To model micropollutants or not to model ... that is the question

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Abstract
Contaminants of Emerging Concern (CECs) in the aquatic environment has become an environmental issue of growing global concern. Their monitoring is discontinuous, costly and time-consuming, strongly depending on the adopted analytical methods, not permitting to have a comprehensive view of their presence and dynamics in the environmental compartments (drinking water, wastewater, natural water, crops). Consequently, the risk for the environment and human health could be even significantly underestimated. Modelling tools are thus fundamental to support monitoring and management of CECs, in an integrated framework oriented to the overall risk minimization. Here, the following modelling tools are presented: (i) methods to manage CECs concentration data under the Limit of Quantification; (ii) stochastic methods to support the generalization and interpretation of literature outputs; (iii) fate models to describe CECs dynamics in interconnected environmental compartments, to be used for forward and backward predictions, and thus supporting CECs prioritization and risk-based corrective actions.

Keywords
Contaminants of Emerging Concern; Modelling; Stochastic methods; Human health risk

INTRODUCTION

In the last decades, the presence of Contaminants of Emerging Concern (CECs) in the aquatic environment has become an environmental issue of growing global concern. CECs comprise more than 700 compounds, present at trace concentrations, including a vast variety of anthropic contaminants, among which there are e.g. Pharmaceuticals and Personal Care Products (PPCPs), Endocrine Disrupting Compounds (EDCs), industrial chemicals, pesticides and all their transformation products. In fact, due to technological and analytical innovations, the list of CECs cannot be exhaustive and needs to be constantly updated.

CECs are often able to produce adverse effects even at very low concentrations, among which there are both short- and long-term toxicity, endocrine disruption effects, and the development of antibiotic-resistance. The uncertainty related to their effects is still very large, especially for humans.

Traditionally, since CECs were not detected being under their respective detection limits, they were not recognized as potential risk sources for the environment and human health. However, the advances in analytical techniques and in the knowledge about both their behaviour in the environment and their toxicity, highlighted the widespread presence of CECs in sensitive environmental compartments, such as drinking water, soil and crops intended for human consumption, even posing a risk for the environment and human health.

Monitoring of thousands of CECs in complex environmental systems can be costly and time-consuming even if only performed discontinuously, and still it does not permit to have a comprehensive view of the contamination level. When experimental studies are performed to investigate the removal options available for CECs concentration reduction in wastewater or drinking water, in order to reduce the exposure concentration, outputs are strongly affected by site-

specific conditions in case of pilot and full-scale work, or by operating conditions and water matrix characteristics in case of lab-scale work. In this framework, quantitative modelling tools can provide valuable complementary information (e.g., filling temporal gaps between measurements), and accounting for the influence of site-specific conditions, enabling a more reliable risk assessment through the prediction of exposure concentrations and accounting for uncertainties.
This work wants to briefly review the statistical and modelling tools available for supporting research aimed at controlling CECs spread in sensitive compartments.

MANAGING DATABASES RICH OF DATA BELOW LOQ

The output of CECs monitoring is strongly affected by the analytical methods adopted and specifically by their Limit of Quantification (LOQ). Consequently, it is common to have databases rich of data below LOQ values, also known as left-censored data. Censored data are usually discarded for further elaboration or substituted with a value equal to half the LOQ. This reduces drastically the reliability of elaboration outcomes, since it affects either the numerosity of the database and its descriptive capacity of the real contamination level of the monitored environmental compartment.
Recently, the advanced Maximum Likelihood Estimation method for (MLE_{LC}) has been proposed to deal with left-censored data. The MLE_{LC} was tested evaluating the estimation errors of the 95th percentile value used for risk assessment (Figure 1), for different datasets characterised by different censored percentages and amplitude of data range (reported as the ratio between the data LOQ and 95th percentile). The MLE_{LC} method appears to be the best in estimating CECs 95th percentiles with fractional errors always lower than 30%. On the other hand, when eliminating censored data, the estimation error is above 100% for all the cases with more than 50% of censored data and LOQ higher than 10% of the 95th percentile.

