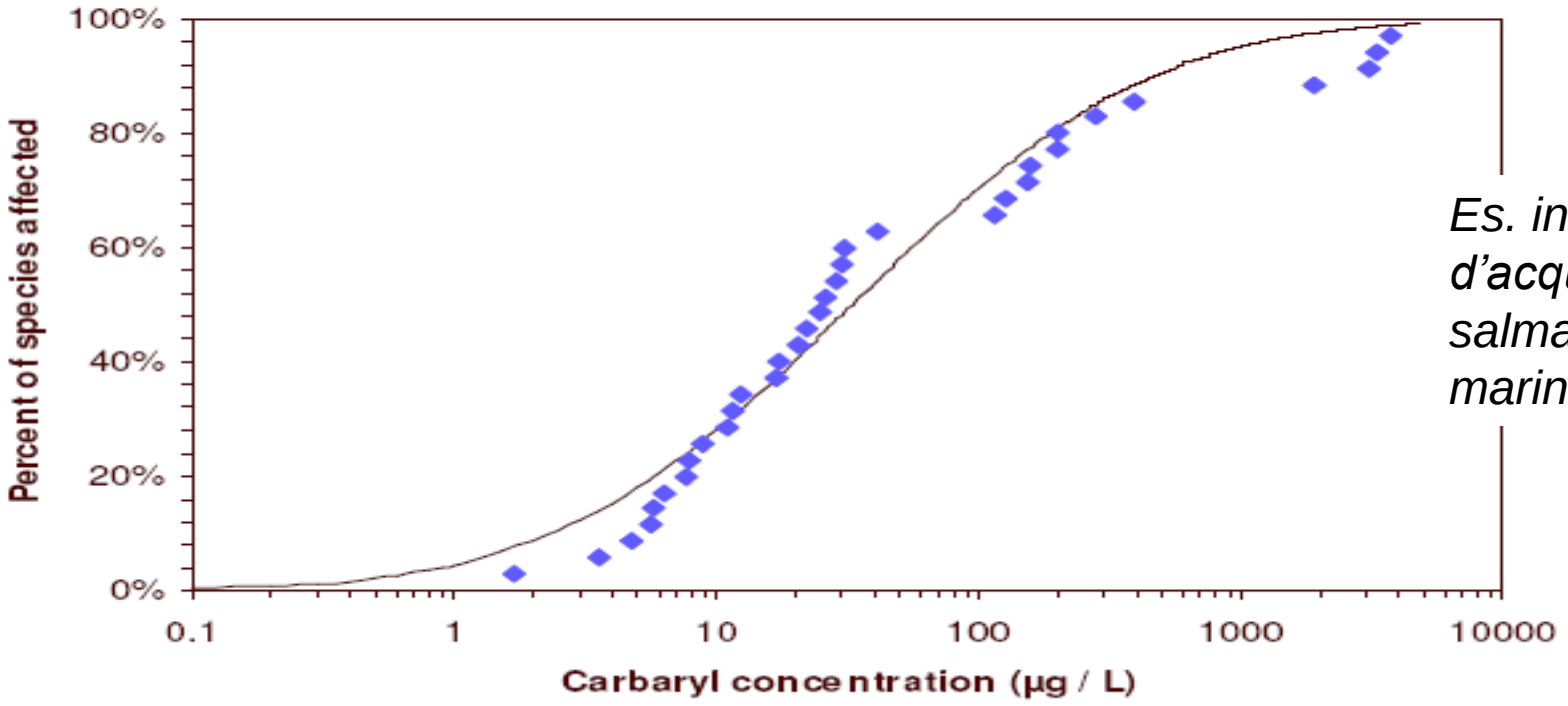
- Collect a consistent measure of toxicity from **a representative set of species**
  - EC50s ***or*** NOECs (not both)
- Fit a distribution (SSD) to these numerical measures
- Estimate concentration, HC5, that protects 95% of species in ecosystem
- Advantages and problems with SSDs



HC5 lower 5th percentile of the estimated hazardous concentration,

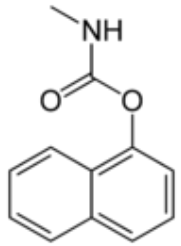
Selection of Toxicity Data

Acute LC_{50} values of Carbaryl for 34 aquatic invertebrate species. The fitted log-normal SSD has a mean of 3.497 and a standard deviation of 2.063.



SSD by Habitat

Es. invertebrati d'acqua dolce, salmastra e marina



insetticida

Visual groupings are not taxonomic classes but defined by habitat , possibly related to mode of action

How Many Species?

- **Newman's method: 40 to 60 species**
  - **Snowball's chance…**
  - **Might reduce this by good choice of groups to model**
- **Aldenberg-Jaworski: 1 species will do**
  - **If you make enough assumptions,…**
- **8 is usual target**
- **5 is common**
- **20-25 in some non-target plant studies**

Which Distribution to Fit?

- **Normal, log-normal, log-logistic, Burr III…?**
  - **With 5-8 data points, selecting the "right" distribution is a challenge**
- **Does it matter?**
  - **Recent simulation study suggests yes**
    - **Various distributions fit**
  - **Actual laboratory data suggests yes**

Which Laboratory Species?

One EUFRAM case study fits an SSD to the following

Species	Toxicity (µg/l)	Test	
Selenastrum capricornutum	43	72h EC50	Alga
Navicula pelliculosa	60	120h EC50	Alga
Skeletonema costatum	69	48-120h EC50	Alga
Myriophyllum heterophyllum	132	14d EC50	Pianta acquatica
Lemna gibba	180	7d EC50	Pianta acquatica
Anabaena flos-aquae	342	72-120h EC50	Batterio/plankton

Aquatic toxicologists can comment (and have) on whether these values belong to a meaningful population

http://www.eufram.com/outputsDraft.cfm

Variability and Uncertainty

Uncertainty reflects *lack of knowledge* of the system under study

- **Ex1: what distribution to fit for SSD**
- **Ex2: what mathematical model to use to estimate ECx**

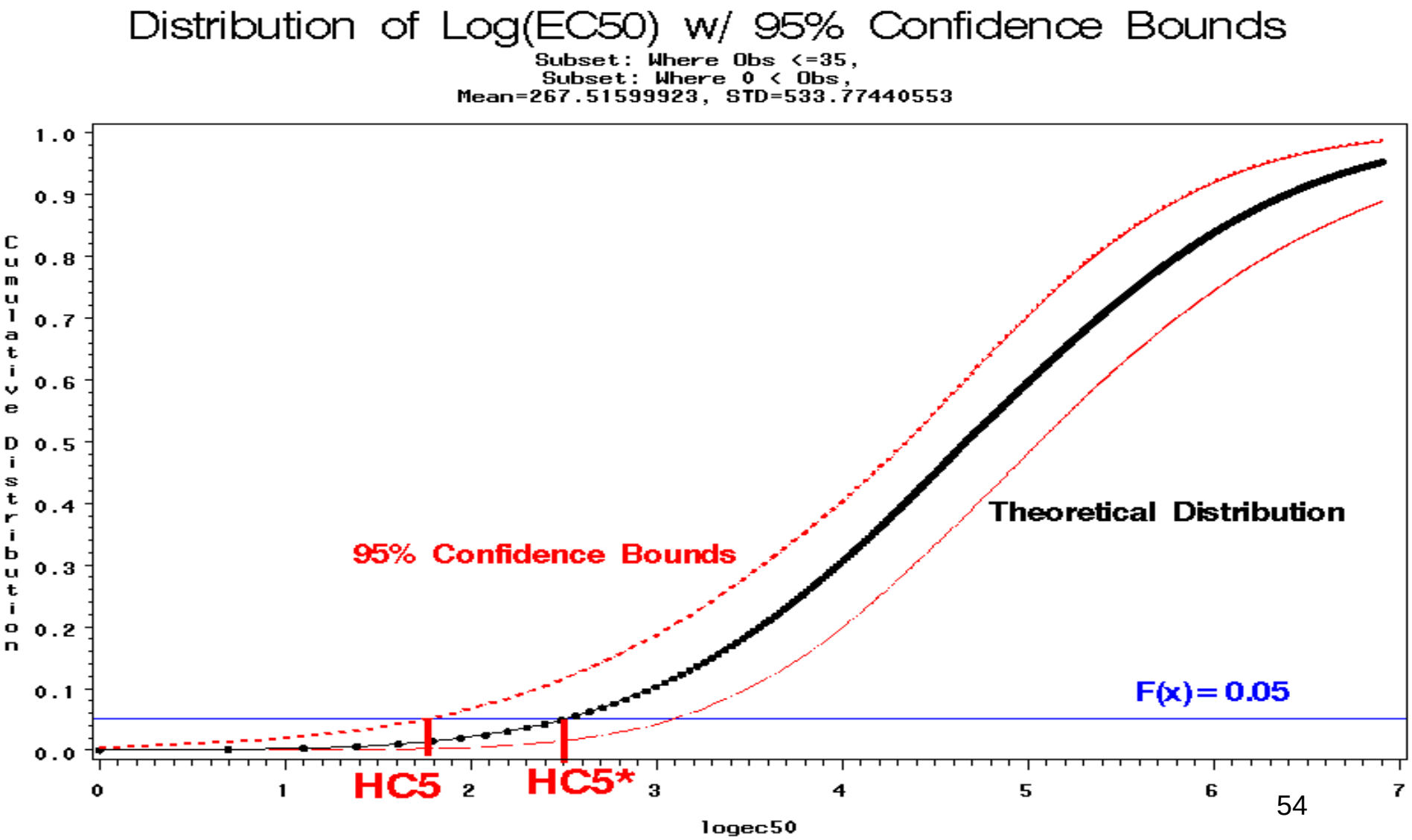
Increased knowledge will reduce uncertainty

