

Trace substance monitoring at the intersection of urban drainage and an urban river in Karlsruhe, Germany

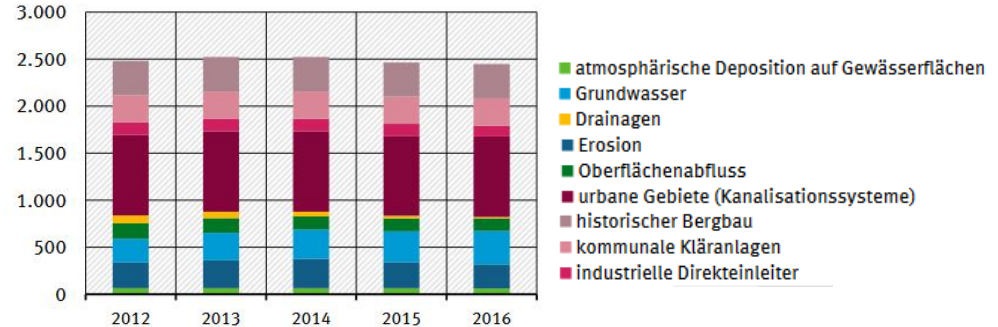
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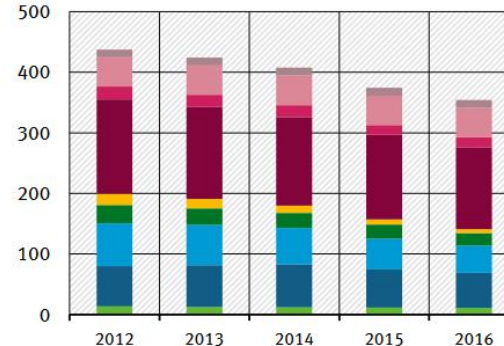
Background

- Multiple substance groups with different sources, transport behaviors and emission pathways may be emitted into surface waters
- Ecological relevance: toxicity/EQS, longterm effects (e.g. heavy metal accumulation in river sediments)
- Past studies showed a significant role of urban emission pathways for various trace substances
- Comprehensive harmonized database often lacking – especially for separate sewer systems

Zink-Einträge in Tonnen/Jahr



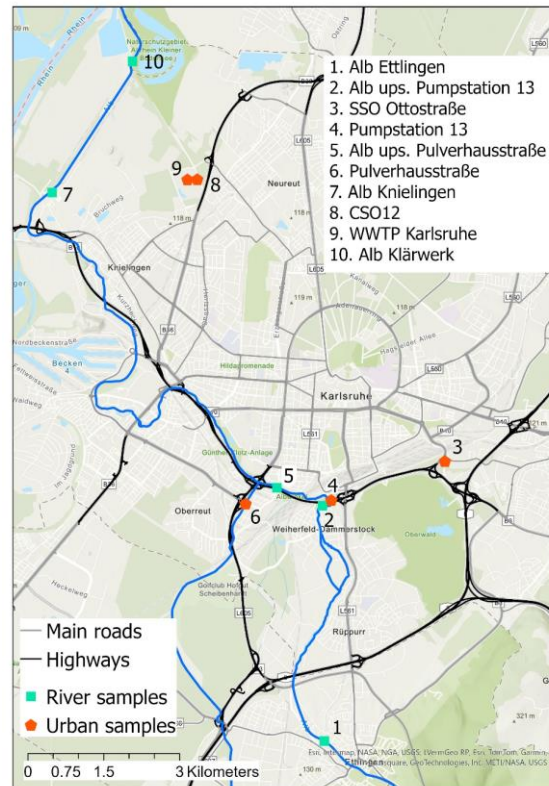
Kupfer-Einträge in Tonnen/Jahr



Source: Umweltbundesamt 2020

Sampling Strategy

- Study Site: river Alb along ist course through Karlsruhe city
- River samples upstream and within the city
- Urban samples covering different pathways:
 - Combined Sewer Overflow (CSO12)
 - Untreated (SSO Ottostraße) and treated seperate sewer runoff (SSO Ottostraße, Pumpstation 13)
 - Street runoff (Pulverhausstraße)
 - WWTP effluent
- Sampling period: over two years (fall 2021 – winter 2023)



