Identifying Key Pathways of Priority Trace Chemicals in the Danube River Basin

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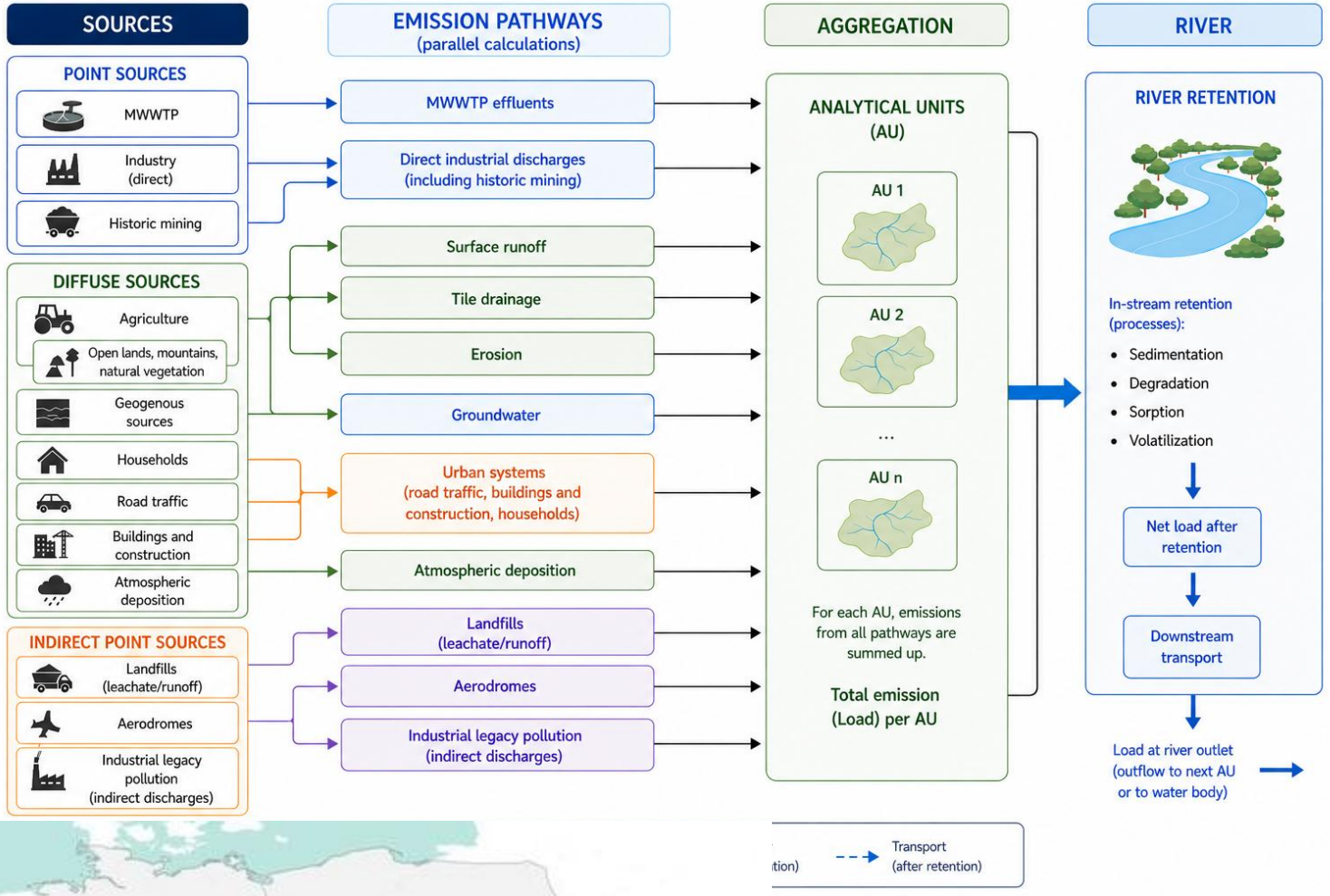
Outline

1. Model structure & input data
2. Model validation
3. Identified emission patterns
4. Outlook: risk analysis

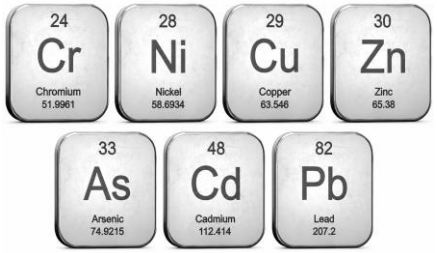
1. **Model structure & input data**
2. Model validation
3. Identified emission patterns
4. Outlook: risk analysis



1727 analytical units
(Visulaization: 52 subbasins)

Temporal coverage: 2015-2020

Cr, Ni, Cu, Zn, As



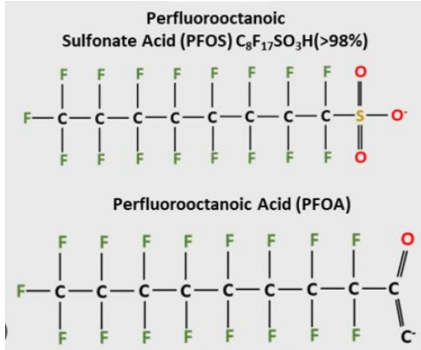
Cd & Pb

- **Dicplophenac (DCF)**

and Carbamazepine (CBZ)

PFOS,

PFOA



Literature data (outside DRB) | Pilot measurements within DRB | Regional dataset | Country dataset | Modelled data

RIVER BASINS

Process	Heavy metals	Pharma	PFAS
Erosion	✓	✗	✓
Surface Runoff	✓	✗	✓
Tile drainage	✓	✗	✓
Urban emission	✓	✓	✓
Groundwater	✓	✗	✓
Atmospheric dep.	✓	✗	✓
Atmospheric dep. - hot spot	✓	✗	✓
Point source - communal	✓	✓	✓
Point source - industrial	✓	✓	✓
Industrial diffuse hot-spots	✓	✗	✓
Landfills	✓	✓	✓
Aerodromes and other fire fighting centres	✗	✗	✓

Point sources data

Industrial emissions to water

IEPR database (2007-2023)

10.445 facilities

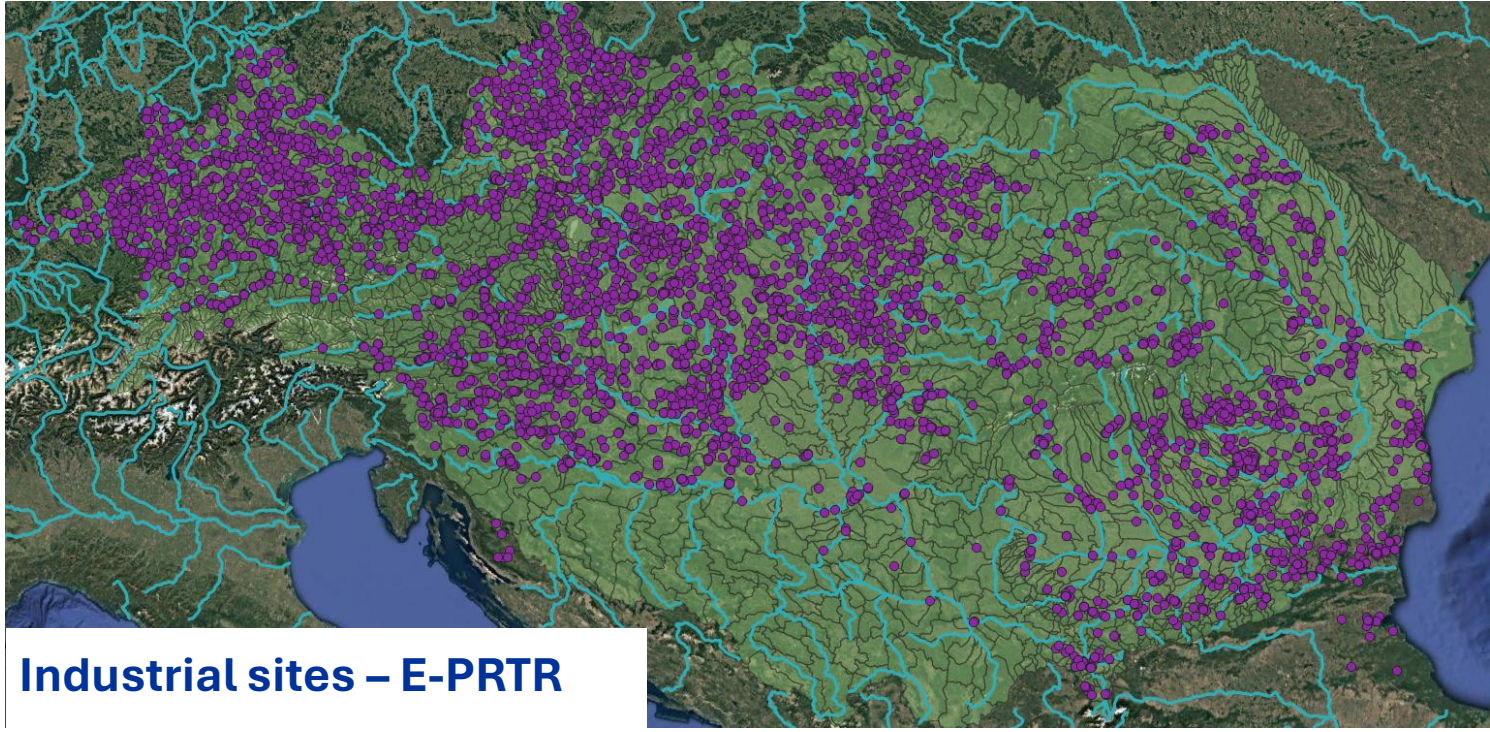
Municipal sewage emissions

ICPDR + EEA UWWTD databases
(2016 /2018 + 2016 – 2020)

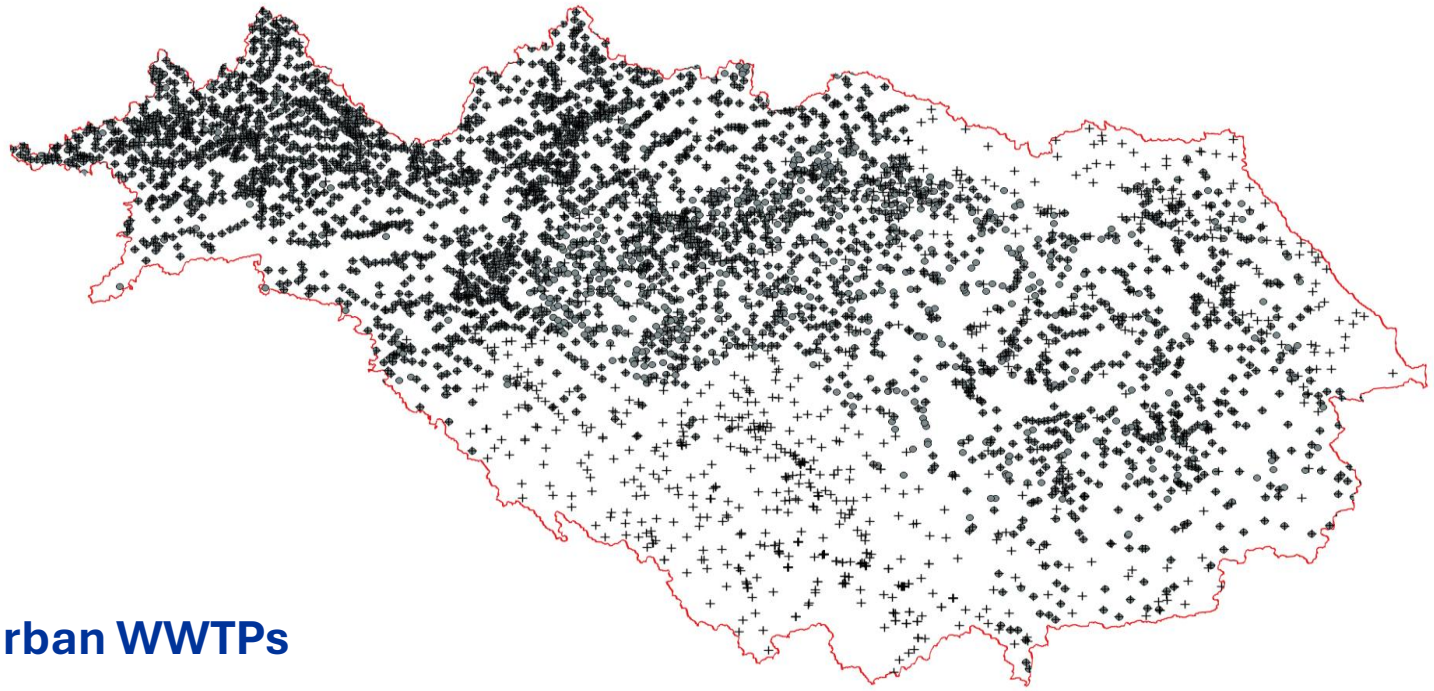
4215 plants

Total load: 68 million PE

Total discharge:
4.6 billion m^3/year = 147 m^3/s

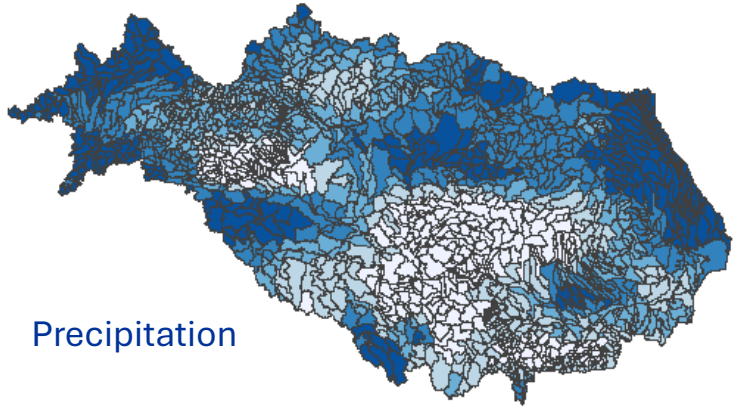


Industrial sites – E-PRTR

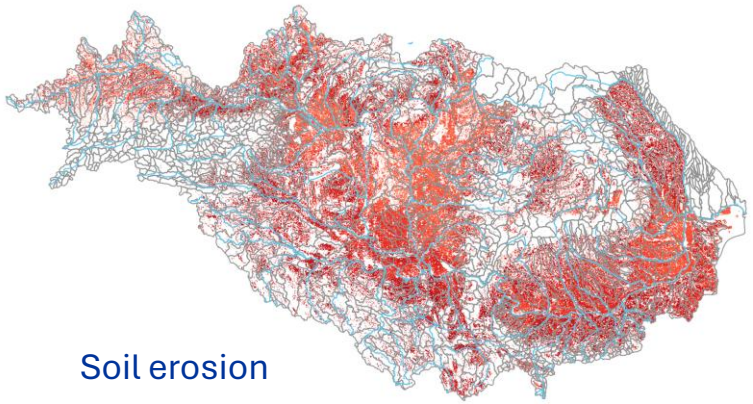


Urban WWTPs

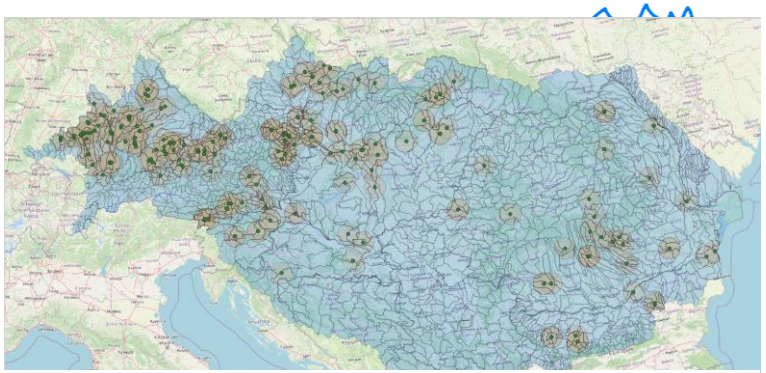
Diffuse source data



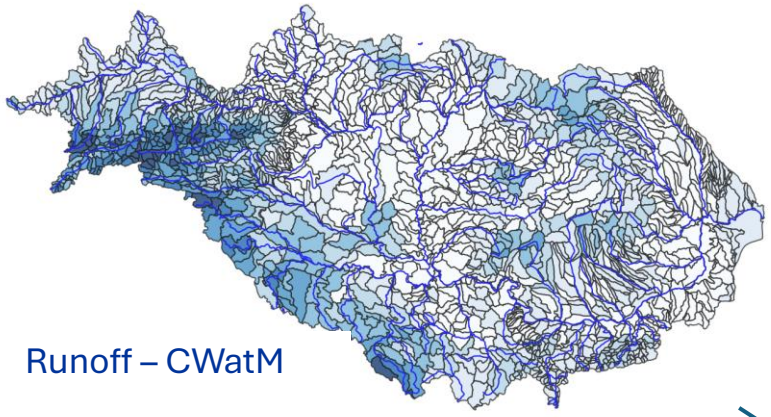
Precipitation



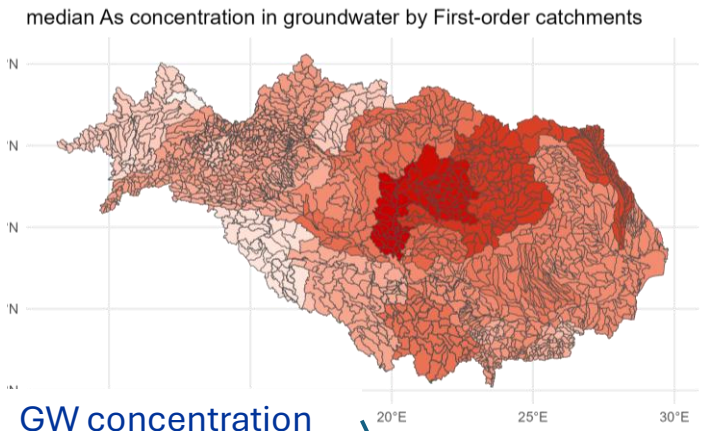
Soil erosion



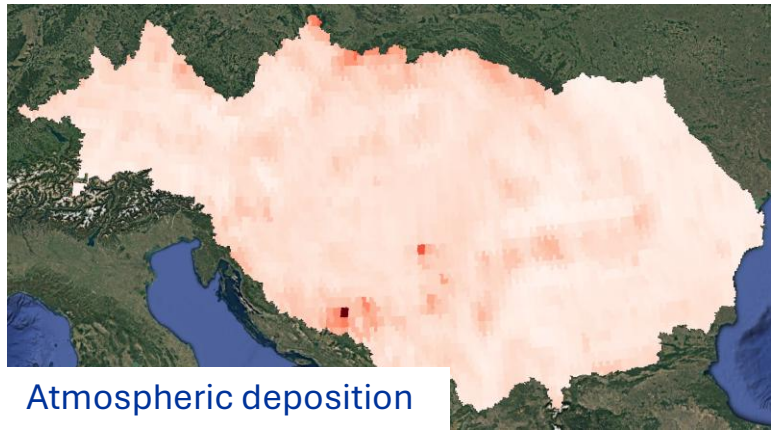
Industrial hot-spot atmospheric deposition



