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University of South Bohemia
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Czech Republic

RESEARCH CENTRE
FOR TOXIC COMPOUNDS
IN THE ENVIRONMENT (RECETOX)
Masaryk University

Field calibration of POCIS: Results of five sampling campaigns and back evaluation of sampling rates under regular monitoring conditions.

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POCIS in regulatory monitoring

Legislation framework

- ISO 5667/23
- Guidance Document No. 19, Guidance on surface water chemical monitoring under the water framework directive,
- Guidance Document No. 25, Guidance on chemical monitoring of sediment and biota under the Water Framework Directive

POCIS vs. grab or composite

- POCIS is integrative sampler provides TWA over relatively long time period
- Simple installation
- Conventional method gives a snapshot of current situation
- Composite sampling is expensive and requires more complicated installation

Challenges

- Limited set of sampling rates is available for regulatory monitoring purpose
- PRC approach with POCIS is principally difficult or impossible
- Questionable relation of POCIS derived concentrations to „whole water“ data requested by EQS directive
- User friendly approach for calculation of aqueous concentrations

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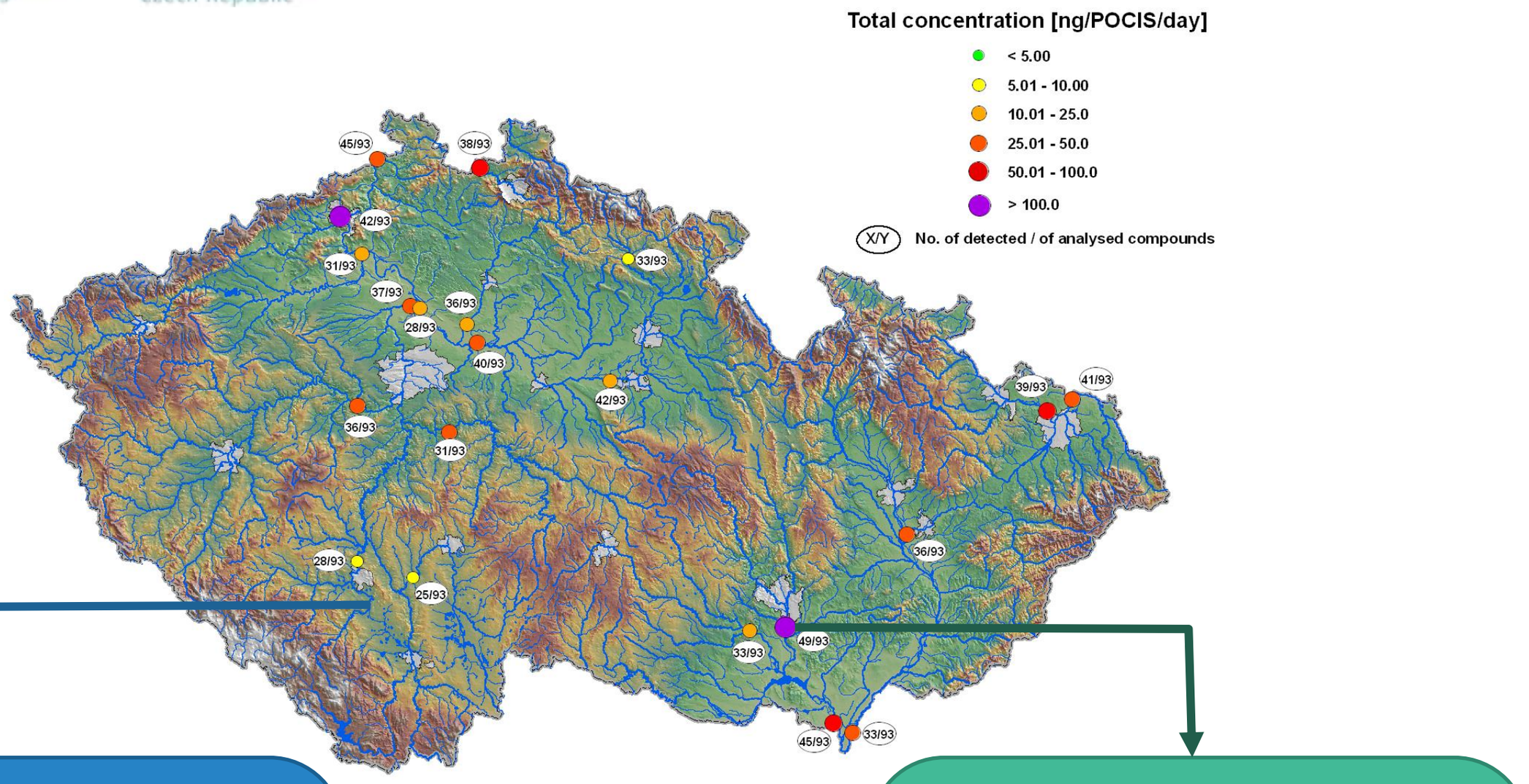
Field calibration design



Heřmaň

Blanice River
rural area with small contribution of effluents, WWTPs located far upstream

Rajhrad

Svratka River
downstream Brno – 500000 inhabitants, effluent contributes up to 15% river flow

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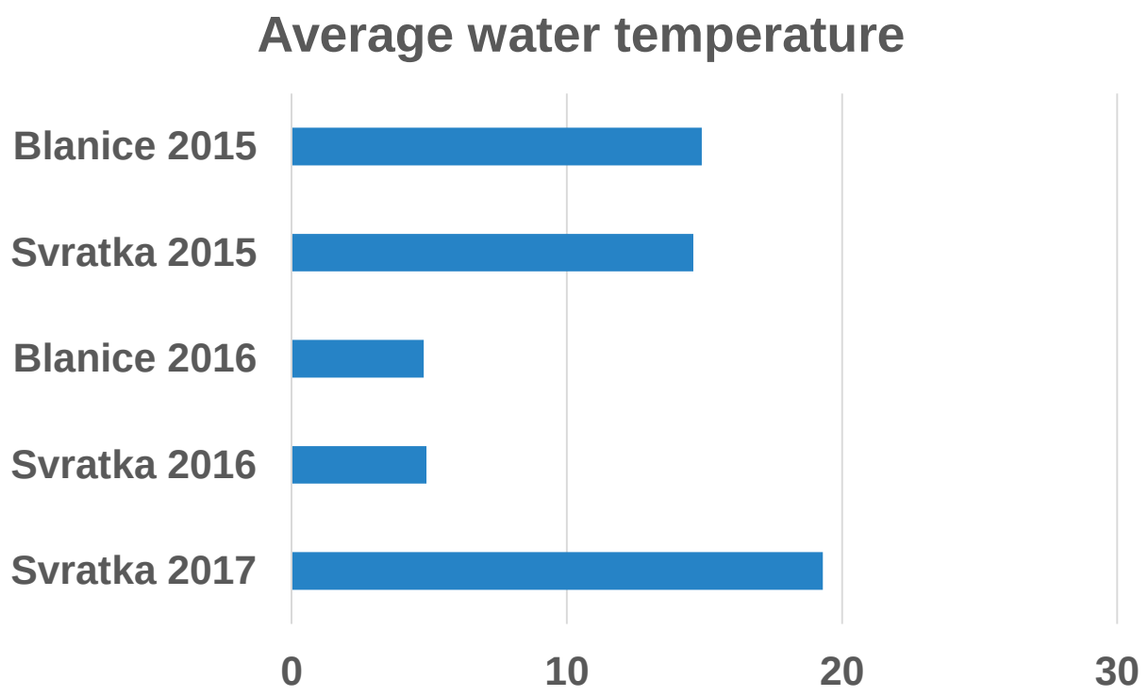
Field calibration design

Calibration was performed at sites selected by CHMI for water quality monitoring - continuous data available on temperature and flow discharge

Continuous time proportional sampling with ISCO automatic sampler, water samples collected as 24 hrs. composite, filtered 0.2 µm RC filter and stored at -18°C

12 POCIS in Pest configuration exposed in parallel, triplicates retrieved after 7, 14, 21, 28 days

	2015											
	1	2	3	4	5	6	7	8	9	10	11	12
Blanice												
Svratka												
	2016											
	1	2	3	4	5	6	7	8	9	10	11	12
Blanice												
Svratka												
	2017											
	1	2	3	4	5	6	7	8	9	10	11	12
Svratka												



