

# Dynamics of mixture effects and causative chemicals during rain events in rivers in agricultural and urban areas

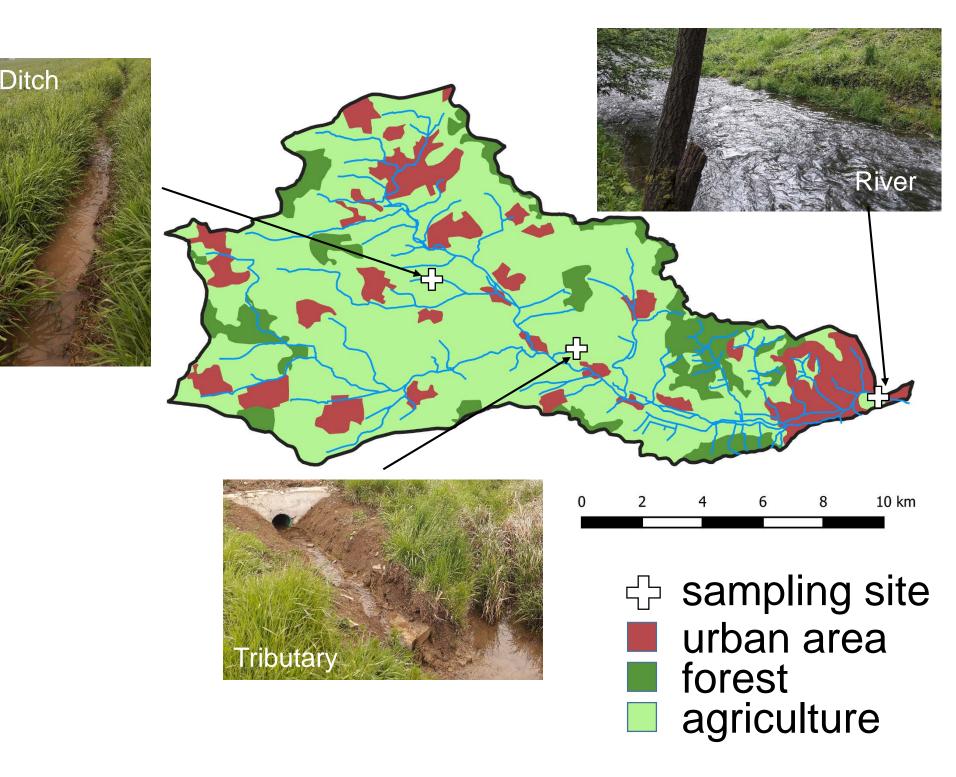
Christiane Zarfl<sup>1</sup>, Claudia Adolphi<sup>1</sup>, Niklas Best<sup>1</sup>, Rosa Degenhardt<sup>1</sup>, Lisa Glauch<sup>2</sup>, Maria König<sup>2</sup>,Rita Schlichting<sup>2</sup>, Marc Schwientek<sup>1</sup>, Martina Werneburg<sup>1</sup>, Christian Zwiener<sup>1</sup>, Beate I. Escher<sup>1,2</sup>

<sup>1</sup> Eberhard Karls Universität Tübingen; <sup>2</sup> UFZ – Helmholtz Center for Environmental Research Leipzig

#### Background

- Rivers integrate pollutant emissions and processes of the whole catchment
- Rivers receive broad spectrum of pollutants via direct and indirect inputs
- During rain events, fast runoff components from agriculture and sealed surfaces of urban areas are additional input sources

