

TERQ: Toxicological Exposure Risk Quantification in case of Environmental Contamination by Pesticide Additives, Impurities and Metabolites:

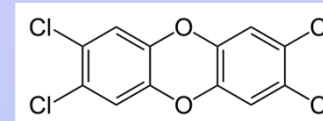
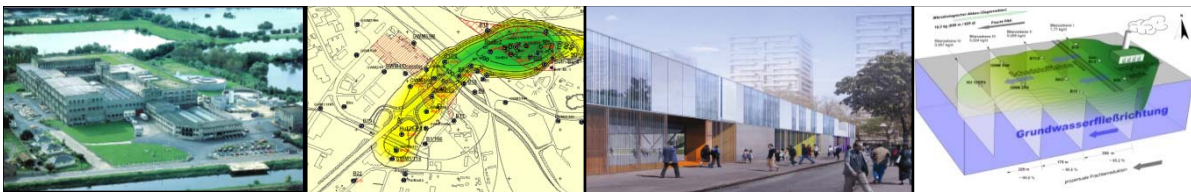
Examples of Picloram, Bromacile Chlordecone, 2,4-D and Glyphosate/AMPA in Europe, Asia (China & Vietnam) and South America

EQRS : Evaluation Quantitative des Risques Sanitaires dans le cas des Pollutions par des additifs, Impuretés et Métabolites :

Exemples : Picloram, Bromacile, Chlordecone, 2,4-D et Glyphosate/AMPA en Europe, Asie (Chine et Vietnam) et Amérique du Sud

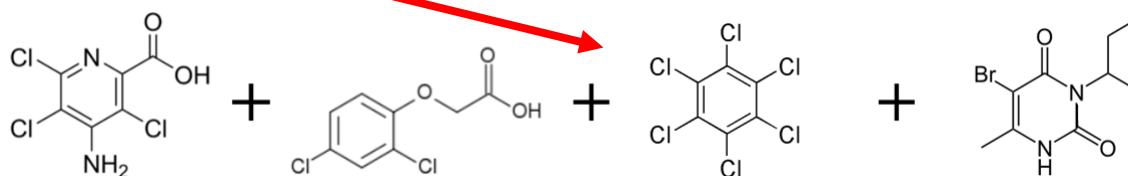
**KARG, Frank / HPC Envirotec S.A. / France
Scientific Director of HPC-Group Germany & International
&**

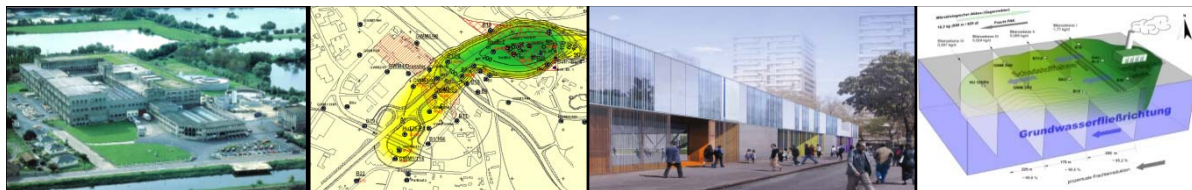
KOPYTYNSKI, Witold / SIM : Servicio Integral de Medioambiente / Argentina



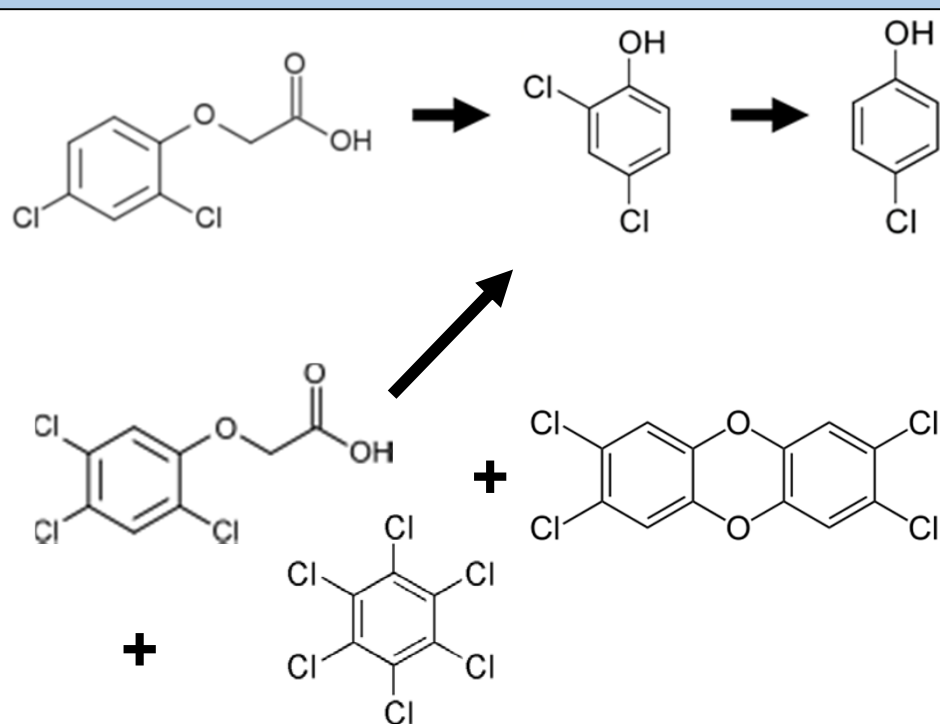
Typical Pesticide Mixtures:

- **Picloram** herbicide (Trade names Tordon & Grazon): Chlorinated derivative of Picolinic acid. In Agriculture (China, India, etc.) & Vietnam War, used together with 2,4-D (2,4-Dichlorophenoxyacetic acid) under the name “**Agent White**”, for **Forest areas which showed resistance** to
- “**Agent Orange**” (Mixture between **2,4-D** and **2,4,5-T** (2,4,5-Trichlorophenoxyacetic acid) used in Viet Nam between 1965 – 1971. Agent Orange shows highly resistant **Dioxin** (2,3,7,8-TCDD, etc.) **impurities**.
- **About 30 + 17 million liters of “Agent Orange” + “Agent White”** were sprayed over Viet Nam by the U.S.-Air Force. As known, impurities with lots of catastrophic Public Health Impacts in Viet Nam.
- The Picloram mixture hides also such impurities, as for ex. **HCB: Hexachlorobenzene (200 ppm)**, which shows also a strong toxicity and bio-accumulation.



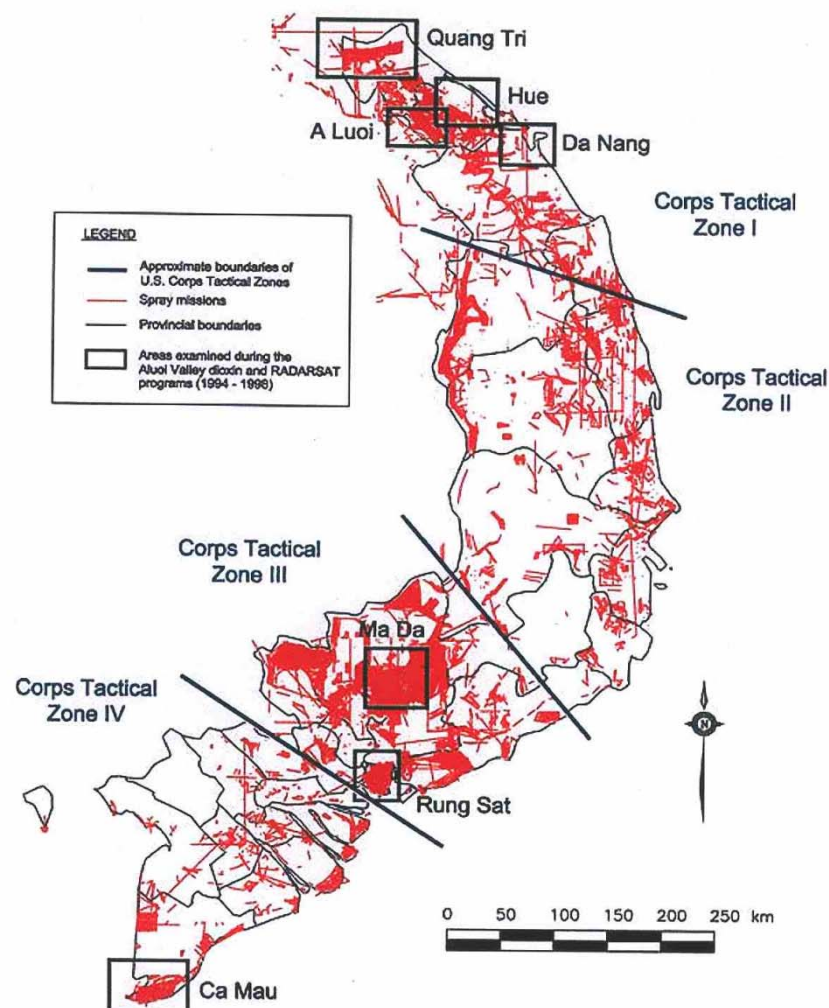


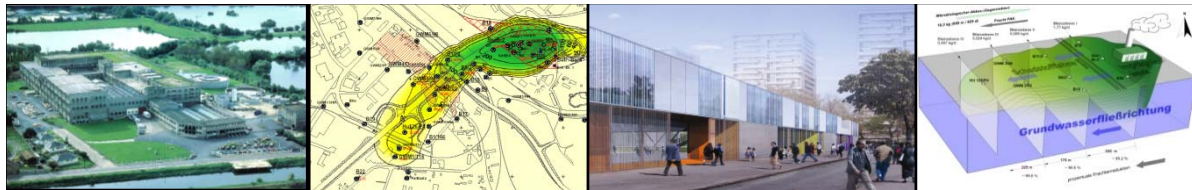
Map of US-Army Pesticide use in Viet Nam: Missions between 1965 - 1971



