The 4th International Conference on Risk Assessment of Pharmaceuticals in The Environment (ICRAPHE2023)
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TOOLS FOR THE EXPLOITATION OF MONITORING DATA

Organic Micropollutants in Three Mediterranean Rivers as Case Study

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Monitoring of contaminants in the environment: Where are we today?

Chemosphere

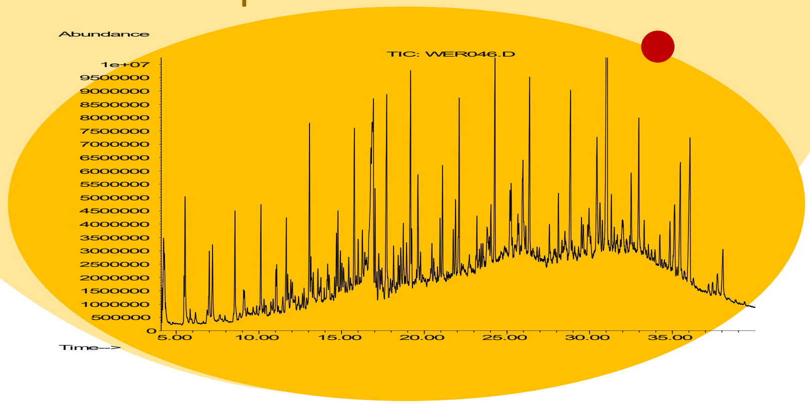
70 mio known chemicals

14 mio commercially available

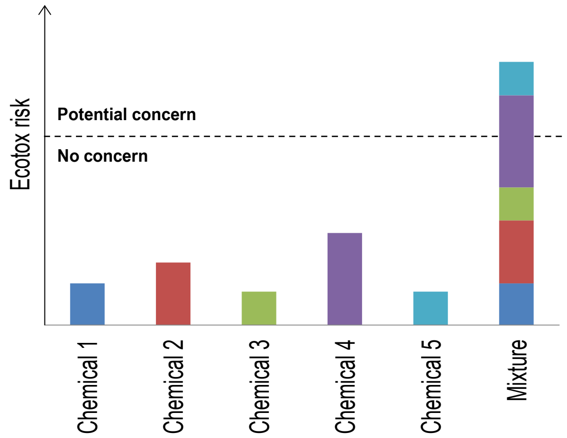
> 140.000 in daily use

≈50 priority pollutants regulated (WFD)

> 10.000 compounds in environmental samples



- **Emerging pollutants** (e.g. pharmaceuticals, personal care products, biocides..., transformation products)
  - in daily use
  - widespread
  - neither regulated nor monitored
  - often polar, ionic, multi-functional, “difficult“ to analyze
  - often poorly retained in WWTPs
  - may exhibit great biological activity
  - occur in mixtures

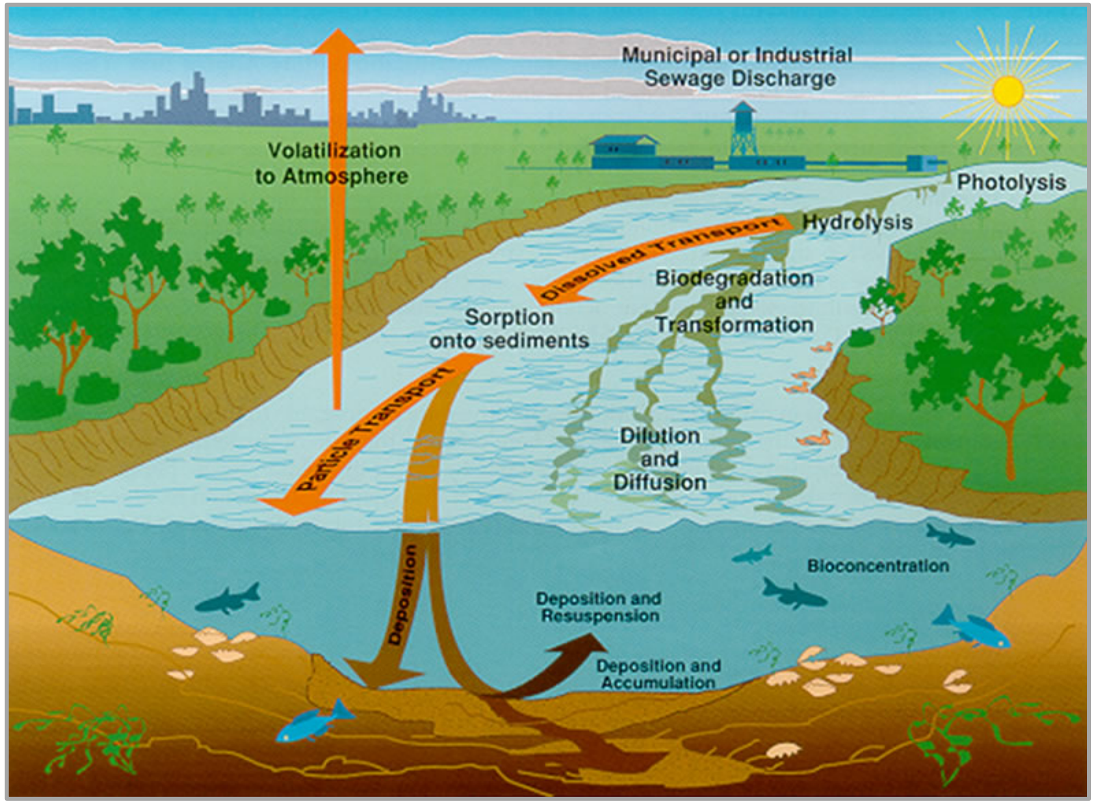


Occurrence and fate of contaminants in the environment:

- Rivers extend more or less continuously through **space** and **time** under the **influence** of their **catchment area.**
- Rivers are net **receivers** of both **point** and **diffuse pollution**, such as nutrients, metals, and emerging pollutants, which are considered one of the main causes of freshwater biodiversity impairment.
- Many pollutants are **not persistent**; rather they may undergo changes due to multiple **biotic** and **abiotic** processes, giving rise to **transformation products.**
- Pollution can be **transferred** alongside the river.

