3rd European Conference on Copper in Plant Protection

15th-16th November in Berlin, Germany

BOLW
Bund Ökologische Lebensmittelwirtschaft

IFOAM EU GROUP
MAKING EUROPE MORE ORGANIC

JKI
Julius Kühn-Institut
Bundesforschungsinstitut für Kulturpflanzen

The repeated dose makes the poison - assessing the risk of copper fungicides towards soil organisms

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3rd European Conference on Copper in Plant Protection
organized by BÖLW, IFOAM EU-Group and JKI
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The Dimorphic Character

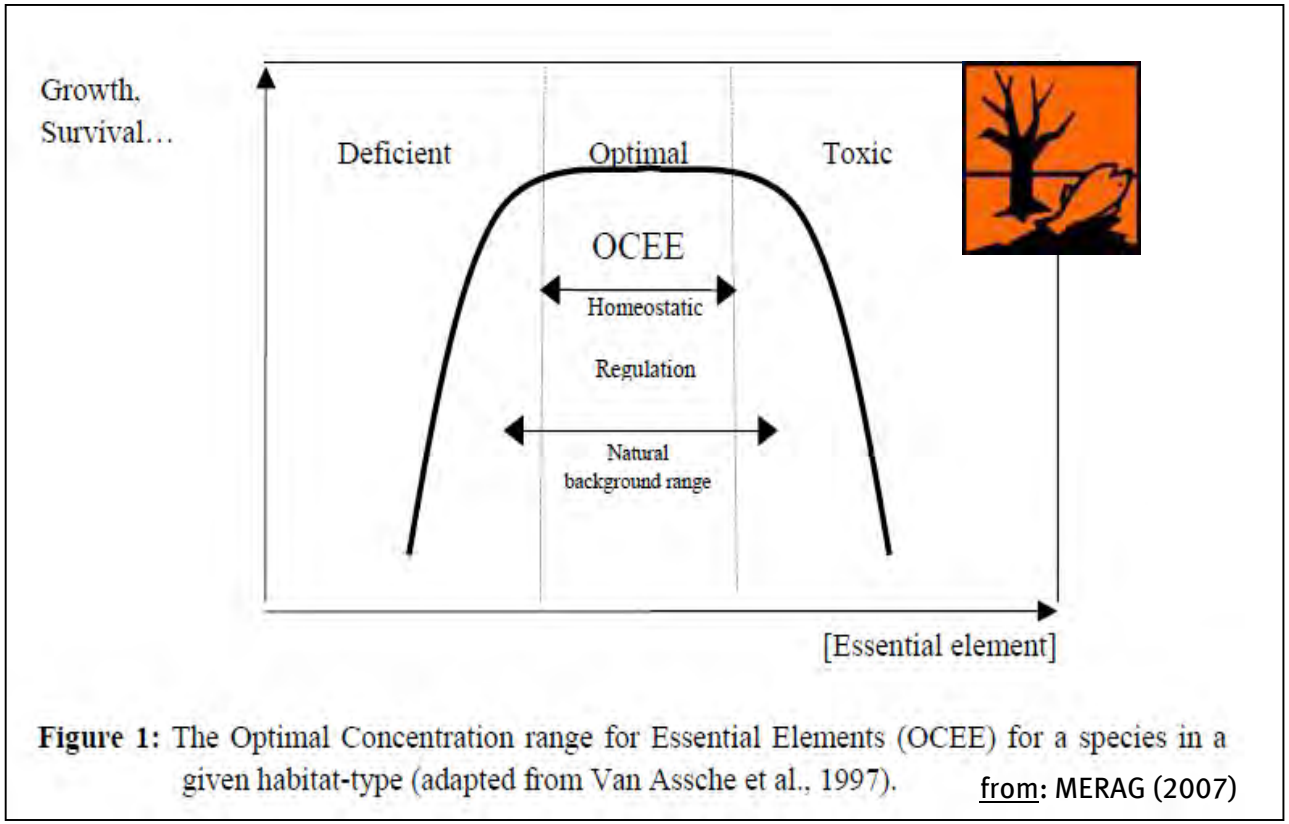


Figure 1: The Optimal Concentration range for Essential Elements (OCEE) for a species in a given habitat-type (adapted from Van Assche et al., 1997).

from: MERAG (2007)

- **essential element, however persistent and toxic…**
- **it´s a question of the dose…**

Precautionary Soil Protection

precautionary values for copper in soil (German Soil Protection Act, 1999)

if exceeded: maximum permissible additional input 360 g Cu/ha per year (∑ of all inputs)

§

soil type	mg/kg dw
sand	20
silt	40
clay	60

- **in derivation considered: ecotox data, ~ bioavailability and natural background copper in German soils (8 – 42 mg/kg dw, median values)**
- **do not apply to agricultural soils – regulatory coherence?**
- **copper pesticides: in-field soils are the major sink**

Environmental Risk Assessment under 1107/2009/EC

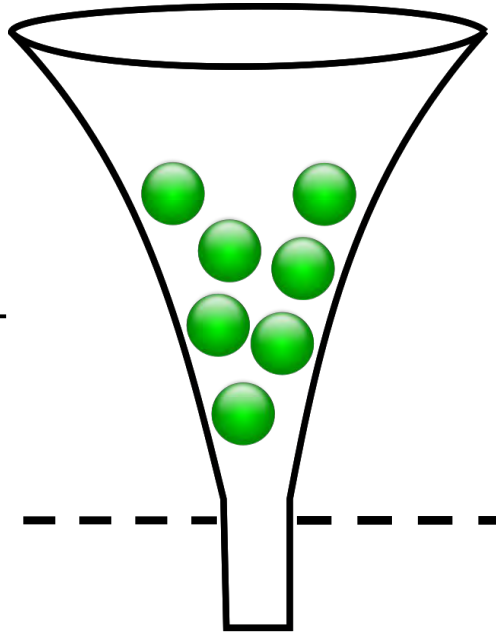
Toxicity-Exposure-Ratio (TER)

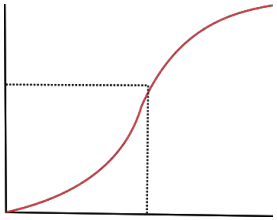
$$TER = \frac{Toxicity}{Predicted\ environmental\ exposure\ (PEC)}$$

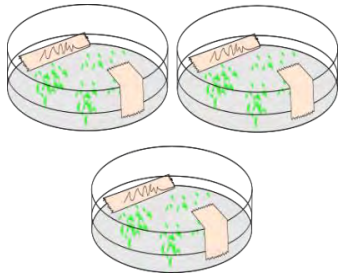
- **if TER at intended application rate above legally defined acceptability trigger (uncertainty factor) = risk acceptable**
- **BUT: relevant guidance document (SANCO 2002) not metal-specific (i.e. no consideration of soil accumulation and bioavailability)**