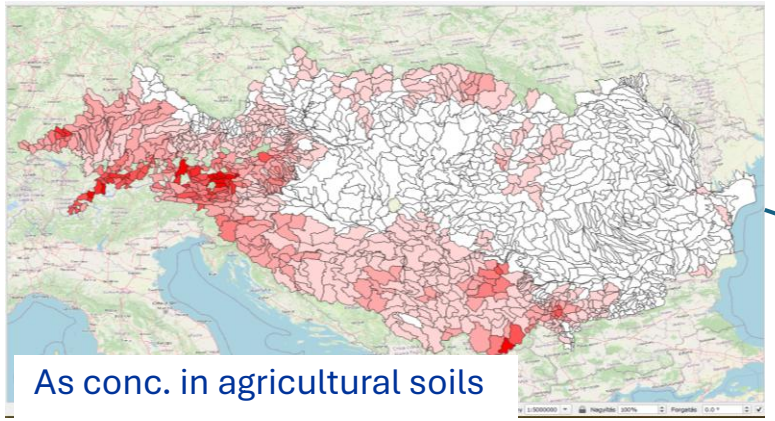
Runoff – CWatM



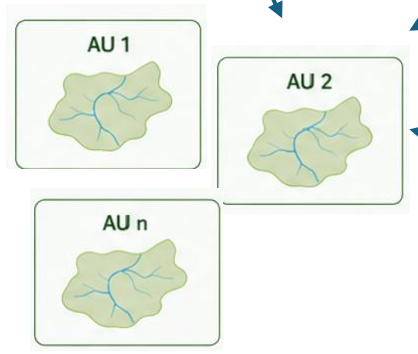
GW concentration

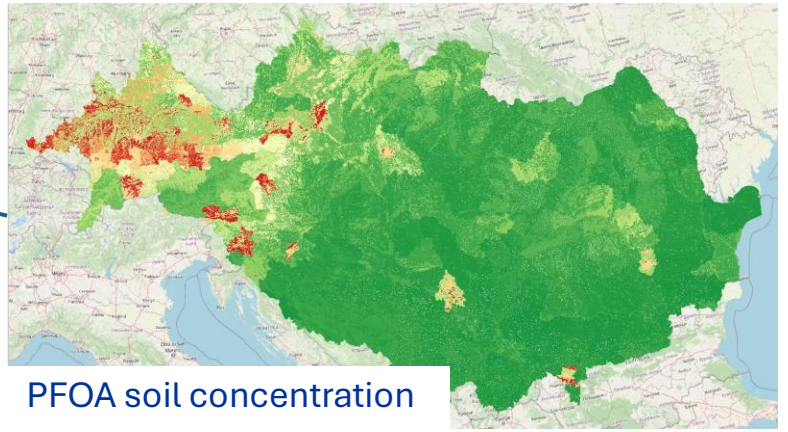


Atmospheric deposition



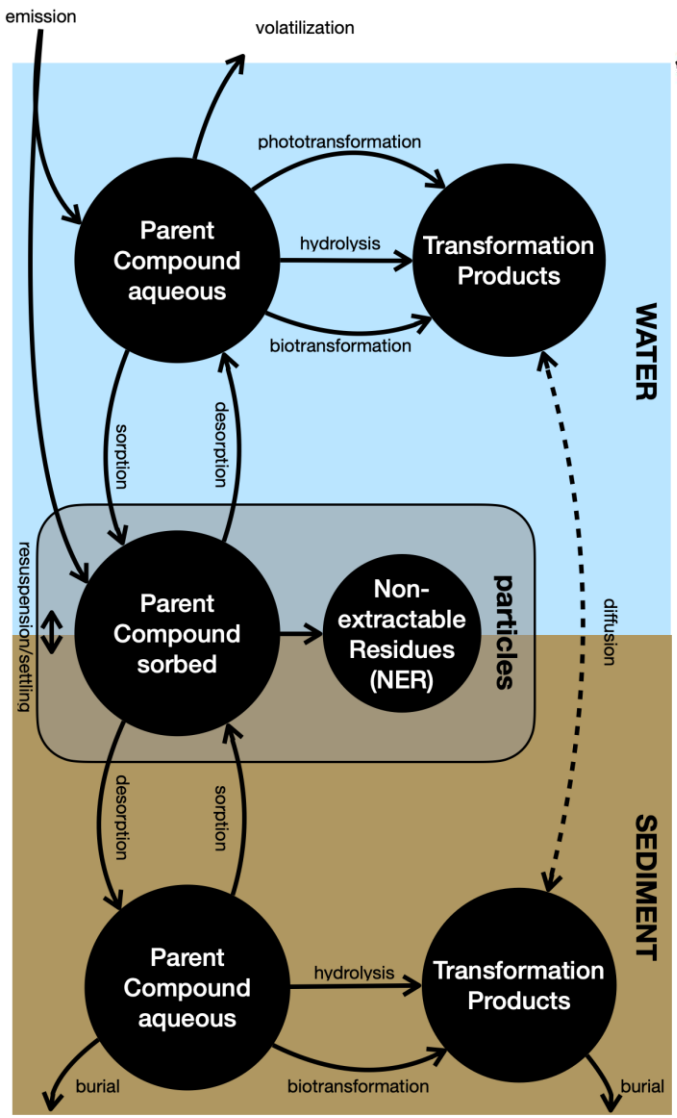
As conc. in agricultural soils

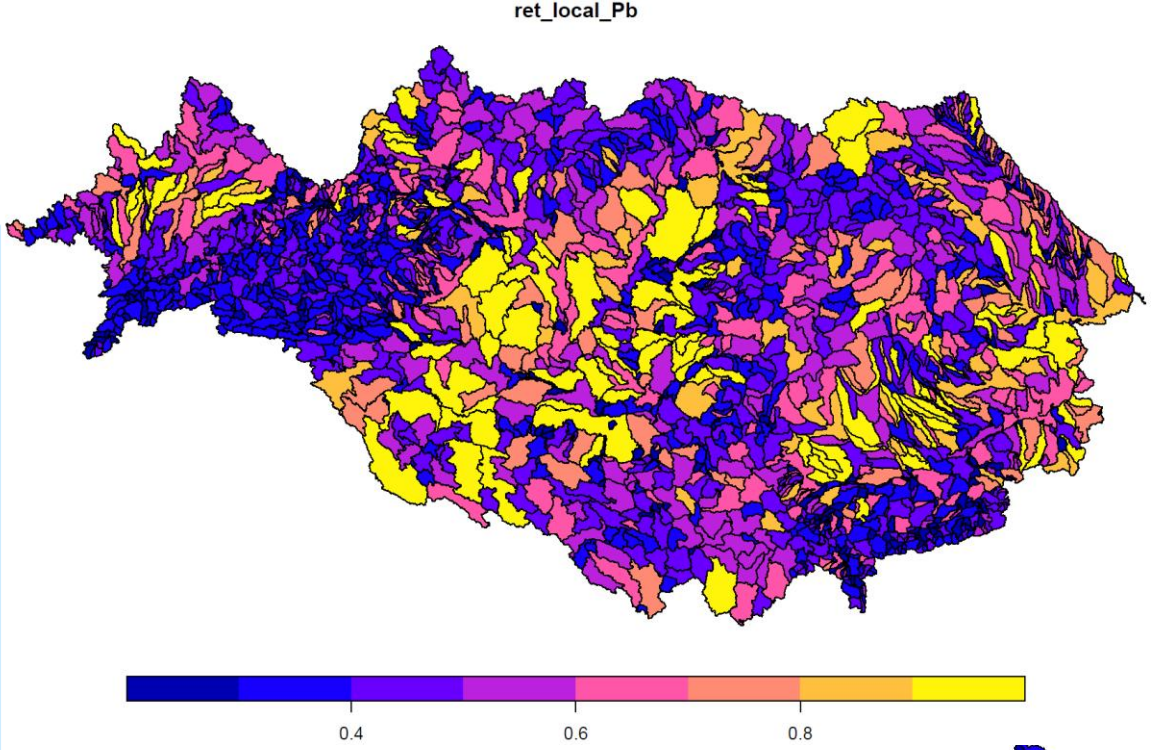


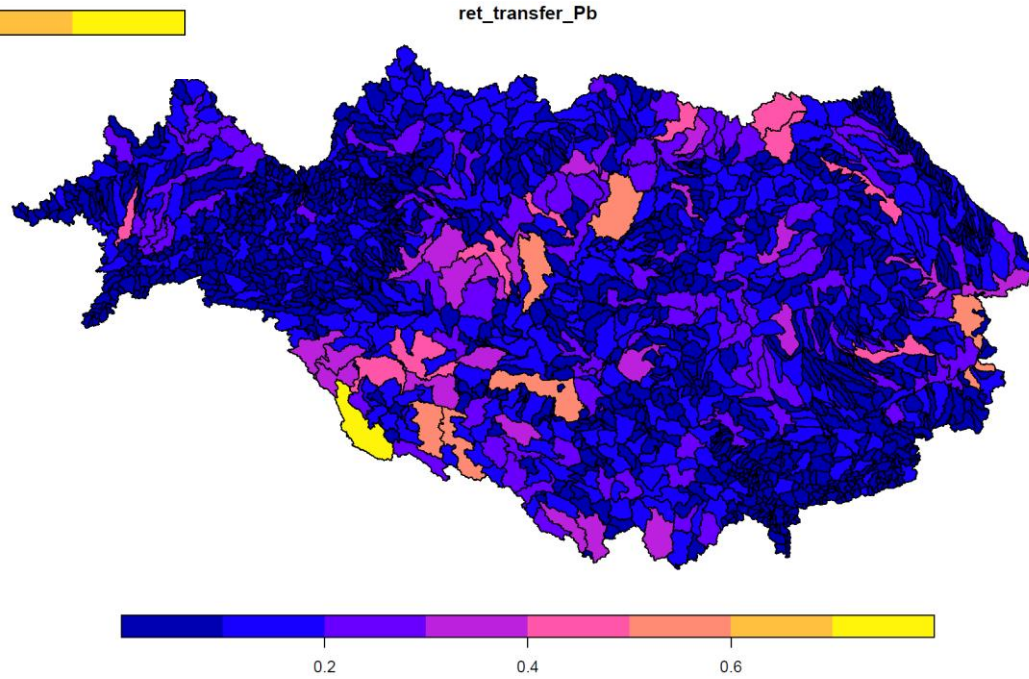


PFOA soil concentration

Retention of HM







1. Model structure & input data
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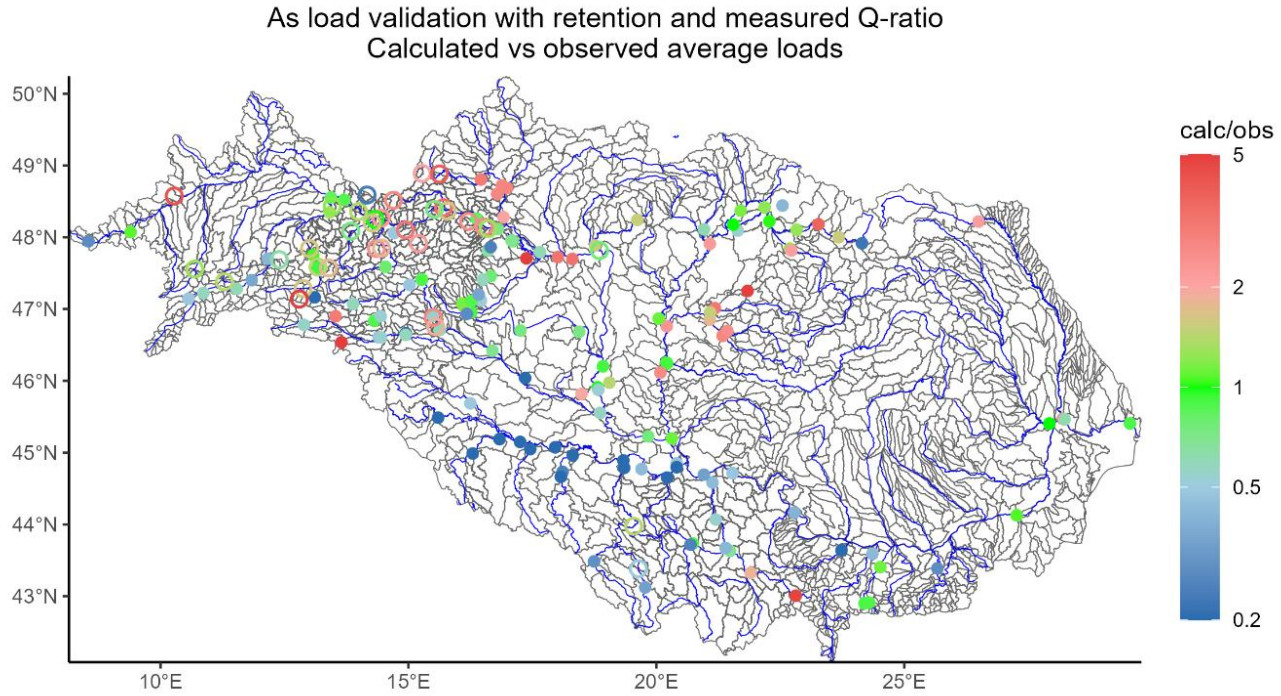
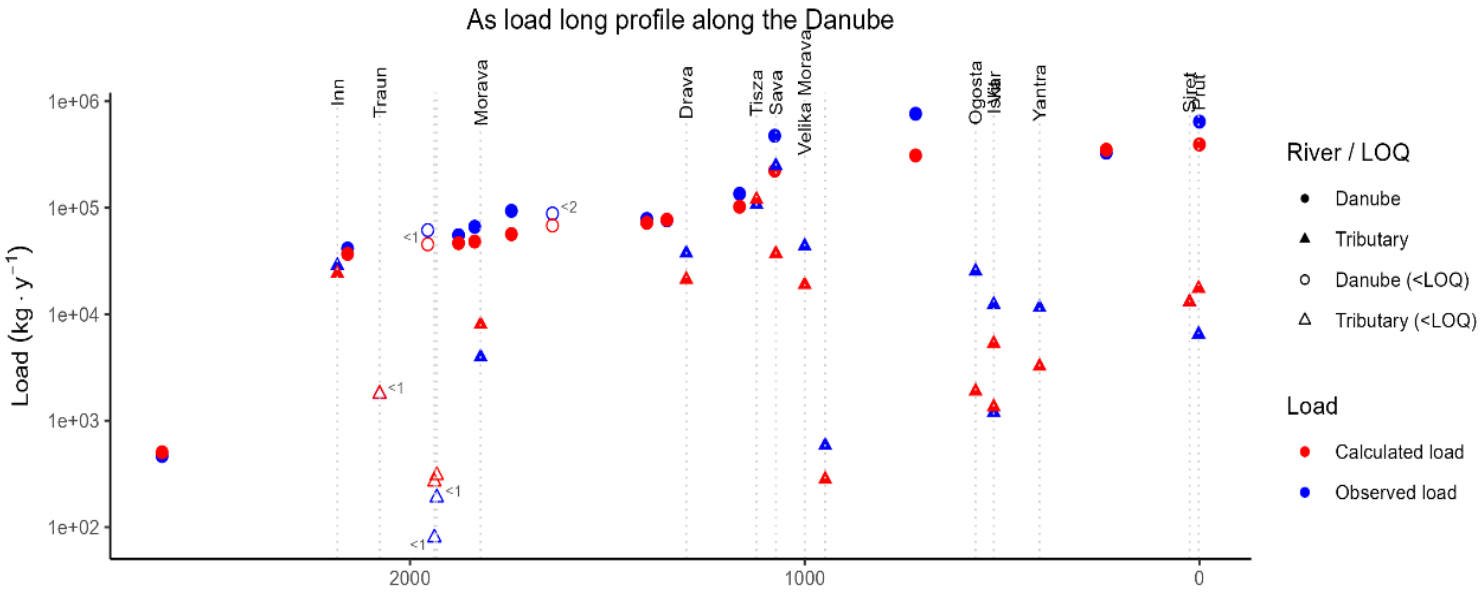
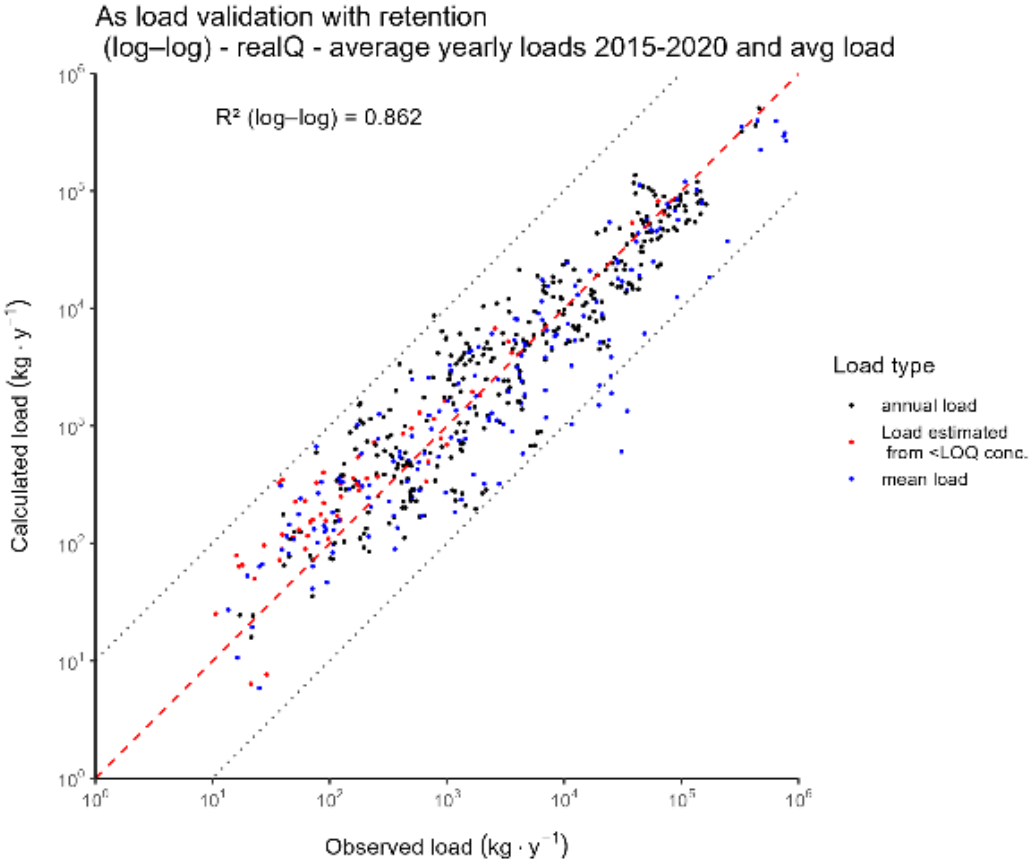
Validation of **As** – (relatively) *well* validated

