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Understanding the behaviour of UV absorbance of natural waters upon chlorination using model compounds

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Supplementary information

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Supplementary text 1: Targeted literature review of the chlorination of the chosen model compounds

1.1.1 PHENOLS: RESORCINOL AND P-CRESOL

Chlorination of resorcinol has been widely studied. Because of its aromatic structure activated by hydroxyl groups, resorcinol has a high UV absorbance in the 270 nm region, and is therefore considered a model for the more complex NOM molecules with high aromaticity, such as humic acids. TCM formation from the reaction between chlorine and meta-dihydroxybenzene precursors, specifically resorcinol, was first suggested by Rook [1]. Norwood et al. [2] confirmed the rapid formation of TCM from resorcinol, and confirmed that TCM is formed by an activated carbon atom located between two hydroxyl groups (OH), for which keto-enol stabilisation of the carbanion is possible. Aromatic structures that lack this carbon between two hydroxyl groups produce less TCM, although their chlorine consumption is still relatively high (3 to 7 mol of Cl_2/mol of compound). This is because of the halogenation of the aromatic ring through the substitution of hydrogen atoms by chlorine atoms [2,3]. The pathway of TCM formation from resorcinol involves three major steps: the incorporation of chlorine into the aromatic ring, the cleavage of the ring, and the release of TCM. Trichloroacetic acid (TCAA) has also been found as a product of the chlorination of resorcinol [2,4].

The impact of chlorination on the UV spectra of resorcinol has been studied previously [5–7]. The general conclusion from these studies is that, at very short reaction times (< 50 s), increasing absorbance with increasing incorporation of chlorine is typical for resorcinol and other phenolic compounds at wavelengths between 250 and 400 nm [5,7](Gonzalez et al., 1996; Li et al., 2000). However, this first step occurs rapidly at chlorine dosages found in drinking water applications. For typical reaction times studied, cleavage of the aromatic ring occurs and UV absorbance steadily decreases over the entire UV-visible spectra.

Gallard and von Gunten [3] exhaustively studied the reaction between chlorine and phenols including p-cresol. They also determined reaction rates and TCM formation rates for many monohydroxybenzenes at various pHs. Generally, monohydroxybenzene reacts more slowly than dihydroxybenzene [3,4,8] and could therefore be responsible for the slowly reacting THM precursors found in natural waters. P-cresol was found to have a very low TCM yield, although its chlorine demand was high [3,4].

1.1.2 ACETYLACETONE

Acetylacetone is a neutral molecule in the sense that its molecular structure does not contain a strong acid or a carboxylic acid group. However, it acts as a weak acid by releasing one of its carbon-bound protons, with a pKa between 8.9 and 9.0. TCM formation upon the chlorination of ketones was first suggested by Morris [9]. De Laat et al. [4] showed that the TCM formation pathway from acetylacetone involves 1,1,1-trichloropropanone (TCP), and to a lesser extent 1,1-dichloropropanone (DCP). The TCP and DCP act as intermediates that form rapidly upon chlorination, and later release TCM. Because TCP can be found in drinking water and has been shown to degrade with time in drinking water systems with a free chlorine residual at pH ≥ 7 [10,11], acetylacetone might be a good model compound for the TCP precursor found in natural and coagulated waters. The UV-visible absorbance spectrum of acetylacetone has not been studied in the context of drinking water DBP formation before.

1.1.3 CARBOXYLIC ACIDS: CITRIC AND MALONIC ACID

Carboxylic acids, specifically those with a β-keto group (a ketone on the second carbon atom from the carbon with the carboxylic acid group) or those that can be converted to such a form, were shown to be precursors of

TCM [4,12,13]. Citric acid gives good yields of chloroform when chlorinated at near neutral pH. Larson and Rockwell [13] suggested a formation pathway involving the formation of the β-keto form of the acid, followed by the rapid halogenation of the carbon between the two keto groups, and then followed by the hydrolysis of the trichloromethyl group. These last two steps are the same as the steps for TCM formation from acetylacetone. TCM yields obtained by Larson and Rockwell [12] and de Laat et al. [4] varied according to initial concentrations of citric acid, probably due to the apparent kinetic rate being proportional to the concentration of the reactants.

In the experiments by de Laat et al. [4], malonic acid had a much lower TCM yield than citric acid, despite having a higher chlorine demand. The UV-visible absorbance spectrum of carboxylic acids has not been studied in the context of drinking water DBP formation before. It is however known that the molar absorptivity of such acids is 2 to 4 orders of magnitude lower than that of aromatic compounds. Finally, in opposition to phenols and acetylacetone, carboxylic acids are not "model" compounds, as they are naturally found in surface and treated waters [14,15].

