

GLYPHOSATE: ARGENTINA CASE

USE OF RISK21 APPROACH

ANALYSIS OF PEER-REVIEW PUBLICATIONS (2000 - 2019)



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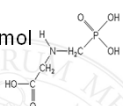
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1

Glyphosate PHYSICOCHEMICAL FEATURES


- Simple structure
- MW, 169.1 g/mol
 - Formulated G-salts, 186.1 - 404.1 g/mol
- pH = 2.5 (1% solution in water)
- Low $K_{o,w}$ = -3.40
- High water solubility = 12 g/L (25°C)
 - Specific gravity, 1.70 g/cm³
- Stable to hydrolysis (pH 3-9; 5-35°C)
- Photostable (soil and air)
- Non volatile



GLYPHOSATE



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Glyphosate PHYSICOCHEMICAL FEATURES AND CONTAMINATION TRENDS

- Not expected to bioaccumulate/biomagnificate

WHO 2005. Glyphosate and AMPA in Drinking-water.
https://www.who.int/water_sanitation_health/dwq/chemicals/glyphosateampa290605.pdf



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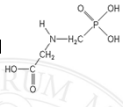


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- Stable to hydrolysis (pH 3-9; 5-35°C)
- Photostable in soil and air
- Non volatile (not expected in the air)




GLYPHOSATE

Solubility
Different G-salts, up to ~10² g/L



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Structural lability - Persistence

- Relatively rapid degradation by soil microbiota:
 - DT50 from days to few weeks.
- Longer stability in particular environmental compartments: DT50 up to few months based on:
 - Some soil texture/composition conditions
 - Diversity and abundance of microbiota
 - Water sediments



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5

High solubility in water....


It may stay for up to few months under some environmental conditions...

Is it worth considering glyphosate as a drinking water-related risk?


Are G concentration levels in water sources used for drinking relevant for total health risk in humans?

Is there a problem?

- 0 -Is there any potential for harm?
- 1 -Is there any chance for occurrence?
- 2 -Is there any chance for exposure?
- 3 -Is there any chance for unsafe exposure?
- 4 -More specific questions

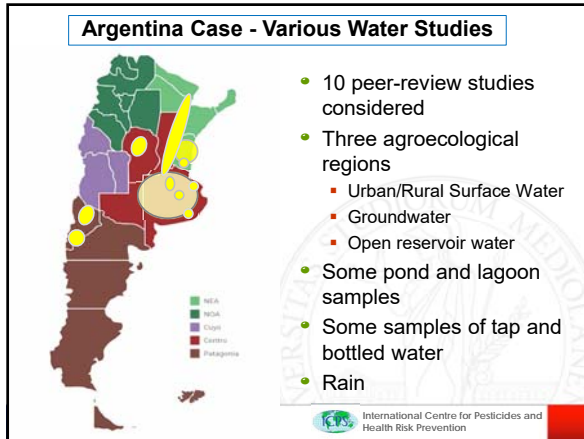


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6



7

Glyphosate in water sources - ARGENTINA

Region	Water System	Produce system	G, pre-application	G, post-application	Reference
Cordoba province,	Suquia River basin	5 sampling sites	3 sites <LOD		Bonasea et al. Toxics 6 (1): 3, 2018
north-central region	Urban and agricultural areas	Several intensive and extensive agricultural uses	2 sites, from <LOD to 125 ug/L	LOD = 0.5 ug/L LOQ = 1.0 ug/L	
Buenos Aires province,	RGW RSW USW	Multiple sampling sites	SW: <LOD to 1.3 ug/L (1.1 - 1.5 ug/L)		Bonetto et al., ISBN 978-950-694-994-5, Universidad de Buenos Aires, 376 pages, 2018.
North-central region	Urban and agricultural areas	Mostly soybean field; other agricultural uses	SW: <LOD to 2 ug/L (1 site/time, 7 ug/L) Lagoon: 1-3 ug/L GW: mostly <LOD to 4 ug/L (in a few sites/times, 10-12 ug/L)		

8

Glyphosate in water sources - ARGENTINA

Region	Water System	Produce system	Sampling sites	Findings	Reference
North-east provinces	Parana and Paraguay Rivers and their tributaries	23 sampling sites			
Buenos Aires province,	Stream water	Mostly soybean field			
southeast, Rio Quequén Grande basin					
Buenos Aires province,	Stream water	16 farms	8-agrifoods	Most sites and sampling times <LOD At different times, 2-15 sites >LOD 4 - 34% samples, trace to 7.6 ug/L LOD = 0.1 ug/L	Aparicio et al. Chemosphere 93: 1866-73, 2013
Southeast region,					
44 sampling					

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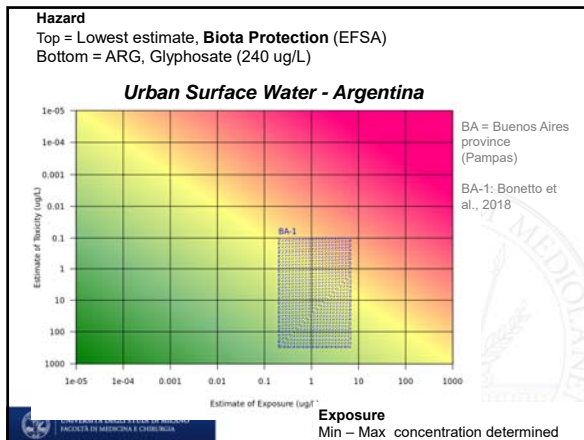
Glyphosate occurrence in water sources

- Surfacewater: ND to $10^0/10^1$ ppb (peak: 10^2 ppb)
- Groundwater: ND to $10^{-1}/10^0$ ppb (peak: 10^1 ppb)
 - Potential use as drinking water: $10^{-1}/10^0$ ppb up to 50 ug/L)
- Rain water: $10^{-1}-10^0$ ppb
- May maximum concentration in multiple Argentine rivers and aquifers be a risk driver for human health and aquatic life?