Sampling Strategy

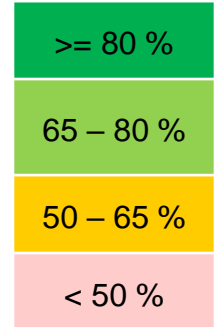
- Large volume samplers to collect homogenized composite samples
- River sites: longterm and wet/dry weather samples
- Urban sites: event-based sampling at each site
- WWTP: weekly composite samples based on methodology by Toshovski et al. (2020)
- Analysis of more than 100 individual substances (e.g. heavy metals, pharmaceuticals and biocides/herbicides)

Sites	Subset	No. of homogenized composite samples
River	Longterm	11
	Wet weather	34
	Dry weather	7
Separate Sewer sites	Untreated	10
	Treated	29
	Street runoff	14
Combined Sewer Overflow	-	10
WWTP effluent	Weekly composite	6

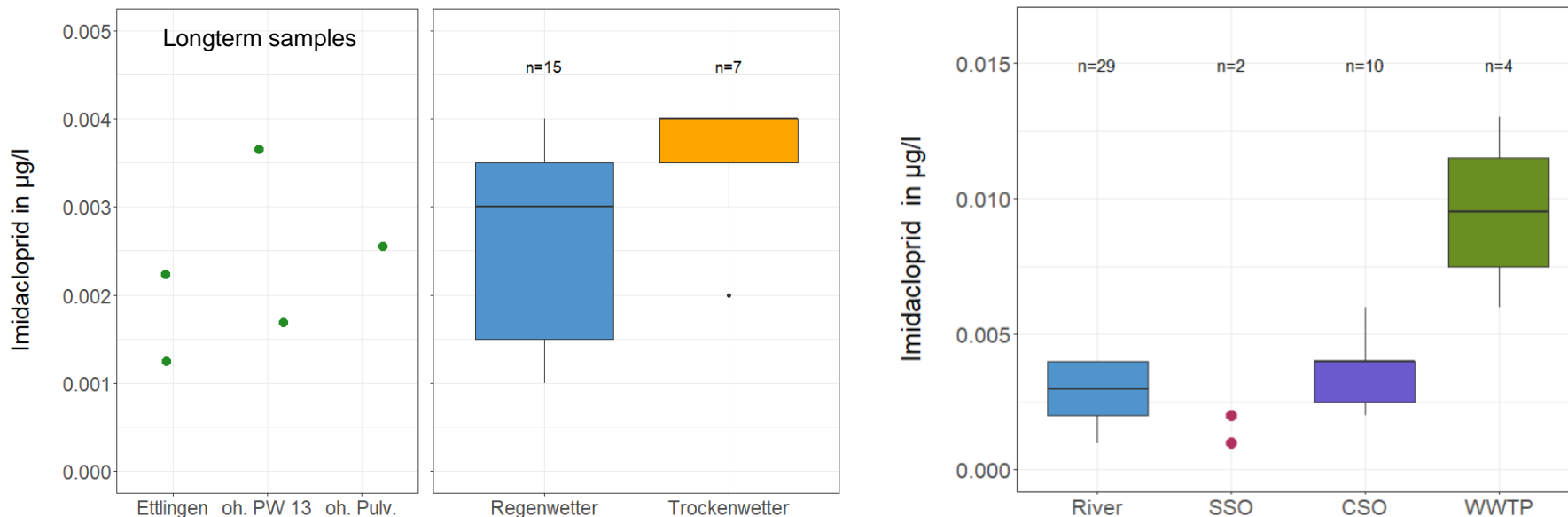
Detections

Substance Group	Number of Substances	Frequently detected substances (> 50 % of samples)			
		River	SSO	CSO	WWTP
Metals	18	14	17	16	13
Pharmaceuticals	14	10	5	14	12
Herbicides	4	1	3	1	1
Disinfectans	6	1	2	3	0
Pesticides	14	2	1	5	1
Preservatives	22	11	13	15	11
PFAS	20	8	14	11	7
Others	8	7	7	8	4