Physical processes:
Dillution
Difusion
Transport (advection)
Volatilization
Adsorption

Abiotic and biotic chemical processes:
Photolysis
Hydrolysis
Biodegradation



Environmental Monitoring

- Pollutants occurrence are determined through **monitoring**
- **Monitoring campaigns** are **expensive**, requiring personnel and analytical resources.
- **Monitoring data** should be regarded as a valuable **asset** that should be **maintained and exploited**

Exploiting Monitoring Data

- **OCCURRENCE**
- **ECOTOXICOLOGICAL RISK ASSESSMENT**
- **RIVER BASIN SPECIFIC POLLUTANTS**
- **DATA-BASED MODELLING**

GLOBAQUA Project: *Managing the effects of multiple stressors on aquatic ecosystems under water scarcity* (2014-2019)

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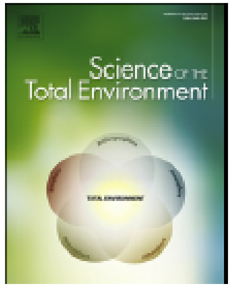

Check for updates

Priority and emerging organic microcontaminants in three Mediterranean river basins: Occurrence, spatial distribution, and identification of river basin specific pollutants

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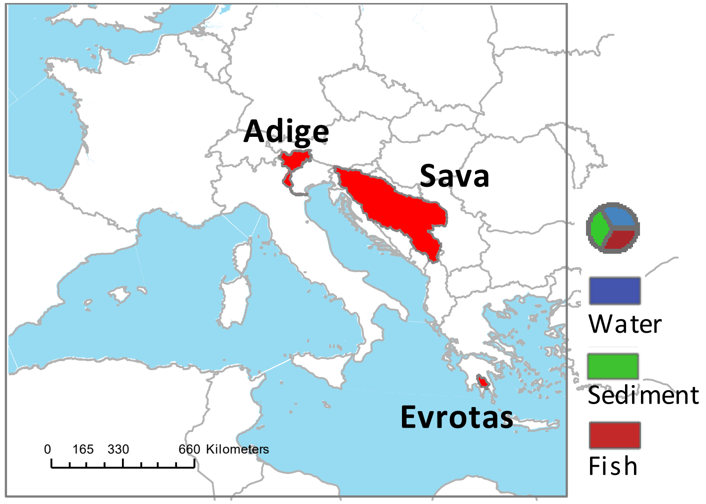
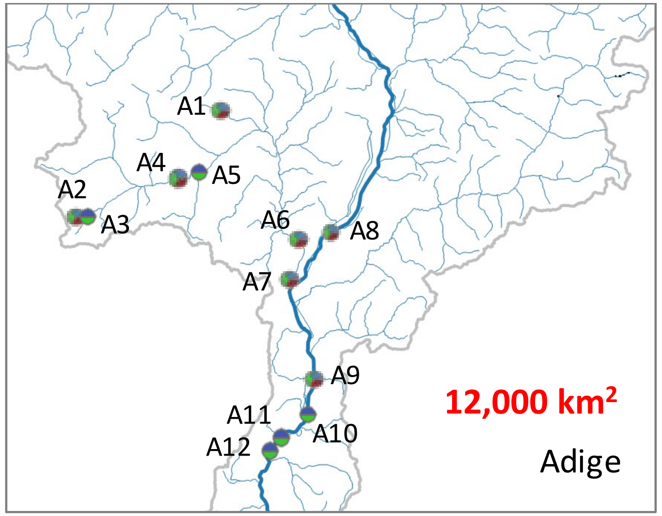
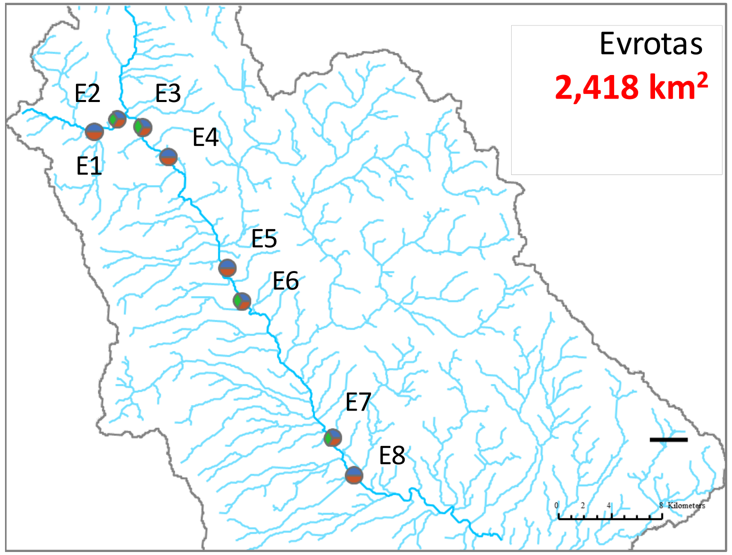
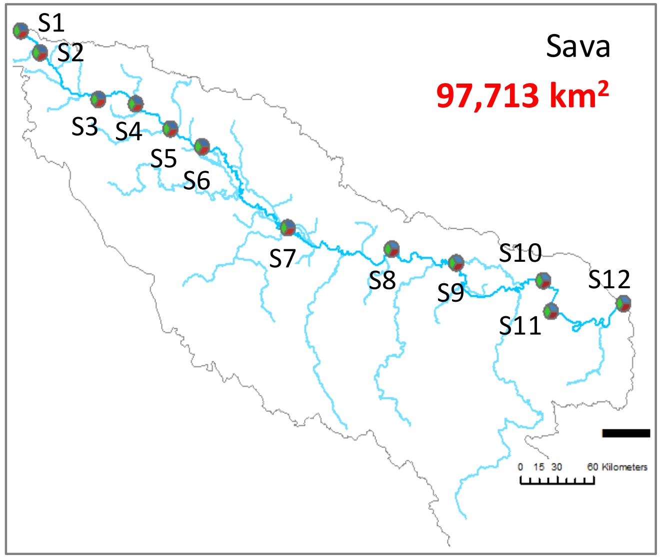
River basins studied









ADIGE Main stressors

- **Diffuse pollution by agriculture** (pesticides used in the apple trees cultivations) in the central and lower course.
- **Hydropeaking** affecting contaminant loads transport.
- **Release of pollutants from the glaciers**
- **Emerging pollutants** from the WWTPs serving the **ski resorts.**