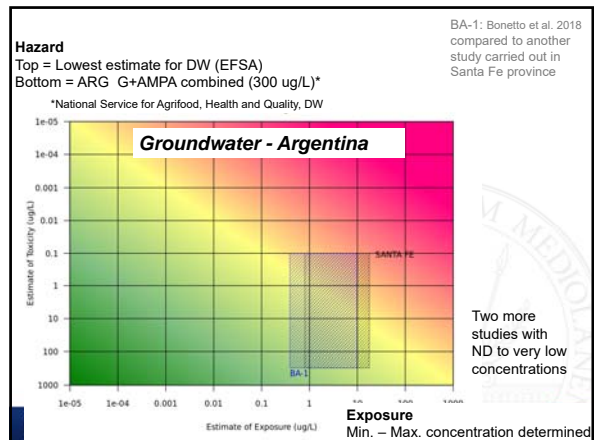
Risk21 approach may help you walk through the problem formulation and refine hypotheses

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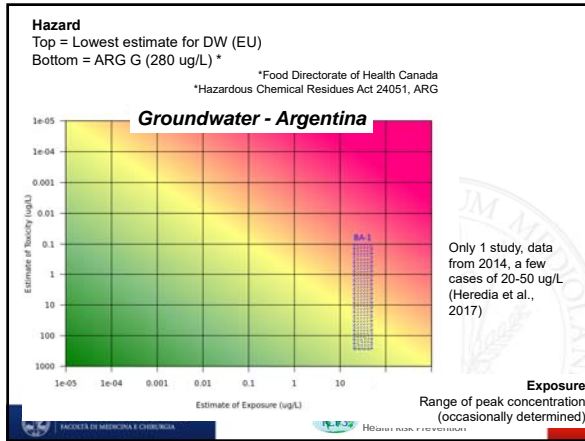
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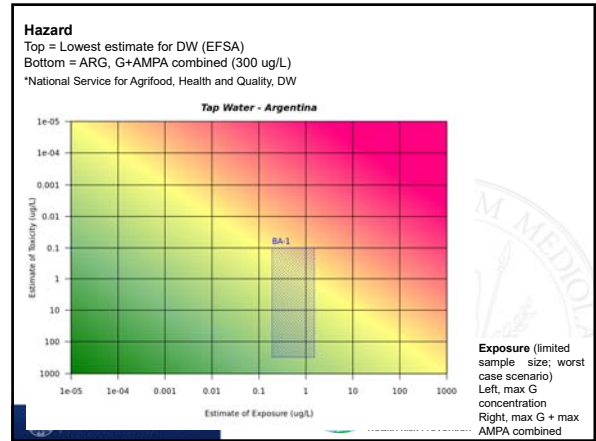
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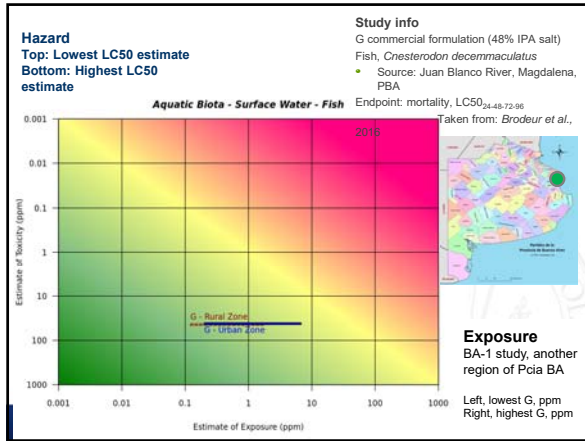
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13



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15

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**GLYPHOSATE
 DIETARY AND ENVIRONMENTAL
 EXPOSURE ASSESSMENT**

RESULTS FROM OFFICIAL CONTROL ACTIVITIES
 CARRIED OUT BY EU MEMBER STATES FROM 2014 TO 2016

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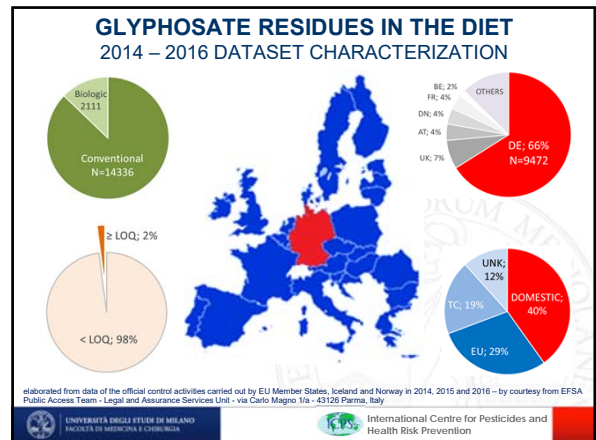
OUTLINE

- EU control activities and the 2014-2016 dataset characterisation
- Results from Groundwater Monitoring
- Dietary Exposure Assessment
- Results from Surface Water Monitoring
- Environmental Exposure Assessment

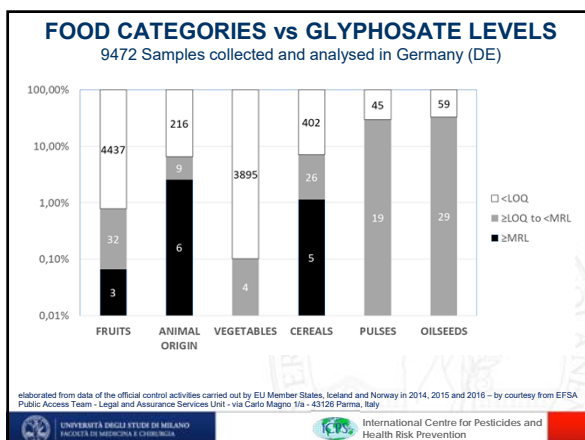
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17



18



19

INHOMOGENEITY OF QUANTIFICATION LIMITS

When averaging residue levels two scenarios were assumed as follows:

- The **lower-bound scenario (LB)** assumes that if not quantified (i.e. samples with residue level <math>< \text{LOQ}</math>), the residues are not present in the food product analysed. This scenario may result in an underestimation of the long term exposure.
- The **adjusted upper-bound scenario (UB)** assumes that even if not quantified (i.e. results <math>< \text{LOQ}</math>), residues are present at the level of LOQ. It consists of a conservative approach which is likely to overestimate the long-term exposure to a pesticide residue.