Environmental Risk Assessment under 1107/2009/EC

Tier 1



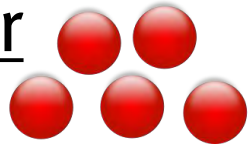


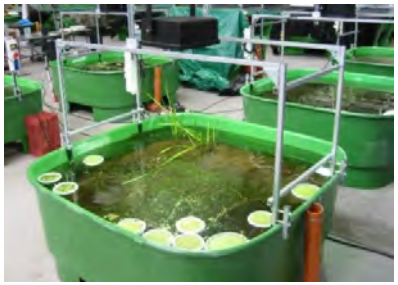


Toxicity data (laboratory) und exposure assessment
standardized

Uncertainty-Factor

Higher Tier





Risk Refinement (Tox / Expo more specific, realistic)
non-standard

Uncertainty-Factor

Original © Klaus Swarowsky (UBA)

Exposure Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Predicted environmental concentration, PEC_{soil} – e.g. Grapes:

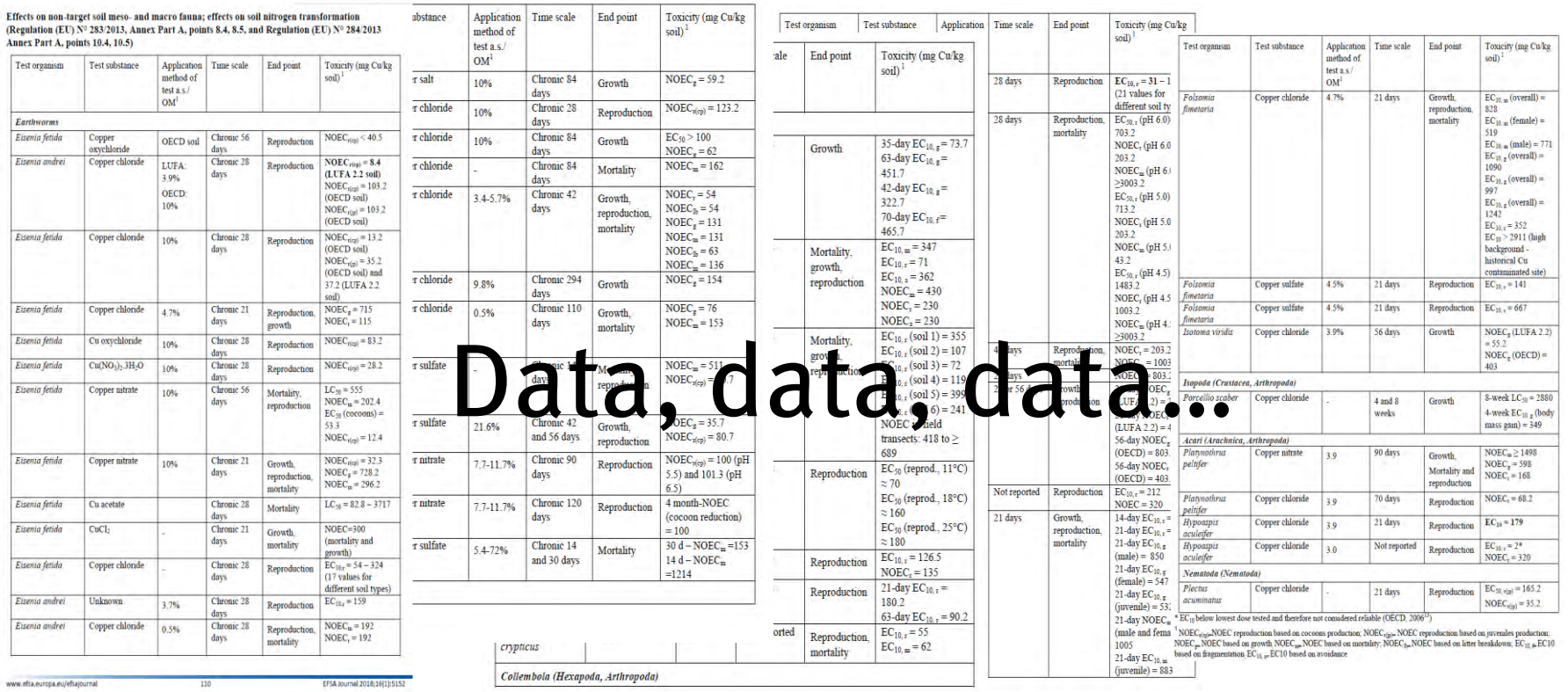
- **application rate: 6000 g Cu/ha/year**
- **soil layer: 5 cm**
- **soil bulk density: 1,5 g/cm^3**
- **no crop interception**
- **no degradation, 10 years accumulation**
- **geo- and anthropogenic Cu background in soil (monitoring data vineyards soils: 10th Percentile 28 mg Cu/kg d.w. and 90th Percentile 160 mg Cu/kg d.w.)**

- **$PEC_{plateau}$ (10 years, 10th Percentile soils): 108 mg Cu/kg d.w.**
- **$PEC_{plateau}$ (10 years, 90th Percentile soils): 240 mg Cu/kg d.w.**

Effect Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Soil macro organism (earthworms and soil arthropods) – Tier 1

- extensive set of acute and chronic toxicity data (lab studies)
- chronic most relevant, earthworms most sensitive group



Effects on non-target soil meso- and macro fauna; effects on soil nitrogen transformation (Regulation (EU) N° 283/2013, Annex Part A, points 8.4, 8.5, and Regulation (EU) N° 284/2013 Annex Part A, points 10.4, 10.5)