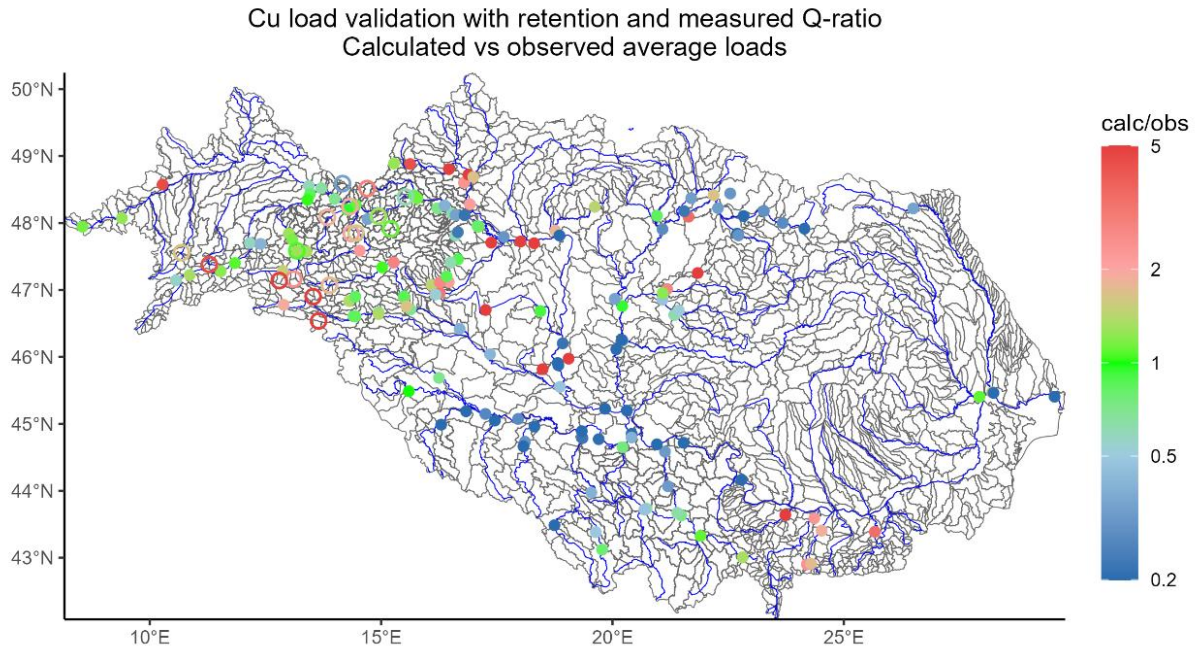


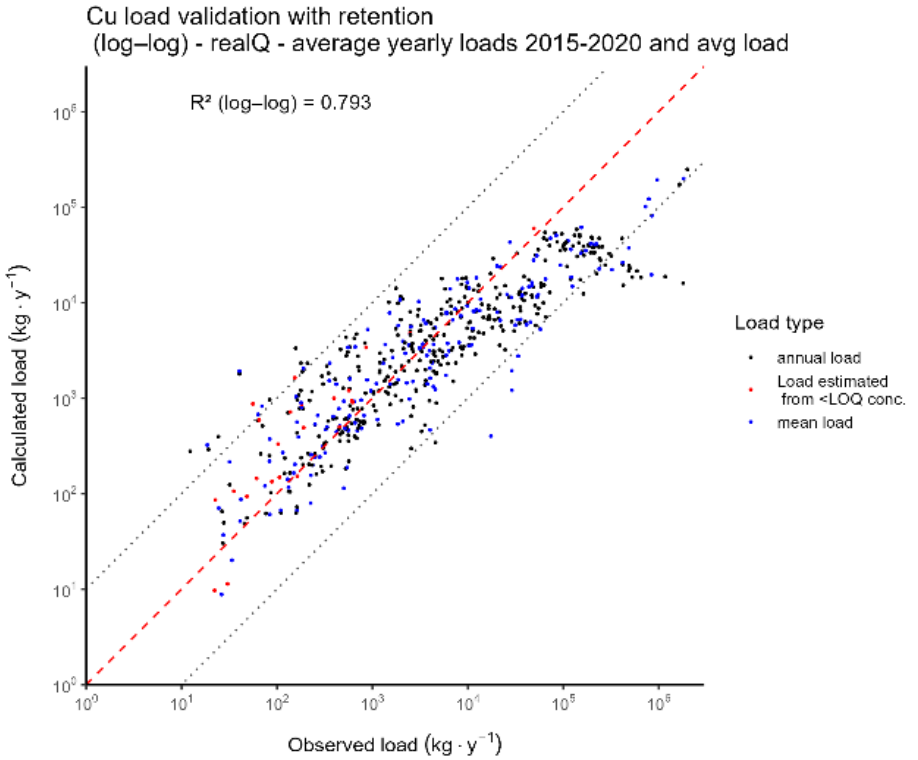


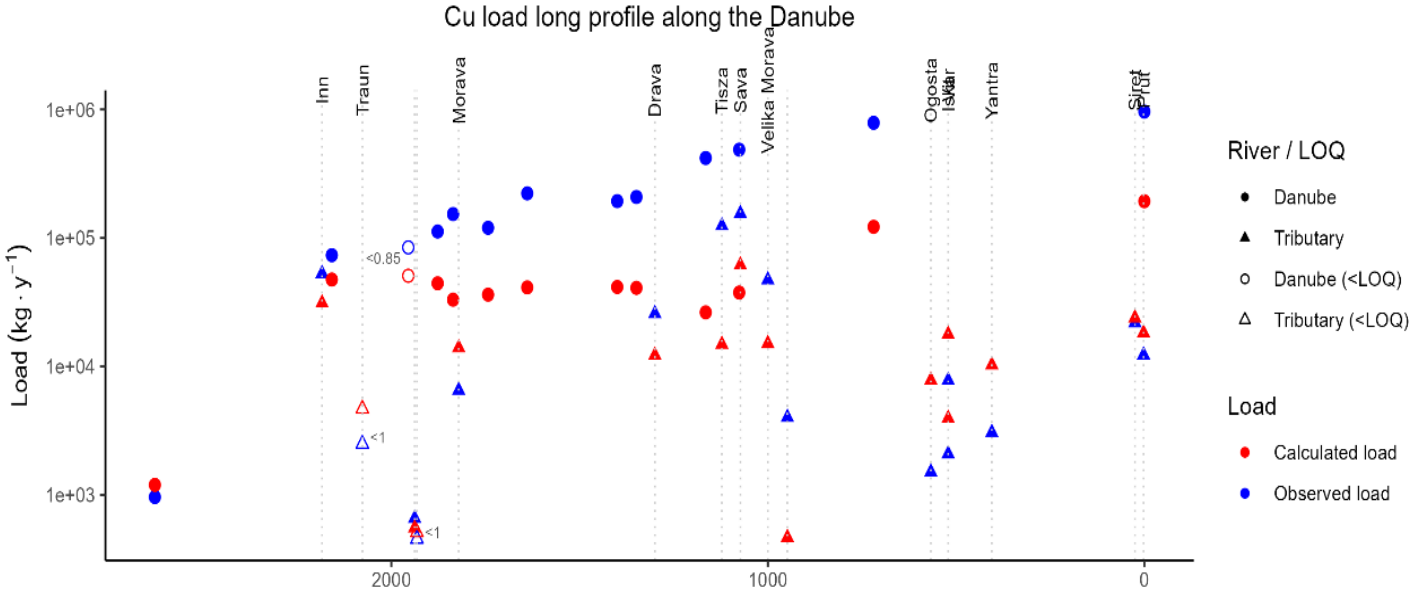


- Clear underestimation of loads in the Sava basin
- Generally good agreement of Danube loads
- Low number of groundwater wells behind derived gw. concentrations are main suspect for the underestimation of loads at Sava and lower Danube tributaries
- Lack of industry data

Validation of **Cu** – the "*worst*" heavy metal

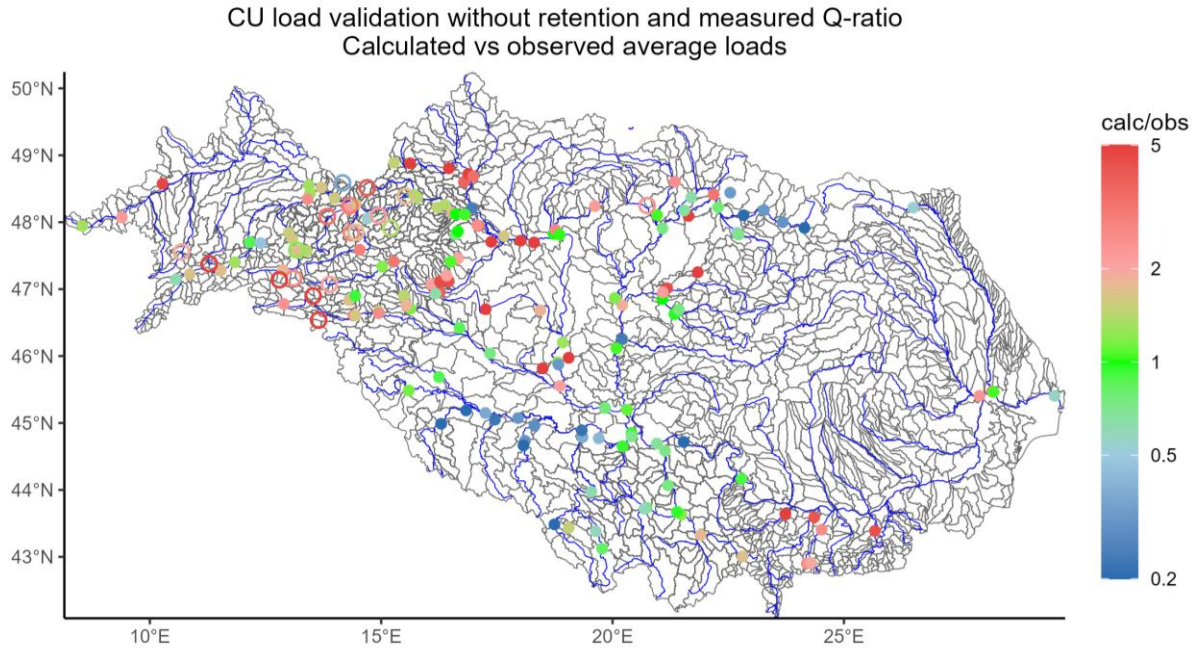


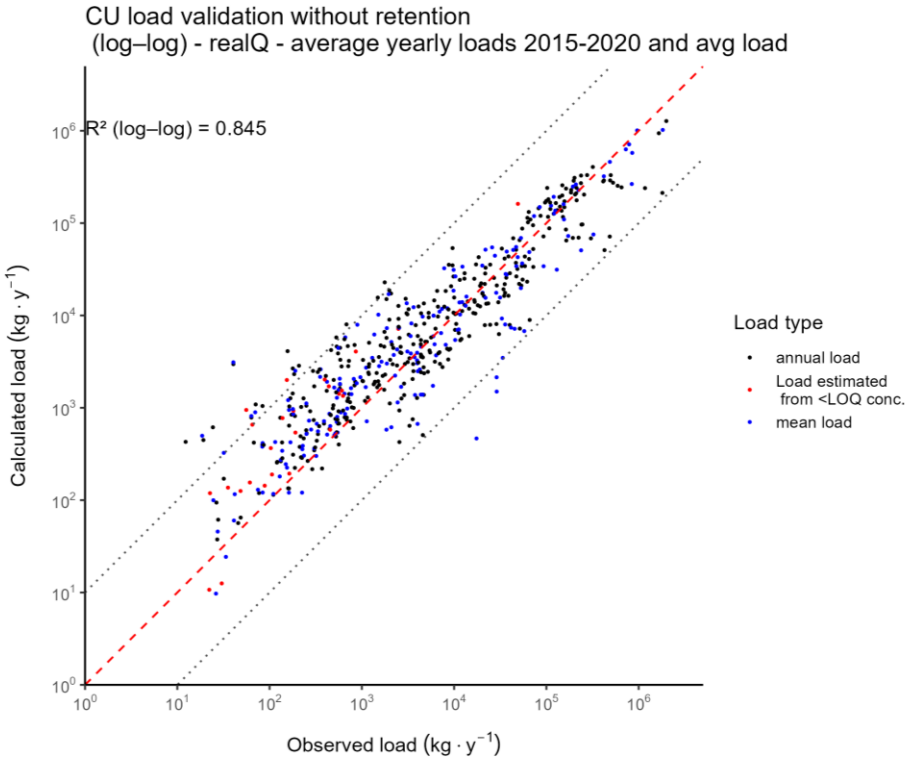


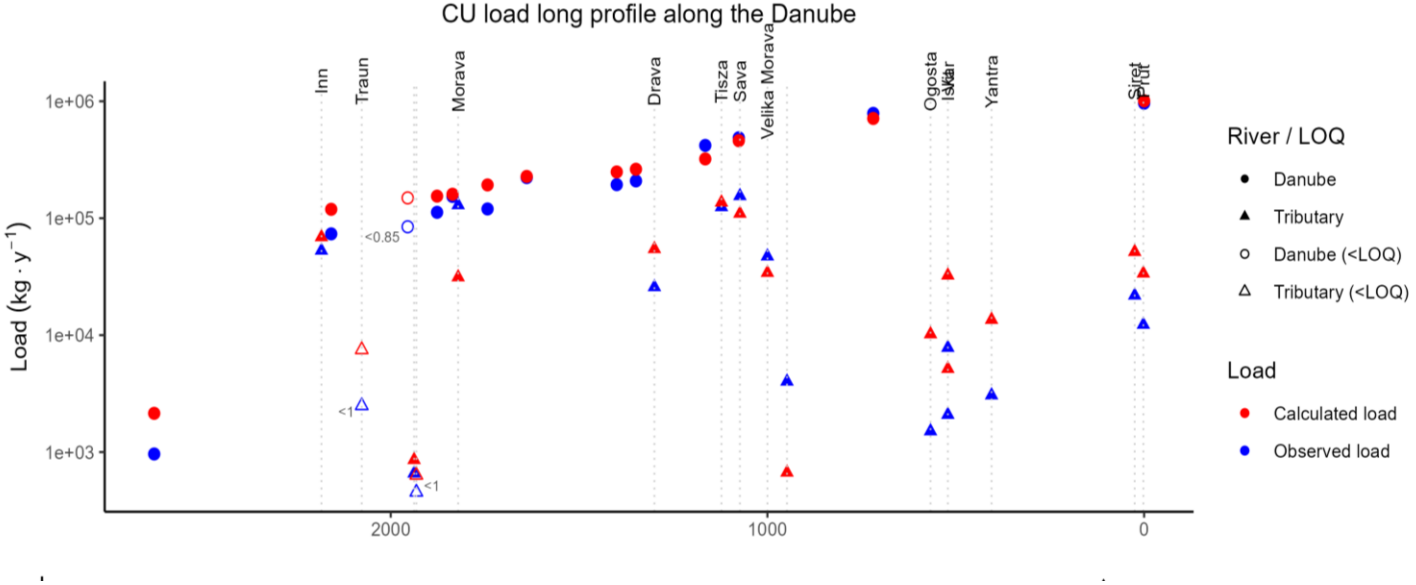


- Clear underestimation of loads in most of the the Sava and Tisza basins
- Strong underestimation of Danube loads
- Lack of industry data → industrial underestimation?
- Orchards/Vinyard soils as hot-spots?

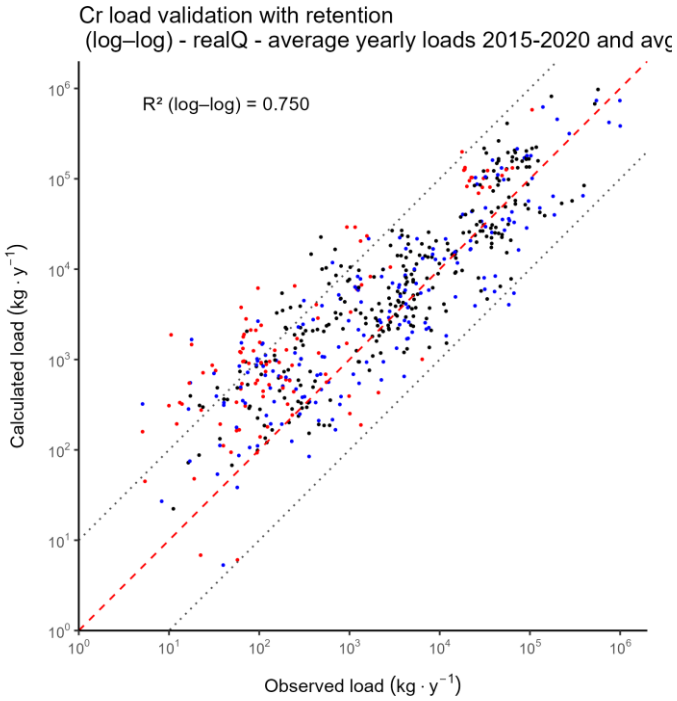
Validation of **Cu** – no retention

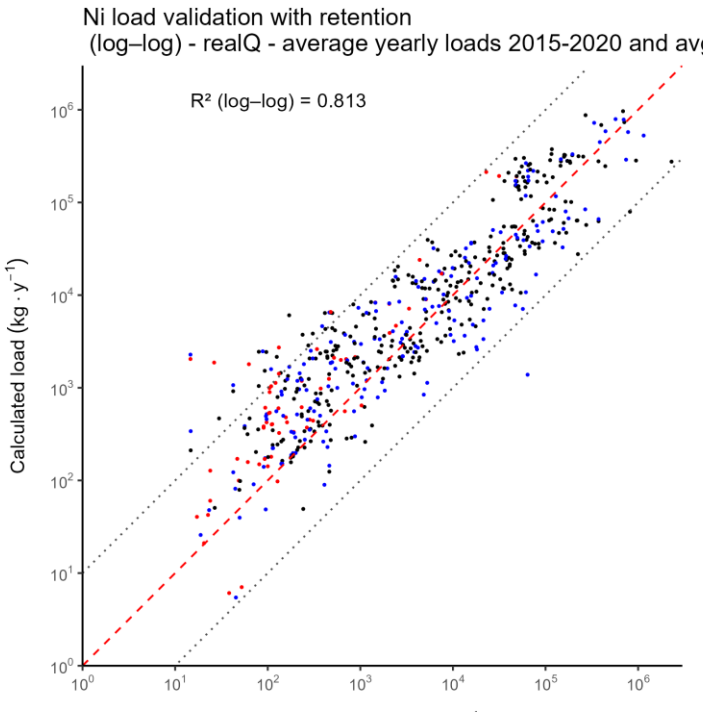


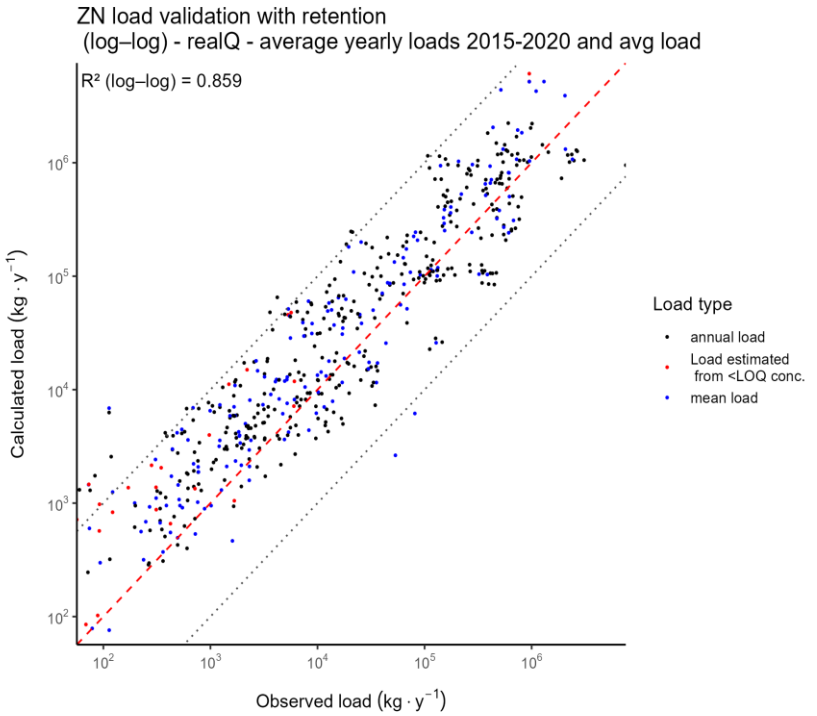


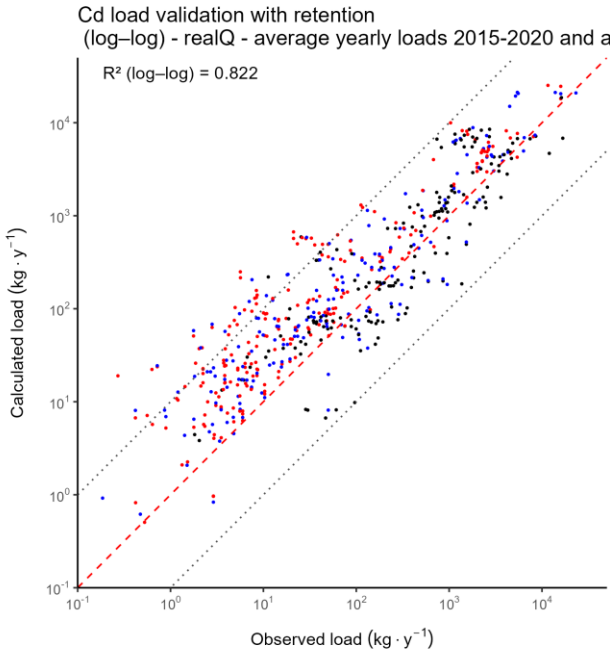


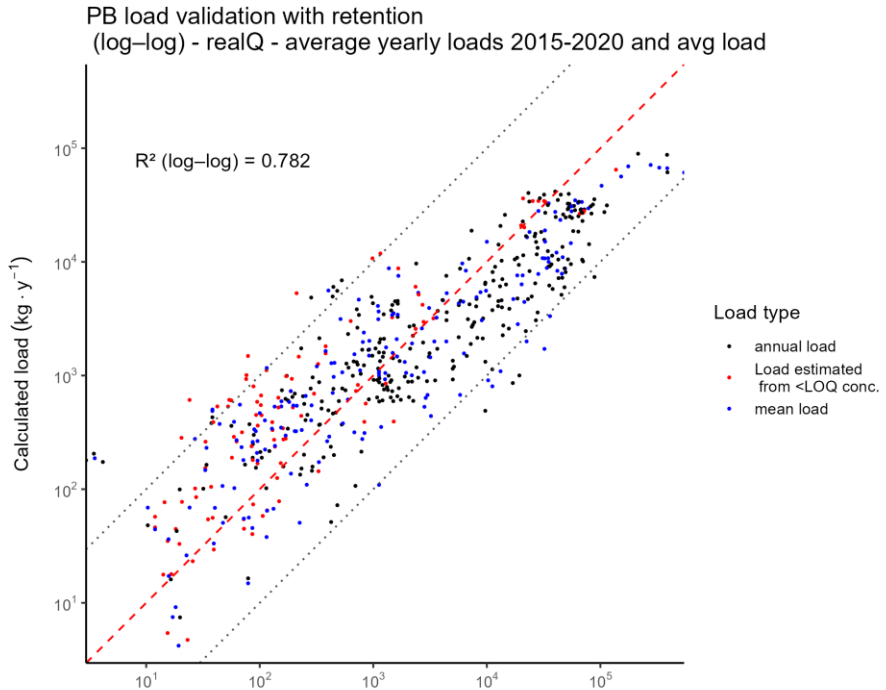
- Much better than with retention
- Mid- and lower Danube OK
- Underestimation in the Balkan region (← missing industrial data?)
- overestimation in the upper basin