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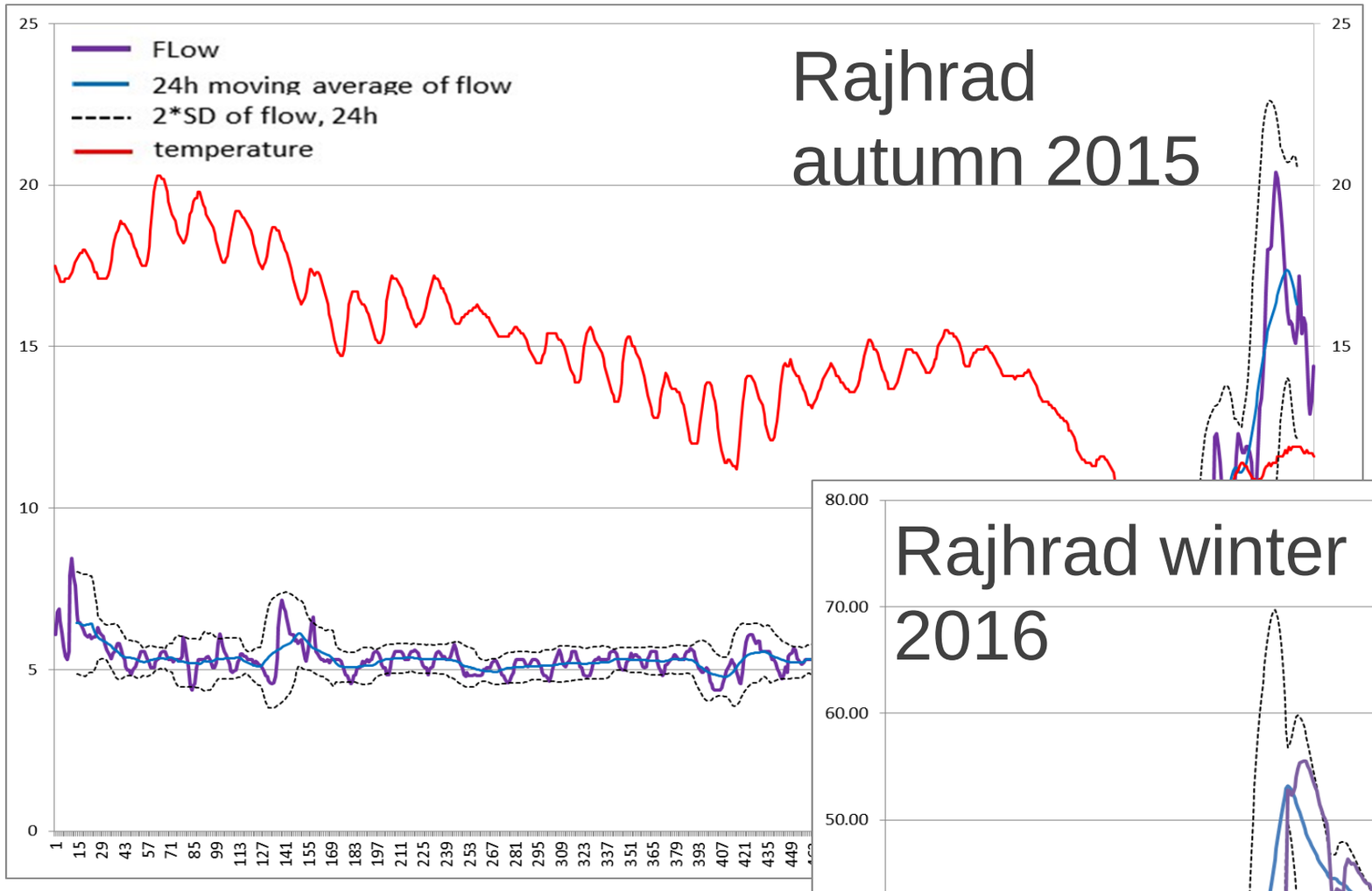
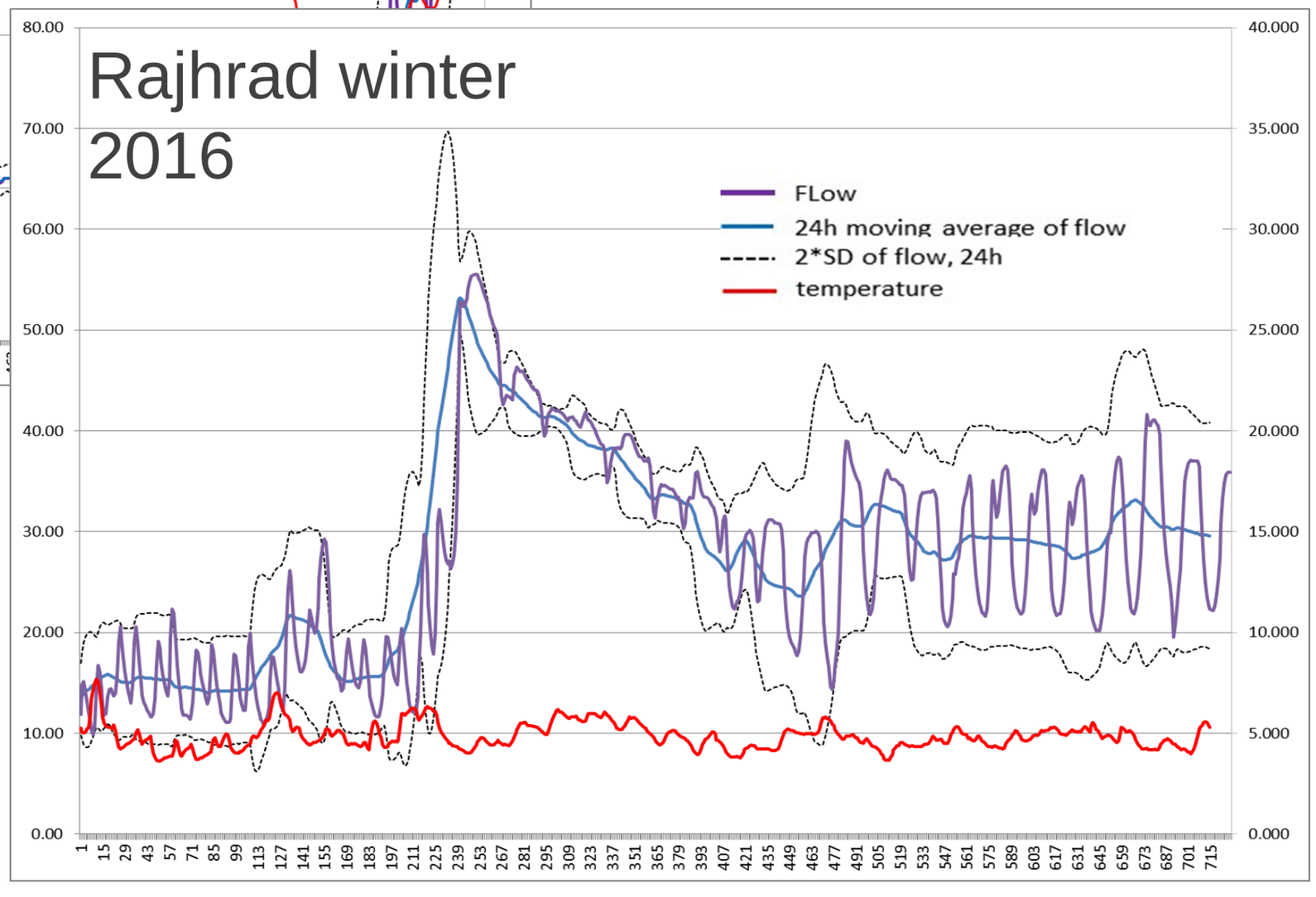
Field calibration result calculation
flow fluctuations