Variability reflects *lack of control*

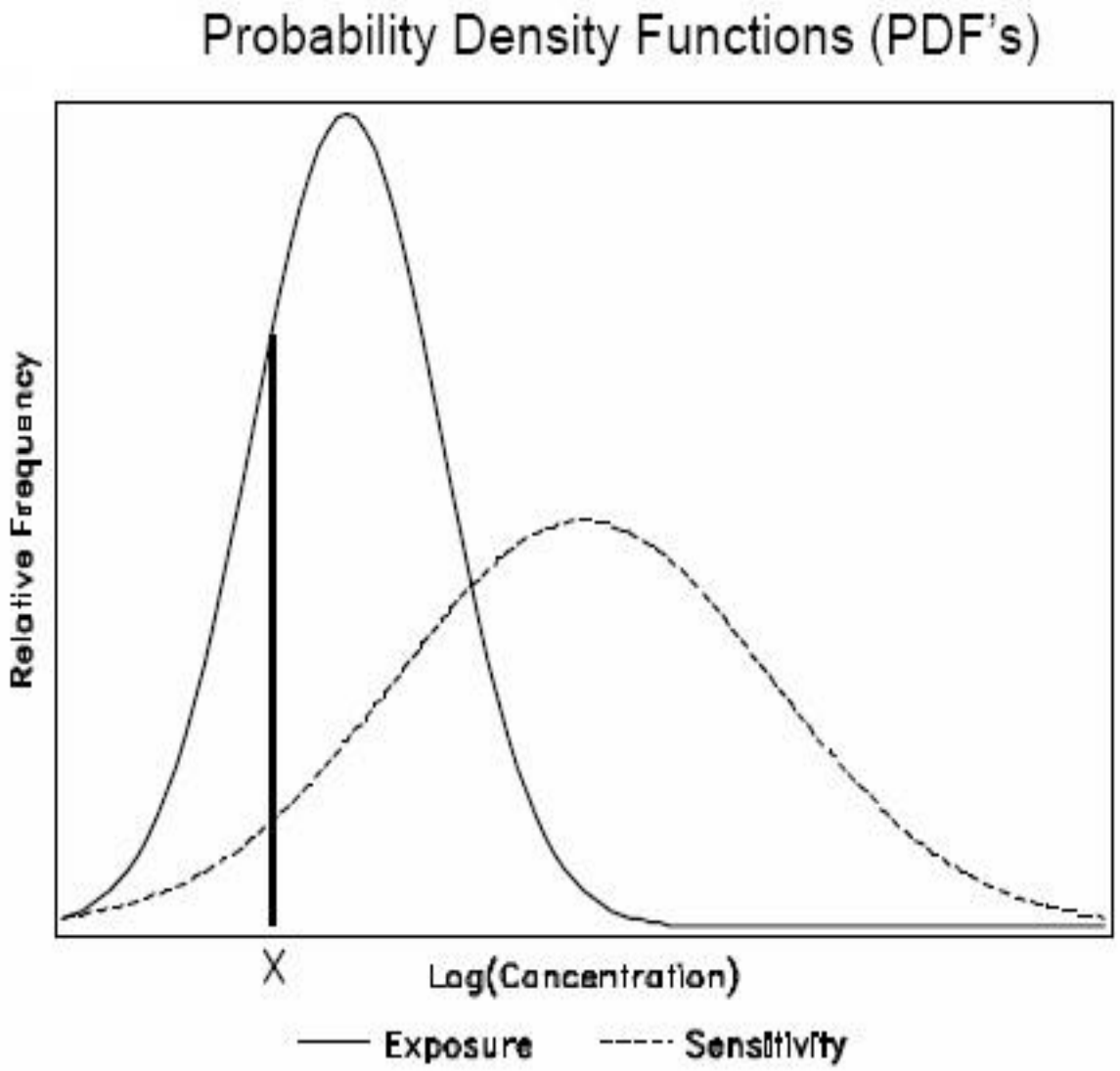
***inherent* variation or noise among individuals.**

Increased knowledge of the animal or plant species will not reduce variability

Summary Plot for SSD



Putting it All Together



Joint Probability Curves

Plot *exposure and toxicity distributions together* to understand the likelihood of the exposure concentration exceeding the toxic threshold of a given percent of the population

Calculating Risk

The risk is given by

$$\Pr[X_e > X_s]$$

where X_e = exposure, X_s =sensitivity or toxicity

This is an "average" probability that exposure will exceed the sensitivity of species exposed

ICE and ACE Software Development

ICE (Interspecies Correlation Estimation)

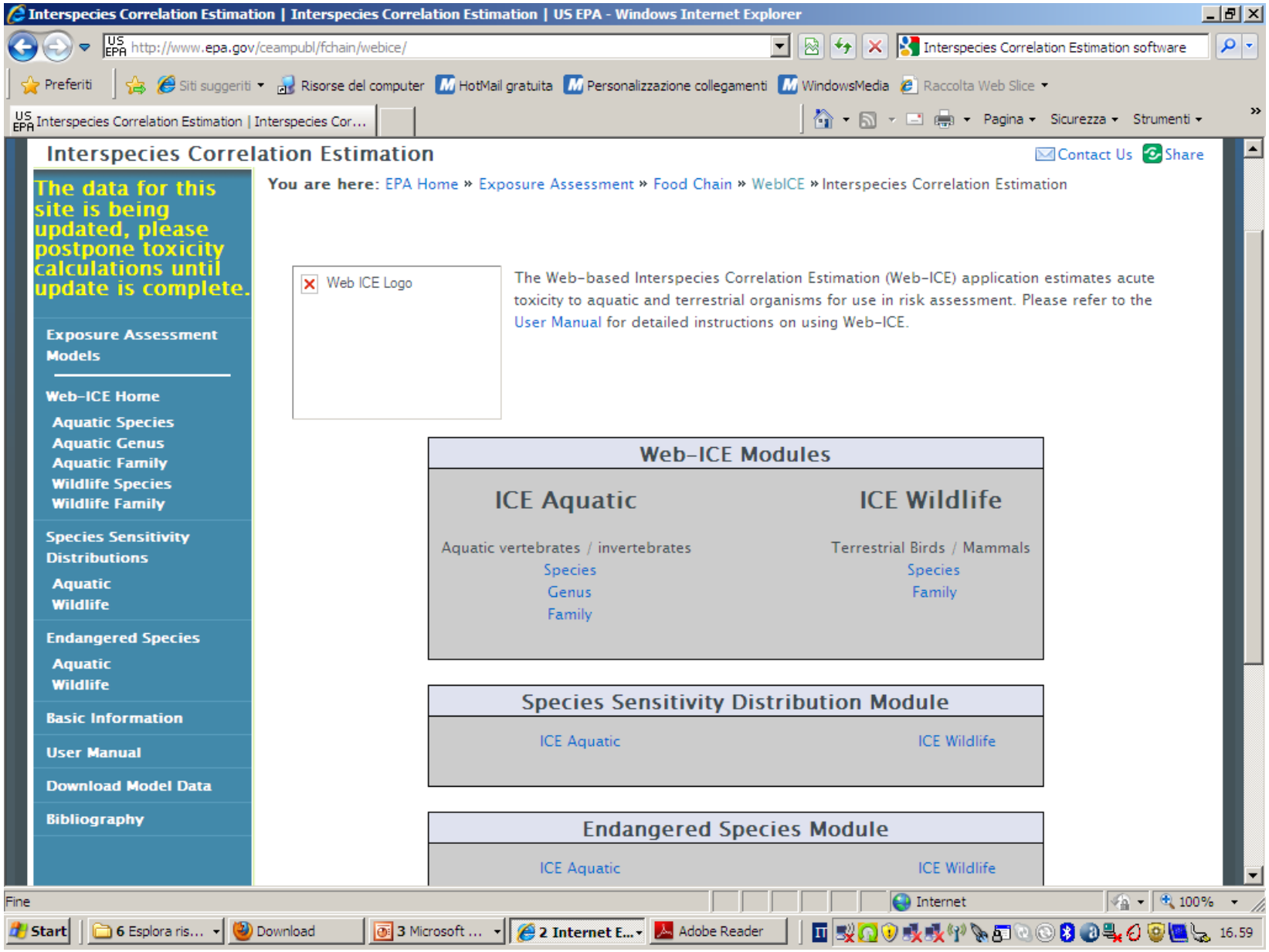
Estimates ***acute toxicity*** for a species, genus or family ***from a surrogate species***

https://www3.epa.gov/webice/ (2016)