Test organism	Test substance	Application method of test a.s./ OM[1]	Time scale	End point	Toxicity (mg Cu/kg soil)[1]
Earthworms					
Eisenia fetida	Copper oxychloride	OECD soil	Chronic 56 days	Reproduction	$NOEC_{r(cp)}$ < 40.5
Eisenia andrei	Copper chloride	LUFA: 3.9% OECD: 10%	Chronic 28 days	Reproduction	**$NOEC_{r(cp)}$ = 8.4 (LUFA 2.2 soil)** $NOEC_{r(cp)}$ = 103.2 (OECD soil) $NOEC_{r(cp)}$ = 103.2 (OECD soil)
Eisenia fetida	Copper chloride	10%	Chronic 28 days	Reproduction	$NOEC_{r(cp)}$ = 13.2 (OECD soil) $NOEC_{r(cp)}$ = 35.2 (OECD soil) and 37.2 (LUFA 2.2 soil)
Eisenia fetida	Copper chloride	4.7%	Chronic 21 days	Reproduction, growth	$NOEC_g$ = 715 $NOEC_r$ = 115
Eisenia fetida	Cu oxychloride	10%	Chronic 28 days	Reproduction	$NOEC_{r(cp)}$ = 83.2
Eisenia fetida	$Cu(NO_3)_2.3H_2O$	10%	Chronic 28 days	Reproduction	$NOEC_{r(cp)}$ = 28.2
Eisenia fetida	Copper nitrate	10%	Chronic 56 days	Mortality, reproduction	LC_{50} = 555 $NOEC_m$ = 202.4 EC_{50} (cocoons) = 53.3 $NOEC_{r(cp)}$ = 12.4
Eisenia fetida	Copper nitrate	10%	Chronic 21 days	Growth, reproduction, mortality	$NOEC_{r(cp)}$ = 32.3 $NOEC_g$ = 728.2 $NOEC_m$ = 296.2
Eisenia fetida	Cu acetate		Chronic 28 days	Mortality	LC_{50} = 82.8 – 3717
Eisenia fetida	$CuCl_2$	-	Chronic 21 days	Growth, mortality	NOEC=300 (mortality and growth)
Eisenia fetida	Copper chloride	-	Chronic 28 days	Reproduction	$EC_{10,r}$ = 54 – 324 (17 values for different soil types)
Eisenia andrei	Unknown	3.7%	Chronic 28 days	Reproduction	$EC_{10,r}$ = 159
Eisenia andrei	Copper chloride	0.5%	Chronic 28 days	Reproduction, mortality	$NOEC_m$ = 192 $NOEC_r$ = 192
Folsomia fimetaria	Copper chloride	4.7%	21 days	Growth, reproduction, mortality	$EC_{10,m}$ (overall) = 828 $EC_{10,m}$ (female) = 519 $EC_{10,m}$ (male) = 771 $EC_{10,g}$ (overall) = 1090 $EC_{10,g}$ (overall) = 997 $EC_{10,g}$ (overall) = 1242 $EC_{10,r}$ = 352 $EC_{10,r}$ > 2911 (high background - historical Cu contaminated site)
Folsomia fimetaria	Copper sulfate	4.5%	21 days	Reproduction	$EC_{10,r}$ = 141
Folsomia fimetaria	Copper sulfate	4.5%	21 days	Reproduction	$EC_{10,r}$ = 667
Isotoma viridis	Copper chloride	3.9%	56 days	Growth	$NOEC_g$ (LUFA 2.2) = 55.2 $NOEC_g$ (OECD) = 403
Isopoda (Crustacea, Arthropoda)					
Porcellio scaber	Copper chloride	-	4 and 8 weeks	Growth	8-week LC_{50} = 2880 4-week $EC_{10,g}$ (body mass gain) = 349
Acari (Arachnica, Arthropoda)					
Platynothrus peltifer	Copper nitrate	3.9	90 days	Growth, Mortality and reproduction	$NOEC_m$ ≥ 1498 $NOEC_g$ = 598 $NOEC_r$ = 168
Platynothrus peltifer	Copper chloride	3.9	70 days	Reproduction	$NOEC_r$ = 68.2
Hypoaspis aculeifer	Copper chloride	3.9	21 days	Reproduction	**EC_{10} = 179**
Hypoaspis aculeifer	Copper chloride	3.0	Not reported	Reproduction	$EC_{10,r}$ = 2* $NOEC_r$ = 320
Nematoda (Nematoda)					
Plectus acuminatus	Copper chloride	-	21 days	Reproduction	$EC_{50,r(cp)}$ ≥ 165.2 $NOEC_{r(cp)}$ = 35.2

* EC_{10} below lowest dose tested and therefore not considered reliable (OECD, 2006[32])

[1] $NOEC_{r(cp)}$=NOEC reproduction based on cocoons production; $NOEC_{r(juv)}$=NOEC reproduction based on juveniles production; $NOEC_m$=NOEC based on growth; $NOEC_m$=NOEC based on mortality; $NOEC_{lb}$=NOEC based on litter breakdown; $EC_{10,lb}$=EC10 based on fragmentation; $EC_{10,av}$=EC10 based on avoidance

Data, data, data…

Effect Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworms – Tier 1

- **Lowest toxicity endpoint: *Eisenia andrei* 28 d-NOEC (reproduction) = 8,4 mg Cu/kg d.w.**

Toxicity-Exposure-Ratio (TER)

RISK !

$$\text{TER (Grapes)} = \frac{Tox}{PEC} = \frac{8{,}4\ \frac{mg\ Cu}{kg\ d.w.}}{240\ \frac{mg\ Cu}{kg\ d.w.}} = 0,035\ (\text{Trigger: } 5)$$

- **BUT: Risk already at background soil copper !?**
- **BUT (as no guidance available): lab-to-field correction factor (4), normalization to reference soil (regression model), geomean approach, HC_5-SSD (species sensitivity distribution) proposed by notifier not accepted**

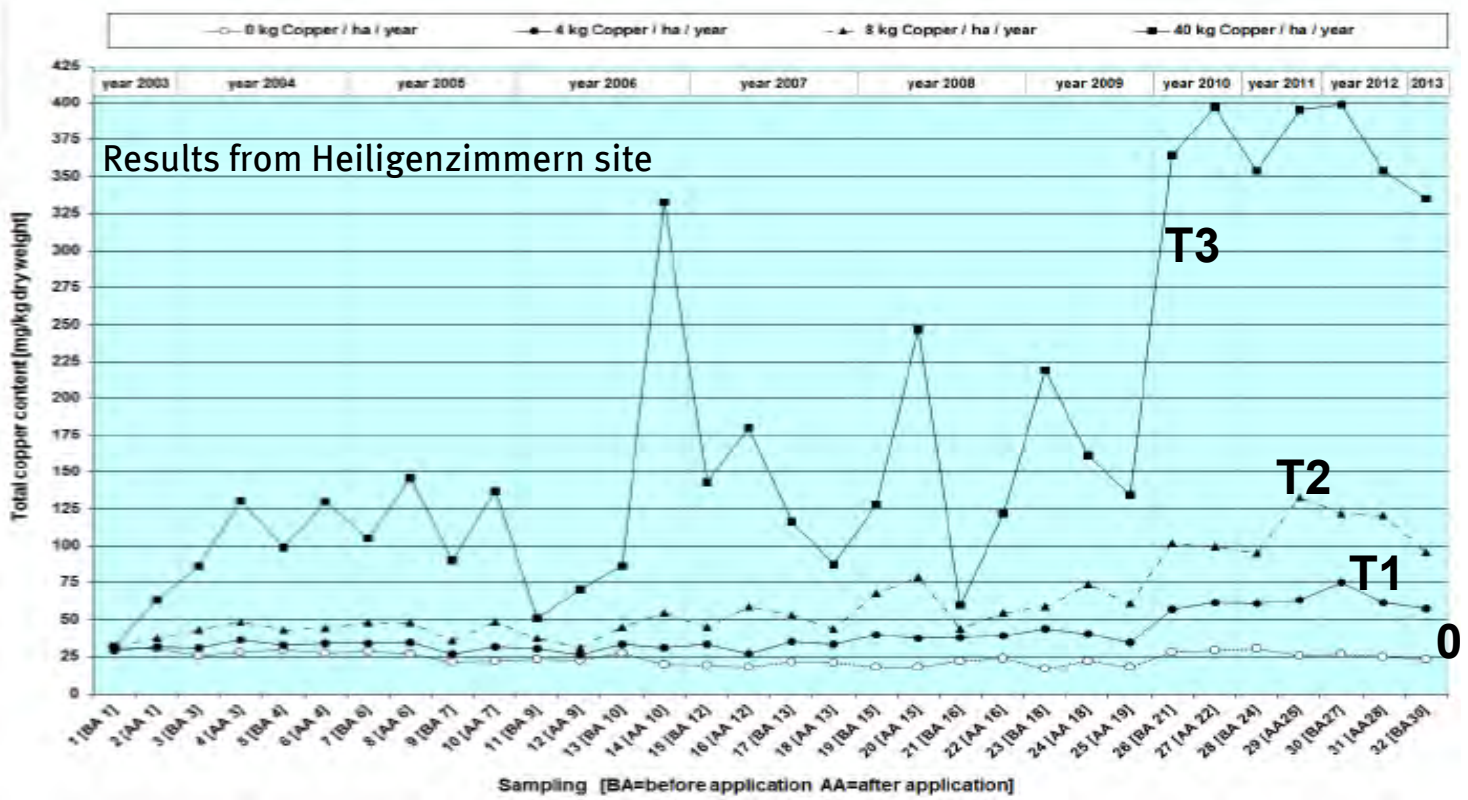
Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworms – Higher Tier (earthworm long-term field study)