#### Study site

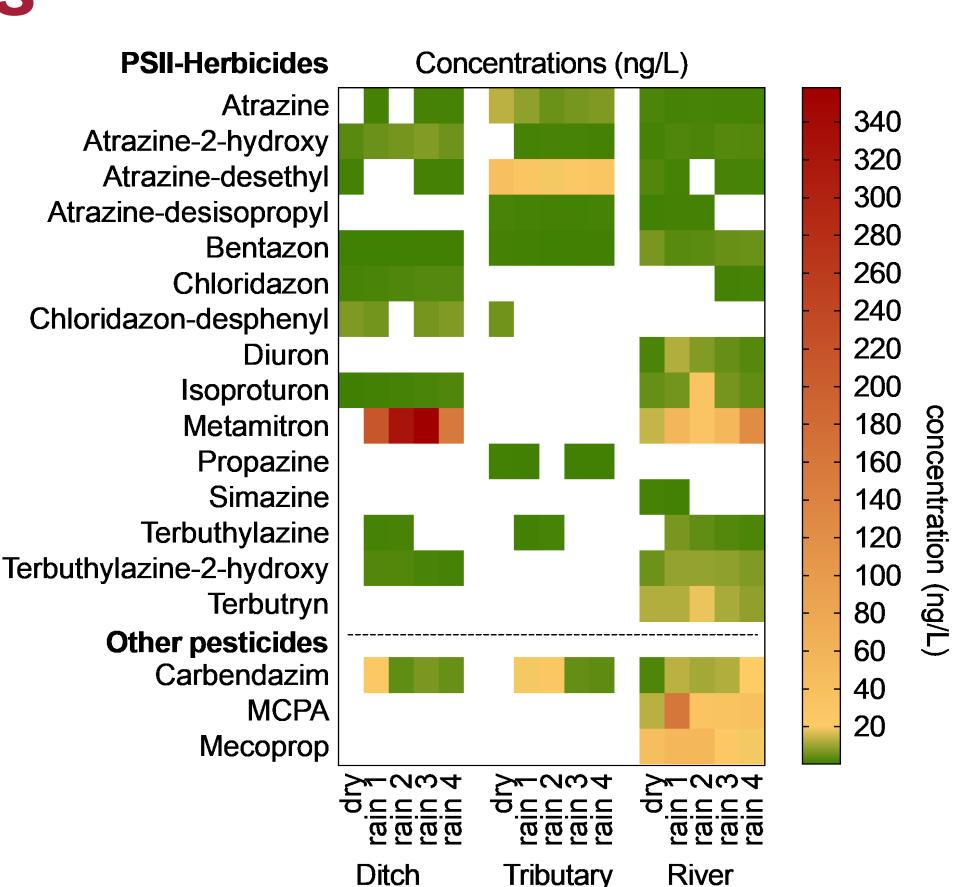


#### Approach

- Grab samples taken in the Ammer river basin, Germany, on four consecutive days ("rain 1" to "rain 4") following a moderate rain event, with a reference sample drawn after a longer dry spell (sample "dry")
- Samples enriched by solid phase extraction
- 51 Pesticides quantified with liquid chromatography and tandem mass spectrometry
  - Bioassays: combined algae assay, oxidative stress response (AREc32), activation of estrogen receptor (ERa), arylhydrocarbon receptor (AhR) and PPARg expressed as effect concentrations EC10

## Pesticide dynamics

- Large dynamics in the ditch: Metamitron (lesser, carbendazim) introduced by rain
- Uneventful tributary: low levels and low dynamics; carbendazim same pattern as ditch
- River shows footprint of upstream WWTP and urban impact (diuron, MCPA, mecoprop)