Share:



Emission pathways - Imidacloprid

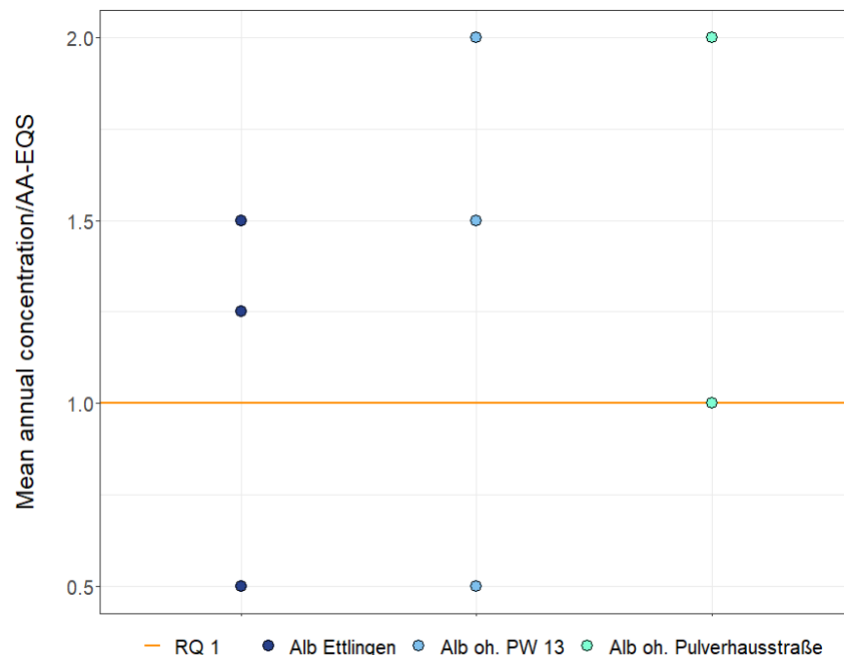


	River	SSO	CSO	WWTP
Imidacloprid (Median) [µg/l]	0,003	(0,0015)	0,004	0,0095

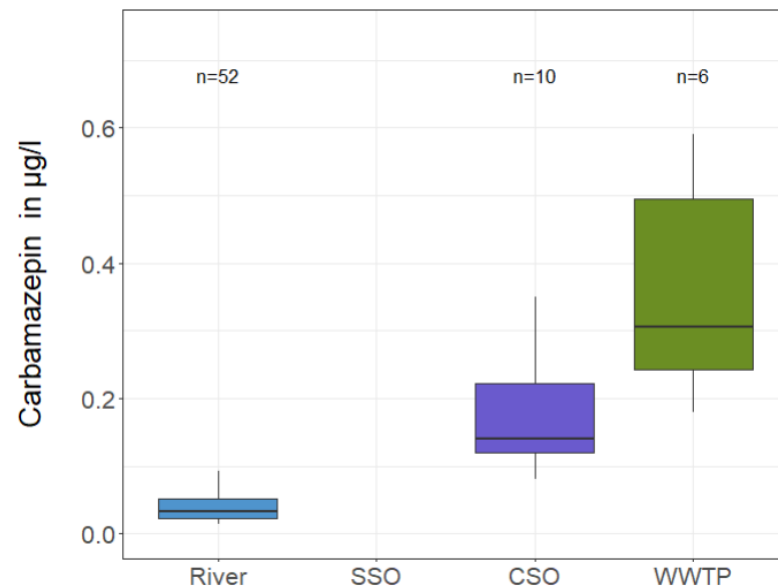
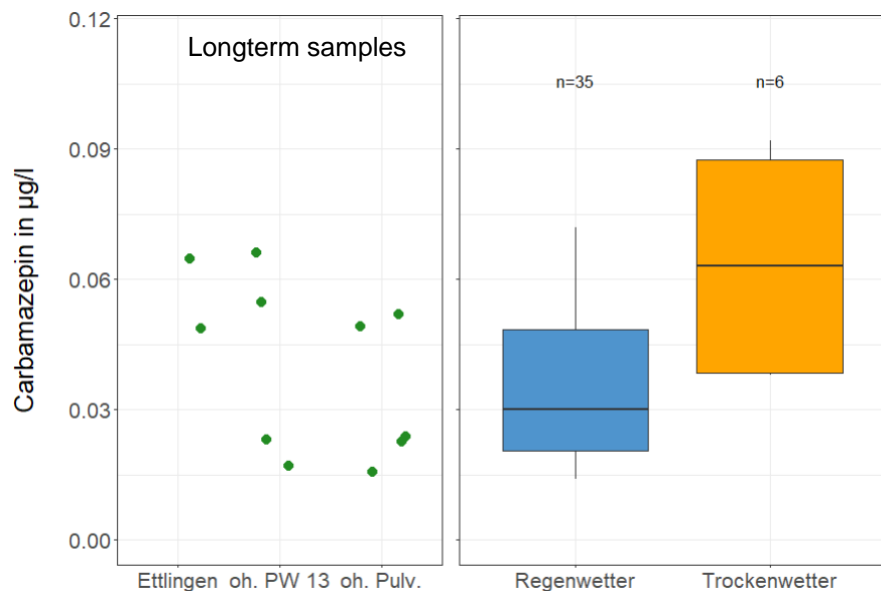
Environmental Quality Standards - Imidacloprid

