

# Rethinking micropollutant removal assessment methods for wastewater treatment plants – how to get more robust data?

Jean-Marc Choubert, Samuel Martin Ruel, Cécile Miege and Marina Coquery

## ABSTRACT

This paper covers the pitfalls, recommendations and a new methodology for assessing micropollutant removal efficiencies in wastewater treatment plants. The proposed calculation rules take into account the limit of quantification and the analytical and sampling uncertainty of measured concentrations. We identified six cases for which a removal efficiency value is reliable and four other cases where result is highly variable (uncertain) due to very low or unquantified concentrations in effluent or when the influent–effluent concentrations differential is below the measurement uncertainty. The influence of the proposed calculation rules on removal efficiency values was scrutinized using actual results from a research project. The paper arrives at detailed recommendations for limiting the impact of other sources of uncertainty during sampling (sampling strategy, cleaning and field blank), chemical analyses (suspended solids and sludge) and data processing according to the targeted objectives.

**Key words** | bioreactor, calculation rules, micropollutants, municipal wastewater treatment, removal efficiency, uncertainty

Jean-Marc Choubert (corresponding author)

Cécile Miege

Marina Coquery

Irstea, UR MALY,

5 rue de la Doua – BP 32108,

69616 Villeurbanne,

France

E-mail: [jean-marc.choubert@irstea.fr](mailto:jean-marc.choubert@irstea.fr)

Samuel Martin Ruel

SUEZ, CIRSEE,

38 rue du Président Wilson,

78 230 Le Pecq,

France

## INTRODUCTION

Accurately assessing the removal efficiency of micropollutants in wastewater and sludge is an important issue from a global environmental point of view. Since the publication of the Water Framework Directive in 2000, various environmental monitoring and research projects have focused on the analysis of priority and emerging substances present at very low concentrations in wastewater, among others (Joss *et al.* 2008; Janex Habibi *et al.* 2009; Choubert *et al.* 2011; Mailler *et al.* 2014). Although some milestone research and review papers have been published, micropollutant removal efficiencies extracted from the literature still suffer high variability (up to 60%) around the average (Martin Ruel *et al.* 2008; Miège *et al.* 2009b; Bertanza *et al.* 2013), as the data have been generated with a wide range of (sometimes inaccurate) methodologies. Consequently, comparing micropollutant removal efficiency could be an irrelevant exercise, despite being crucial for stakeholders, regulators and life cycle analysts (Metz & Ingold 2014; Muñoz *et al.* 2017). Removal efficiency for hydrophobic (adsorbable) substances

cannot be reliably calculated without considering both dissolved and particulate concentrations, as well as both water and sludge lines for the evaluation of fate through wastewater treatment plants (WWTP), which is rarely done in practice.

In the last decade, powerful analytical techniques have been developed for the analysis of inorganic and organic micropollutants in aqueous phase of samples. Nevertheless, a representative sample is still a prerequisite for providing meaningful analytical results (Ort *et al.* 2010; Richardson & Kimura 2016). Moreover, evaluating the treatment by full-scale WWTP requires a data processing phase, which will be more or less complex depending on the objectives targeted. The amount of information needed to get more robust data is more than expected. Some can be found in technical reference guides, as detailed below, but a lot of information is still ‘orphan’. The next section details the big pitfalls and the care to be taken to prevent errors during sampling (sampling strategy, cleaning and field

blank), chemical analyses (suspended solids and sludge) and data processing.

This paper first focuses on the key issues for limiting how far micropollutant concentrations are impacted by the different sources of uncertainty during sampling and chemical analyses, which are collapsed here under the term 'measurement'. We then introduce a new methodology for accurately assessing micropollutant removal efficiencies by WWTPs that takes into account the 'measurement' (i.e. sampling and analytical) uncertainty. Calculations of removal efficiency of water line ( $R_W$ ) and water & sludge lines ( $R_T$ ) were considered in this approach. Finally, we evaluate how the proposed calculation rules can provide more robust data on removal efficiencies for wastewater facilities. Applications are proposed on real data.

## SAMPLING AND ANALYTICAL ISSUES

### Existing good practices

A successful sampling step is based on first setting up flow-proportional composite samples on each point of the WWTP (Harvey 2008), even if some teams unfortunately still use grab samples, as reported by Ort *et al.* (2010). Good sampling practice has to include suitable settings of the automatic samplers, like location and frequency of sampling, and fluid velocity (FD T 90-523-2 2008). Duration of sampling should also fit the residence time distribution, with consideration of water inflow rate pattern in sewers (Ort *et al.* 2010; Majewsky *et al.* 2011; Rossi *et al.* 2011) and also process hydraulic retention time (Petrie *et al.* 2015), which may be short for some processes (e.g. biofilters) but long for others (e.g. ponds). It should also include the use of specific materials (e.g. glass and Teflon for organic micropollutants) and preparation procedures (specific cleaning and field blank checks) for the automatic samplers (US Geological Survey 2002; Eymery *et al.* 2011).