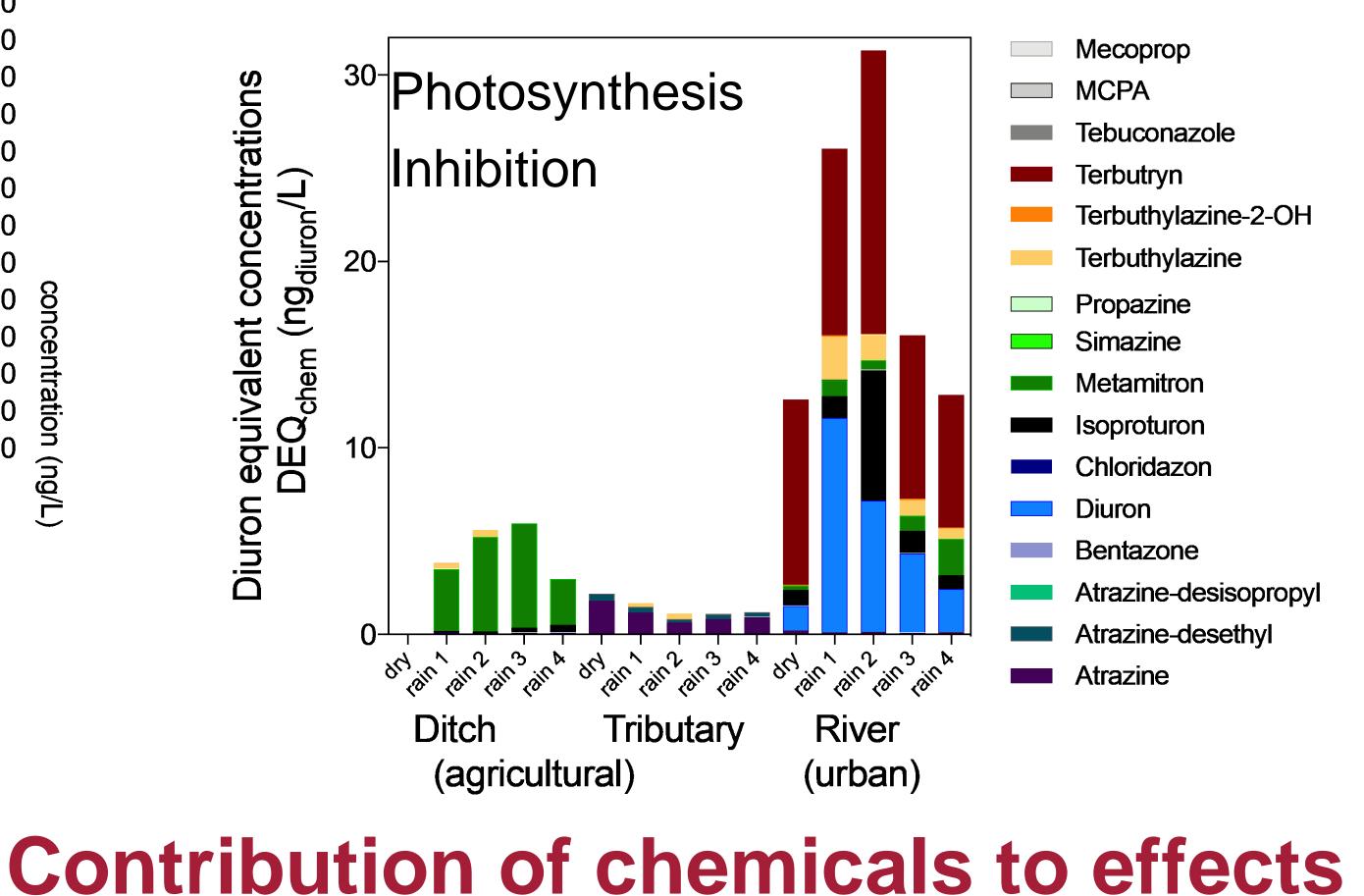


(agricultural)