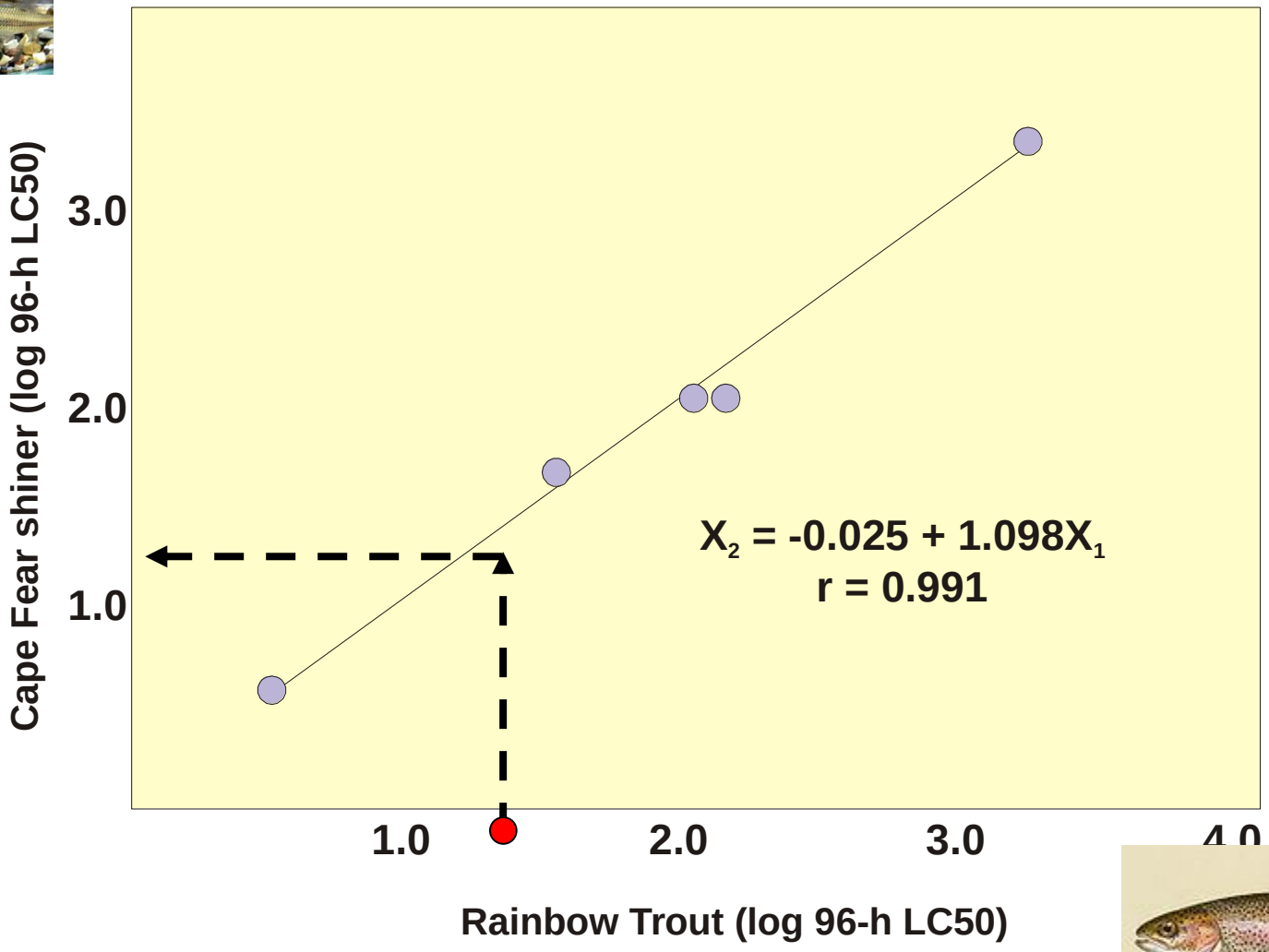
ACE (Acute to Chronic Estimation)

Estimates ***chronic*** toxicity ***from raw acute toxicity data***

https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=62534


Interspecies Correlation Estimation | Interspecies Correlation Estimation | US EPA - Windows Internet Explorer
http://www.epa.gov/ceampubl/fchain/webice/
Interspecies Correlation Estimation software
Preferiti
Siti suggeriti
Risorse del computer
HotMail gratuita
Personalizzazione collegamenti
WindowsMedia
Raccolta Web Slice
Interspecies Correlation Estimation | Interspecies Cor...
Pagina
Sicurezza
Strumenti
Interspecies Correlation Estimation
Contact Us
Share
The data for this site is being updated, please postpone toxicity calculations until update is complete.
You are here: EPA Home » Exposure Assessment » Food Chain » WebICE » Interspecies Correlation Estimation
Exposure Assessment Models
Web-ICE Home
Aquatic Species
Aquatic Genus
Aquatic Family
Wildlife Species
Wildlife Family
Species Sensitivity Distributions
Aquatic
Wildlife
Endangered Species
Aquatic
Wildlife
Basic Information
User Manual
Download Model Data
Bibliography
Web ICE Logo
The Web-based Interspecies Correlation Estimation (Web-ICE) application estimates acute toxicity to aquatic and terrestrial organisms for use in risk assessment. Please refer to the User Manual for detailed instructions on using Web-ICE.
Web-ICE Modules
ICE Aquatic
Aquatic vertebrates / invertebrates
Species
Genus
Family
ICE Wildlife
Terrestrial Birds / Mammals
Species
Family
Species Sensitivity Distribution Module
ICE Aquatic
ICE Wildlife
Endangered Species Module
ICE Aquatic
ICE Wildlife
Fine
Internet
100%
Start
6 Esplora ris...
Download
3 Microsoft ...
2 Internet E...
Adobe Reader
16.59

Acute toxicity estimates using interspecies correlations



You are here: EPA Home > Exposure Assessment > Food Chain > ACE > ACE

Exposure Assessment Modeling

Modeling Products
- Groundwater
- Surface Water
- Food Chain
- Multimedia
- Tools & Data

Information Sources
- About CEAM
- Frequent Questions
- CEAM Discussion
- Related Links
- Distribution & Support Policy

ACE

ICE and ACE were developed by the U.S. EPA in collaboration with other federal agencies, industry, and universities to address data gaps in species sensitivity and reduce reliance on uncertainty factors in ecological risk assessment.

The Acute-to-Chronic Estimation (ACE) with Time-Concentration-Effect Models software allows prediction of chronic toxicity from acute toxicity datasets. ACE uses linear regression and accelerated life testing to predict no-effect and low-effect concentrations for chronic mortality.

Specifications

Current Version:	2.0
Release Date:	December 2003
Development Status:	General Release
Development Information:	Release Notes - changes and known deficiencies
Operating System:	Win 9x, NT, 2000, XP
Development Language:	Visual Basic, Fortran
Intended Audience:	Scientist/Biologist
Key Words:	acute, chronic, toxicity, concentration, exposure
Related Web Sites:	Web-ICE Model Page EPA National Health and Environmental Effects Research Laboratory (NHEERL)

Text Files (ASCII Format)

File Name	File Description

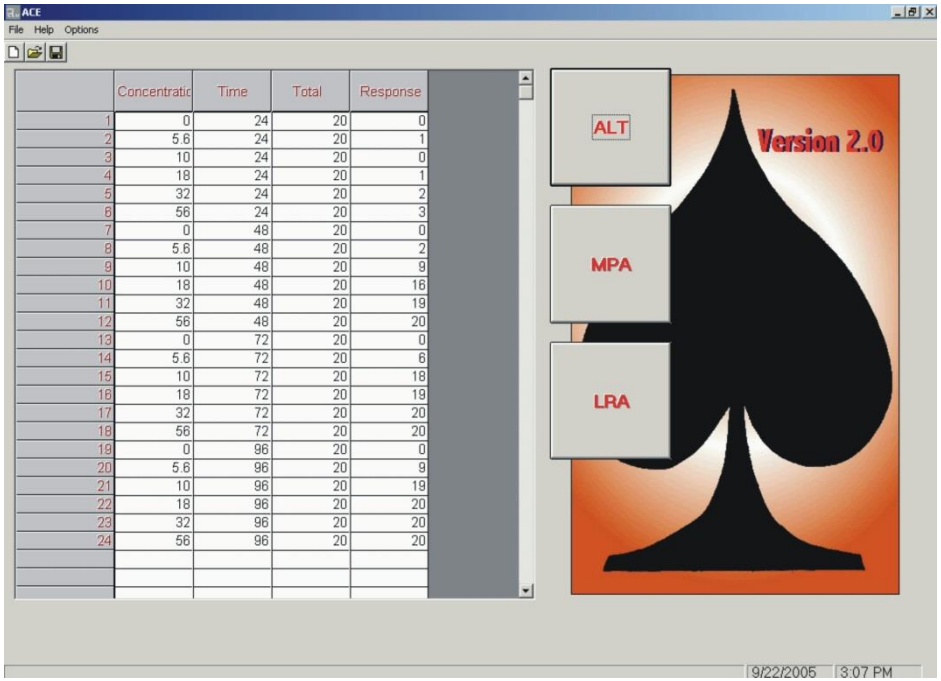
ACE:
Acute to Chronic Estimations

Significance:

Provides estimated chronic toxicity for species with only acute data

Acute: ie.96-hour LC50/ LD50

Chronic: long-term, sublethal



Tossicologia acquatica

Gli studi sugli organismi acquatici sono di prima generazione, i più diffusi, i più consolidati
Misure basate su effetti a breve termine, o Saggi acuti:
da pochi minuti (batteri luminescenti) a 24 o 96 h (pesci, crostacei).

