

Occurrence and distribution of pharmaceuticals in intermittent rivers in Spain using LC-HRMS/MS Orbitrap

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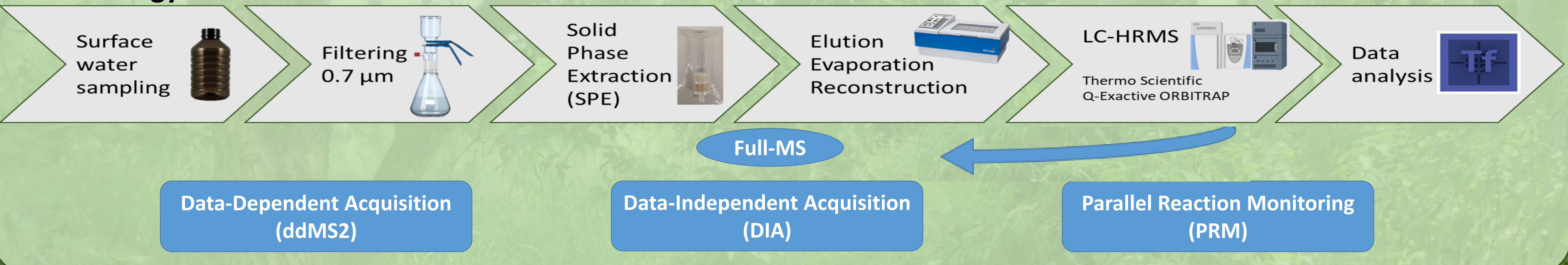


Introduction

Intermittent rivers are defined by seasonal flooding and drying, where climate and geomorphic characteristics have a direct influence on structural and functional features. At the same time, effluents from industrial and municipal wastewater treatment plants (WWTPs) play an important role as they are a continuous source of contamination. WWTPs are not designed to remove pharmaceuticals from wastewater, consequently, pharmaceuticals are detected in surface water at concentrations up to $\mu\text{g L}^{-1}$. Their continuous discharge into the aquatic environment makes them pseudo-persistent contaminants and may cause adverse effects on living organisms and the environment. Hence, the determination of these compounds in the environment is essential to characterize the quality of surface water and the changes it undergoes.

This study aims to evaluate three HRMS data acquisition modes using Q-Exactive Orbitrap MS for simultaneous full-scan MS in combination with MS2 analysis in detecting and identifying 113 pharmaceuticals and to evaluate the effect of different WWTP discharges along the watercourse of intermittent rivers in Spain.

Methodology



Results – acquisition analysis and method validation

Acquisition methods were evaluated by determining how well 113 targeted compounds could be detected and identified. In Fig. 1, we can observe the number of compounds detected with at least one product ion observed.

