XIII Symposium in Pesticide Chemistry

3-6 September 2007 - Piacenza, Italy

FOOTPRINT

FuncTional tOOls for Pesticide RIsk assessmeNt and managemenT

WP1: Integrated knowledge reviews

Activity 1.3: State of the art on bound residues

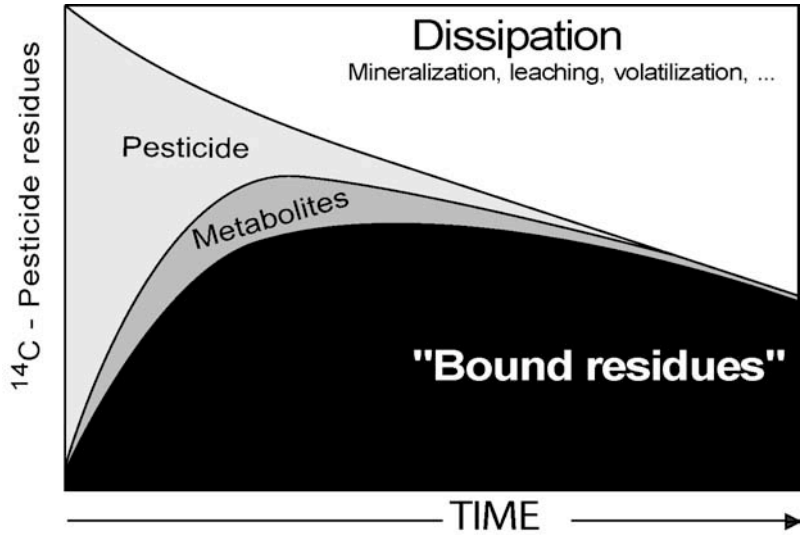
Current knowledge and future challenges in considering **bound residues** in pesticide risk assessment and modeling

E. Barriuso, P. Benoit & I. Dubus

INRA brgm

Bound residues (BR) formation - main questions for risk assessment

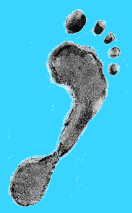
- Risk assessment for pesticides=> dissipation (DT50)
- BR: decrease of soil availability of pesticide residues!



- *Pesticide dissipation?*
- *Stabilisation process?*
- *Reversibility?*
- *Chemical nature?*
- *Factors controlling their formation and evolution?*

Objective:
Synthesize available data from published literature to …

- Build a database with available and coherent data on BR formation
- Propose an approach and parameters for estimation of BR formation and their potential release
- Identify factors controlling BR formation and evolution:
  - Structural (chemical) factors
  - Soil and environmental factors
  - Agronomic factors

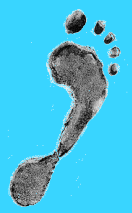


Data used for this review

- CAB Abstracts: *1973-present*

Main journals Field: Source Title	Record Count	% of 411	Bar Chart
Journal of Agricultural and Food Chemistry	53	12.9 %	
Chemosphere	28	6.8 %	
Journal of Environmental Science and Health. Part B, Pesticides, Food Contaminants, and Agricultural Wastes	27	6.6 %	
Pesticide Science	21	5.1 %	
Environmental Pollution	12	2.9 %	
Journal of Environmental Quality	12	2.9 %	
Journal of Pesticide Science	10	2.4 %	
Soil Biology & Biochemistry	9	2.2 %	
Bulletin of Environmental Contamination and Toxicology	8	1.9 %	
Environmental Science & Technology	8	1.9 %	

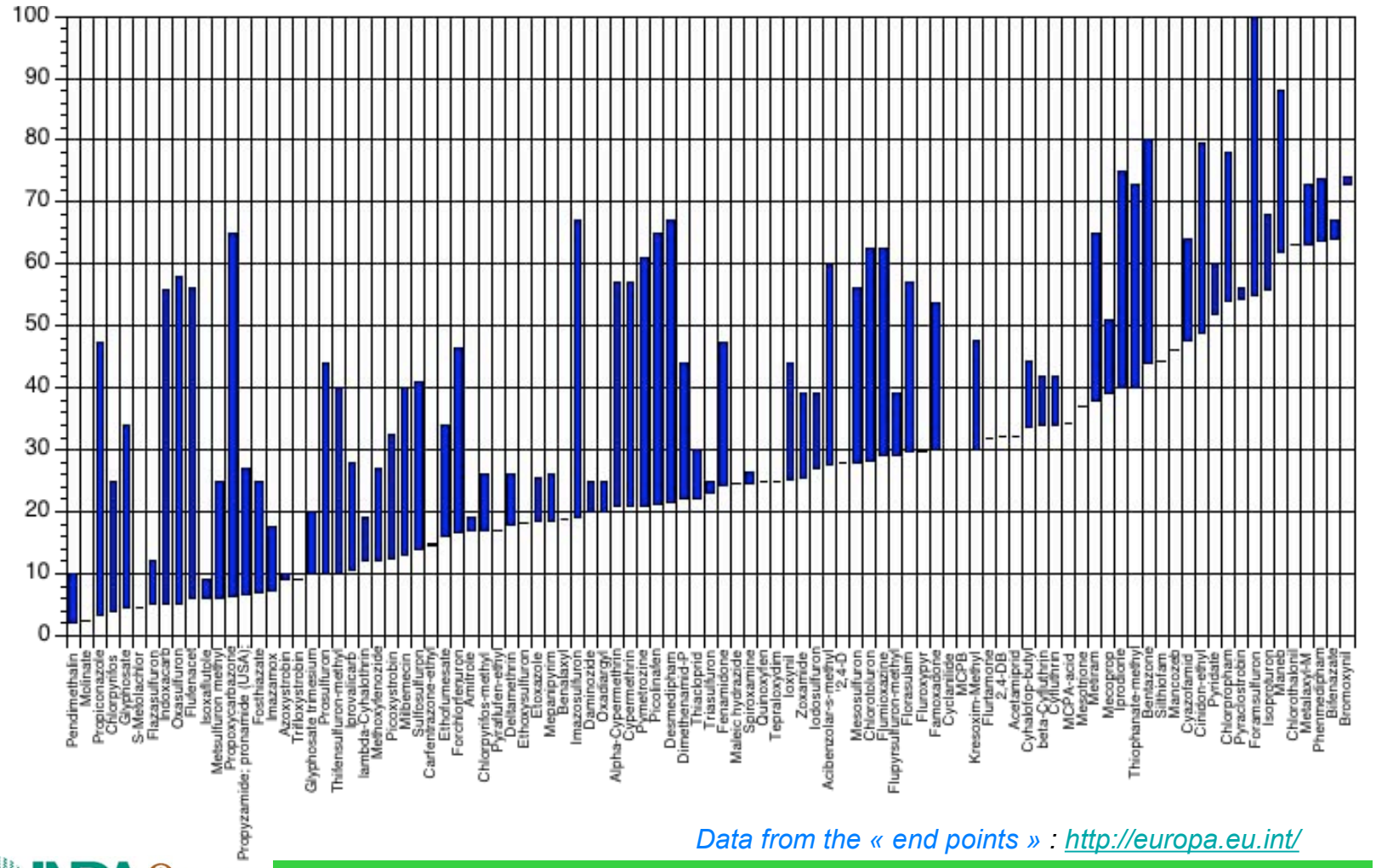
- Data from the review reports for EU registration http://europa.eu.int /