Valutazioni: effetti prodotti da immissioni, più o meno accidentali, di sostanze diverse, di pesticidi, di reflui industriali o domestici

Specie animali: pesci, invertebrati
Specie vegetali: microalghe

Scopo: rilevare la concentrazione o la dose di una sostanza o di una miscela, di un agente fisico (torbidità, livello termico, radiazioni ionizzanti) che hanno effetto avverso misurabile per gli organismi considerati

Motivazioni dell'uso di saggi di tossicità con organismi acquatici

a) Sollecitazioni di carattere legale –
controllo della qualità delle acque superficiali ai fini della *tutela della fauna ittica e della pesca*

b) Formulazione di criteri di qualità:
saggi *preventivi all'immissione sul mercato di nuovi prodotti chimici*. Bersagli biologici – saggi con pesci e crostacei

c) Tutela ambientale:
giudizi di *accettabilità di effluenti* di cui non è nota la composizione

Specie test

ACQUA DOLCE

Pesci

Salmonidi Oncorhyncus mykiss, Salvelinus fontinalis
Ciprinidi Pimephales promelas
Ictaluridi Ictalurus punctatus
Centrarchidi Lepomis macrochirus

Invertebrati

Cladoceri Daphnia magna, D.pulicaria, D.pulex
Anfipodi Gammarus lacustris, G.fasciatus, G.pseudolimnaeus
Decapodi Orconects sp., Cambarus sp.
Ditteri Chironomus sp.
Gasteropodi Physa integra

ACQUA DI MARE

Pesci

Ciprinodontidi Cyprinodon variegatus, Fundulus heteroclitus, F.similis
Aterinidi Menidia sp.

Invertebrati

Copepodi Acartia tonsa, A.clausi
Decapodi Peneus setiferus, P.duorarum, Palaemonetes pugio, P.vulgaris, Crangon septemspinosa, Mysidiopsis bahia, Callinectes sapidus, Uca sp.
Lamellibranchi Crassostrea virginica, C.gigas
Policheti Capitella capitata, Neanthes sp.

Introduction: experimental

The toxicity towards **Fathead Minnow (*Pimephales promelas*) – a freshwater fish from north America** - has been tested [1] for

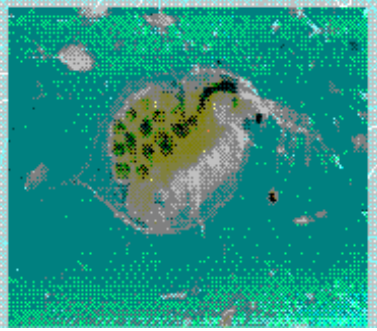
•562 compounds representing a cross section of industrial organic chemicals [2], and

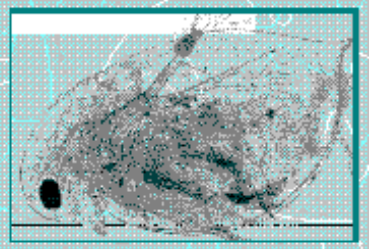
•Toxicity has been reported as median lethal concentrations LC50 (mmol/l) after 96 hours exposure

1. C.L. Russom, S.P. Brandbury, S.J. Broderius, D.E. Hammermeister, D.A. Drummond, *Environmental Toxicology and Chemistry*, 16 (1997) 948-967.

2. G.D. Veith, B. Greenwood, R.S. Hunter, G.I. Niemi, R. Regal, *Chemosphere*, 17 (1988) 1617-1630 .

Daphnia magna, D.pulex e le altre





Effetto rilevato: morte, a volte si sceglie *l'immobilizzazione* (dafnie). Per gli organismi monocellulari si sceglie la *diminuzione della crescita* (alghe) o la *compromissione della luminescenza* (batteri)

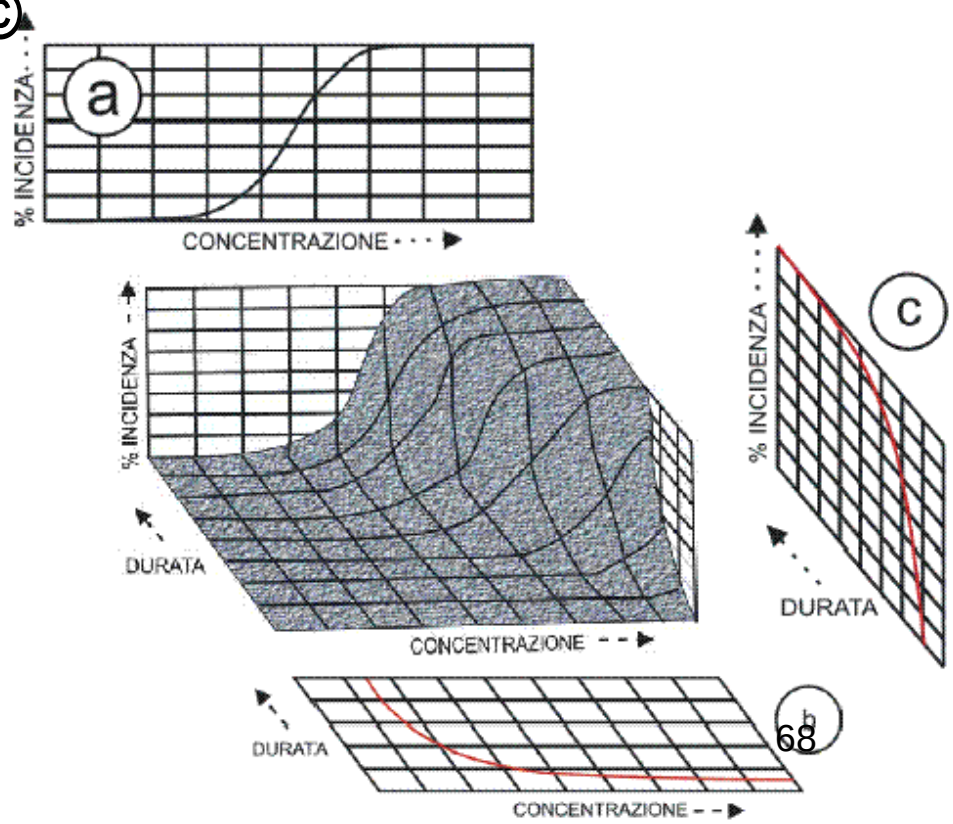
Somministrazione: Nei saggi con organismi acquatici si contamina l'acqua *(effective concentration* – concentrazione efficace).

Tre sono i possibili tipi di approccio:
- **test statici.** Si allestiscono una serie di soluzioni con concentrazioni diverse senza ulteriori aggiunte di contaminante. *Sono impiegati per i saggi di breve durata*
- **test con rinnovo periodico della soluzione**: si procede come con i test statici, ma dopo 24 h si procede ad una sostituzione dell'acqua a cui viene aggiunto di nuovo il tossico per ripristinare la concentrazione.
- **test a flusso continuo**: la soluzione test viene mantenuta in stato stazionario mediante un sistema di alimentazione automatico. *Sono i più utilizzati per gli esperimenti a lungo termine*

Si suppone che la sostanza impiegata nel test sia la causa dell'effetto osservato.

Nel corso del test deve essere verificato se a carico di tale sostanza si verificano *trasformazioni* chimiche **(b)**. Si suppone che la *risposta* osservata e la sua intensità siano *in funzione della concentrazione* della sostanza in esame nell'acqua in cui vengono posti gli organismi-test **(a)**. *Livelli* di esposizione *non efficaci a breve termine possono produrre danni con tempi di trattamento più lunghi*. ©

Tuttavia, in genere, si tiene costante il tempo ma si varia la concentrazione.