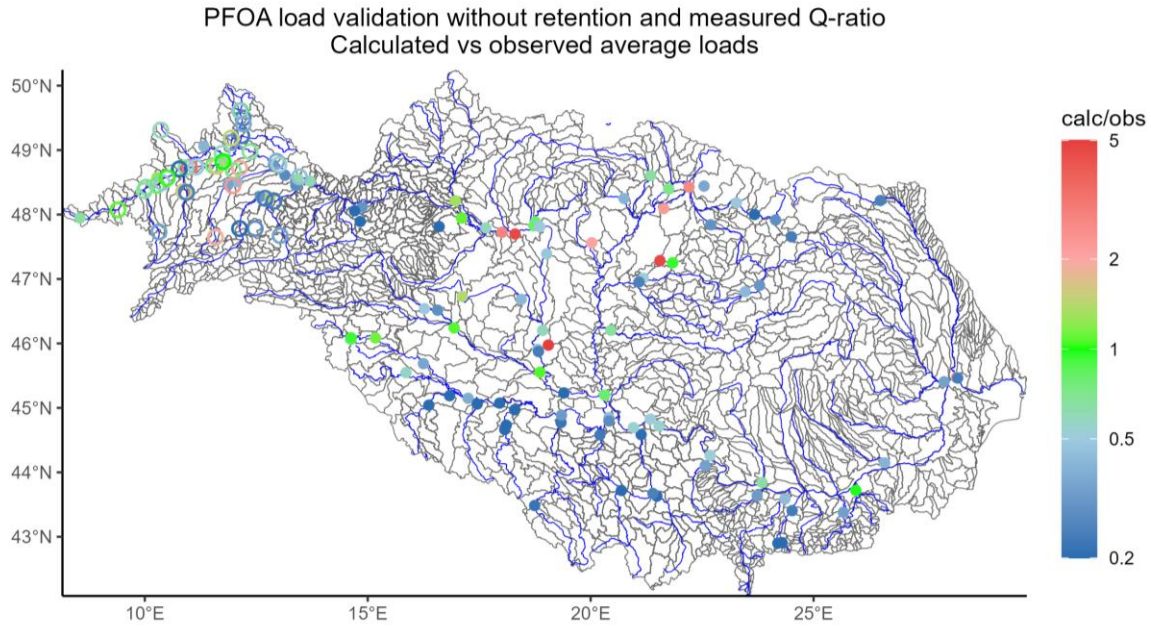


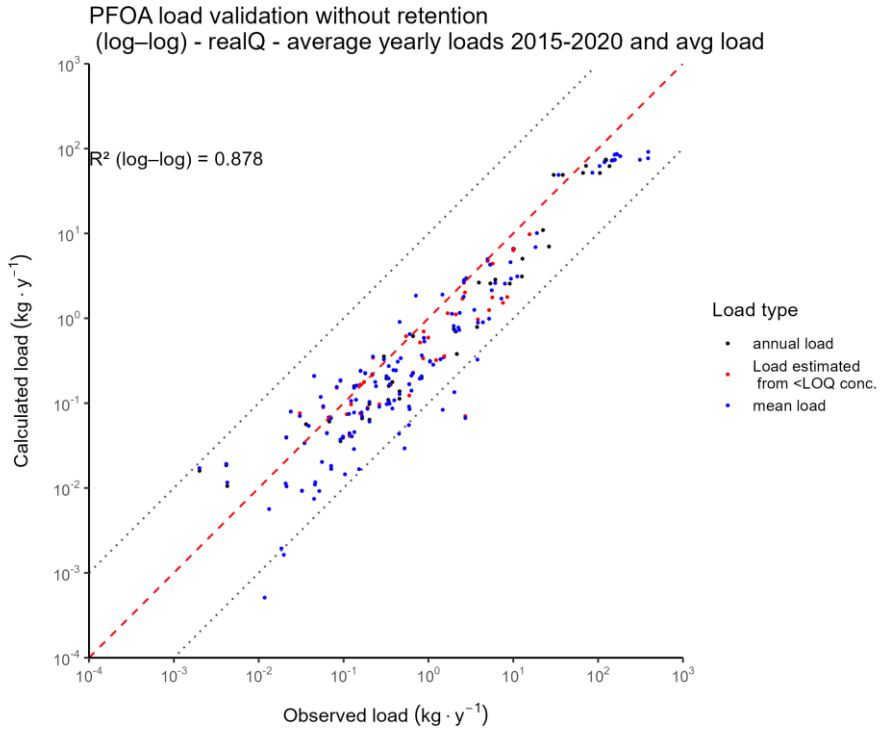


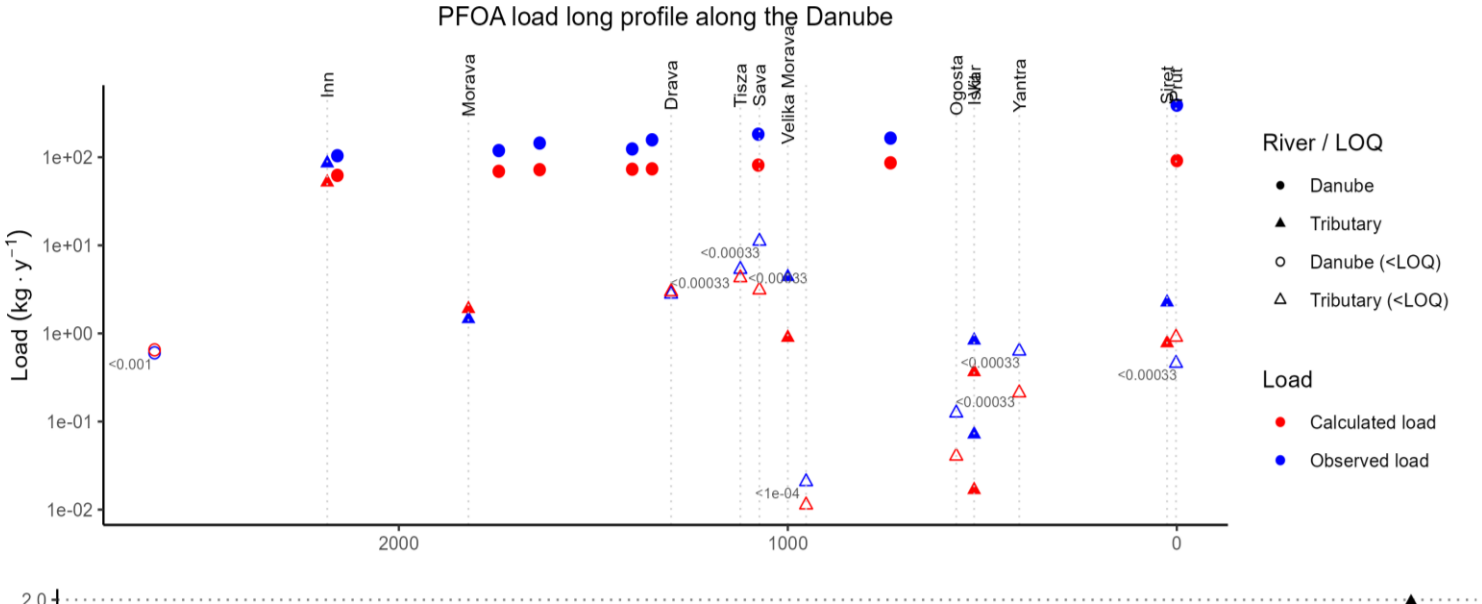


- As and Zn mostly within +/- 1 oom
- Cr, Ni, Cu and Pb: Overestim in small, underestim in large rivers – retention problem?
- Cd: tendential overestimation but relatively accurate in lower Danube main river

Validation map – **PFOA**

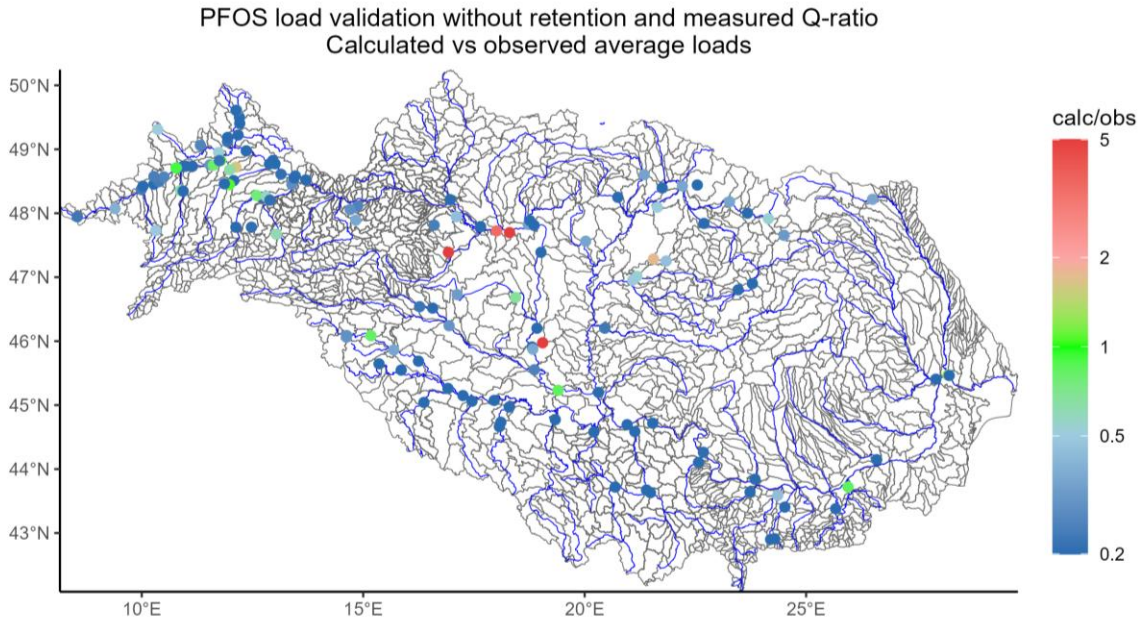


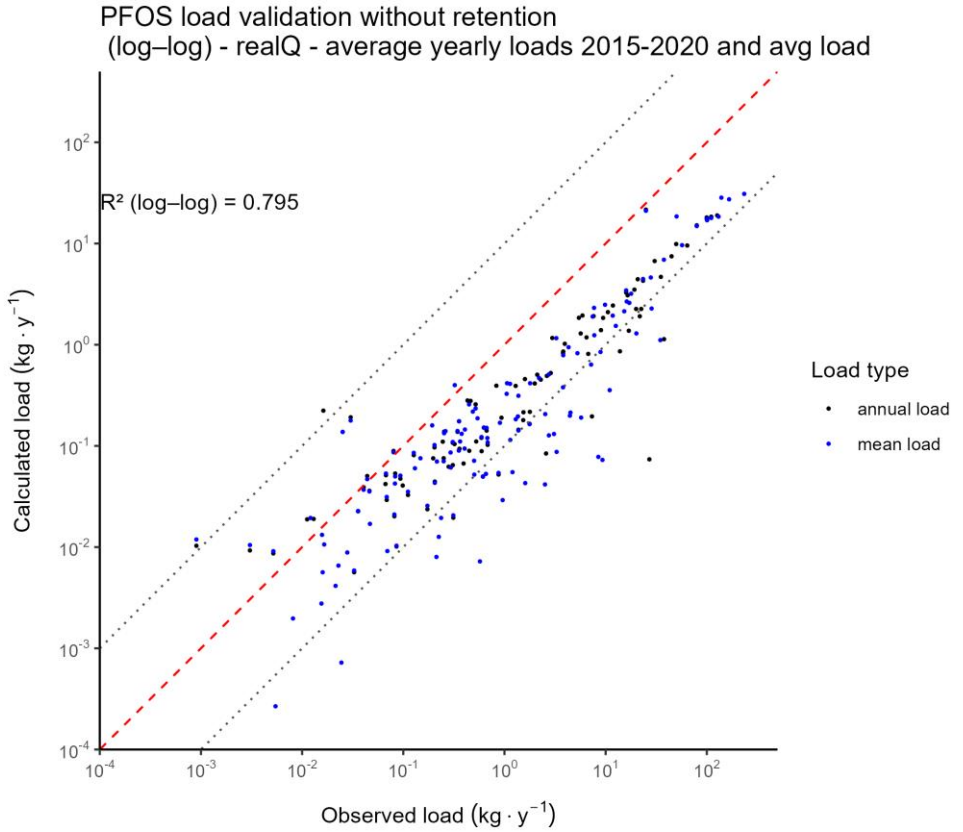


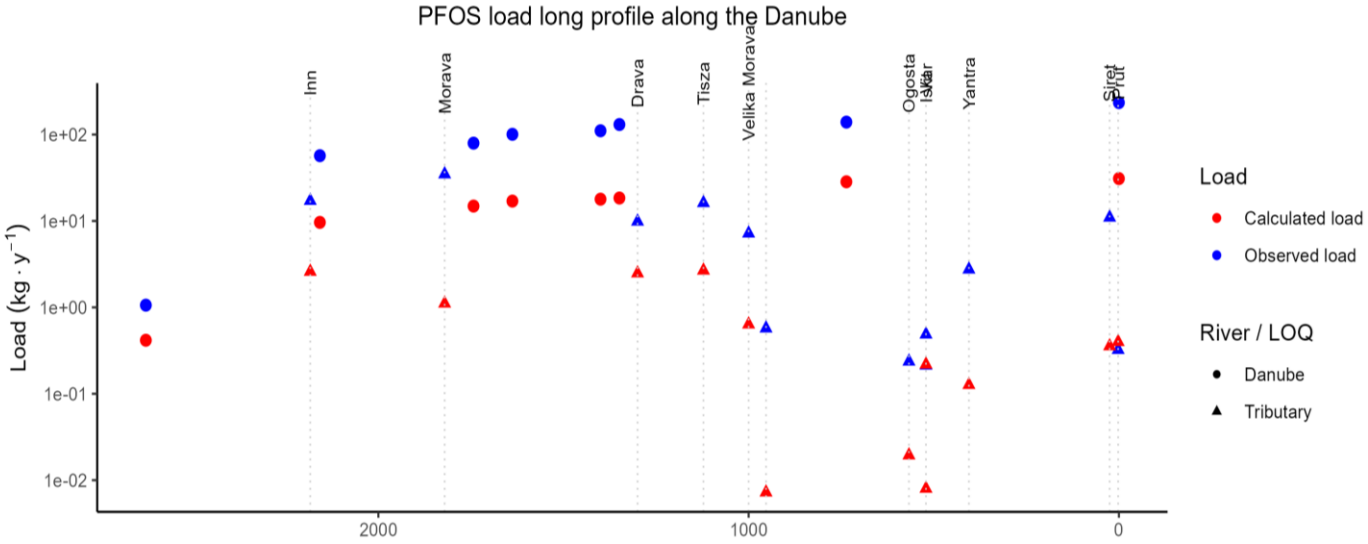


- Some underestimation, except for upper Danube
- Strong overestimation at some small-medium sized rivers
- Some underestimation along the Danube
- Most loads come from upper Danube region
- Less reliable validation datasets (1,2 measurements per year in some cases)

Validation map – **PFOS**

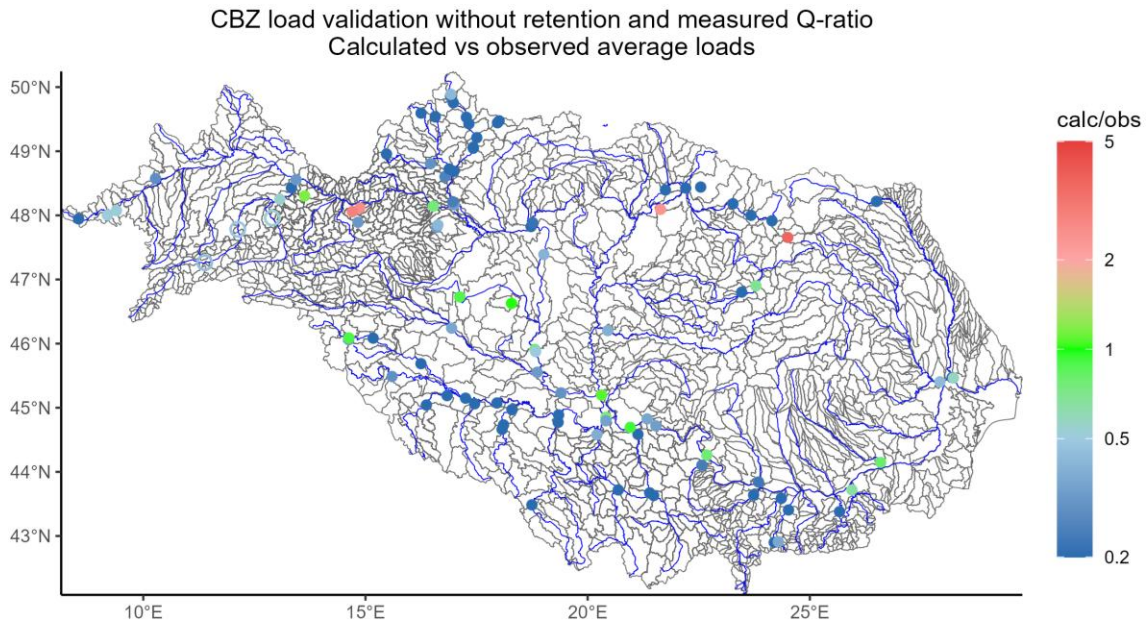


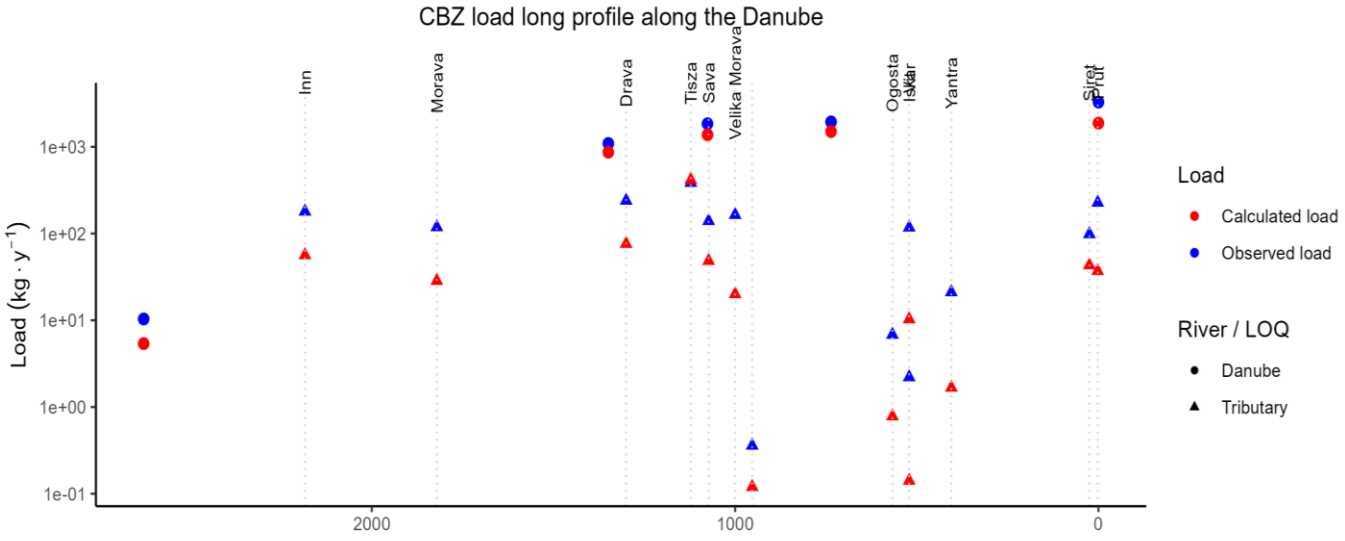


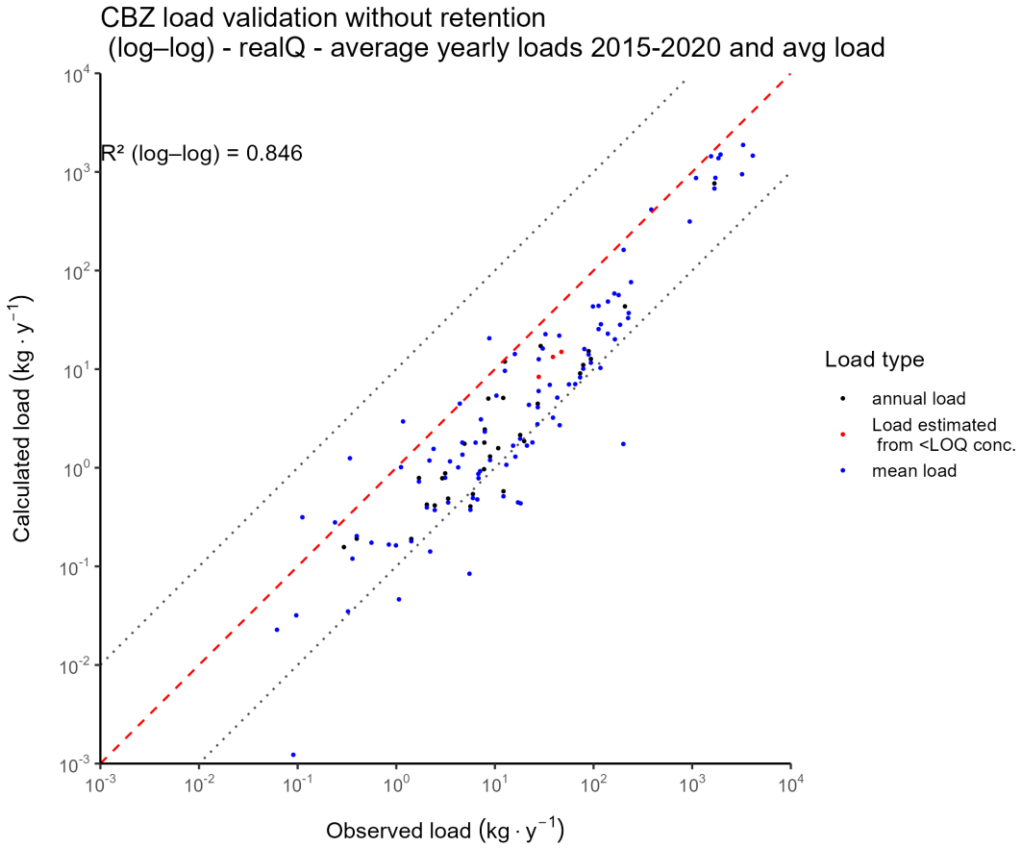


- Heavy underestimation !
- Less reliable validation datasets (1,2 measurements per year in some cases)
- Strong regional differences in model performance