	Imidacloprid
AA EQS rivers [$\mu\text{g/l}$]	0,002
MAC EQS rivers [$\mu\text{g/l}$]	0,1

- Mean annual concentrations at three river sites exceeded the AA EQS in 2022/2023
- All 4 measured concentrations from WWTP exceeded the AA EQS

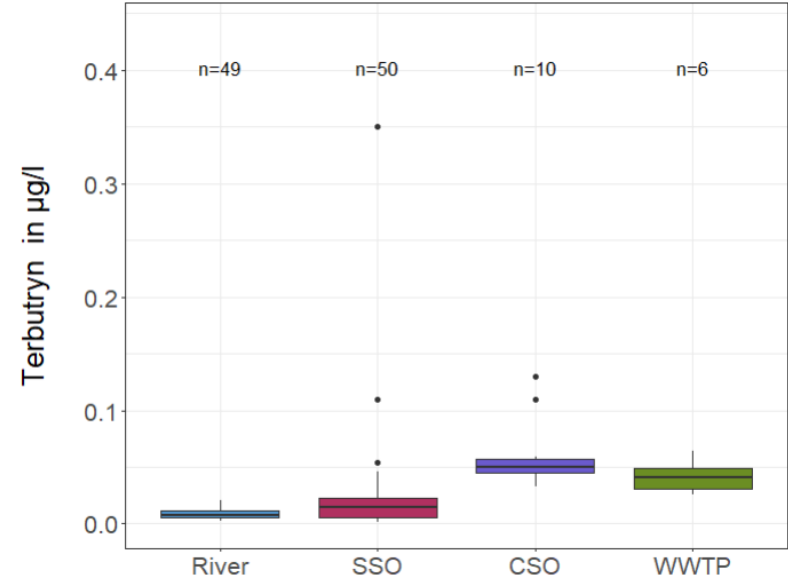
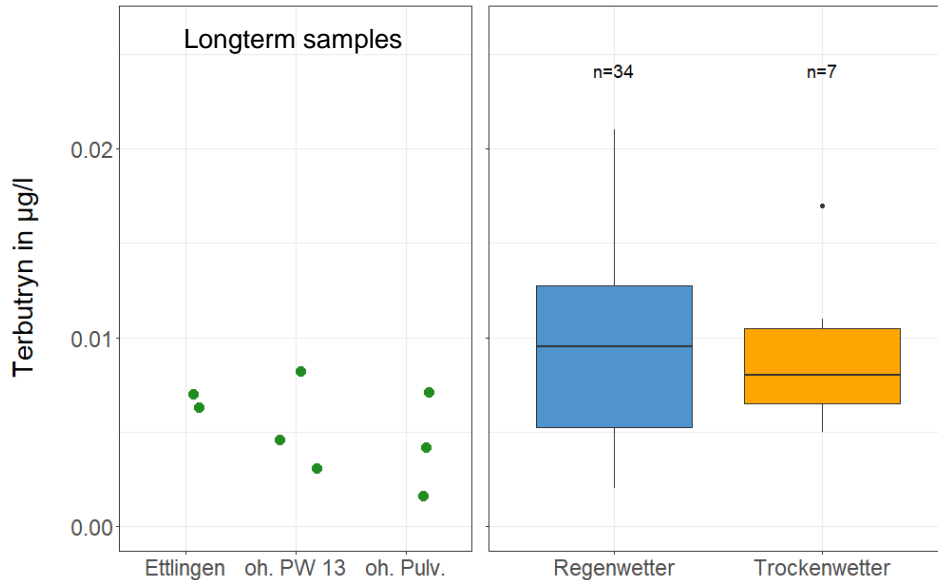