2,4-D & 2,4,5-T – Impurities and Metabolites :
2,4-Dichlorophenol & 4-Chlorophenol
+ 2,3,7,8-TCDD (+general PCDD/F) + HCB

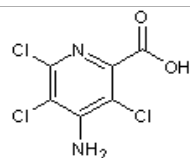
Aerial herbicide spray missions in southern Viet Nam, 1965 to 1971
(Source: U.S. Dept. of the Army).



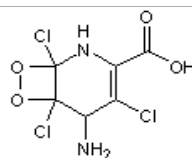


Prior Picloram use

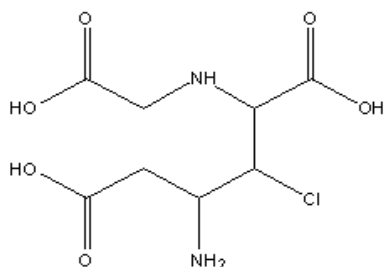




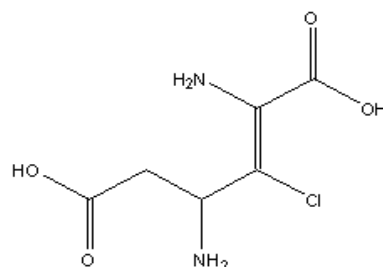
4-amino-3,5,6-trichloropyridine-2-carboxylic acid



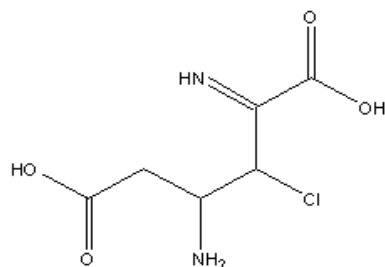
5-amino-1,4,6-trichloro-7,8-dioxabicyclo[4.2.0]oct-3-ene-3-carboxylic acid



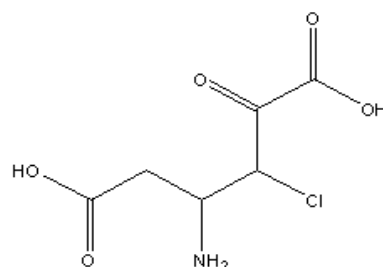
4-amino-2-[(carboxymethyl)amino]-3-chlorohexanedioic acid



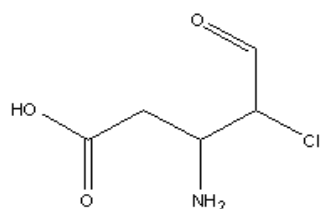
(2E)-2,4-diamino-3-chlorohex-2-enedioic acid



4-amino-3-chloro-2-iminohexanedioic acid



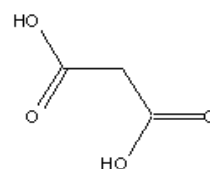
4-amino-3-chloro-2-oxohexanedioic acid



3-amino-4-chloro-5-oxopentanoic acid



(2E)-3-aminoprop-2-enal



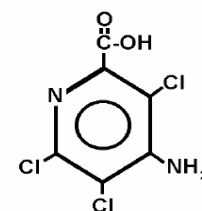
propanedioic acid



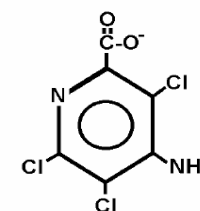
Picloram Forms and Degradation

Only 1 µg/kg

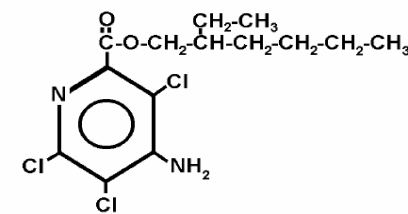
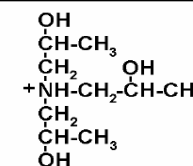
of Picloram, can be lethal to garden plants such as peas, beans, lettuce, spinach, tomatoes and potatoes.