Boun residues as a general process, with different extend depending on pesticide

% of BR after 100 days

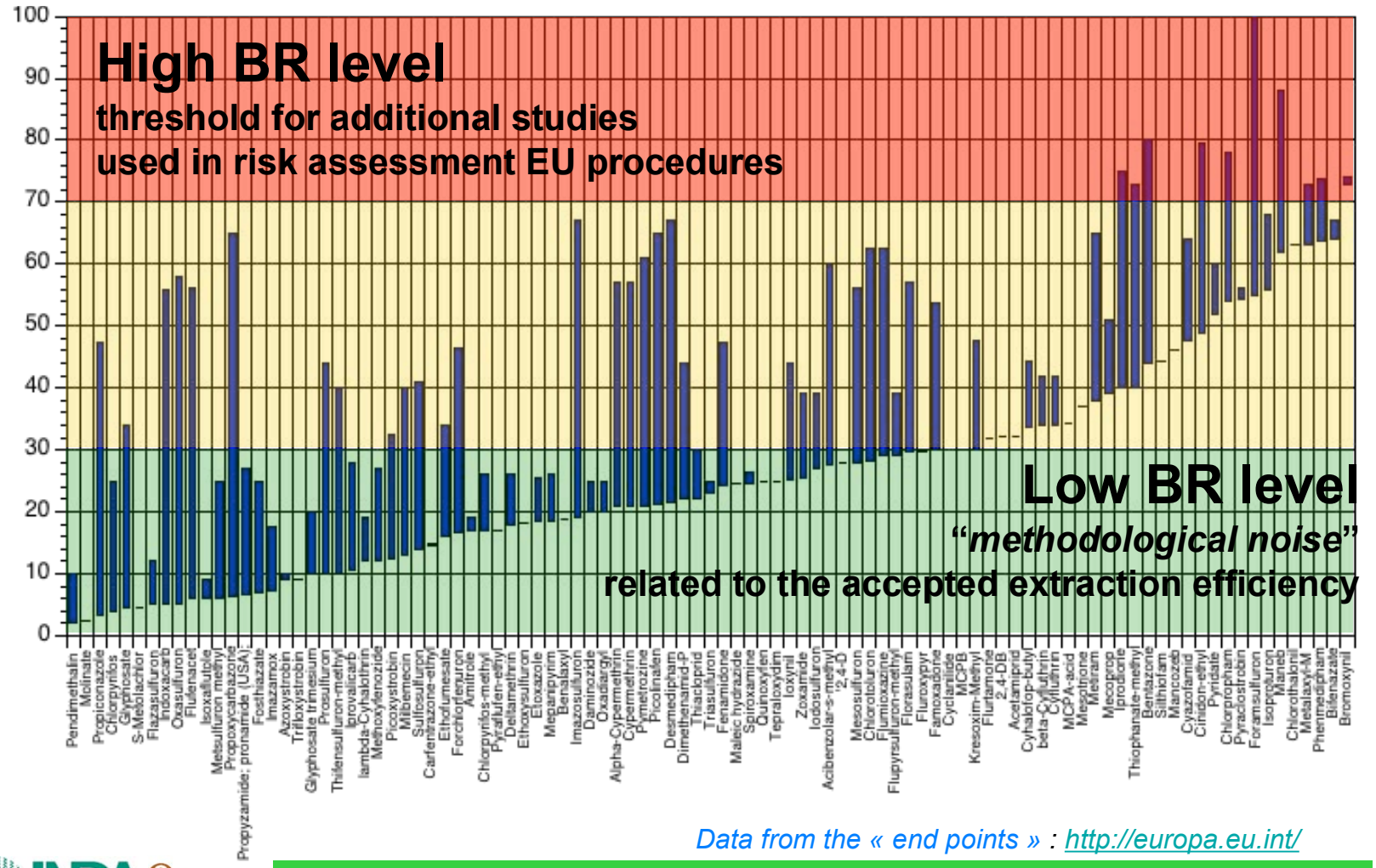
Extend of BR formation for a duration target



