



# Pharmaceutical residues in crop irrigation water: a potential threat to groundwater

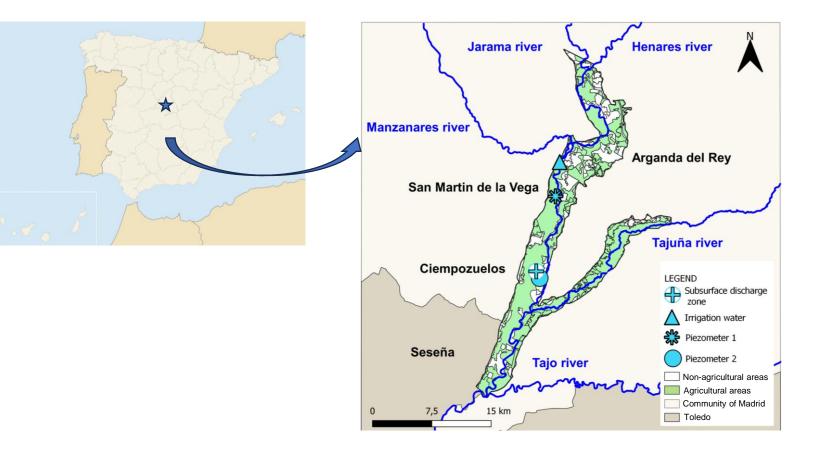
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## CONTEXT

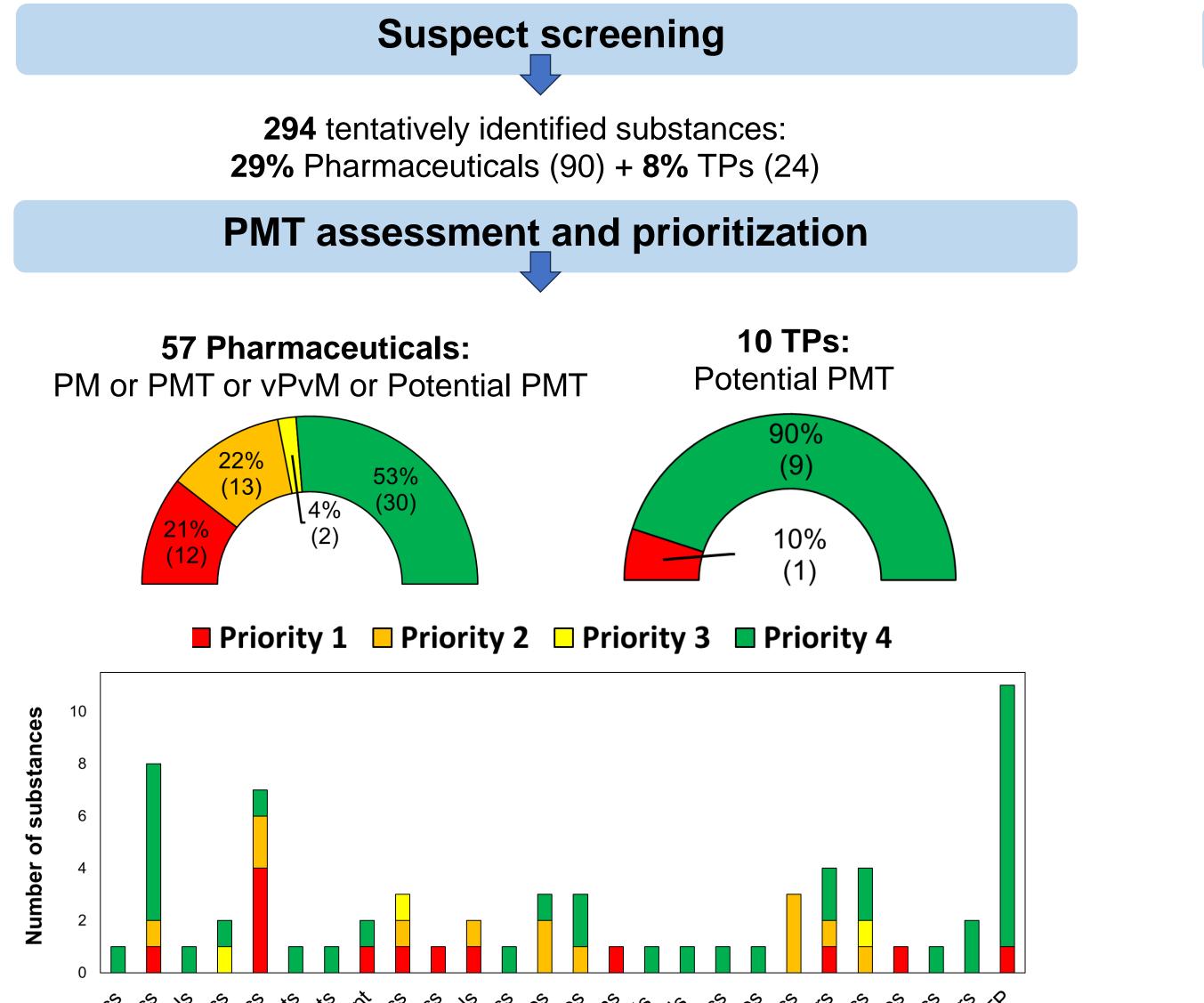
Unplanned reuse of surface water affected by wastewater treatment plant (WWTP) effluents for crop irrigation can easily spread pharmaceutical residues in the environment. These pharmaceuticals may show properties that are typical of substances defined as persistent, mobile, and toxic (PMT) category. PMT substances has gained considerable attention from both scientific and regulatory perspectives due to their potential adverse effects on ecosystem and, though them, to humans. This study focuses on assessing the presence of pharmaceutical residues and their associated transformation products (TPs), previously classified as PMT substances, in irrigation water and their spread to groundwater. The agricultural scenario selected for the study is the Vega Baja of the Jarama river, whose water is strongly impacted by the effluents of the main WWTPs of the Community of Madrid (Spain).



