A virtual full-scale ozonation plant for micropollutant removal: how to reduce (eliminate?) piloting efforts

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Abstract
The AMOZONE kinetic ozonation model was applied to answer key questions for assessing the suitability of ozonation for the removal of micropollutants (MPs) from the effluent of a full-scale Water Resource Recovery Facility (WRRF). The model was calibrated and validated with bench-scale experiments on the real water matrix. Different control strategies for MP removal (considering the complete list of 11 guide MPs of the current Dutch legislation and an extended set of 19 MPs) and BrO_3 formation were tested. Results unravelled the complex dynamics behind O_3 and HO* reactions in this specific water matrix. The virtual full-scale experiments revealed the potential MP removal, the extent of production of BrO_3 (average levels varied between 1 and 3 µg/L), and the influence of the upstream WRRF dynamics. OpEx and CapEx of the virtual ful-scale installation were also assessed (the total cost varied between 9.6 and 10.8 cEUR/m³). No onsite piloting or MP analyses were needed and innovative controls could be tested.

Keywords
Virtual piloting, ozonation, micropollutants, bromate, AMOZONE

INTRODUCTION
Properly sizing a water treatment installation is of crucial importance, especially when the removal of micropollutants (MPs) must be completed with expensive technologies such as ozonation and introduced in an existing treatment site. Mechanistic models are nowadays supporting important decisions in design, optimization, revamping, and scale-up, and can be a powerful tool to save time and resources from long and expensive pilot testing. In addition to this, mechanistic models provide in-depth understanding of the complex net of reactions taking place in every point of an installation, which would be impossible to study in real-life testing. In this work the potential MP removal, the bromate (BrO_3) formation risk, and the costs of an ozone installation for the Water Resource Recovery Facility (WRRF) effluent matrix were assessed within one month. This was possible by building and operating a virtual full-scale plant with the novel AMOZONE model.

MATERIALS AND METHODS
The AMOZONE model (Audenaert et al., 2019) mechanistically describes the complex net of reactions leading to the formation of BrO_3 (*inter alia:* von Gunten, 2003a; von Gunten, 2003b), hydroxyl radical (HO*) formation and scavenging, O_3 reaction with the organic and inorganic water matrix, and a potentially limitless list of MPs which can be easily integrated.

Model calibration and validation
Four 24h secondary effluent composite samples of the Soerendonk WRRF (operated by Waterboard De Dommel, Netherlands) were provided, along with one month of high-resolution online data, and weekly lab analysis of the effluent quality. Dedicated ozonation batch tests were performed in replicates on these 4 samples at Ghent University lab in Kortrijk (Belgium) to assess reaction kinetics at two O_3 dosages. During the batch testing, O_3 and UVA_{254} decay, BrO_3 production, and HO* concentrations (probe component Alachlor) were measured as function of time. Out of eight bench experiments, four were used to calibrate the AMOZONE model and the remaining four were used to validate the model.

Full/scale plant operational scenario analysis
The model layout of the virtual O_3 installation was conceived with side stream injection (SSI) and

sized to ensure the necessary retention time for the O_3 reactions to occur and for O_3 to deplete completely (i.e. no final residual in effluent).

Simulations of different control strategies for O_3 dosage were run: i) flow proportional; ii) O_3/DOC proportional; iii) delta-UVA proportional; iv) MP removal-based). Results were then compared in terms of O_3 demand and OPEX. The MP removal-based control is a very novel control strategy as it implies the direct control of the O_3 dose on MP at a specific removal (not feasible without the model as MPs cannot be measured in real-time). The simulations also considered the contribution by the upstream biological treatment on MP removal (i.e. between 10% (worst case) and 30% (best case)). Finally, an overview of CapEx and OpEx was provided in terms of volume of treated water (cEUR/m^3) and yearly costs (kEUR/y).

All the scenarios were run for 1 month of real plant operation. The online and offline data collected by WSDD were processed and used as model input to observe the effect of real dynamics on the different control scenarios.