- 2 grassland-sites (SE Germany), start 11/2003 (data analysis: 10 years)
- test substance: Copper Hydroxide WP (50%)
- 3 applications per year (yearly treatment rate splitted)
- 3 treatments: 4 kg Cu/ha/y (T1) / 8 kg Cu/ha/y (T2) / 40 kg Cu/ha/y (T3), plus water control (negative) and reference toxicant (benomyl)
- 4 replicates per treatment
- 4 samplings per replicate
- 3 assessments per year
- Cu residue analysis (soil, earthworms)
- earthworm sampling (formalin extraction + hand sorting)
- earthworm endpoints: abundance, species, biomass

Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworm long-term field study: Cu accumulation in soil (0-5 cm)

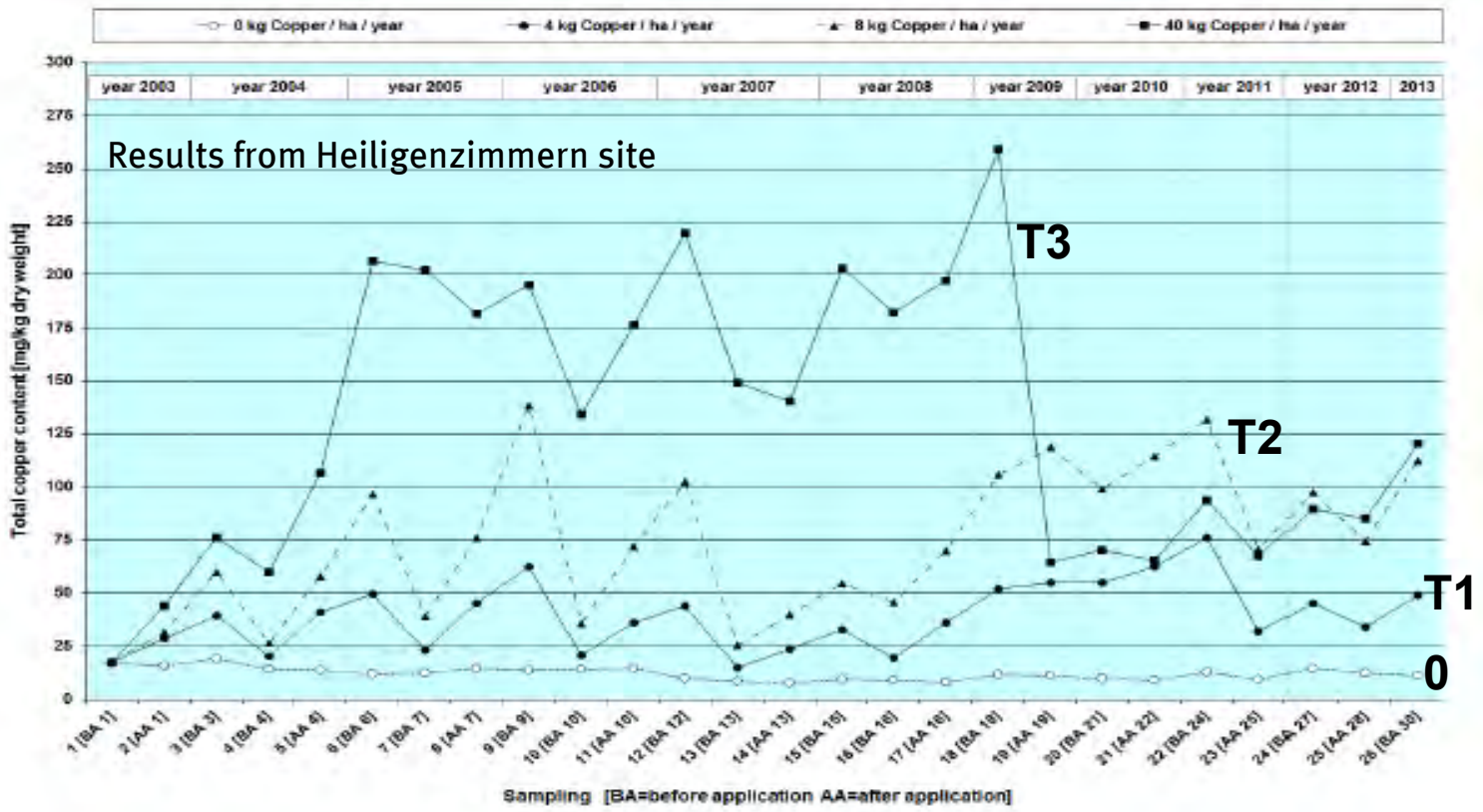


0 = Water (negative control)

T1 = 4 kg Cu/ha/year; T2 = 8 kg Cu/ha/year; T3 = 40 kg Cu/ha/year (stop in 2009)

Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworm long-term field study: Cu accumulation in earthworms