LOQ = f(lab) mg/kg	N
0.05	107
0.01	1537
0.02	6214
0.03	806
0.04	95
0.05	336
0.1	299
0.14	68

LOQ: Limit of Quantification

20

THEORETICAL MAXIMUM DAILY INTAKE

TMDI and EU-MRLs set for PRE-HARVEST USES

Pre-harvest uses include uses for weed control (higher doses) and harvest aid, sometimes also referred to as desiccation (lower doses), to enhance ripening on non-determinate crops to reduce crop losses, and to help manage determinate crops in wet seasons.

For these uses, and based on an adequate number of metabolism studies and residue trials, EU-MRL were set as follows.

CATEGORY	kg as/ha	PHI	CROP	MRL
CEREALS	2,16	7	barley, oat, sorghum	20
			wheat	10
OILSEEDS	2,16	14	sunflower seeds, soybeans	20
			rapeseeds/canola, mustard and cotton seeds, linseeds	10
PULSES	1,44	7	lentils, peas, lupins	10

The Theoretical Maximum Daily Intake (TMDI) is an overestimate of the true pesticide residue intake, calculated by multiplying the established or proposed MRLs by the estimated average daily consumption for each food commodity and then summing the products.

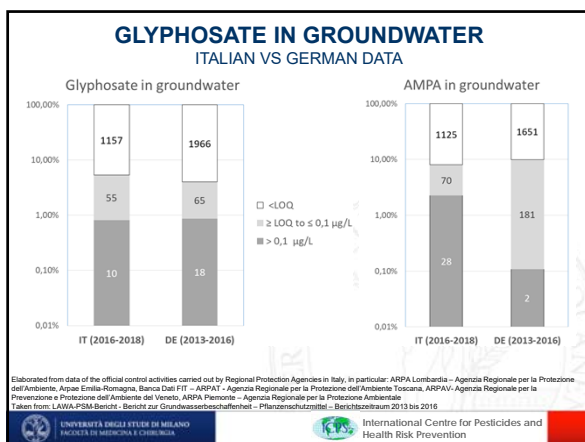
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DIETS CONSIDERED IN THE ASSESSMENT

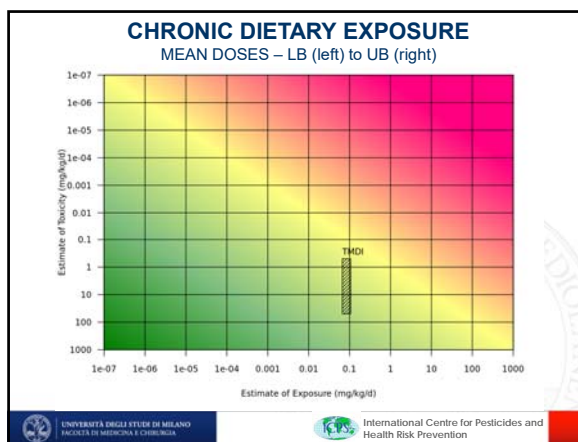
DIET	BW (kg)	DIET	BW (kg)	DIET	BW (kg)
DE child	16,2	IT adult	66,5	GEMS/Food G06	60,0
DE general	76,4	IT toddler	41,6	GEMS/Food G07	60,0
DE women 14-50 yr	67,5	LT adult	70,0	GEMS/Food G08	60,0
DK adult	75,1	NL child	18,4	GEMS/Food G10	60,0
DK child	21,8	NL general	65,8	GEMS/Food G11	60,0
ES adult	68,5	NL toddler	10,2	GEMS/Food G15	60,0
ES child	34,5	PT general	62,8		
FI 3 yr	15,2	RO general	60,0		
FI 6 yr	22,4	SE general	60,0		
FI adult	78,1	UK adult	76,0		
FR adult	66,4	UK infant	8,7		
FR child 3-15 yr	18,9	UK toddler	14,6		
FR infant	9,1	UK vegetarian	66,7		
FR toddler 2-3 yr	13,6				
IE adult	75,2				
IE child	20,0				

