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Supporting Information for

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Photodegradation of micropollutants by vacuum-UV (VUV) radiation in potable reuse waters: Promotive and inhibitory effects of free chlorine oxidant

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Section S1. Additional materials

Free chlorine was prepared freshly from a stock NaOCl solution (13% as Cl_2 w/v, Fisher Scientific, Canada). 1,4-dioxane (1,4-D) (+99% ACS reagent), 1,4-dioxane-d8, carbamazepine (CBZ), nitrobenzene (NB) (+99% ACS reagent), *tert*-butanol (t-BuOH) (+99% ACS reagent), methanol (MeOH) (HPLC plus, ≥99.9%), dichloromethane (DCM) (HPLC plus, ≥99.9%), and sodium sulphate (anhydrous) were purchased from Sigma-Aldrich, Canada. Sodium chloride, sodium sulfite, monobasic sodium phosphate (anhydrous), and sodium phosphate dibasic (anhydrous) were obtained from Fisher Scientific, Canada. Experiments were carried out in ultrapure water (resistivity 18.2 MΩ.cm) from an Elga Pure water Option-Q system (Elga Labwater, UK). O_3/BAC direct potable reuse effluent was obtained from a pilot plant at Colorado School of Mines (Golden, CO). Reverse osmosis (RO) permeate was collected from an indirect potable reuse facility in California. Water samples were pre-filtered on 0.45 µm pre-rinsed membrane filters (Millex-HV Syringe Filters, Catalog number: SLHV033RS, Duluth, GA, USA) and stored in the dark at 4°C for up to three weeks. For VUV experiments ultrapure nitrogen (Praxair, Canada) was purged inside the VUV lamp housing to prevent absorption of 185 nm photons by oxygen and consequent ozone formation.

For UV control experiments a low-pressure (LP) mercury amalgam lamp (LightSouces Inc., Orange CT USA) with a doped quartz sleeve – to prevent the emission of 185 nm radiation – was used. According to the manufacturer's comment, the mercury amalgam mix is used to control mercury vapor pressure inside the lamp. This yields up to three times the UVC output of a standardLP mercury lamp of the same length. For the VUV experiments, two identical 10 W lamps with undoped quartz envelopes, transparent to both 254 and 185 nm wavelengths, were used (Sterilight S212ROL Lamp, HomePlus Products Inc., Canada).

Section S2. Chemical actinometry at 254 nm

Iodide/iodate actinometry is used to determine the fluence rate at 254 nm (E'). In this technique, a standard solution, consisting of 0.6 M KI, 0.1 M KIO_3 and 0.01 M $Na_2B_4O_7.10H_2O$ at pH 9.25, is prepared from 9.96 g KI, 2.14 g KIO_3 and 0.38 g $Na_2B_4O_7.10H_2O$ brought to 100 mL volume with distilled water. The reagents on exposure to UV form triiodide, the proposed reaction having the following stoichiometry:

$$8KI + KIO_3 + 3H_2O \overset{h\nu}{\rightarrow} 3I^- + 6OH^- + 9K^+ \qquad \text{(S1)}$$

The absorbance of triiodide can be determined spectrophotometrically at 352 nm and used to calculate the UV irradiance:

$$E' = 23.373\,\frac{A_{352\,nm}(sample) - A_{352\,nm}(blank)}{Area\ (cm^2) \times Exposure\ time\ (s)} \times Volume\ (mL)\ \ [mW.cm^{-2}] \qquad \text{(S2)}$$

where $A_{352\,nm}(blank)$ is the initial absorbance of the standard actinometry solution and $A_{352\,nm}(sample)$ is the absorbance of the standard solution after irradiation both measured at 352 nm. As described by Rahn (1997), the constant 23.373 is the result of dividing the energy of a mole of photons at 254 nm (4.716×10^5 J Es^{-1}) over the product of the quantum yield of triiodide (0.73) at 254 nm and the molar absorption coefficient of triiodide at 352 nm (27600 M^{-1} cm^{-1}) (Rahn, 1997).