Data from the « end points » : http://europa.eu.int/

Used reference levels of BR formation for risk assessment

% of BR after 100 days



Data from the « end points » : http://europa.eu.int/

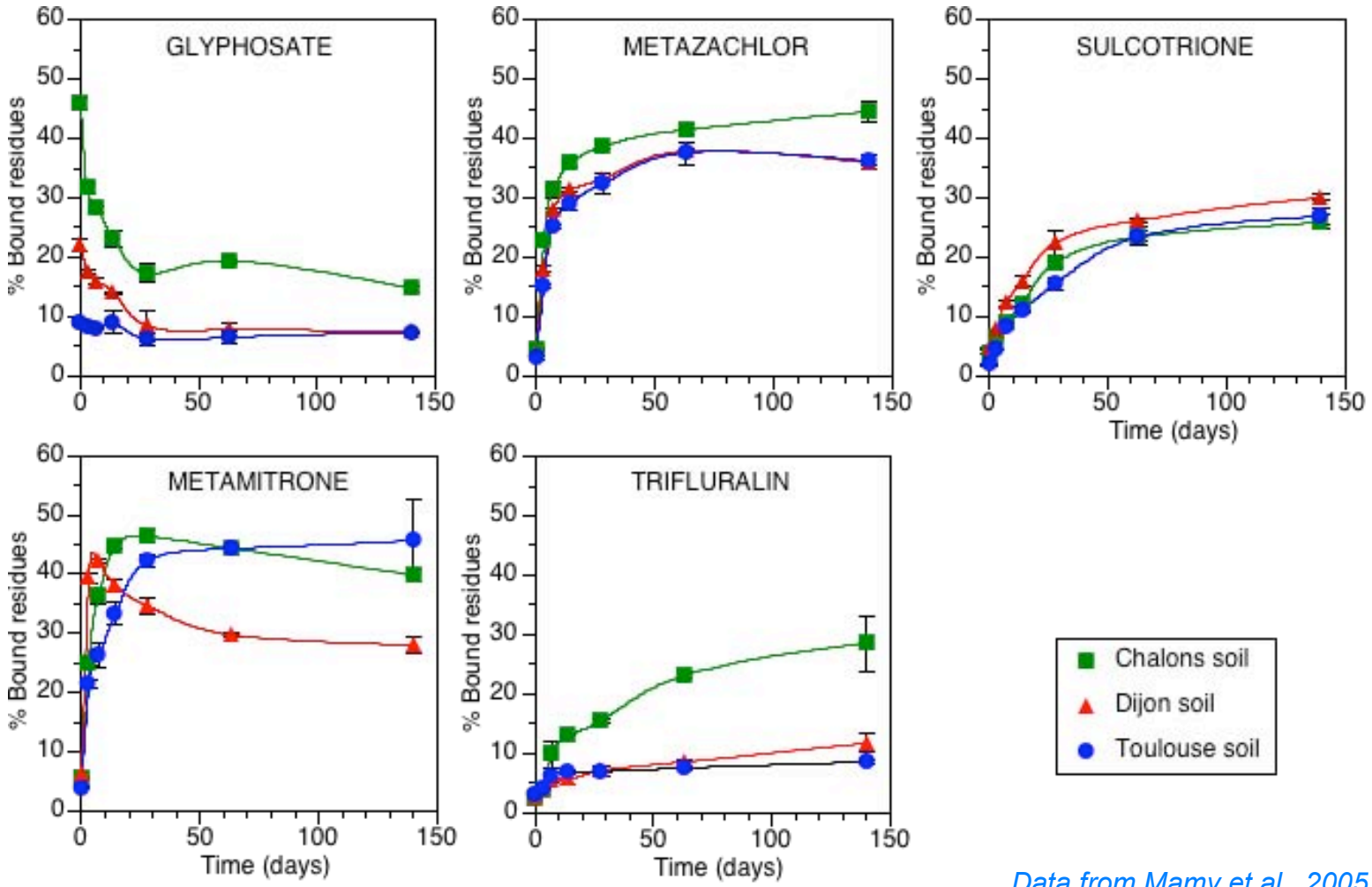
Pesticide classification

« Methodological noise » Low BR level < 30 %	Intermediate situation 30 % < BR < 70 %	Threshold risk assessment High BR level > 70 %
Molinate	Acetamiprid	Thiophanate-methyl
S-Metolachlor	Glyphosate	Metalaxyl-M
Isoxaflutole	Ethofumesate	Phenmedipham
Trifloxystrobin	MCPA-acid	Bromoxynil
Pendimethalin	Mesotrione	Iprodione
Azoxystrobin	Flupyrsulfuron-methyl	Chlorpropham
Carfentrazone-ethyl	Prosulfuron	Cinidon-ethyl
Imazamox	Dimethenamid-P	Bentazone
Ethoxysulfuron	Ioxynil	Maneb
Benalaxyl	Cyhalofop-butyl	Foramsulfuron
Amitrole	Silthiofam	
Glyphosate trimesium	Mancozeb	
Chlorpyrifos	Propiconazole	
Metsulfuron methyl	Mecoprop	
Fosthiazate	Pyraclostrobin	
Triasulfuron	Flufenacet	
Quinoxyfen	Mesosulfuron	
Chlorpyrifos-methyl	Cypermethrin	
Deltamethrin	Florasulam	
Propyzamide	Oxasulfuron	
Methoxyfenozide	Pyridate	
2,4-D	Chlorotoluron	
Fluroxypyr	Chlorothalonil	
Thiacloprid	Propoxycarbazone	
Cyclanilide	Imazosulfuron	
MCPB	Desmedipham	
	Isoproturon	