BW: Bodyweight

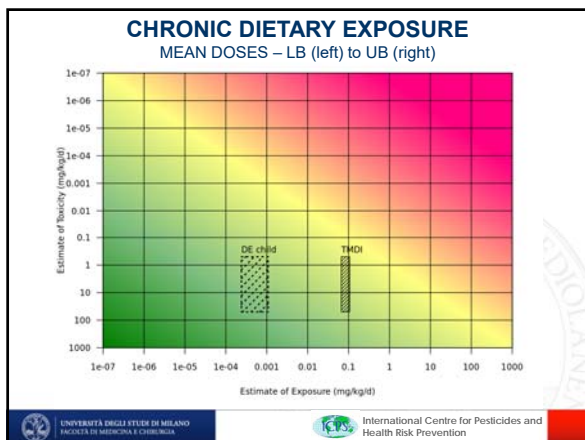
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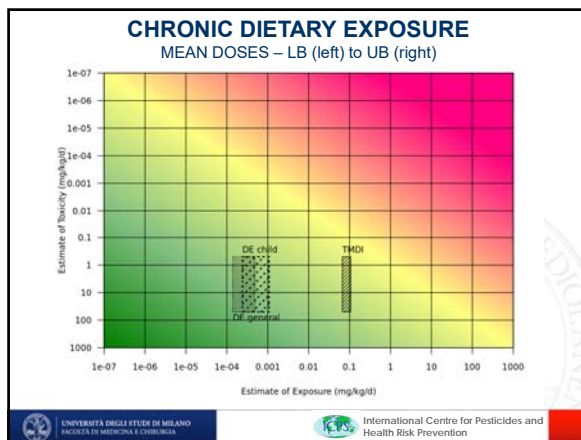
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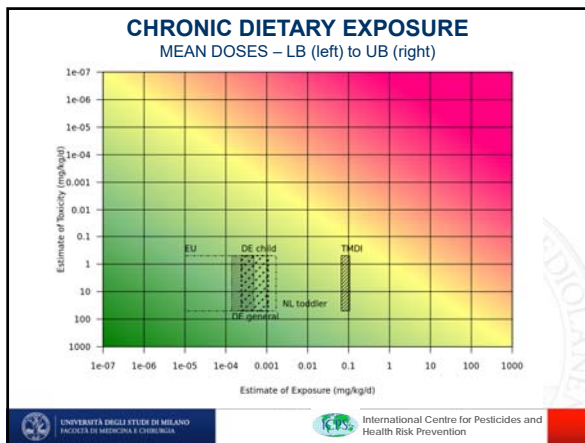
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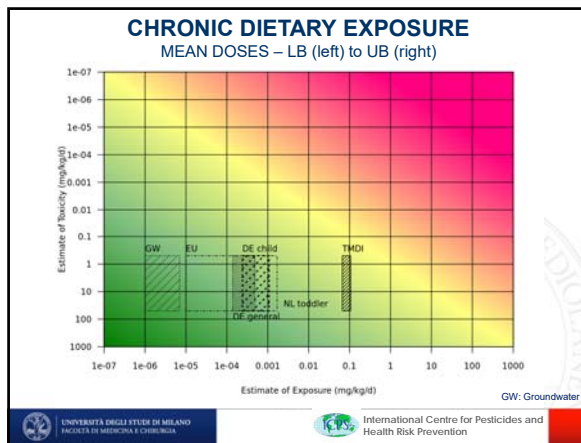
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28

CHRONIC DIETARY EXPOSURE

CHILDS: MAIN CONTRIBUTORS

DIET	Exposure $\mu\text{g/kg bw}$	1 st	2 nd	3 rd
NLtoddler	1,69	Wheat	Maize	Apples
DKchild	1,12	Rye	Wheat	Apples
DEchild	1,08	Wheat	Apples	Rye
NLchild	1,08	Wheat	Sunflower seeds	Apples
FRchild	1,03	Wheat	Lentils	Sunflower seeds

MEAN LEVELS

Crop	UB $\mu\text{g/kg}$
Lentils	970
Sunflower seeds	507
Soyabeans	95
Rye	92
Wheat	75
Apples	22

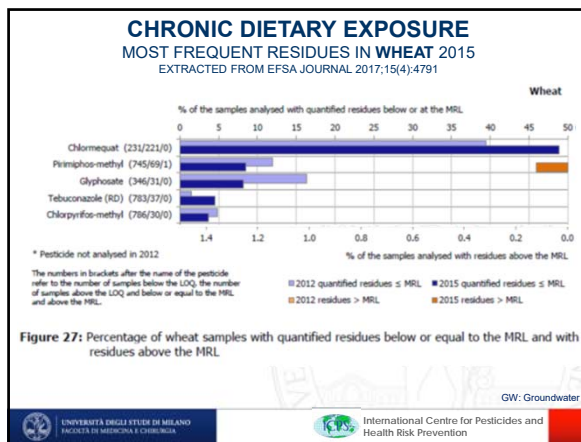
ADULTS: MAIN CONTRIBUTORS

DIET	Exposure $\mu\text{g/kg bw}$	1 st	2 nd	3 rd
GEMSFoodG06	1,45	Wheat	Soyabeans	Sunflower seeds
GEMSFoodG08	1,35	Wheat	Sunflower seeds	Soyabeans
GEMSFoodG15	1,27	Wheat	Sunflower seeds	Soyabeans
GEMSFoodG10	1,25	Soyabeans	Wheat	Sunflower seeds
DEgeneral	0,49	Wheat	Rye	Apples

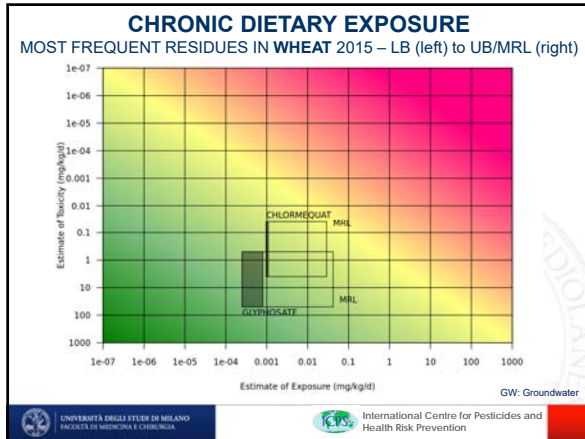
WHEAT

Origin	% > LOQ
Ireland	32
UK	22
Italy	14
Lithuania	11
Denmark	5
Germany	4
France	1

