Using small to large scale monitoring data to identify priority mixtures in surface water bodies

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Round table: “Ecosystem health and chemical mixture risk assessment and management”

Background

Actually, European Union regulations take into account risks and impacts of chemical substances **one by one**, disregarding an overall evaluation of the cumulative effects of mixtures

Several studies in scientific literature and many reports from International Scientific Bodies demonstrate that mixtures may have a **more than additive** effect on non-target organisms

In 2019 European Council of Environment Ministry delegated the European Commission to propose **new specific regulations** to introduce the evaluation of combined exposure of chemicals in mixtures either in human beings and the environment.

Italian Ministry of Environment delegated IRSA CNR to propose a **methodology** that could help **local and regional Authorities** to identify priority mixtures and their potential effects

↓

Management

The current project

«Accordo di collaborazione per la definizione di un approccio metodologico alla valutazione degli effetti combinati delle sostanze chimiche»
«Collaboration agreement for the implementation of a methodological approach for the evaluation of combined effects of chemical substances»

Consiglio Nazionale delle Ricerche - Istituto di Ricerca sulle Acque (**CNR-IRSA**)
in collaboration with
University of Milano Bicocca - Department of Earth and Environmental Science (**DISAT**)
Istituto di Ricerche Farmacologiche Mario Negri (**IRFM**)
Istituto Superiore di Sanità (**ISS**)
Istituto Superiore per la Protezione e la Ricerca Ambientale (**ISPRA**)
Istituto Sull'inquinamento Atmosferico-**CNR**

Preliminary data

Types of input

- Mixtures from urban wastewater
- Mixtures from industrial wastewater
- Mixtures from agricultural sources
- Mixtures from landfills or incinerators

Non-target organisms considered

Surface water

- Algae (EC50)
- Daphnia (EC50)
- Fish (LC50)

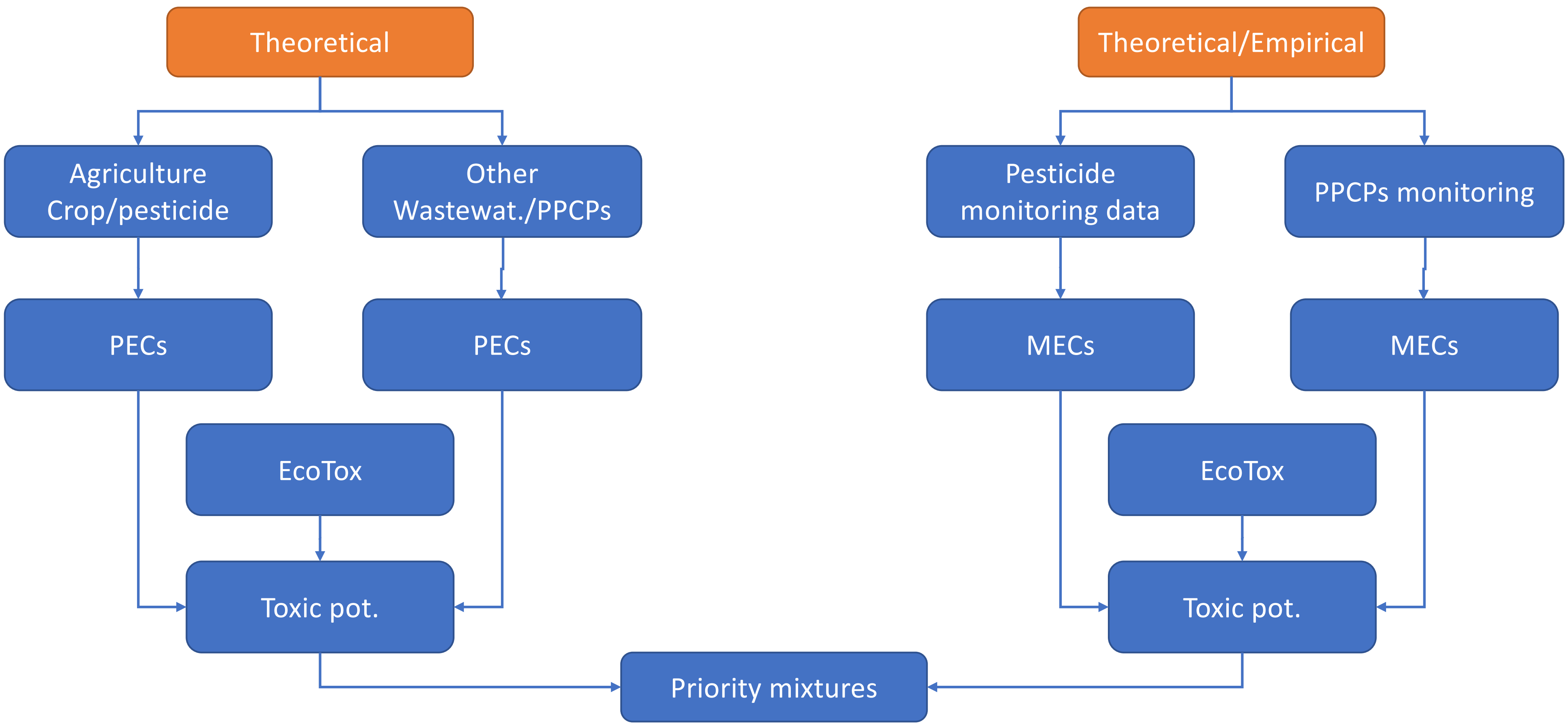
What spatial scale?