Validation map - **CBZ**

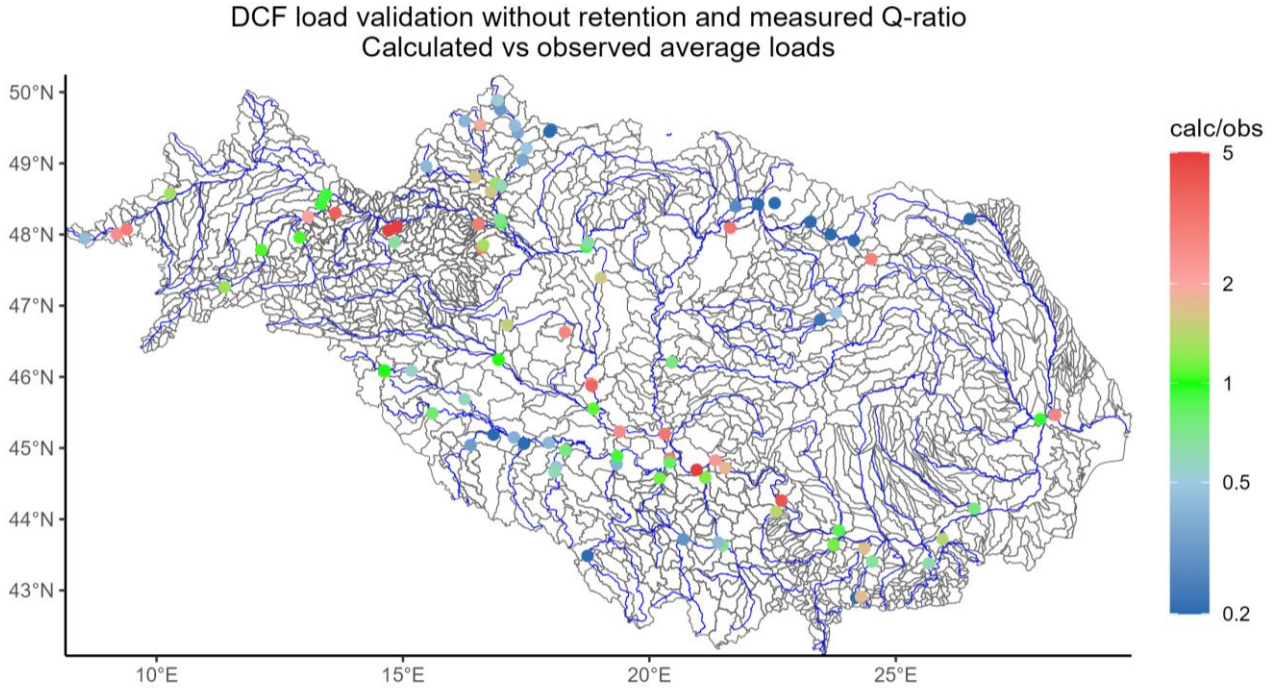


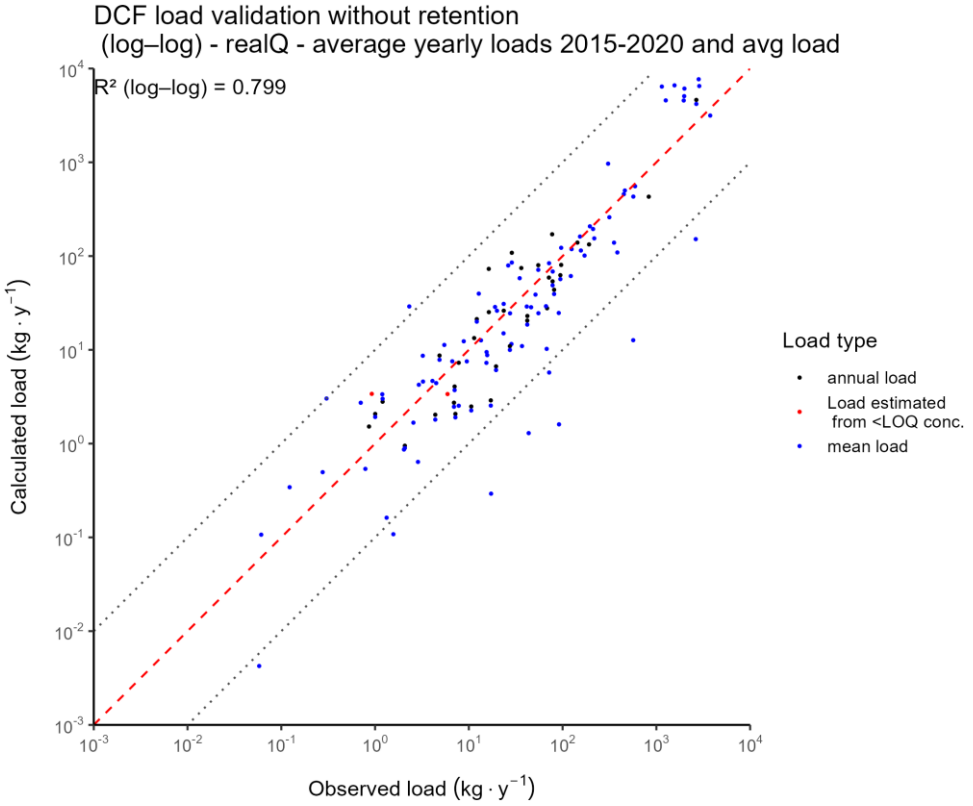


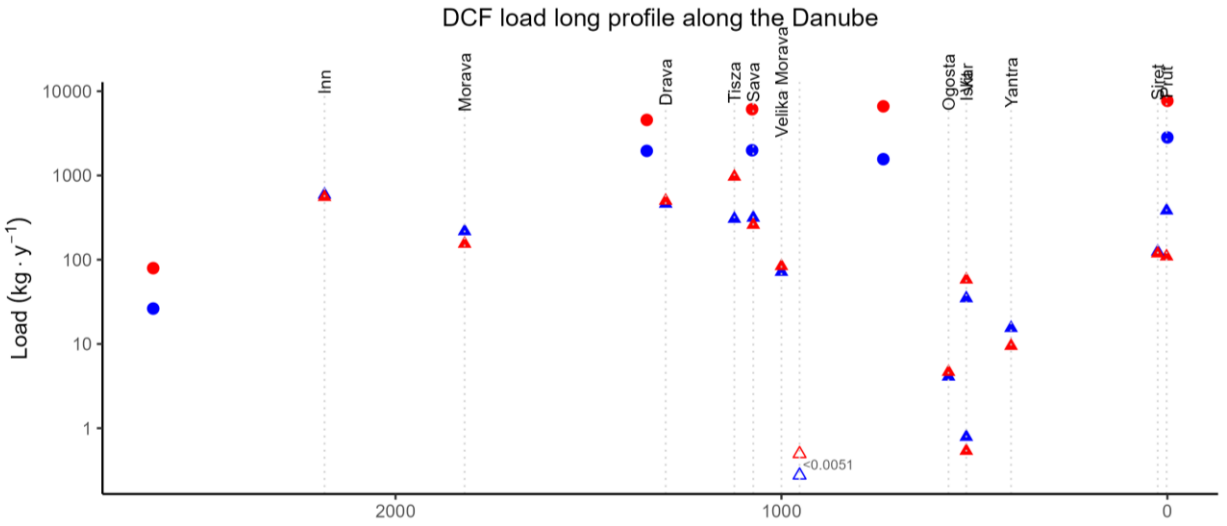


- Correct estimation of loads in the Danube river
- Obvious underestimation in major tributaries (Morava, Sava)
- No significant retention in rivers
- Less reliable validation datasets:
  1-2 measurements per year in some cases

Validation map - **DCF**







- Overestimation of loads in the Danube river
- Riverine retention for Danube is very likely, not yet in the model!!
- Less reliable validation datasets
  1-2 measurements per year in some cases

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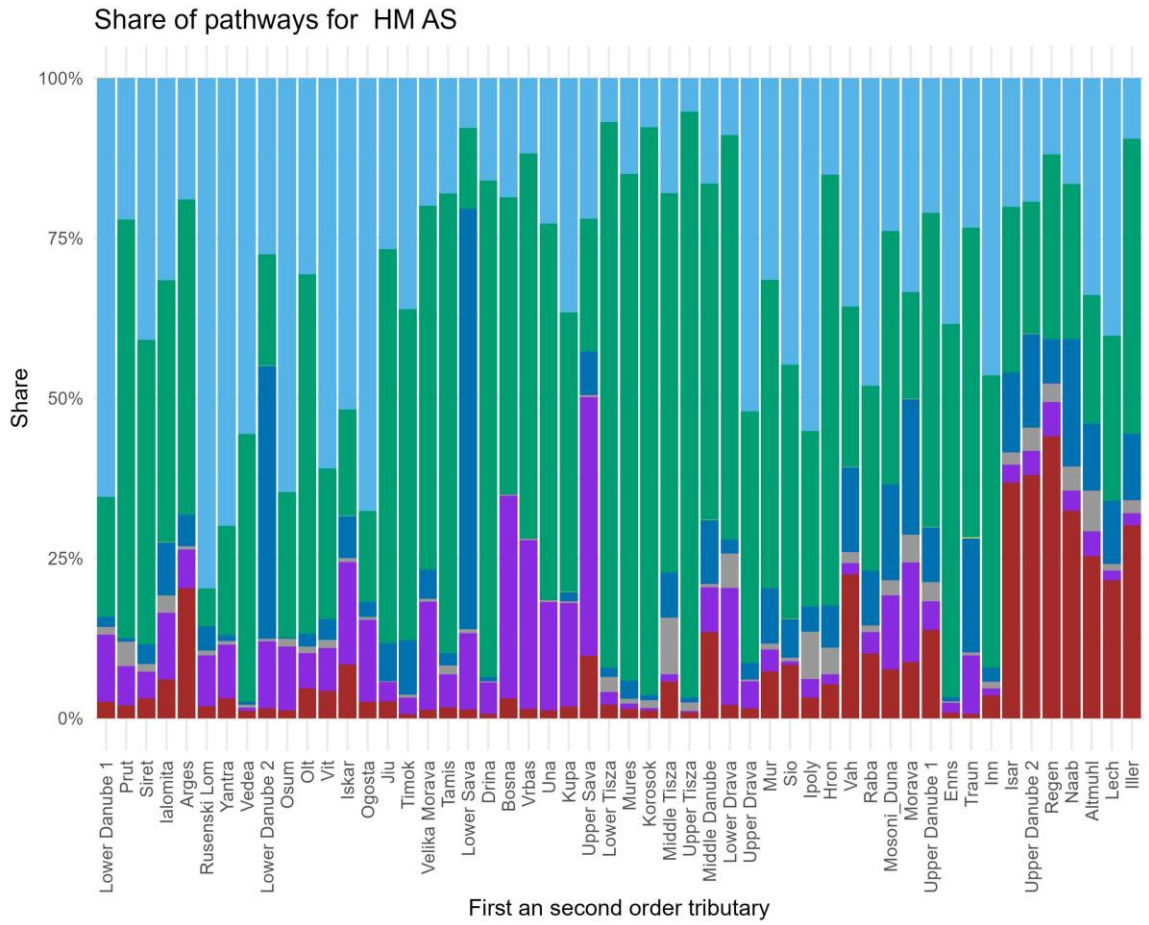
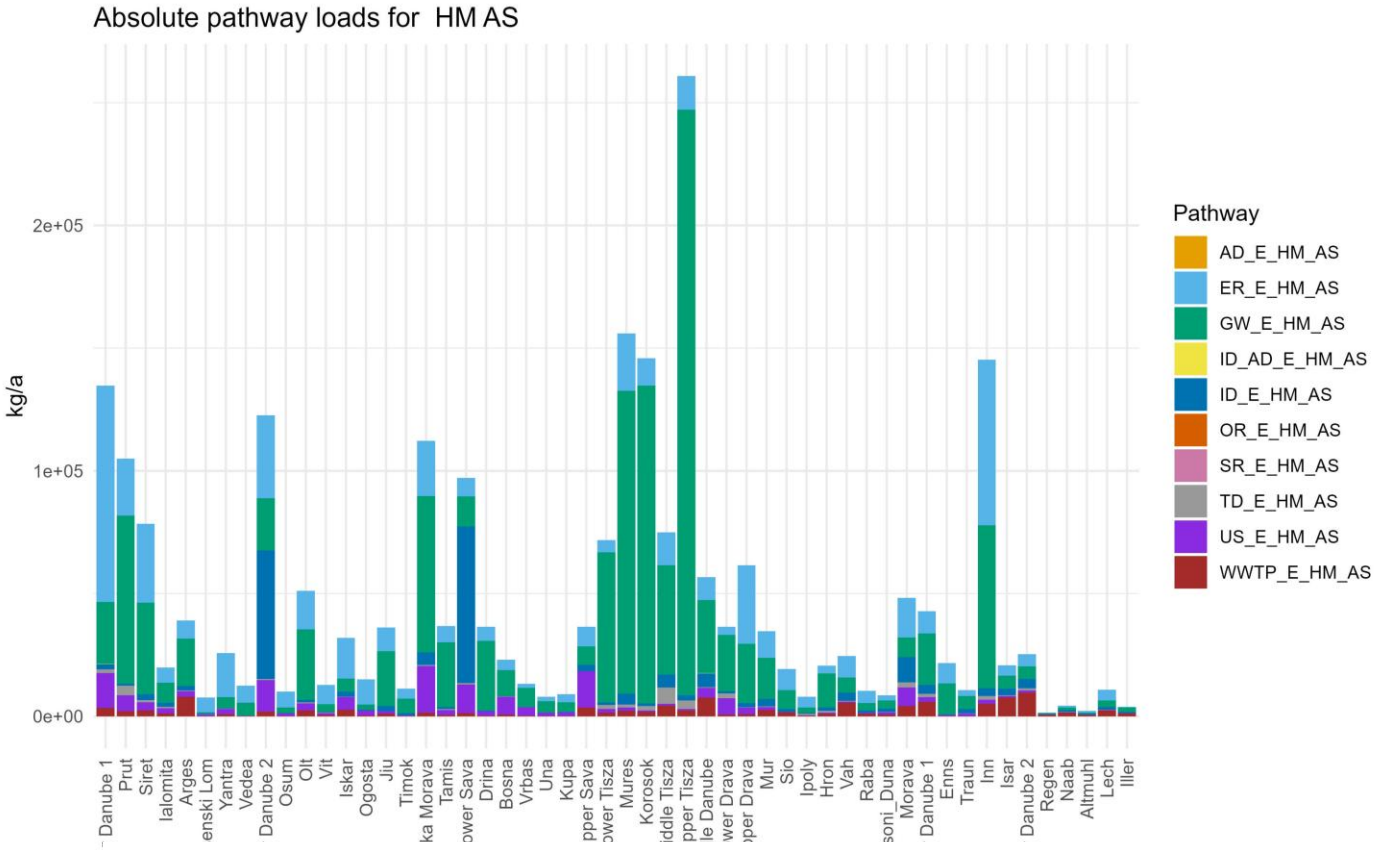
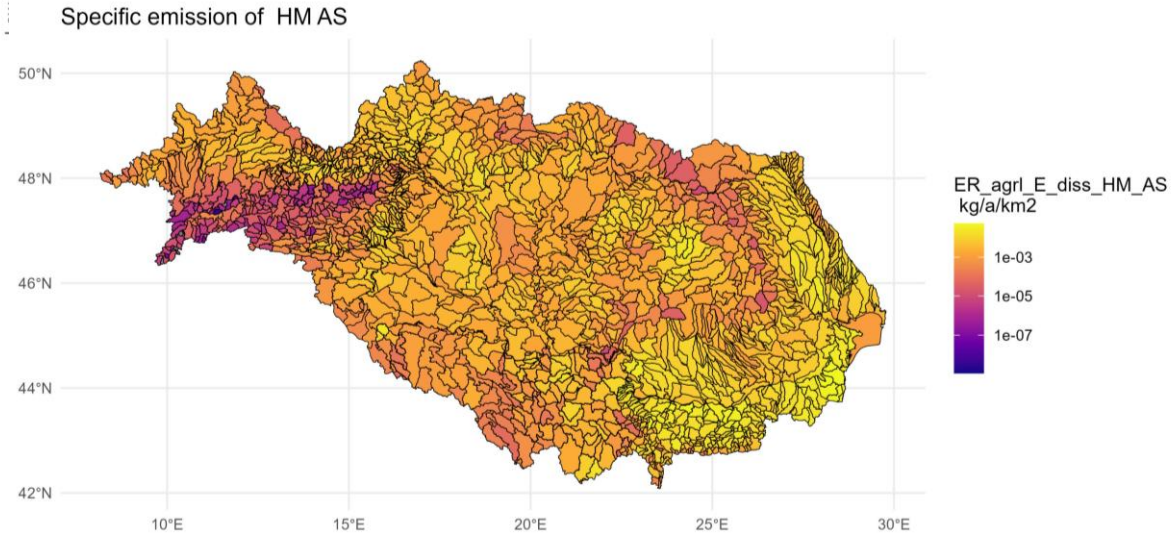
As emissions in the DRB