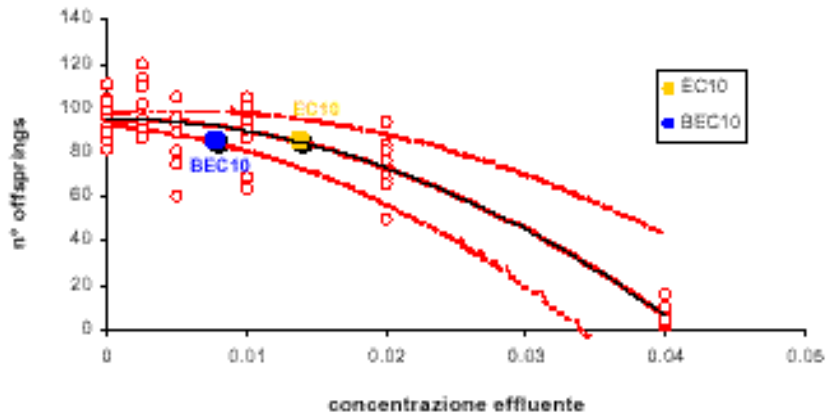
Produrre uno o più effetti sugli organismi tenuti in condizioni controllate

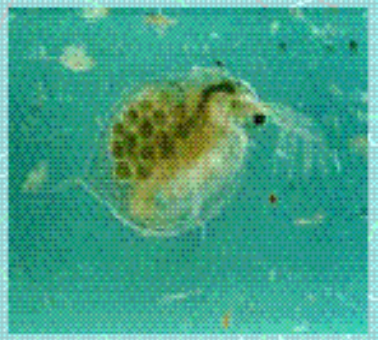
Esperimenti con più repliche:
- Variazione della concentrazione della sostanza in esame
- Scelta dei tempi
- Lettura dei danni prodotti allo scadere dei tempi prefissati
- Curva di tossicità
-EC 50 *(Median effective concentration – Concentrazione efficace mediana*)
- Quando l'effetto è la morte allora EC 50 = LC 50 *(Median lethal concentration – Concentrazione letale mediana*)
- Mediana indica che la risposta biologica è pari al 50%; alla LC 50 ci si aspetta la morte del 50% dei trattati.

- Generalmente si prendono come riferimento dei parametri fisiologici e/o riproduttivi (es. vel. di nuoto, tasso respiratorio, parametri indicativi del metabolismo) dell'organismo utilizzato nei test e se ne confrontano statisticamente i valori rispetto ad un gruppo di controllo.

Definizione del NOEC

- Ad esempio può essere assunto come endpoint una diminuzione del 10% del tasso riproduttivo





PREGI

Il saggio tossicologico diviene estremamente utile ai fini della valutazione delle interazioni tra le componenti tossiche e le caratteristiche naturali del corpo idrico ricevente.

LIMITAZIONI

L'approccio tradizionale basato sull'utilizzazione di *una singola specie* può essere riduttivo rispetto alla complessità degli ecosistemi

L'utilizzazione di un *numero maggiore di specie lascia comunque irrisolti i problemi di incertezza* rispetto alla capacità di tolleranza delle innumerevoli specie (micro e macrospiche) di un ecosistema acquatico

I saggi a *breve termine*, prevalentemente utilizzati, non permettono di prevedere quali siano invece gli effetti derivanti da esposizione a lungo termine

Soglia di tossicità. Dose o concentrazione alla quale o al di sotto della quale non si manifesta un danno misurabile dopo un determinato tempo prestabilito. Tale concetto non si applica per quelle sostanze o agenti fisici (radiazioni ionizzanti) che agiscono sul DNA, per le sostanze mutagene, per quelle che producono un'inibizione enzimatica e dei meccanismi di trasporto, per quelle cancerogene.

No-observed-effect level. Max livello di esposizione ancora non efficace
Lowest-observed-effect level. Livello più basso tra quelli efficaci

Per definizione la soglia di tossicità si colloca tra NOEL e LOEL

No-observed-adverse-effect level. Concentrazioni che non producono effetti necessariamente dannosi *(adverse effect)* e pertanto anche se presenti non vengono considerati ai fini della valutazione della soglia di tossicità.
La conoscenza del NOEL **per gli organismi più sensibili di una comunità** consente di ricavare criteri di protezione accettabili. La difficolt è rappresentata dalla possibilità di includere le specie più sensibili tra gli organismi con cui si effettuano i test di tossicità.

Individuazione *a priori* dei **percorsi critici** degli inquinanti (quelli in cui si prevedono le contaminazioni maggiori) e dei **gruppi critici** (specie o insiemi di individui più esposti alla contaminazione).

Si controllano gruppi critici e/o i percorsi critici, e si assume che se per essi sono verificate condizioni accettabili, allora anche altre specie, individui, siti si trovino in condizioni di sicurezza.

Possibili forme di distorsione delle prove di tossicità:
- l'impiego di un basso numero di animali può portare a valutazioni di tipo ottimistico.
- l'insorgenza di effetti a basse concentrazioni può confondersi con le risposte dei controlli
- il trasferimento dei risultati ricavati dal campione sperimentale all'intera popolazione (inferenza statistica).
-l'estrapolazione dei risultati conseguiti con una specie ad altre

Fattori di sicurezza

Ai NOEL sperimentali si applicano *fattori di incertezza o fattori di sicurezza* (1/5, 1/10, 1/100 del suo valore)

Spesso si effettuano ***test tossicologici su organismi posti a diversi livelli della catena trofica***.

Ad esempio:
1 test su batteri (es. *Vibrio Fisheri* inibizione luminescenza)
1 test su alghe (es. *Dunaliella Tertiolecta* inibizione crescita)
1 test su invertebrati (es. *Daphnia Magna* inibizione mobilità)
1 test su pesci (es. *Pimephales promelas* LD_{50}*)*

SEDIMENTI

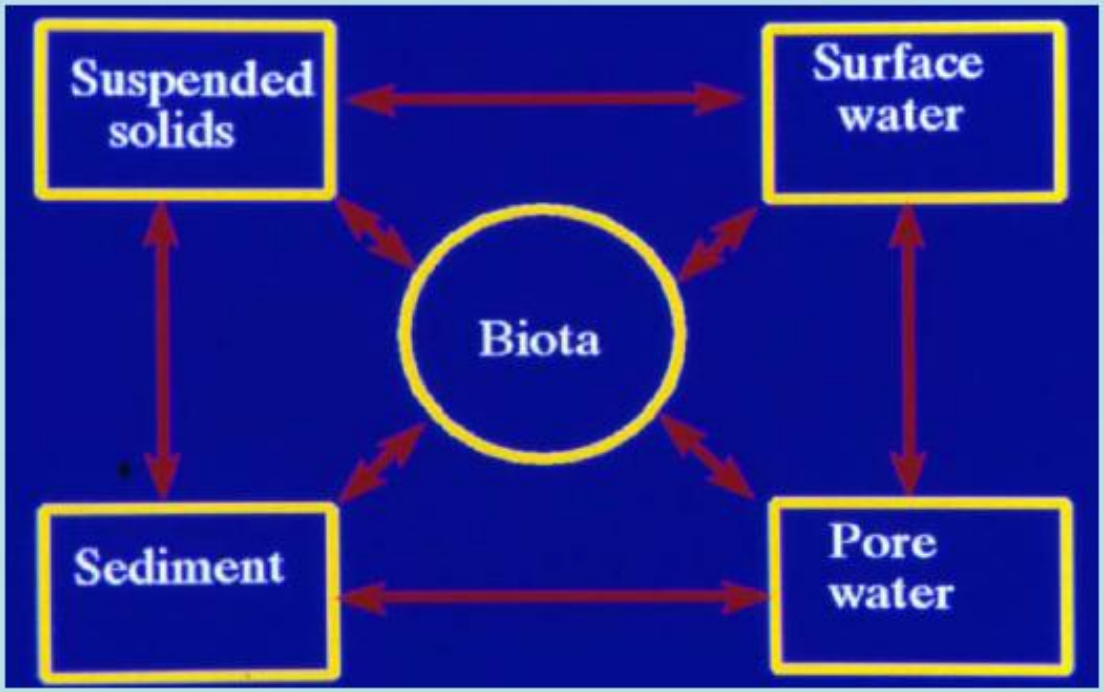


Fig. 7.26. Compartments and their interrelationships

EQUILIBRIUM-PARTITIONING

(Van der Kooy et al., 1990)

CONCENTRATIONS IN WATER AND SOLIDS ARE RELATED THROUGH A PARTITION COEFFICIENT:

$$K_{sw} = \frac{C_s}{C_w}$$

WHERE:

Ksw = SOLIDS-WATER PARTITION COEFFICIENT (L/KG)

CS = CONCENTRATION IN THE SOLID PHASE (MG/KG)

CW = CONCENTRATION IN THE WATER PHASE (MG/L)

Sediment Quality Guidelines developed for the National Status and Trends Program

Because guidelines were needed that were based on measures of biological effects associated with toxicants, data were compiled that included both chemical measures and biological effects.