Emission pathways - Carbamazepin



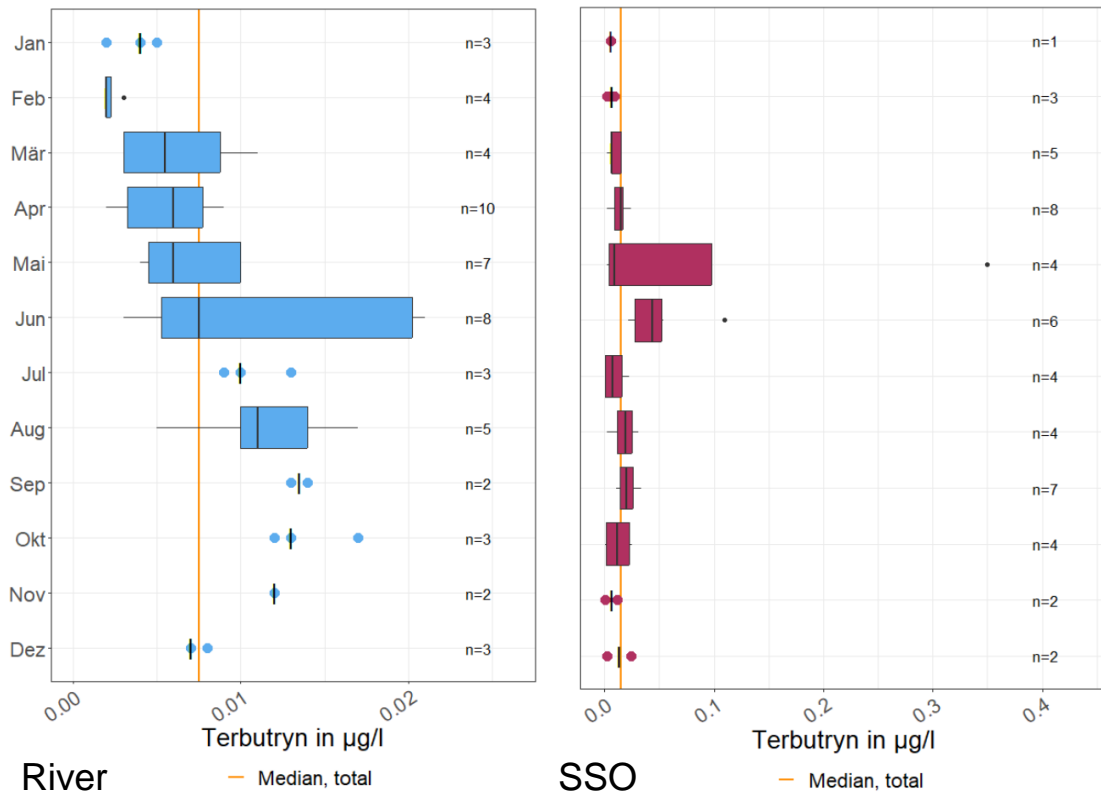
	River	SSO	CSO	WWTP
Carbamazepin (Median) [$\mu\text{g/l}$]	0,03		0,14	0,3