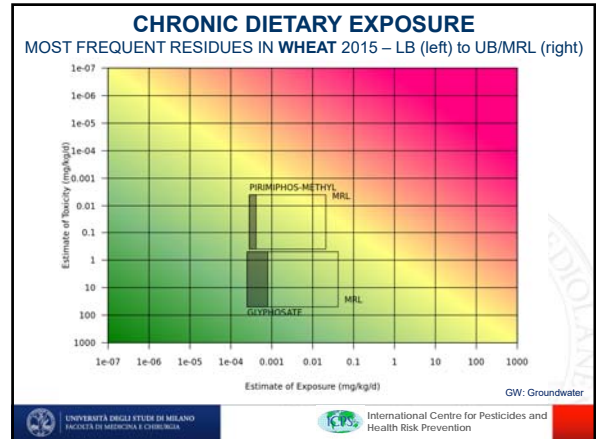
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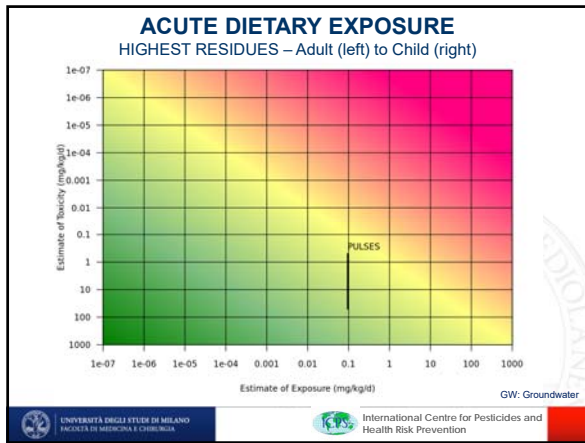
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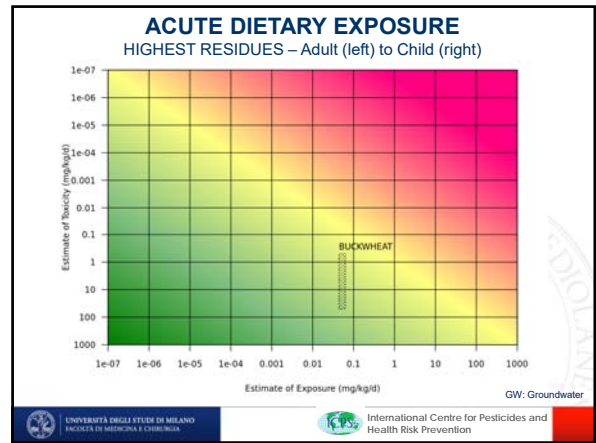
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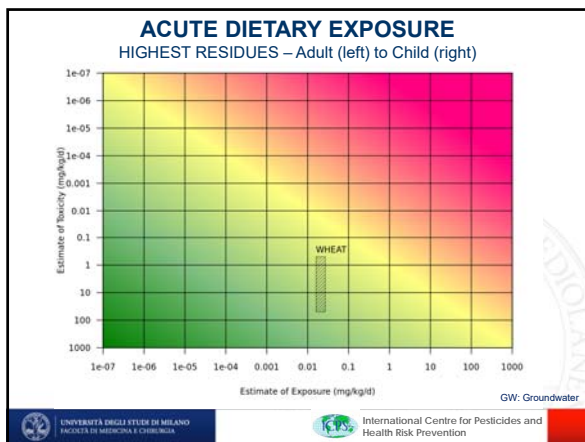
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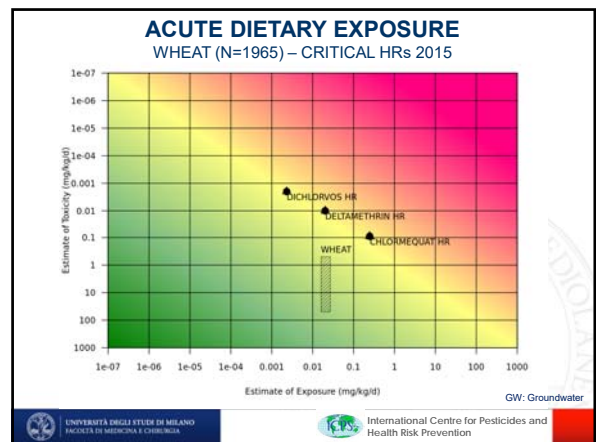
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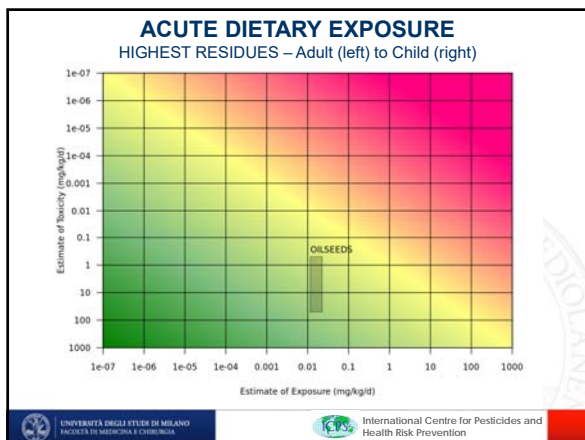
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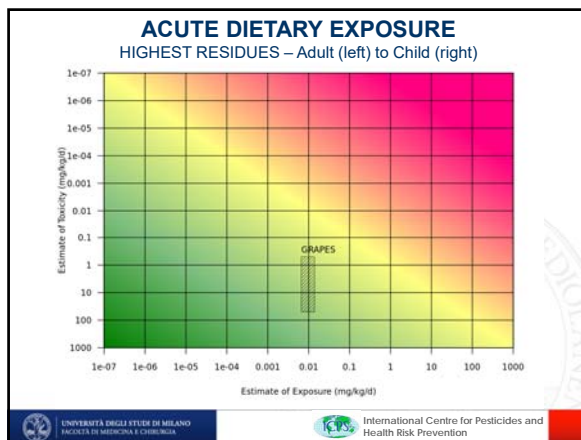
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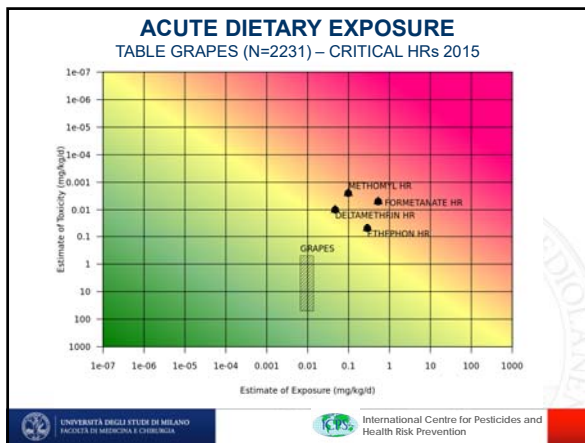
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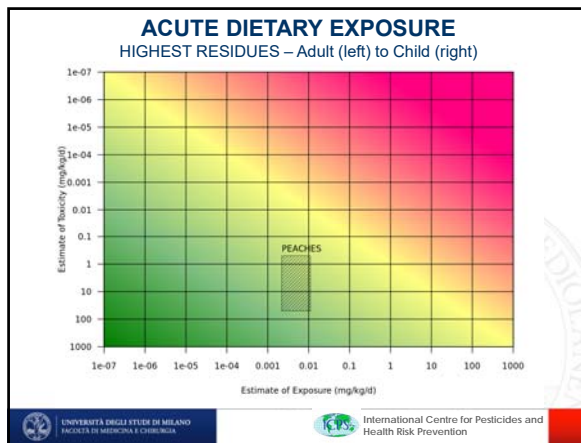