SQGs were derived initially using a database compiled from studies performed in both saltwater and freshwater and published in NOAA Technical Memorandum NOS OMA 52 (Long and Morgan 1990). A larger database compiled from many studies perform
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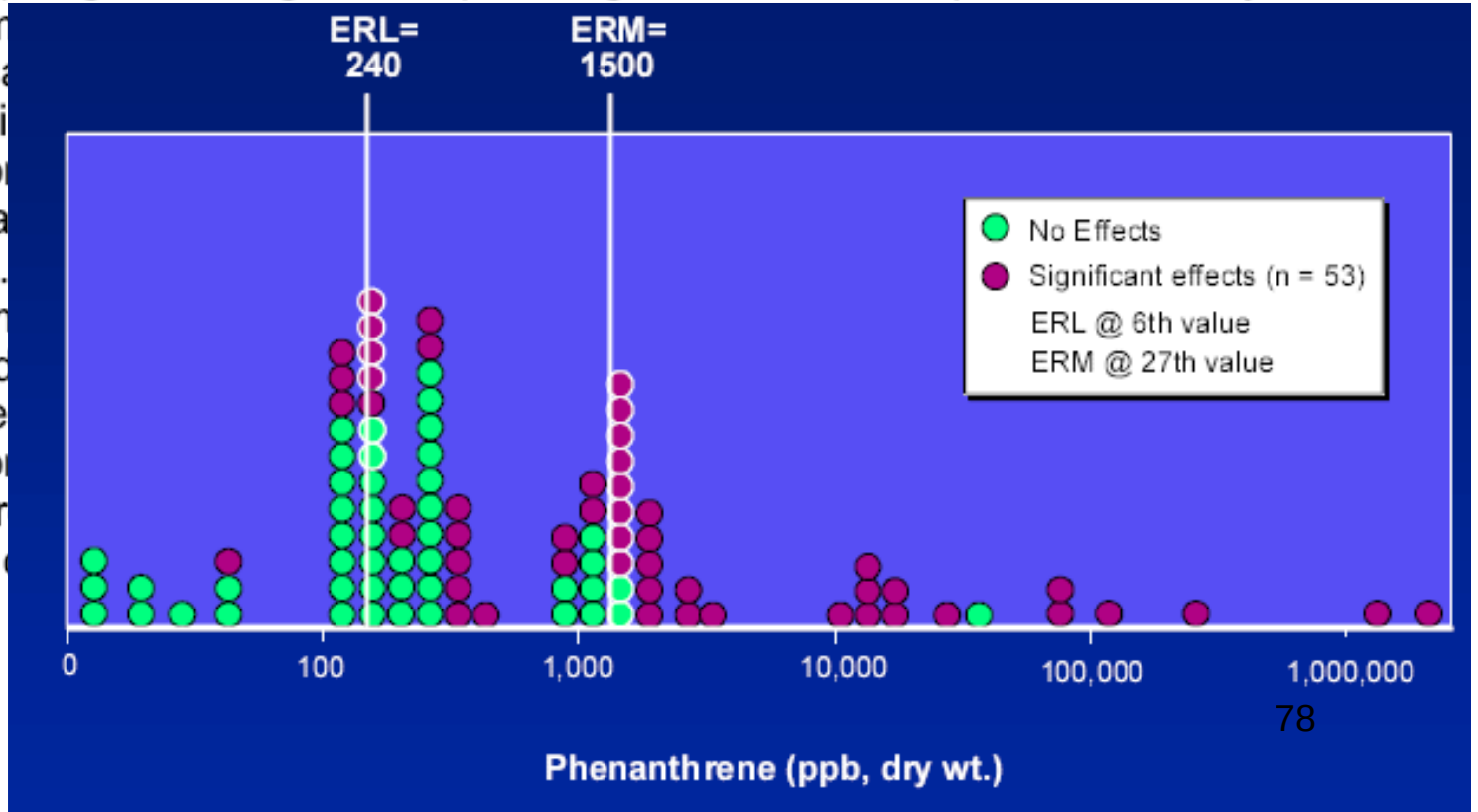

Table 1. ERL and ERM guideline values for trace metals (ppm, dry wt.) and percent incidence of biological effects in concentration ranges defined by the two values (from Long et al., 1995). ERL= Effects Range-Low; ERM= Effects Range-Median.

	Guidelines		Percent incidence of effects*		
Chemical	ERL	ERM	<ERL	ERL - ERM	>ERM
Arsenic	8.2	70	5.0	11.1	63.0
Cadmium	1.2	9.6	6.6	36.6	65.7
Chromium	81	370	2.9	21.1	95.0
Copper	34	270	9.4	29.1	83.7
Lead	46.7	218	8.0	35.8	90.2
Mercury	0.15	0.71	8.3	23.5	42.3
Nickel	20.9	51.6	1.9	16.7	16.9
Silver	1.0	3.7	2.6	32.3	92.8
Zinc	150	410	6.1	47.0	69.8

*Number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range.

Table 2. ERL and ERM guideline values for organic compounds (ppb, dry wt.) and percent incidence of biological effects in concentration ranges defined by the two values (from Long et al. 1995). ERL= Effects Range-Low; ERM= Effects Range-Median.

	Guidelines		Percent incidence of effects*		
Chemical	ERL	ERM	<ERL	ERL--ERM	>ERM
Acenaphthene	16	500	20.0	32.4	84.2
Acenaphthylene	44	640	14.3	17.9	100
Anthracene	85.3	1100	25.0	44.2	85.2
Fluorene	19	540	27.3	36.5	86.7
2-methyl naphthalene	70	670	12.5	73.3	100
Naphthalene	160	2100	16.0	41.0	88.9
Phenanthrene	240	1500	18.5	46.2	90.3
Sum LPAH	552	3160	13.0	48.1	100
Benz(a)anthracene	261	1600	21.1	43.8	92.6
Benzo(a)pyrene	430	1600	10.3	63.0	80.0
Chrysene	384	2800	19.0	45.0	88.5
Dibenzo (a,h) anthracene	63.4	260	11.5	54.5	66.7
Fluoranthene	600	5100	20.6	63.6	92.3
Pyrene	665	2600	17.2	53.1	87.5
Sum HPAH	1700	9600	10.5	40.0	81.2
Sum of total PAH	4022	44792	14.3	36.1	85.0
p,p'-DDE	2.2	27	5.0	50.0	50.0
Sum total DDTs	1.58	46.1	20.0	75.0	53.6
Total PCBs	22.7	180	18.5	40.8	51.0

*Number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range.

Preliminar Results From a Sediment Quality Triad Study in the Gulf of Trieste:

the Choice of the Reference Site.

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Title anticipated in the Book of Abstracts:

"Sediment Quality Triads and the Integration of Information from Analytical Chemistry with Ecological Community Structure and Toxicological Data in Risk Assessment of Coastal Sites."

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Environmental quality criteria

Aiming at the classification of ecosystems on the base of their environmental degradation, *environmental quality criteria* (numerical values) are required in order to determine if a zone is degraded or not.

Questions arise when the environmental quality criteria is based only on the assessment of chemical contamination of a certain environmental compartment since *chemical contamination does not necessarily imply effects on biological communities*. Moreover effects on biological communities are related to several factors, conditioning also the concentrations of contaminants, as – in aquatic systems – hydrodynamics, grain size of sediments, species being considered, etcetera.

Sediments

Within aquatic ecosystems, sediments achieve importance in consideration of:

- Accumulation of contaminants (low solubility – affinity for particulate matter
- High residence time of c. (difficult biodegradation in reducing medium) → benthic organisms exposed to high levels of c.
- Sediment bound contaminants can be released to water if environmental conditions do vary.

Environmental agencies - as U.S.E.P.A. - thus consider *sediments as key environmental components within aquatic compartments.*

Criteria classically determined for environmental quality characterisation derive from approaches listed in Table 1, where examples and main limitations of each are reported.

Table1

APPROACH	***EXAMPLE OF MEASUREMENTS***	***LIMITATIONS***
Sediment chemical analyses	- Individual contaminants - Complementary analyses (TOC, surface of grains etc.)	- Assumes that all chemical contaminants are measured - Contamination do not inform about biological effects
Organism tissue chemical analyses	- Individual contaminants - Complementary analyses (biometrical etc.)	- *Idem* as above - Organisms mobility
Sediment toxicity tests	- Survival - Sublethal effects (malformation, burial)	- Conditions different from reality; - Assumes that considered tests cover all responses - Toxicity is not linked causally to specific toxic agent
Histopathological alterations	- Individual pathological conditions - Complementary analyses (biometrical etc.)	- Organisms mobility - Disease is not linked causally to specific chemical agent
Structure of the Benthic community	- Taxa (Mollusca, Polichaeta etc.) - Biomass; indices of biodiversity	- Difficult to discriminate between natural and anthropogenic effects

Each single approach presents pros and cons; consequently two or more of the cited type of measurements can be applied on samples acquired simultaneously thus allowing *an integrated assessment*.

The case study

The growing degree of connection of urban and industrial sites of the Plain of the Isonzo River to the local sewage treatment plants and the high environmental pressure on the coast line of the Gulf of Trieste have brought to *plan the building of a new off-shore diffusor* that will be completed before the end of 2002.

Other diffusors within the same Gulf were demonstrated to bring metals to offshore sediments, thus extending the radius of impact of human activities, beside lowering the environmental strain on the coastline [].

An *integrated environmental assessment* has been performed before the building and exersice of the offshore dispersion device *at four sites located nearby* it -locations are ISO1, ISO2, ISO3 and ISO4 in Figure 1 - so to provide a reference for a future evaluation the possible impact of treated waters on benthic life. *Measurements describing chemical contamination of sediments, ecotoxicity tests with sediment elutriates, and quali-quantitative assessment of macrobenthic population have been produced*.