Local scale: easily characterization of substances and their amount

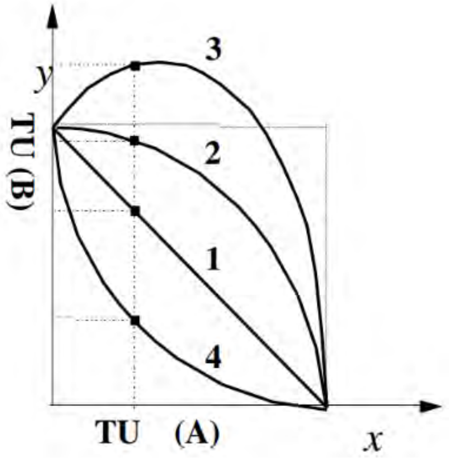
Basin scale: preliminary analysis of land uses to identify potential «priority mixture», i.e. mixtures which have a high probability to be formed.

Regional scale: too many sources → mixtures cannot be easily identified

Methodology overview



Methodological approach



The approach is based on the **Concentration Addition** (CA) model

Hypothesis:
a) substances have the same Mode of Action (MoA)
b) mixture toxicity for a non-target organism (*org*) is expressed as:

$$TU_{org} = \sum_{1}^{n} i \frac{Conc_i}{EndPoint(org)_i}$$

Where:

TU is “Toxit Unit” concept

Conc$_i$ is the concentration of the i-th substance expressed as:

MEC (Measured Environmental Concentration) when dealing with monitoring data

PEC (Predicted Environmental Concentration) when obtained from modelling data

EndPoint(org)$_i$ is the toxicological end point for the selected organism (generally LC50 or EC50)

Characterization of results

Best case/worst case

Two different cases, dependent on the LOQ (Limit of quantification)

Best case: only substances with a measure above the LOQ

Worst case: also substances not quantified are taken into account, with the value LOQ/2

Assessment factors

Uncertainties due to the selection of ecotox data should be considered

Algae → 0.1 * EC50
Daphnia → 0.01 * EC50
Fish → 0.01 * LC50

Theoretical/empirical approach

1) Definition of 5 baseline **scenarios** representative of
different contamination sources and territories (North and South Italy)

2) Acquisition of **monitoring data** from certified sources
- pesticides from Regional Environmental agencies
- emerging contaminants from scientific literature

3) **Georeferencing** of monitoring stations

4) **Calculation** of mixtures toxicity with CA method:
mixtures are characterised considering monitoring data in one place **and** in one time
and applying the worst and best case

5) **Calculation** of mixture fractions to identify the most influencial substances