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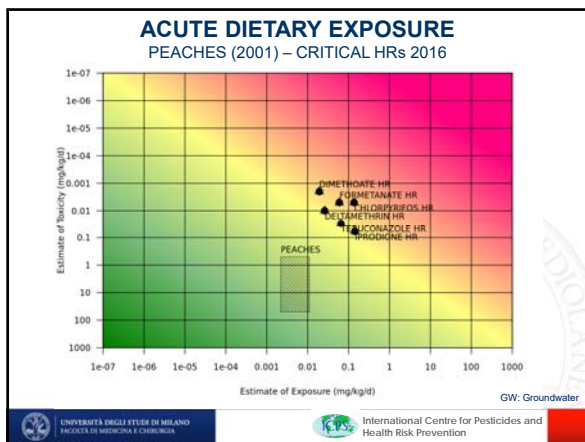
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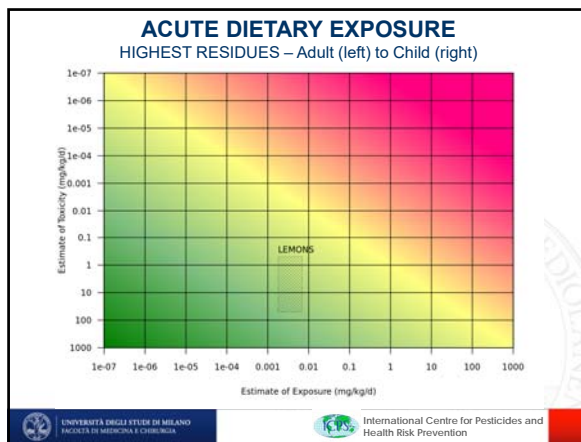
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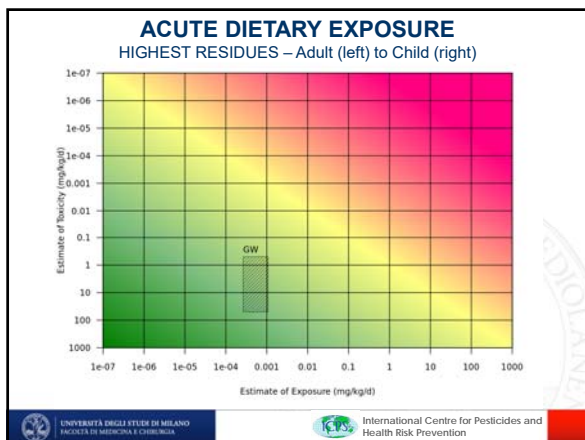
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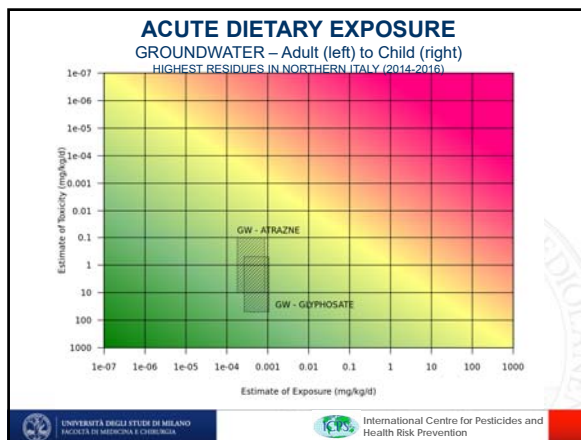
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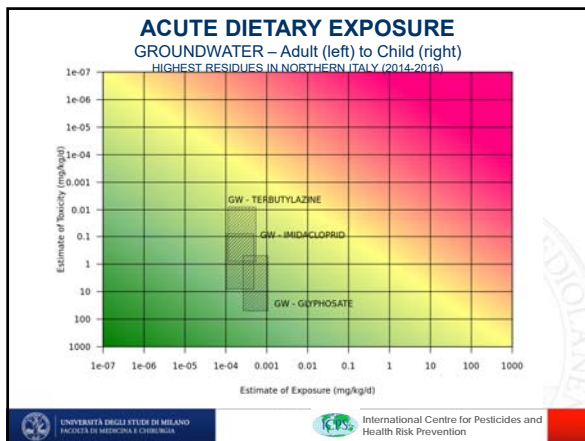
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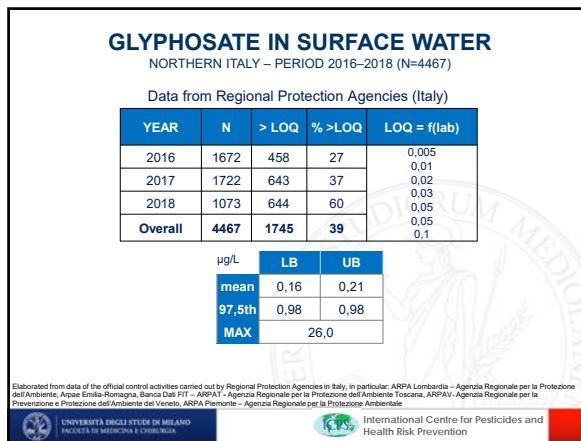
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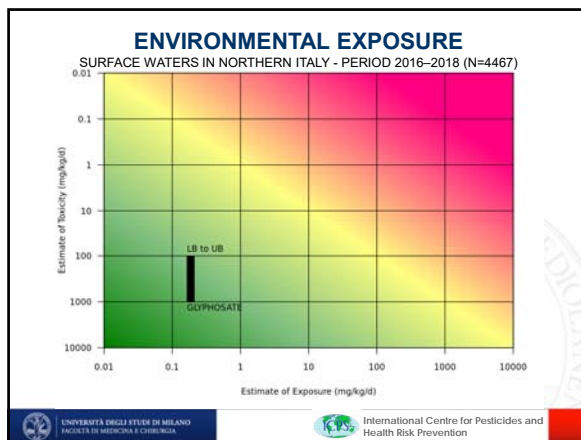
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REGULATORY ACCEPTABLE CONCENTRATION RAC OF GLYPHOSATE