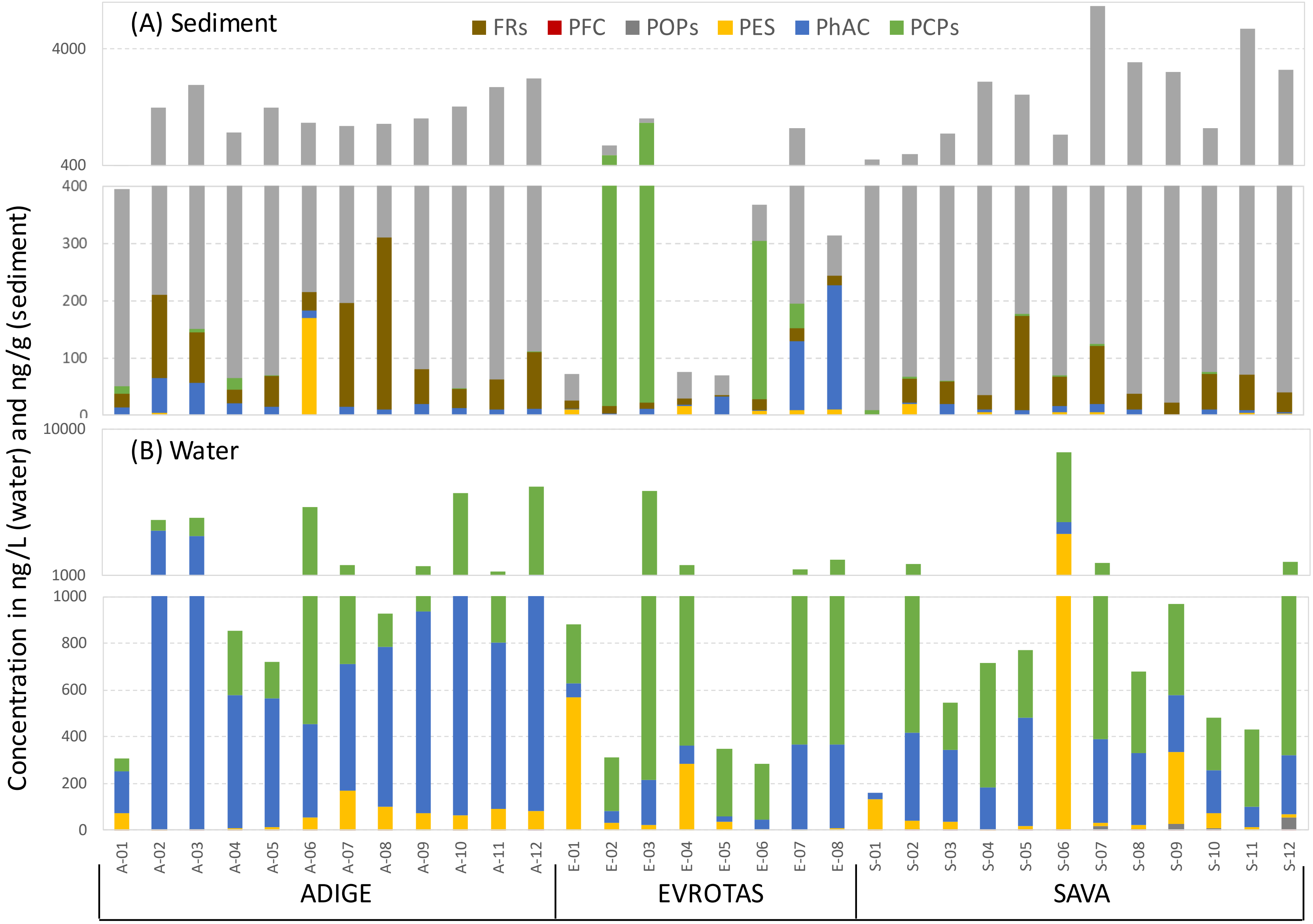
EVROTAS Main stressors

- **Agricultural activities**
Overexploitation of both **ground** and **surface waters**
Disposal of **agro-industrial wastes** (mainly oil mills)
agrochemical pollution (pesticides)
hydromorphological alterations.

SAVA Main stressors

- **Urban pollution.** Untreated sewage discharge (Belgrade)
- In the middle and lower part, **oil refinery, heavy metal industry, site mining industry and agricultural activities**.

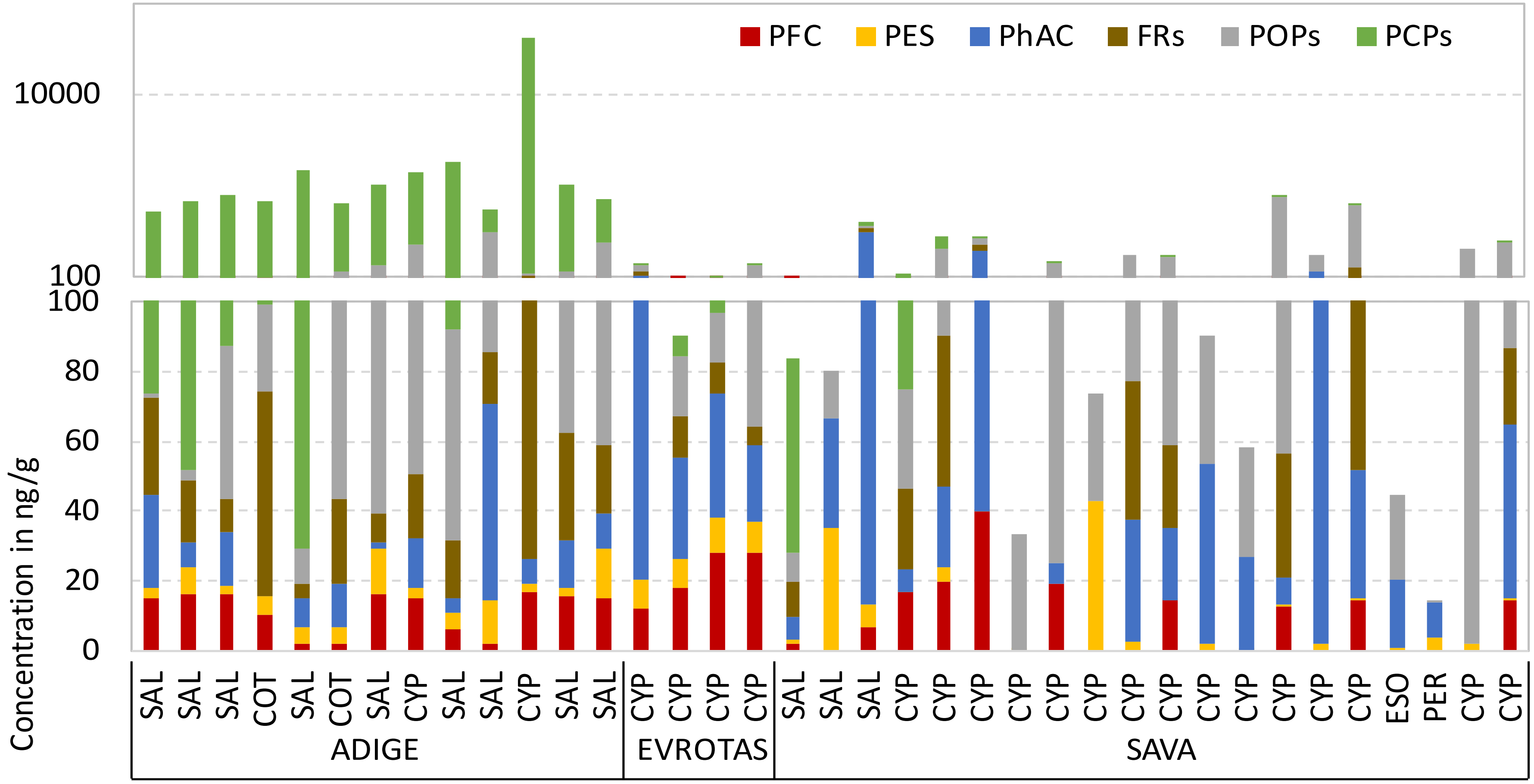
Ocurrence in Water and Sediments



PFC, perfluorinated
PES, pesticides
PhAC pharmaceuticals
FR, flame retardants
POP, persistent organic
PCP, personal care products.