1.1.4 Amino acids: tyrosine and histidine

Amino acids are constituents of proteins, found in all living organisms, and hence are ubiquitous in natural waters. Chinn and Barrett [16] found 16 different amino acids at the microgram level in two drinking water sources. Amino acids react with chlorine in different ways depending on their molecular structure. Hurekei et al. [17] found that the initial chlorine demand of the primary amine was 2 mol/mol, leading to the formation of dichloramine, with a chlorine demand that increased slowly thereafter. Other amines, when present on the structure, also had an initial chlorine demand of 2 mol/mol. Hydroxyl functions demand 3 to 4 mol/mol, while the presence of double bonds and aromatic structures increases the chlorine demand from 4 to 8 mol/mol. The highest 72-h chlorine demand (16 mol/mol) was obtained with tryptophan, an amino acid with an aromatic structure and a secondary amine with a double bond. Finally, Hurekei et al. [17] found that amino acids were globally low precursors of THM, but contributed to the total organic halide (TOX) formation potential, which include HANs. Selbes et al. [18] confirmed the formation potential of DCAN of various amino acids. CPK is not usually found upon the chlorination of amino acids, but ozonation followed by chlorination produces CPK [18–20]. The UV-visible absorbance spectrum of amino acids has not been studied before in the context of drinking water DBP formation.

1.1.5 Methylcellulose

Methylcellulose was chosen as a model compound for carbohydrates. Carbohydrates represent between 5 and 12 % of dissolved organic carbon (DOC) in surface waters, and cellulose is probably the most abundant polysaccharide [15]. Methylcellulose was preferred over cellulose because of its higher solubility. To our knowledge, chlorination of cellulose in water has not been reported before. Based on its molecular structure, low reactivity with chlorine is expected.

Table S. 1 : Classification, reactivity and chlorination by-products of the selected model compounds identified in the literature

Classification			Data from the literature								
	Polarity*	Acidity	Chlorination conditions				Chlorine consumption		DBPs formed		Reference
			pH	Cl_2 dose	T°	Contact time	Initial (< 60 s)	Total	Compound	Molar yield	
				mol/mol	°C	(h)	mol/mol	mol/mol		mol/mol	
Resorcinol	HPB	Acid	7.5	6-8	10	4	n.a.	n.a.	TCM	0.75	[1]
			11.0	6-8	10	4	n.a.	n.a.	TCM	0.80	
			7.0	11.6	5	4.17	n.a.	6.60	TCM	0.877	[2]
			7.5	20	20	15	6.85	7.2	TCM	0.9	[4]
				<5					Chlororesorcinol	0.002-0.015	
				8					Monochloro-maleic acid	0.6	
									TCAA	<0.1	
			11.5	10	22	1s-18min	n.a.	n.a.	Tri and tetra chlorinated resorcinol Tetra-, penta-, and hexachlorinated pentenones	n.a.	[5]
			7.0	0.9-9.0	25	n.a.	n.a.	n.a.	n.a.	n.a.	[6]
			7.0	44	20±2	0-50s	n.a.	n.a.	n.a.	n.a.	[7]
p-cresol	HPB	Acid	7.0	20	20	15	n.a.	3.3	TCM	0.4	[4]
			8.0	35	23±2	45	5.0	10.5	TCM	0.02	[3]
Acetylacetone	HPB	Neutral (acid)	7.5	20	20	60s	3	3	TCP	1	[4]
			7.5	20	20	15	3	4	TCM	0.085	
Citric acid	HPL	Acid	7.0	10	20	2	n.a.	n.a.	TCM	0.8	[13]
			7.0	10	ambient	2	n.a.	n.a.	TCM	0.779	[12]
			5.5							0.212	
			9.3							<0.01	
			7.0	20	20	15	n.a.	0.8	TCM	0.145	[4]
Malonic acid	HPL	Acid	7.0	20	20	15	n.a.	1.8	TCM	<0.001	[4]

Classification			Data from the literature								
	Polarity*	Acidity	Chlorination conditions				Chlorine consumption		DBPs formed		Reference
			pH	Cl_2 dose	T°	Contact time	Initial (< 60 s)	Total	Compound	Molar yield	
				mol/mol	°C	(h)	mol/mol	mol/mol		mol/mol	
Methyl-cellulose	HPL	Neutral	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Tyrosine	HPB	Base	7.0	20	20	15	n.a.	11.4	TCM	0.013	[4]
			8.0	15	20	72	n.a.	13.4	TCM	0.347	[17]
Histidine	HPL	Base	8.0	15	20	72	n.a.	12	TCM	0.023	[17]
			8.0	>20	22	24	n.a.		TCM	0.00	[18]
									HNM	0.00	
									DCAN	173 µg/mgC	
									DCAA	336 µg/mgC	
									TCAA	45 µg/mgC	