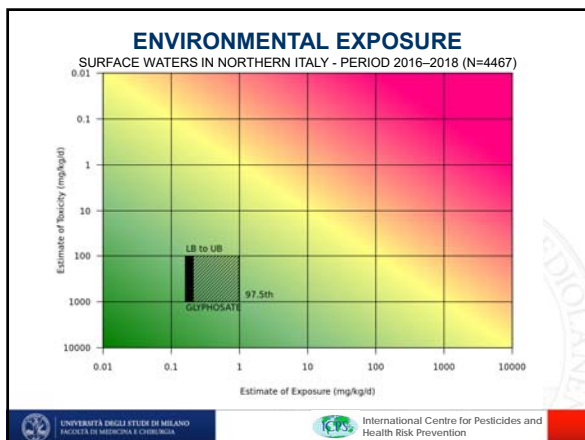
Setting of Environmental Toxicity endpoint for most sensitive species
Data from EFSA Journal 2015;13(11):4302

Test organism	Species	Endpoint	Conc. (µg/L)	Annex VI trigger value	RAC (µg/L)
Fish acute	<i>O. mykiss</i>	LC50	38000	100	380
Fish prolonged	<i>B. rerio</i>	NOEC	1000	10	100
Fish prolonged	<i>P. promelas</i>	NOEC	25700	10	2570
Daphnia acute	<i>D. magna</i>	EC50	40000	100	400
Daphnia prolonged	<i>D. magna</i>	NOEC	12500	10	1250
Algae acute	<i>A. flosaquae</i>	Ebc50	8500	10	850
Aquatic plants	<i>M. aquaticum</i>	Ebc50	4400	10	440

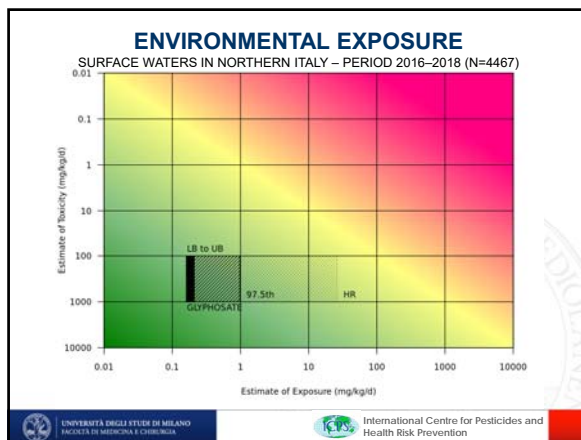
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48



49



50

REGULATORY ACCEPTABLE CONCENTRATION
RAC OF TERBUTYLAZINE

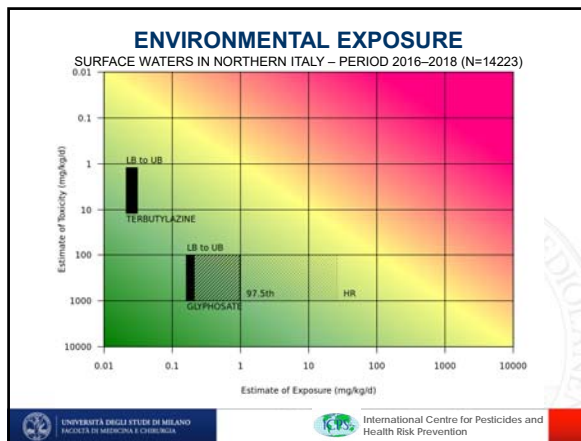
Setting of Environmental Toxicity endpoint for most sensitive species
Data from EFSA Journal 2019;17(9):5817

Test organism	Species	Endpoint	Conc. (µg/L)	Annex VI trigger value	RAC (µg/L)
Fish acute	<i>Oncorhynchus mykiss</i>	LC50	2200	100	22
Fish prolonged	<i>Oncorhynchus mykiss</i>	NOEC	90	10	9
Daphnia chronic	<i>Daphnia magna</i>	NOEC	19	10	1,9
Algae chronic	<i>Pseudokirchnerella subcapitata</i>	EbC50	12	10	1,2
Aquatic plants Chronic	<i>Lemna gibba</i>	EbC50	12,8	10	1,28