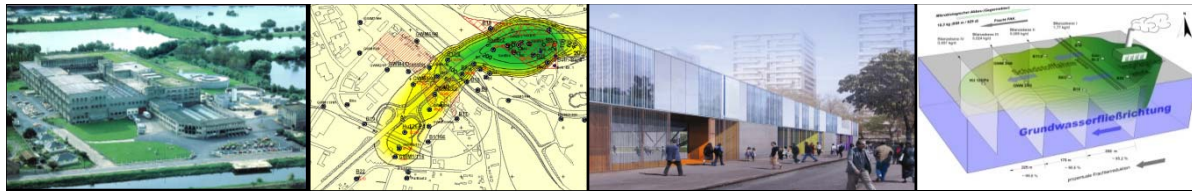
Picloram acid



Picloram triisopropanolamine salt

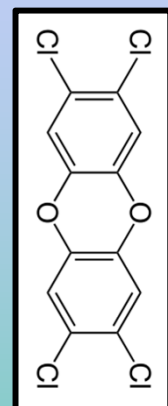
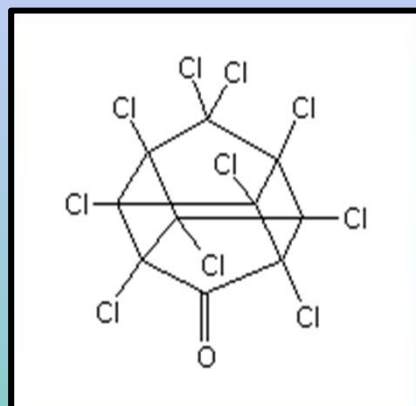
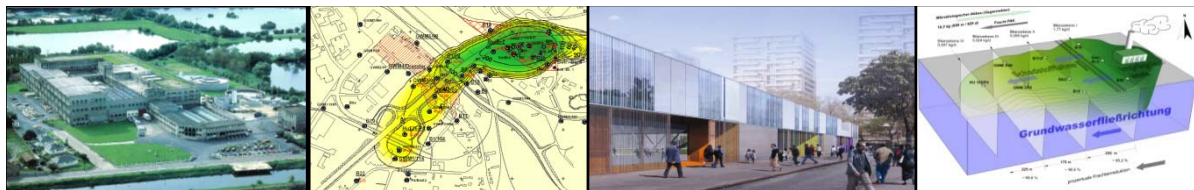


Picloram isooctyl ester



Prior historical Chlordecon use

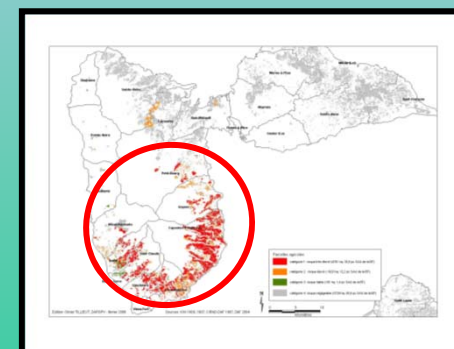
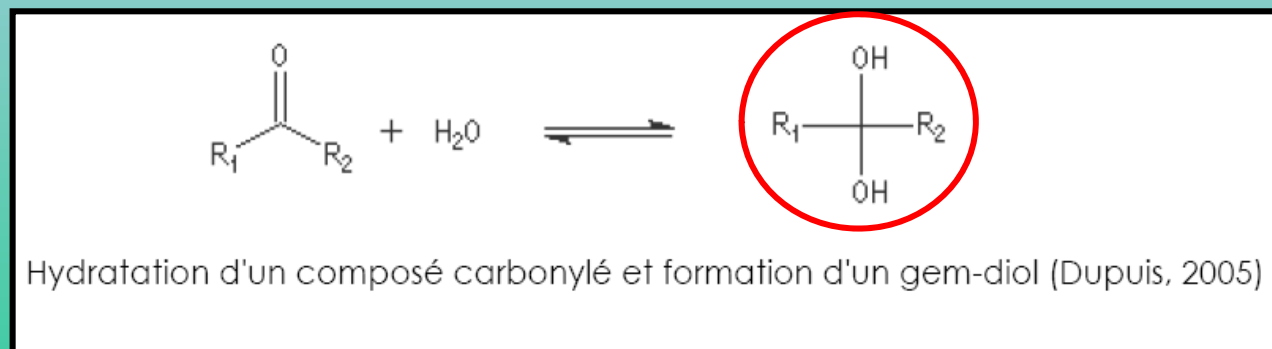
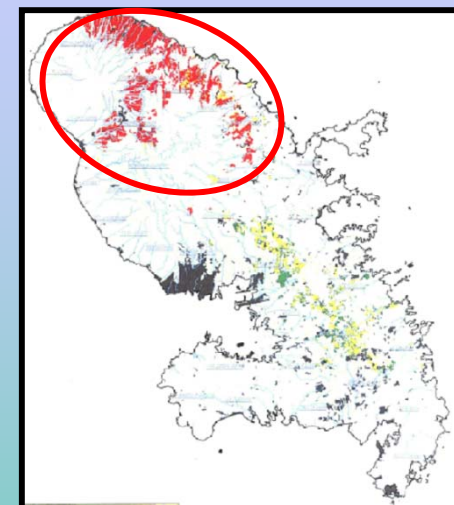