A successful analysis step is based on first selecting suitable and powerful preparation and analysis techniques to apply to liquid and sludge samples, which will involve (among others) extraction, purification, chromatographic separation and mass spectrometry detection for organic micropollutants (Dimpe & Nomngongo 2016; Richardson & Kimura 2016). Low limits of quantification (LoQ) are necessary in the aqueous phase of samples (from  $\mu\text{g/L}$  to sub- $\text{ng/L}$  range depending on laboratory and substance). Good data quality practice actually requires comparison of the analytical LoQ to actual concentrations of

micropollutants in wastewaters. Furthermore, measurement uncertainty has to be determined and ranges from 20% up to 100% according to laboratory, substance, matrix and concentrations. In addition, analytical methods need to be developed and validated for the analysis of micropollutants in solid phases (suspended solids in water and in sludge) so that process engineers can compute full mass balance (Carballa *et al.* 2007; Miège *et al.* 2009b).

### Pitfalls and preventive solutions

Reaching low LoQ for a wide range of inorganic and organic micropollutants often present at trace levels in complex mixtures such as raw influent, treated effluent and sludge is still a challenge. Consequently, there is some bias in the literature data that might explain some of the more irrelevant concentration or removal efficiency data. Fortunately, there are good-practice precautions that can limit this bias when determining micropollutant concentrations. Table 1 and the discussion below briefly present possible sources of bias and preventive solutions that can help obtain more robust data quality in sampling and chemical analyses.

### Sampling

Schemes sampling the water line of WWTP with unsuitable equipment, duration or frequency of collection of composite sample are a major source of error. To limit the contamination during sampling and when conditioning samples of influent and effluent into the bottles sent to the laboratory, specific materials have to be used, such as plastic bottles (polyethylene or polypropylene) for metals or amber glass bottles for organic substances, along with Teflon tubing. All materials used also require a thorough cleaning procedure (rinsed with detergent, acidified water, then acetone and finally with water to sample). Moreover, field blanks need to be used to verify absence of adsorption and contamination of all the sampling material (US Geological Survey 2002; Eymery *et al.* 2011).

It is essential to thoroughly homogenize the sample while filling the bottles to send to the laboratory when the total micropollutant concentrations are analysed, including particulate matter. The variations of influent flow rate and concentrations can affect the reliability of the removal efficiency of water line ( $R_W$ ) when calculated at day-scale (for one day only). Variability of concentrations during a sampling period (e.g. intra-day variability) can be eliminated by choosing an appropriate sampling mode and frequency. To do so, automatic samplers deliver 24-h volume-proportional

**Table 1** | Pitfalls and solutions for minimizing measurement uncertainty on micropollutant removal efficiency in WWTP

POSSIBLE BIAS	PREVENTIVE SOLUTIONS
1–Sampling	
Biased sampling strategy	<p><u>Liquid samples:</u></p> <ul style="list-style-type: none"> <li>– Check individual volume for flow-proportional composite samples</li> <li>– Increase sampling frequency (dynamics of sudden-release patterns)</li> <li>– Adapt sampling duration and refer to the hydraulic residence time distribution</li> <li>– Thoroughly homogenize the sample while filling bottles to send to the laboratory</li> </ul> <p><u>Solid sludge:</u></p> <ul style="list-style-type: none"> <li>– Adapt sampling duration and refer to solid residence time distribution. Sludge from heaps must be collected in all the strata with a minimal number of samples</li> <li>– Ensure homogeneity by thorough mixing, coning and quartering methods (before filling containers to send to the laboratory)</li> </ul>
Contamination of sample (sample integrity)	<ul style="list-style-type: none"> <li>– Use specific materials (e.g. Teflon tubing, glass containers for organics)</li> <li>– Execute a thorough cleaning procedure (detergent, acidified water, acetone)</li> <li>– Implement regular verification of sampling material (field blanks)</li> </ul>
2–Chemical analyses	
Ill-adapted instrumental methods (quantification)	<ul style="list-style-type: none"> <li>– Select the appropriate instrumental apparatus for analysis (i.e. with the lowest LoQ) of trace-level concentrations</li> <li>– Use validated methods for trace chemicals (control laboratory blanks, use certified reference materials when available, and perform inter-laboratory comparison)</li> <li>– Regularly check the values of the analytical blanks and actual LoQ</li> </ul>
Matrix effects	Account for matrix effects, especially for organic micropollutants in influents and sludge (use of deuterated internal surrogates, control by systematic spiking and dilution) and also for trace metals (control by systematic spiking or dilution checks)
Sample not homogeneous (solid-phase pre-treatment)	<p><u>Liquid samples:</u></p> <ul style="list-style-type: none"> <li>– Thoroughly homogenize the sample at every step of sample preparation to prevent settling</li> <li>– Use the same one protocol to determine particulate matter (centrifugation or filtration, but not both)</li> <li>– Filter a sufficiently large volume of sample</li> <li>– Measure filtered volume instead of dry weight on filter (or preferably both for checks) and express micropollutants in µg/L or ng/L for removal efficiency calculations</li> </ul> <p><u>Solid sludge:</u> Get homogeneous DM by using specific equipment like dry freezers, agate mortar grinders or other non-contaminating apparatus</p>
3–Data processing	
Aberrant values	Eliminate aberrant values due to higher uncertainty of chemical analyses at low concentrations, or wrong substitution of not-quantified effluent concentration (this work)

composite samples to collect and merge a minimum number of individual samples of a minimum volume each (Eymery *et al.* 2011). Duration of effluent sampling should also be aligned to the mean hydraulic retention time in order to sample during a period of time that corresponds to the distribution and treatment of the influent load. As an example, an inter-day variability of 20% was determined for estrogens and betablockers in WWTP influent (Gabet *et al.* 2010), whereas an inter-day variability was below 35% for metals (Coquery *et al.* 2011). We thus recommend sampling and measuring over consecutive days to estimate

removal efficiency with sufficiently low uncertainty (Majewsky *et al.* 2011; Bertanza *et al.* 2013), as this strategy should buffer the day-on-day variations of concentrations.

