Evaluation of the impact of urban wet weather discharges (UWWD) on the Seine River by high resolution mass spectrometry (HRMS) and development of predictive models

Julien Sade, Sabrina Guérin-Rechdaoui, Stéphane Mottelet, Vincent Rocher, R. Moilleron, Anthony Marconi, Julien Le Roux

Evaluation of the impact of urban wet weather discharges (UWWD) on the Seine River by high resolution mass spectrometry (HRMS) and development of predictive models

Julien Sade[1], Sabrina Guerin[2], Stéphane Mottelet[3], Vincent Rocher[2], Régis Moilleron[1], Anthony Marconi[2], Julien Le Roux[1]

[1]LEESU,Univ Paris Est Créteil, Ecole des Ponts, F-94010 Créteil, France ; [2]Service public de l'assainissement francilien, DI, F- 92700 Colombes, France ; [3]Université de Technologie de Compiègne, TIMR, F-60200 Compiègne, France

Introduction

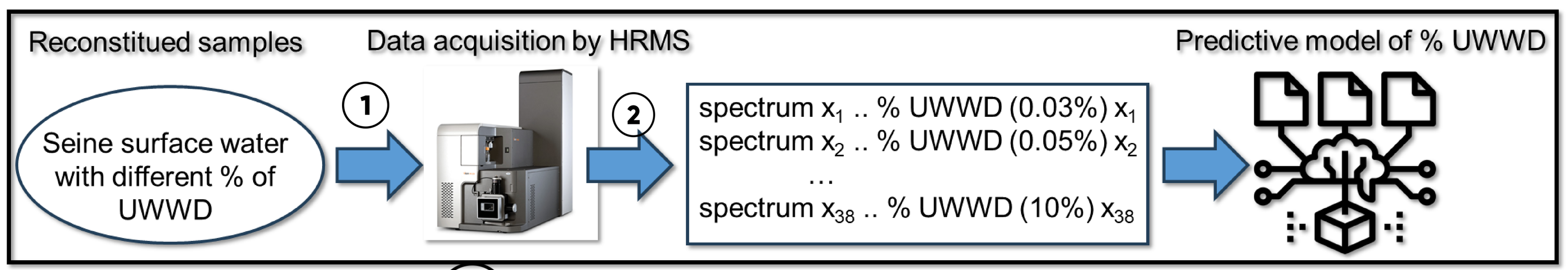
Background

- **Urban pollutant discharge**: During rainfall events, urban environments release a mix of pollutants into aquatic systems, especially from combined sewer overflows, known as urban wet weather discharges (UWWD).
- **Composition & Origin** [1]: UWWD include contaminants like heavy metals, hydrocarbons, and microplastics or organic micropollutants (including traffic-related pollutants or pharmaceutical residues) originating from urban activities.
- **Threat to water systems** [2]: During intense rainfall, these discharges act as a significant contamination source for surface waters, thus requiring monitoring and effective management.
- **Surveillance by SIAAP**: The wastewater treatment plants operator in the Île-de-France region monitors the quality of surface waters through ecotoxicological tests, but the frequency of these assessments is limited, thus preventing tracking of many potential toxic events.

Objectives

- **Detection and quantification**: Utilizing non-targeted HRMS analysis, our primary objective is to detect and quantify the UWWD in the Seine river.
- **Predictive model development**: Based on HRMS data, these predictive models aim to anticipate the influence of UWWD on the Seine river, and offer a more frequent tool of water quality monitoring.
- **Methodological questions**: Can HRMS correctly "quantify" the % of UWWD present in a sample, and what is the minimal level of detection?

Methods



1 Analytical preparation:

- **Sample collection**: Both surface water from the Seine River and UWWD from wastewater treatment plants were sampled across various seasons.
- **UWWD Addition**: Multiple UWWD additions (ranging from 0.03% to 10%UWWD) were made to surface water to simulate wastewater-impacted samples and to evaluate the influence on the HRMS fingerprint.
- **Sample preparation post-addition of UWWD**:
  - Filtration (0.2 µm) and solid phase extraction using multiphasic cartridges [3]
  - Evaporation with N_2 gas and reconstitution in solvent ($MeOH/H_2O$)
- **HRMS**: The samples were analyzed using UPLC-IMS-QTOF with a C18 column and data acquisition in data-independent analysis mode.