Baseline scenarios

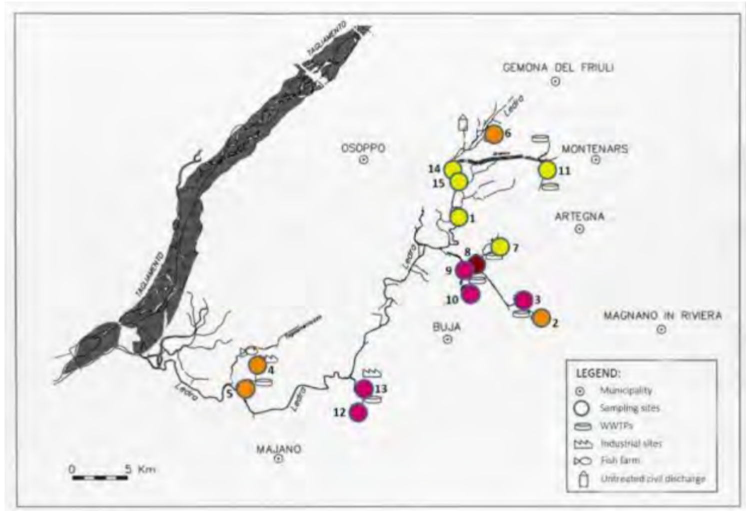
a) last section of the **ADDA river** (Po tributary) --> agricultural input, 3 years data, 17 monitoring stations

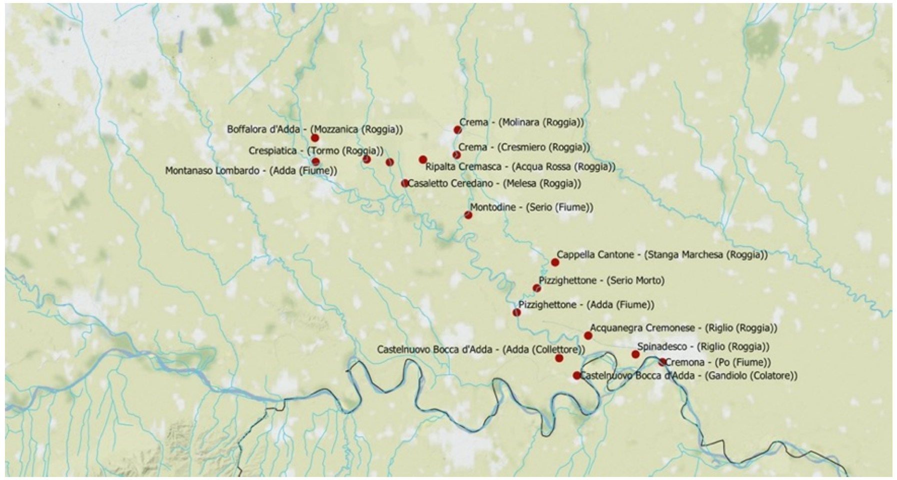
b) a 50 Kms section of the **Tevere river** --> mixed agricultural and wastewater, 3 years, several stations

c) one monitoring station on **Tevere river** downstream to a wastewater treatment plant, south of Rome, 1 year

d) Ledra river (Friuli Venezia Giulia), wastewater, several stations, 1 sampling

e) Seveso and Olona river (near Milan), wastewater TP, 2 years data.





Implementation of a procedure to calculate and visualise mixture toxicity

Objectives:

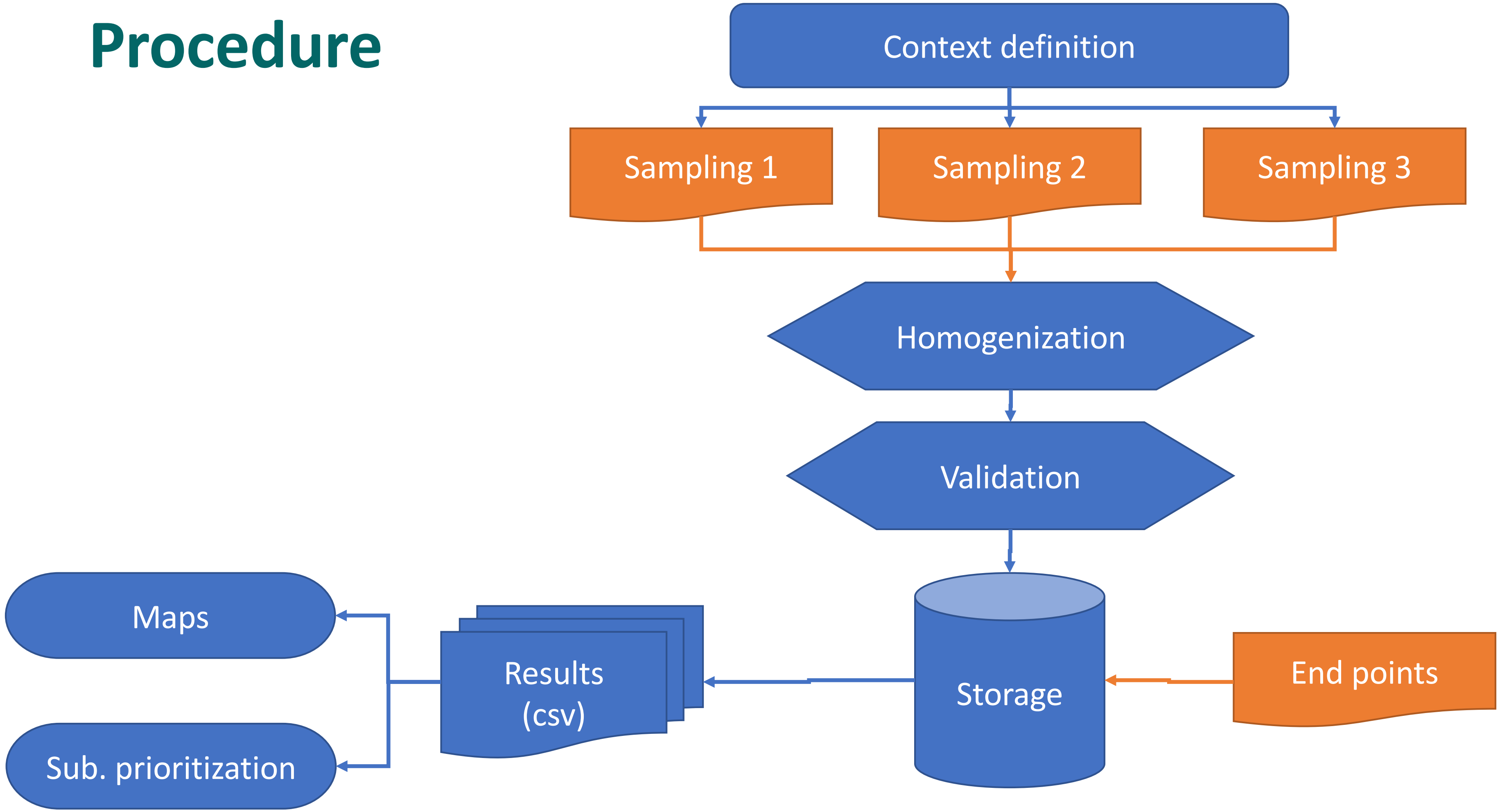
a) collect **in one place** all the information of a specific evaluation

b) provide a **simple and repeatable** procedure to technicians

c) estimate the **contamination level** for each non-target organism (TU calculation)

d) prioritization of substances within the mixture (TU fraction calculation)

Procedure



Context definition
Sampling 1
Sampling 2
Sampling 3
Homogenization
Validation
Storage
End points
Results
(csv)
Maps
Sub. prioritization

Input data

Mandatory Monitoring data

→ Station ID
→ Sampling Date
→ Geographical coordinates
→ Sampled value (and its unit of measure)

Eco-tox end points (surface water)

→ LC 50 fish
→ EC 50 algae
→ EC 50 daphnia

Sources (example)

Scientific literature

Pesticide Property Data Base (PPDB)

Veterinary Medicine Property Data Base (VPDB)

ECOTOX (EPA)

Homogenization and validation

Substance	CAS number	LoQ
Trifluralin	1582-09-8	<0,01
Trifluralin	1582-09-8	<0,02
Trifluralin	1582-09-8	<0,03
Trifluralin	1582-09-8	<0,05