Sampling in the sludge line also requires representative samples. As suggested in existing standards (ISO 5667-13 2011), sludge from heap must be collected in all the strata with a minimal number of samples. Moreover, periodic sampling requires a maximal interval between each sample. The sludge needs to be mixed thoroughly to ensure homogeneity by coning and quartering methods. Sampling duration should also be considered when dealing

with removal in sludge, and it has to be aligned to residence time, otherwise micropollutant concentrations measured in sludge will not correspond to the pollution load entering the process.

## Analysis

Some precautions should also limit biases when analyzing the micropollutant concentrations. It is essential to select an appropriate instrumental apparatus (i.e. with the lowest LoQ and uncertainty). When analyzing wastewaters, this will require comparison of analytical LoQ against actual micropollutant concentrations. For instance, even for metals that have been extensively studied, it is necessary to use the most powerful methods (e.g. ICP-MS, or CV-AFS for mercury), especially for toxic metals present at low (i.e. down to ng/L) levels in the aqueous phase (such as cadmium and mercury). Moreover, it is well known that the analytical uncertainty depends upon the sample matrix and the concentration level (Miège *et al.* 2009a; NF EN ISO 11352 2013). The complexity of the WWTP influents leads to matrix effects and can result in apparently lower (or higher) measured concentrations than actual concentrations (sometimes lower than effluents), which has as a knock-on effect of apparent negative removal (e.g. Gabet *et al.* 2010). Therefore, it is crucial to use deuterated internal surrogates when available, or to spike each type of sample in order to compensate for the matrix effect by using protocol recoveries.

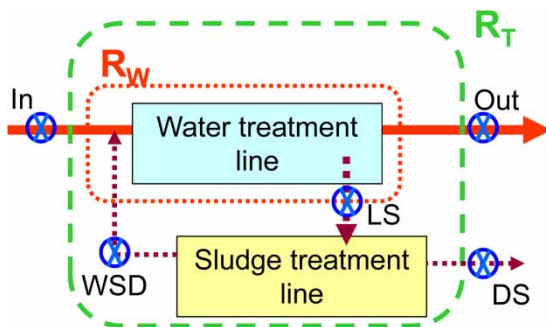
Analysis of the suspended particulate matter in water is a key issue, and even the sample pre-treatment stage can be optimized to afford better-quality concentration data. Even if the samples are homogenized before each volume taken to limit settling, it is still vital to use the same one protocol to estimate the suspended solids loads of samples. Indeed,

a basic bias comes from the use of centrifugation for determining suspended solids while the particulate phase of the micropollutants is determined after filtration (typically through glass fiber filters, 0.7 µm), which introduces differences of measurement. Filtering a sufficiently large volume of sample is particularly critical for influents, which are often very heterogeneous, to get a representative particulate matter sample, such as by using several filters for each sample. Conversely, for effluents, the filtered volume needs to be large enough to ensure a sufficient mass of particulate phase collected on the filter for subsequent micropollutant analysis. We also strongly recommend working with filtered volume instead of dry weight of filter in order to provide concentration in the particulate phase expressed in µg/L (instead of mg/kg dry matter (DM)). This is particularly important for secondary effluent (or tertiary influent) samples with very low suspended particulate matter content (typically below 30–10 mg/L or even 5 mg/L).

Specific attention, practice and equipment are required to get homogeneous DM and thus limit the final uncertainty of measured concentrations. Here, thorough agate mortar grinding limits the heterogeneity in DM samples, but in some cases an automatic grinder (cryogenic or ball-mill type), is necessary when woody bulking agent is mixed in sludge (composting) or for fibrous sludge (e.g. containing leaves of reeds or septage). In the future, laboratories should be able to more precisely quantify some of the organics (those still not yet quantified or not precisely enough).

## Data processing

This step consists in calculating the micropollutant removal efficiencies of the WWTP. An illustration and equations are proposed in Figure 1.



**Figure 1** | Calculations of micropollutant removal efficiency by a water line ( $R_W$ ) and by overall WWTP ( $R_T$ ), and layout of the WWTP with sampling points (⊗). In: influent (raw wastewater); Out: effluent (treated water); LS: liquid sludge; DS: dewatered sludge; WSD: water from sludge dewatering;  $F_{tot,In}^{water}$ : micropollutant flux received by the WWTP;  $F_{tot,Out}^{water}$ : micropollutant flux released by water line;  $F_{LS}^{sludge}$ : micropollutant flux received by sludge line;  $F_{WSD}^{sludge}$ : micropollutant flux released by sludge line.