2 Data preparation:

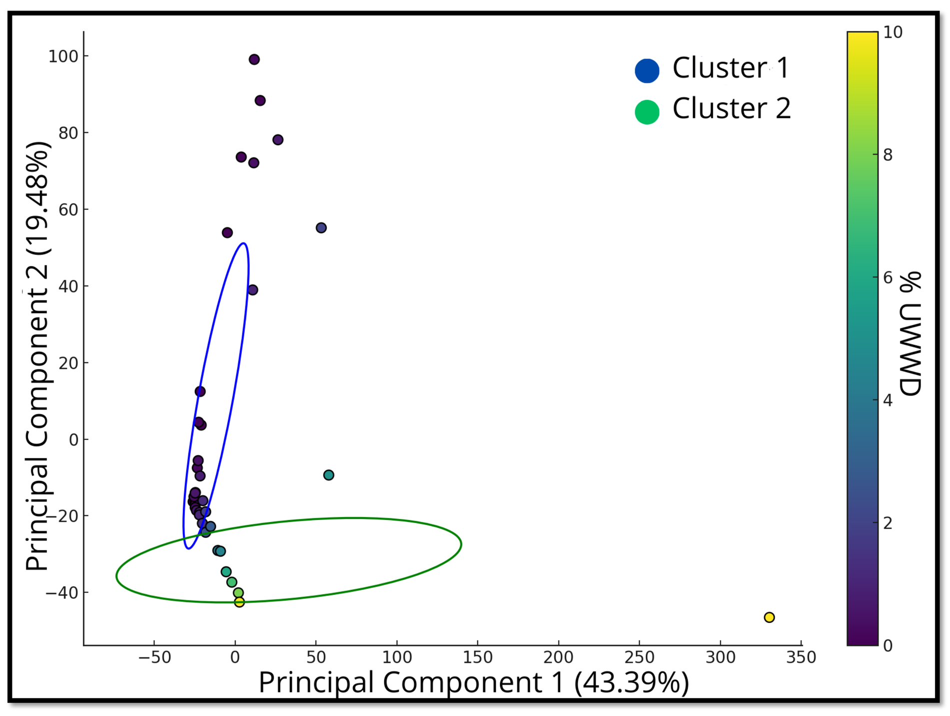
- **HRMS spectra**: Peak detection was conducted by the UNIFI (Waters) software.
- **Marker filtration**: Based on replicates and blank subtraction, markers were filtered using R software.
- **Marker Matching**: 8117 common markers were identified across different sampling and analysis campaigns. A marker is defined by its m/z, retention time, drift time (ion mobility), and intensity.
- **Standardization & modeling**: Dataset from 38 unique samples was standardized, followed by the development and comparison of various predictive models based on selected markers.

Results

Correlation between markers and % UWWD

- **High linearity**: A significant number (120) of markers shows a strong linear relationship (r > 0.8) with %UWWD.
- **Potential for model simplification**: These linear relationships show the possibility of leveraging simpler models based on a reduced number of markers.