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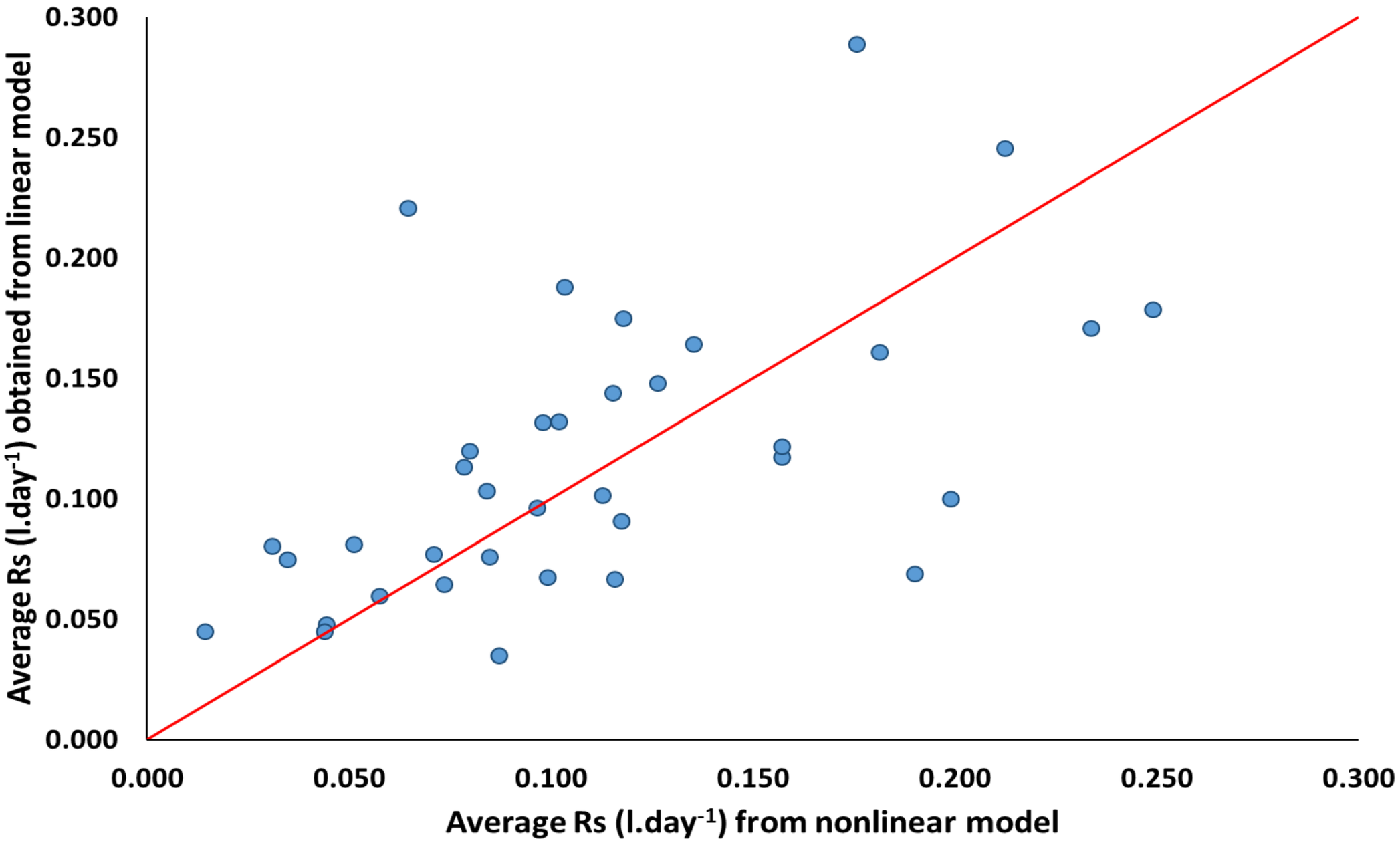
Field calibration result calculation

calculation models

Linear uptake model

Nonlinear model based on numerical integration of differential uptake equation



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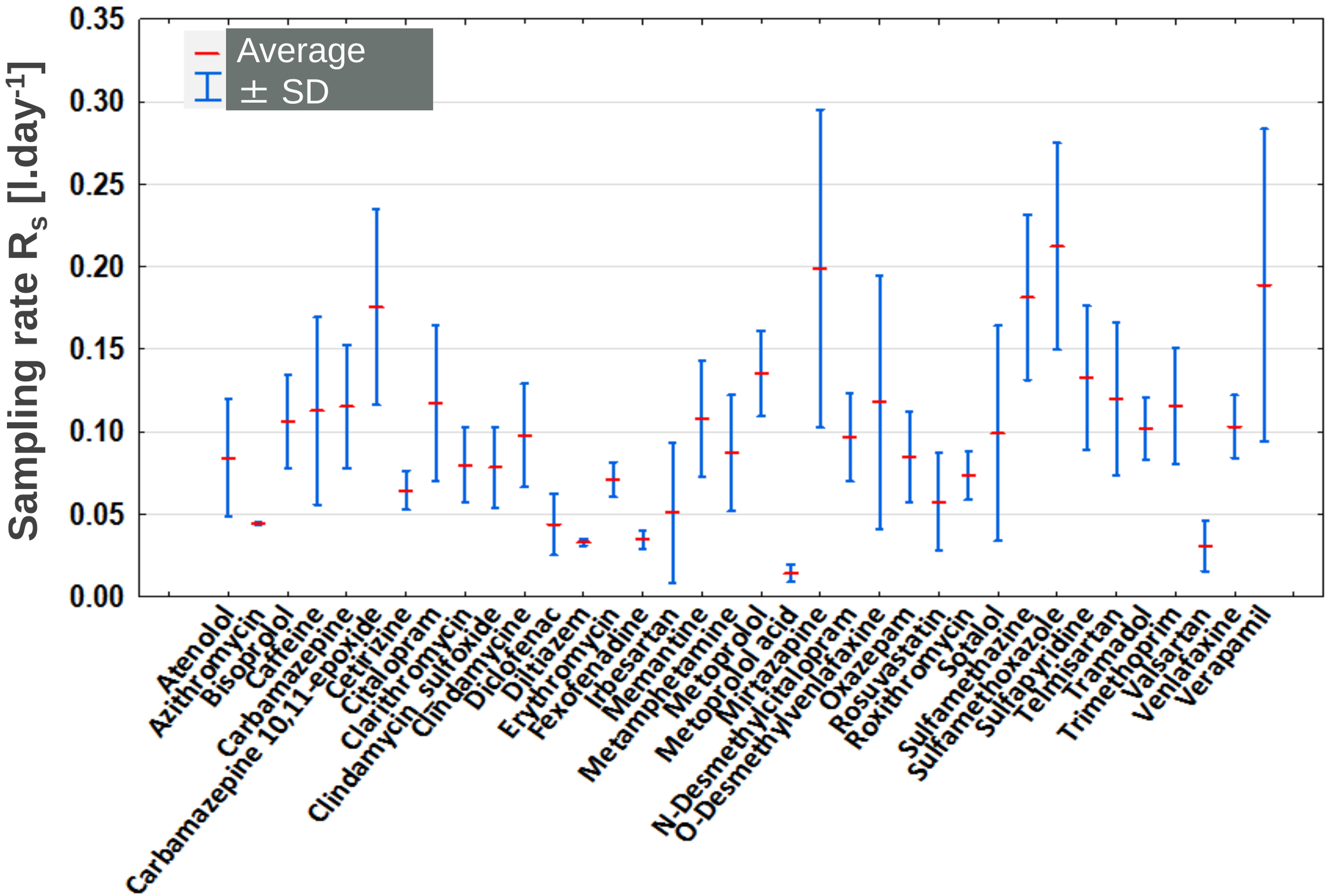
Results pharmaceuticals