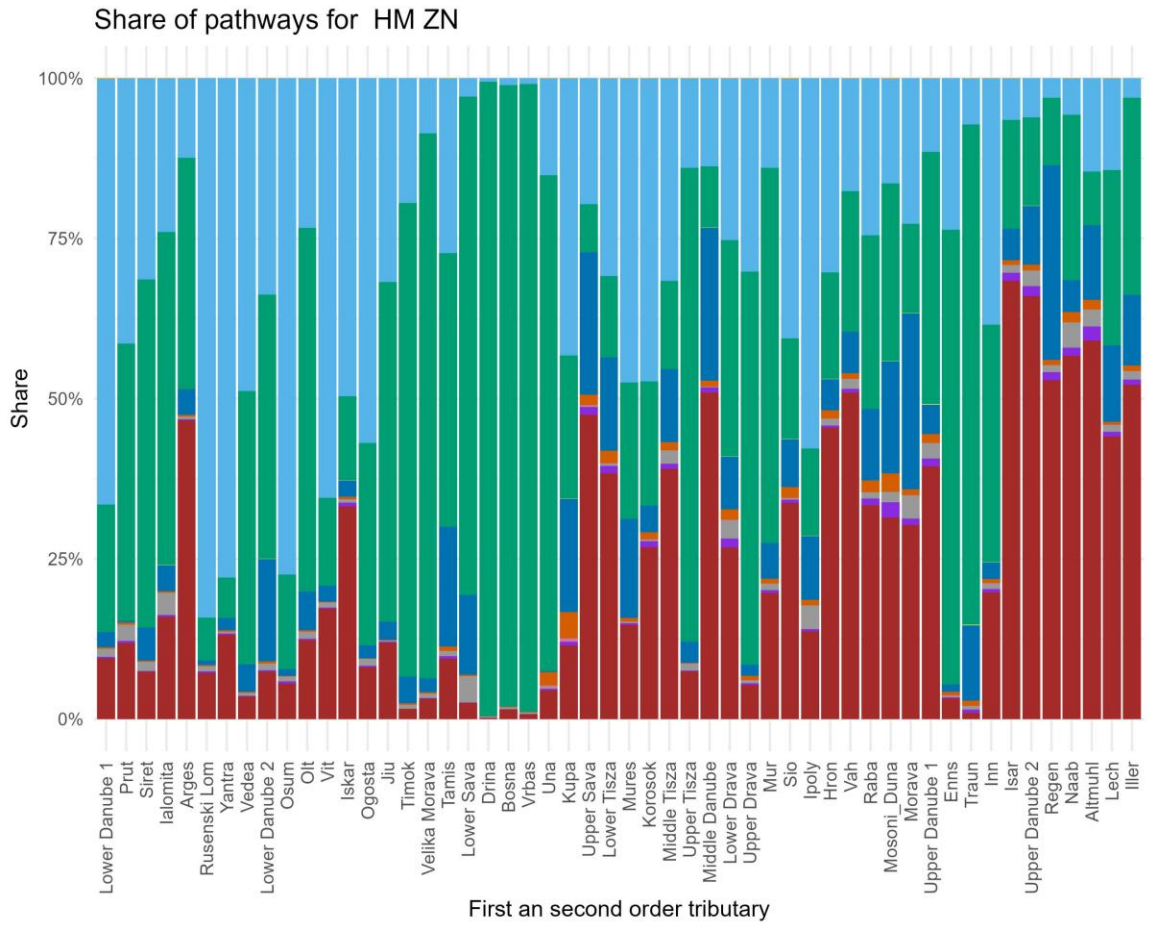


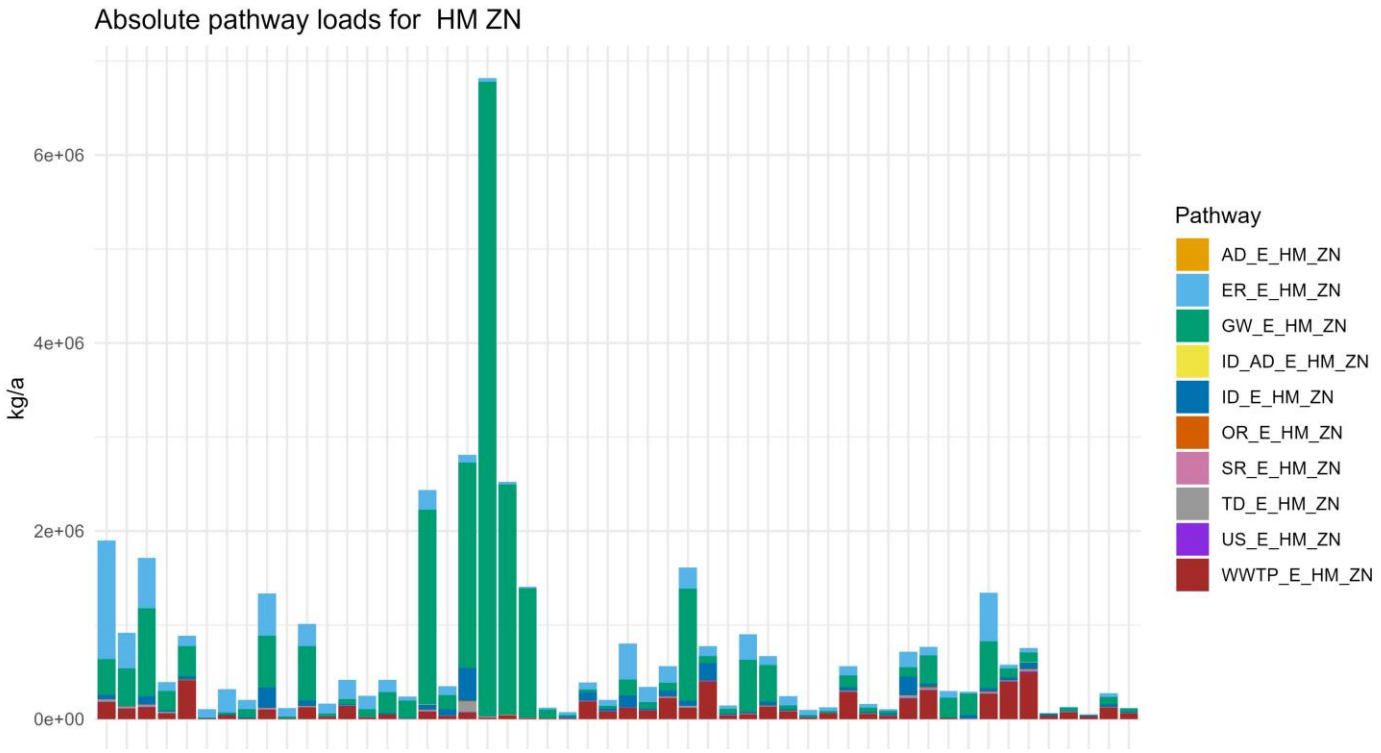


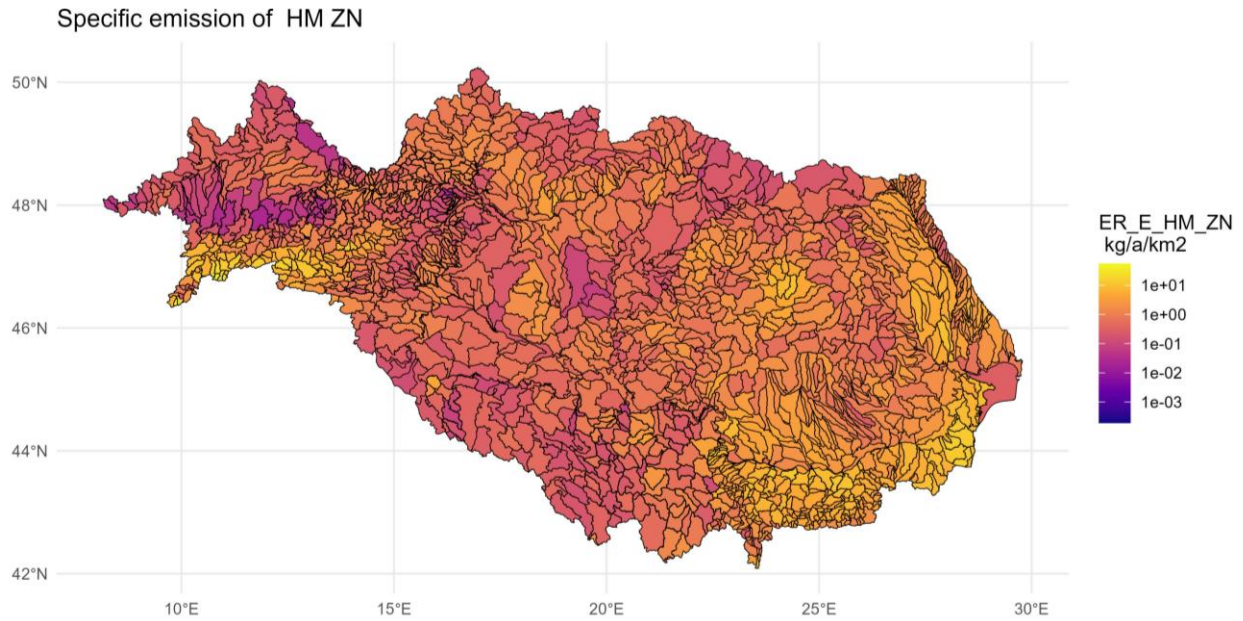


- Strong regional patterns in total loads
- Groundwater is the main overall source, especially in the middle Danube
- Erosion is significant, especially in the lower Danube
- WWTP load is a small share in total terms

Zn emissions in the DRB



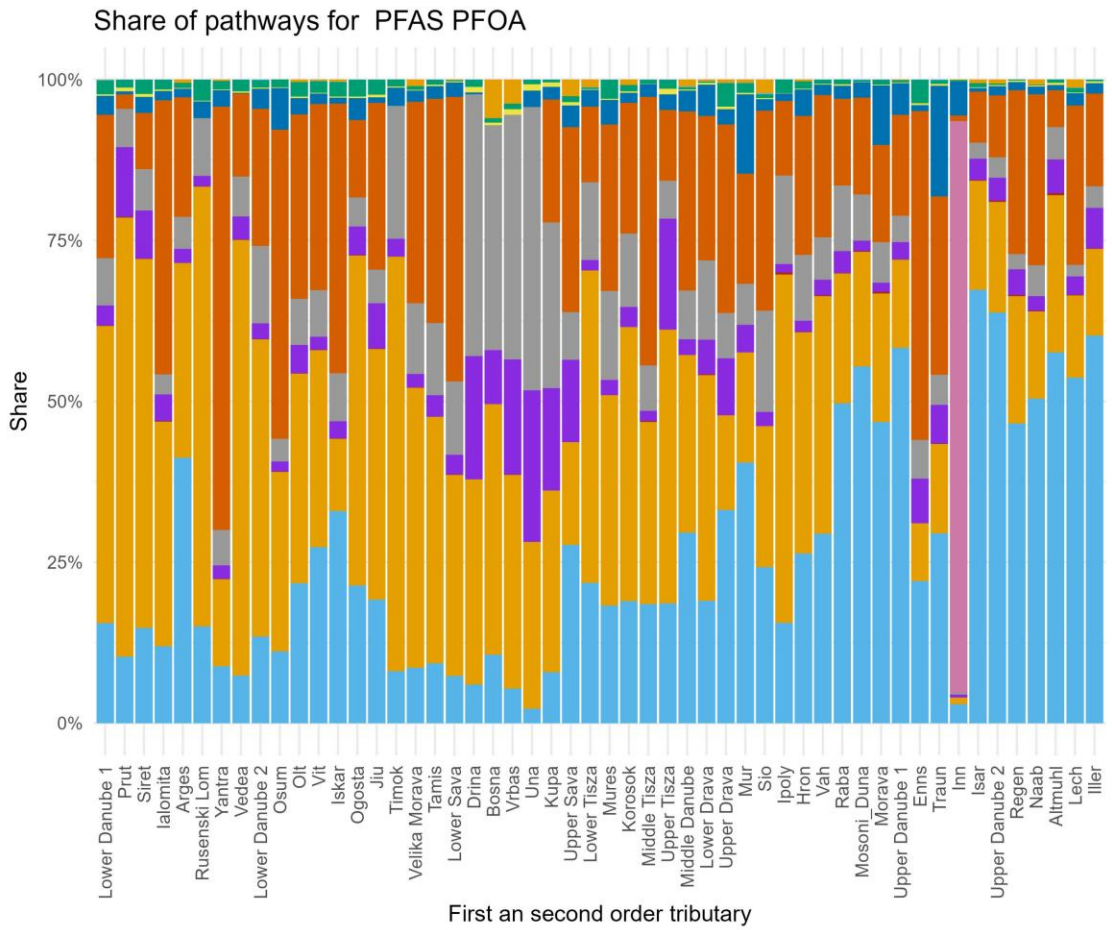


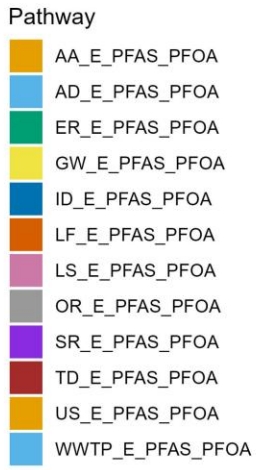


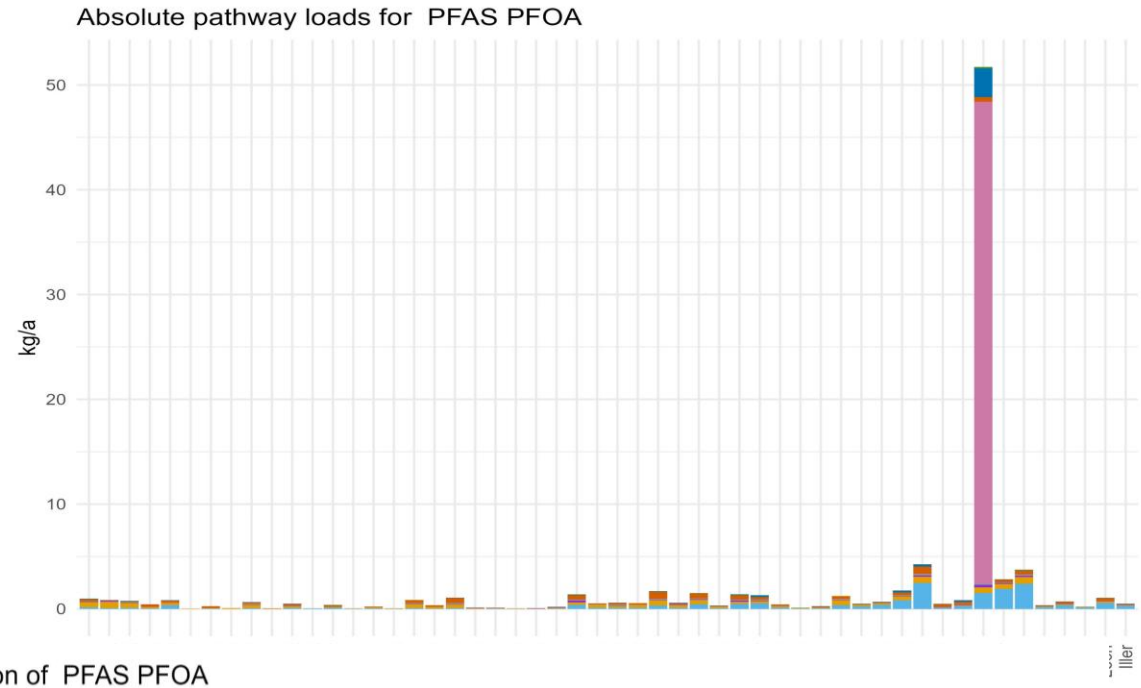
Main observations

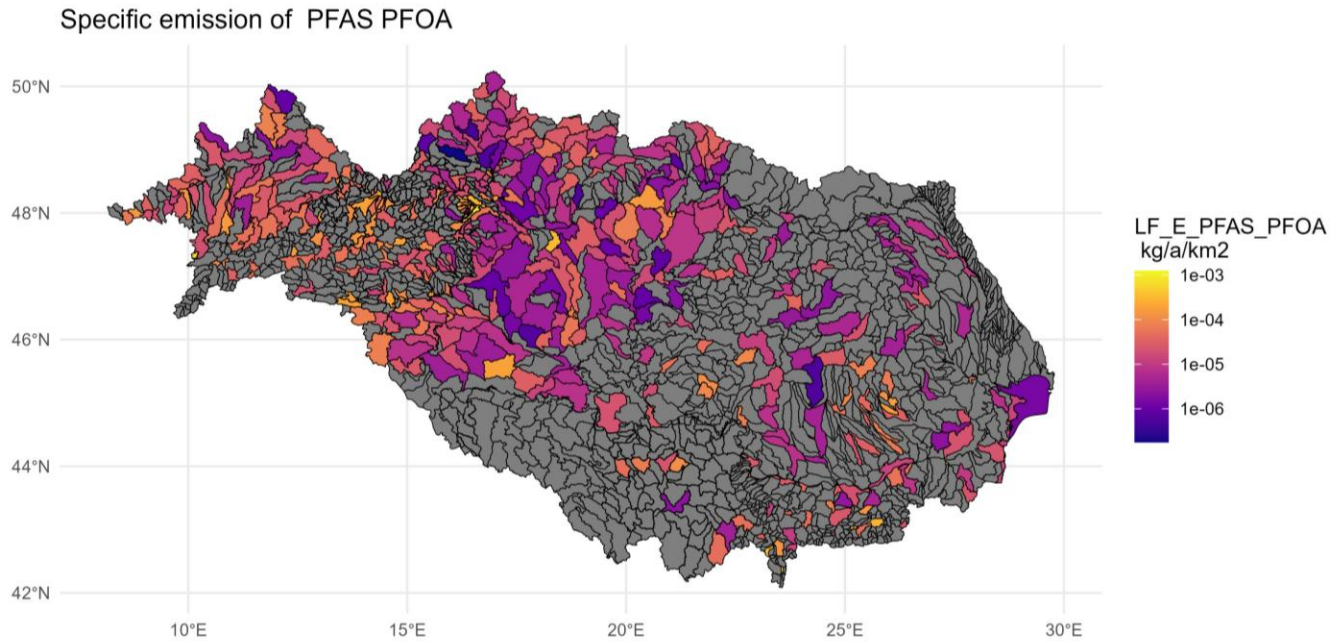
- Overestimation of GW loads in the Bosnian rivers
- Erosion and waste water loads are the most significant
- Groundwater is locally significant.