The average fluence rate will then be calculated by applying the necessary correction factors (Bolton and Linden, 2003):

$$E'_{avg} = E' \times Water\ Factor \times Divergence\ Factor \qquad \text{(S3)}$$

where water factor (WF) corrects for the attenuation of the incident fluence rate due to the water absorption in the irradiated column and divergence factor (DF) accounts for the fact that the beam is not fully collimated. The correction factors WF and DF are calculated as following:

$$WF = \frac{1 - 10^{-al}}{al\ \ln(10)} \qquad \text{(S4)}$$

$$DF = \frac{L}{L + l} \qquad \text{(S5)}$$

In the above equations, a is defined as the product of molar absorption coefficient and concentration of water ($a = \varepsilon.C$ = 0.0365 cm^{-1} at 254 nm), l is the pathlength of the light (1 cm) and L is the distance from the lamp to the irradiated surface (the value of L was adjusted at 29.5 cm and 22.5 cm in the UV and VUV/UV collimated beams, respectively).

In this study, the average 254 nm fluence rates in the UV collimated beam and VUV/UV collimated beams were measured at 0.40 and 0.61 mW cm^{-2}, respectively.

Section S3. Determining the molar absorption coefficients at 185 nm

A VUV radiometer was used to measure the irradiance passing through the samples at 185 nm and determine the molar absorption coefficients of the solution components at this wavelength (Figure

S2). Radiometry experiments were carried out in a 1 cm path length quartz cuvette, while the temperature was maintained at 20°C using a temperature controller. The measured irradiances were then converted to absorbance of the samples at 185 nm by applying the Beer-Lambert law (equation S6). Finally, the slope of the absorbance versus the concentration data was calculated by linear regression and was used to determine the molar absorption coefficients of HOCl and OCl^- at 185 nm. For each of HOCl and OCl^- species, the measured values of $\varepsilon_{185\ nm}$ were 3900 M^{-1} cm^{-1} and 4700 M^{-1} cm^{-1}, respectively (Masjoudi and Mohseni, 2022).

$$\log\left(\frac{I_{0,185\ nm}}{I_{185\ nm}}\right) = A_{185\ nm} = \varepsilon_{185\ nm}.C.l \qquad \text{(S6)}$$

where $I_{0,185\ nm}$ and $I_{185\ nm}$ (W cm^{-2}) are the measured irradiances at 185 nm for the blank and the sample, respectively. Also, $A_{185\ nm}$ and $\varepsilon_{185\ nm}$ (M^{-1} cm^{-1}) are the solution absorbance and the molar absorption coefficient of the solution, respectively, both measured at 185 nm. C is the molar concentration of the solution (M), and l is the light pathlength (cm).

Section S4. Sample preparation and analytical method for 1,4-dioxane

To prepare 1,4-dioxane-containing samples for analysis, 5 mL of the water sample was placed in a 60 mL separatory funnel and 5 mg sodium sulfite was added and dissolved to quench free chlorine residual. 1,4-dioxane-d8 was added as the internal standard at a constant concentration of 200 μg/L. For improving the liquid-liquid extraction efficiency, 1 g sodium chloride (NaCl) was added and dissolved to help better separation of phases by salting out. The samples were then extracted into 20 mL dichloromethane (DCM) in two steps by shaking vigorously for 2 minutes. After separating and discarding the aqueous layer, 1 g of anhydrous sodium sulphate (Na_2SO_4) was added to the organic extracts to remove any residual water. Then, 5 mL of the extract was further concentrated by nitrogen blowdown to 0.5 mL and kept in the freezer prior to analysis. The total sample preparation procedure is shown in Figure S7.

The DCM extracts were analyzed by gas chromatography/mass spectrometry (GC/MS, Shimadzu, USA) using a Shimadzu GC-2030/GCMS-QP2020 NX equipped with an SH-Rxi-5ms column (30 m × 0.25 mm ID × 0.25 μm film thickness). Helium was used as the carrier gas at a flow rate of 1 mL/min. A volume of 1 μL of the extracted sample was injected into a splitless injection port at 280°C. Oven temperature program initially started at 35°C for 4 min, subsequently increased to 70°C at 5°C/min to a final temperature of 280°C and hold for 2 min. Ion source was set in the electron ionization mode at 200°C and an interface temperature of 250°C. Data acquisition was performed in selected ion monitoring (SIM) mode scanning for *m/z* 58 and 88 for 1,4-dioxane (target), and *m/z* 62 and 96 1,4-dioxane-d8 (internal standard). The ratio of the peak area of quantifier ions at *m/z* 88 to that of *m/z* 96 was used for quantification of 1,4-dioxane.

A series of mixed standards were prepared in the working concentration range of 25 μg/L to 2 mg/L and were used to build a 10-point calibration curve. During a sequence of sample analyses, the linearity was periodically checked by including the standard solutions in the sequence.