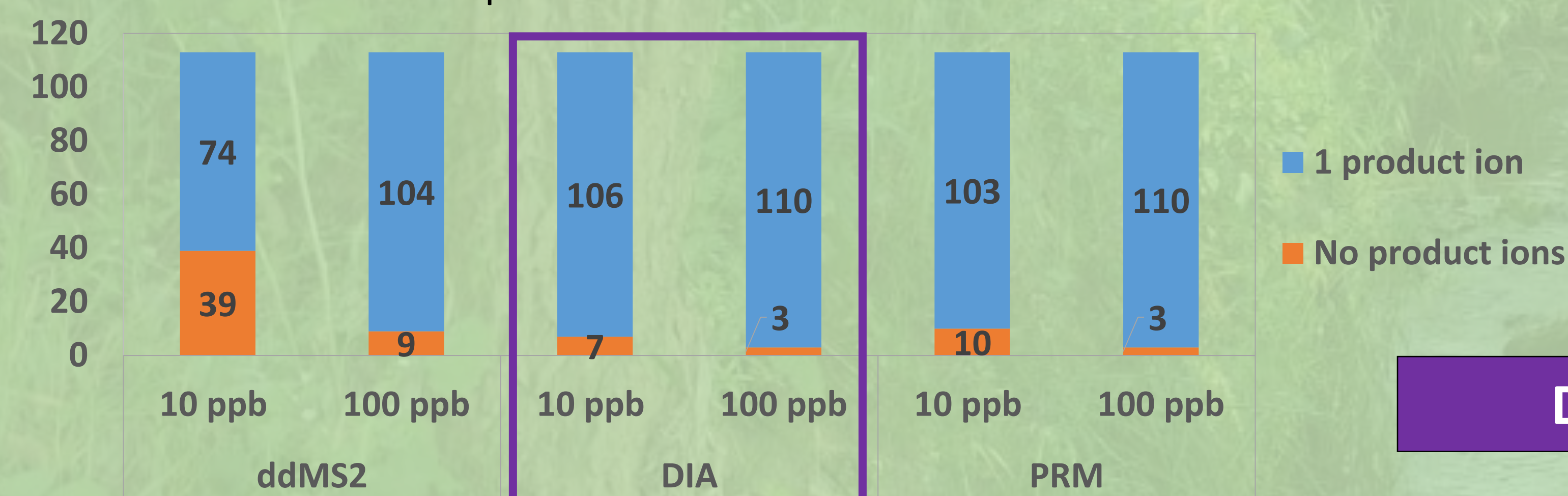
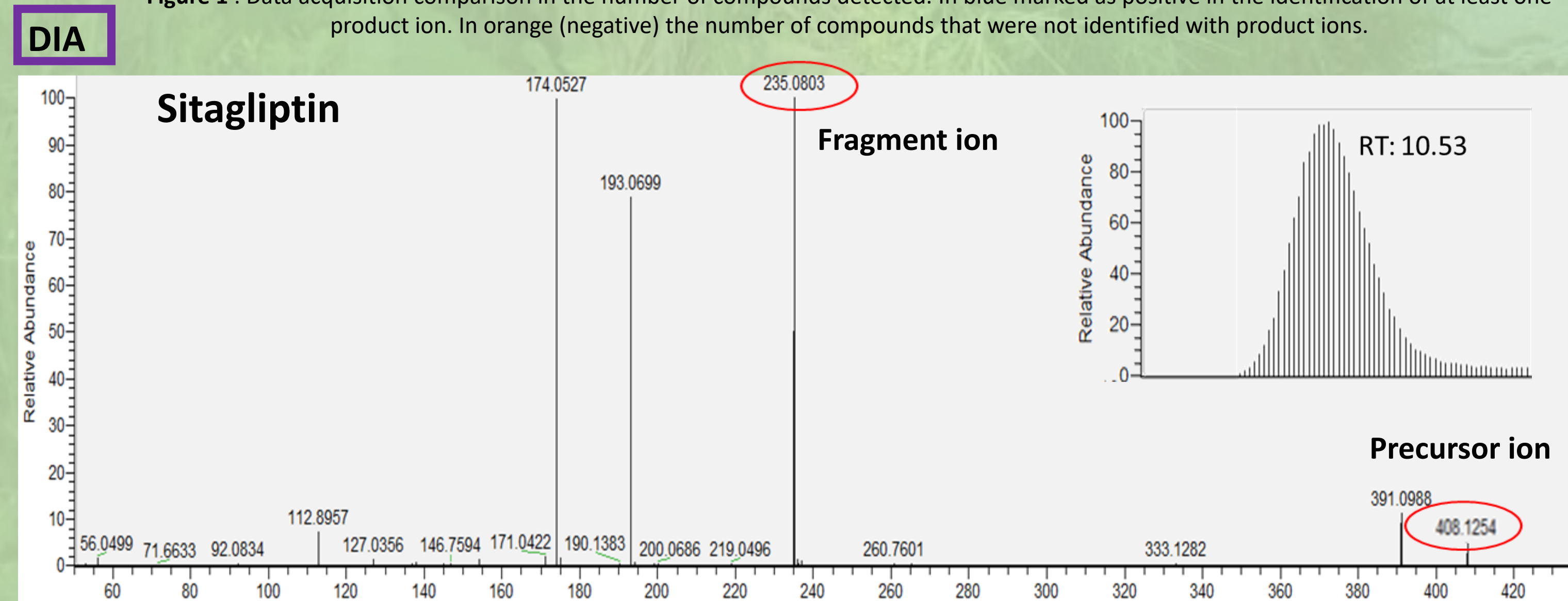