Mean concentration of target pollutants in sediment (A) and water (B) samples from the three river basins.

Ocurrence in Biota (fish)



PFC, perfluorinated
PES, pesticides
PhAC pharmaceuticals
FR, flame retardants
POP, persistent organic
PCP, personal care products.

Mean concentration of target pollutants in fish: **SAL**: Salmonidae; **COT**: Cottidae; **CYP**: Cyprinidae; **ESO**: Esocidae; **PER:** Percidae.

Assessing the chemical risk of water bodies

- Under the **WFD**, the characterization of the **“chemical status”** of the European water bodies relies on the monitoring of **priority pollutants**, as well as on pollutants of regional or local relevance **specific to each river basin (RBSP)**.

- For risk mitigation purposes it is crucial **to identify which compounds** are the **most relevant** ones in terms of **ecotoxicological risk** for each river basin.

Of all the compounds present in the environment **typically only a few are responsible** for the majority of the **risk** for **biological communities**.

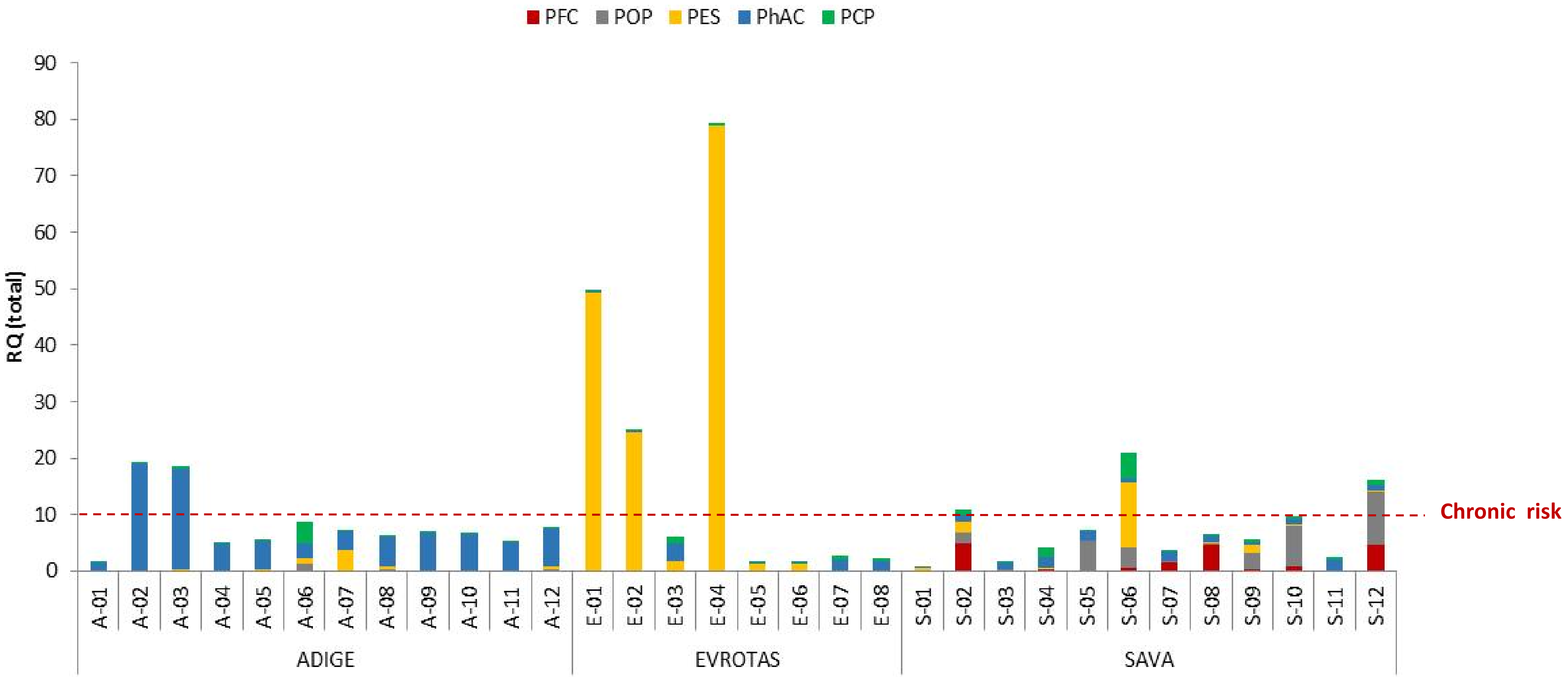
$$RQ_i = \frac{MEC_i}{PNEC_i}$$

$$RQ_{site} = \sum_i RQ_i$$

(Conc. Addition)

Prioritization

Ecotoxicological Risk Assessment



Cumulated risk per site for the three river basins, showing the contribution of the different compound families: **PFC**, perfluorinated compounds; **POP**, persistent organic pollutants; **PES**, pesticides; **PhAC**, pharmaceutical active compounds; **PCP**, personal care products.

NORMAN prioritization methodology

https://www.norman-network.com/nds/ecotox/

- Considering the **specific pollutants of each river basin,** two risk indicators were proposed for the prioritisation in the water phase

Frequency of Exceedance (FoE)

Considers the spatial distribution of potential effects of a certain compound, *i.e.* the **frequency of sites** with observations **above** the lowest **PNEC**.
The maximum observed concentration at each site (MEC_{site}) is compared to the lowest PNEC.