Table S1. Fraction of 185 nm photons absorbed by solutes in the O_3/BAC effluent and RO permeate.

Solute	H_2O	HCO_3^-	DOC	Cl^-	NO_3^-	SO_4^{2-}
$f_{O_3/BAC,185\ nm}$	0.117	0.015	0.075	0.465	0.322	0.006
$f_{RO,185\ nm}$	0.747	0.016	0.021	0.140	0.076	$< 10^{-4}$

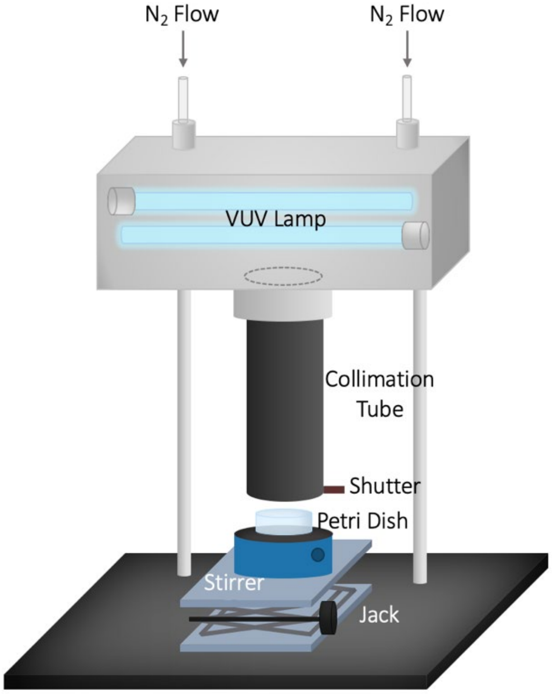

Figure S1. VUV/UV collimated beam setup.

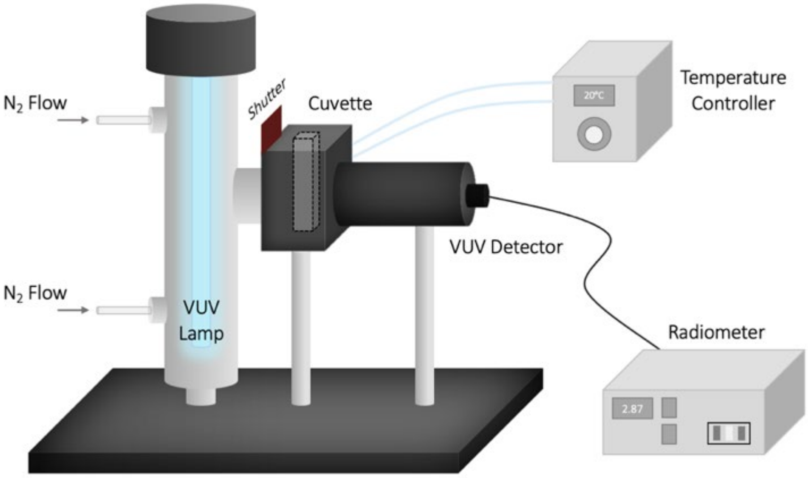

Figure S2. VUV 185 nm radiometry setup.