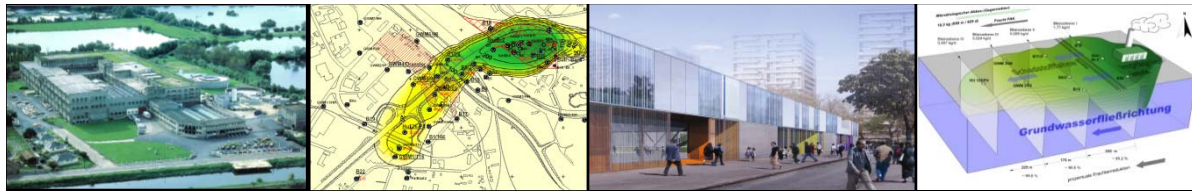


Chlordecon degradation :

Chlordecon was principally used in Germany (potatoes) and South of USA, Brazil and Martinique & Guadeloupe (bananas)

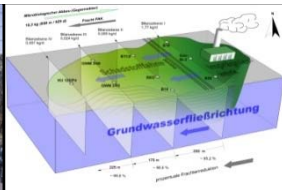
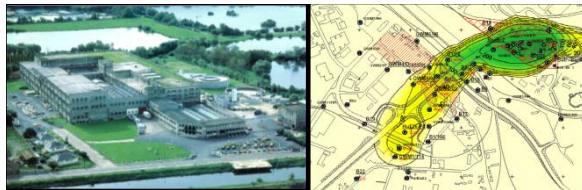
**CDE is very stable and toxic.
PCDD/F Impurities are existing.**



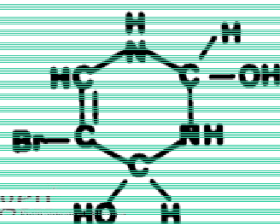
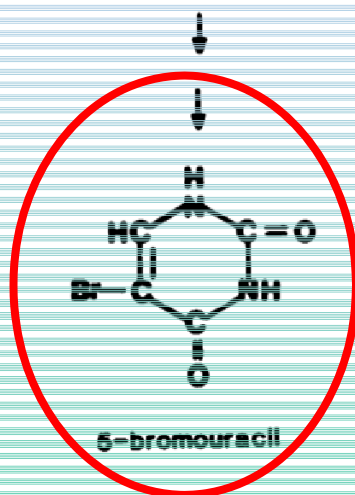
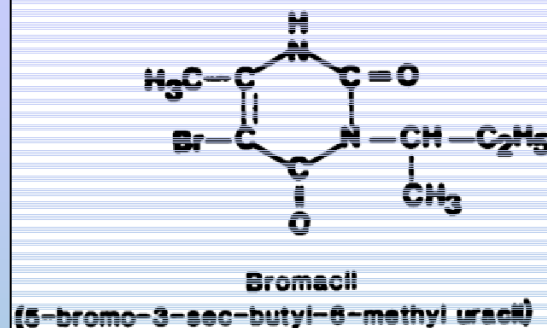


Prior Bromacil use

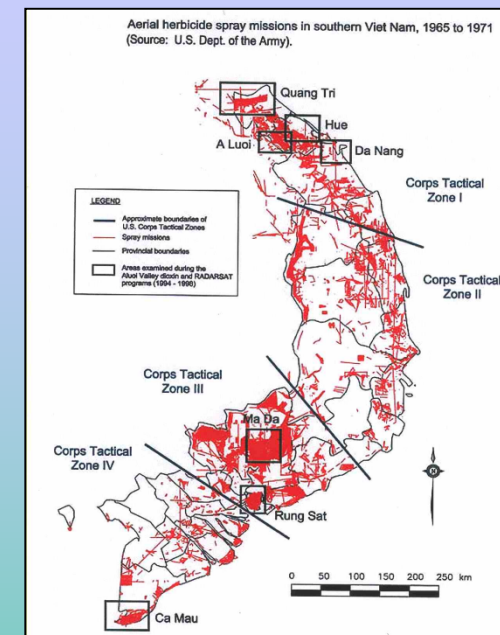
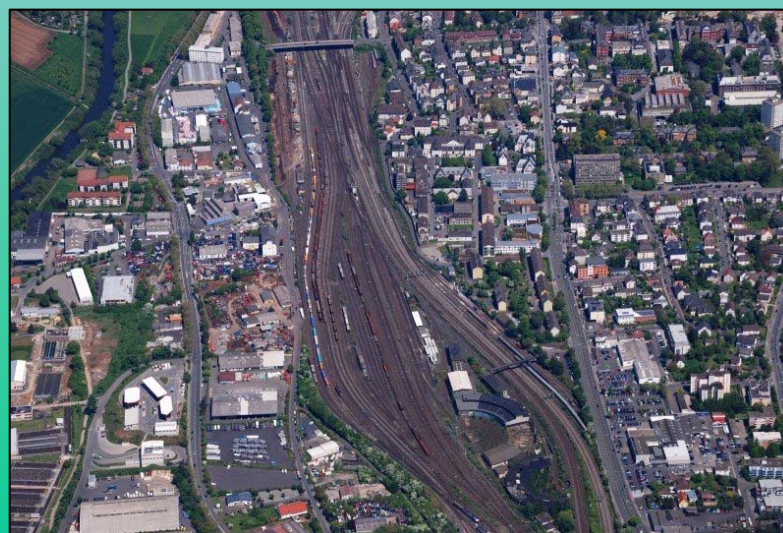