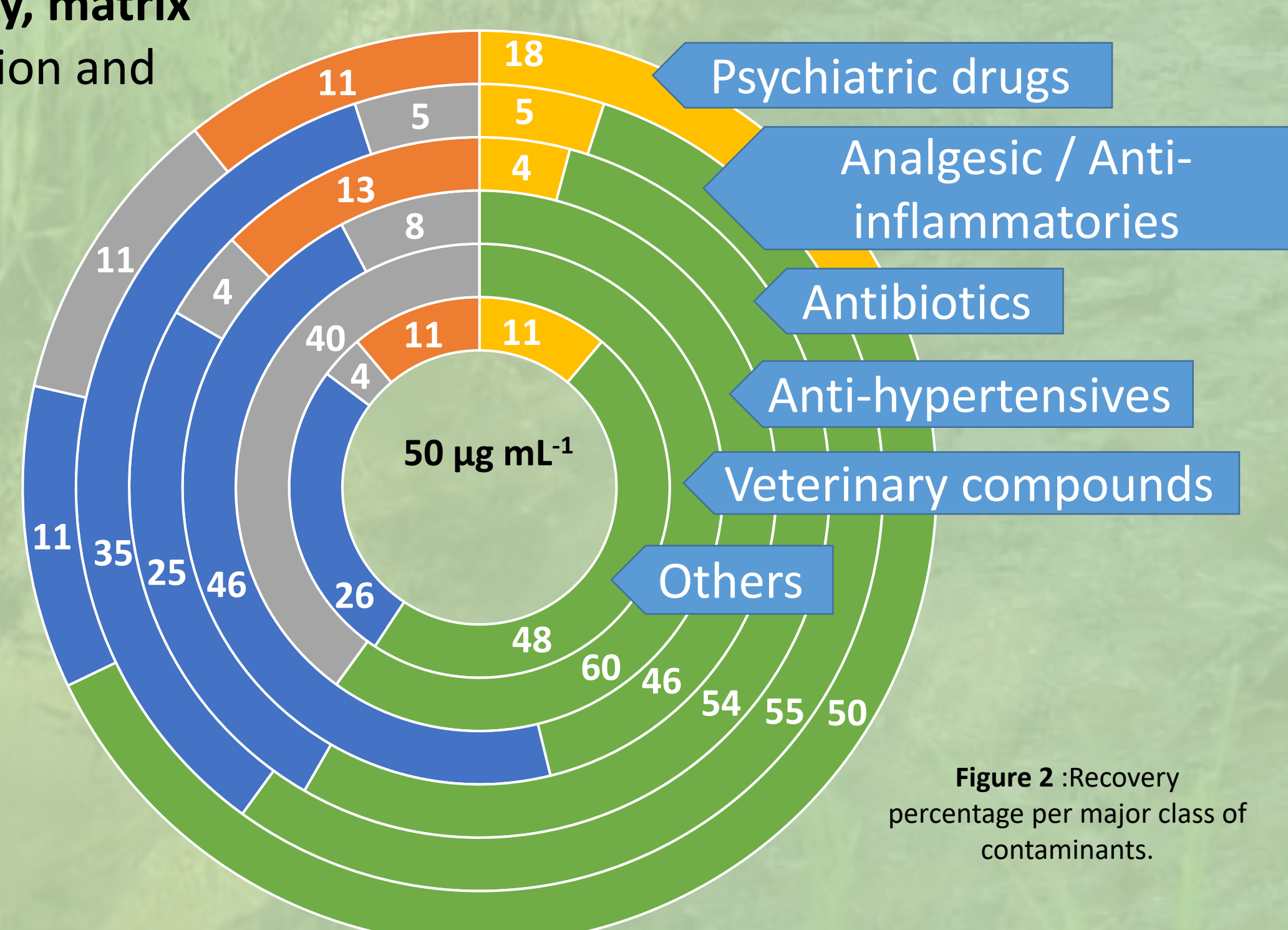