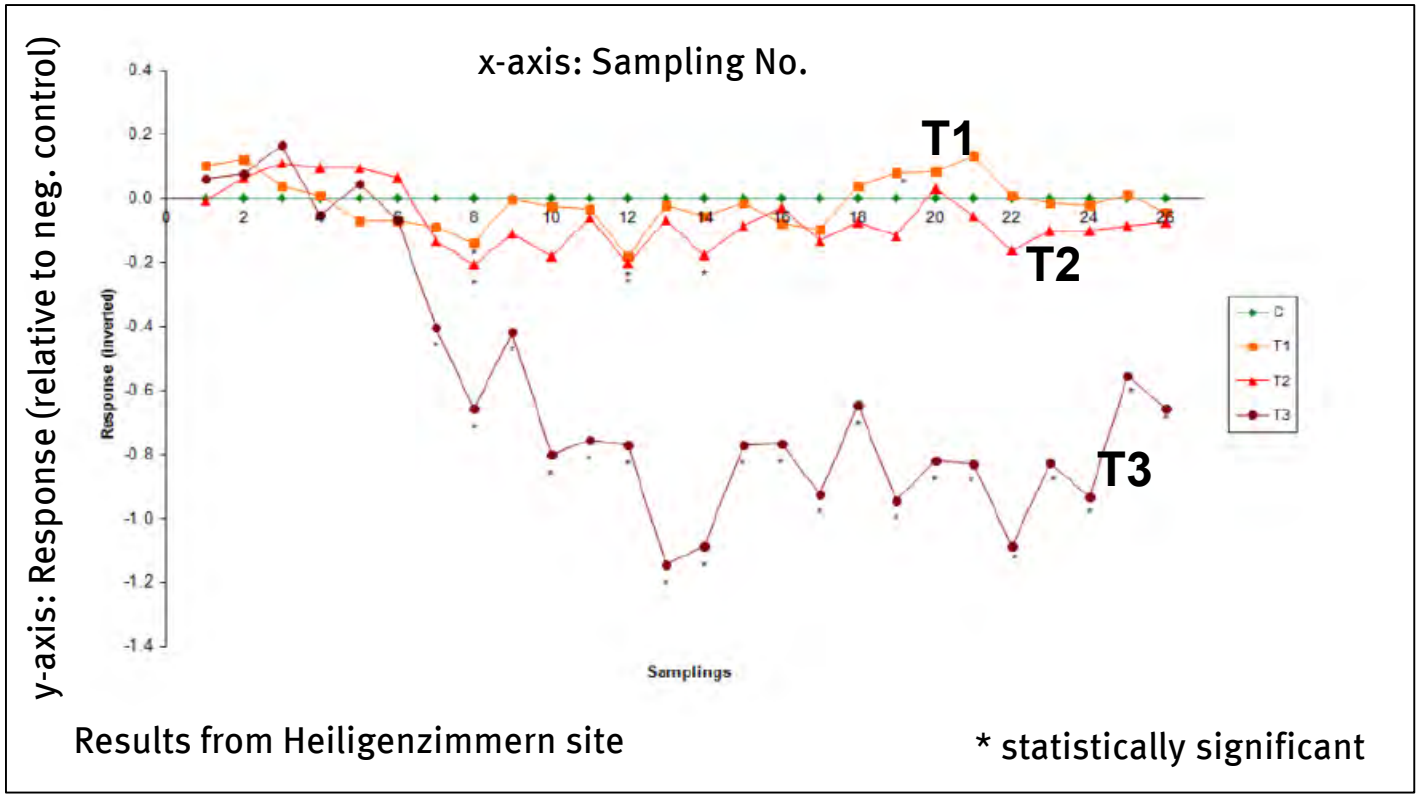


0 = Water (negative control)

T1 = 4 kg Cu/ha/year; T2 = 8 kg Cu/ha/year; T3 = 40 kg Cu/ha/year (stop in 2009)

Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworm long-term field study: Community analysis (PRC)



T1 = 4 kg Cu/ha/year; T2 = 8 kg Cu/ha/year; T3 = 40 kg Cu/ha/year

Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworm long-term field study: Abundance (reduction compared to control)

G03N047N (Heiligenzimmern)	Sampling																								
treatment T1 (4 kg copper/ha/year)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Ap. caliginosa								(*)				(*)														
A. chlorotica[n]																										
A. rosea[n]																										
L. terrestris																										
L. castaneus																										
O. lacteum[n]																										
tanylobous juveniles[n]																										
epilobous juveniles		(*)																								
epigeic earthworms																										
endogeic earthworms								(*)				(*)					(*)									
anecic earthworms																										
total juvenile earthworms[n]																										
total adult earthworms								(*)				(*)														
total earthworms[n]																										

Results from Heiligenzimmern site

T1 = 4 kg Cu/ha/year

T2 = 8 kg Cu/ha/year

T3 = 40 kg Cu/ha/year

G03N047N (Heiligenzimmern)	Sampling																								
treatment T2 (8 kg copper/ha/year)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Ap. caliginosa							(*)	(*)		(*)		(*)										(*)	(*)	(*)	(*)	(*)
A. chlorotica[n]																										
A. rosea[n]																										
L. terrestris							(*)																			
L. castaneus				(*)	(*)			(*)																		
O. lacteum[n]																										
tanylobous juveniles[n]																										
epilobous juveniles														(*)		(*)	(*)									
epigeic earthworms				(*)	(*)			(*)																		
endogeic earthworms								(*)		(*)				(*)			(*)					(*)				
anecic earthworms							(*)																			
total juvenile earthworms[n]																										
total adult earthworms								(*)		(*)		(*)					(*)									
total earthworms[n]																										

G03N047N (Heiligenzimmern)	Sampling																								
treatment T3 (40 kg copper/ha/year)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Ap. caliginosa							(*) *	(*) *	(*)	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *
A. chlorotica[n]																										
A. rosea[n]																										
L. terrestris							(*)	(*)	(*)	(*)	(*)	(*) *	(*)	(*) *	(*)		(*)	(*)	(*)			(*)				
L. castaneus								(*)	(*)	(*)	(*)	(*)				(*)			(*)							
O. lacteum[n]																										
tanylobous juveniles[n]																										
epilobous juveniles					(*)				(*)	(*)	(*)	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *
epigeic earthworms								(*)	(*)	(*)	(*)	(*)				(*)			(*)							
endogeic earthworms							(*) *	(*) *	(*)	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *
anecic earthworms							(*)	(*)	(*) *	(*)	(*)	(*) *	(*)	(*) *	(*)		(*)	(*)	(*)							
total juvenile earthworms[n]																										
total adult earthworms							(*) *	(*) *	(*)	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *		(*) *	(*) *	(*) *	(*) *
total earthworms[n]																										

* significant for Tukey Test ($p \leq 0.05$)
(*) significant for LSD Test ($p \leq 0.05$)
[n] not evaluated because of lack of normality

Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworm long-term field study: Effects on Abundance (Ind./m²)

G03N047N (Heiligenzimmern)	Sampling																									
treatment T1 (4 kg copper/ha/year)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Ap. caliginosa								(*)				(*)														
A. chlorotica[n]																										
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endogeic earthworms								(*)				(*)					(*)									
anecic earthworms																										
total juvenile earthworms[n]																										
total adult earthworms								(*)				(*)														
total earthworms[n]																										