Water line:

$$R_W = \frac{F_{tot,In}^{water} - F_{tot,Out}^{water}}{F_{tot,In}^{water}} \quad (\text{Eq. 1})$$

Water & Sludge lines:

$$R_T = \frac{F_{tot,In}^{water} - F_{tot,Out}^{water} + F_{WSD}^{sludge} - F_{LS}^{sludge}}{F_{tot,In}^{water}} \quad (\text{Eq. 2})$$

Removal by the 'water line' (called  $R_W$ , Equation (1)) represents the elimination of micropollutants from water by the WWTP, and the driving forces of micropollutant removal assessed are adsorption, removal of solids, biotransformation, and stripping for volatiles. When the sampling strategy also includes sludge samples, then the micropollutant removal efficiencies can be calculated considering a larger scale, including the 'water and sludge lines' (called  $R_T$ ). This consists of a mass balance (Equation (2)) using the micropollutant concentrations transferred into sludge (Carballa *et al.* 2007; Martin Ruel *et al.* 2010). In the case of  $R_T$ , the driving forces of the elimination pathways assessed are biotransformation and stripping for volatiles. Thus, the comparison of  $R_W$  against  $R_T$  gives some information on the fate of the micropollutants and, in particular, indicates whether the removal was caused by sorption onto sludge only, or whether it was also influenced by biodegradation.

Even if adapted sampling and validated sophisticated analytical methods are required to obtain robust (valid) data, correct methods for data processing are also more than necessary. Despite several sets of guidelines published in recent years on sampling strategy and mass balance calculation for specific micropollutant families (Carballa *et al.* 2007; Ort *et al.* 2010; Estrada-Arriaga & Mijaylova 2011), various cases have still not been clarified, for instance when a concentration obtained in influent or effluent, or in sludge, is too low or unquantified. The literature only counts one paper that discusses substituting values for nondetects, and the rule given concerns the calculation of average concentration data in the environment (Helsel 2006), not removal calculations. Consequently, some removal calculations today are meaningless given the LoQ of analytical methods and measurement uncertainty of the concentrations. To address this issue, the next section presents an original methodology for considering both LoQ and uncertainty of WWTP influent and effluent concentrations for calculating removal efficiency.

## CONSOLIDATING REMOVAL EFFICIENCIES

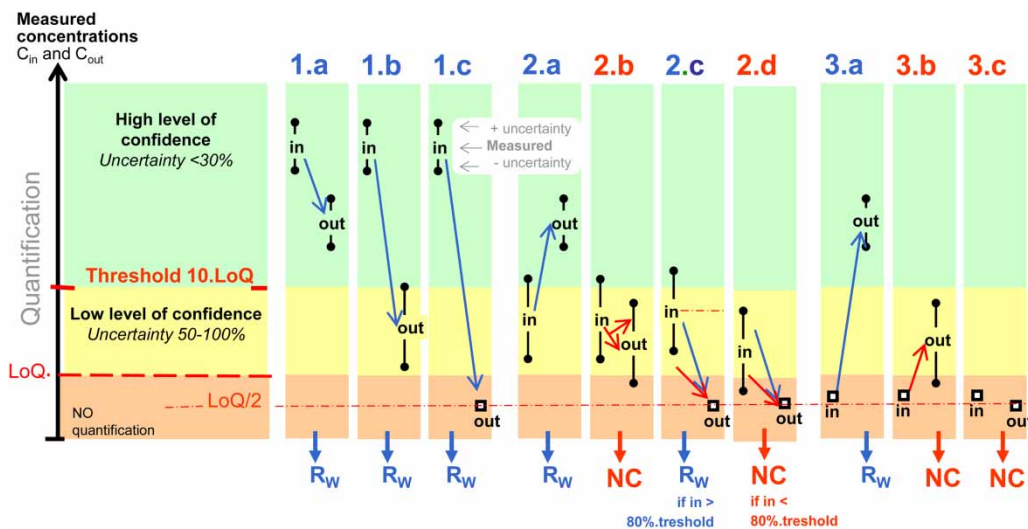
### Proposed rules

Here we propose a novel ruleset for calculating micropollutant removal efficiencies in WWTP ( $R_W$  and  $R_T$  using fluxes (Equations (1) and (2)). Both calculations accounts for measurement uncertainty of the micropollutant concentration, which will differ depending on concentration

level and sample type. We defined a threshold (depending on LoQ) for each micropollutant:  $10 \times \text{LoQ}$  for influent and secondary effluent. Above the thresholds, we have defined a high level of confidence (noted 'high level'), where micropollutant concentrations were determined with a low level of uncertainty ranging between 20% and 30%. Below these thresholds, there is a low level of confidence (noted 'low level') which corresponds to measurement uncertainty ranging between 50% and 100%. The proposed threshold and measurement uncertainty values are low, as laboratories in charge of analyses used state of the art methods suited to measuring low concentrations of micropollutants in wastewaters and sludge (i.e.  $\mu\text{g/L}$  to sub- $\text{ng/L}$  levels in the aqueous phase) (Martin Ruel *et al.* 2010; Choubert *et al.* 2011). The LoQ and uncertainties should be checked for each study and could differ between laboratories and also between sampling campaigns and samples types (e.g. due to matrix effects, see Table 1). As explained above, the uncertainty depends upon the sample matrix and the micropollutant concentration level, so the threshold value needs to be adapted (e.g. we suggest to use  $5 \times \text{LoQ}$  for tertiary effluent (i.e. cleaner samples than secondary samples).

