PESTICIDES TRANSFER FROM TEA LEAVES TO TEA BREW:

IDENTIFICATION OF CRITICAL INFUSION PARAMETERS AND DATABASE CREATION



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The problematic

Samples of tea & herbal tea:

- More than 90 different pesticide residues have been detected between 2017 and 2019

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Pesticides the most detected on the 54 studied:

Pyrethrinoid	Neonicotinoid	others
Cyhalothrin (-L)	Thiamethoxam	Anthraquinone
Bifenthrin	Acetamiprid	Carbendazim (∑)
Cypermethrin (∑)	Thiachloprid	Chlorfenapyr
	Imidacloprid	Chlorpyrifos
		Propargite
		2,4-D
		Tolfenpyrad
		Dinetofuran

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In some cases, pesticides exceeded MRLs

The problematic

- MRL exceedance is not necessarily synonym of risk for consumer health
- Risk analysis must take into account that tea leaves/herbal tea is first infused before consumption of the brew.

⇨ Necessity to use transfer factor (infusion factor)

$$\text{Transfer factor (\%)} = \frac{Quantity\ of\ pesticides\ (tea\ brew)}{Quantity\ of\ pesticides (tea\ leaves)} \text{ X } 100\%$$

The problematic

- Transfer factors already available in the scientific literature

But!

- Transfer factors not available for several pesticides frequently detected in tea/herbal tea on the Belgian market => difficult to perform a risk analysis

- Transfer factors have not always been acquired with infusions practices representative of the Belgian population's behaviour

Objectives

- Compilation of relevant transfer factors
- Experimental determination of unknown transfer factors
- Creation of predictive model to determine transfer factors still unknown

=> Risk analysis more refine and representative of the Belgian consumers in case of MRL exceedance.

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EXPERIMENTAL DETERMINATION OF TRANSFER FACTORS

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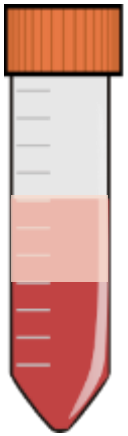
Experimental determination of transfer factors



2 g of tea

Quechers extraction



Determination of pesticide content



1.5 g of tea

Infusion



20 ml taken for analysis via QuEChERS extraction

Determination of pesticide content

Determination of pesticide's transfer factor

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Experimental determination of transfer factors

Fortification of organic tea & herbal tea with a pesticides mix at known concentration

Determination of pesticide's transfer factor



Wait until dried



Infusion



Tea leaves spiked with pesticides

1.5 g in tea bag

20 ml taken for analysis via QuEChERS extraction

Experimental determination of transfer factors

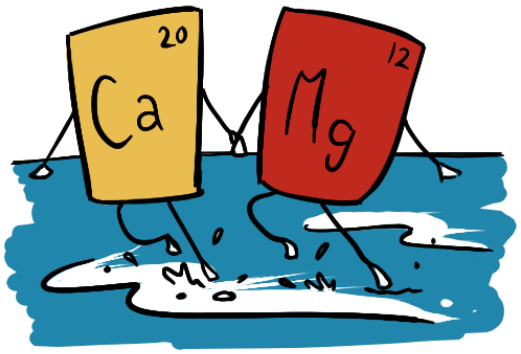
Influence of different parameters:



Green tea

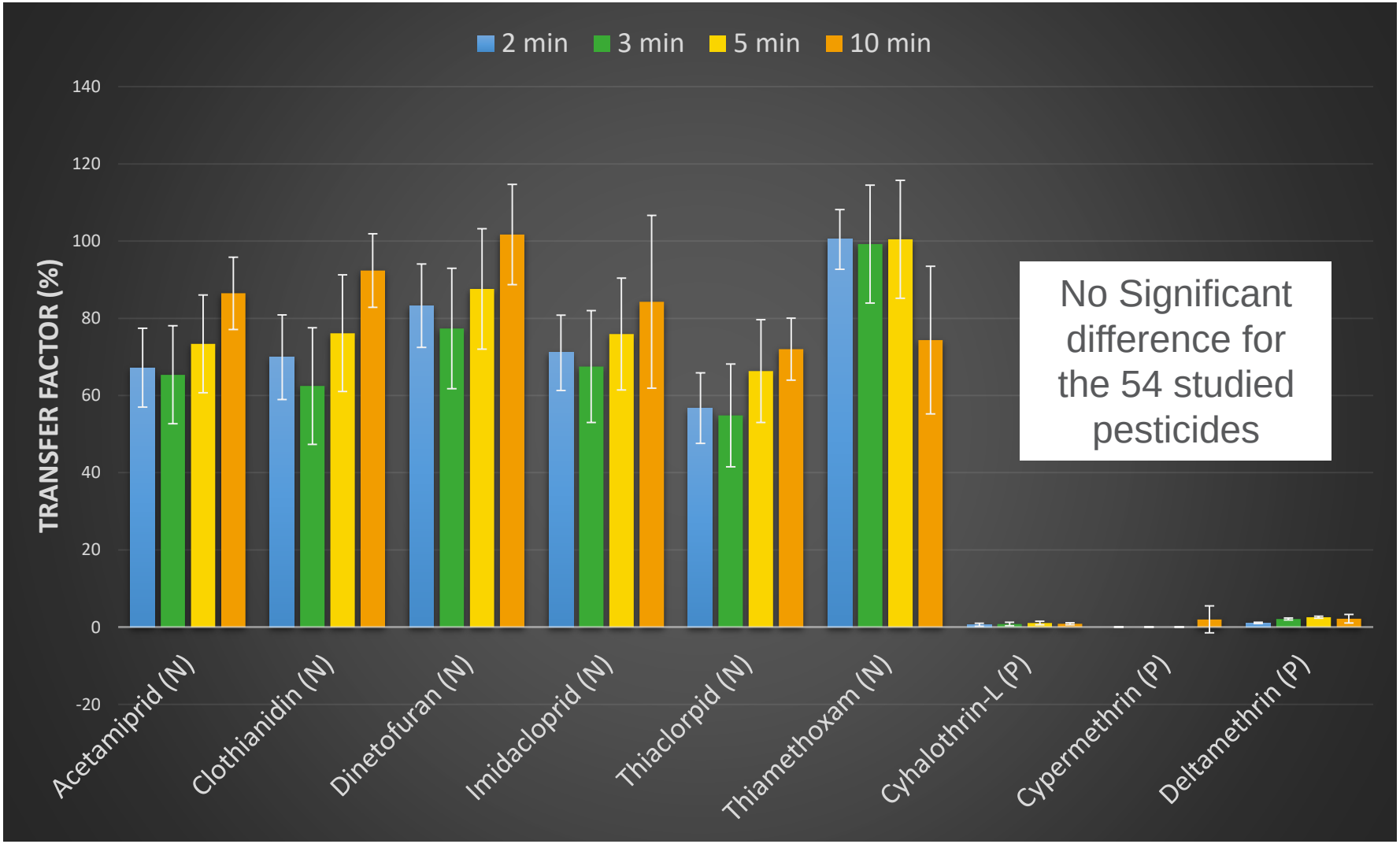
Black tea



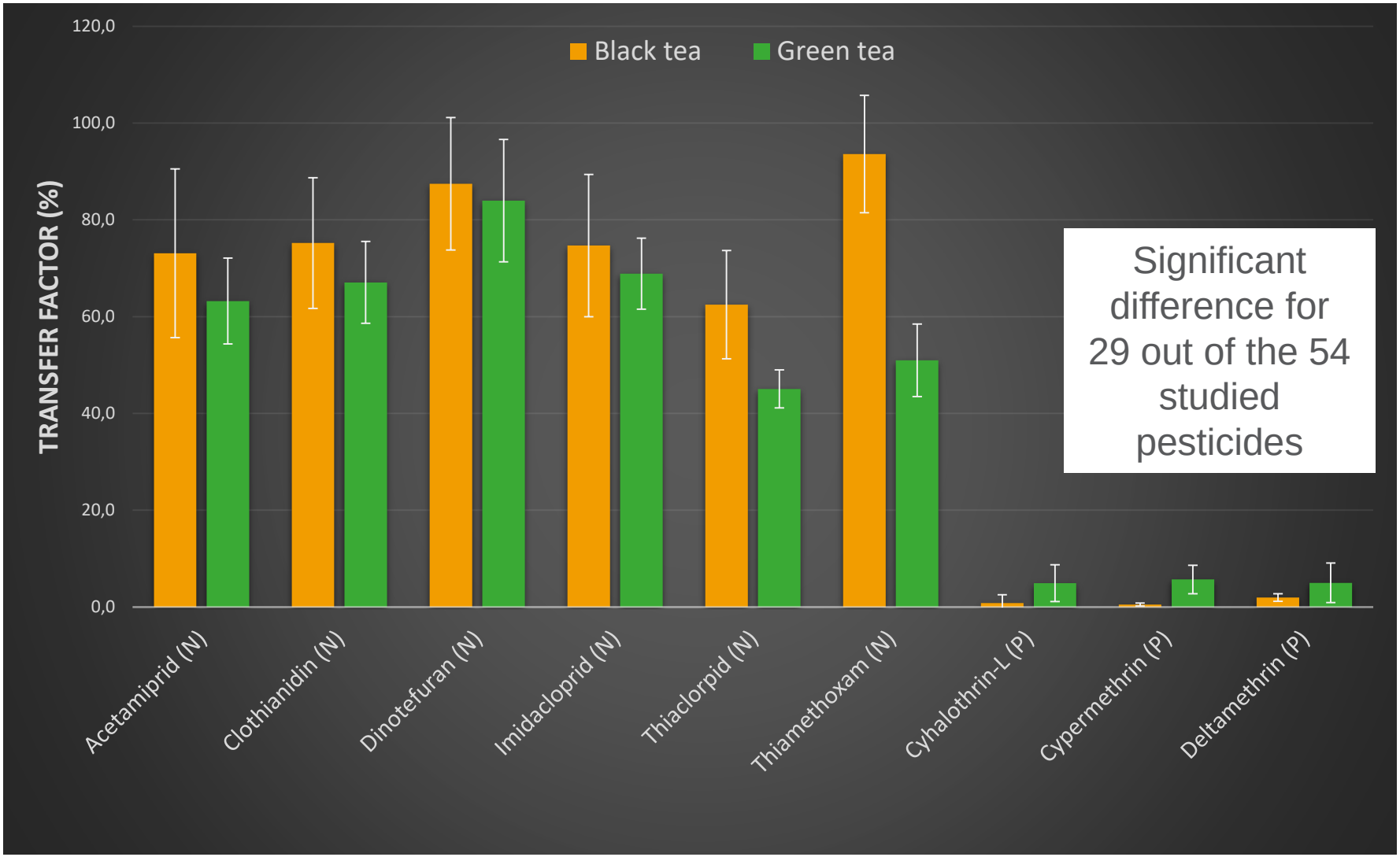




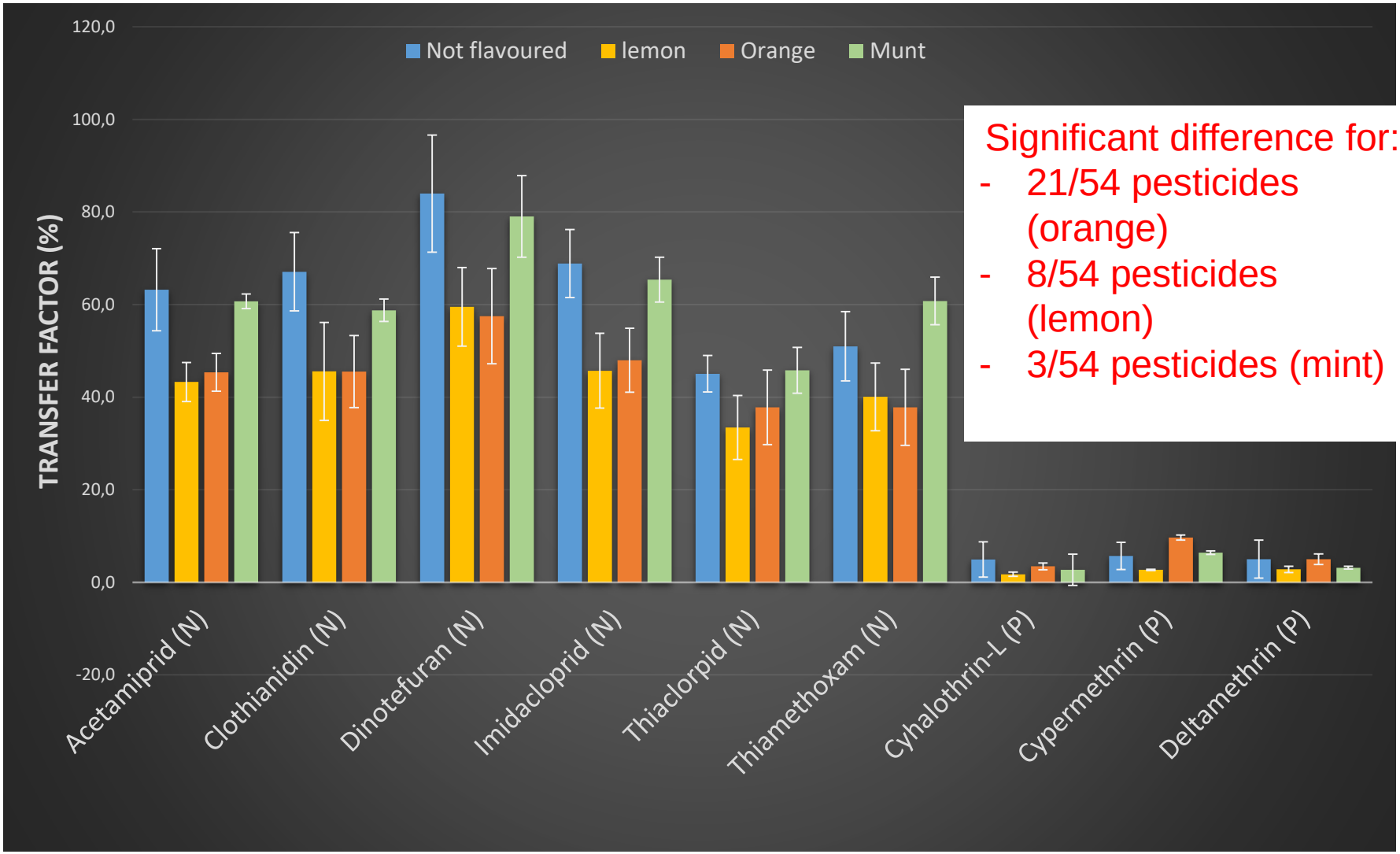
Influence of infusion time



Comparison black tea- green tea



Comparison Green tea & flavoured green tea



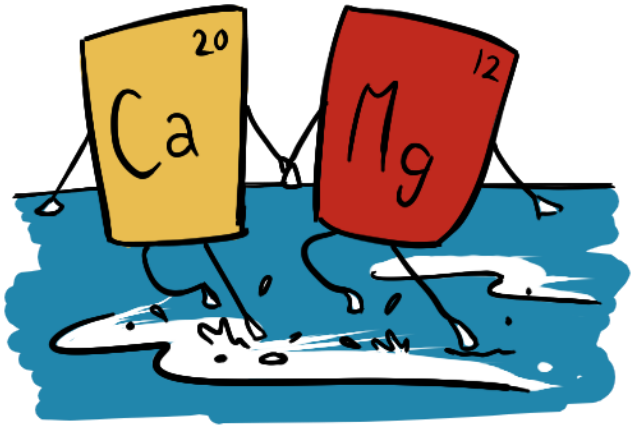
Significant difference for:

- 21/54 pesticides (orange)
- 8/54 pesticides (lemon)
- 3/54 pesticides (mint)

Influence of water hardness

Water hardness:

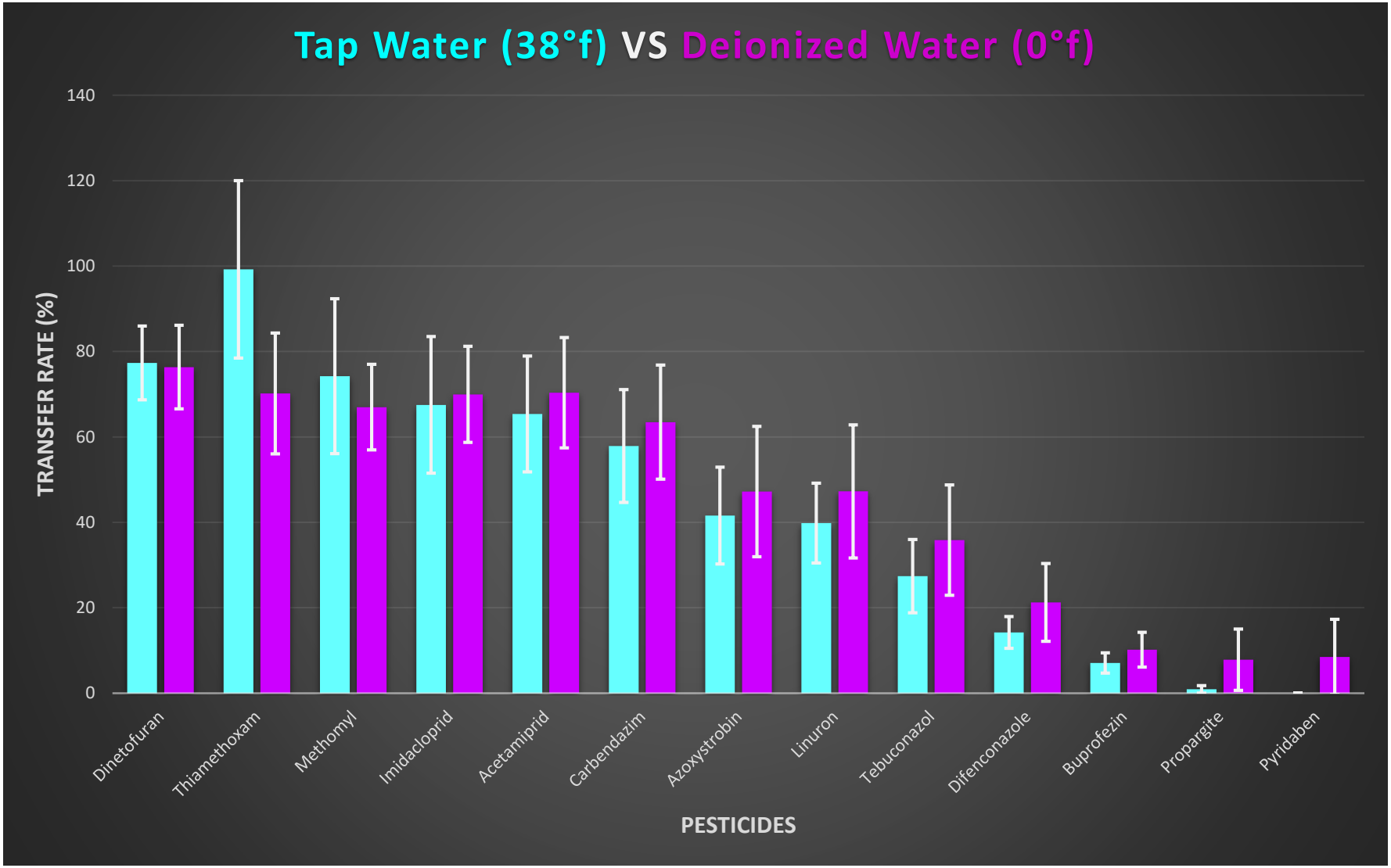




Two extreme cases:

- *Tap Water (38°f)*
- *Deionised Water (0°f)*

Comparison Tap Water VS deionized Water



COMPARISON OF TRANSFER FACTOR WHEN TEA ARE SPRAYED IN FIELD, SPIKED IN LABORATORY OR DETECTED IN SAMPLE MARKET

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Comparison of transfer factor when tea are sprayed in field, spiked in laboratory or detected in sample market

Acetamiprid (Log P = 0.8)			
Source	Infusion time	Sample type	Transfer factor
M. Gupta et al 2009	2 min	Tea sprayed in field	47%
	5 min	Tea sprayed in field	51%
	10 min	Tea sprayed in field	53%
X. Wang et al. 2019	5 min	Tea sprayed in field	59%
H. Chen et al. 2015	5 min	Market sample	54%
	5 min	Market sample	51%
Sciensano	multiple	Spiked tea	57% ± 10%
	2 min	Market sample	42% ± 17%

Comparison of transfer factor when tea are sprayed in field, spiked in laboratory or detected in sample market

Bifenthrin (Log P = 7.3)			
Source	Infusion time	Sample type	Transfer factor
S. Yadav et al. 2017	2 min	Spiked tea	1%
	5 min	Spiked tea	2%
	10 min	Spiked tea	2%
H. Chen et al. 2015	5 min	Market sample	0%
	5 min	Market sample	1%
S.K. Cho et al. 2014	5 min	Tea sprayed in field	0%
	5 min	Tea sprayed in field	0%
	5 min	Tea sprayed in field	0%
Sciensano	Multiple 2 min	Spiked tea Market sample	2% ± 2% <5%

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THEORETICAL DETERMINATION OF TRANSFER FACTORS

Claire Demoury

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Theoretical determination of transfer factors