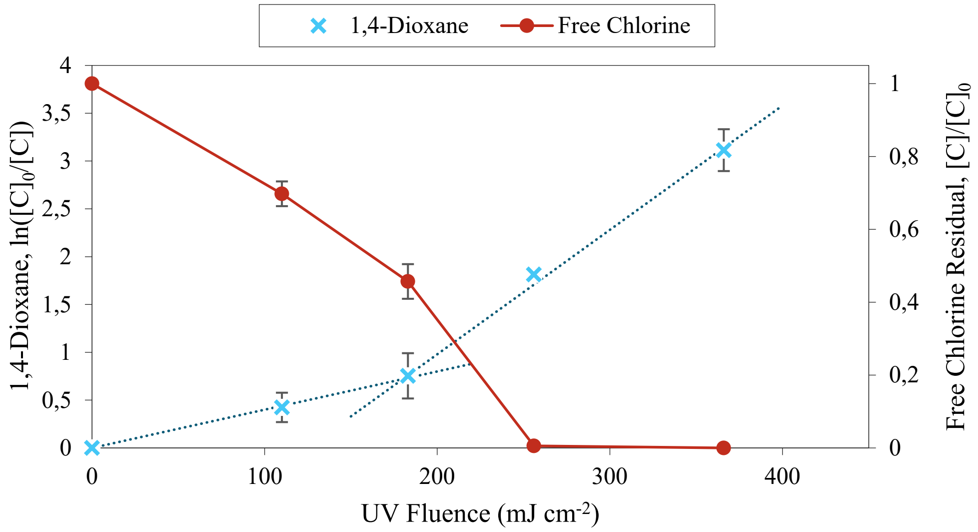

Figure S3. Enhancement of 1,4-D removal with consumption of free chlorine in the VUV/UV/Cl AOP in DI water ($[C]_{1,4\text{-D},0}$ = 6 µM, $[C]_{\text{free chlorine},0}$ = 70 µM, Average pH = 6.5 (unadjusted)). Dotted lines indicate the trend lines for 1,4-D removal before and after chlorine depletion in the solution.

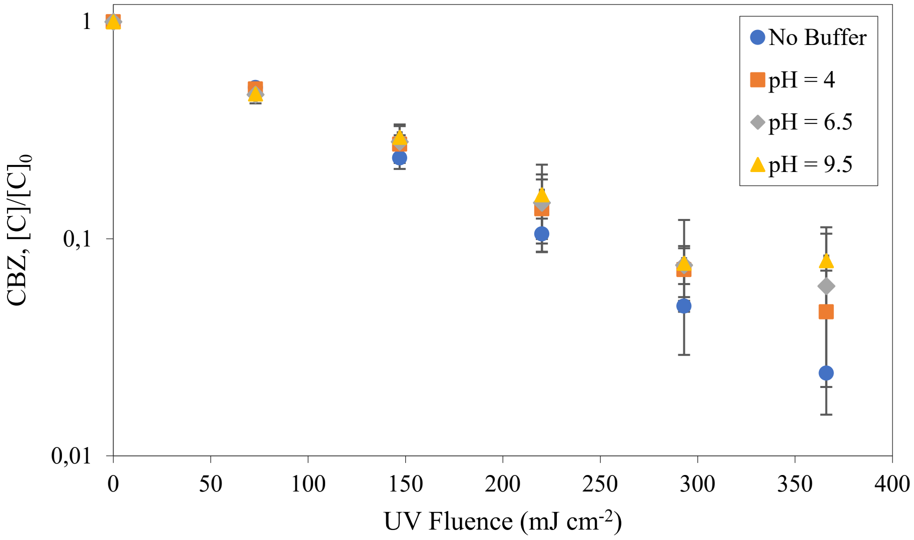

Figure S4. Degradation of CBZ in the VUV/UV AOP at different pH levels ($[C]_{\text{CBZ},0}$ = 1 ppm, $[C]_{\text{phosphate buffer}}$ = 2 mM).

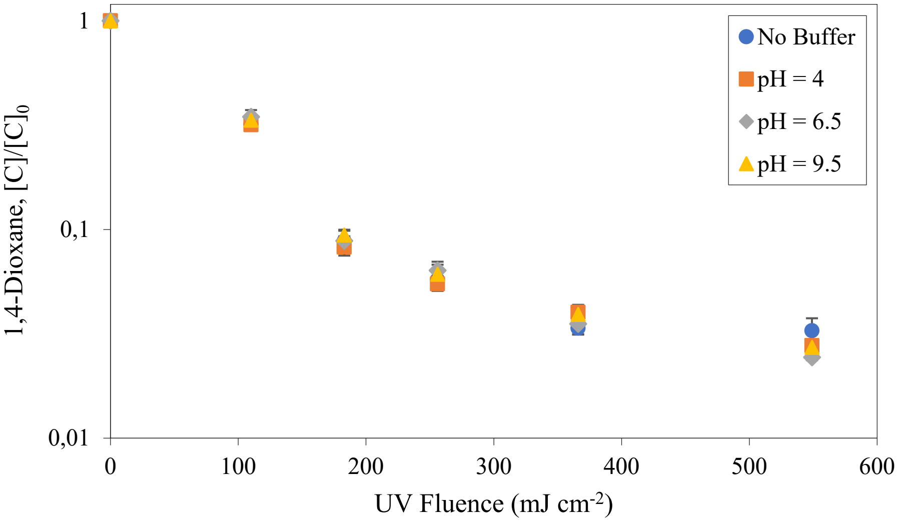

Figure S5. Degradation of 1,4-D in the VUV/UV AOP at different pH levels ($[C]_{1,4\text{-}D,0}$ = 0.5 ppm, $[C]_{\text{phosphate buffer}}$ = 2 mM).