The proposed rules for calculating robust micropollutant removal efficiency values are fully detailed in Figure 2, which charts 10 different cases depending on concentration in the influent ( $C_{\text{in}}$ ) and effluent ( $C_{\text{out}}$ ), LoQ and threshold. The calculations are possible in six cases when the difference between the micropollutant concentrations,  $C_{\text{in}}$  and  $C_{\text{out}}$ , of a WWTP is substantial compared to the measurement uncertainty. This is the case for situations where  $C_{\text{in}}$  is quantified in the high level of confidence (1.a, 1.b and 1.c). Calculation is also feasible in situations where  $C_{\text{in}}$  is quantified in the low level of confidence but  $C_{\text{out}}$  is quantified in high level of confidence or  $C_{\text{in}}$  is quantified close to the threshold (2.a and 2.c). Calculation is also possible in situations where  $C_{\text{in}}$  is not quantified whereas the  $C_{\text{out}}$  quantified is in high level of confidence (3.a), typically when quantifying a by-product.

In four other cases, the removal efficiency should not be calculated (noted NC in Figure 2), especially when the uncertainty might explain the concentration differential between influent and effluent. This is the case where  $C_{\text{in}}$  and  $C_{\text{out}}$  are in the low level of confidence (2.b), or in situations where  $C_{\text{in}}$  is quantified below 80% of the threshold and  $C_{\text{out}}$  is unquantified (2.d). Finally, no calculation is recommended in situations where  $C_{\text{in}}$  is unquantified while  $C_{\text{out}}$  is quantified in the low level of confidence (3.b) or below the LoQ (3.c).



**Figure 2** | Detailed cases for the calculation (or not) of micropollutant removal efficiency taking into account measurement uncertainty. LoQ: limit of quantification;  $R_W$ : calculable removal efficiency; NC: non-calculable  $R_W$ ; in: influent; out: effluent.

To improve the confidence on the calculation of removal efficiencies in the low level of confidence (e.g. in case 2.b), the threshold could be dropped slightly when the removal efficiency calculation ruleset is applied on a dataset covering a period of time of several days, or several periods of time.

To calculate removal efficiencies by the water line (i.e.  $R_W$  values), we substituted unquantified values in effluent with  $LoQ/2$ . To calculate removal efficiencies by the water and sludge lines (i.e.  $R_T$  values), we substituted unquantified values in sludge by zero (not  $LoQ/2$ ). Indeed, even if  $LoQ$ s are as low as possible in sludge, using  $LoQ/2$  as for water often led to negative  $R_T$  values, thus wrongly inferring a higher quantity of micropollutants transferred in sludge than was received by the influent. The next section illustrates these choices and proposes examples of real data.

### Influence of the proposed rules on the quality of removal efficiency values

In this section, we demonstrate how the proposed removal efficiency calculation rules could decrease bias and improve data quality for  $R_W$  and  $R_T$ . We also detail the dependency of the removal efficiency results on the measurement uncertainty of micropollutant concentrations.

The proposed calculation rules were tested on the data from the AMPERES project (Analysis of priority and emerging pollutants in wastewater and surface waters, 2006–2009, France), which investigated 127 micropollutants through 21 municipal WWTPs of different types previously published (Martin Ruel et al. 2010; Choubert et al. 2011). Representative samples of water and sludge were collected. For

water, flow-proportional composite samples (24 h) were collected in WWTP influent and effluent during 2 days with an automatic refrigerated sampler (Hach-Lange Bühler 5010) operating with 240 individual samples of 180 mL each per day, and equipped with Teflon tubings and glass containers. For sludge, representative samples were collected mixing several grab samples taken over time and mixed in glass containers. Micropollutant concentration in aqueous and solid phases of samples were determined with specific analytical methods adapted to complex wastewater and with  $LoQ$  of a few ng/L for organic micropollutants (Coquery et al. 2011).

An example of application of the proposed calculation rules for these data is fully detailed in the supplementary material (SPM, available with the online version of this paper). Sixty-five data were consolidated and 18 were rejected.

### On the importance of eliminating aberrant values in the low-level-of-confidence interval

This section illustrates case 2.b (Figure 2) where a substance is quantified with high uncertainty in influent and effluent (i.e. within the low level of confidence), so the difference between micropollutant concentrations may be due to the measurement uncertainty rather than to actual elimination by the WWTP.  $R_W$  should not be calculated in this case.

For a given micropollutant in influent and effluent for which  $LoQ$  is  $0.20 \mu\text{g/L}$ , a 50–100% measurement uncertainty is considered for all concentrations below  $2 \mu\text{g/L}$  (with threshold at  $10 \times LoQ$ ). For concentrations of  $0.90 \mu\text{g/L}$  in influent and  $0.45 \mu\text{g/L}$  in effluent, the simple mathematical calculation would lead to a  $R_W$  value of 50%.

However, considering, for instance, that 100% uncertainty would decrease the concentration in the effluent by 50% (i.e. to 0.23  $\mu\text{g/L}$ ), the calculation would give a  $R_W$  value of 75%. Thus, in this case, the  $R_W$  should not be calculated as the calculated  $R_W$  values are excessively variable (uncertain).