Elaboration of predictive model

Link transfer factors to different physico-chemical parameters

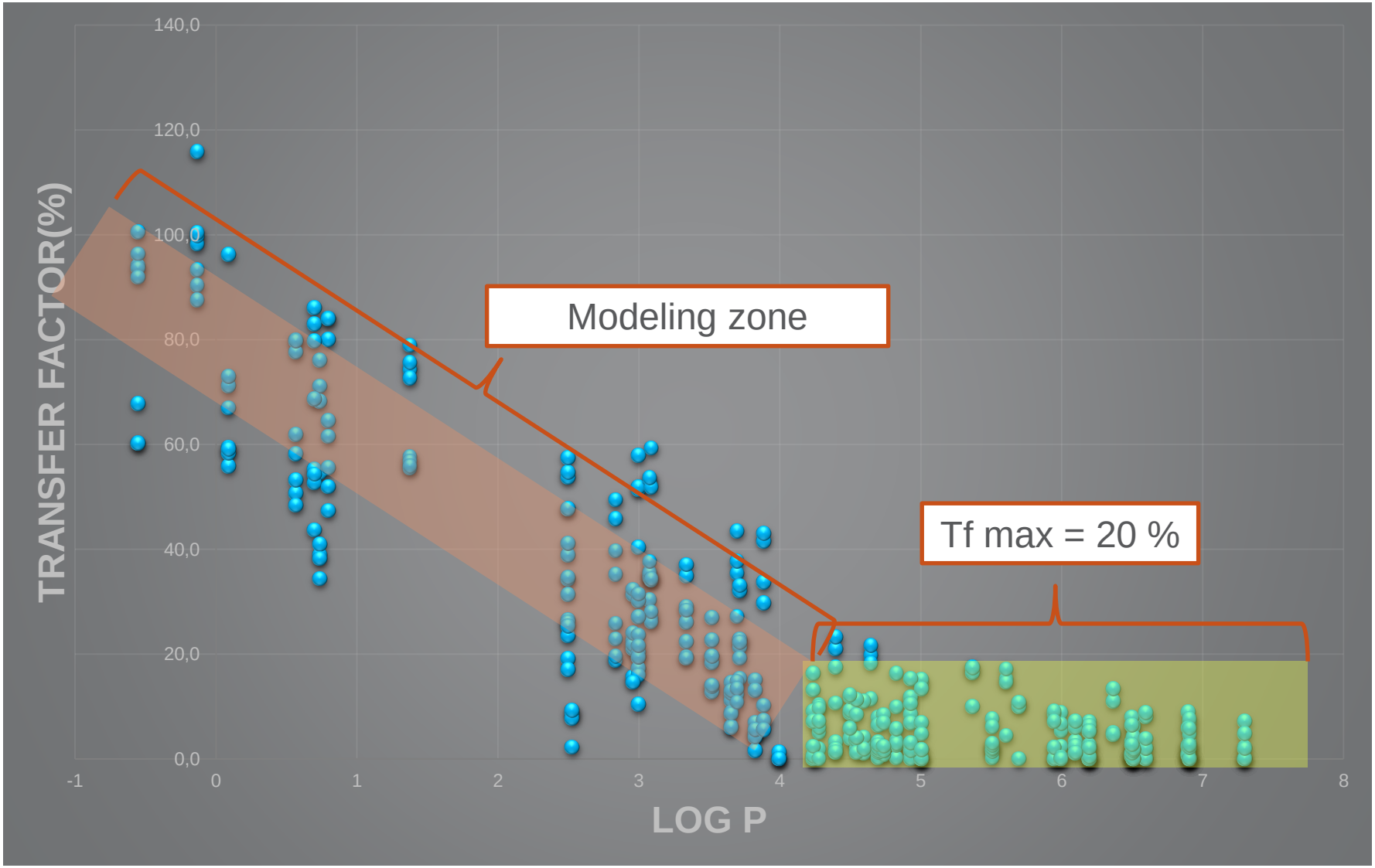
- Log P = pesticides affinity for water
- Solubility
- Vapour pressure

Multiple linear regression:

- One for each tea type (black, green, flavoured)

$$\text{Log(TR)} \sim \beta_0 + \beta_1 \log(P) + \beta_2 \log(\text{vapour pressure}) + \beta_3 \log(\text{solubility})$$

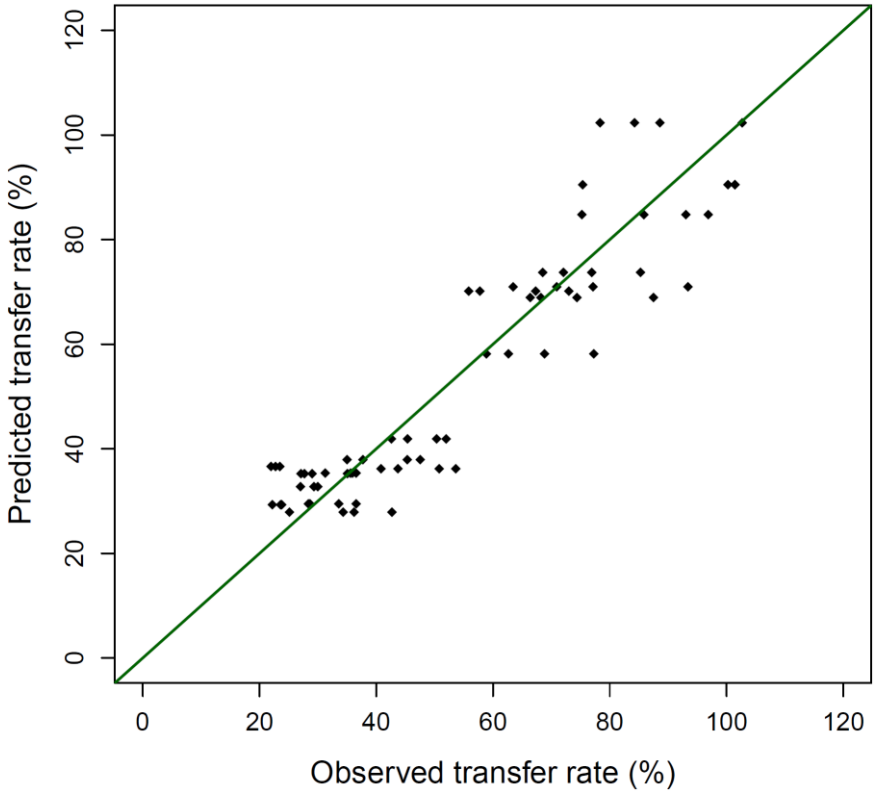
Theoretical determination of transfer factors