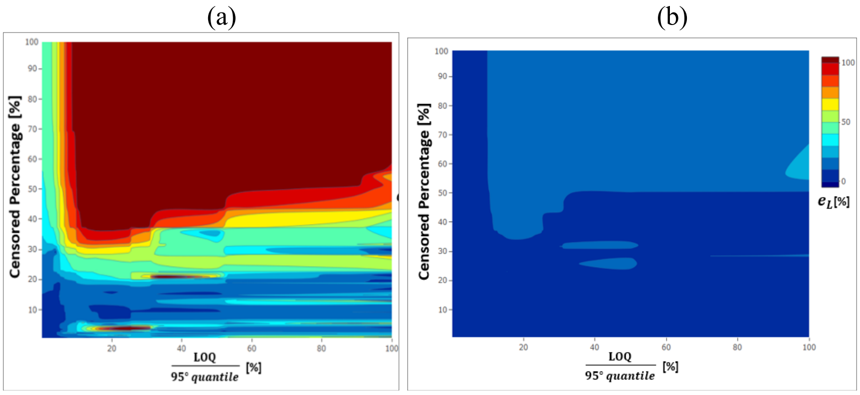

Figure 1: Contour plot of the estimation error (e) of health risk as a function of the percentage of censored data and amplitude of data range for elimination (a) and MLE_{LC} (b) methods [1].

MULTIVARIATE REGRESSION FOR LITERATURE DATA GENERALIZATION

Many studies are available in literature about CECs removal, especially in wastewater. Anyway, most of these studies are performed in non-realistic conditions, with regard to CEC concentration, water matrix characteristics and process operating conditions, or are strongly affected by site-specific conditions. For instance, considering studies focused on CECs removal by activated carbon adsorption, oxidation/advanced oxidation processes and pressure-driven membrane separation (nanofiltration, reverse osmosis) as summarised in Figure 2a, about 62% were carried out using synthetic water (mainly, deionized water) spiked with a single compound usually at concentrations greater than at least one order of magnitude with respect to environmental concentrations; besides, in synthetic water, no competitors are present, such as organic matter, conventional micropollutants or other CECs. This strongly limits the outputs' generalization, making results not fully representative of full-scale conditions, as it can be noted in Figure 2b, where removal efficiency values are reported for activated carbon adsorption in synthetic and real water matrices.

An attempt to overcome this barrier relies on metanalysis, which uses multivariate regression models, to generalize literature results highlighting common behaviours and trends. An example is summarized in Figure 3, where data show that carbon load (q_e) measured for 18 pharmaceuticals compounds in drinking water highly depends on the main test boundary conditions (compound mixture concentrations, activated carbon doses, organic matter). Data were preliminarily grouped in cluster by a cluster analysis, to highlight studies performed in comparable testing conditions: clusters 4 and 5 refer to not-realistic test conditions, with estimated q_e excessively high, but comprise more than 70% of the studies.