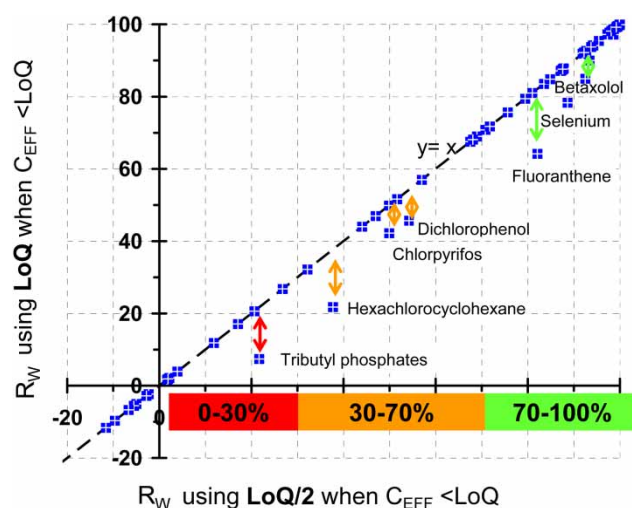
Among the 127 substances analyzed during the AMPERES project, 109 micropollutants were quantified in the influents and 96 were quantified in the effluents. A total of 91  $R_W$  removal efficiency values could be determined. The proposed rules thus led us to eliminate a further 18 aberrant  $R_W$  values, as influent and effluent concentrations were not within the high confidence level.

### On the interest of substituting ‘unquantified’ concentrations in effluent by $\text{LoQ}/2$

This section illustrates cases 1.c and 2.c presented on Figure 2. We compared the advantage of substituting unquantified concentrations in effluent by  $\text{LoQ}/2$  (Helsel 2006) or by  $\text{LoQ}$ , which would look a ‘safer’ practice as probably including a security factor. For case 1.c, considering a micropollutant quantified in influent of a WWTP at a concentration of 3.9  $\mu\text{g/L}$  but unquantified in the effluent ( $\text{LoQ} = 0.20 \mu\text{g/L}$ ), substituting unquantified effluent concentration with  $\text{LoQ}/2$  gives a  $R_W$  of 97% while substituting with  $\text{LoQ}$  gives a  $R_W$  value of 95%. In this example, we obtained practically similar removal efficiency values, as  $C_{\text{in}}$  was higher than the threshold. For case 2.c, in the case of a concentration of 0.39  $\mu\text{g/L}$  in influent (i.e.  $C_{\text{in}} = 2 \times \text{LoQ}$ ) and again an unquantified concentration in the effluent, the  $R_W$  value was calculable, although with higher analytical uncertainty (low confidence level). Substituting unquantified effluent concentration with  $\text{LoQ}/2$  gives a  $R_W$  of 75%, but substituting with  $\text{LoQ}$  gives a  $R_W$  of only 50%. In this last situation, no calculation is recommended.

Figure 3 presents overall  $R_W$ -based removal efficiencies calculated for one activated sludge WWTP by substituting below- $\text{LoQ}$  concentrations by  $\text{LoQ}$  (Y-axis) or by  $\text{LoQ}/2$  (X-axis). The figure shows that for a large majority of the micropollutants analyzed, there was no impact of the choice of substitution rule. Nonetheless, for seven micropollutants,  $R_W$  was 10% to 20% higher than the removal efficiency when using  $\text{LoQ}/2$  than when using  $\text{LoQ}$ , as  $\text{LoQ}$ s for these substances were not low enough compared to measured concentrations.

In contrast,  $R_T$  was not sensitive to choice of  $\text{LoQ}$  or  $\text{LoQ}/2$  in effluent. Nevertheless,  $R_T$  was highly influenced by the substitution rule for the unquantified micropollutants in sludge. The extent of this influence was dependent on



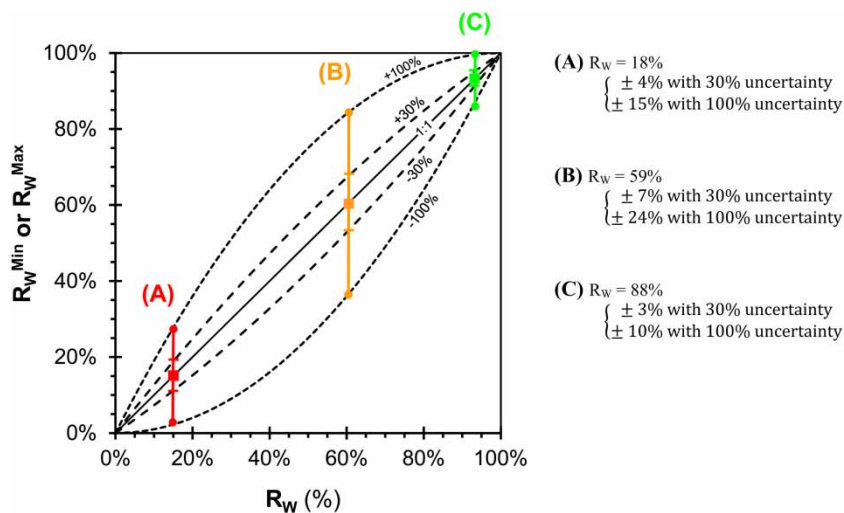
**Figure 3** |  $R_W$  values calculated by substituting unquantified values in effluent ( $C_{\text{EFF}}$ ) with  $\text{LoQ}$  (Y-axis) or with  $\text{LoQ}/2$  (X-axis) [data from one activated sludge WWTP studied during the AMPERES project].

$\text{LoQ}$  value in sludge but was also strongly dependent on daily flux of the micropollutant received by the WWTP, mass of the micropollutant transferred in sludge, and fate of the micropollutant by sorption and biotransformation.