Figure 1 : Data acquisition comparison in the number of compounds detected. In blue marked as positive in the identification of at least one product ion. In orange (negative) the number of compounds that were not identified with product ions.



Optimized method was validated in terms of linearity, recovery, matrix effect and limits of detection and quantification at three concentration levels.

- Recoveries >120%
- Recoveries 70-120 %
- Recoveries 40-70 %
- Recoveries 20-40 %
- Recoveries 0-20%



Results – intermittent rivers

3 intermittent rivers were analysed, for each, 4 samplings points were monitored; upstream (UP), WWTP discharge point (DP), 20m after DP (DW1) and finally 200m after DP (DW7).

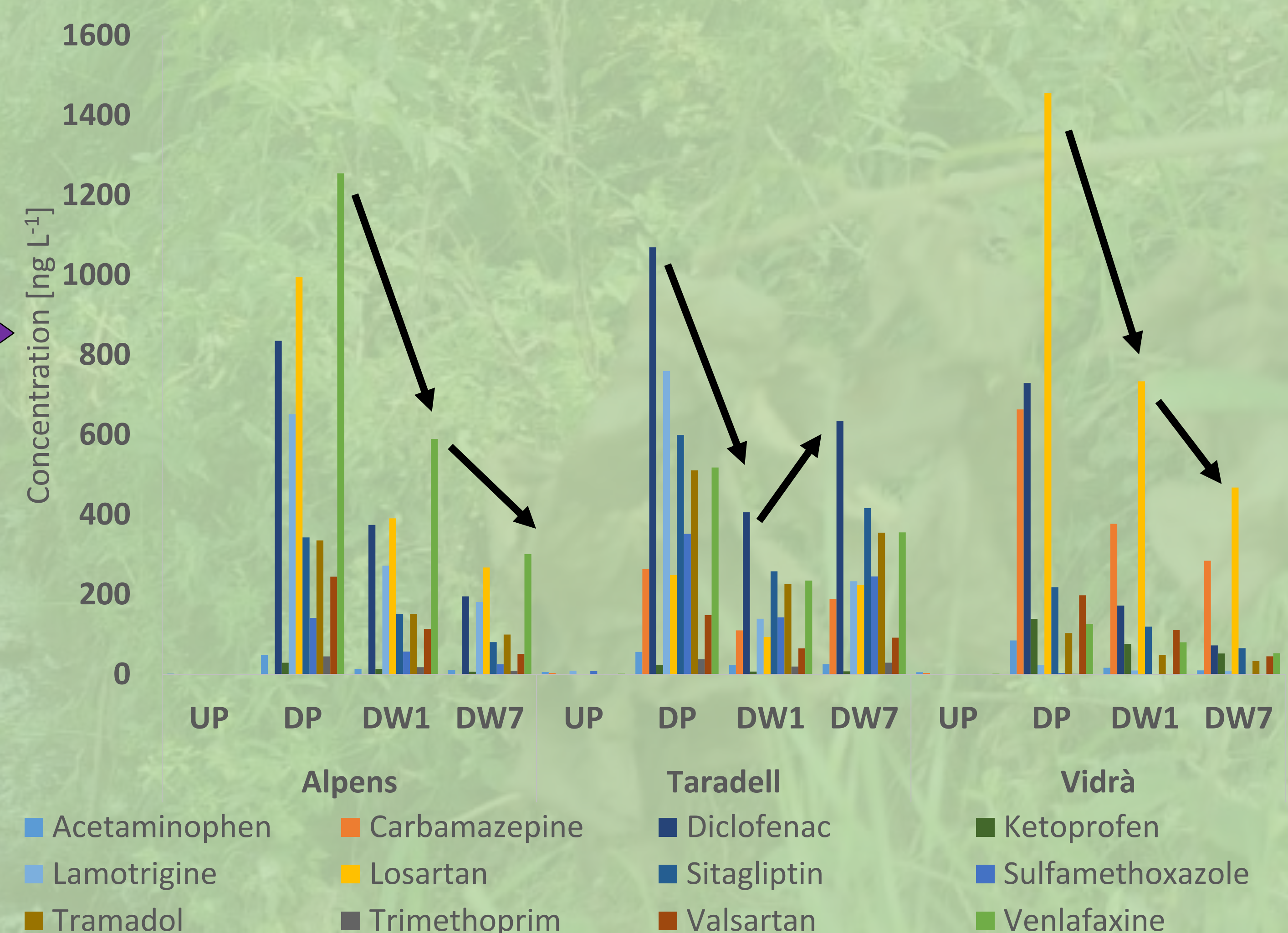


Figure 3 : Concentration of 10 main pharmaceuticals found in all intermittent rivers and permanent river studied.

Preliminary results report the presence of over 50 pharmaceuticals in all studied rivers. In Fig. 3 we can observe 9 of the most representative and the clear impact of the WWTP at the DPs.

Conclusions:

- ✓ The comparison of the data acquisition methods proved that DIA enabled to find a higher amount of product ions as well as better selectivity generating higher quality MS2 spectrums. Also enables the performance of retrospective analysis to search unknowns.
- ✓ Good recovery percentages between 70-120 % were obtained for the vast majority of compounds proving the effectiveness of the developed analytical method.
- ✓ Sporadic detection of over 50 pharmaceuticals along the different rivers was observed and quantified as well as a clear impact of the different WWTP and other surface run-offs on intermittent rivers.

References:

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