PFOA emissions in the DRB





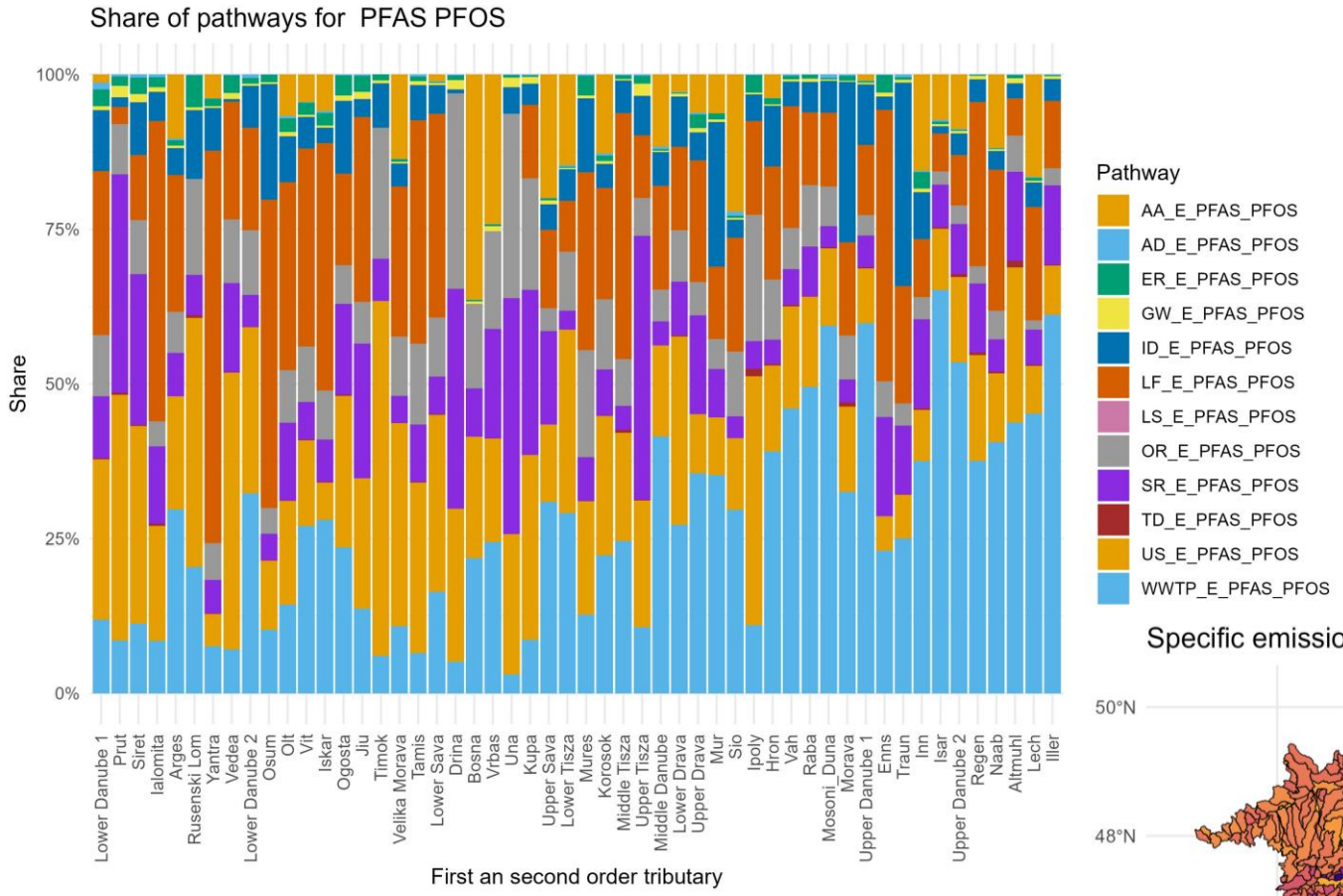


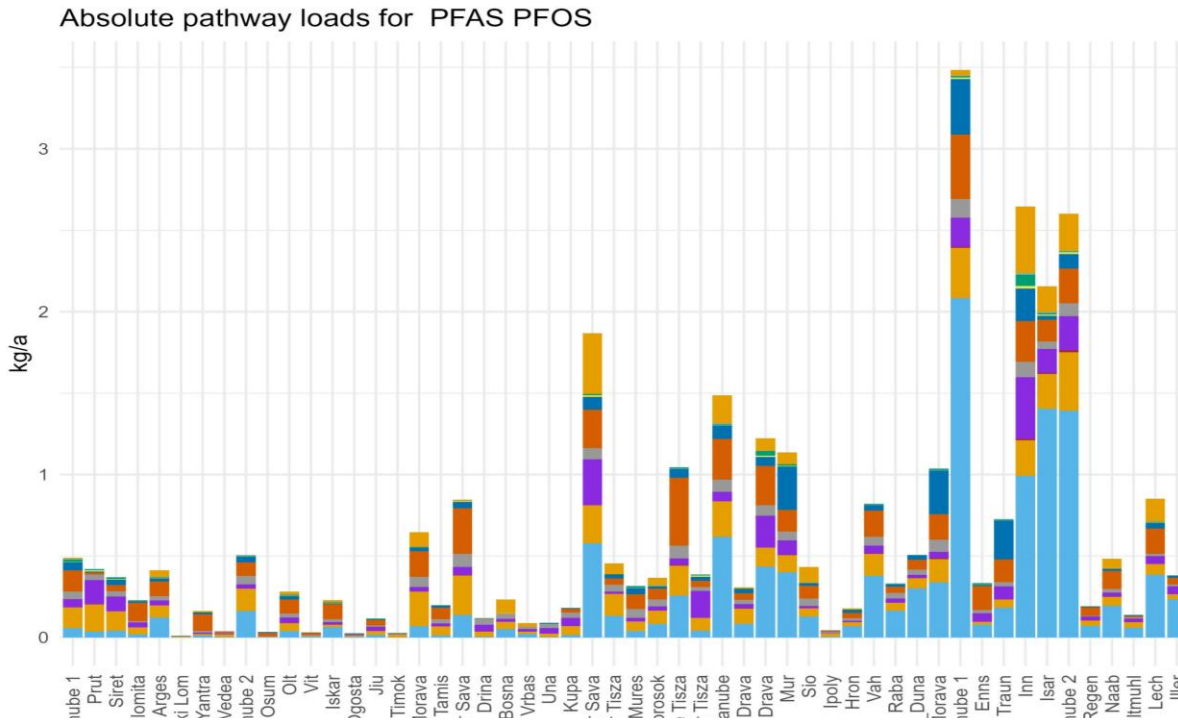


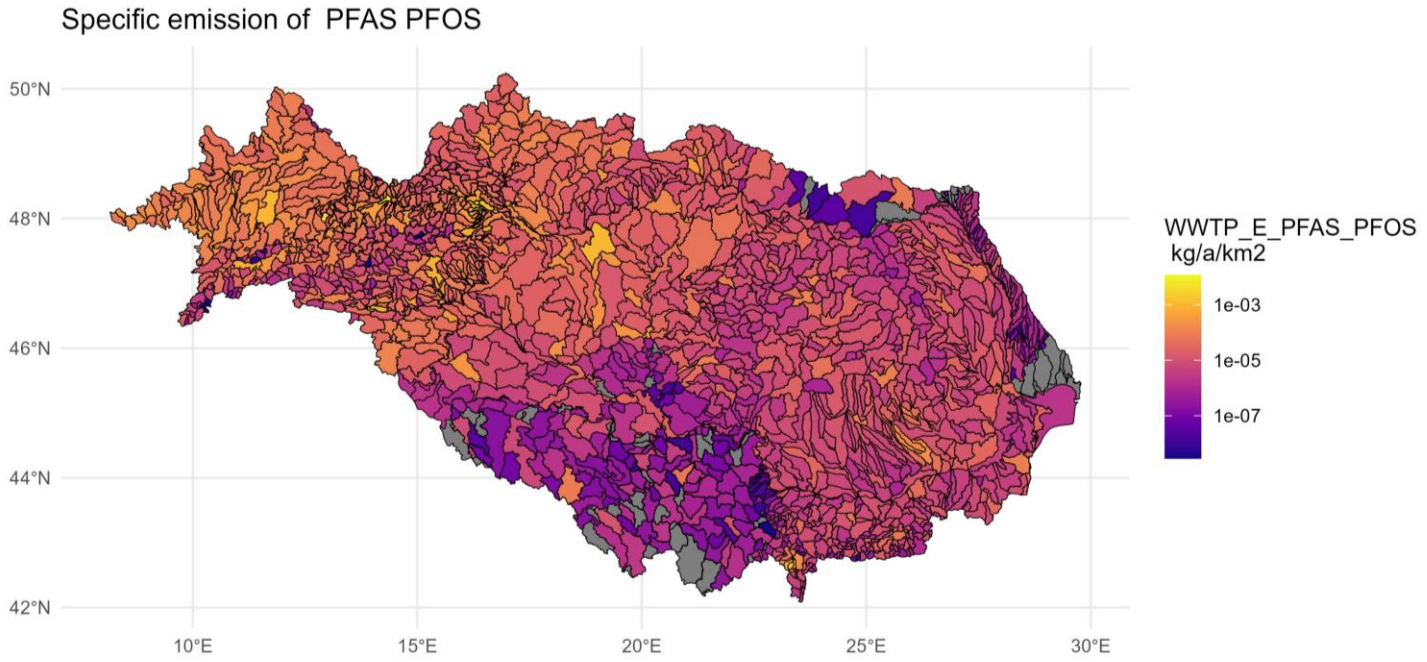
Main observations

- Gendorf legacy hot spot is a dominant source
- WWTP loads dominate river loads in the upper Danube
- Urban systems related emissions dominate river loads in the middle and lower Danube
- Landfill hot-spots give a significant share (high uncertainty)

PFOS - strongly underestimated!!!!



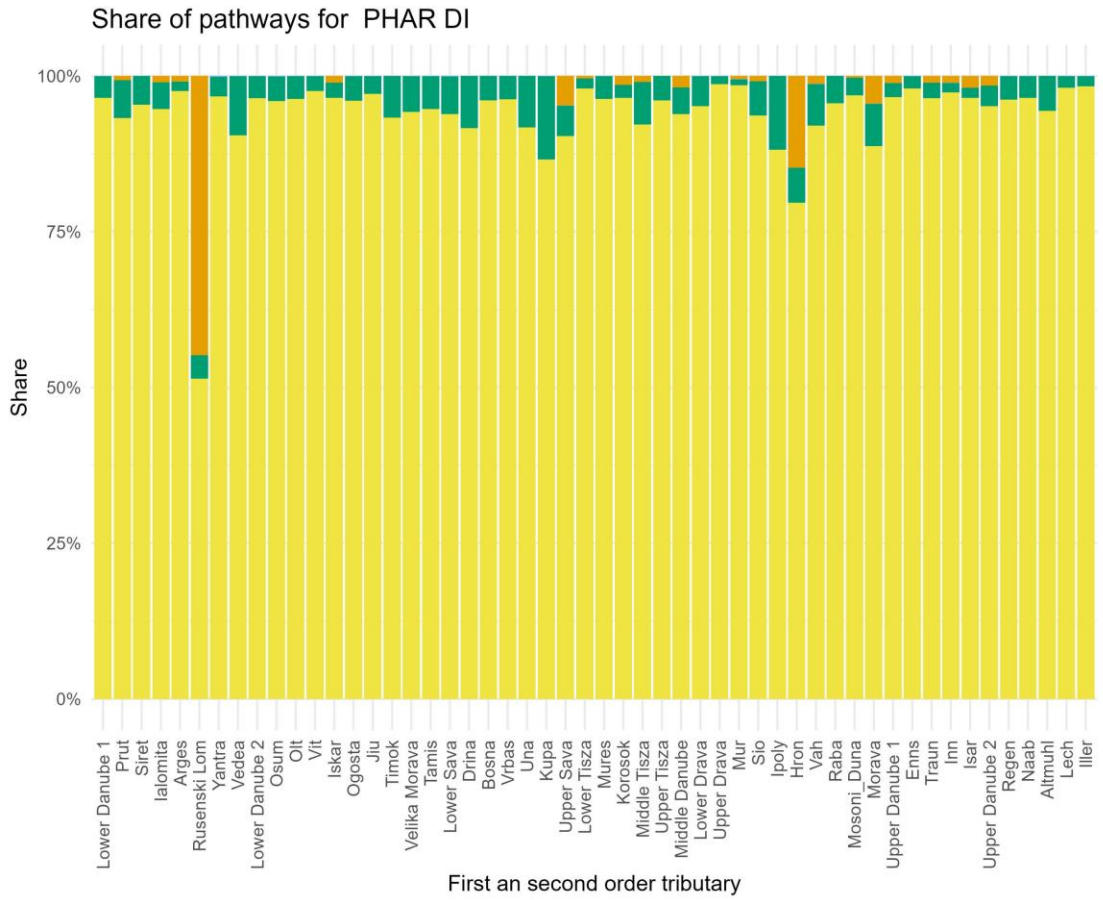


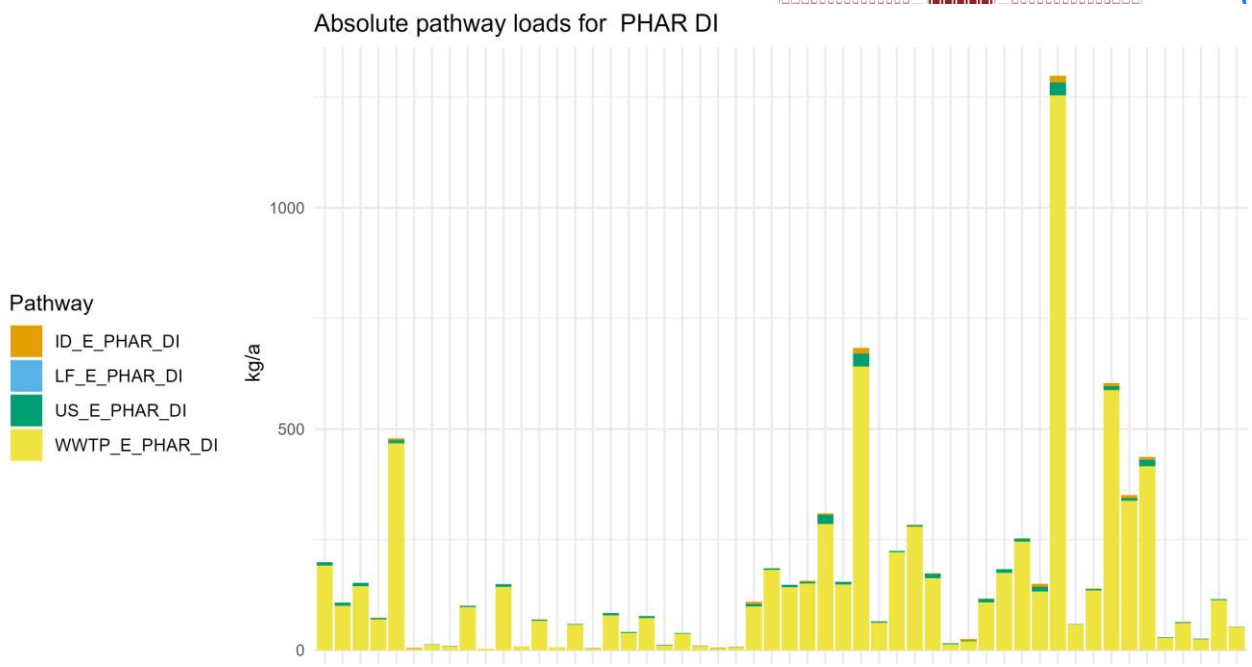


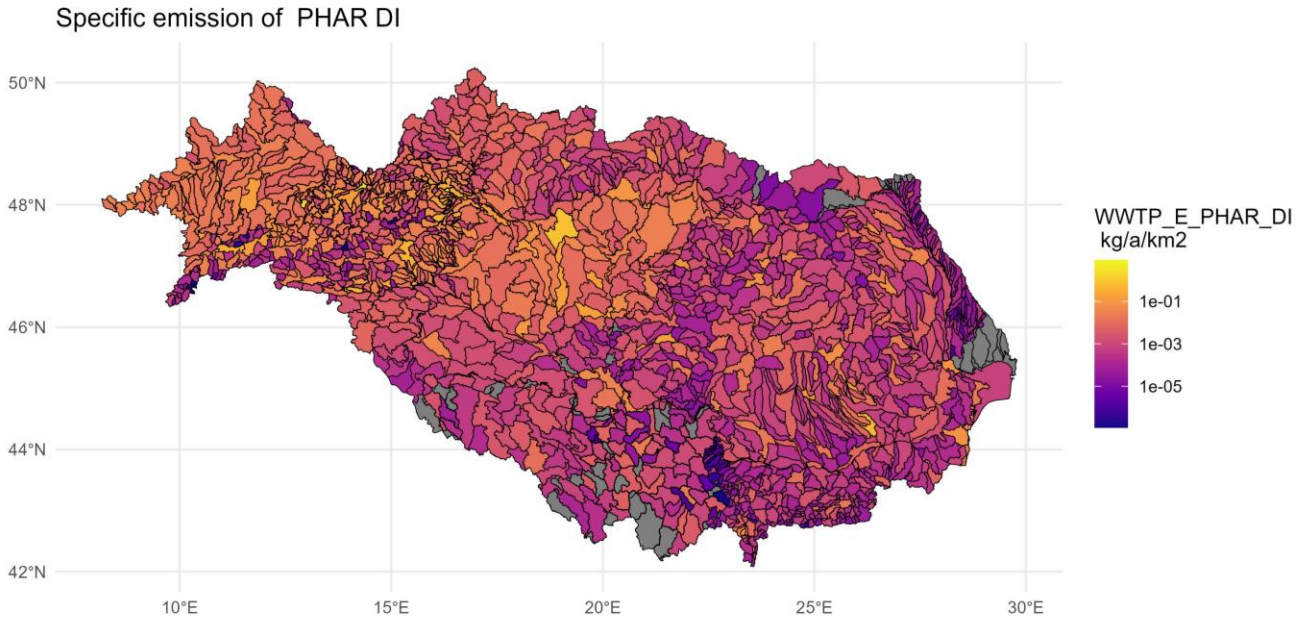
Main observations

- WWTP loads dominate river loads in the upper Danube
- Loads from urban systems are very relevant in the lower Danube region
- Landfill/Aerodrome hot-spots give a significant share (high uncertainty)

DCF emissions in the DRB





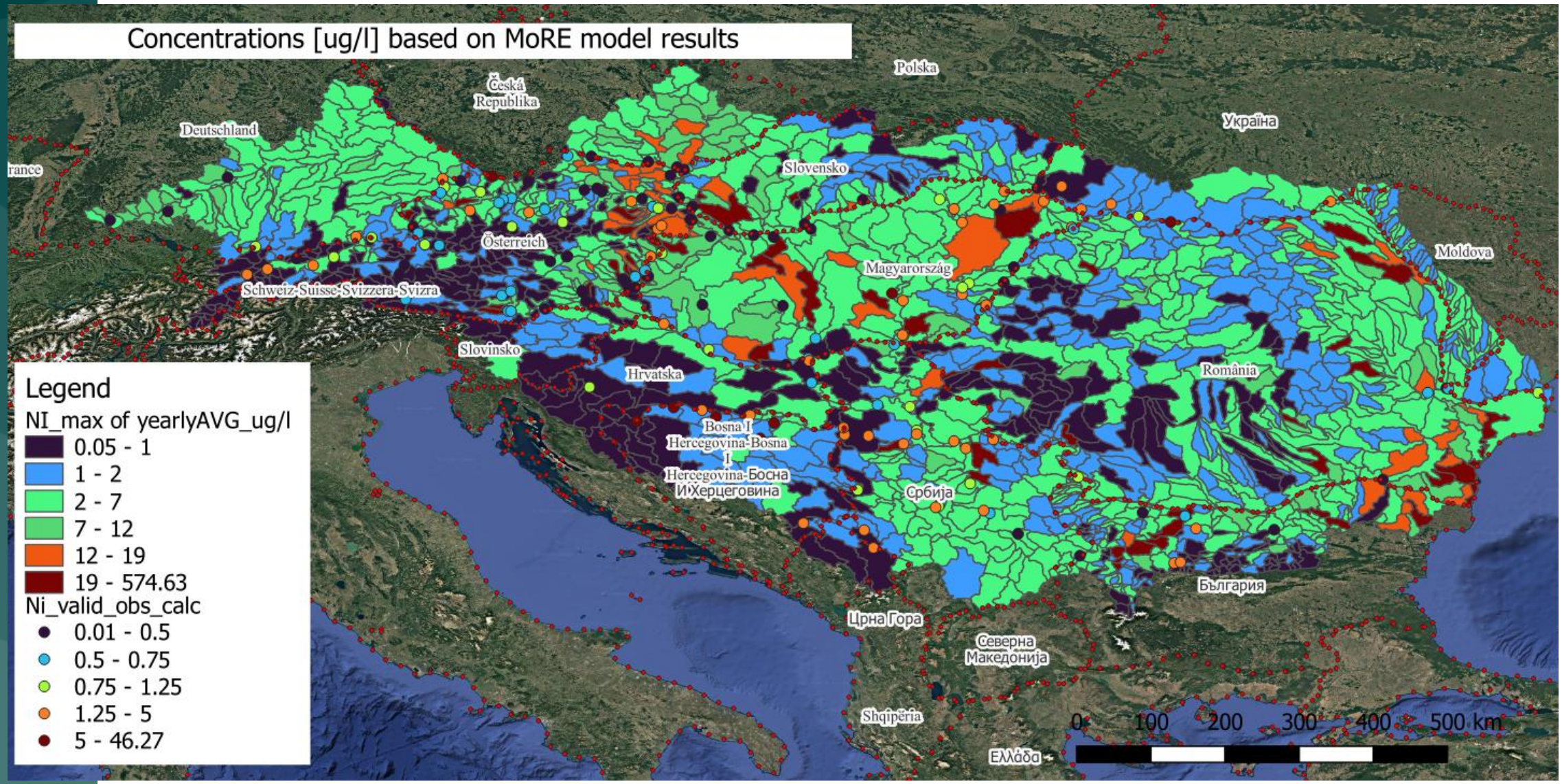


Main observations

- Beside WWTPs, urban systems may play an important part in total loads
- Due to lower share of sewege treatment, share of urban systems related diffuse load might be important in the lower Danube
- Industrial discharges show strong hot-spot loads in a few catchments

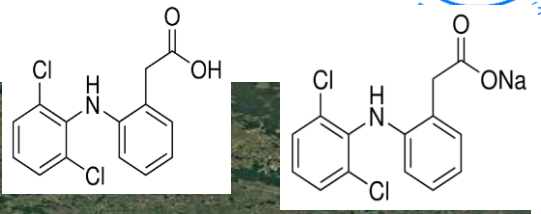
1. Model structure & input data
2. Model validation
3. Identified emission patterns
4. **Outlook: risk analysis**

Risk analysis - **Ni**



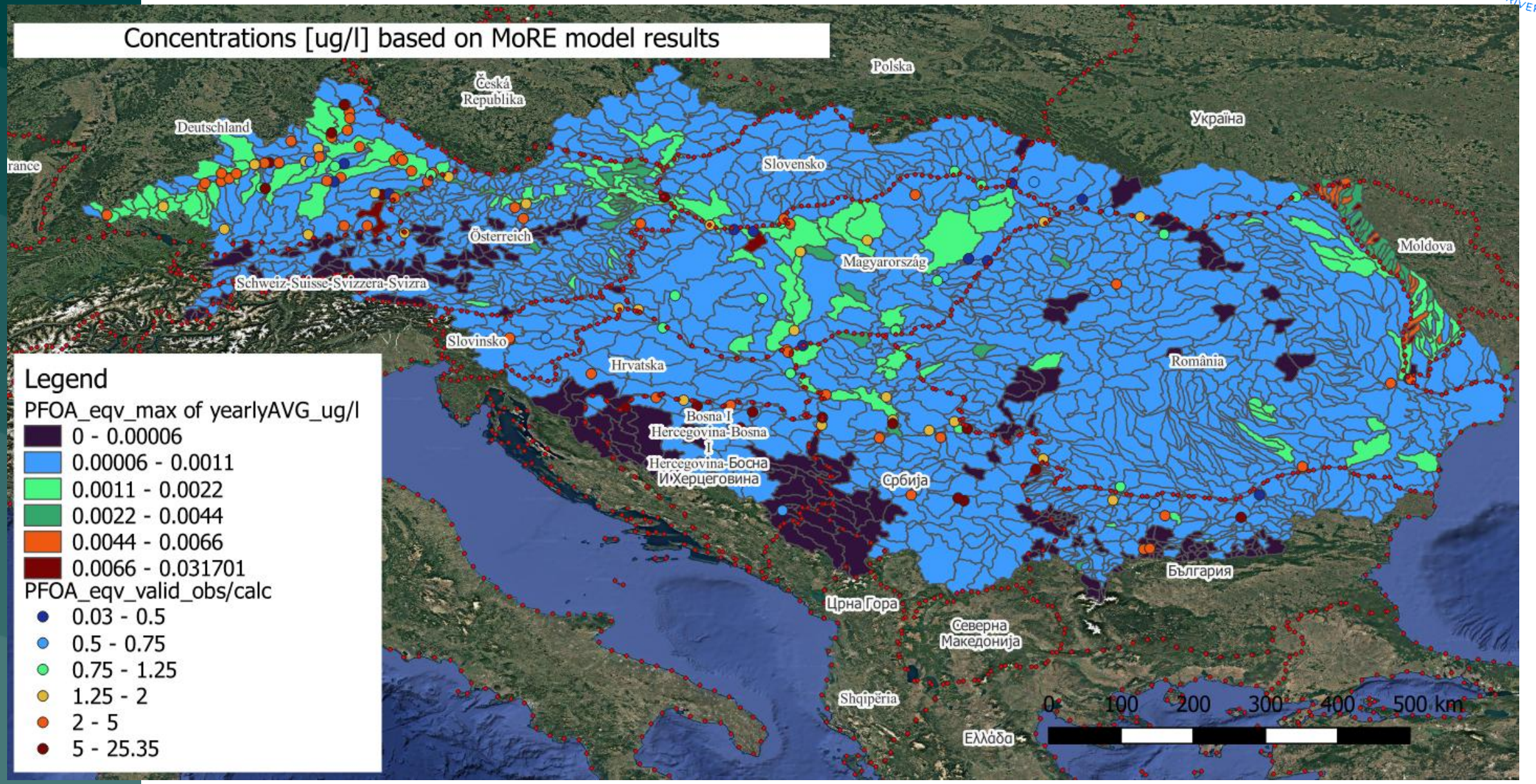
Risk analysis - **DCF**

AA-EQS = 0.04 µg/l



Risk analysis – **PFOA-eqv**

AA-EQS = 0.0044 µg/l (sumproduct of 25 PFAS compounds)



Summary 1/2 - Validation

Input data deficiencies

- Groundwater concentrations of organics (except AT & DE)
- Industrial emissions in SE Europe
- Landfills and fire-fighting centres
- Need to increase river sampling frequency to improve validation data

Heavy metals

Validation performance varies between substances.