The Soerendonk WRRF bromide levels varied between 42 and 480 μg/L. In all the scenarios, a rather worst-case condition of a continuous inflow of 400 ug/L of bromide was used.

RESULTS

Calibration and validation

An extensive model calibration and validation was performed on the results of the batch experiments (Figure 1 and Figure 2). AMOZONE contains the net of O_3 reactions leading to organics depletion, and resulting in HO* radicals production, ultimately allowing to assess MPs exposure to O_3 and HO*. Nonetheless, also BrO_3 formation (data not shown)

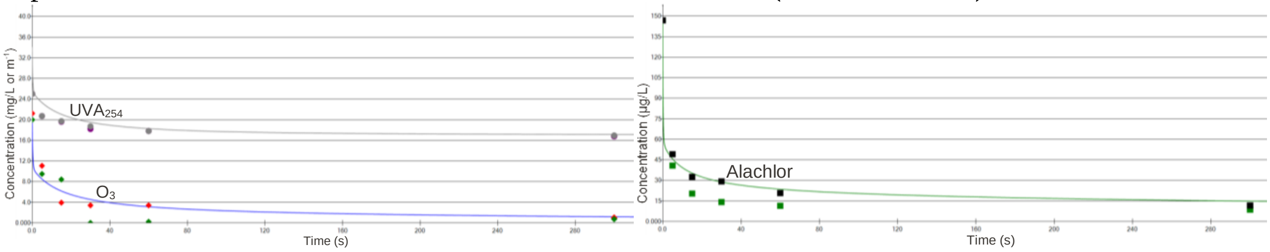

Figure 1. Model calibration on the 2nd sample, O_3 dose of 20 mg/L. Measured concentration in time (seconds) of O_3 (diamonds, mg/L) and UVA_{254} (circles, 1/m) (left), and alachlor (squares, μg/L) (right). Model results are reported as lines.

Figure 2 shows one of the model validations performed comparing model results with the measured data.

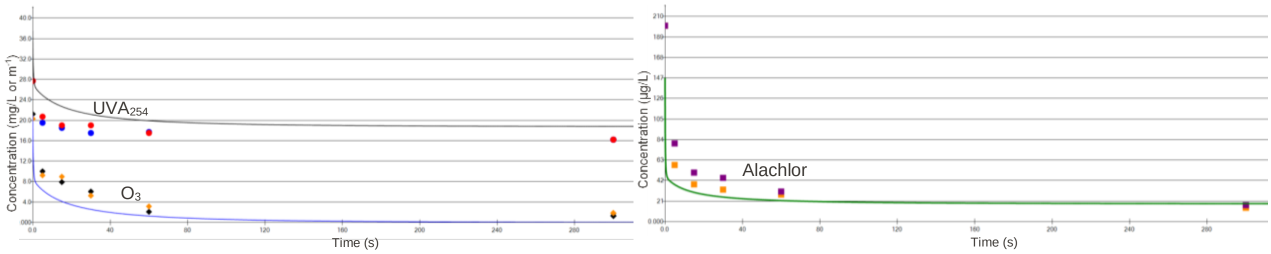

Figure 2. Model validation on the 3rd sample, O_3 dose of 16 mg/L. Measured concentration in time (seconds) of O_3 (diamonds, mg/L) and UVA_{254} (circles, 1/m) (left), and alachlor (squares, μg/L) (right). Model results are reported as lines.

An additional cross-project validation of the model prediction capabilities was made comparing the results from this study with the results of the European CWPharma project (Sehlén et al., 2020). In Figure 3, can be observed how the measured and simulated data of the first Swedish full-scale effluent ozonation plant (the Linköping WRRF, operated by Tekniska verken in Linköping) compare with the results of the Dutch plant of this study.