### **METHODS**

<b>Sampling</b> From June to September 2022 (maize irrigation campaign), biweekly samples of : - Irrigation water (IW) - Water from subsurface discharge zone (D\	3. Data processing	PMT assessment and prioritization - Multi-pillar approach for prioritization	Confirmation and quantification - Confirmation with standards - Development of the analytical method (LC-MS/MS)
- Groundwater (GW)	1. Extraction protocol (SPE)	- <b>Persistent</b> (P), <b>Mobile</b> (M) and <b>Toxic</b> (T) substances assessment proposed by	42 water samples
Out of the irrigation campaign, GW sample were taken once a month to cover on hydrological year.		Neumann and Schliebner [1] combined with European Commission criteria [2]. - Use of experimental and predicted data	Analytical methodology: - SPE: HLB cartridge
Irrigation canal W DW Fiezometer	Preconcentration factor: 200-100-20    2. Atlantis C18 column   Kinetex F5 column	from multiple QSAR models <b>Priority 1</b> : PM, PMT, vPvM, vPvMT and Potential PMT present included in the 2022 watch list and/or classified as T by more than	Mobile phase:
	Zic-HILIC column Ion paring modifier: HFBA vs formic a Ionization mode: ESI +, ESI -	one toxicity criteria and/or included in the	
	Library search: NIST 2017 (> 14.000 substances)	Priority 3: Potential PMT with the highest signal to noise value in the chromatogram	