Emission pathways - Terbutryn



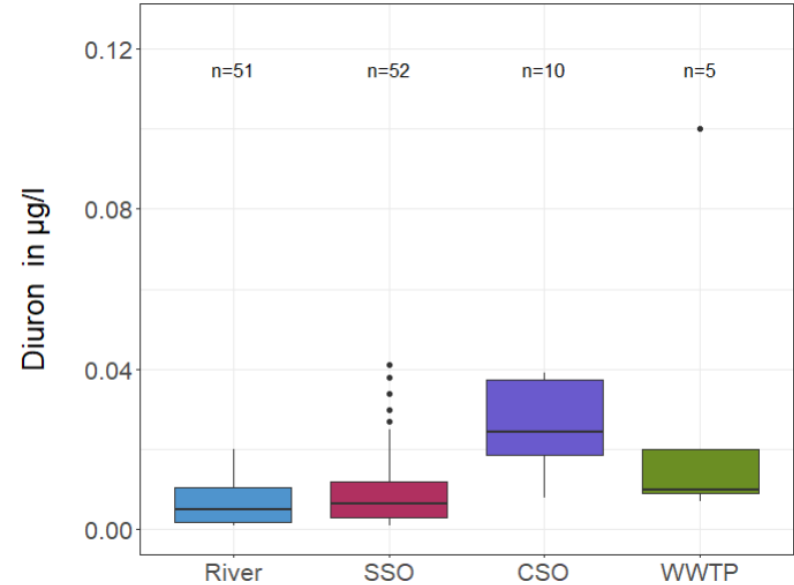
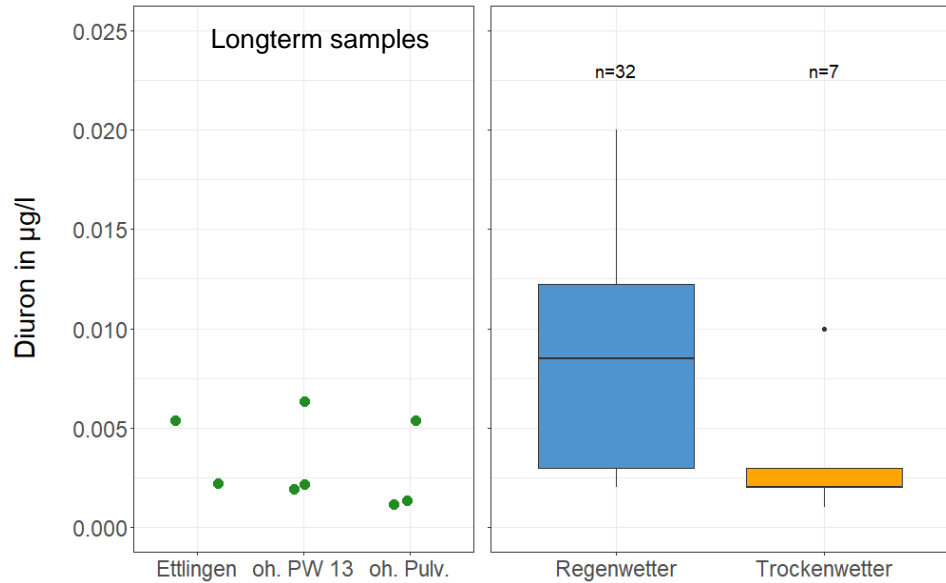
	River	SSO	CSO	WWTP
Terbutryn (Median) [$\mu\text{g/l}$]	0,008	0,015	0,05	0,041