Bromacil degradation (very slowly) to 5-Bromouracil & 5-Bromo-dihydroxy-uracil

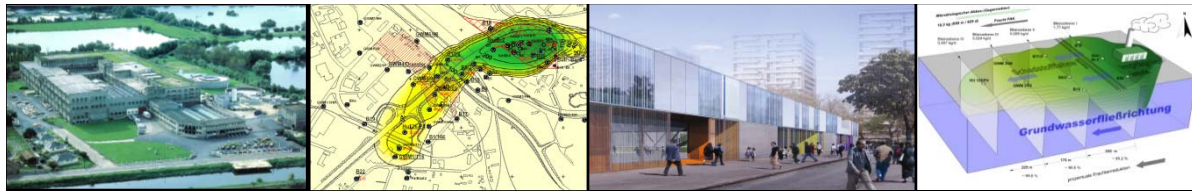


Prior Bromacil use **USA,** **Germany: Railways,** **Viet Nam War**



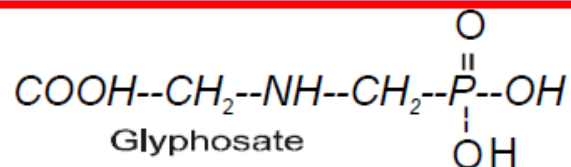
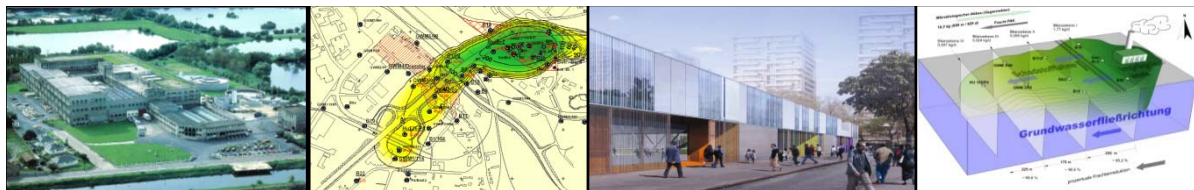
Map of US-Army Pesticide use in Viet Nam: Missions between 1965 - 1971





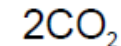
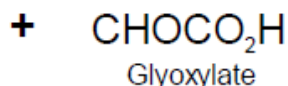
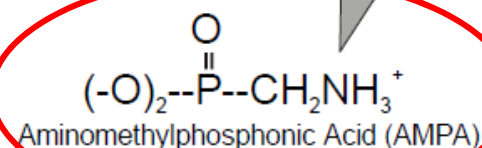
Prior Glyphosate use



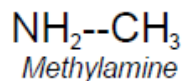


Enzyme(s)

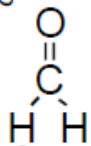
Degrades rapidly in soil (Large number of microbes)
Minimal degradation in water (Smaller number of microbes)