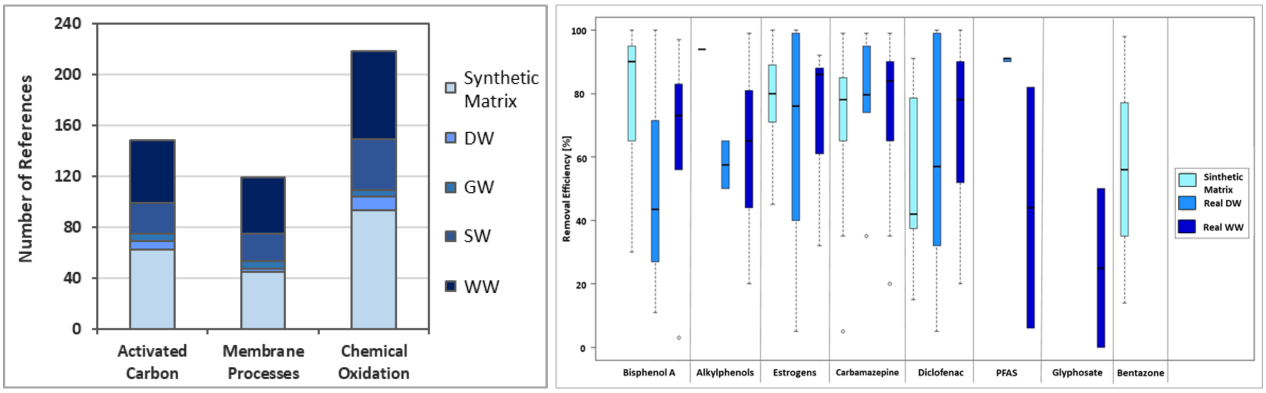

Figure 2. (a) Literature data (251 studies from 2000 to 2020) about CECs removal by activated carbon adsorption, oxidation, pressure-driven membrane separation, grouped based on the type of water matrix adopted for tests; (b) CECs removal efficiencies by activated carbon adsorption in synthetic and real water matrices.

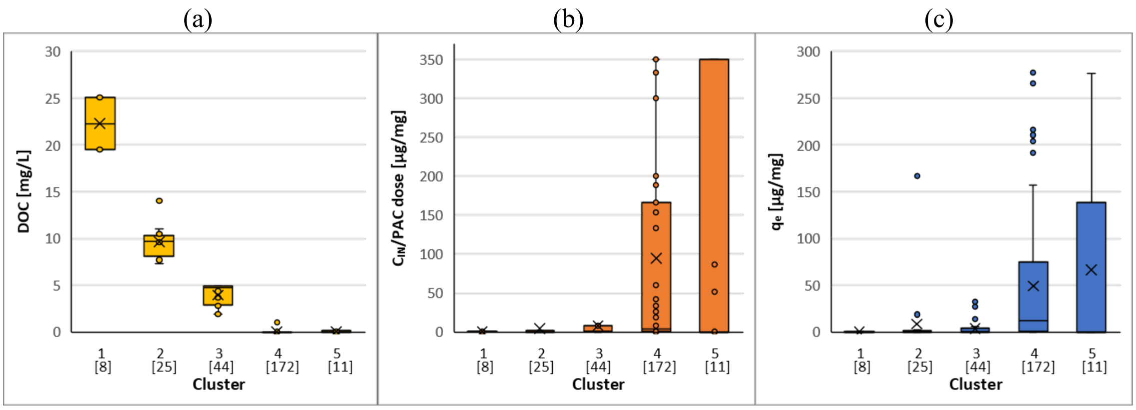

Figure 3. Boxplot of water matrix DOC concentration (a), ratio between initial CECs mixture concentration (C_{in}) and activated carbon dosage (PAC dose) (b), and equilibrium carbon load (q_e) (c) for 260 literature data in which isotherms were determined. Numbers in brackets report the number of data falling in each cluster.

INTEGRATED MODELLING FOR CECs FATE IN THE ENVIRONMENT

The possibility of identifying and quantifying CECs in environmental compartments depends on a multiplicity of factors. Firstly, the adopted analytical methods and their LOQ. Several studies report CECs concentrations, but only a fraction of these studies reports the LOQs of the analytical methods used for the measurements, which are highly variable as shown in Figure 4. Thus, it is impossible a quantitative comparison of data or drawing general conclusions about the presence/absence of a CEC. In addition, about the monitoring plan, the selection of the monitoring frequency and the sampling instants is usually semi-arbitrary, not guaranteeing the identification of the actual contaminant concentrations or the extent of the variations in fast-responding water systems, potentially leading to erroneous evaluations of process performances or human health risk.