Seasonal patterns - Terbutryn



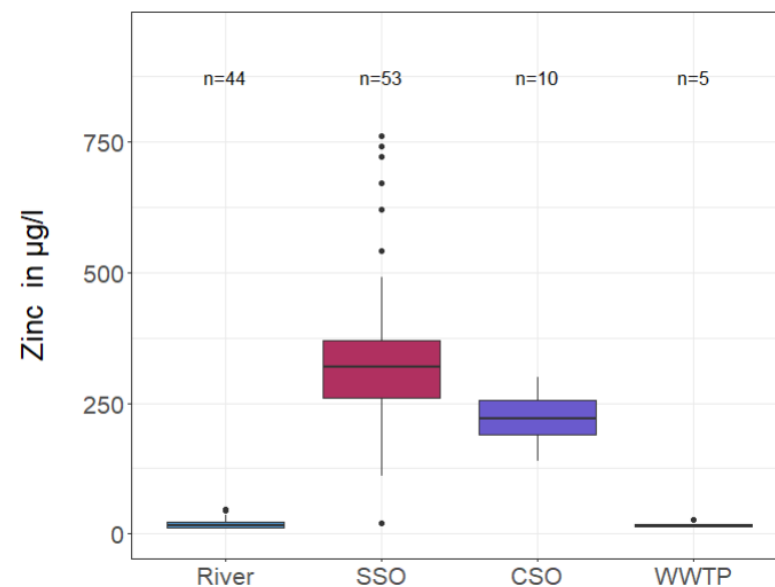
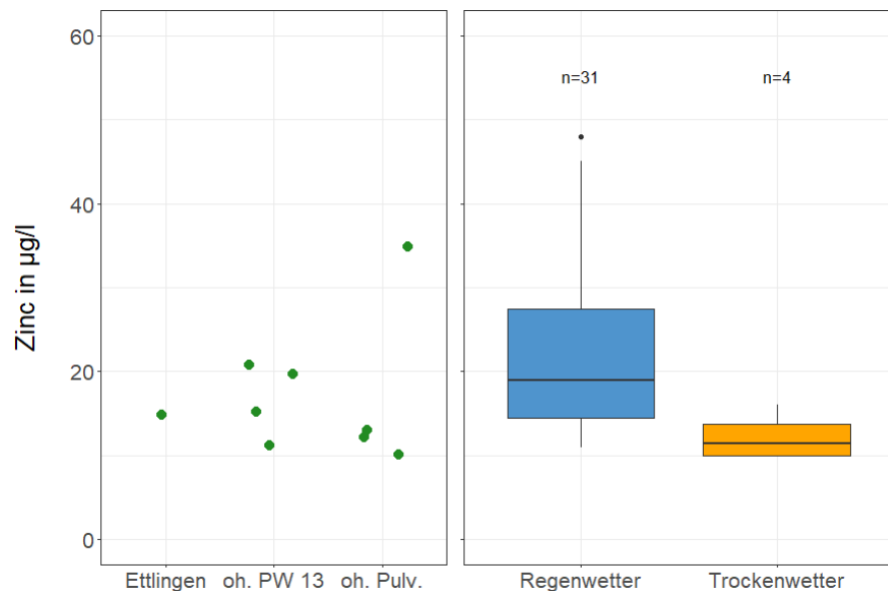
- Increased release from surfaces with increased temperatures
- Consistent with findings by Fuchs und Toshovski 2020; Landesanstalt für Umwelt Baden-Württemberg (LUBW) 2023