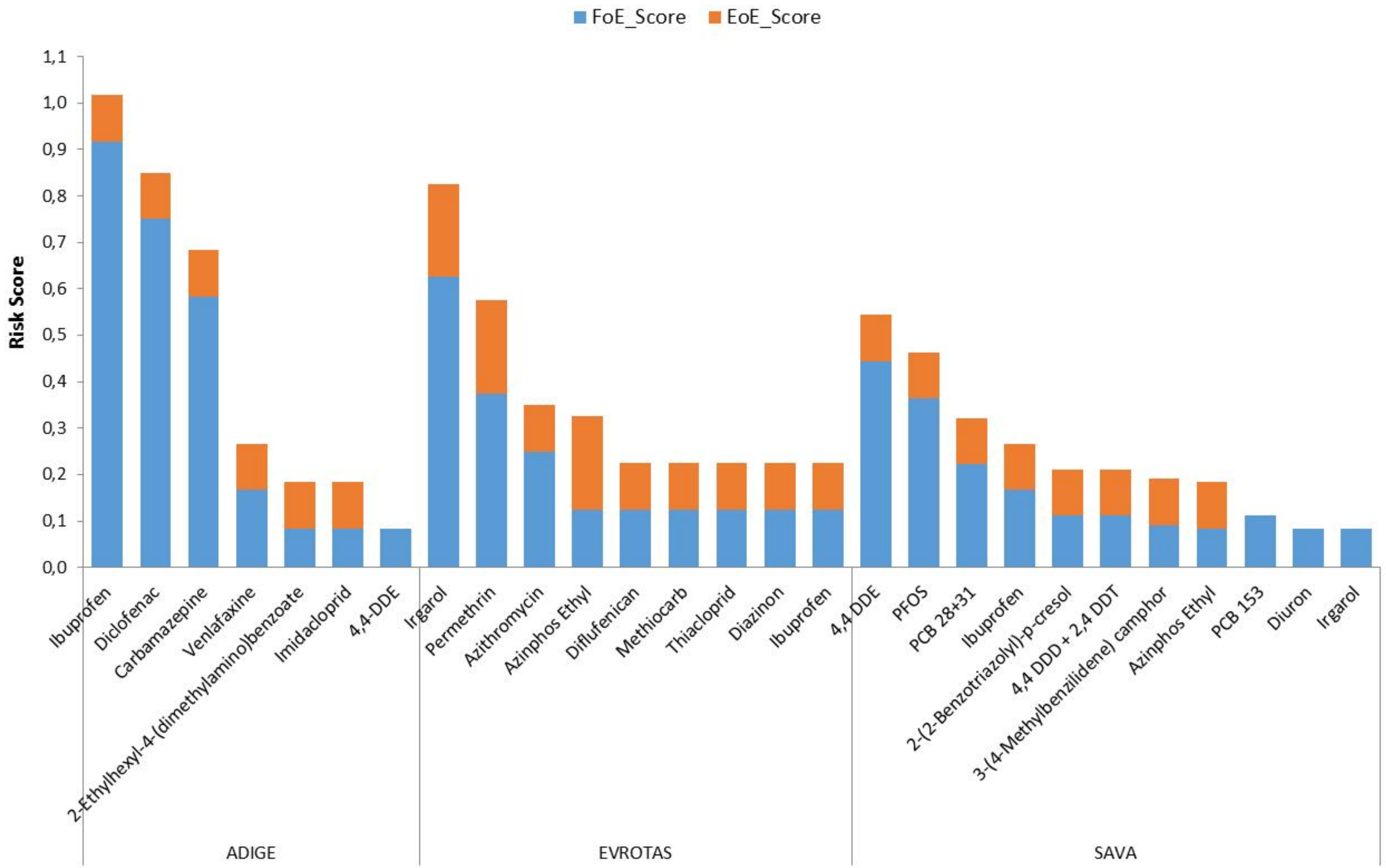
Extent of Exceedance (EoE),

Considers the **extent (intensity)** of local effects.
All concentration data above the LOQ is pooled and used to calculate a MEC_{95}.
The MEC_{95} is then divided by the lowest PNEC to derive the "*Extent of Exceedance*".

FoE and *EoE* lie within 0 and 1 and are added to yield the final Risk Score $RS = FoE + EoE$ $(0 \leq RS \leq 2)$

Dulio, V., Slobodnik, J., 2015. *Environ. Toxicol. Chem.* 34, 2183–2185.

River Basin Specific Pollutants (prioritization)

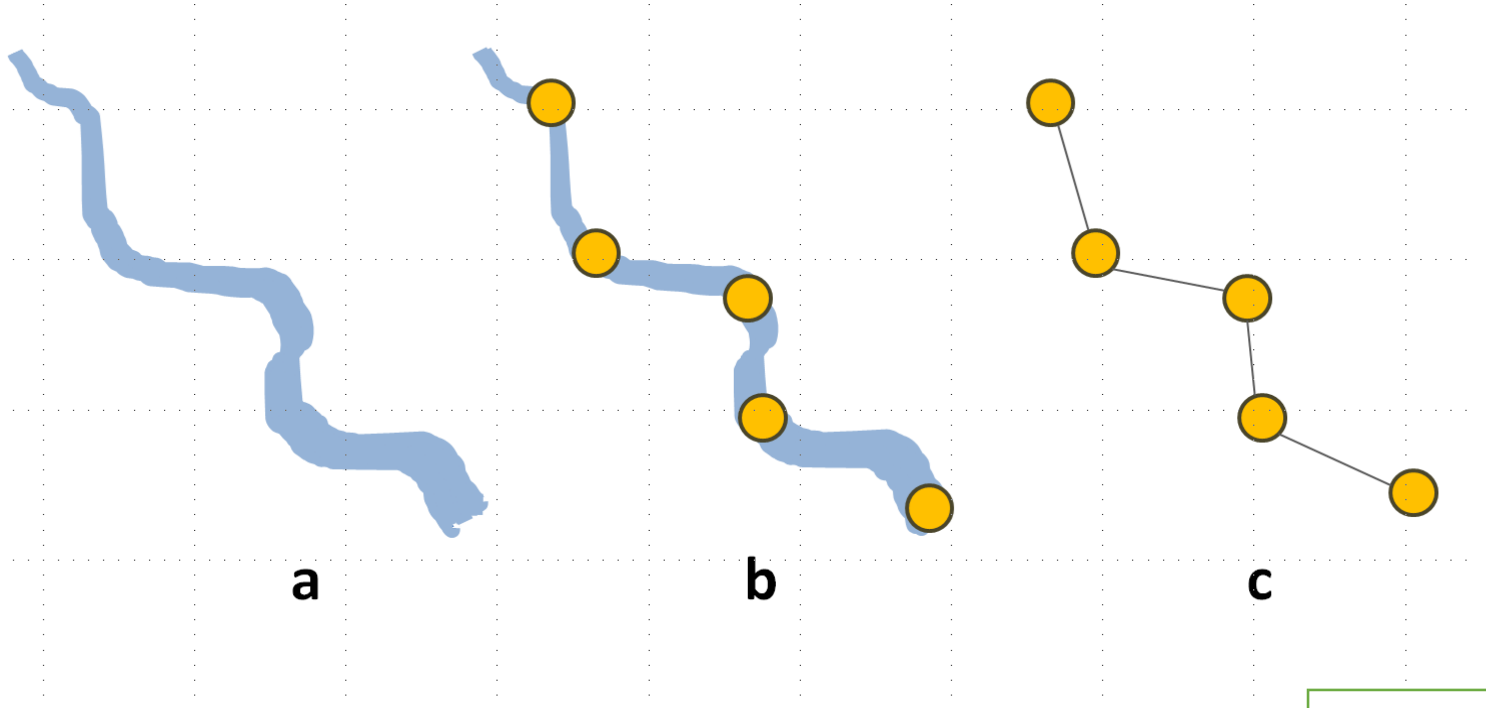


River basin specific pollutants prioritized according to the NORMAN methodology for the three investigated rivers.