Data from the « end points » : http://europa.eu.int/

Bound residues formation - as a kinetic process

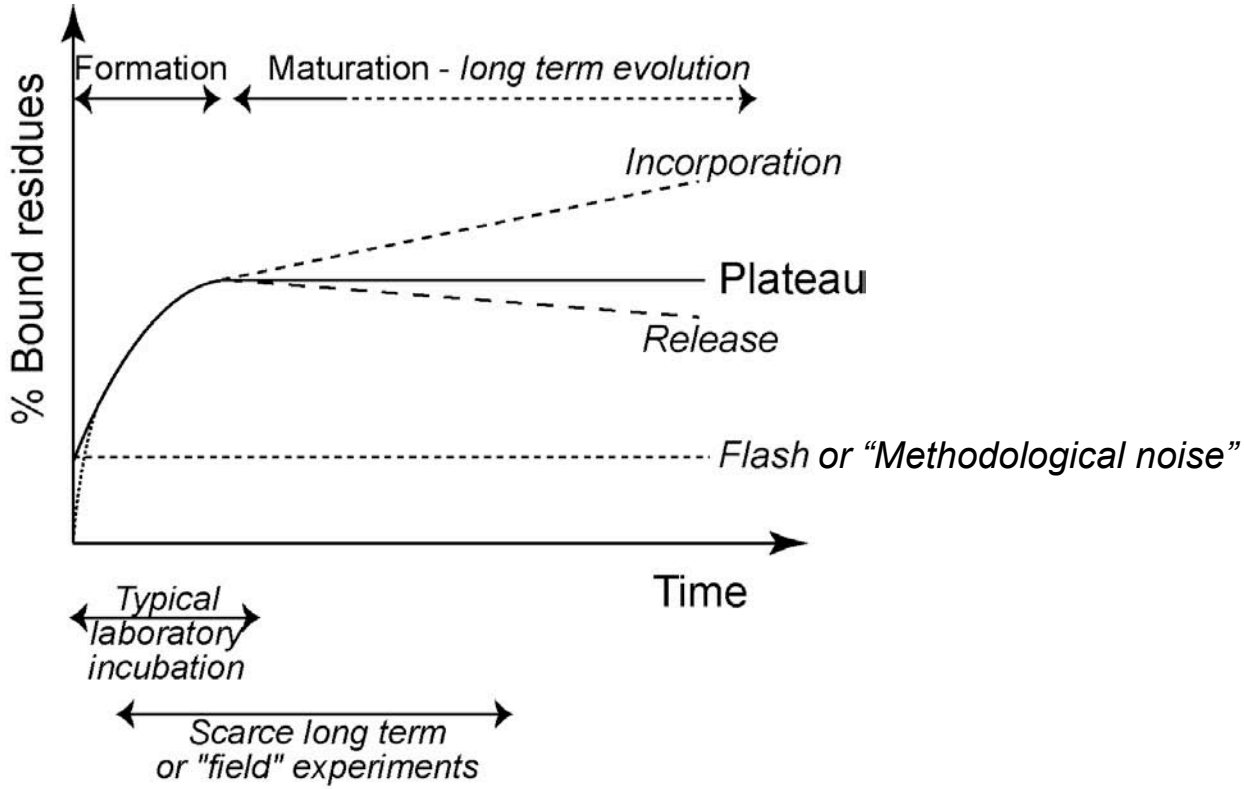
Example of kinetics of BR formation



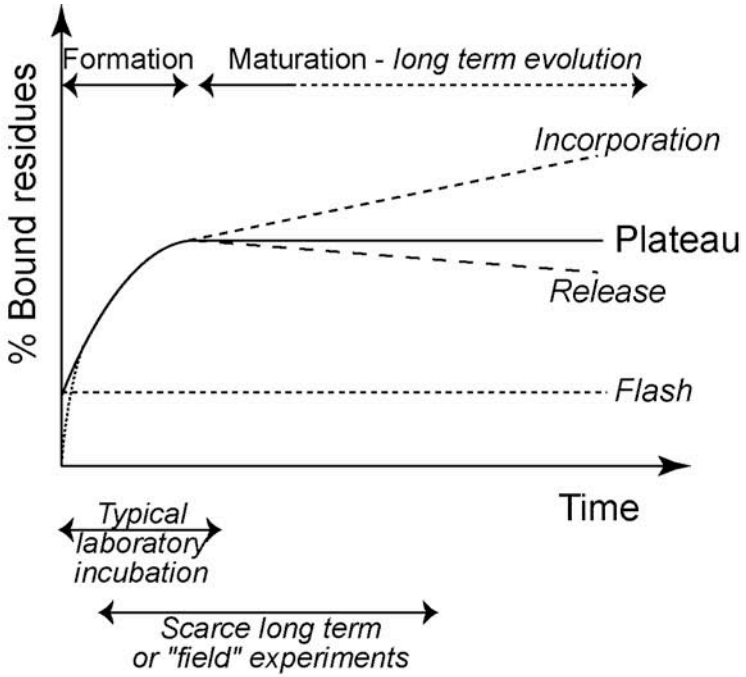
Data from Mamy et al., 2005

Bound residues formation - as a kinetic process

Main characteristics of the BR kinetics



Pesticide classification in relation to theirs BR kinetics characteristics

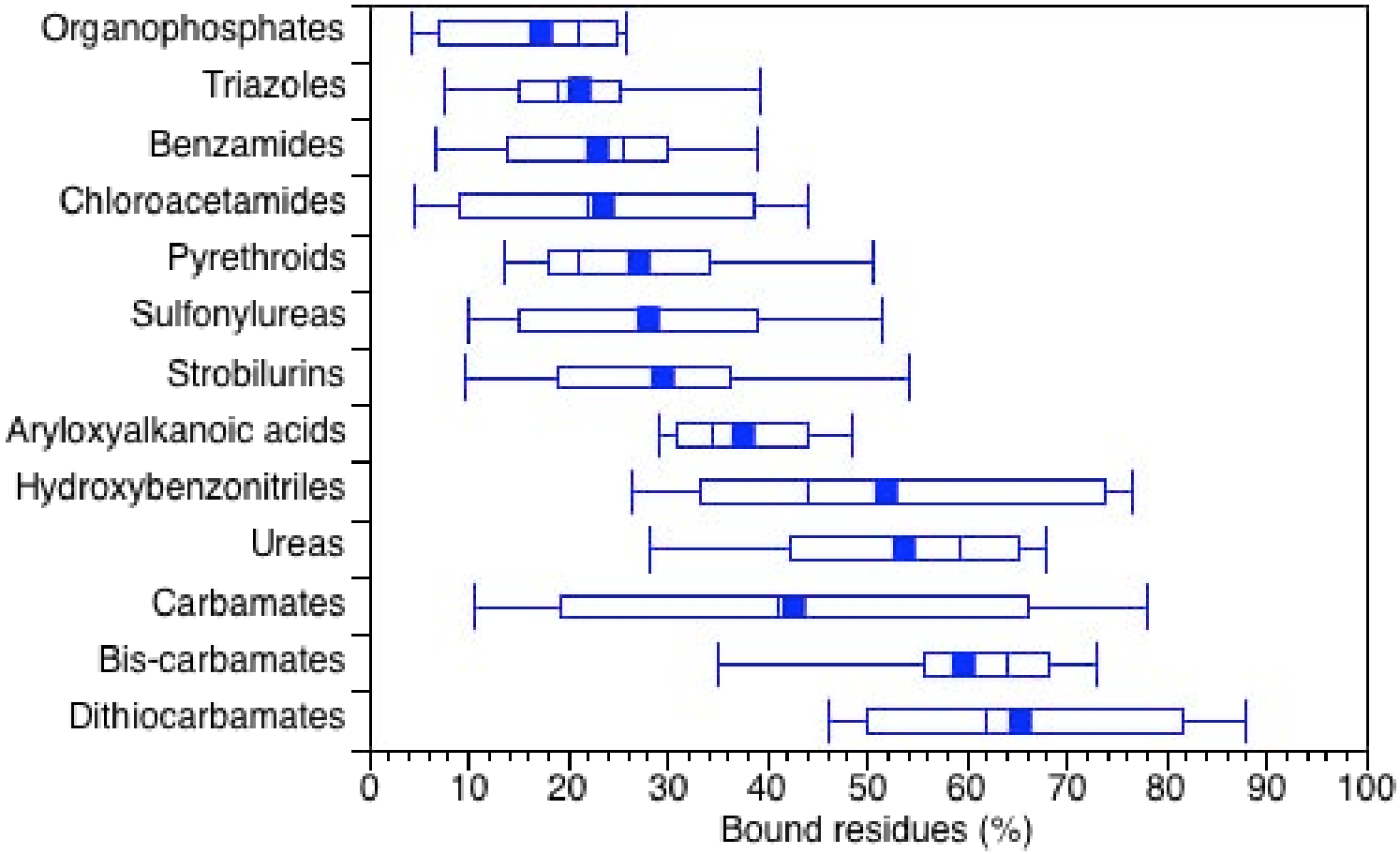


Rate of BR formation	Pesticide	Initial BR	Plateau time	Maturation (final time)	
High	Alachlor	< 5 %	28 d	Incorporation	(80 d)
	DDT	< 5 %	7 d	Incorporation	(28 d)
	Metsulfuron	< 5 %	20 d	Incorporation	(100 d)
	Parathion	< 5 %	7 d	Incorporation	(28 d)
	Phosalone	< 5 %	14 d	Incorporation	(84 d)
	Chlorothalonil	< 40 %	7 d	Stable	(90 d)
	Dimethenamid	< 10 %	30 d	Stable	(142 d)
	Dyfonate	< 5 %	14 d	Stable	(28 d)
	Metazachlor	< 5 %	14 d	Stable	(84 d)
	Monocrotofos	< 5 %	4 d	Stable	(80 d)
	Paraquat	< 5 %	1 d	Stable	(91 d)
	Prosulfuron	< 20 %	20 d	Stable	(105 d)
	2,4-D	< 5 %	10 d	Release	(60 d)
	Acetochlor	< 5 %	90 d	Release	(371 d)
	Atrazine	< 10%	60 d	Release	(154 d)
	Atrazine	?	60 d	Release	(360 d)
	Cloransulam	< 5 %	120 d	Release	(357 d)
	Dialllate	< 5 %	28 d	Release	(210 d)
	Dicamba	< 5 %	40 d	Release	(91 d)
	Dicamba	<10 %	14 d	Release	(90 d)
	Metamitron	< 5 %	28 d	Release	(84 d)
	Triallate	< 5 %	140 d	Release	(365 d)
Low	Isoproturon	< 5 %	40 d	Incorporation	(91 d)
	Simazine	< 5 %	50 d	Incorporation	(80 d)
	Sulcotrione	< 5 %	56 d	Incorporation	(84 d)
	Atrazine	< 10 %	200 d	Stable	(326 d)
	Bentazone	< 10 %	60 d	Stable	(160 d)
	Deltamethrin	< 10 %	30 d	Stable	(80 d)
	Triticonazole	<10 %	100 d	Stable	(130 d)
	Lindane	< 5 %	70 d	Release	(91 d)