Results from Heiligenzimmern site

T1 = 4 kg Cu/ha/year

T2 = 8 kg Cu/ha/year

T3 = 40 kg Cu/ha/year

G03N047N (Heiligenzimmern)	Sampling																									
treatment T2 (8 kg copper/ha/year)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Ap. caliginosa							(*)	(*)		(*)		(*)										(*)	(*)	(*)	(*)	(*)
A. chlorotica[n]																										
A. rosea[n]																										
L. terrestris							(*)																			
L. castaneus				(*)	(*)			(*)																		
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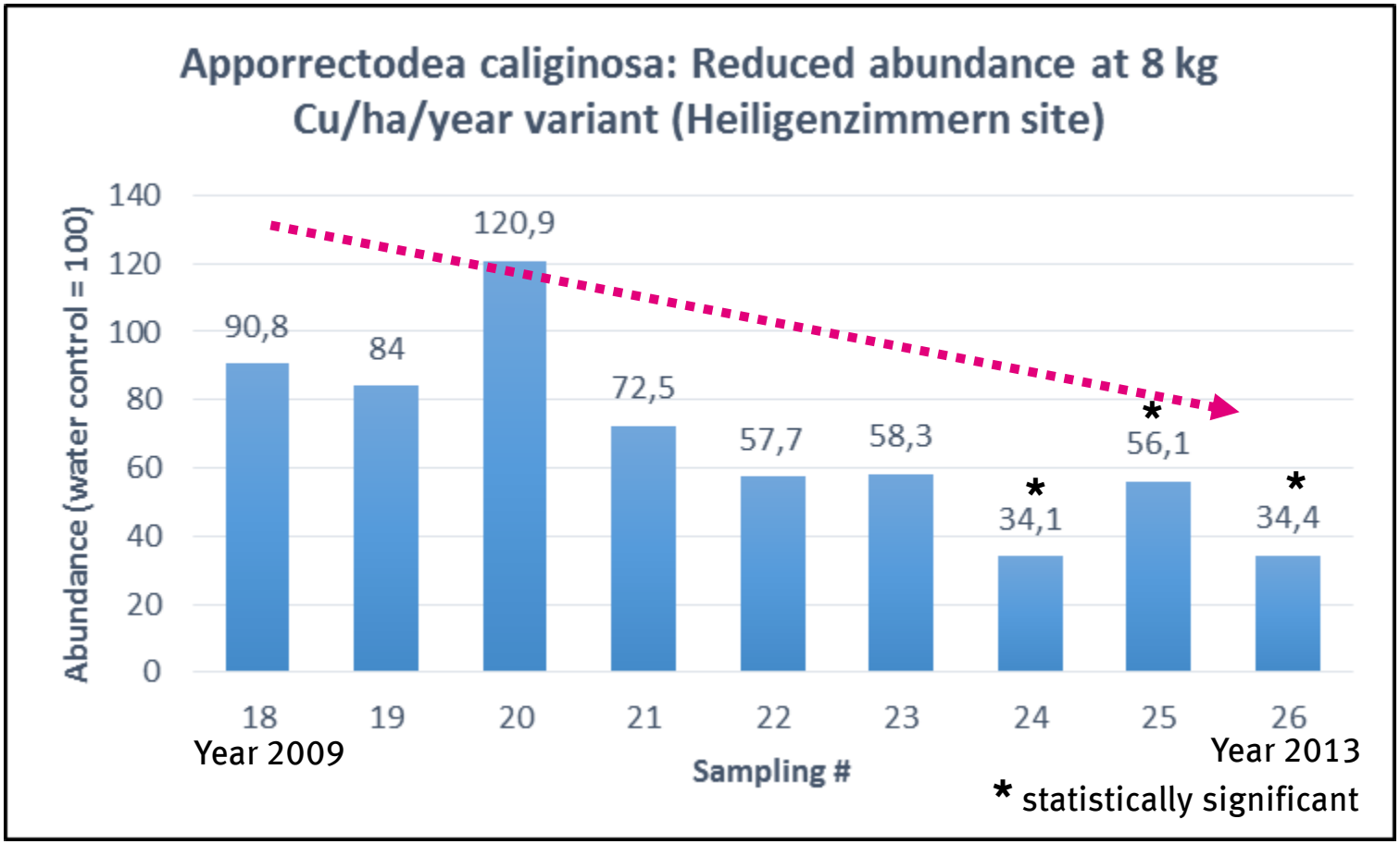
epilobous juveniles														(*)		(*)	(*)									
epigeic earthworms				(*)	(*)			(*)																		
endogeic earthworms								(*)		(*)				(*)			(*)					(*)				
anecic earthworms							(*)																			
total juvenile earthworms[n]																										
total adult earthworms								(*)		(*)		(*)					(*)									
total earthworms[n]																										

G03N047N (Heiligenzimmern)	Sampling																									
treatment T3 (40 kg copper/ha/year)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
Ap. caliginosa							(*) *	(*) *	(*)	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *
A. chlorotica[n]																										
A. rosea[n]																										
L. terrestris							(*)	(*)	(*)	(*)	(*) *	(*) *	(*)	(*) *	(*)		(*)	(*)	(*)			(*)				
L. castaneus								(*)	(*)	(*)	(*)	(*)				(*)			(*)							
O. lacteum[n]																										
tanylobous juveniles[n]																										
epilobous juveniles					(*)				(*)	(*)	(*)	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *
epigeic earthworms								(*)	(*)	(*)	(*)	(*)				(*)			(*)							
endogeic earthworms							(*) *	(*) *	(*)	(*)	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *
anecic earthworms							(*)	(*)	(*) *	(*)	(*)	(*) *	(*)	(*) *	(*)		(*)	(*)	(*)					(*)		
total juvenile earthworms[n]																										
total adult earthworms							(*) *	(*) *	(*)	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *	(*) *		(*) *	(*) *	(*) *	(*) *
total earthworms[n]																										

* significant for Tukey Test ($p \leq 0.05$)
(*) significant for LSD Test ($p \leq 0.05$)
[n] not evaluated because of lack of normality