C-P lyase



Methylamine
dehydrogenase



Formaldehyde

Transamination



Phosphate

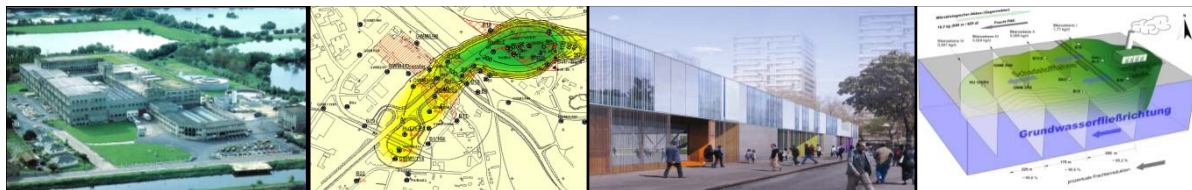
Glyoxylate &
Citric Acid Cycles

Amino Acids
Carbohydrates
Natural Acids
 CO_2

**Glyphosate and
glyphosate
Impurities
and Metabolites
(AMPA, etc.)**

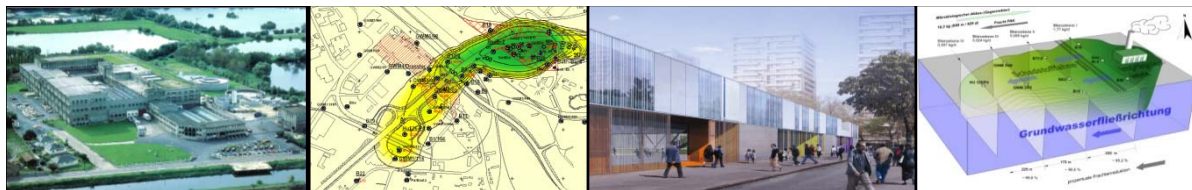
**Very strong use
in Corn (Mais)
Agriculture, as in
USA, Europe,
South-America
and especially in
Argentina**





**TERQ: Toxicological Exposure-Risk-Quantification
(HRA: Health Risk Assessment)**





TERQ: Toxicological Exposure-Risk-Quantification (HRA: Health Risk Assessment)

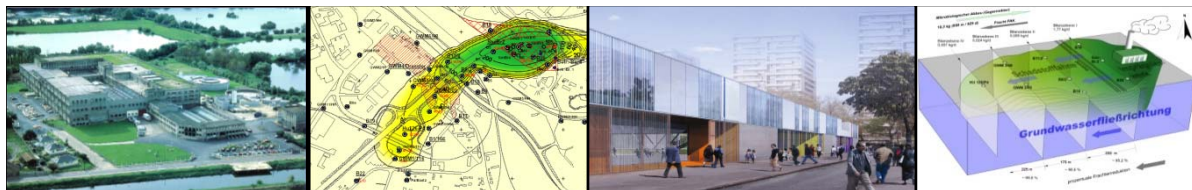
- Toxic Risks without Effect Threshold Dose (Carcinogenic risk etc.):

The carcinogenic risk, or individual cancer risk (ICR), is calculated by multiplying the daily dose of exposure with a slope factor (Sf) or an unit risk (UR) from the U.S.-EPA, UBA, and WHO etc.:

The individual cancer risk is compared with the limit of 10^{-5} (*) which represent the limit of an acceptable carcinogenic risk (1:100 000):

$$\text{ICR} = \text{DED (mg/kg/d)} * \text{Sf (mg/kg/d)}^{-1} \text{ or } \text{ICR} = \text{DED (mg/kg/d)} * \text{UR (mg/m}^3\text{)}^{-1}$$

- $\text{ICR} \leq 10^{-5}$: risk acceptable,
- $\text{ICR} > 10^{-5}$: risk unacceptable



TERQ: Toxicological Exposure-Risk-Quantification (HRA: Health Risk Assessment)

- Toxic Risks with Effect Threshold Dose (Non carcinogenic risk):

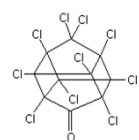
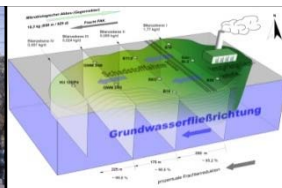
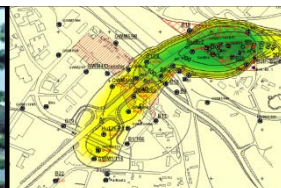
The non-carcinogenic risk, or risk index (RI), is defined according to the ratio of the daily exposure dose (DED) divided by the acceptable daily intake (ADI) or the acceptable concentration (AC) as following:

The risk index is compared to the limit of $RI = 1$ for which the daily exposure dose is equal to the acceptable daily intake dose:

$$RI = DED \text{ (mg/kg/d)} / ADI \text{ (mg/kg/d)} \quad \text{or} \quad RI = DED \text{ (mg/kg/d)} / AC \text{ (mg/m}^3\text{)}$$

$RI \leq 1$: the risk is acceptable,

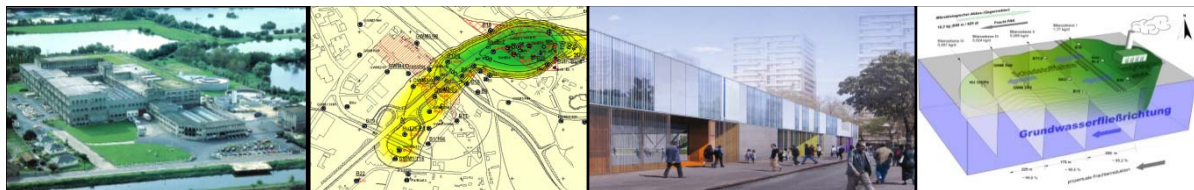
$RI > 1$: the risk is unacceptable.