References are in the proceedings

BR and structural classification

Chemical family

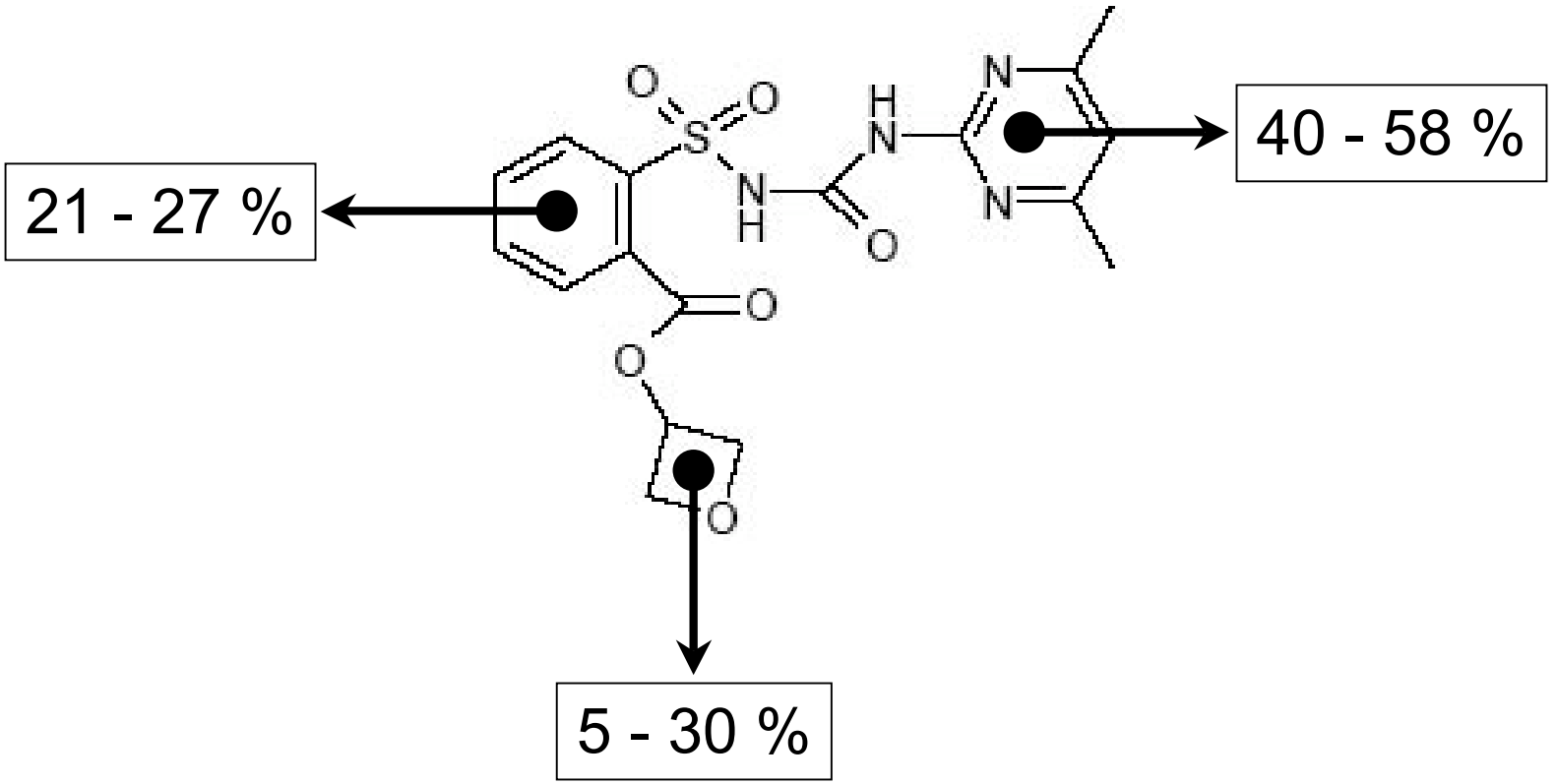


Barriuso et al. - submitted to Environ. Sci. Technol.