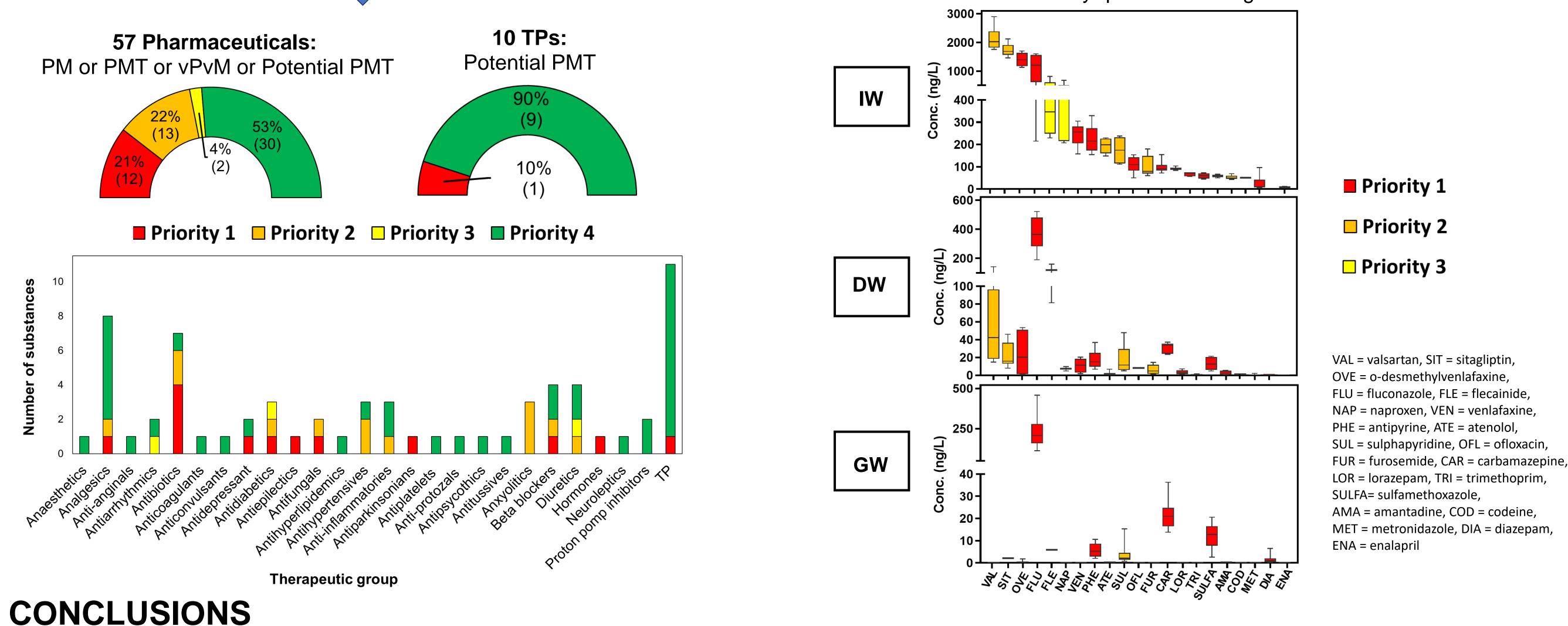
#### RESULTS



#### **Confirmation and quantification**

**Priority 4**: Potential PMT

The 28 pharmaceuticals with priority 1, 2 and 3 were selected for quantification in collected water samples. Among these substances, four were not confirmed when using the corresponding analytical standards. Instead, three pharmaceuticals have to be temporally withdrawn from the study due to analytical issues not yet overcome. Ultimately, 21 substances were successively quantified in target water matrices.



- The screening employing a library with over 14,000 compounds has identified 294 substances in IW. Among these substances, 67 Pharmaceuticals and TPs fulfill the criteria for persistence, mobility and toxicity.
- □ Although concentrations of the studied PMT pharmaceuticals are generally in the ng/L range in IW, certain exceptions exist. Substances such as the TP of venlafaxine OVE, the antifungal FLU, the antidiabetic SIT, and the antihypertensive VAL deviate from this trend, exhibiting concentrations in the order of µg/L.
- Despite their intrinsic characteristics, identified PMT pharmaceuticals undergo natural attenuation processes capable of reducing their concentrations during infiltration through the soil. However, the unplanned water reuse for crop irrigation causes the spread of some of these contaminants to the GW.
- Among studied pharmaceuticals, the two most persistent are FLU and CAR, both classified as priority 1 substances. These contaminants arise particular concern due to their potential impact on the integrity of water resources and associated ecosystems.

## REFERENCES

[1] Neumann and Schliebner (2019), German Enviroment Agency (UBA) [2] Chemicals Strategy for Sustainability Towards a Toxic-Free Environment European Commission (2020) Acknowledgements

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