- As and Zn mostly within +/- 1 oom
- Cr, Ni, Cu and Pb:
  Overestim in small, underestim in large rivers – retention problem?
- Cd: tendential overestimation but relatively accurate in lower Danube main river

PFOA

- slight overall underestim. (~0.5 o.o.m)
- relatively adequate in main river Danube and large tributaries
- accurate in upper Danube Basin

PFOS

- heavy overall underestim (1-2 o.o.m)
- accurate in a few mid-size tributaries

CBZ

- tendential underestimation
- accurate in Central European tributaries

DCF

- Generally within +/- 1 o.o.m
- strong underestimation at some points

Summary 2/2 - Emission patterns

As: GW-dominated + ER

Zn: OR dominates in upper DRB, GW and ER in lower DRB

PFAS

- very diverse pattern of emission sources
- PFOA: vast majority comes from the Gendorf location
- PFOS: larger emissions in the upper DRB

Pharmaceuticals

- MWWTP emssions dominate but vary by country
- urban diffuse loads secondary
- in some catchments, ID also substantial

Risk analysis

Ni: high risk in some areas

DCF: high risk almost overall

PFOA: high risk + calculation challenge

Interreg Danube Region

Co-funded by the European Union

Tethys

MŰEGYETEM 1782

RIVER BASINS

Thank you for your attention!

"Identifying Key Pathways of Priority Trace Chemicals in the Danube River Basin"

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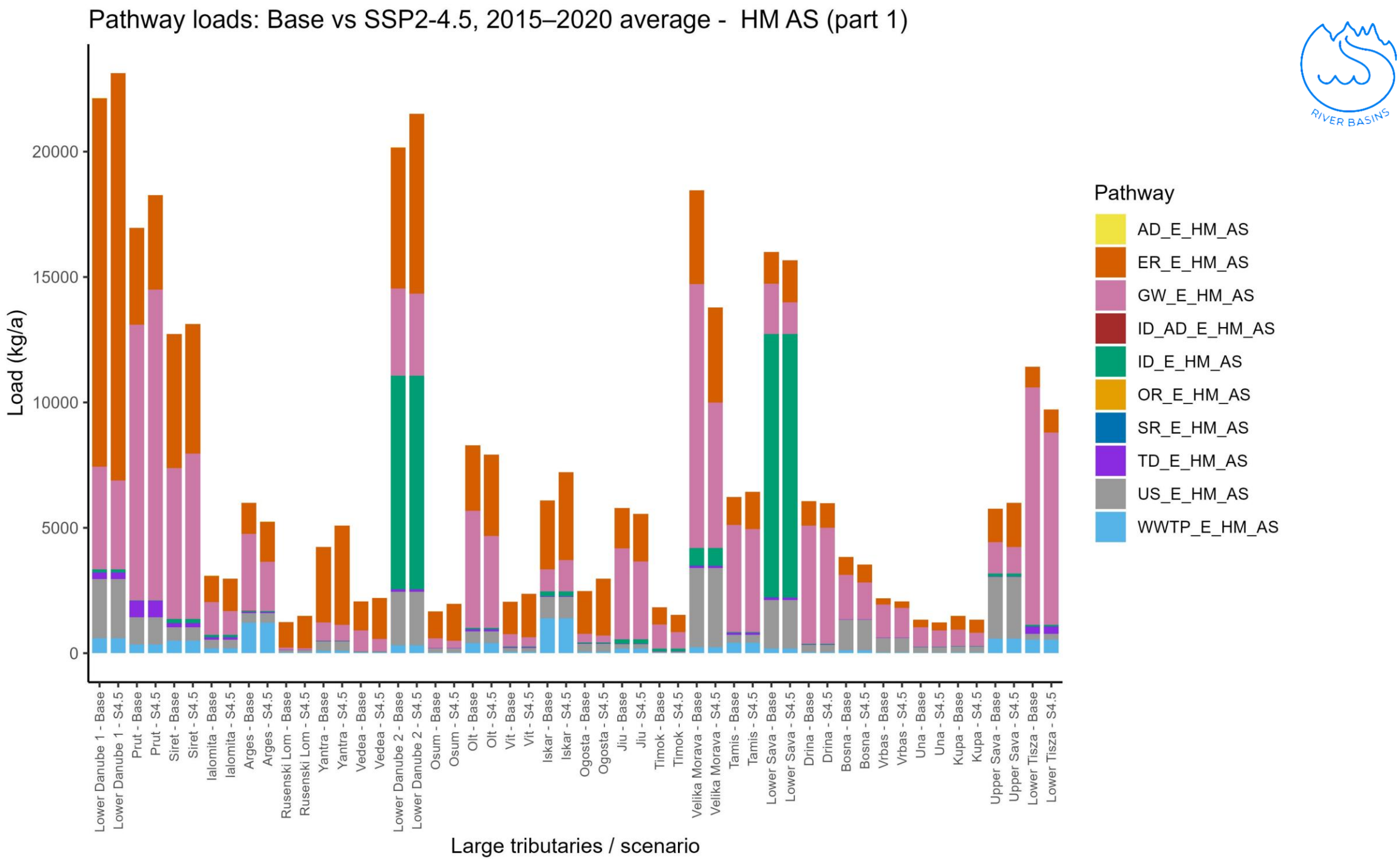
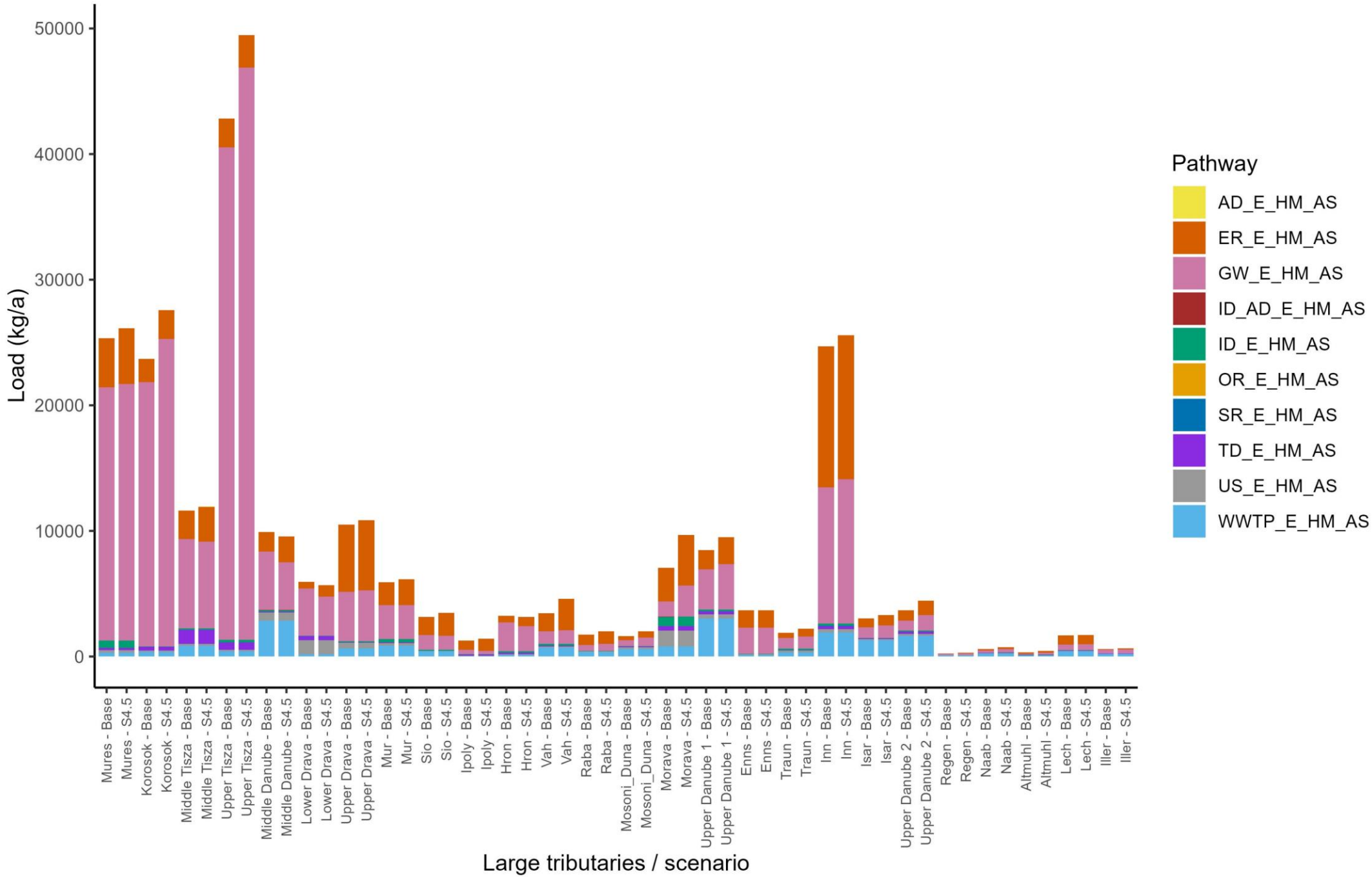
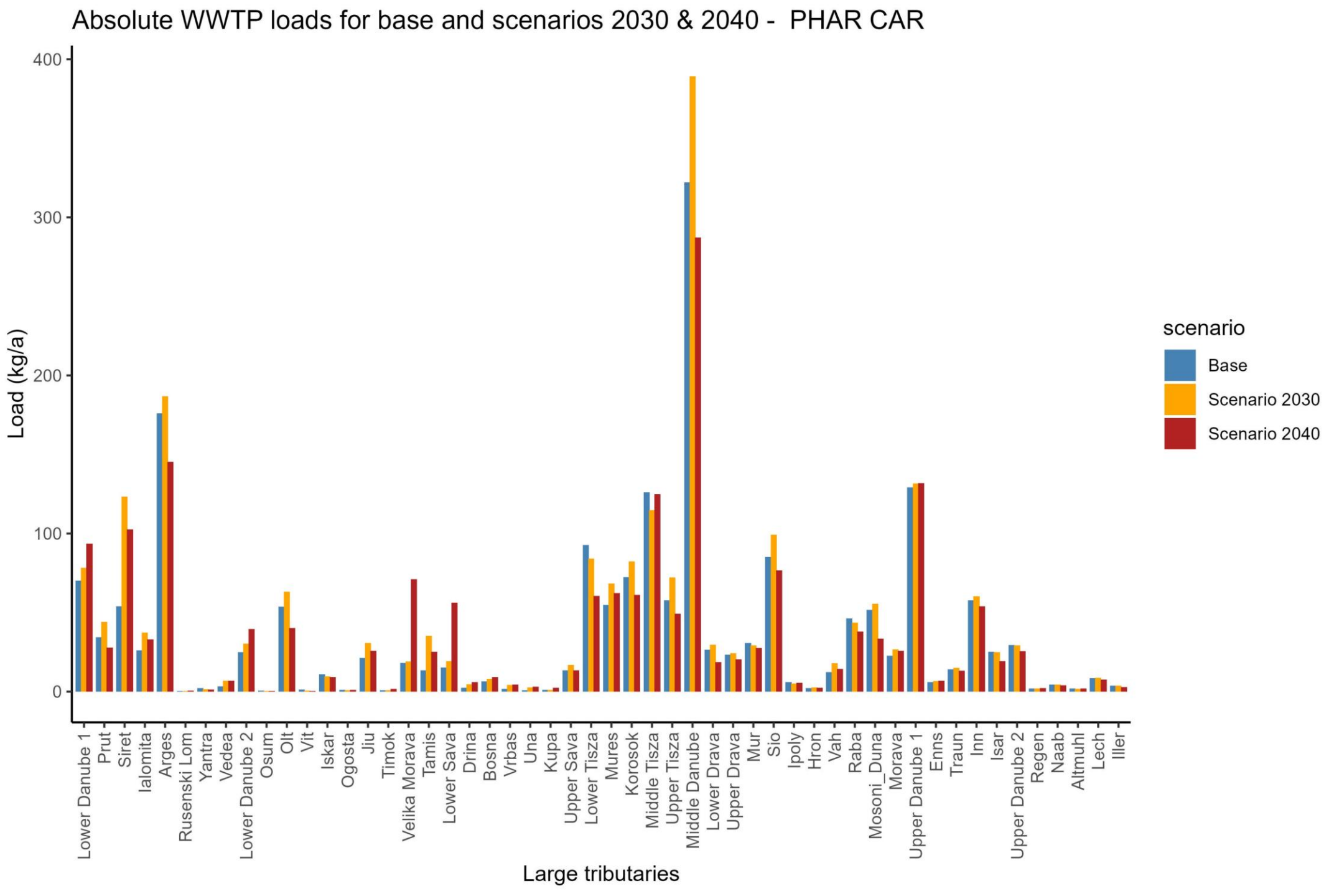
Climate projection & Erosion forecast by 2050

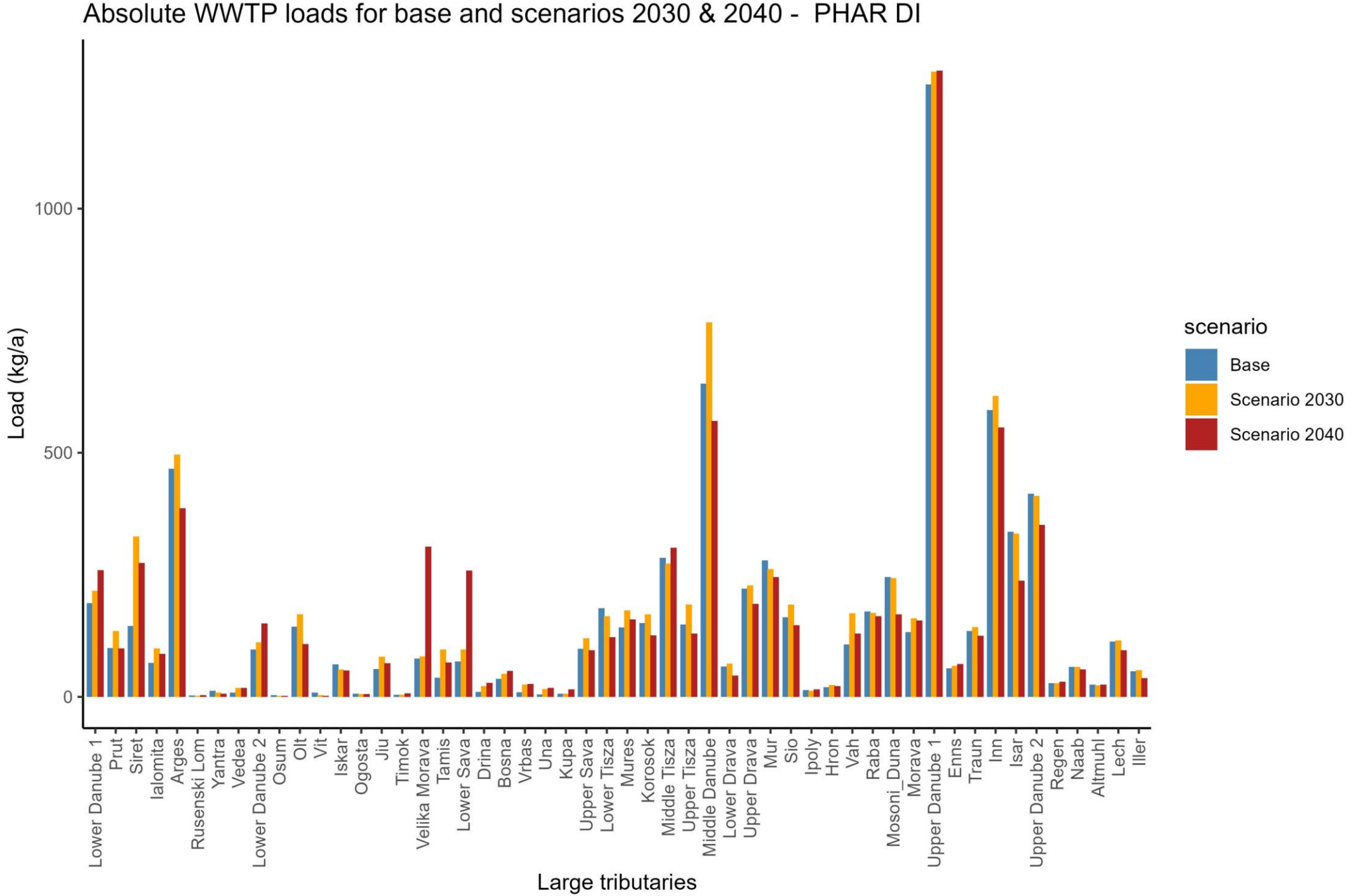
- Hydrological input from IIASA CWatM for 2015 to 2100:
    - biascorrected ISIMIP IPSL-CM6A-LR General Circulation Model - Ssp2.45 & SSP5.85 scenarios
    - Later: Biascorrected Restore4life ec_earth3_veg GCM - Ssp2.45 & SSP5.85 scenarios
- Comparison now: against present condition and not against GCM historical data
- JRC forcast:
    - 19 GCM to assess future rainfall erosivity
    - Ssp2.45 & SSP5.85 scenarios
    - CAPRI forecast for land use change and crop dynamics


Pathway loads: Base vs SSP2-4.5, 2015–2020 average - HM AS (part 1)
Load (kg/a)
0
5000
10000
15000
20000
Large tributaries / scenario
Lower Danube 1 - Base
Lower Danube 1 - S4.5
Prut - Base
Prut - S4.5
Siret - Base
Siret - S4.5
Ialomita - Base
Ialomita - S4.5
Arges - Base
Arges - S4.5
Rusenski Lom - Base
Rusenski Lom - S4.5
Yantra - Base
Yantra - S4.5
Vedea - Base
Vedea - S4.5
Lower Danube 2 - Base
Lower Danube 2 - S4.5
Osum - Base
Osum - S4.5
Olt - Base
Olt - S4.5
Vit - Base
Vit - S4.5
Iskar - Base
Iskar - S4.5
Ogosta - Base
Ogosta - S4.5
Jiu - Base
Jiu - S4.5
Timok - Base
Timok - S4.5
Velika Morava - Base
Velika Morava - S4.5
Tamis - Base
Tamis - S4.5
Lower Sava - Base
Lower Sava - S4.5
Drina - Base
Drina - S4.5
Bosna - Base
Bosna - S4.5
Vrbas - Base
Vrbas - S4.5
Una - Base
Una - S4.5
Kupa - Base
Kupa - S4.5
Upper Sava - Base
Upper Sava - S4.5
Lower Tisza - Base
Lower Tisza - S4.5
Pathway
AD_E_HM_AS
ER_E_HM_AS
GW_E_HM_AS
ID_AD_E_HM_AS
ID_E_HM_AS
OR_E_HM_AS
SR_E_HM_AS
TD_E_HM_AS
US_E_HM_AS
WWTP_E_HM_AS
RIVER BASINS

Pathway loads: Base vs SSP2-4.5, 2015–2020 average - HM AS (part 2)




Absolute WWTP loads for base and scenarios 2030 & 2040 - PHAR CAR
RIVER BASINS
Load (kg/a)
400
300
200
100
0
Large tributaries
Lower Danube 1
Prut
Siret
Ialomita
Arges
Rusenski Lom
Yantra
Vedea
Lower Danube 2
Osum
Olt
Vit
Iskar
Ogosta
Jiu
Timok
Velika Morava
Tamis
Lower Sava
Drina
Bosna
Vrbas
Una
Kupa
Upper Sava
Lower Tisza
Mures
Korosok
Middle Tisza
Upper Tisza
Middle Danube
Lower Drava
Upper Drava
Mur
Sio
Ipoly
Hron
Vah
Raba
Mosoni_Duna
Morava
Upper Danube 1
Enns
Traun
Inn
Isar
Upper Danube 2
Regen
Naab
Altmuhl
Lech
Iller
scenario
Base
Scenario 2030
Scenario 2040


Absolute WWTP loads for base and scenarios 2030 & 2040 - PHAR DI
Load (kg/a)
1000
500
0
Lower Danube 1
Prut
Siret
Ialomita
Arges
Rusenski Lom
Yantra
Vedea
Lower Danube 2
Osum
Olt
Vit
Iskar
Ogosta
Jiu
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Kupa
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Iller
Large tributaries
scenario
Base
Scenario 2030
Scenario 2040
RIVER BASINS