In summary, the choice of a  $\text{LoQ}/2$  or  $\text{LoQ}$  substitution rule for unquantified data could have a strong influence on  $R_W$  results for micropollutants with high  $\text{LoQ}$  in comparison with usual concentrations in wastewaters. We suggest using  $\text{LoQ}/2$  rather than  $\text{LoQ}$ , as we feel that it offers a better compromise from an analytical point of view. Thus, we strongly advocate choosing an adequate analytical method (with sufficiently low  $\text{LoQ}$ ) to analyze the targeted micropollutants. To improve  $R_T$  data, we also encourage the development of analytical methods with lower  $\text{LoQ}$ s in sludge and lower uncertainties, and to decrease the uncertainty linked to sampling strategy and heterogeneity of sludge.

### On the sensitivity of $R_W$ removal efficiency to measurement uncertainty

Considering the uncertainty on the micropollutant concentration for influent and effluent, we estimated the possible inferred bias on  $R_W$  values. To do this, we calculated the extreme values for removal efficiencies, noted  $R_W^{\text{Min}}$  and  $R_W^{\text{Max}}$ , considering two values for the measurement uncertainty on concentrations in influent, i.e. 30% and 100%. Two envelopes were plotted, as shown on Figure 4. These values should be compared to the  $R_W$  calculated with the measured concentrations given by the laboratory (represented on the X-axis) and also obtained by the 1:1 line.



**Figure 4** | Extreme  $R_W$  values (Min or Max) according to  $R_W$  calculated with measured concentrations (i.e. provided by the laboratory). Calculations obtained with the absolute sensitivity of  $R_W$  (i.e.  $\Delta R_W = (1 - R_W) * R_W * \Delta C_{in} / C_{in}$ ) using the measurement uncertainty on the influent concentrations ( $\Delta C_{in} / C_{in} = \pm 30\%$  and  $\pm 100\%$ ). Three cases are considered: low (A), partial (B) and high (C) removal efficiencies.

We discuss the robustness of  $R_W$  removal efficiencies using the example of three micropollutants with low (A), partial (B) and high (C) removal efficiencies, i.e. for instance carbamazepine, sulfamethoxazole and nonylphenol, respectively.

Through this example, we show that the calculated  $R_W$  are the most robust for substances with low (<30%, A) and high (>70%, C) removal efficiencies, with for example 3–4% uncertainty on  $R_W$  with a 30% uncertainty on the influent concentration, and with 10–15% uncertainty on  $R_W$  with a 100% uncertainty on the influent concentration. We conclude that  $R_W$  is not very sensitive to the measurement uncertainty in these ranges of  $R_W$ . In contrast, for a substance with partial removal efficiency (B) ranging from 30 to 70%, the calculated  $R_W$  values have higher uncertainty with, for instance, 7% uncertainty on  $R_W$  with a 30% uncertainty on the influent concentration, and with 20% uncertainty on  $R_W$  with a 100% uncertainty on the influent concentration. We deduce that calculated removal efficiency values for partially-removable micropollutants should be taken with care.

## CONCLUSIONS

This paper discussed different challenges to consider during the assessment of micropollutant removal efficiencies for WWTP. Pitfalls and preventive solutions for the sampling strategy and analytical methods are scrutinized to remind research and process engineers of the importance of these steps. New recommendations are proposed for data processing that should be disseminated and discussed to reach a

procedure internationally accepted. We have proposed preventive solutions to ensure unbiased water/sludge sampling, micropollutant analyses and new calculations ruleset to limit the sources of uncertainties. However, it needs to be understood that all of the uncertainty and threshold values covered here need to be adapted to every micropollutant project. We also advised to evaluate the sensitivity of calculation rules on the dataset and to adapt them according to the objectives of the project. We strongly advocate choosing adequate analytical methods (with sufficiently low LoQ) to analyze the targeted micropollutants. Also, more efforts should be spent to develop analytical methods in sludge with lower LoQ and lower uncertainties, and to decrease the uncertainty linked to sampling strategy and heterogeneity of sludge.

## ASSOCIATED CONTENT SPM

Example of application of the proposed calculation rules.