Unsupervised analysis: PCA & KMEANS clustering

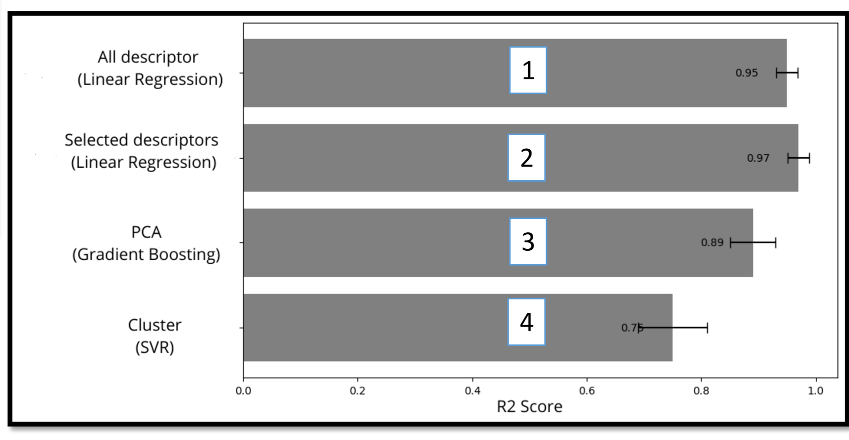


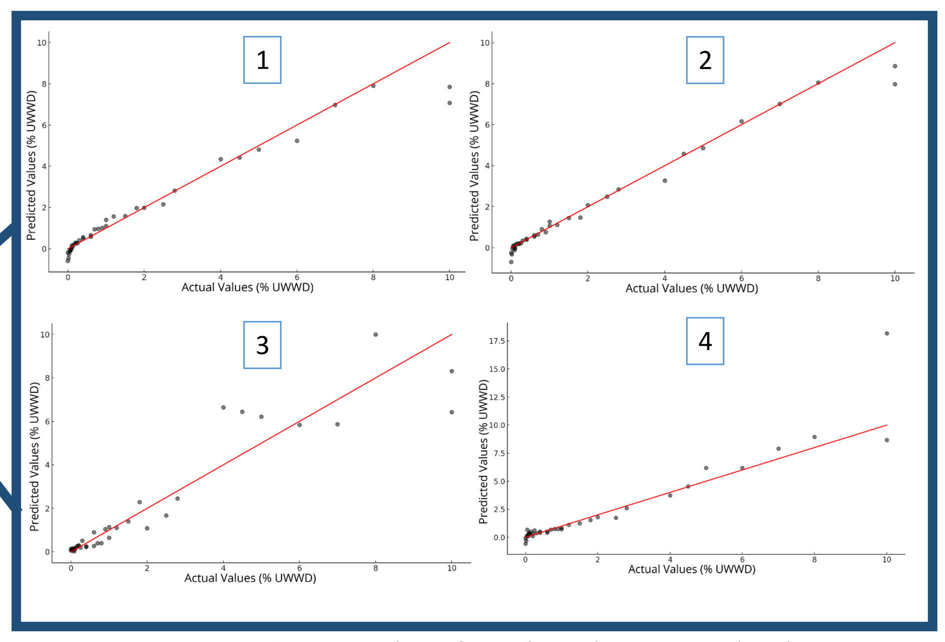
PCA Plot with K-MEANS clustering

- **Variability**: A clear trend is visible between the %UWWD and Principal Component 2, showing good potential for a precise model of %UWWD prediction, even at the lowest concentrations.
- **Dilution distinction**: The results from the clustering indicate a clear division where low dilutions cluster distinctly from high dilutions.
- **Binary assignment**: Using the KMEANS clustering, a simple binary assignment can be made to act as an initial tool, classifying future samples into either low or high dilution categories.

Supervised analysis : Predictive models

Performance comparison chart of predictive models





Scatter plot of predicted vs. actual values

- **High linearity**: High performance of the model based on linear regression.
- **Consistent high performances**: Across various methodologies/models, substantial R^2 values indicate accurate and reliable prediction models for % UWWD.
- This is encouraging for developing further models to predict other impacts (toxicity) even at the lowest %UWWD, demonstrating the **sensitivity of the approach**.

Further Exploration

- **Ecotoxicity prediction model**: Experiments are underway to develop a predictive model to forecast ecotoxicity values from HRMS data.
- **Model design**: The model will be based on ecotoxicity tests focusing on endocrine disruption, general toxicity, and genotoxicity. 36 samples from the Seine and Marne rivers, collected over three different seasons, will undergo toxicity induction with the addition of UWWD. These samples will then be used for the development of the model

Research and solutions in NTS

References

[1] Masoner, J. R. and al. (2019). Urban Stormwater: An Overlooked Pathway of Extensive Mixed Contaminants to Surface and Groundwaters in the United States. Environ Sci Technol, 53(17), 10070-10081. https://doi.org/10.1021/acs.est.9b02867
[2] Kayhanian, M. et al. (2008). Toxicity of urban highway runoff with respect to storm duration. Science of the Total Environment, 389(2-3), 386-406. https://doi.org/10.1016/j.scitotenv.2007.08.052
[3] Singer, H. P. and al (2016). Rapid Screening for Exposure to "Non-Target" Pharmaceuticals from Wastewater Effluents by Combining HRMS-Based Suspect Screening and Exposure Modeling. Environmental Science and Technology, 50(13). DOI: 10.1021/acs.est.5b03332.

Contact
SCAN ME