Data from the « end points » : http://europa.eu.int/

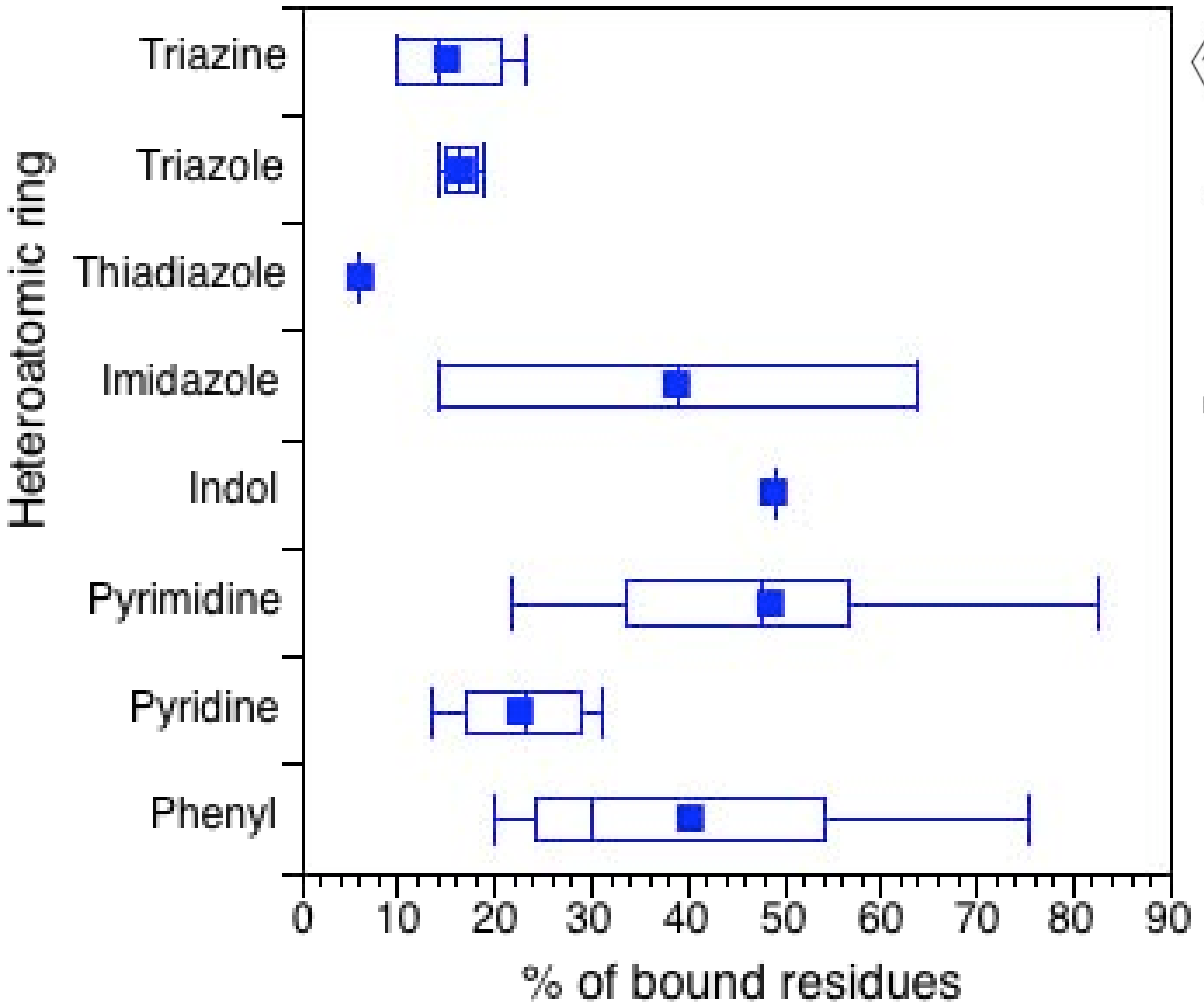
BR and structural factors - dependency on the ^{14}C-labelling position

Oxasulfuron

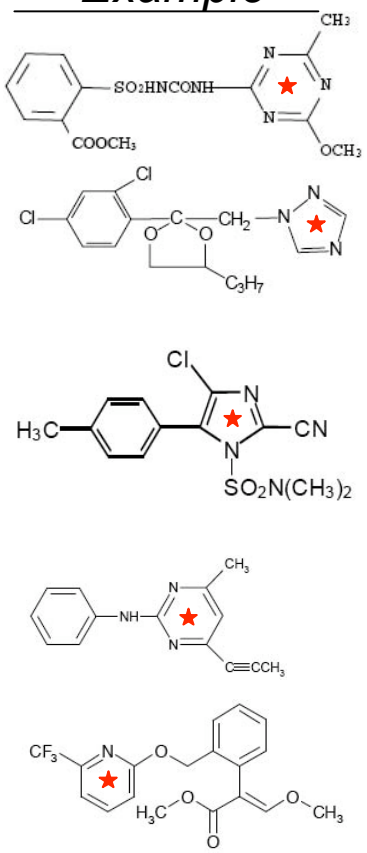


Data from the « end points » : http://europa.eu.int/

BR proportion in relation to the nature of the heteroatomic moiety ^{14}C-labelled( )*



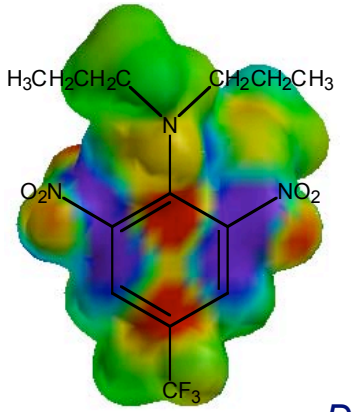
Example



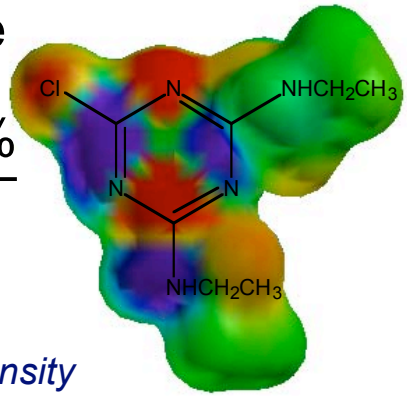
Barriuso et al. - submitted to Environ. Sci. Technol.

Data from the « end points » : http://europa.eu.int/

BR and structural factors related to the electron molecular distribution

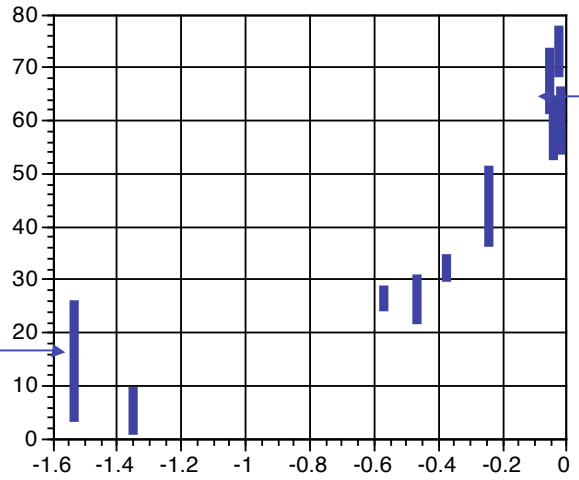


Trifluraline	Simazine
Bound residues	
5 - 25 %	50 - 70 %
3 halogens	1 halogen
Dipole moment (D)	
5,22	2,99



Distribution of the electronic charge density

% Bound residues (100 d incubation)



LUMO energy (eV)

(Energy of the lowest unoccupied molecular orbital)

Barriuso et al., 2005

Soil and agronomic factors - general statements

> Pesticide BR are associated to soil organic constituents

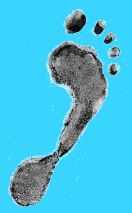
- Amount and nature (humification degree) are concerned

> BR amounts are related to soil microbial activity, mainly that of the pesticide degrading microorganisms

- Metabolisation giving reactive intermediates can favour BR formation

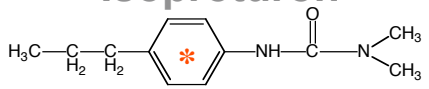
> Physicochemical and environmental factors influencing through the modification of both soil organic matter and biological activity