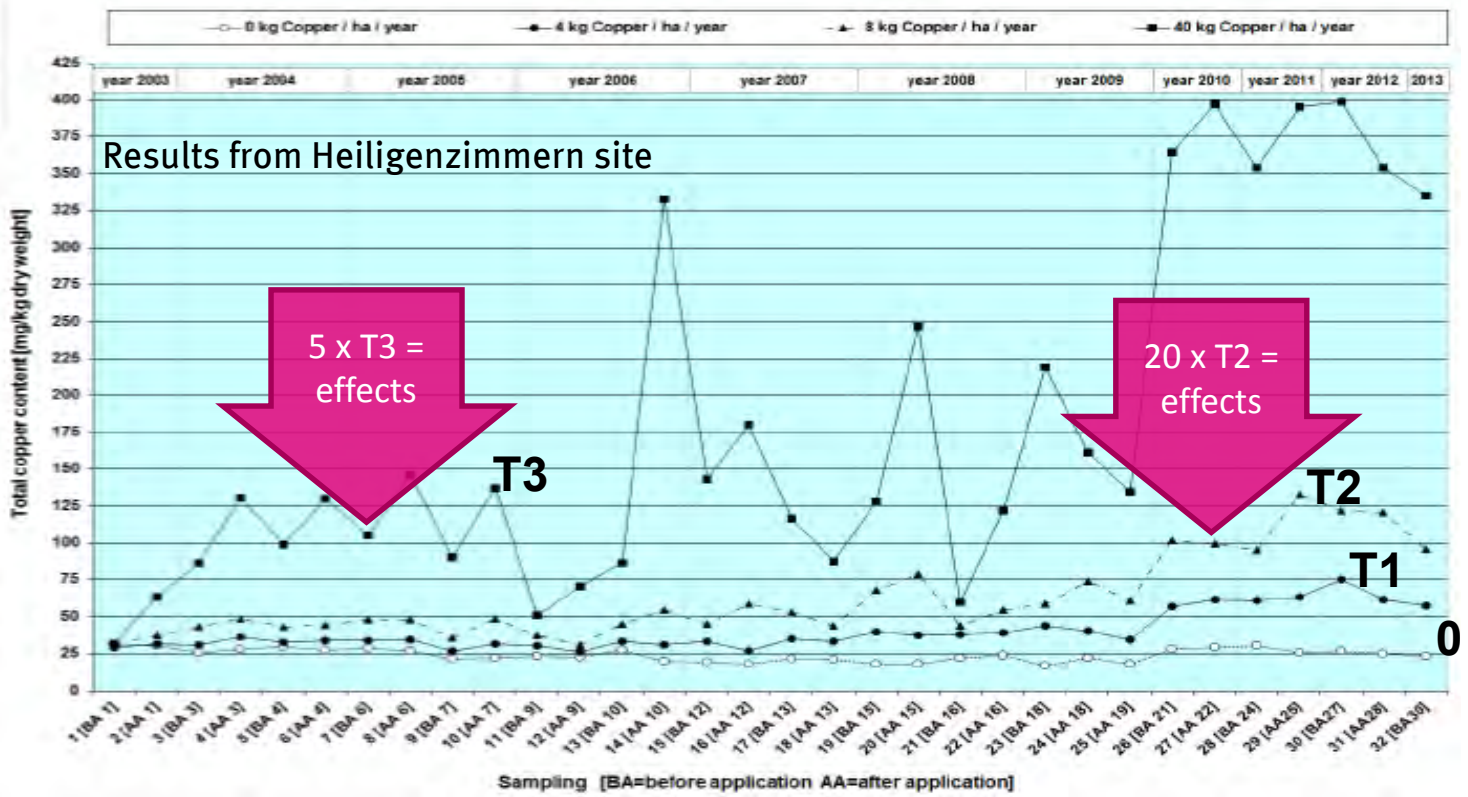
Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworm long-term field study: Effects on Abundance (Ind./m²)



Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworm long-term field study: The repeated dose makes the poison



0 = Water (negative control)

T1 = 4 kg Cu/ha/year; T2 = 8 kg Cu/ha/year; T3 = 40 kg Cu/ha/year (<u>stop in 2009</u>)

Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

Earthworm Risk Assessment – Conclusion RMS + EFSA (1):

"(…) taking into account all the effects observed (…) in the field study at 8 and 40 kg/ha/y, and the slight effects observed at 4 kg/ha/y, a no observed adverse effect concentration (NOAEC) of 4 kg Cu/ha/y should be set for earthworms."

Effect/ Risk Assessment Copper Compounds (RAR 2017 + EFSA 2018)

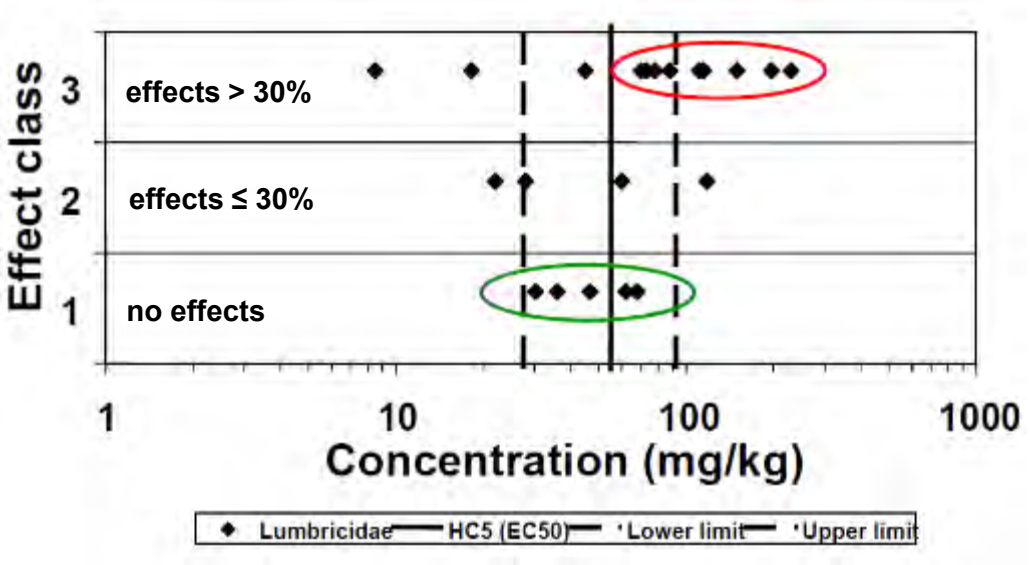
Earthworm Risk Assessment – Conclusion RMS + EFSA (2):

Available field monitoring data:

"Those studies give indication of an effect of copper content in soil on earthworm species abundance and diversity especially for endogeic earthworm's species, such as *Aporrectodea caliginosa* for soils with total copper content > 100 mg Cu/kg d.w."