average nonlinear R_s from 4 experiments



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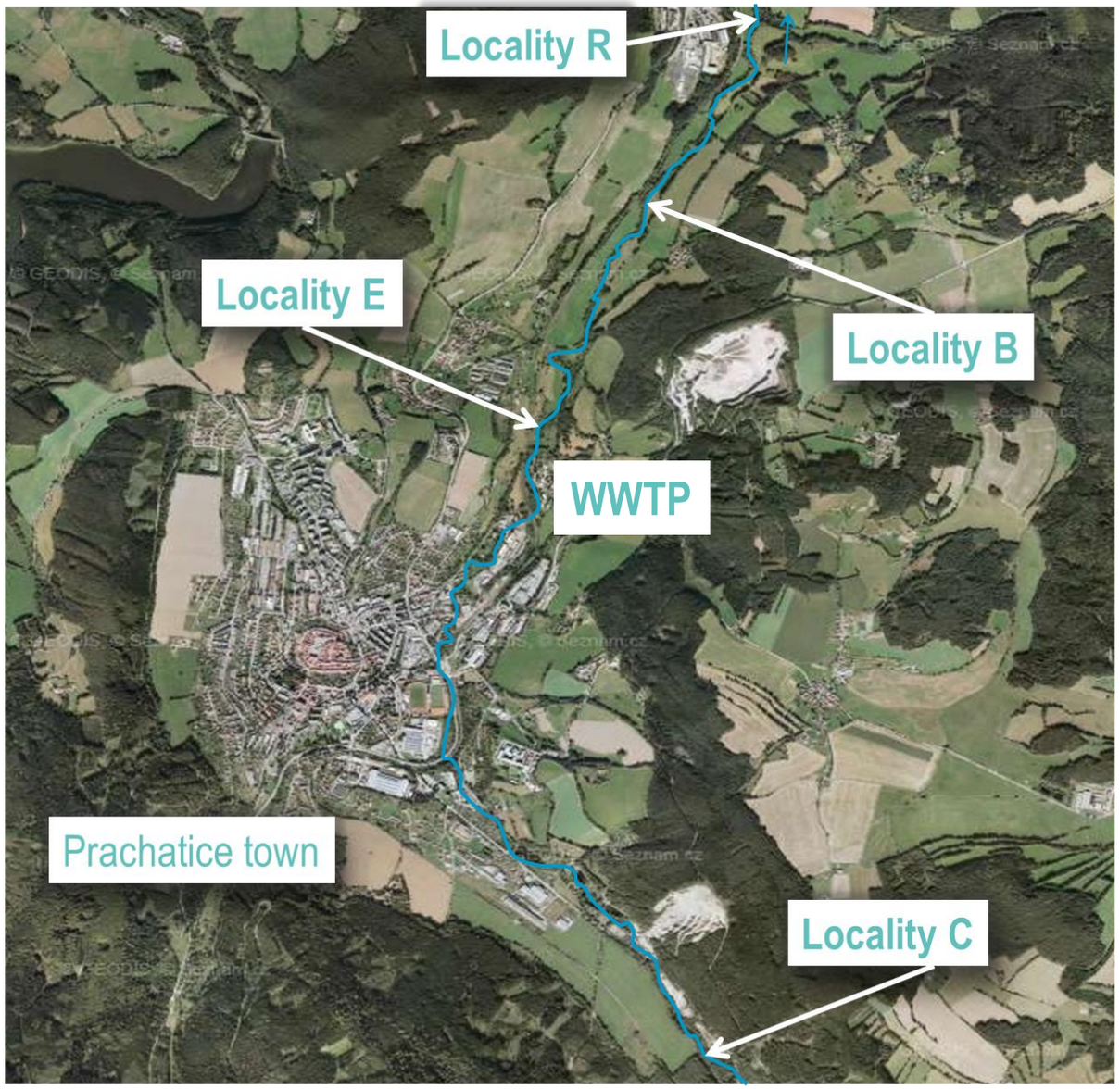
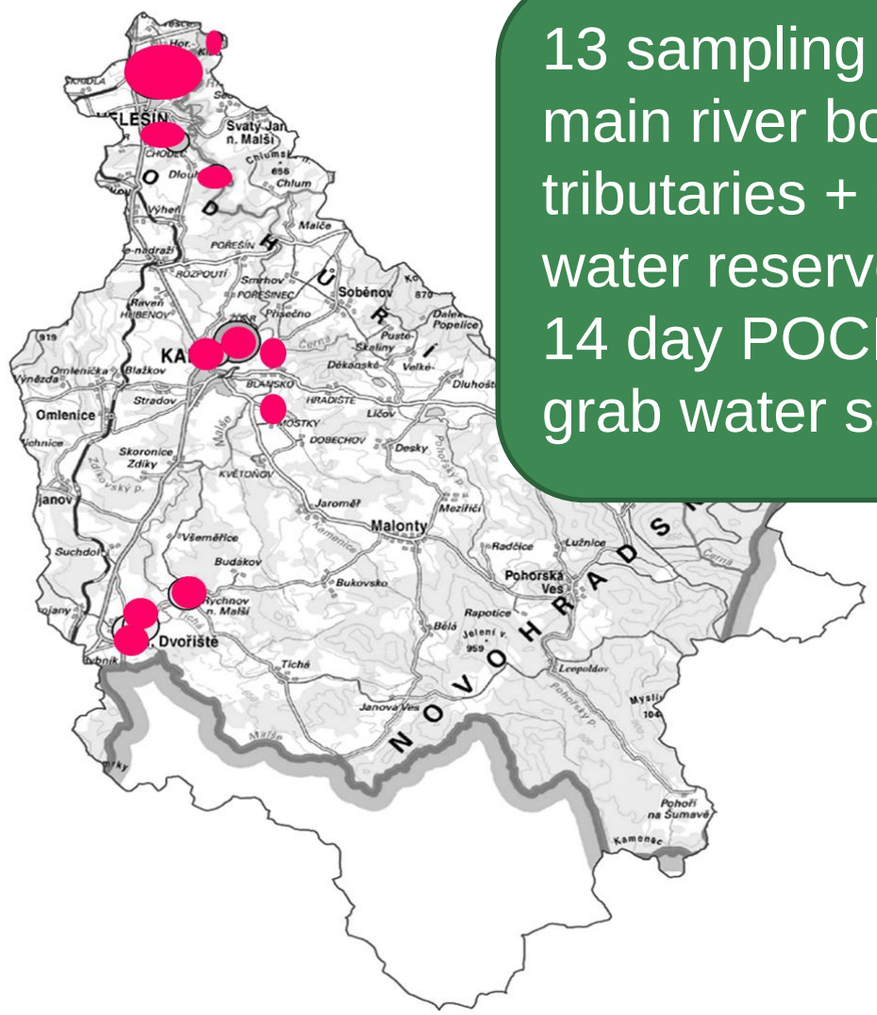
Results pharmaceuticals evaluation



http://www.mapy.cz

Malše River basin



13 sampling sites at main river body + tributaries + drinking water reservoir
14 day POCIS + 3 grab water samples

Month	X			XI				XII			I				II			III			IV		
Week																							
No. of grab samples				3	3	1					2	3	2								3	2	2
POCIS exposure																							
Average temperature			9.2 ± 2.1 °C								4.9 ± 1.0 °C										10.8 ± 1.4 °C		

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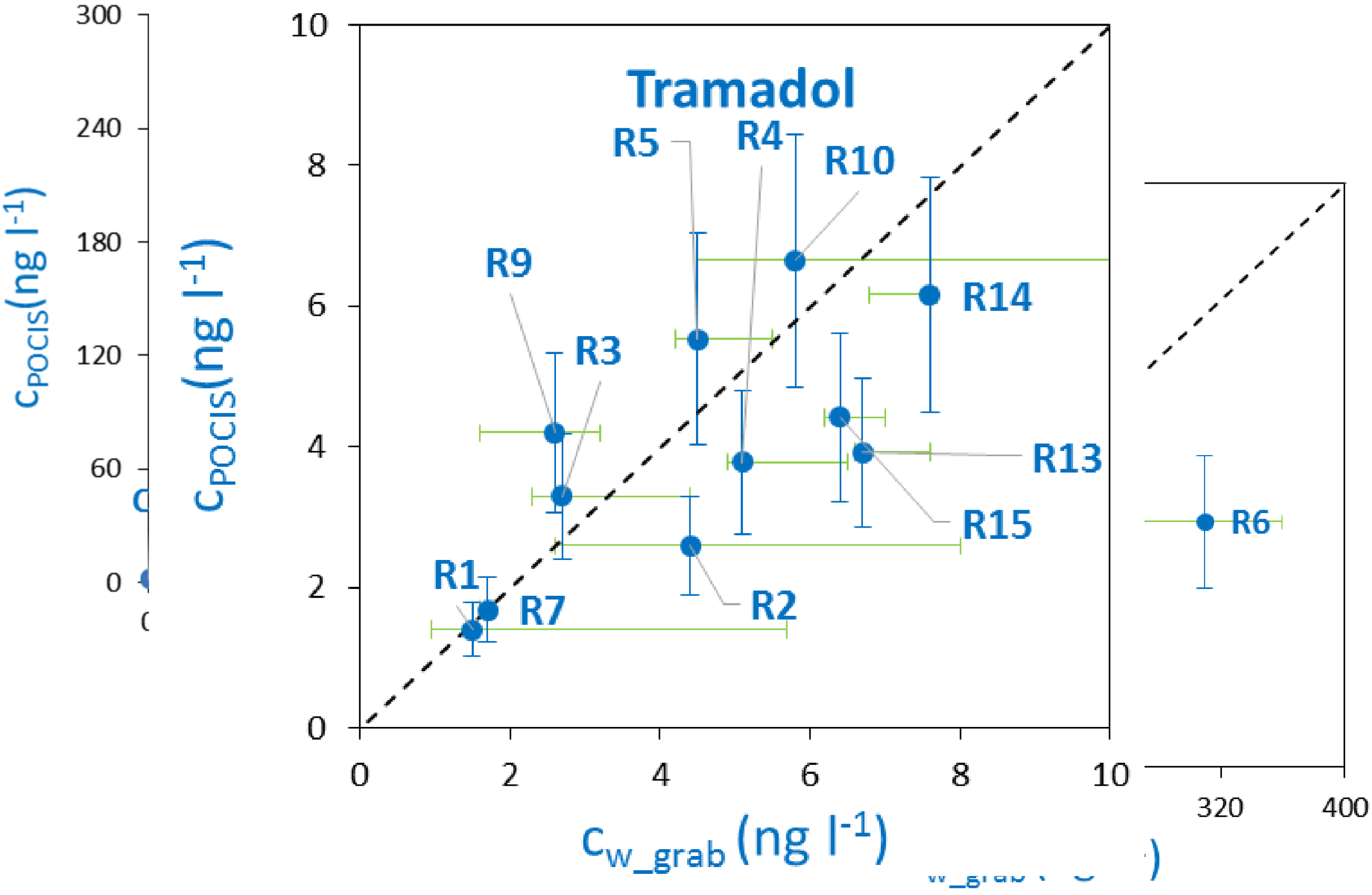