Homogenization

→ Data format
→ Geographical coordinates
→ LOQ differences (between regions or time of samping)

Validation

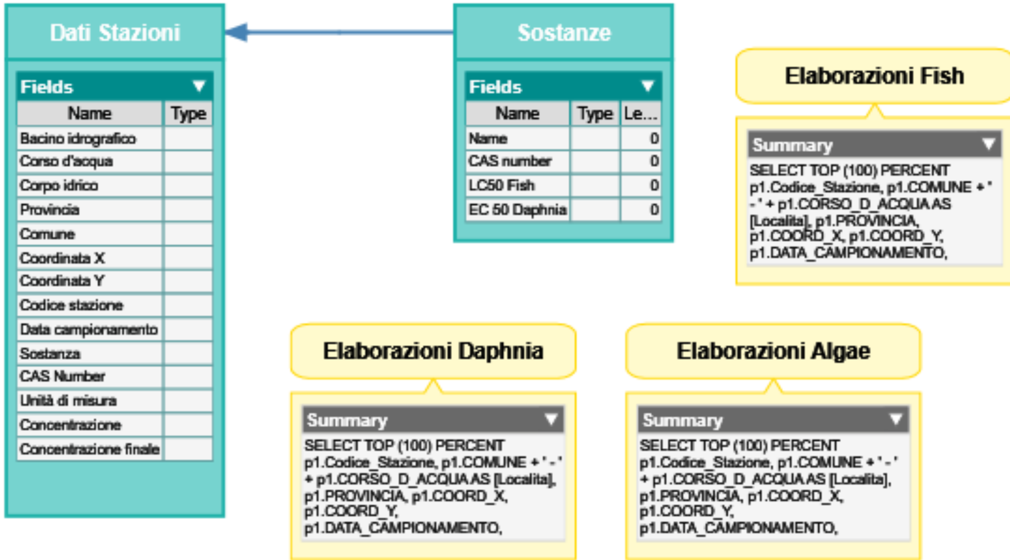
→ Check for values beyond admissible range
→ Check the Unit of measure of concentration by years and by regions

TU calculation

Checked data flush into a **database** (tables in green)

Database **queries** ("views" in yellow) calculates TU for each non-target organism

Resulting data are exported in **csv tables** with essential information for GIS representation



An **Excel** file provides functionalities for visualize TU fractions values both for worst and best case

TU results

Field	Example
Station ID	0013311ir_1
Station name	Acquanegra Cremonese - Riglio (Roggia)
Province	CR
X coordinate (WGS 84 – UTM 32N)	569644
Y coordinate (WGS 84 – UTM 32N)	5000750
Sampling date	10/08/2015
Substance removed due to no ecotox data provided	Chlorides, Orthophosphate
TU «Best case»	**0.008575281**
N# substances considered [TU «Best case»]	3
Substances list [TU «Best case»]	Metolachlor, Terbuthylazine, Desetil Terbuthylazine
TU «Worst case»	**0.017830407**
N# substances considered [TU «Worst case»]	20
Substances list [TU «Worst case»]	Alachlor, Atrazine, Clorpirifos, Clorpirifos Metile, Dieldrin, Eptacloro, Esaclorobenzene, HCH alfa, HCH gamma (lindano), Metolachlor, Molinate, Oxadiazon, Paration etile, Pendimetalin, Pentaclorobenzene, Terbutilazina, Terbutilazina desetil, Trifluralin

TU fractions results

TU provides an overall value of the mixture toxicity, but it hides the information behind each substance

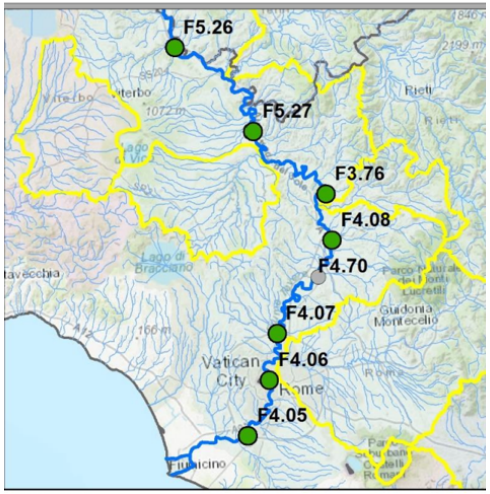
The detailed analysis of the mixture component (fractions of toxic unit) gives information about relevant contributions and what can be neglected