TERQ: Toxicological Exposure-Risk-Quantification

Definition of SS-RG (CMA): Exemple Chlordecon

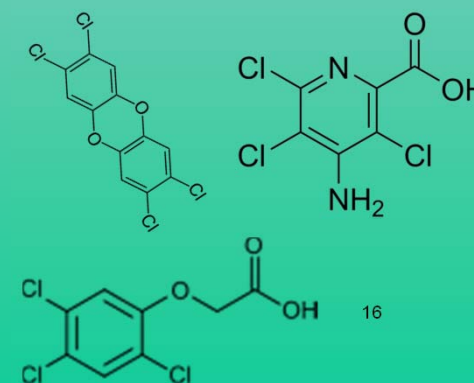
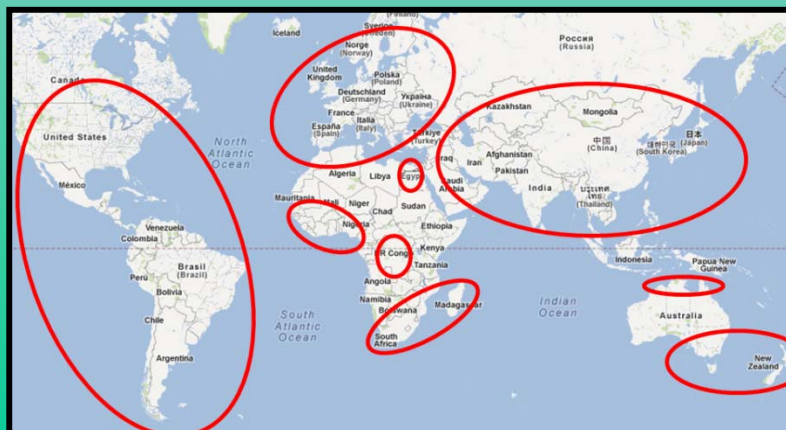
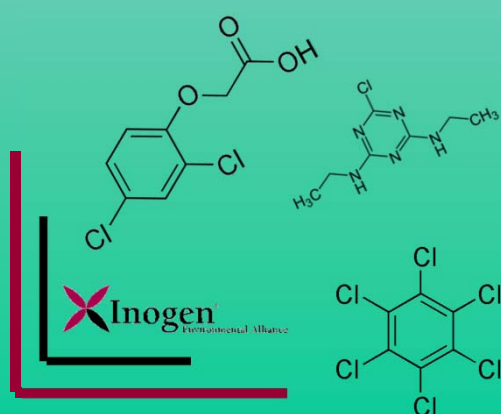
Chlordecone			
Scénario	Milieu source	CMA-A	unité
Scénario résidentiel avec jardin potager	Sols superficiels avec jardin potager	0,033	mg/kg
	Sols profonds partie cultivable	0,033	mg/kg
	Sols superficiels espaces verts	1,3	mg/kg
	Sols profonds hors parties cultivables	24	mg/kg
	Eaux souterraines tous usages sauf eau de boisson	0,00009	mg/l
	Eaux souterraines tous usages avec eau de boisson	0,000015	mg/l
Scénario espace vert	Sols superficiels espaces verts	1,5	mg/kg
	Sols profonds	118	mg/kg
Scénario crèche / école maternelle	Sols superficiels espaces verts	2,9	mg/kg
	Sols profonds	92	mg/kg
Scénario ERP / commercial	Sols superficiels espaces verts	6,6	mg/kg
	Sols profonds	420	mg/kg

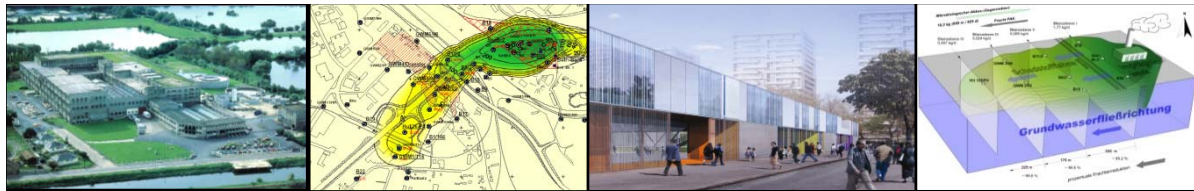


Recommendations

In case of Pesticide pollution !,

- as for ex. by 2,4-D, Picloram, Bromacil, Chlordecone, etc. ;
- Co-contaminants & toxic Metabolites,
as HCH: Hexachlorobenzene, PCDD/F, 2,4-dichlorophenol,
4-chlorophenol, etc.
- must be also assessed (site investigations & TERQ or HRA)
- and integrated in corrective actions,
as shown by the examples from Europe, South America
(Argentina, Brazil, etc.) and Asia (China, India, Viet Nam, etc.).





ZEN ?