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## REFERENCES

- Bertanza, G., Papa, M., Pedrazzani, R., Repice, C., Mazzoleni, G., Steimberg, N., Feretti, D., Ceretti, E. & Zerbini, I. 2013 EDCs, estrogenicity and genotoxicity reduction in a mixed (domestic + textile) secondary effluent by means of ozonation: a full-scale experience. *Science of the Total Environment* **458–460**, 160–168.
- Carballa, M., Omil, F. & Lema, J. 2007 Calculation methods to perform mass balances of micropollutants in sewage treatment plants: application to pharmaceutical and personal care products (PPCPs). *Environmental Science & Technology* **41**, 884–890.
- Choubert, J. M., Martin Ruel, S., Esperanza, M., Budzinski, H., Miège, C., Lagarrigue, C. & Coquery, M. 2011 Limiting the emissions of micropollutants: what efficiency can we expect from wastewater treatment plants? *Water Science & Technology* **63** (1), 57–65.
- Coquery, M., Pomiès, M., Martin Ruel, S., Budzinski, H., Miège, C., Esperanza, M., Soulier, C. & Choubert, J. M. 2011 Concentrations and fluxes of micropollutants in wastewaters and sludge: methodology and main results of the AMPERES project [in French]. *Techniques Science Méthodes* **1/2**, 25–43.
- Dimpe, K. M. & Nomngongo, P. N. 2016 Current sample preparation methodologies for analysis of emerging pollutants in different environmental matrices. *Trends in Analytical Chemistry* **82**, 199–207.
- Estrada-Arriaga, E. B. & Mijaylova, P. 2011 Calculation methods to perform mass balance of endocrine disrupting compounds in a submerged membrane bioreactor: fate and distribution of estrogens during the biological treatment. *Water Science & Technology* **64** (11), 2158–2168.
- Eymery, F., Choubert, J. M., Lepot, B., Gasperi, J., Lachenal, J. & Coquery, M. 2011 *Technical Guide: Sampling and Conditioning for the Measurement of Micropollutants in Wastewater*. <http://www.aquaref.fr>, p. 85, Irstea/Cemagref.
- FD T 90-523-2 2008 *Water Quality – Sampling Guide for Monitoring Quality of Waters in the Environment – Part 2: Sampling of Wastewater*, p. 21.
- Gabet, V., Miège, C., Choubert, J. M., Martin Ruel, S. & Coquery, M. 2010 Occurrence and removal of estrogens and beta blockers by various processes in wastewater treatment plants. *Science of the Total Environment* **408** (19), 4257–4269.
- Harvey, D. 2008 *Analytical Chemistry 2.0*, pp. 285–354.
- Helsel, D. R. 2006 Fabricating data: how substituting values for nondetects can ruin results, and what can be done about it. *Chemosphere* **65**, 2434–2439.
- ISO 5667-13 2011 *Water Quality – Sampling – Part 13: Guidance on Sampling of Sludges*. AFNOR, p. 27.
- Janex Habibi, M. L., Huyard, A., Esperanza, M. & Bruchet, A. 2009 Reduction of endocrine disruptor emissions in the environment: the benefit of wastewater treatment. *Water Research* **43** (6), 1565–1576.
- Joss, A., Siegrist, H. & Ternes, T. A. 2008 Are we about to upgrade wastewater treatment for removing organic micropollutants? *Water Science & Technology* **57** (2), 251–255.
- Mailler, R., Gasperi, J., Rocher, V., Gilbert-Pawlik, S., Geara-Matta, D., Moilleron, R. & Chebbo, G. 2014 Biofiltration vs conventional activated sludge plants: what about priority and emerging pollutants removal? *Environmental Science and Pollution Research* **21** (8), 5379–5390.
- Majewsky, M., Gallé, T., Bayerle, M., Goel, R., Fischer, K. & Vanrolleghem, P. A. 2011 Xenobiotic removal efficiencies in wastewater treatment plants: residence time distributions as a guiding principle for sampling strategies. *Water Research* **45** (18), 6152–6162.
- Martin Ruel, S., Choubert, J. M., Ginestet, P. & Coquery, M. 2008 Semi-quantitative analysis of a specific database on priority and emerging substances in wastewater and sludge. *Water Science & Technology* **57** (12), 1935–1944.
- Martin Ruel, S., Esperanza, M., Choubert, J. M., Valor, I., Budzinski, H. & Coquery, M. 2010 On-site evaluation of the efficiency of conventional and advanced secondary processes for the removal of 60 organic micropollutants. *Water Science & Technology* **62** (12), 2970–2972.
- Metz, F. & Ingold, K. 2014 Sustainable wastewater management: is it possible to regulate micropollution in the future by learning from the past? A policy analysis. *Sustainability* **6** (4), 1992–2012.
- Miège, C., Bados, P., Brosse, C. & Coquery, M. 2009a Method validation for the analysis of estrogens (including conjugated compounds) in aqueous matrices. *Trends in Analytical Chemistry* **28** (2), 237–244.
- Miège, C., Choubert, J. M., Ribeiro, L., Eusèbe, M. & Coquery, M. 2009b Fate of pharmaceuticals and personal care products in wastewater treatment plants – Conception of a database and first results. *Environmental Pollution* **157**, 1721–1726.
- Muñoz, I., Otte, N., Van Hoof, G. & Rigarsford, G. 2017 A model and tool to calculate life cycle inventories of chemicals discharged down the drain. *The International Journal of Life Cycle Assessment* **22**, 986–1004.
- NF EN ISO 11352 2013 *Water Quality – Estimation of Measurement Uncertainty Based on Validation and Quality Control Data*, p. 26.
- Ort, C., Lawrence, M., Reungoat, J. & Mueller, J. F. 2010 Sampling for PPCPs in wastewater systems: comparison of different sampling modes and optimization strategies. *Environmental Science & Technology* **44** (16), 6289–6296.
- Petrie, B., Barden, R. & Kasprzyk-Hordern, B. 2015 A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. *Water Research* **72**, 3–27.
- Richardson, S. D. & Kimura, S. Y. 2016 Water analysis: emerging contaminants and current issues. *Analytical Chemistry* **88**, 546–582.
- Rossi, L., Rumley, L., Ort, C., Minkkinen, P., Barry, D. A. & Chèvre, N. 2011 Samplinghelper a web-based tool to assess the reliability of sampling strategies in sewers and receiving waters. *Water Science & Technology* **63** (12), 2975–2981.
- US Geological Survey 2002 National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A10, available online at <http://pubs.water.usgs.gov/twri9A>.