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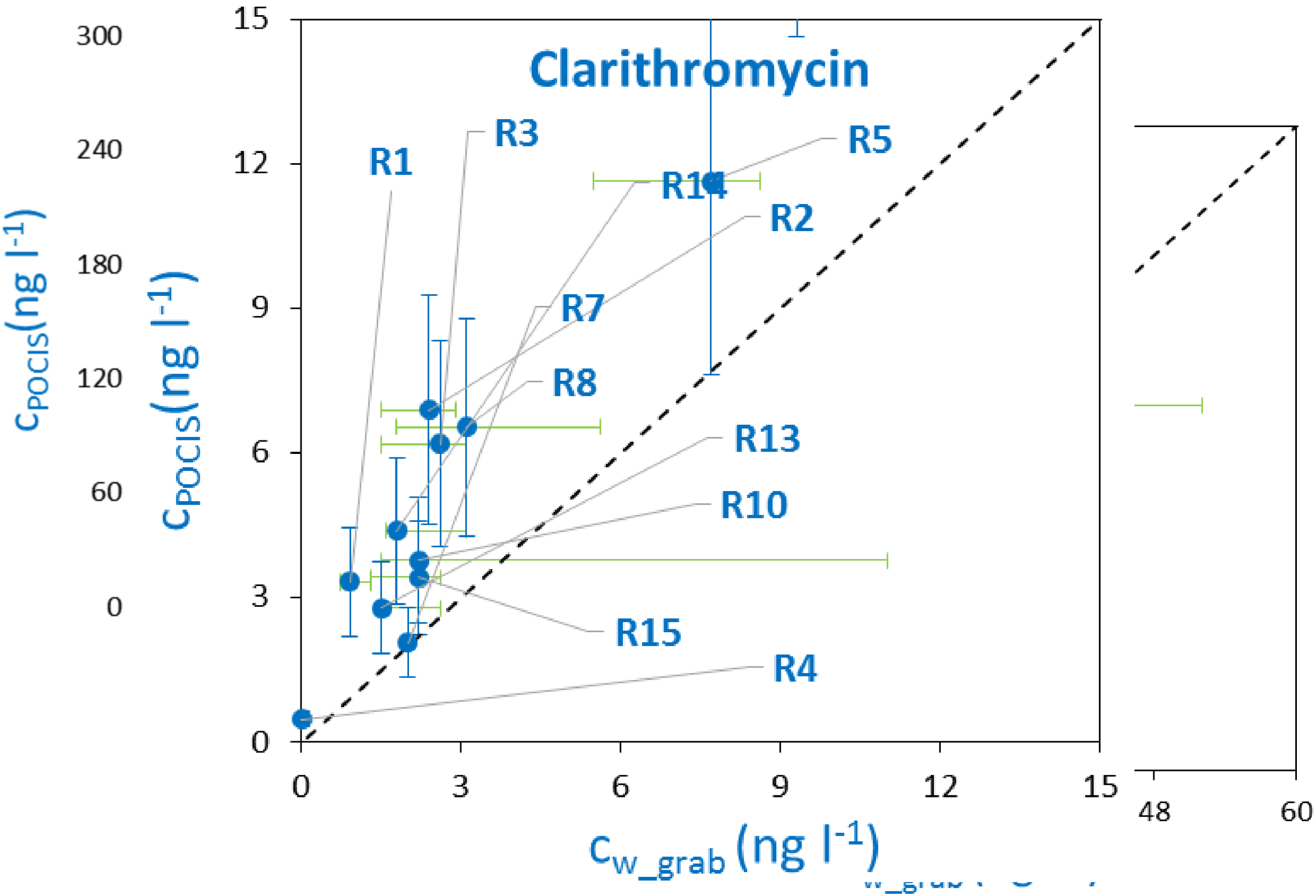

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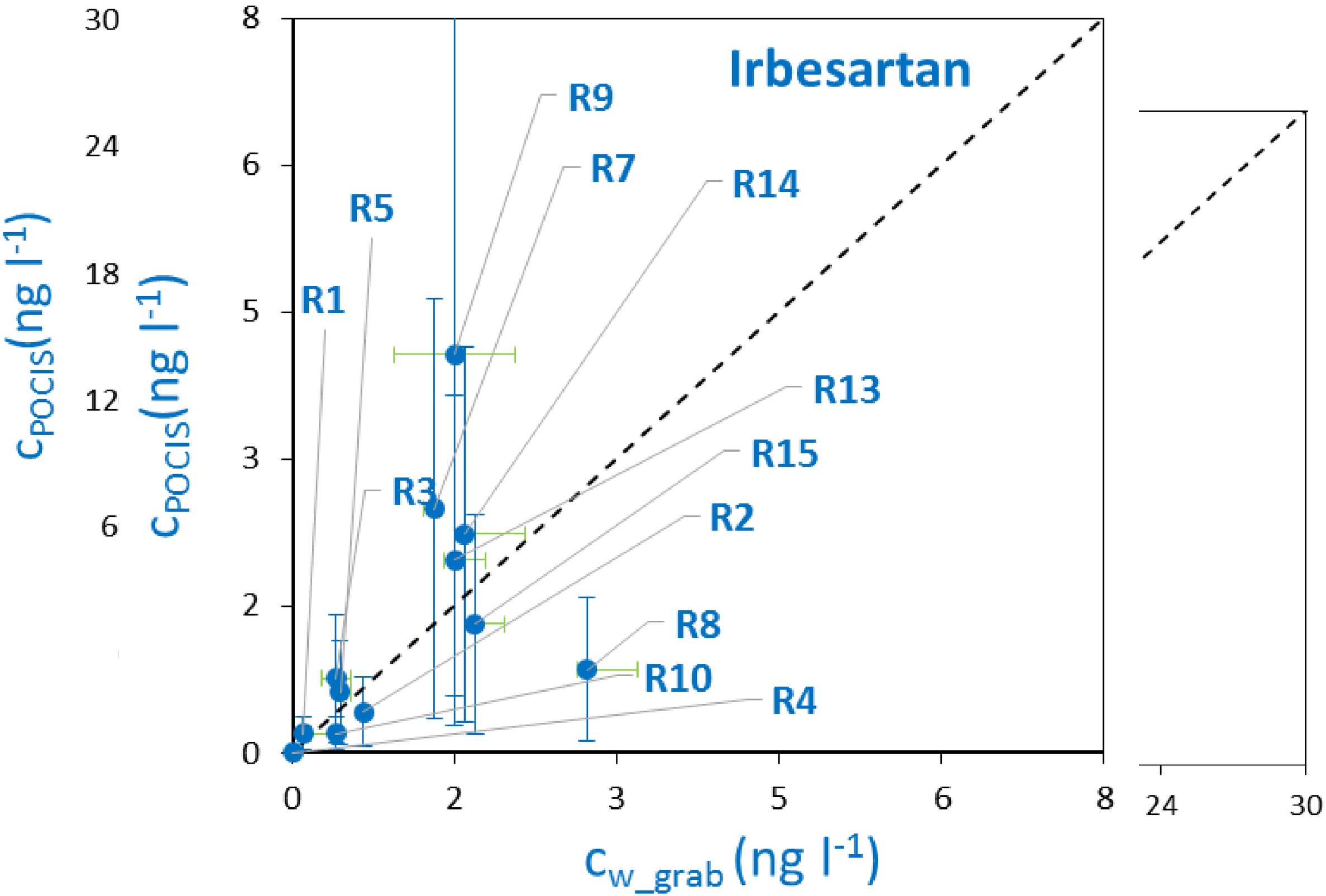
Results pharmaceuticals evaluation



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Results pharmaceuticals simple R_s list for end users

Pharmaceutical	Rs ($l.den^{-1}$)	No. of Rs	Extened uncertainty (%)	Živný potok	Malše basin
Atenolol	0.084	4	47	x	
Azithromycin	0.044	2	20	x	
Bisoprolol	0.106	3	33	x	
Caffeine	0.113	4	54		
Carbamazepine	0.115	4	38		
Carbamazepine 10,11-epoxide	0.176	2	39	x	
Cetirizine	0.064	2	27	x	
Citalopram	0.117	3	45	x	
Clarithromycin	0.080	4	35		
Clindamycin_sulfoxide	0.078	4	37	x	
Clindamycine	0.098	4	38	x	
Diclofenac	0.044	4	47		
Diltiazem	0.033	2	21	x	
Erythromycin	0.071	3	25	x	
Fexofenadine	0.035	4	26		
Irbesartan	0.051	4	86		
Memantine	0.108	2	38	x	
Metamphetamine	0.087	3	45	x	
Metoprolol	0.135	4	28		
Metoprolol acid	0.014	4	42	x	
Mirtazapine	0.199	3	52	x	
N-Desmethylcitalopram	0.097	3	34	x	
O-Desmethylvenlafaxine	0.118	4	68	x	
Oxazepam	0.085	4	38	x	
Rosuvastatin	0.058	3	55	x	
Roxithromycin	0.073	2	28	x	
Sotalol	0.099	4	69	x	
Sulfamethazine	0.181	4	34	x	
Sulfamethoxazole	0.212	4	36		
Sulfapyridine	0.133	3	38		
Telmisartan	0.120	4	44		
Tramadol	0.102	4	27		
Trimethoprim	0.116	3	36	x	
Valsartan	0.031	4	53		
Venlafaxine	0.103	4	27		
Verapamil	0.189	3	54	x	