Effect/ Risk Assessment Copper Compounds

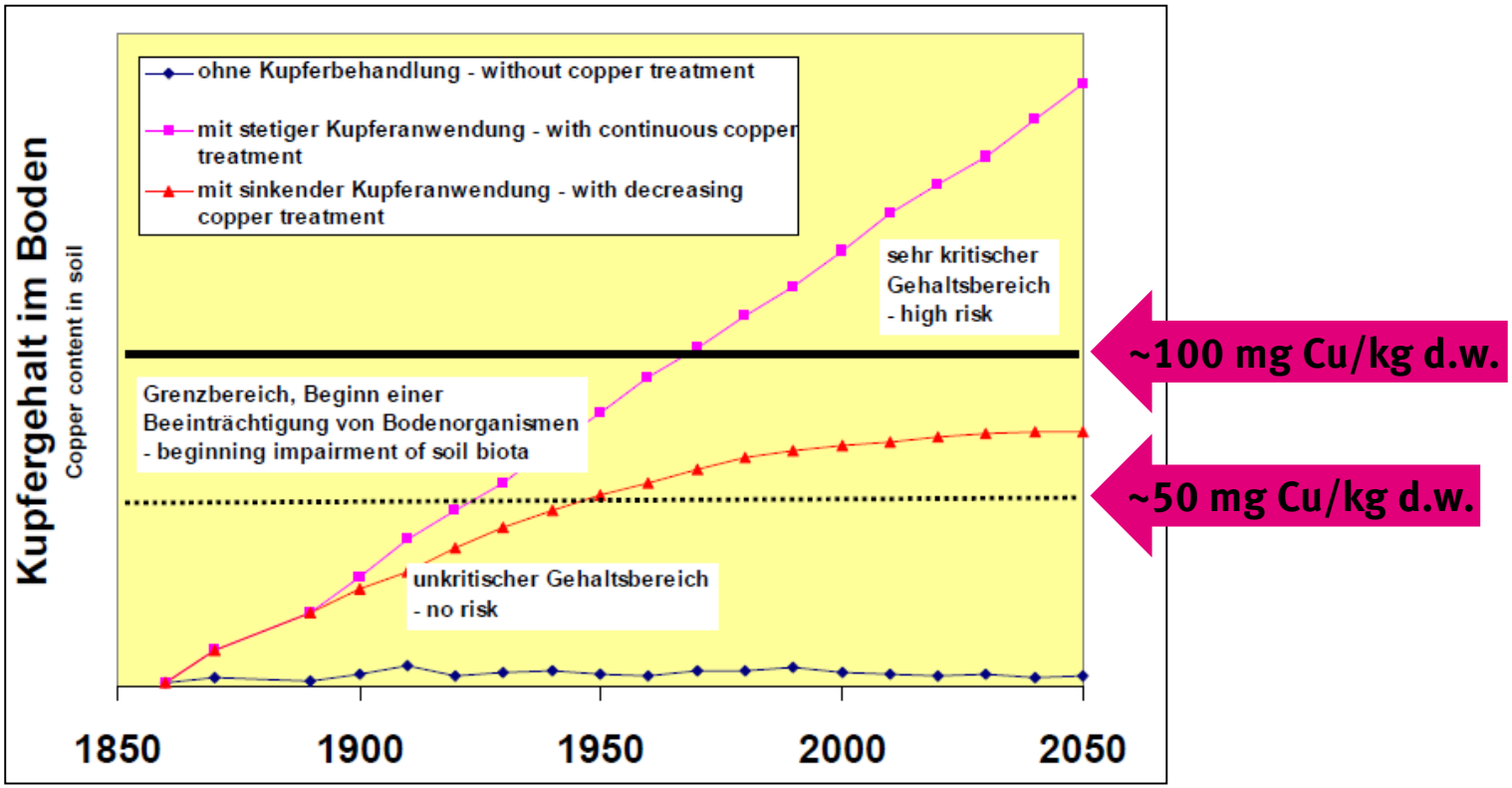
Literature review (2009) commissioned by UBA



from: Jänsch et al. (2009)

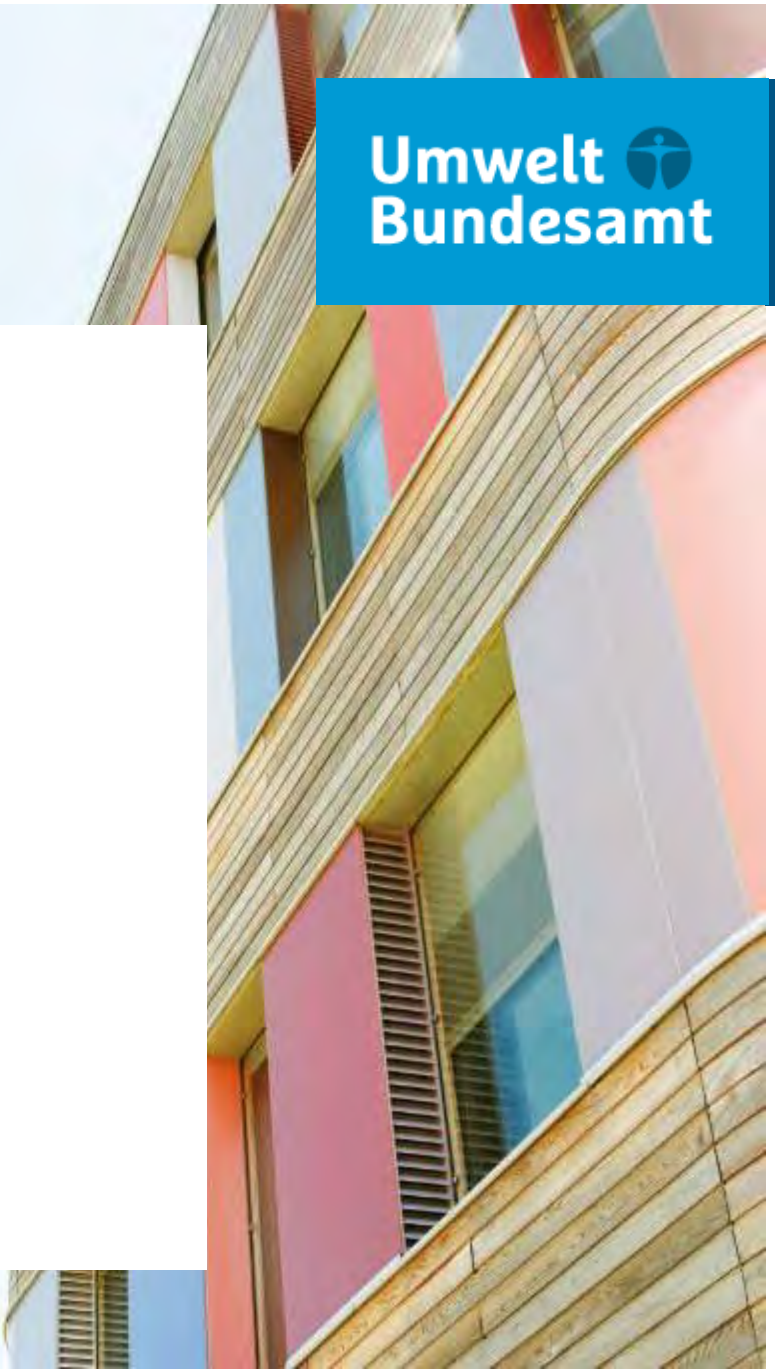
- **field effects on earthworm populations** (and other soil macro-organism)
- **reduced abundance and species diversity at ≥ 50 mg/kg**

Outlook “The repeated dose…”



copied from: Journal für Kulturpflanzen, Band 61 (4) 2009

- **Where do we go in the upcoming (seven) years?**



Thank you.

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Representative PPPs and intended uses

FUNGURAN OH 50 WP (Copper hydroxide), NORDOX 75 WG (copper oxide), CURENOX 50 WG (copper oxychloride), CUPROXAT SC (tribasic copper sulfate) POLTIGLIA CAFFARO 20 DF NEW (Bordeaux mixture)

Crop/ crop group	Application method	Spray volume [L/ha]	Maximum individual application rate [kg a.s./ha]	Number of applications	Application timing (growth stage)
Vineyards	Airblast sprayer	400-1000	1.25	8 (7-d interval)	BBCH 12-89
Vineyards	Airblast sprayer	400-1000	1.25	3 (21-d interval)	BBCH 91-11
Tomato	Foliar spraying	200-1000	0.85	8 (7-d interval)	BBCH 10-89
Cucurbits	Foliar spraying	200-1500	0.85	8 (7-d interval)	BBCH 10-89

Maximum total rate per year (kg Cu/ha/year)

- **Grapes: 6.0 (8.0)** = flexible dosing regime: max. 30 kg Cu/ha/year in any rolling 5 year period and 8 kg Cu/ha/year in any single year
- **Tomato/Cucurbits: 6.0**