#### **Algal toxicity**

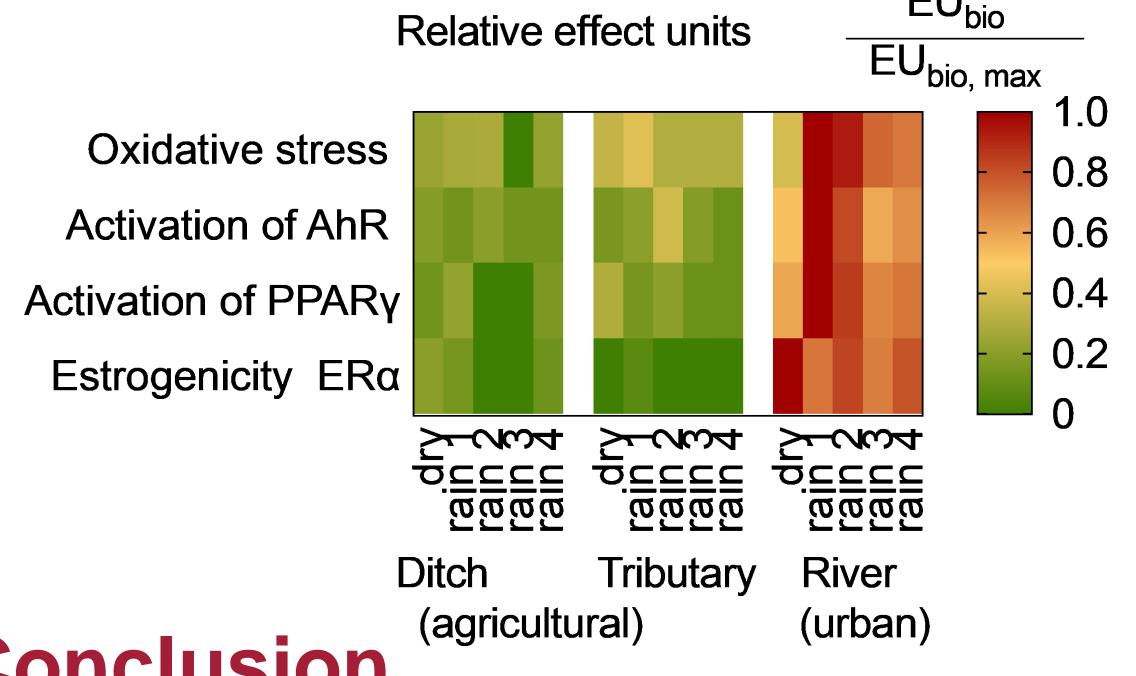
herbicides

Algal toxicity dominated by PSII herbicides



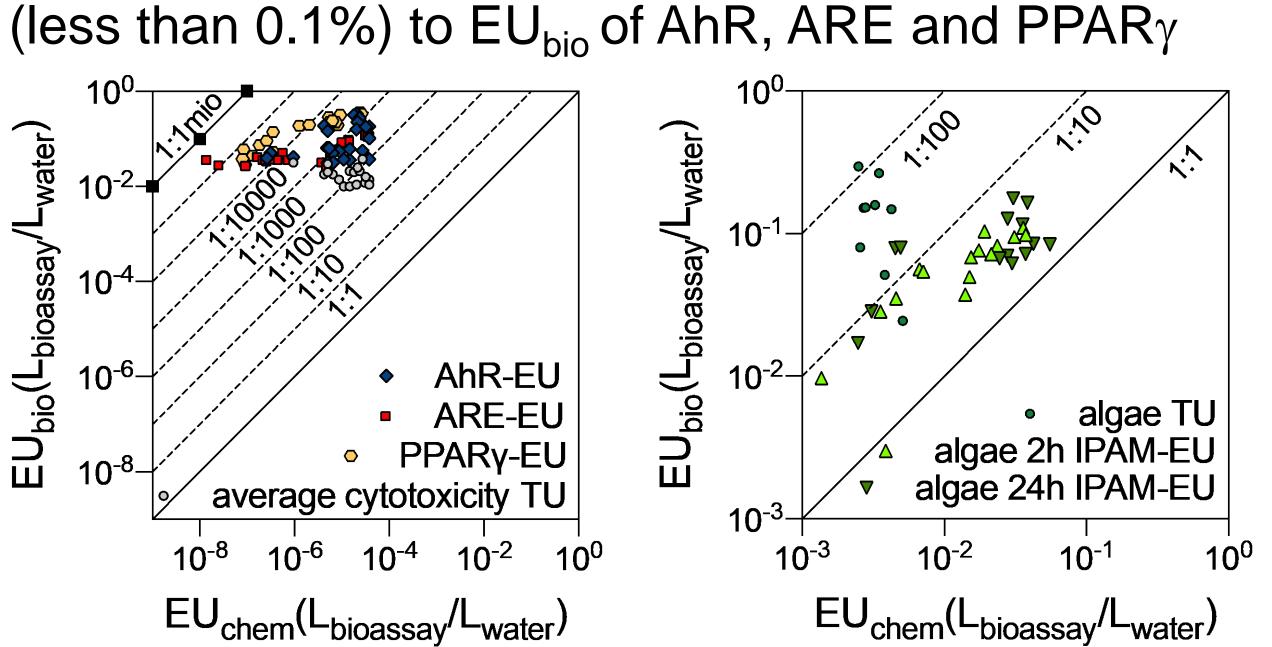
# Other biological effects

- All biological endpoints were highest in river
  - Estrogenicity (mainly from WWTP) highest @ dry weather
  - All other endpoints impacted by rain event
- No dynamics by rain in agriculturally influenced sites



# Effect Units $EU_{bio} = \frac{1}{EC10_{sample}}$ $EU_{chem} = \sum_{i=1}^{C_i} \frac{C_i}{EC_i}$

(urban)



Up to 30% of algal toxicity EU<sub>bio</sub> explained by detected

Detected pesticides contributed to a very small fraction

#### Conclusion

Moderate rain events led to substantial increase in individual pesticides' concentrations almost without changing the non-specific toxicity and modes of action that are not necessarily associated to pesticides (AhR, ER) but had a influence on algal toxicity when there was additional input of herbicides

## Acknowledgements

This work was supported by the Collaborative Research Centre 1253 CAMPOS funded by the German Research Foundation (DFG, SFB 1253/1 20147). The bioassays were performed with the robotic platform CITEPro (Chemicals in the Environment Profiler) funded by the Helmholtz Association