It is therefore of paramount importance to develop mathematical models for CECs fate in selected environmental compartments, supporting various important applications: (i) development of costeffective monitoring campaigns to capture contaminant dynamics in the environmental compartments, especially when interconnected in a complex multiple-use system; (ii) evaluation of environmental and human health chemical risk, permitting the prioritization of CECs to be regulated, based on their contribution to the overall risk; (iii) scenario analysis about the effect of mitigation actions, acting as a decision-support tool for the identification of optimal water management strategies in view of risk minimization. In fact, mathematical models support a more robust risk assessment, enabling the calculation of statistical indicators from the predicted exposure concentrations, e.g. the probability of exceedance of certain thresholds.

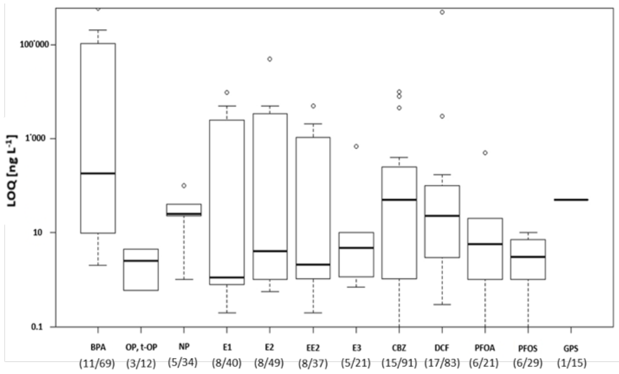

Figure 4. LOQ values (ng/L) reported in examined references (251 references between 2000 and 2020 about CECs removal by activated carbon adsorption, ozonation, advanced oxidation processes, nanofiltration, reverse osmosis) as a function of the 12 investigated CECs. In brackets the number of studies reporting the analytical method LOQ with respect to the total number of studies analysing the specific CEC is displayed.

An example of integrated model framework to estimate CECs exposure concentration and related risk is reported in [2]. In this case an indirect wastewater reuse system was conceptualized and modelled, to evaluate the risk associated to CECs spread in natural waters and in agricultural fields, and to human consumption of irrigated crops due to CECs uptake. One of the proposed outputs is related to the execution of monitoring campaigns. CECs (e.g. diclofenac and sulfamethoxazole) predicted attenuation rates showed monthly (lower concentrations during summer) and daily (night-time/daytime) variations, leading to median monthly rates which varied by more than one order of magnitude throughout the year (Figure 5), highly affecting downstream concentrations. This suggests that using data derived from a summer sampling campaign would lead to an underestimation in CECs concentrations in the irrigation water and thus in the risk for the environment and human health.

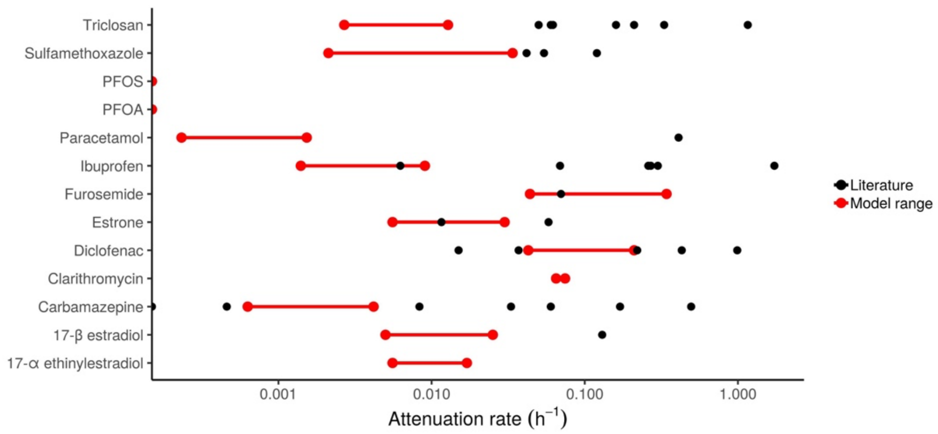

Figure 5. Literature surface water CECs attenuation rates and predicted yearly ranges for the simulated scenario.

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