The river as a network

- Few variables can be measured with the highest resolution in time (i.e., online sensors) or space (i.e., remote sensing), and none in both dimensions.

- Therefore, our **knowledge** of the river's **qualitative status** relies on **discrete spatial and temporal** observations of a set of physical, chemical, or biological parameters, organized under what is commonly known as a **“monitoring network”**



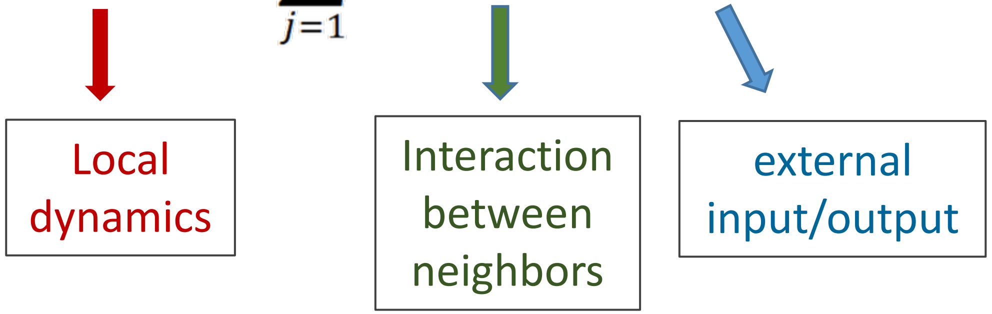
Real river

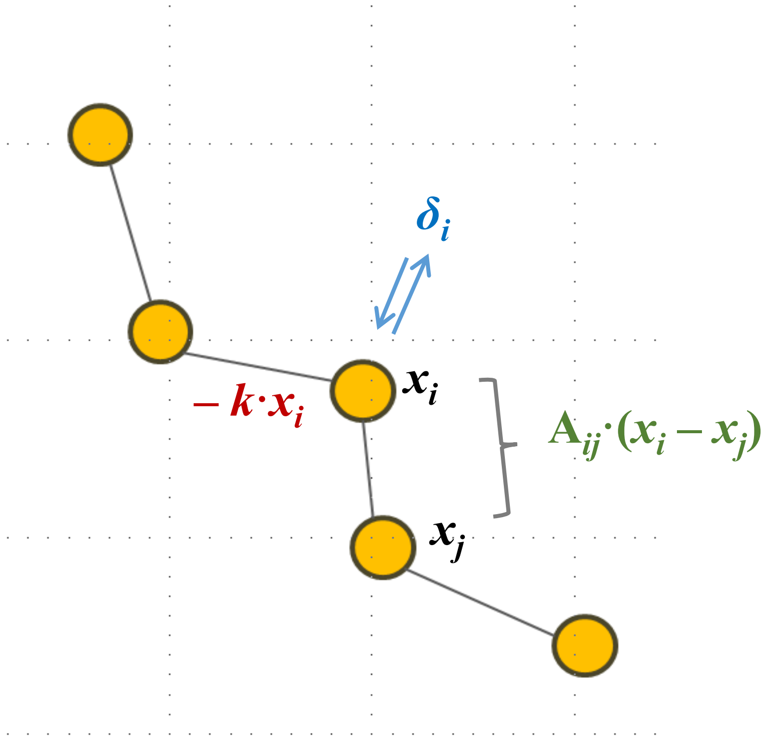
Monitoring network
(our observations)

Network graph
(topological representation)

A simple data-based advection-reaction *(reactive transport)* model

$$\frac{dx_i}{dt} = -k \cdot x_i + \bar{v} \cdot \sum_{j=1}^{n} A_{ij}(x_i - x_j) + \delta_i$$





x_i : variable x measured at sampling site i

Assuming steady-state ($\dot{\mathbf{x}} = \mathbf{0}$), rearranging, and dividing both sides by k :

$$\mathbf{x} = \bar{v}/k \cdot \mathbf{Lx} + \boldsymbol{\delta}/k$$

$$\mathbf{x} = \ell \cdot \mathbf{Lx} + \boldsymbol{\varepsilon}$$

- ℓ and $\boldsymbol{\varepsilon}$ are obtained by **ordinary least squares regression** of $\mathbf{x}$ over $\mathbf{Lx}$
- The error vector $\boldsymbol{\varepsilon}$ provides information on the **external inputs/outputs** at each site.

Calculations

$$\rho = \frac{k}{\bar{v}} = 1/\ell$$

ℓ Characteristic length

$$\rho = \frac{\mathbf{x}^{\mathrm{T}}\mathbf{L}\mathbf{x}}{\mathbf{x}^{\mathrm{T}}\mathbf{x}}$$

$$0 \leq \rho \leq \lambda_{max}$$

Spectral decomposition:

Expanding **x** in terms of the normalized eigenvectors **u** and eigenvalues λ of **L**

$$c_i = \mathbf{u}_i^{\mathrm{T}}\mathbf{x}$$

$$\rho = \sum_i c_i^2 \lambda_i$$

$$\sum_i c_i^2 = 1$$

Entropy:

$$S = -\sum_i c_i^2 \ln c_i^2$$

Synchronization contribution:

$(x_1 = x_2 = \dots x_n)$:

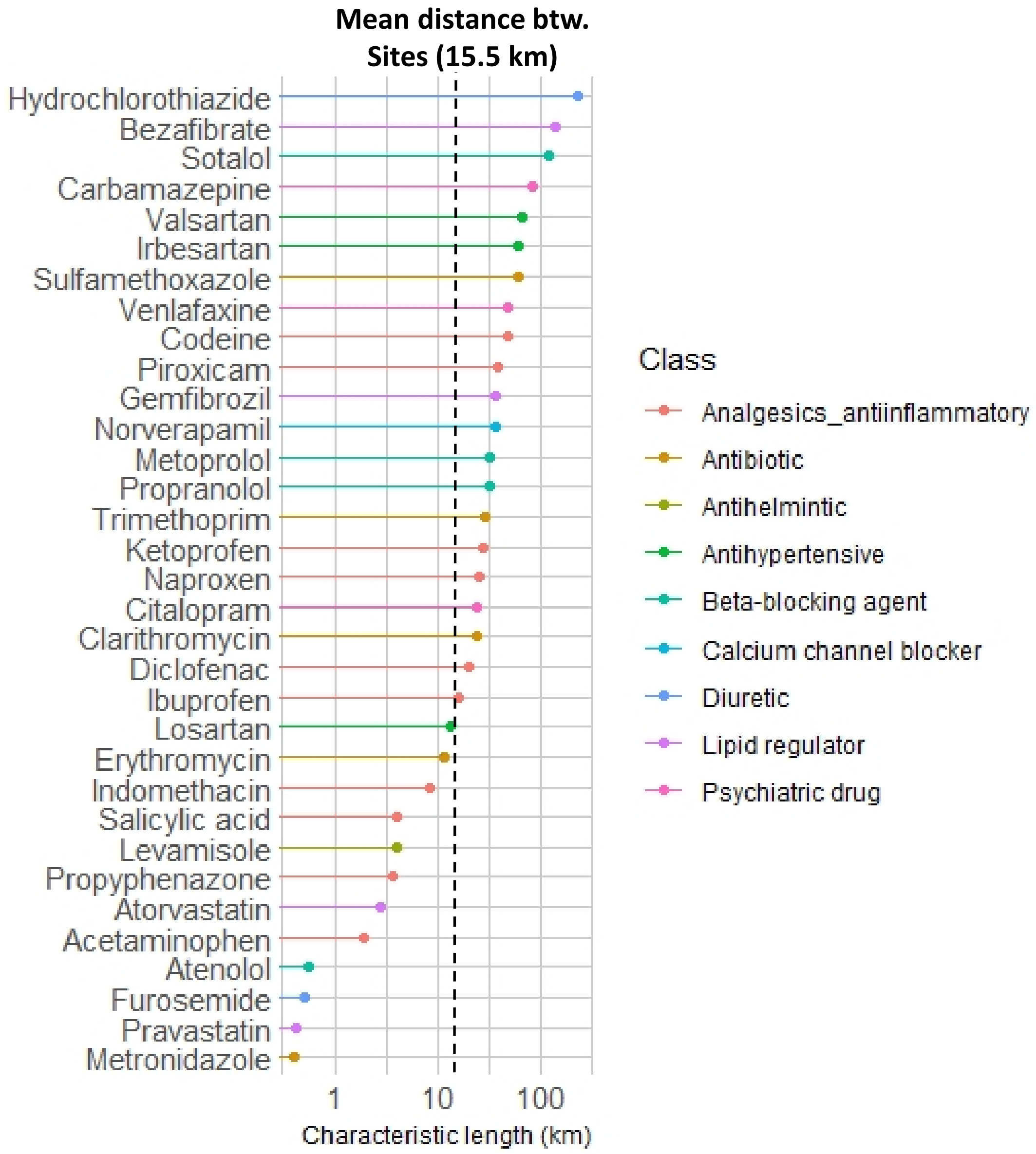
c_1^2

Ginebreda A, et al. *MethodsX* 10 (2023) 101948 https://doi.org/10.1016/j.mex.2022.101948

Labad F, et al. *Environ. Pollution* 316 (2023) 120504 https://doi.org/10.1016/j.envpol.2022.120504

Ginebreda A, Barceló D. *Water Emerg Contam Nanoplastics* (2022)1:12 https:// doi: 10.20517/wecn.2022.07c

Characteristic length ℓ (km)



$$\rho = \frac{k}{\bar{v}} = 1/\ell$$

Interpretation:

- Distance (km) to which the advection process is active in relation to the local decay process
- Ratio between the advection and the local decay process
- Ideally, the mean distance between monitoring sites $\leq \ell$

Comments:

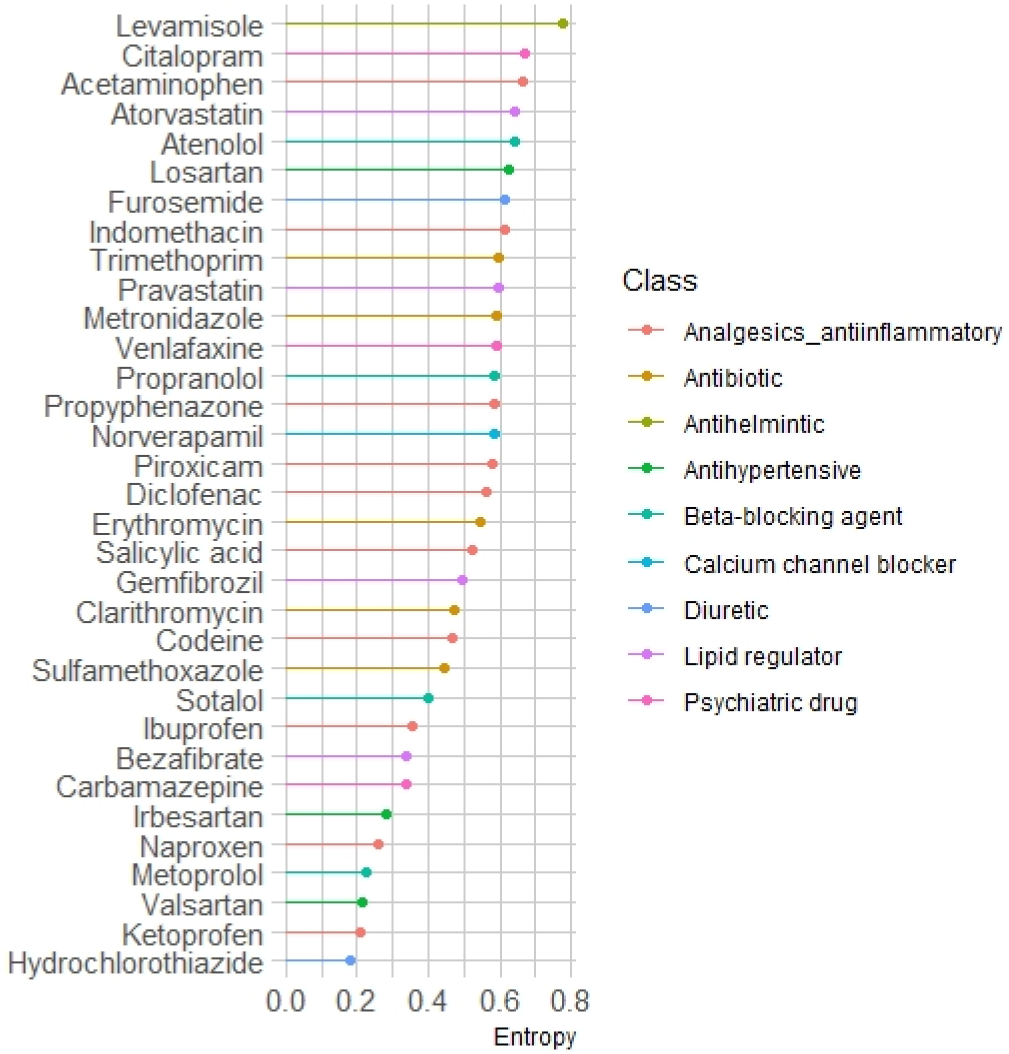
- ℓ of the whole compound set was comprised between 231 km and 0.4 km, with a median of 25 km (same order of mean distance between monitoring sites ≈ 15.5 km)