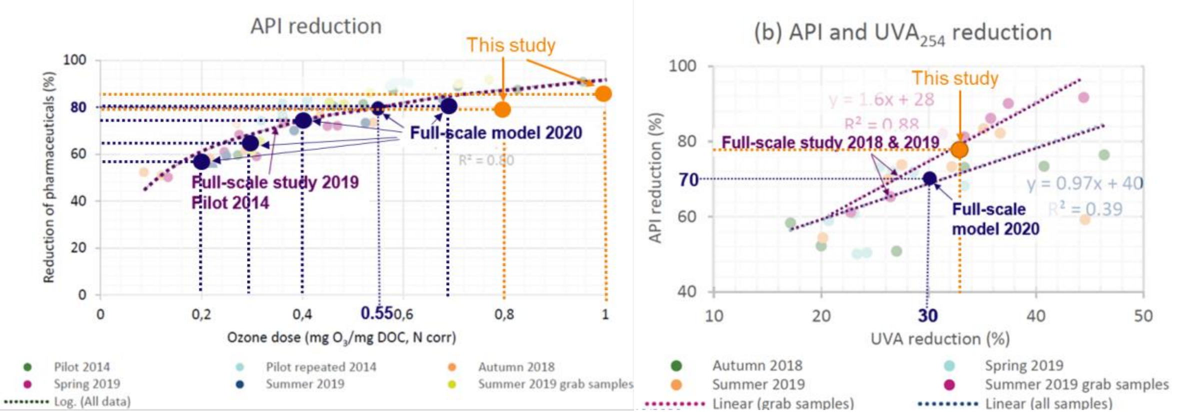

Figure 3. validation of the AMOZONE model performance (dark blue dots) against the Linköping full-scale installation data in terms of MP reduction as function of O_3 dose (left) and as function of UVA removal (right) (adapted from Sehlén et al., 2020) –data from this study fell within the expected ranges (orange dots).

Dynamic simulations

Dynamics simulations were run feeding the model with online data measured onsite. Knowing the detailed dynamics of the upstream WWTP helped in assessing its potential effect on the performance of the ozonation plant. In particular, the fluctuations in NH_4 concentration, resulting from the combined effect of the influent dynamics and the WWTP airflow controller action, have a relevant effect on BrO_3 formation (Figure 4, left). On the other hand, rain events and fluctuations in the water matrix (e.g. DOC, UVA) can also affect the removal of MPs (Figure 4, right).

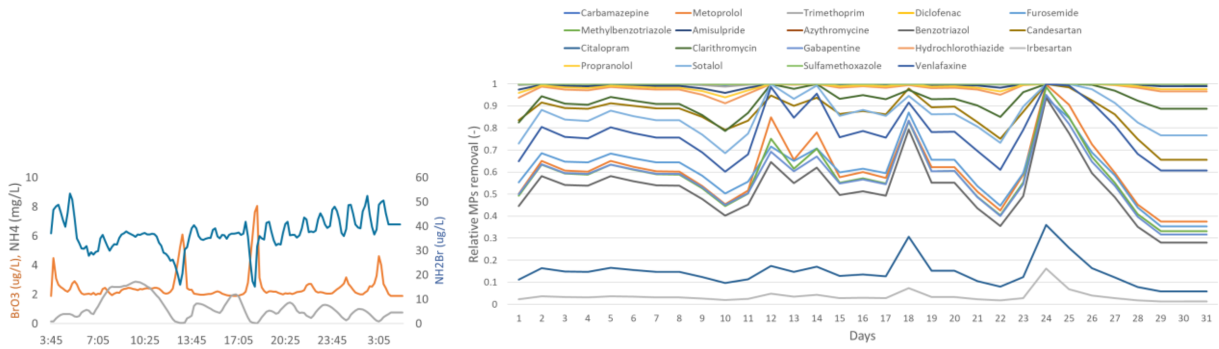

Figure 4. Dynamic simulation with flow proportional controller (8 mg/L). Left: 24h dynamics of BrO_3, NH_4 (left axis) and NH_2Br (right axis). Right: 30d dynamics of MP removal.