- Direct effect of soil water content, temperature, …



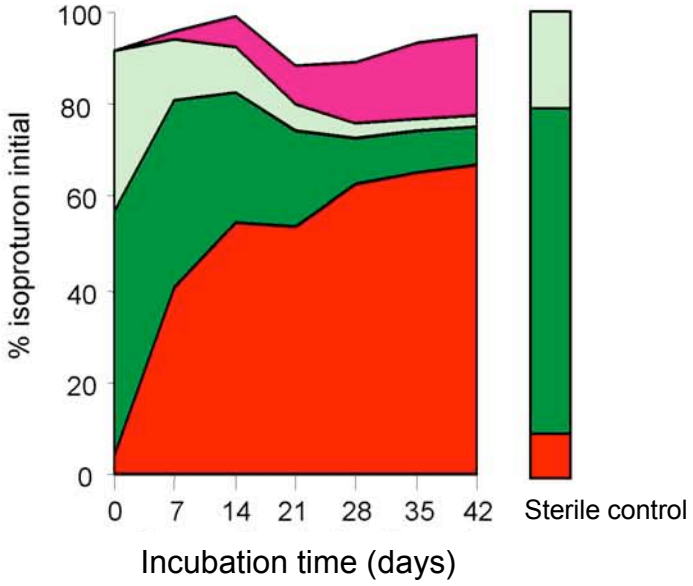
Environmental factors inducing soil microbiological and BR modifications

Isoproturon

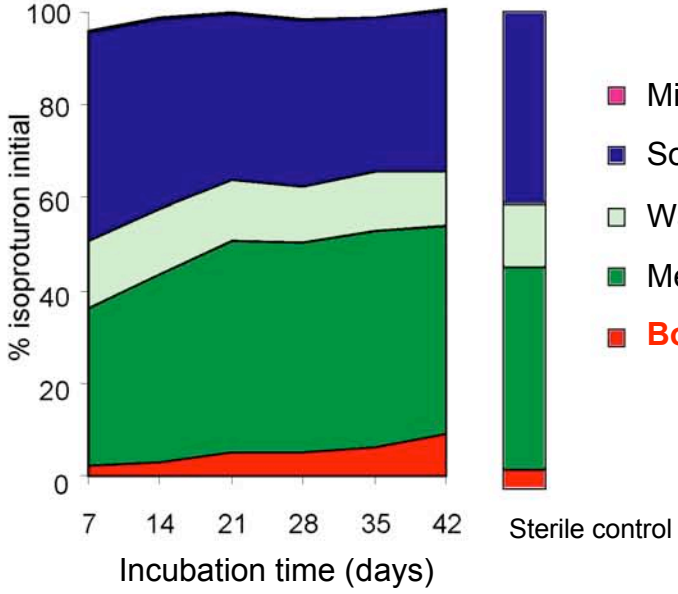


Example:
Isoproturon fate in relation to the Redox potential

Spring aerobic conditions
Redox potential: ***500 mV***



Fall anoxic conditions
Redox potential: ***150 mV***



Charnay et al., 2001

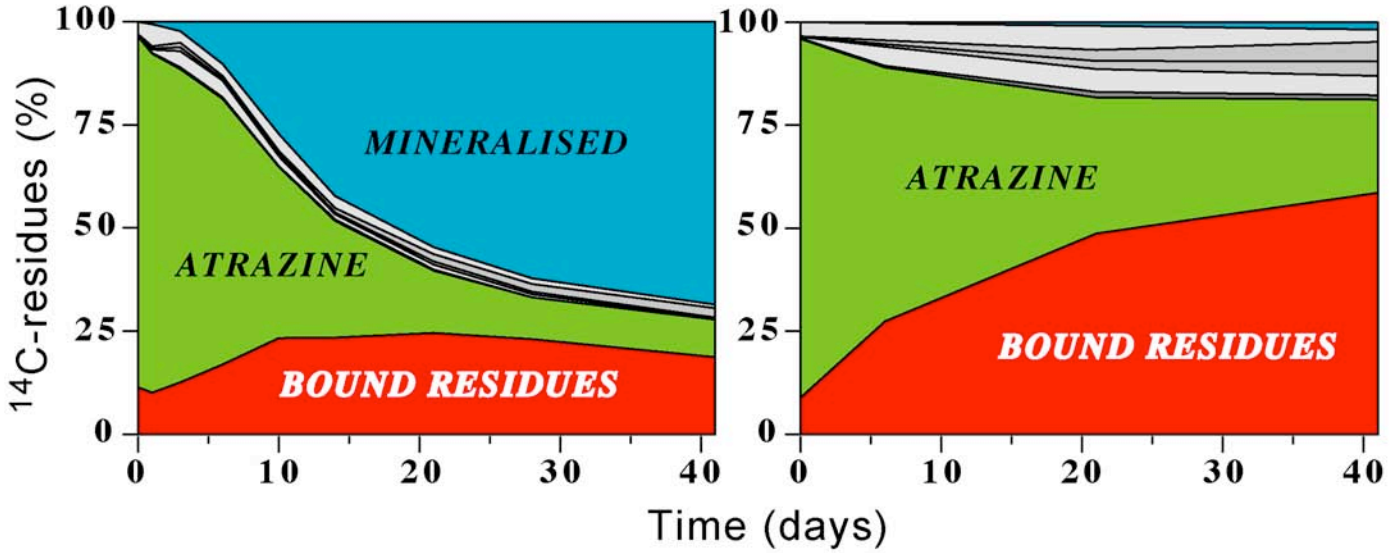
Agronomic factors inducing soil microbiological and BR modifications

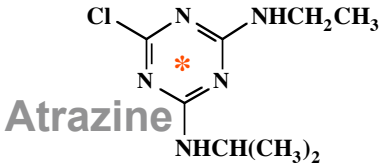
Example: microbial adaptation to accelerated pesticide degradation