Pharmaceuticals in the Adige

Entropy

Entropy:

$$S = -\sum_i c_i^2 \ln c_i^2$$



Interpretation:

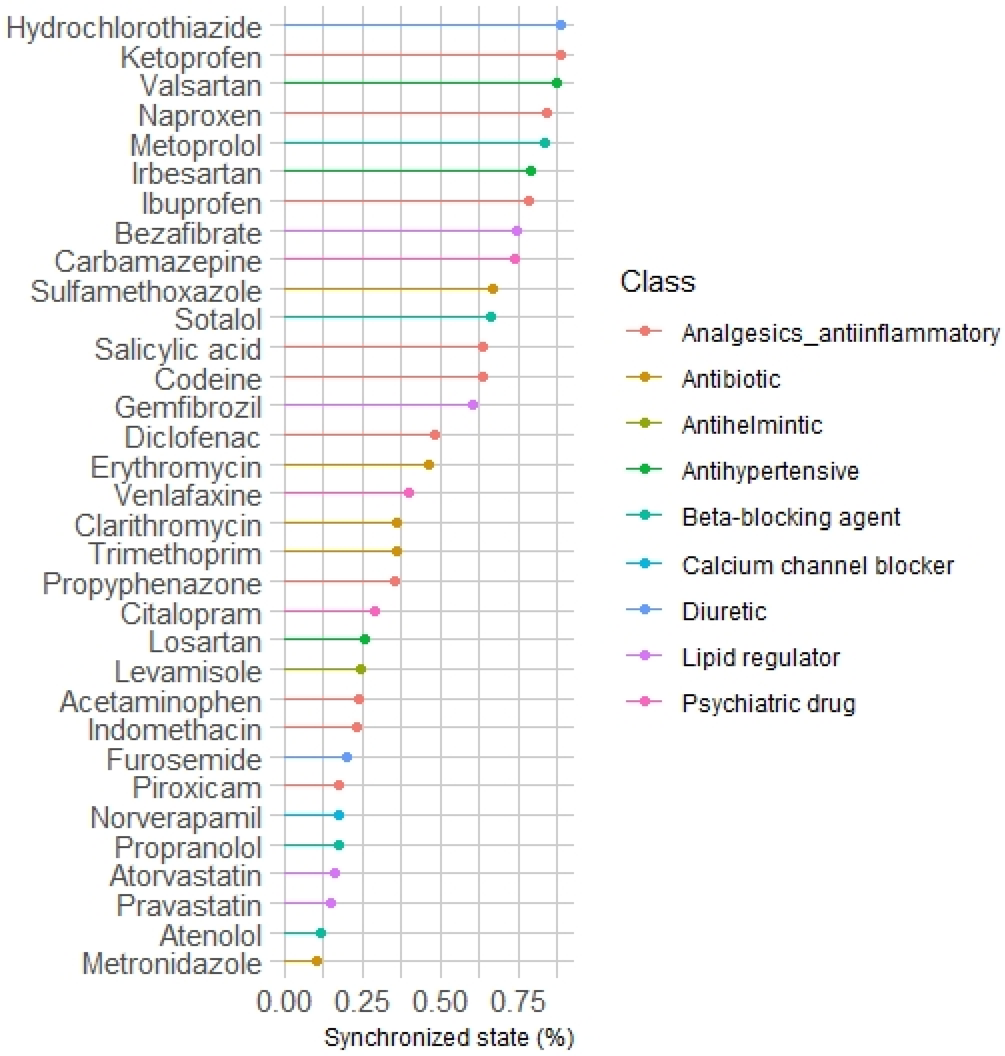
- Captures the system 'complexity' providing a quantitative measure on how the different eigenstates of the Laplacian matrix contribute to the description of the system.
- Entropy takes its maximum value when all the eigenstates are equally allocated $c_1 = c_2 = ... = c_n$

Pharmaceuticals in the Adige

Synchronization

$$\rho = \lambda_1 c_1^2 + \lambda_2 c_2^2 + \ldots + \lambda_n c_n^2$$

with $\sum_{i=1}^{n} c_i^2 = 1$



Interpretation:

- Synchronization corresponds to the equilibrium state in which $x_1 = x_2 = \ldots = x_n$
- Synchronization corresponds to the lowest eigenvalue of $\mathbf{L}$ $(\lambda_1 = 0)$
- The equilibrium state has $\rho = 0$ and hence $\ell = \infty$

Ongoing work

- **PRIORITY MIXTURES:**
  - Identification of the most relevant **pollutant mixtures** at basin scale in terms of risk using multivariate statistical analysis with advanced chemometric tools (MCR-ALS).
    - ***Loadings*** *(eigenvectors) resulting from multivariate analysis (linear combinations of measured variables) may be regarded as mixtures*

- **MODELLING:**
  - **Extension of the advection-reaction (reactive transport) model** to other site-measured variables (microplastics, biological, etc.), matrices (sediments, biota), or waterbodies (groundwater).

    MethodsX 10 (2023) 101948 https://doi.org/10.1016/j.mex.2022.101948

    Environ. Pollution 316 (2023) 120504 https://doi.org/10.1016/j.envpol.2022.120504

Conclusions

- Typically **>50 compounds were detected per site** indicating that the targeted chemicals generally occur in mixtures in the environment and likely originate from a variety of uses and sources
- The **ecotoxicological risk per site** was estimated using **RQs**. Sites with RQ>10 indicative of **chronic ecotoxicological** risk were present in the three rivers assessed.
- **NORMAN Prioritization methodology** was conveniently used to identify the compounds of highest relevance for each river basin
- **Prioritization** resulted in lists of relevant compounds (**RBSP required by the WFD**) that differed among three rivers……. Good **agreement** with **predominant stressors in each river.**
- A simple **advection-reaction (reactive transport)** model is derived based on **network-theoretical** concepts that are applicable to **data** obtained from **monitoring networks** with **known spatial topology**.
- This modelling approach provides useful **quantitative information** regarding the **dynamic behaviour** of the variables monitored **local decay kinetics**, the **distance of influence of the neighbour sites** (quantified as a *characteristic length*), the relative **contribution of the different network modes or states** (quantified as an *entropy*), and specifically, that of the fully ***synchronized state*** , and the **external input/output** to the system.
- The presented approach can be **useful for water managers** for the design and **optimization of river monitoring networks.**
- **Monitoring networks are crucial** for the surveillance of both the environment and human health (**One Health perspective**)

Thanks for your attention!

Acknowledgements

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