TU BC: 1.41E-03

Fish - Best Case					
Station ID	**Sampling date**	**Substance**	**Concentration**	**End-Point**	**TU fraction**
POAD3ACCA1lo1	14/04/2016	Terbutilazina	2.75	2200	1.25E-03
POAD3ACCA1lo1	14/04/2016	Flufenacet	0.2	2130	9.39E-05
POAD3ACCA1lo1	14/04/2016	Metolachlor	0.26	3900	6.67E-05
POAD3ACCA1lo1	14/04/2016	Terbutilazina desetil	0.06	18000	3.33E-06
POAD3ACCA1lo1	14/04/2016	Simazina	0.02	90000	2.22E-07

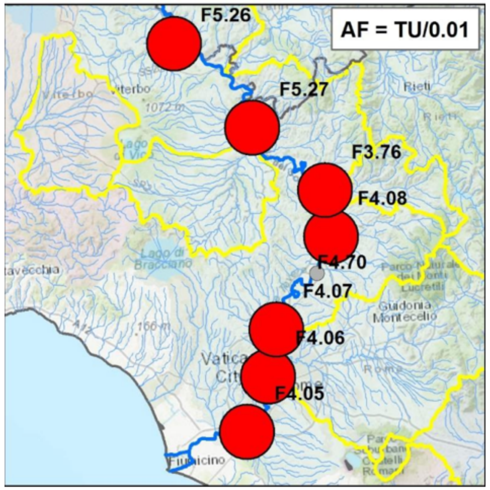
Geographical representation

TU without assessment factor

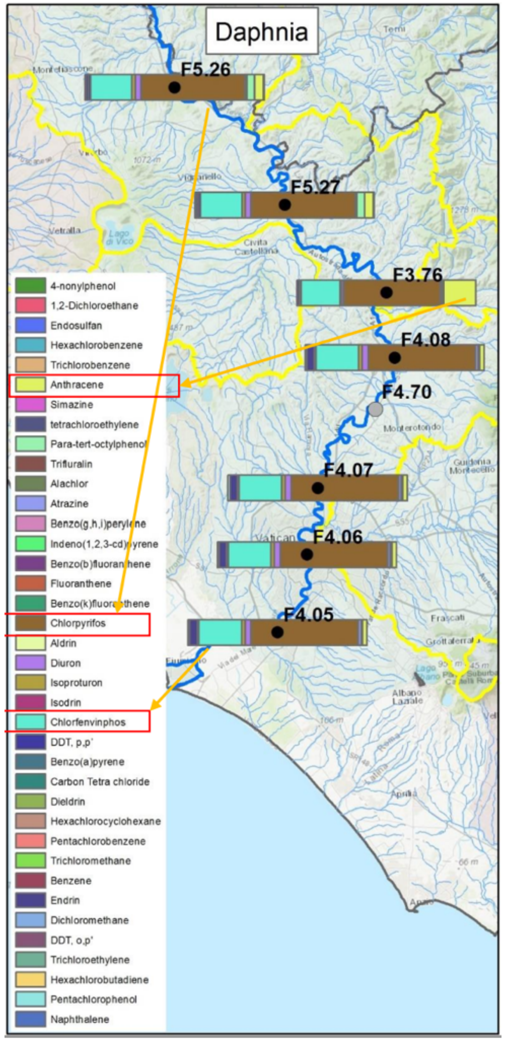


TU Daphnia

TU with assessment factor



TU fractions



Conclusions

The methodology (and the correlated procedure) provides:

a) simple and reliable way to calculate contamination from mixtures with a certain degree of **automatization**

b) prioritization of substances within each mixture

c) immediate **visualization** of the results through GIS techniques

d) mixture **distribution in the territory** (also in spatial relation with the eventual input)

e) mixture **differentiation in time** (for example seasonal changes)

Thank you for listeni