Approved for robust estimation of water concentration - 27

Applicable, but with higher uncertainty - 3

POCIS is not suitable sampler for this compound - 1

Lack of the data due to low water concentration - 6

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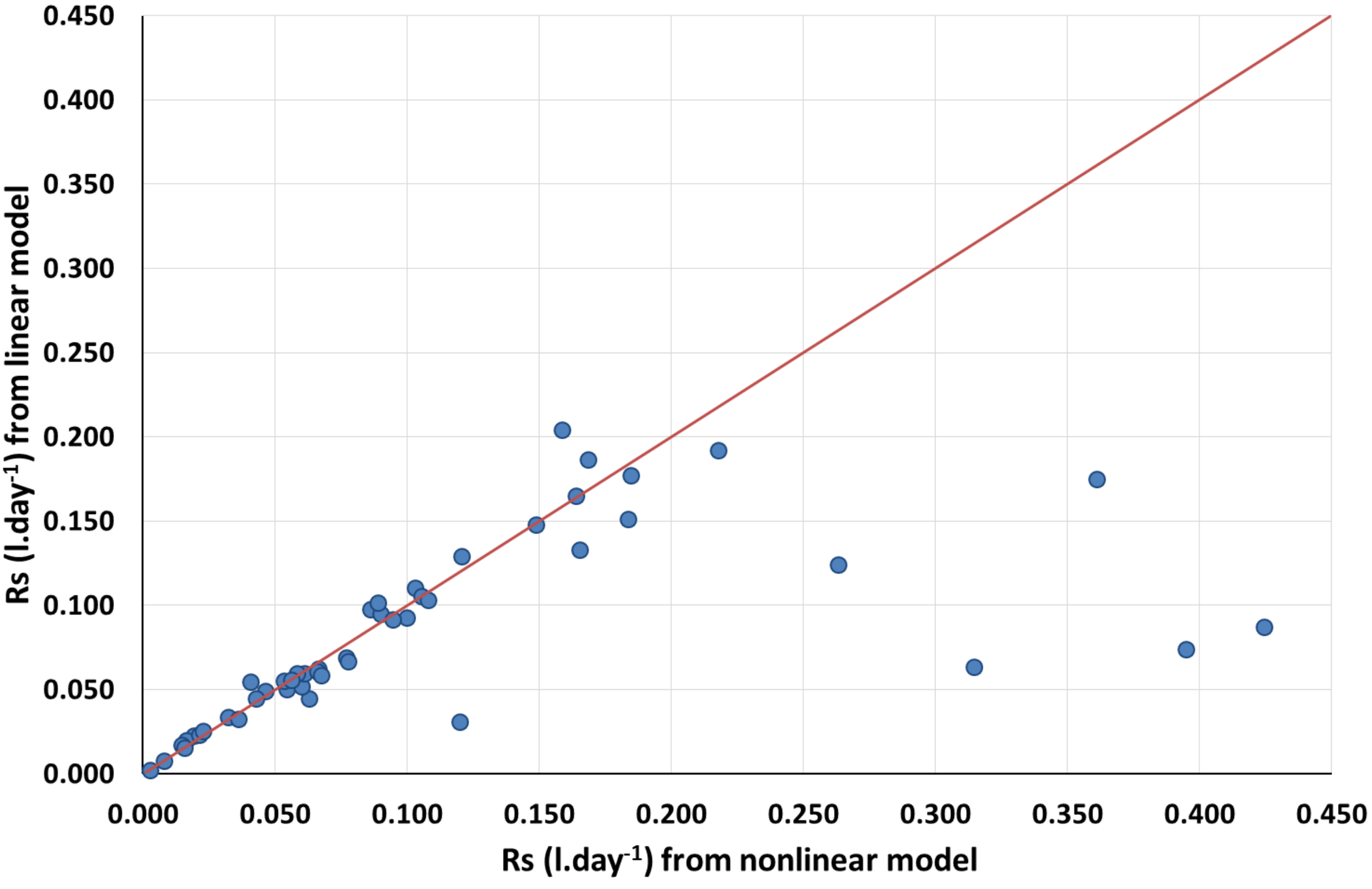
Field calibration pesticides



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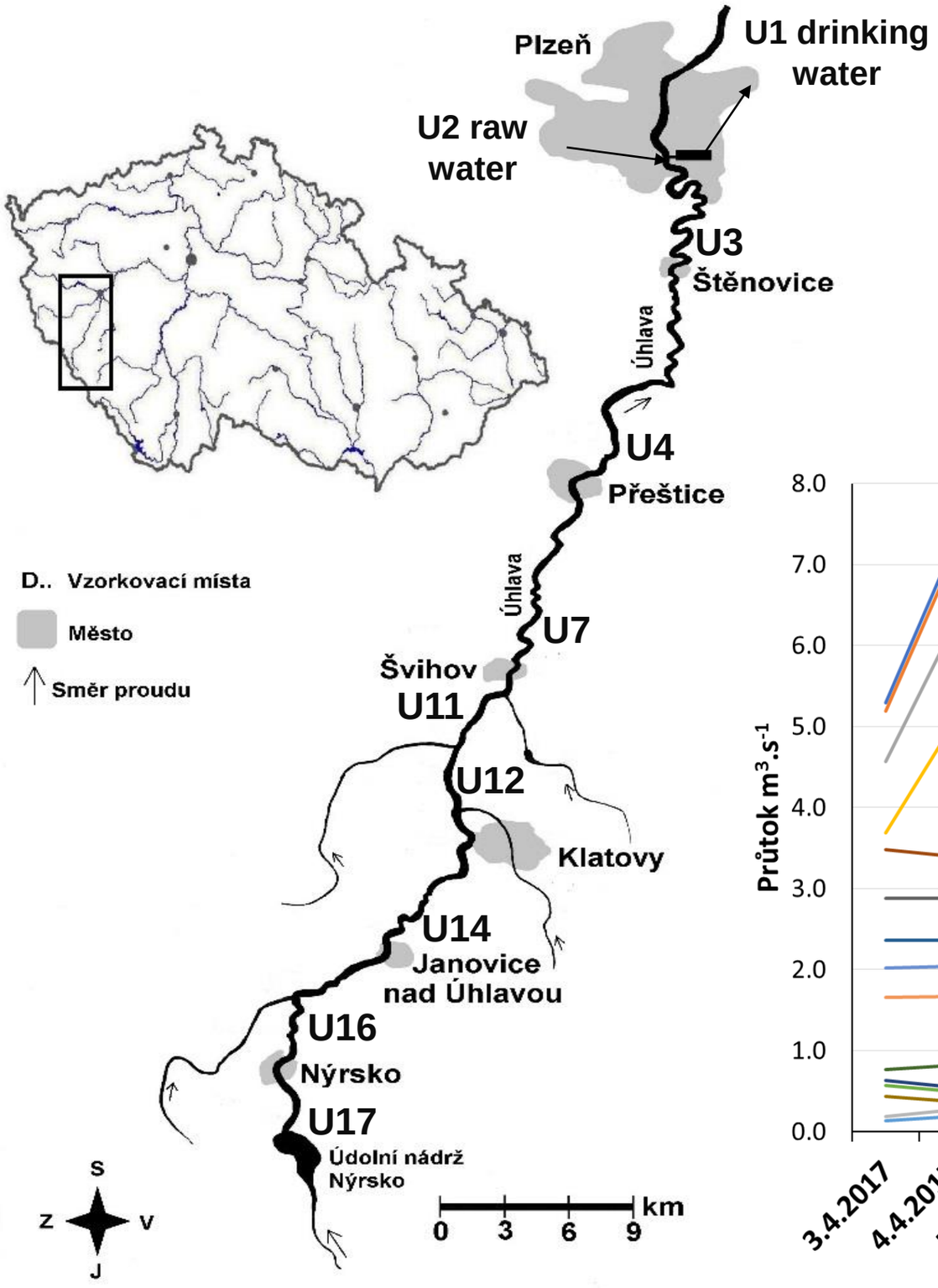
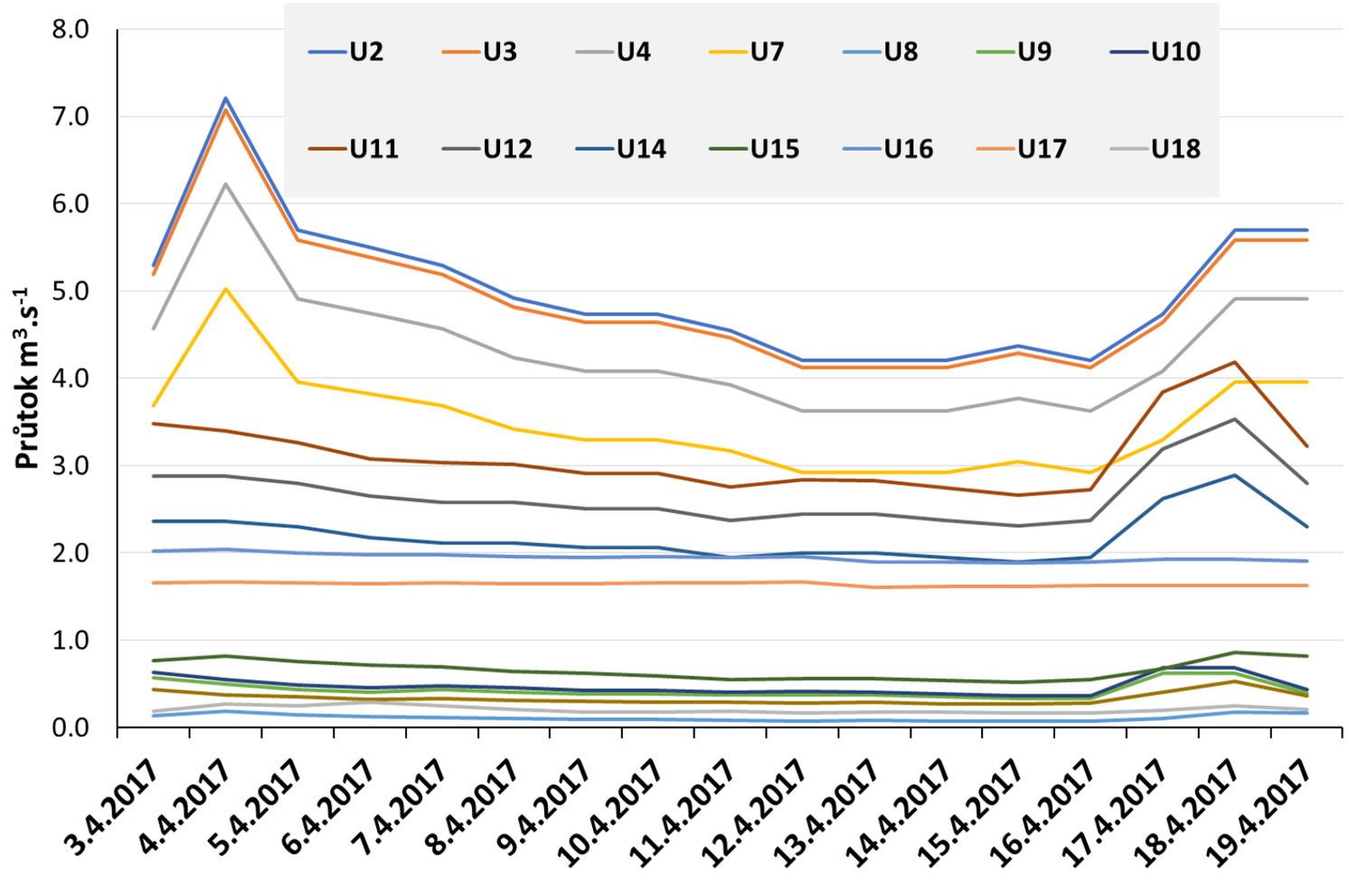
Field calibration pesticides evaluation