Same soil with different history of pesticide treatment since 30 years…

… under maize with repeated atrazine applications

… under wheat without atrazine applications

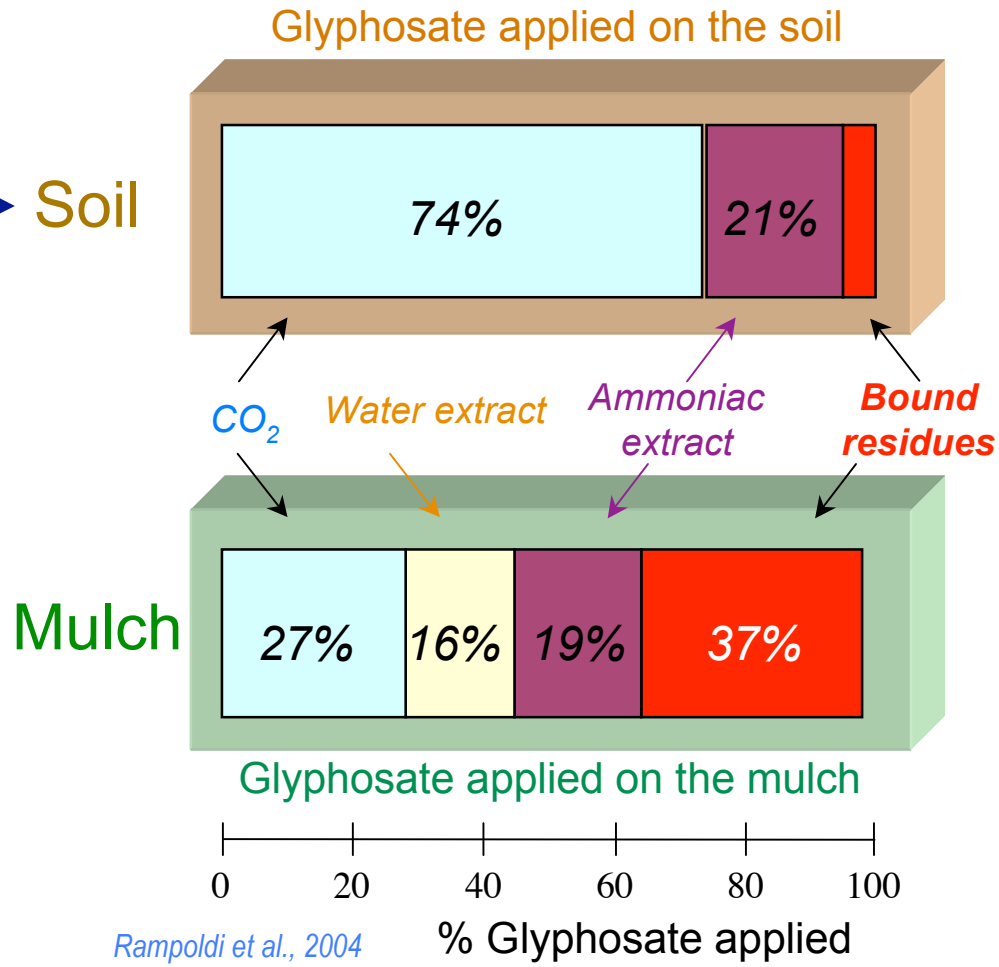




Barriuso & Houot, 1996

Agronomic practices inducing soil properties and BR modifications

Example: pesticide interception by mulch (crop residues)

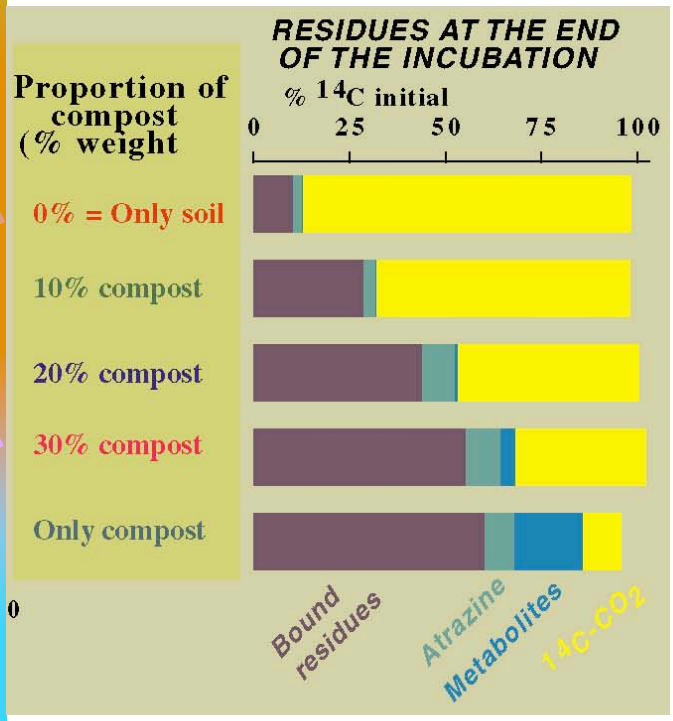


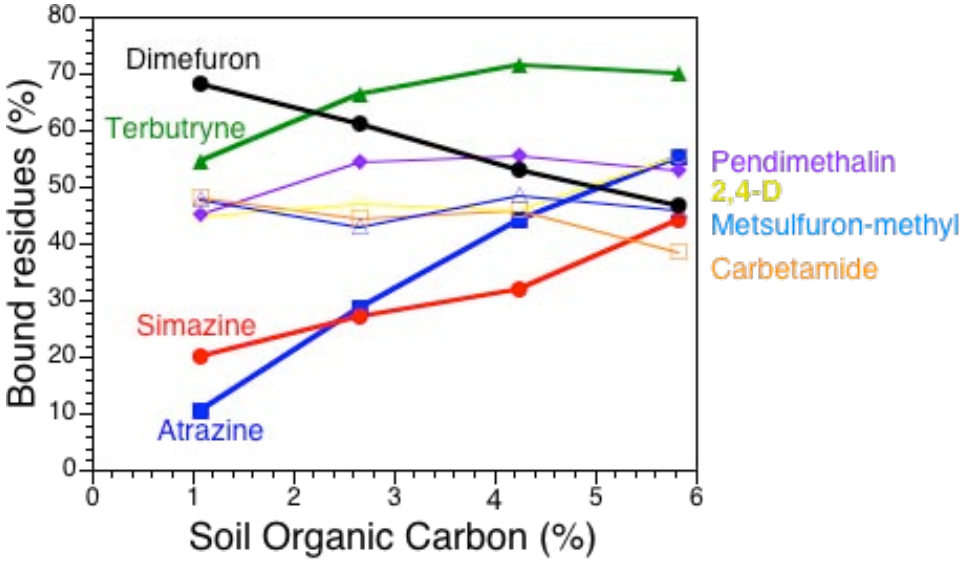
Rampoldi et al., 2004

Agronomic practices inducing soil properties and BR modifications

Example: use of organic amendments

Modification of content and nature of the soil organic matter





Data from Barriuso et al., 1997

Concluding remarks

- Data set:
  - High variability of the experimental conditions
  - Data on BR mainly coming from laboratory incubations
- Pesticide structure factors:
  - Indicators from chemical structure only qualitatively usable
  - Giving indication of the chemical reactivity of the initial pesticide
  - Usable only for BR formed by chemical interactions
- Soil factors:
  - BR mostly related to soil microbial activity
  - Environmental factors influencing through modifications of this activity
  - Content and nature of soil organic matter influence depending on pesticide
- Agronomic factors:
  - They interact through modifications of soil properties (microflora, OM, pH)
  - Interception by crops or weeds can modify drastically the BR formation

Concluding questions

- What can be a reasonable principle to convert ^{14}C data into pesticide or metabolite concentrations?
  - *Nature of BR*
- What is the targeted time scale for laboratory incubation, and how is it reasonable to extrapolate them for long-term risk assessment?
  - *Transposition lab-field,*
  - *Standardisation of methods*
- How the used models can take into account BR?
  - *Non-reversible sorption, slow sorption kinetics, …*

Thank you for your attention

FOOTPRINT

FuncTional tOOls for Pesticide RIsk assessmeNt and managemenT