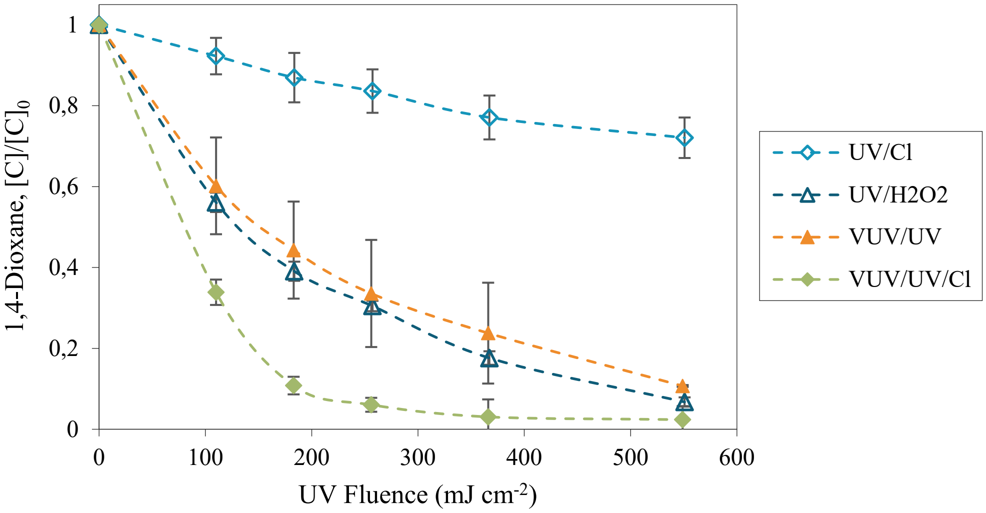

Figure S6. Degradation kinetics of 1,4-D in the VUV/UV and VUV/UV/Cl AOPs compared to the commonly used UV/Cl and UV/H_2O_2 treatments in RO permeate water matrix ($[C]_{1,4\text{-}D,0}$ = 6 µM, $[C]_{\text{free chlorine},0}$ = 70 µM, $[C]_{H2O2,0}$ = 88 µM).

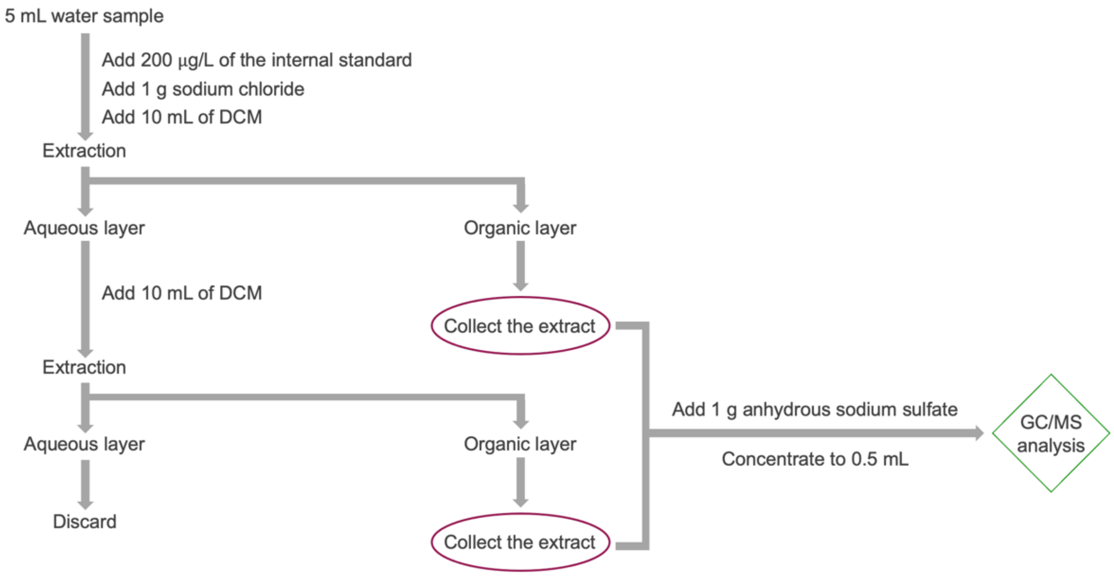

Figure S7. The flowchart of 1,4-dioxane sample preparation overview.

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