Emission pathways - Diuron



	River	SSO	CSO	WWTP
Diuron (Median) [µg/l]	0,005	0,0065	0,025	0,01

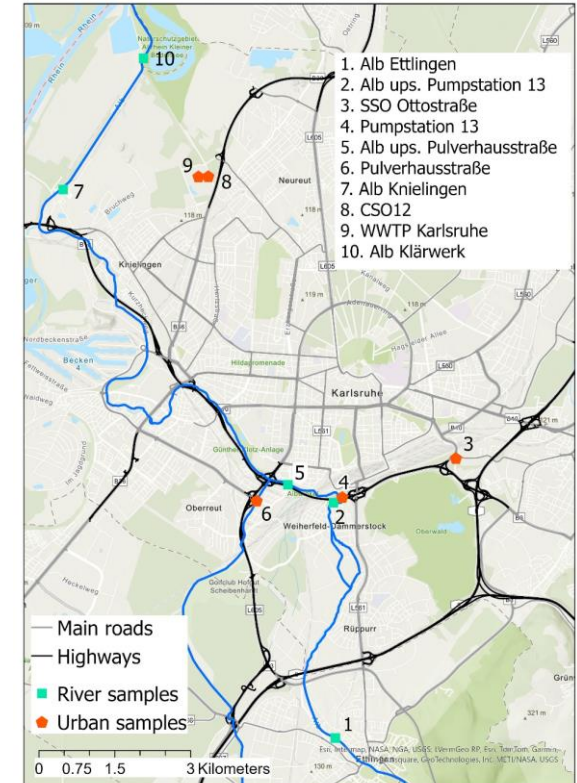
Emission pathways - Zinc



	River	SSO	CSO	WWTP
Zinc (Median) [µg/l]	16	320	220	17

Estimating annual loads

- Alb Ettlingen (upstream of Karlsruhe)
 - Pumpstation 13 and Pulverhausstraße (SSO/street runoff)
 - CSO12
 - Σ 65 intersections within Karlsruhe (excl. CSO12)
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- Alb Ettlingen: total yearly runoff from the official gauge (2022)
 - CSO12: measured yearly overflow volume (2019 – 2022)
 - Urban intersections: effective precipitation based on average annual precipitation (721 mm)



Estimating annual loads

Site	Runoff volume [m ³ /a]	Median concentration [µg/l]				
		Imidacloprid	Carbamazepin	Terbutryn	Diuron	Zinc
Alb Ettlingen	56.692.271	0,003	0,0365	0,008	0,007	16
Pumpstation 13	229.033	-	-	0,014	0,008	250
Pulverhaus- straße	8.026	-	-	0,002	0,002	355
CSO12	1.196.665	0,004	0,14	0,05	0,0245	220
∑ 65 inter- sections *	1.787.964	-	-	0,015	0,0065	320

* median concentrations of all SSO samples

Estimating annual loads

Site	Estimated loads in g/a				.. and kg/a
	Imidacloprid	Carbamazepin	Terbutryn	Diuron	Zinc
Alb Ettlingen	170	2.069	454	397	907
Pumpstation 13			3,2	1,8	57
Pulverhaus- straße			0,016	0,016	2,8
CSO12	4,8	168	60	29	263
∑ 65 inter- sections			27	11,6	572

Summary & Recommendations

WWTP	CSO	SSO
Primary source of pharmaceuticals & some biocides (Imidacloprid)	Highest concentrations for multiple biocides (e.g. Terbutryn)	Highest concentrations and emissions of heavy metals
	Relevant source for metals & pharmaceuticals	Source for material preservatives, but less pronounced

- Homogenized composite samples: easier, reduced cost and mistakes during sample treatment
- Prioritizing longer sampling campaigns enables capturing variability and seasonal differences
- Coupling sites with robust hydrological/background information → estimating loads

Thank you!



References

- Fuchs, Stephan; Kaiser, Maria; Kiemle, Lisa; Kittlaus, Steffen; Rothvoß, Shari; Toshovski, Snezhina et al. (2017): Modeling of Regionalized Emissions (MoRE) into Water Bodies: An Open-Source River Basin Management System. In: *Water* 9 (4), S. 239. DOI: 10.3390/w9040239.
- Fuchs, Stephan; Toshovski, Snezhina (2020): Belastung der Umwelt mit Bioziden realistischer erfassen - Schwerpunkt Einträge über Kläranlagen.
- Landesanstalt für Umwelt Baden-Württemberg (LUBW) (2023): Spurenstoffinventar der Fließgewässer in Baden-Württemberg. Ergebnisse der Untersuchung von Fließgewässern 2013 - 2021. Hg. v. Landesanstalt für Umwelt Baden-Württemberg (LUBW).
- Nickel, Jan Philip; Fuchs, Stephan (2021): Large-Volume Samplers for Efficient Composite Sampling and Particle Characterization in Sewer Systems. In: *Water* 13 (20), S. 2831. DOI: 10.3390/w13202831
- Umweltbundesamt (2020): Einträge von Nähr- und Schadstoffen in die Oberflächengewässer. <https://www.umweltbundesamt.de/daten/wasser/fliessgewaesser/eintraege-von-naehr-schadstoffen-in-die#nahrstoffeintrage-sinken-wieder-langsam>