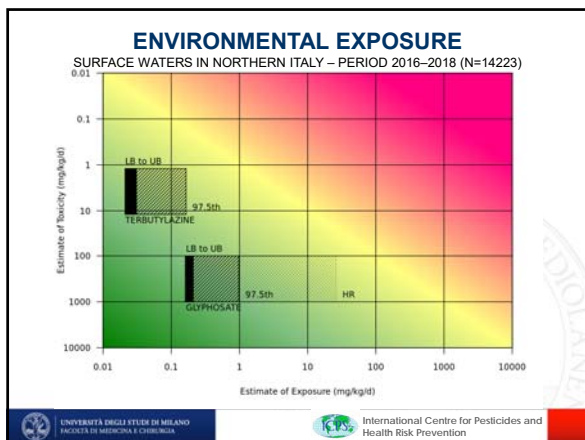
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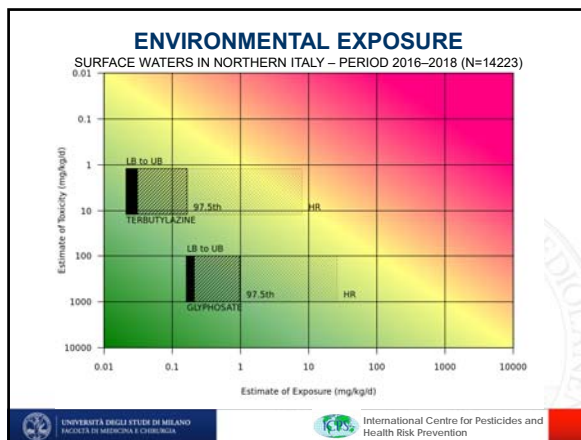
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52



53



54

Conclusions for Europe

- Glyphosate has been monitored extensively (at least in Germany) in crops and water (surface and ground-water)
- Estimated consumers' exposure is well below the ADI
- The risk from the estimated consumer exposure is very low, and generally lower than risks from other pesticides used in the same crops
- The risk for the environment is low
- The risk for the environment is generally lower than the risk estimated for other herbicides

55

Many thanks to: Christian Schlitt, Azzurra Milano, Federica Tagni, Francesca Vellere

ORIGIN OF ITALIAN DATA ON SURFACE and GROUNDWATER

ARPA Lombardia – Agenzia Regionale per la Protezione dell'Ambiente
<https://www.arpalombardia.it/Pages/Ricerca-Dati-ed-Indicatori.aspx>

ARPA Emilia-Romagna
https://www.arpae.it/elenchi_dinamici.asp?tiposdati_acqua&idivello=2020

Banca Dati FIT – ARPAT - Agenzia Regionale per la Protezione dell'Ambiente Toscana
<http://sira.arpap.toscana.it/apev2/?p=121-3-0>

ARPAV - Agenzia Regionale per la Prevenzione e Protezione dell'Ambiente del Veneto
<https://www.arpa.veneto.it/dati-ambientali/open-data/indice/risorse-sotterranee/acque-sotterranee-qualita-chimica>

ARPA Piemonte – Agenzia Regionale per la Protezione Ambientale
<http://webgis.arpa.piemonte.it/geoportale/index.php?tema=chiesacqua>

ORIGIN OF GERMAN DATA ON SURFACE and GROUNDWATER

LAWA-PSM-Bericht - Bericht zur Grundwasserbeschaffenheit – Pflanzenschutzmittel – Berichtszeitraum 2013 bis 2016
beschlossen auf der 157. LAWA-Vollversammlung am 03.04.04.2019 in Gotha

56

SUMMARY OF GLYPHOSATE DATA

DIETARY EXPOSURE

Over the period 2014 to 2016, 3.4% of the samples analysed for glyphosate contained quantified residues of this active substance (2014: 4.3%; 2015: 3.1%; 2016: 3.1%) (DE: 2014: 1.9%; 2015%: 0.8; 2016: 1.2%)

Considering the individual food products analysed over the period 2014-2016, the highest quantification rate was observed for dry lentils (42.7% of the samples containing quantified levels of glyphosate, i.e. 67 samples of 157 samples analysed), followed by sunflower seeds (26.4%; 14 of 53 samples). In cereals, glyphosate was mainly found in barley (15.3% of the samples; 33/215 samples), followed by wheat (10.4% samples; 283/2725), barley (8.4%; 9/107) and rye (4.4%; 33/756). Buckwheat (flour), analysed mainly in 2016, was found in 22.7% of the samples (15/66).

Among the 16743 samples analysed (14336 non-organic and non-baby-food samples), 26 samples (0.16%) exceeded the MRL for glyphosate:

- 5 samples of honey from Germany containing up to 0.61 mg/kg glyphosate (MRL=0.1 mg/kg);
- 4 samples of buckwheat from Lithuania containing up to 2 mg/kg glyphosate (MRL=0.1 mg/kg);
- 2 samples of lentils from Canada containing 12.2 and 12.4 mg/kg glyphosate (MRL=10 mg/kg);
- 1 sample of limes from Brazil with a glyphosate residues of 0.2 mg/kg (MRL=0.1 mg/kg);
- 1 sample of beans from China with a glyphosate residues of 2.3 mg/kg (MRL=2 mg/kg);

Glyphosate was quantified in 14 out of 2111 organic samples (0.7%), but not found in food for infants and young children (478 samples).

No data were reported to EFSA on the presence in samples of N-acetyl-glyphosate and N-acetyl-AMPA, metabolites formed in some genetically modified (GM) crops tolerant to glyphosate.

57