	Start water temperature °C	End water temperature°C
September 8th to 22th	16.6	12.6
April 4th to 18th	9.3	6.4



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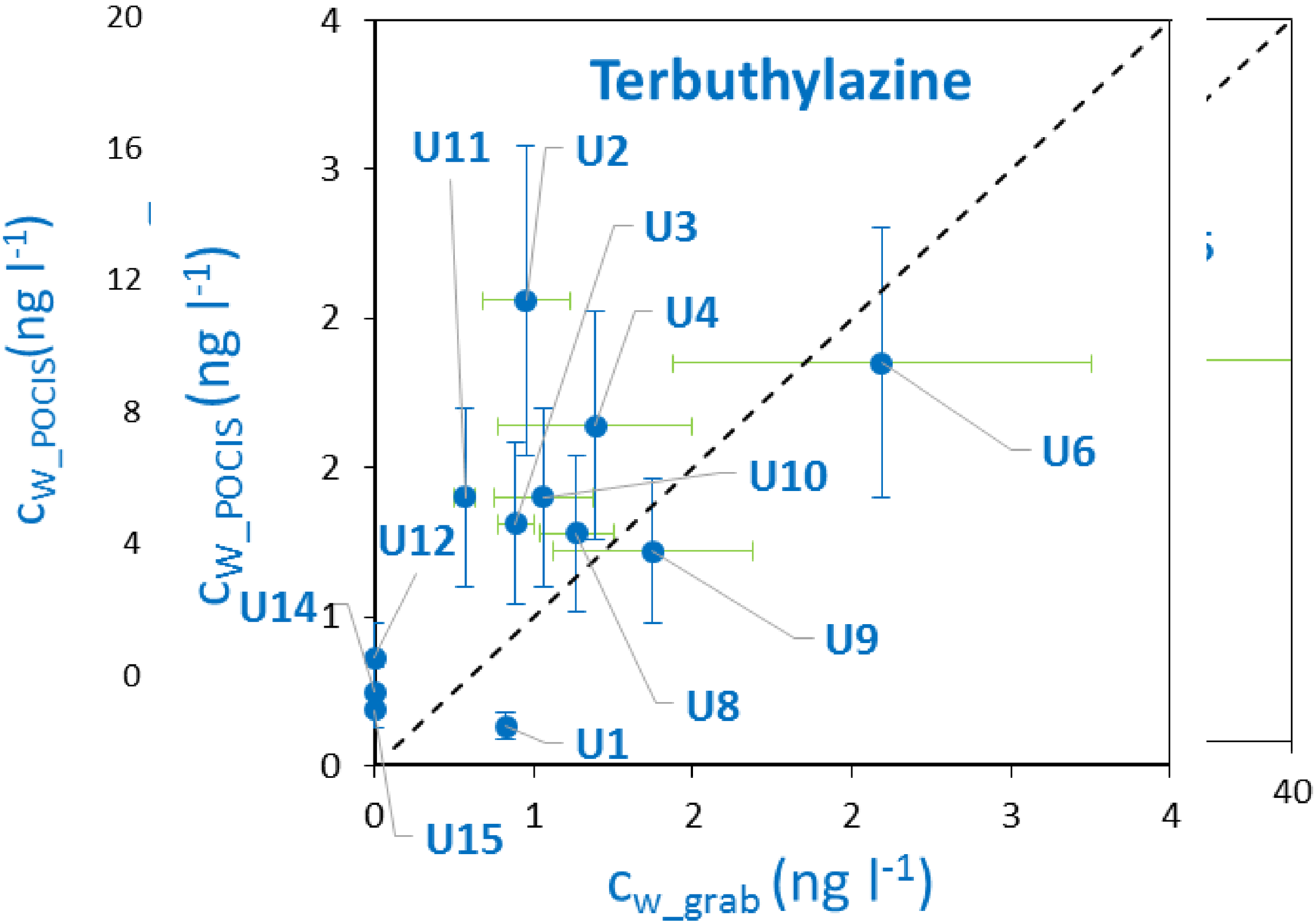
Field calibration pesticides