	Long.	Lat.
ISO1	13°35’.43	45°42’.08
ISO2	13°35’.17	45°41’.86
ISO3	13°35’.91	45°42’.13
ISO4	13°35’.33	45°42’.73

	Depth (m)	Sand %	Silt %	Clay %
ISO1	13.7	0.00	33.47	63.53
ISO2	13.7	0.00	33.16	66.84
ISO3	14.6	0.00	37.05	62.95
ISO4	11.5	0.00	42.82	57.18

Experimental methods:

Samples for chemical and toxicological analyses have been collected by a Kc HAPS bottom corer with a sample area of 127 cm^2; for the analysis of benthos three samples have been collected with a 0.1 m^2 van Veen grab.

Chemical analyses: metals (Cd, Ni, Pb, Ag, Cu, Cr, Fe, Zn, As and Hg) have been released from sediments and analysed according to I.R.S.A. methodologies []. The spectrometer was a PE-5100PC.

PAHs (Phenantrene, Fluoranthene, Pyrene, Benzo(a)anthracene, Crysene, Benzo(b)fluoranthene, Benzo(a)pyrene), PCBs, 4,4'-DDE, 4,4'-DDD, 4,4'-DDT have been extracted again according to I.R.S.A. methods []; PCBs have been quantified as PCB1254 mixture. The separation were conducted by gas chromatography, with ECD for chlorinated compounds and MS for PAHs. PE-AutoSystem XL and HP-6980/5973 instruments were used.

Toxicological analyses on sediment elutriates considered here are the Microtox assay® [] and the assay on the alga *Dunaliella tertiolecta* [].

In situ alteration of the benthic community has been assessed by the *analysis of macrobenthos.* Macrobenthic organisms (Mollusca, Polychaeta, Crustacea, Echinodermata) have been determined to species level; furthermore abundance values of specimens were computed. From these data diversity indices (Shannon, Pielou) have been calculated.

Chemistry, Toxicity and Infauna Data from the four different sites can be combined into *the Sediment Quality Triad* (SQT) [] in order to determine the degree of degradation at each site. The normalization of data from the sampling sites towards those of one of them that is considered as an unpolluted reference makes the comparison relatively easy. For each site and for each parameter determined, the datum is converted into a *Ratio To Reference* (RTR) value:

$$(RTR_i)_k = (v_i)_k / (v_i)_0$$ where:

$(RTR_i)_k$ is the RTR for parameter i-me at site k-me;

$(v_i)_k$ is the datum determined for parameter i-me at site k-me;

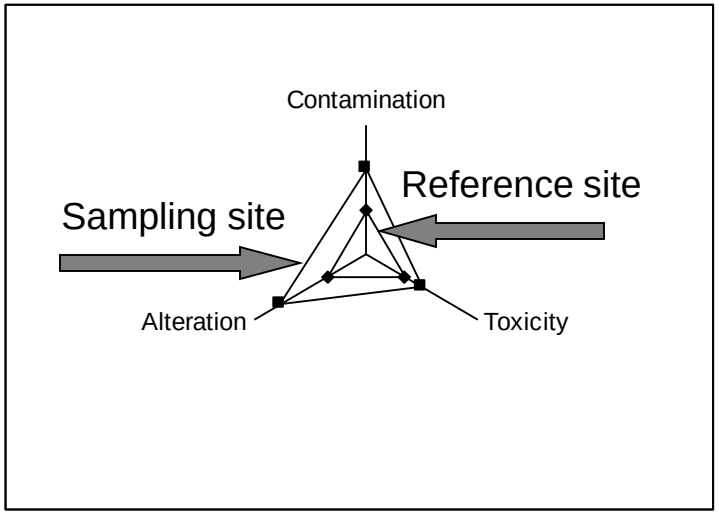
$(v_i)_0$ is the datum determined for parameter i-me at site chosen as reference.

This is straightforward for chemical parameters, while toxicological and infaunal parameters have been transformed so to show increase with biological damage. For instance, in a Microtox® test the result (endpoint) is expressed as EC20, the percentage of interstitial water sample causing a 20% inhibition of bioluminescence of the population of *Vibrio Fisheri;* this means that EC20 is low when sediment is highly polluted; the inverse ($EC20^{-1}$) is thus considered.

$(RTR_i)_k$ for all i parameters describing chemical contamination are averaged, thus providing a single *Index of Contamination for each site, IC ;* the same is done for parameters describing sediment toxicity and *in situ* alteration; The result is a *Index of Toxicity (IT) and a Index of Alteration (IA) for each site*.

The three indices for each sampling site can be displayed in graphical form as three segments (for Contamination, Toxicity and Alteration) departing from a central point, where the lenghts of each segment equals the averaged values of the RTR for the three group of determined parameters.

Two triangles are identified; the inner one represents the reference site, the outer is one of the site for whom the environmental quality must be assessed. The difference between the areas of the outer and inner triangles can be retained as a synthetic ***index of degradation*** with respect of the reference site []. The difference between the sums of the three indices IC, IT and IA. for the site under investigation and the reference is a measure of degradation as well.



Del Valls et al. [] proposed a modified normalization procedure, where:

$$(RTM_i)_k = (RTR_i)_k / RTRmax_i$$

$(RTM_i)_k$ is the new normalized value for parameter i-me at site k-me;
$(RTR_i)_k$ is the RTR for parameter i-me at site k-me;
$RTRmax_i$ is the maximum value of RTR for parameter i-me;
The new indices of Contamination, Toxicity and Alteration for site k are computed as:

$NIC_k=(\Sigma RTM_{ic})_k / (\Sigma RTM_{i\,c})_0$; ic = index running between chemical parameters;
$NIT_k=(\Sigma RTM_{it})_k / (\Sigma RTM_{i\,t})_0$; it = index running between toxicological parameters;
$NIA_k=(\Sigma RTM_{ia})_k / (\Sigma RTM_{i\,a})_0$; ia = index running between alteration parameters

It is clear how results depend on the choice of the reference site, but no formal procedure has been proposed to select it, at the best of our knowledge.

The problem is not trivial, since in practical cases it is frequent to choose the reference site between stations which are not “completely unpolluted”; the quest for a “truly unpolluted” reference could lead to select a station being too heterogeneous from others.

A formal procedure for selecting the reference site is as follows:

1) for each possible reference site i

compute IC, IT, IA (or NIC, NIT, NIA) and index of degradation P_{ij} (based on areas of triangle or on sums of indices) for each sampling site j

2) the selected reference site i is the one for which

a) $P_{\underline{ii}} = \min P_{ij}$;

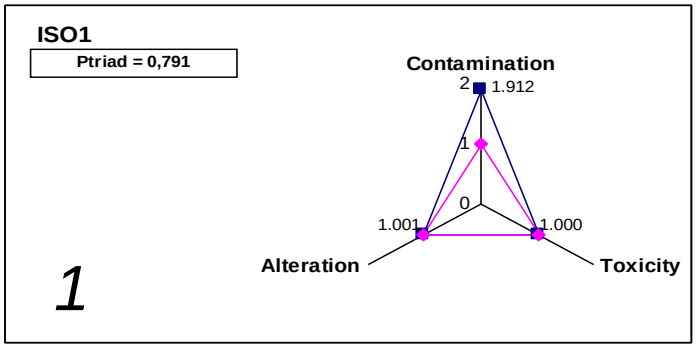
b) $P_{ij} \geq 0$.

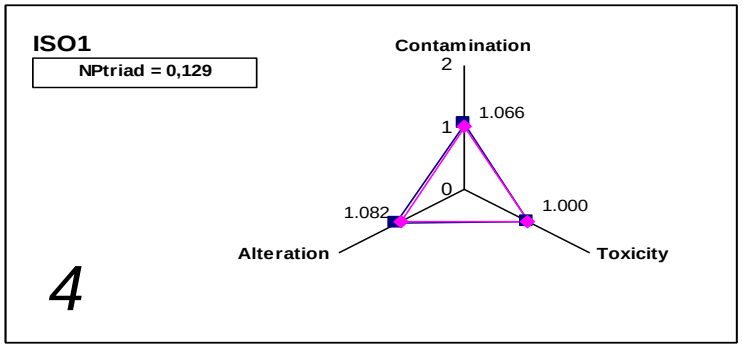
The results of the procedure described above for our data, using RTR, the areas for defining the index of degradation, are as follows:

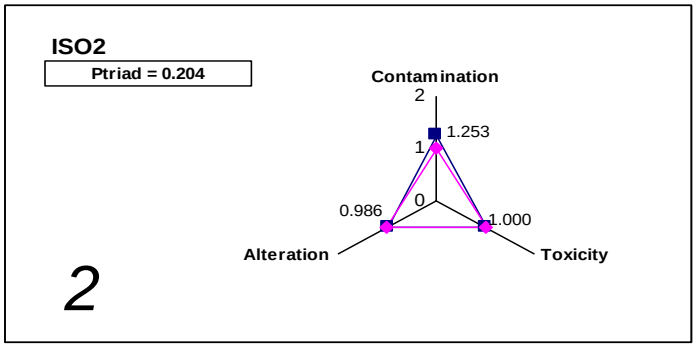
Rif.	**ISO1**				**ISO2**				**ISO3**				**ISO4**			
	ISO1	**ISO2**	**ISO3**	**ISO4**	**ISO1**	**ISO2**	**ISO3**	**ISO4**	**ISO1**	**ISO2**	**ISO3**	**ISO4**	**ISO1**	**ISO2**	**ISO3**	**ISO4**
IC	1.000	0.980	1.760	0.908	1.193	1.000	2.423	0.903	1.193	1.000	2.423	0.908	1.912	1.253	3.995	1.000
IT	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
IA	1.000	0.992	0.791	0.939	1.016	1.000	1.001	1.015	1.016	1.000	1.001	1.015	1.001	0.986	0.987	1.000
Ptriad	**0.000**	**-0.017**	**0.407**	**-0.131**	**0.181**	**0.000**	**1.233**	**-0.073**	**0.181**	**0.000**	**1.233**	**-0.073**	***0.791***	***0.204***	***2.564***	***0.000***

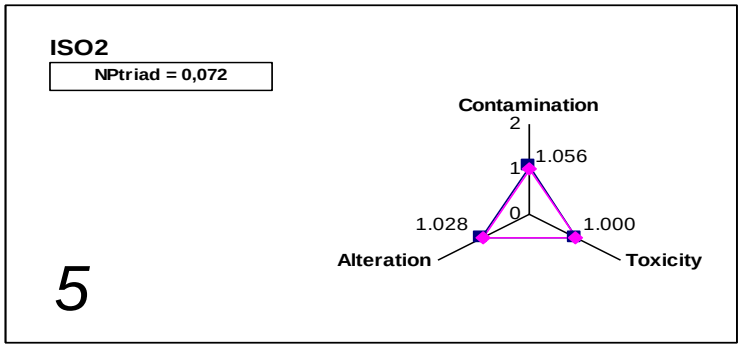
Underlined numbers stand for condition (a), Italics stand for condition (b), from the table above, *ISO4 is selected as reference site.*

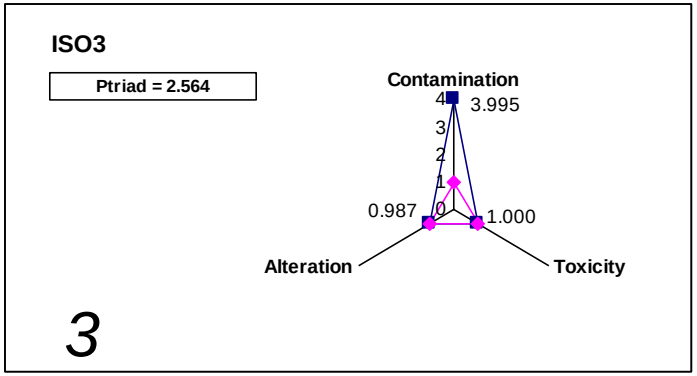
Sediment Quality Triad Plots

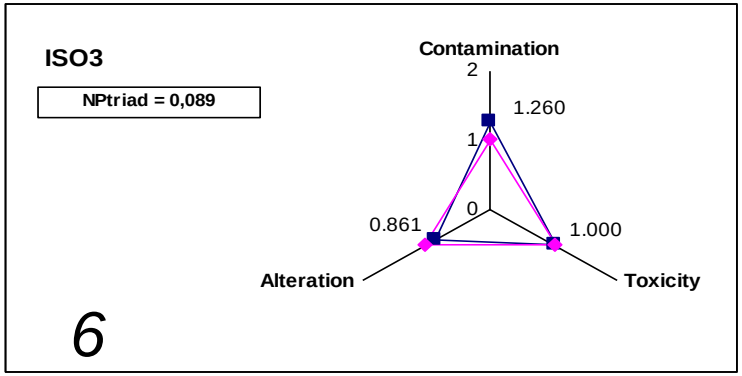












Plots 1, 2, 3 report results derived after RTR normalization; plots 4, 5, 6 report results derived after RTM normalization; Degradation Indices (P or NP) are differences between areas of triangles defined for the sampling sites ISO1, ISO2, ISO3 , and the reference site ISO4.

Conclusions

Examining the plots it can be seen how the three sites are very similar to the reference station; some differencies can be appreciated with respect to the chemical contamination, but they seem not to be severe enough to alter in a significative way population of macrobenthos, and neither to determine a significative toxicity of sediments. This scenario will be compared with SQT analysis obtained when the wastewater diffusor will be operative.

From a methodological point of view, the SQT approach present an interesting way of synthetising complementary information, providing a rich -informative- comparison between sites of a certain area.

In order to gain more widespread acceptance of the methodology, detailed guidelines are needed so to apply SQT “on objective bases”.

Clear indications (“how to”) on the selection of contaminants to be considered, on ecotoxicological tests to be applied, and on measures of the *in situ* alteration should be set. Moreover an exaustive study on benefits of the different normalization procedures and a general criterium for the selection of the reference site are required.

In this work we have proposed a procedure for the choice of the reference station.

Bibliography

1. P. Barbieri, G. Adami, S. Predonzani, E. Reisenhofer, “Heavy metals pollution assessment in surface sediments nearby urban and industrial discharges collectors in the gulf of Trieste”, Tox. Env. Chem., 71, 105-114 (1999).
2. G. Adami, P. Barbieri, S. Piselli, S. Predonzani, E. Reisenhofer, “Detecting and characterising sources of persistent organic pollutants (PAHs and PCBs) in surface sediments of an industrialized area (harbour of Trieste, Northern Adriatic)”, J. Env. Monit., 2, 261-265, (2000).
3. G. Adami, F. Aleffi, P. Barbieri, A. Favretto, S. Predonzani, E. Reisenhofer, “Bivalves and heavy metals in polluted sediments: a chemometric approach”, Wat. Air Soil Poll., 99, 615-622, (1997).
4. T.A. Del Valls, L.M. Lubian, J.M. Forja, A. Gomez-Parra, “Comparative Ecotoxicity of Interstitial Waters in Littoral Ecosystems using Microtox ® and the rotifer *Brachionus Plicatilis”,* Env. Tox. Chem., 16, 2323-2332, (1997).
5. P.M. Chapman, “ The Sediment Quality Triad Approach to determining pollution Induced Degradation” Sci. Total Environ., 97, 815-825 (1990) .
6. T.A. Del Valls, J.M. Forja, A. Gomez-Parra, “Integrative Assessment of Sediment Quality in Two Littoral Ecosystems from the Gulf of Cadiz, Spain”, Env. Tox. Chem., 17, 1073-1084, (1998).
7. P.M. Chapman, “The Sediment Quality Triad: then, now and tomorrow” Int. J. Environment and Pollution, 13, 351-356 (2000).
8. C.N.R.-I.R.S.A. Quaderno 64 (1985) Roma.
9. C.N.R.-I.R.S.A. Quaderno 39 (1978) Milano.
10. G. Sbrilli, L. Brilli, S. Milani “La metodologia di saggio algale nel monitoraggio marino costiero e nella classificazione delle acque marine.” Biologi Italiani, 6, 45-51 (2000).

- **Relative Taxa Sensitivity (RTS) of aquatic invertebrates with respect to organic and metal compounds. (39)**
- **Von der Ohe, P. & Liess, M. 2004. Environmental Toxicology and Chemistry. 23, 150-156.**
- In the field, a multitude of species can be exposed to numerous toxicants; thus, the sensitivity of individual species to particular toxicants must be known to predict effects and to analyze changes in species composition. For most species, no information about their toxicant sensitivity is available. To address this limitation, we have grouped the available information to assign sensitivities to aquatic invertebrate taxa relative to Daphnia magna. With respect to organic compounds, most taxa of the orders Anisoptera, Basommatophora, Coleoptera, Decapoda, Diptera, Ephemeroptera, Eulamellibranchiata, Heteroptera, Hirudinea, Isopoda, Oligochaeta, Prosobranchia, Trichoptera, Tricladida, and Zygoptera are less sensitive than D. magna. Some taxa of the Amphipoda, Plecoptera, and Cladocera (other than D. magna) are significantly more sensitive. For organic compounds, approximately 22% of the investigated taxa were more sensitive than D. magna. Most taxa of the orders Amphipoda, Basommatophora, Diptera, Ephemeroptera, Eulamellibranchiata, Heteroptera, Isopoda, Oligochaeta, and Tricladida are significantly less sensitive than D. magna to metal compounds. The taxa belonging to the Crustacea, with the exception of the order Isopoda, are much more sensitive. For metal compounds, approximately 30% of the investigated taxa were more sensitive than D. magna. Hence, D. magna is among the most sensitive taxa regarding both groups of toxicants. The sensitivities for several taxa are listed, and use of the relative sensitivity distribution to link toxicant effects in mesocosm studies and field investigations is discussed.