Scenario analysis

All the scenarios were run dynamically feeding the model with data from the online sensors. Results in terms of cost and performance were then analysed and compared for each of the scenario. Figure 5 shows the peak demand of O_3 for each of the scenarios. For this study, the peak demands resulted from the control strategy based on the O_3/DOC ratio of 1.2. On the other hand, basing the control strategy on a flow proportional dose of 8 mg/L or on a target MP might mitigate the peak O_3 demands

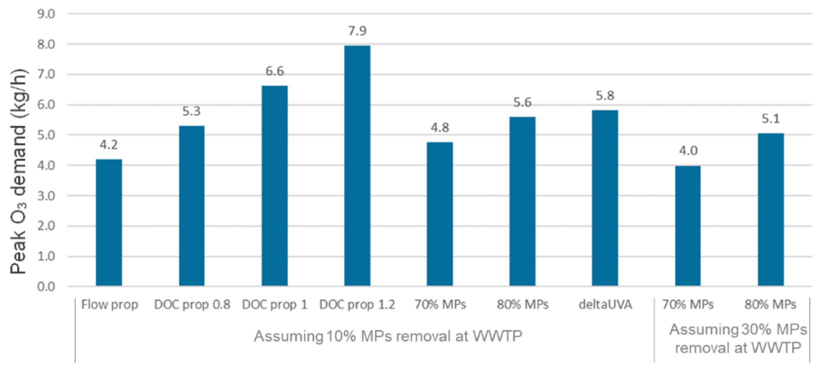

Figure 5. Peak O_3 demand (kg O_3/h) per scenario

For each of the scenarios the relative MP removal was also assessed with the dynamic simulation and compared with current regulatory limits (Figure 6). Interestingly, the highest dose of the O_3/DOC based controller shows that even 10 MPs are removed more than 70%, 9 for the delta-UVA controller. The novel '70% or 80% MP' controllers directly targeted regulatory compliance and showed the potential to save at least 10% OPEX.

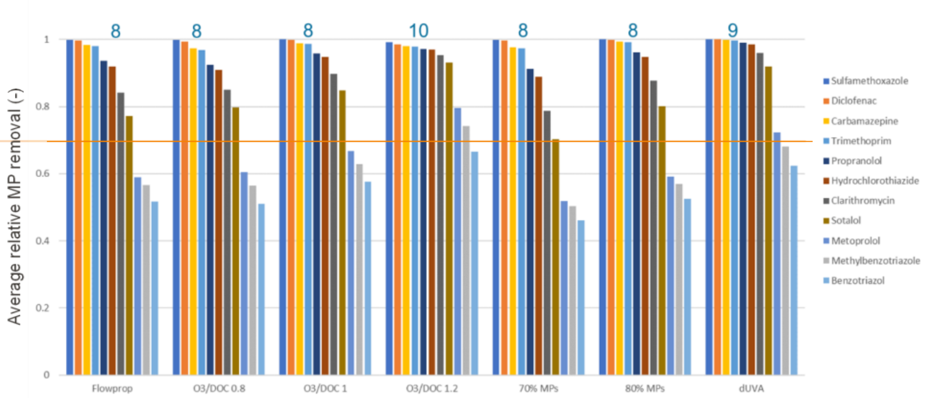

Figure 6. Whole-plant relative MP removal for the different control scenarios assuming 10% contribution of the upstream WRRF. For the 11 guide MPs. Numbers above the graph indicate how many MPs are removed according to the 70% regulatory threshold (orange line).

CONCLUSIONS

For the first time, an ozone installation was modelled prior to building any pilot or full-scale installation, and based on literature knowledge a large amount of information was extracted concerning the water matrix reactions with O_3 and HO*, the potential formation of BrO_3, the removal of MPs, and cost analysis. The virtual O_3 installation showed that the BrO_3 formation risk at Soerendonk is low. The calculated OpEx varied between 2.2 and 3.5 cEUR/m³ treated. The total cost (OpEx + CapEx) varied between 9.6 and 10.8 cEUR/m³. A smart control based on the removal of Sotalol (i.e. the 8th component in the list) can potentially save around 10% OpEx compared to scenarios that are conventionally used.

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