R_s evaluation



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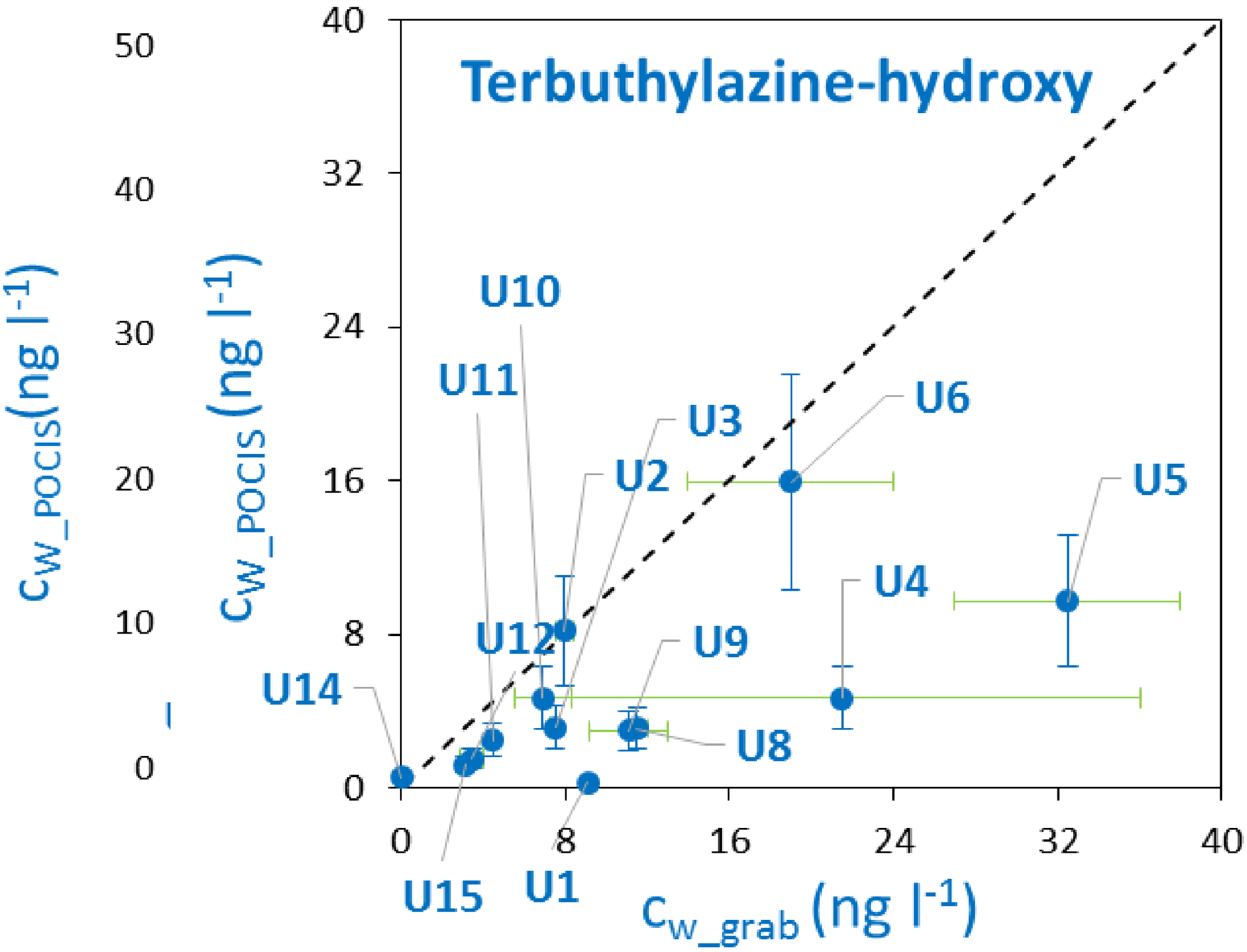

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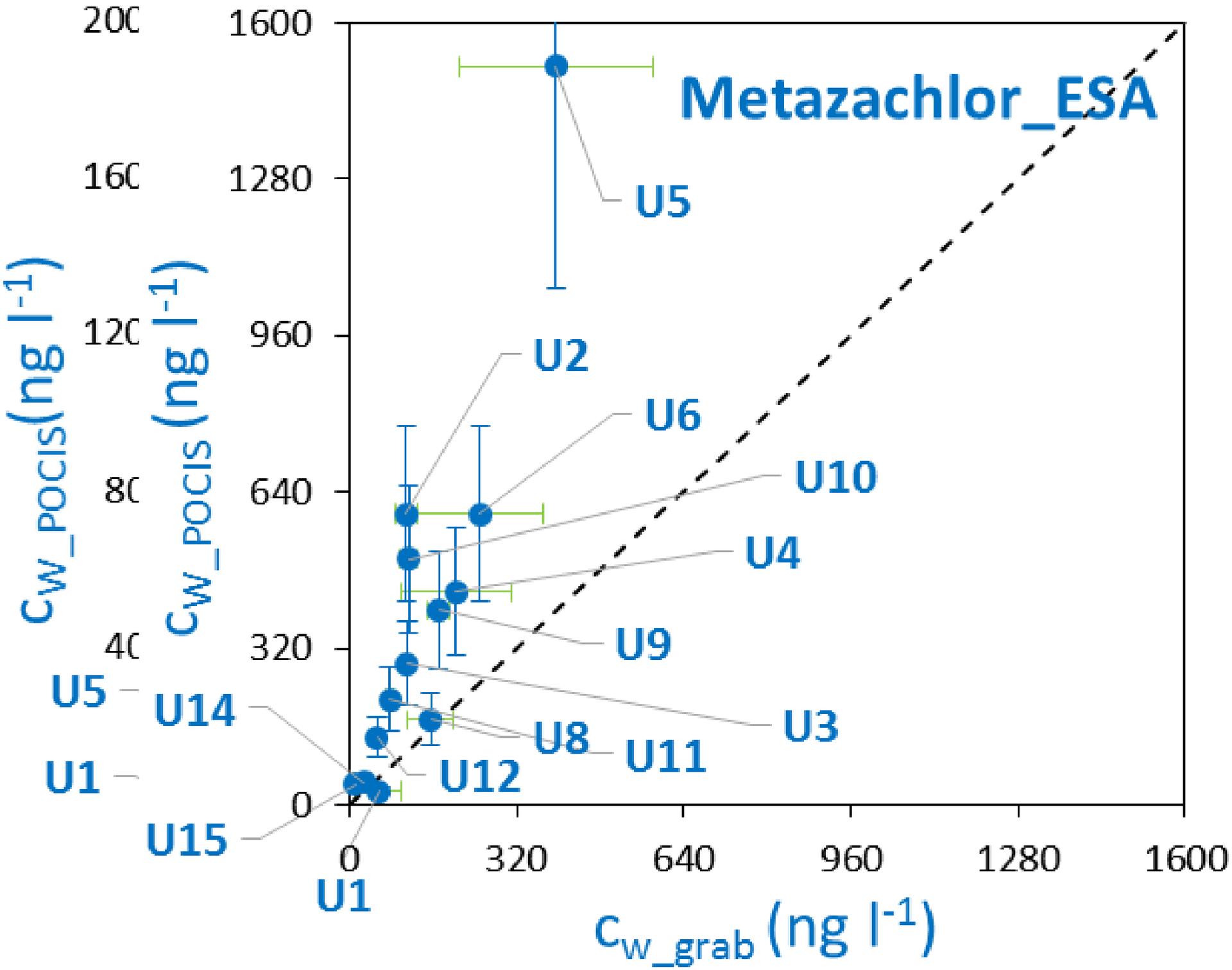

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Field calibration result calculation

R_s evaluation

Compoound	Rs (l.day^{-1})	Extended uncertainty (%)	September	April
4 a 5-methyl-1H-benzotriazol	0.103	31		
1-(3.4-Dichlorophenyl) urea	0.063	30		
2.4-D	0.019	31		
Acetochlor ESA	0.032	31		
Alachlor ESA	0.032	31		
Alachlor OA	0.361	32		
Atrazine	0.041	31		
Atrazine-desethyl	0.090	32		
Azoxystrobin	0.055	30		
Bentazone	0.003	31		
Clomazone	0.100	32		
Cyproconazole	0.060	31		
DEET	0.046	31		x
Diazinon	0.105	30		
Dimethachlor ESA	0.017	32		
Dimethenamid ESA	0.021	31		
Dimethomorph	0.061	33		
Diuron	0.218	31		
Epoxiconazole	0.077	31		
Fenuron	0.121	32		
Foramsulfuron	0.120	32		
Hexazinone	0.043	31		
Chloridazon	0.395	31		
Chloridazon-desphenyl	0.086	31		
Chloridazon_methyl desphenyl	0.053	31		
Chlortoluron	0.169	31		
Imidacloprid	0.089	31		
Isoproturon	0.164	31		
Lenacil	0.424	32		
Linuron	0.066	31		
MCPA	0.015	31		
Metalaxyl	0.263	30		
Metazachlor ESA	0.016	32		
Metazachlor OA	0.023	31		
Metolachlor	0.159	31		
Metolachlor OA	0.036	31		
Metribuzin desamino	0.078	31		
Pirimicarb	0.058	31		
Propazine-2-hydroxy	0.108	33		
Propiconazole	0.066	31		
Simazine	0.095	31		
Tebuconazole	0.067	31		
Terbuthylazine	0.149	31		
Terbuthylazine-desethyl	0.185	31		
Terbuthylazine-desethyl-2-hydroxy	0.165	31		
Terbuthylazine-hydroxy	0.184	31		
Warfarin	0.056	32		

Approved for robust estimation of water concentration - 16

Applicable, but with higher uncertainty - 18

POCIS is not suitable sampler for this compound - 5

Lack of the data due to low water concentration 14

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POCIS field calibration summary

- Pharmaceuticals *R*s were obtained from 4 campaigns under variable conditions, pesticides *R*s for only one campaign
- Nonlinear calculation model enable to use data from variable exposure (aqueous concentration) condition

- In spite the expectation that there would be two datasets – for cold and warm season it was possible to average all data to a single set – end user friendly for calculation

- Back evaluation provided good agreement for most pharmaceuticals *R*s
- Pesticides *R*s data set must be extended (HRMS data collected) to be provide more robust data

- Pesticides seem to be more problematic due to their diffusive sources
- Some acidic compounds with low *R*s seem to be trapped in PES membrane only – low *R*s variability and overestimation of water conc.

Thank you for your attention!

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