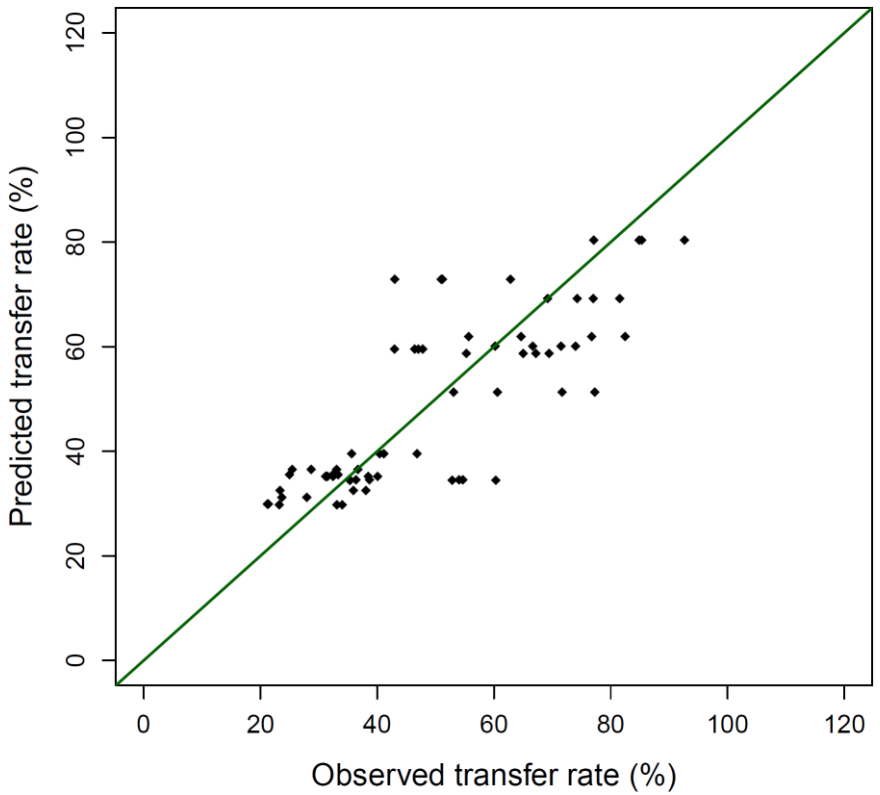
Theoretical determination of transfer factors

Predictive model for transfer rate > 20 %

Black Tea



Green Tea



Theoretical determination of transfer factors

Predictive model

$$\log(TR) \sim \beta_0 + \beta_1 \log(P) + \beta_2 \log(\text{vapour pressure}) + \beta_3 \log(\text{solubility})$$

Coefficients		Green tea	Black tea	Flavored tea
		TR>20%	TR>20%	TR>20%
β_0	Intercept	4,26	4,47	3,37
β_1	log(P)	-0,23	-0,29	NS
β_2	log(vapor pressure)	NS	NS	NS
β_3	log(solubility)	NS	NS	0,07

NS: not significant variable

Theoretical determination of transfer factors

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β_3	log(solubility)	NS	NS	0,07

NS: not significant variable

Theoretical determination of transfer factors

Model validation:

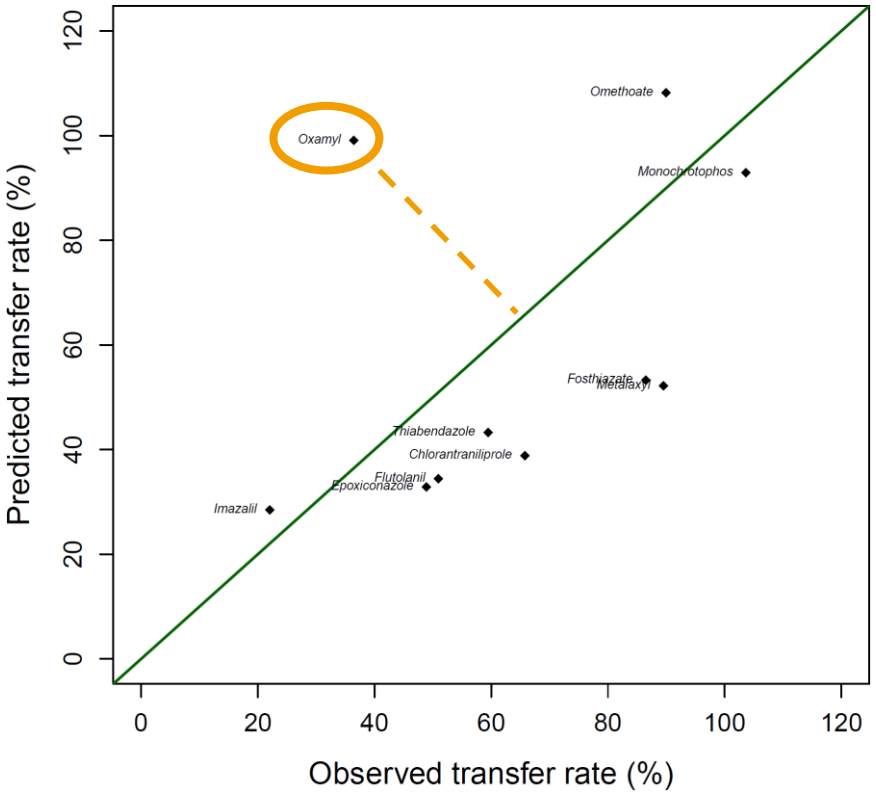
Validation on independent dataset

Pesticides	log P	S (mg/l)	Vapour Pressure (mPa)
Omethoate	-0,74	500000	3,285E+00
Oxamyl	-0,44	280000	3,046E+01
Monochrotophos	-0,22	1000000	2,900E-01
Thiabendazole	2,39	30	5,298E-03
Fosthiazate	1,68	9850	5,563E-01
Metalaxyl	1,75	8400	7,444E-01
Chlorantraniliprole	2,76	0,95	1,589E-09
Flutolanil	3,17	8,01	1,762E+00
Epoxiconazole	3,33	6,63	3,500E-04
imazalil	3,82	210	1,580E-01
pencycuron	4,7	0,3	4,967E-07
spirodiclofen	5,8	5,1	7,000E-04

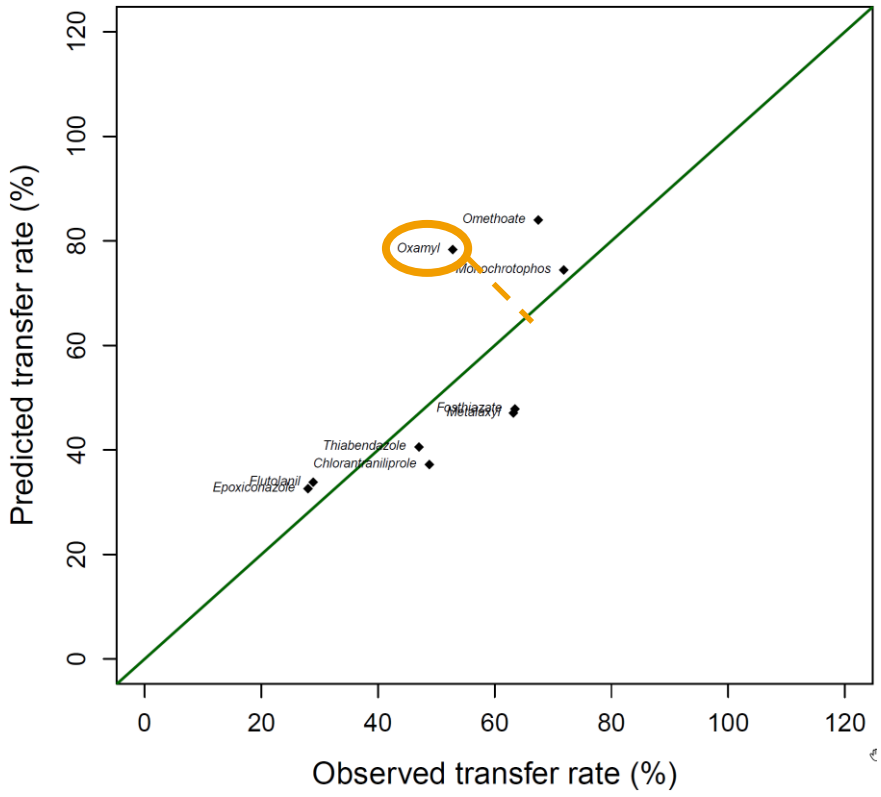
Theoretical determination of transfer factors

Model validation:

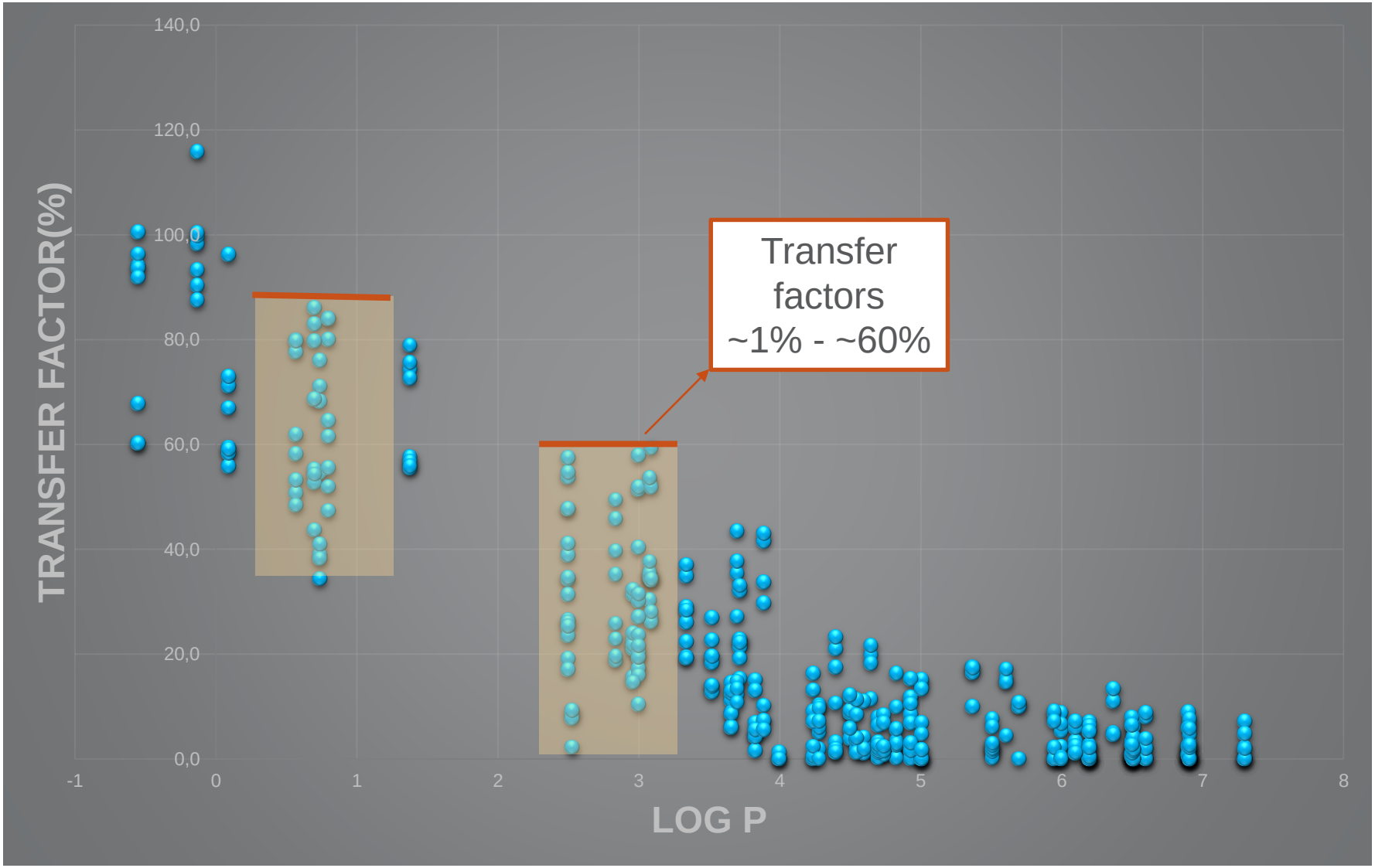
Black Tea



Green Tea



Theoretical determination of transfer factors



DATABASE - Creation

DATA Collection

- Pesticide name
- Source + link: Scientific litterature / database / sciensano experimental
- Sample type: sprayed tea, market sample, fortified sample
- Tea type: black, green, oolong, mix, herbal tea
- Infusion protocol: amount of tea/water, temperature, infusion time
- Average transfer factor and RSD when available

1206 TF collected for 108 pesticides residues and for different type of tea

DATABASE - Summary

Active substance	Black Tea				Green Tea				Herbal Tea			
	min	max	Mean	N	min	max	Mean	N	min	max	Mean	N
2,4-D	55%	58%	56%	2	41%	61%	51%	2	26%	49%	36%	3
3-Hydroxycarbofuran	-	-	-	0	-	-	-	0	-	-	-	0
4-Bromo-2-Chloro-phenol	-	-	-	0	-	-	-	0	-	-	-	0
Acephate	-	-	-	0	77%	77%	77%	1	-	-	-	0
Acetamiprid	47%	86%	64%	10	42%	78%	56%	13	74%	105%	86%	3
Alachlor	-	-	-	0	-	-	-	0	-	-	-	0
Anthraquinone	13%	20%	18%	4	14%	35%	22%	7	40%	57%	49%	3
Atrazine	-	-	-	0	-	-	-	0	-	-	-	0
Azoxystrobin	30%	43%	37%	5	30%	98%	47%	11	36%	49%	43%	3
Bifenazate	-	-	-	0	19%	19%	19%	1	-	-	-	0
Bifenthrin	0%	5%	1%	6	0%	15%	3%	13	4%	6%	5%	3
Boscalid	16%	22%	20%	4	15%	32%	25%	7	14%	20%	18%	3
Buprofezin	3%	6%	4%	5	2%	9%	4%	10	4%	9%	6%	3
Butachlor	-	-	-	0	-	-	-	0	-	-	-	0
Carbaryl	-	-	-	0	-	-	-	0	-	-	-	0
Carbendazim	50%	76%	63%	5	38%	89%	60%	14	70%	99%	81%	3
Carbosulfan	-	-	-	0	7%	7%	7%	1	-	-	-	0
Chlorfenapyr	0%	3%	2%	4	3%	16%	7%	7	3%	4%	4%	3

DATABASE – Predictive model

Compound Information		
active substance:	Thiamethoxam	
Log P	-0,13	
Solubility	4100	mg/L
vapor Pressure	0,0000066	mPa
Type of tea	Green tea	
Transfer Rate	65,3	%

Unit Converter

Pressure:	760	torr
		mm Hg
		Pa

Pressure:	101325000	mPa
	0	mPa
	0	mPa

Solubility:		g/L
		µg/L
		ppm
		ppb

Solubility:	0	mg/L
	0	mg/L
	0	mg/L
	0	mg/L

$$\log(TR) \sim \beta_0 + \beta_1 \log(P) + \beta_2 \log(\text{vapour pressure}) + \beta_3 \log(\text{solubility})$$

Coefficient	Black tea	Green tea	Perfumed green tea	Herbal tea
β0	2,63641	2,7823	2,7126	3,82132
β1				-0,30256
β2	-0,0399			-0,03734
β3	0,11731	0,1697	0,1537	

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CONCLUSIONS & RECOMMENDATIONS

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Conclusions & recommendations

Parameters influencing transfer rate

- No significant influence of infusion time on the TF and water hardness
- Contrary to tea type and flavours (case by case)

Predictive model & risk assessment

- Log P best explains the pesticides behavior

In case of MRL exceedance:

If data available: apply the maximum TF for pesticide/tea combination

If no data available:

- Log P > 4: TF max= 20% is a good approximation
- Log P < 4: the model allows a good approximation of TF when no data are available in the database

Consumer exposure

- 1206 TF collected for 108 pesticides residues and for different type of tea
- More refined exposure assessment for consumers in case of MRL exceedance

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