*HPB: hydrophobic; HPL: hydrophilic

References in Supplementary text 1 and Table S.1

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In Figures S.1 to S.8, R represents the deprotonated species of the compound (e.g., R of p-cresol is CH_3-C_6H_4-O^-), RH_1 represents the compound with 1 proton added (e.g., RH_1 of p-cresol is CH_3-C_6H_4-OH), RH_2 represents the compound with 2 protons added (when applicable), etc.

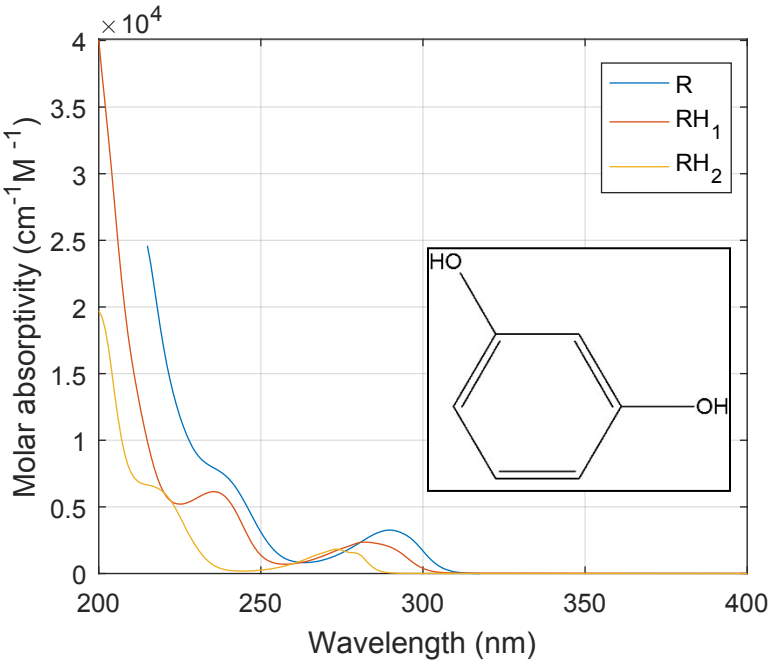

Figure S. 1 : Molar absorptivity spectra of resorcinol deprotonated species (R) and protonated species (RH1, RH2) in nanopure water (Dominant species at near neutral pH : RH2).

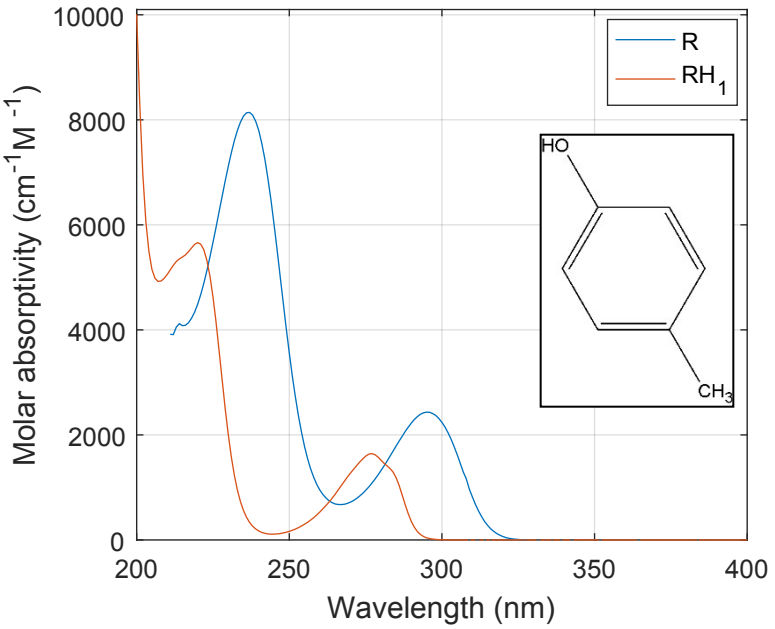

Figure S. 2 : Molar absorptivity spectra of p-cresol deprotonated species (R) and protonated species (RH1) in nanopure water (Dominant species at near neutral pH : RH1).

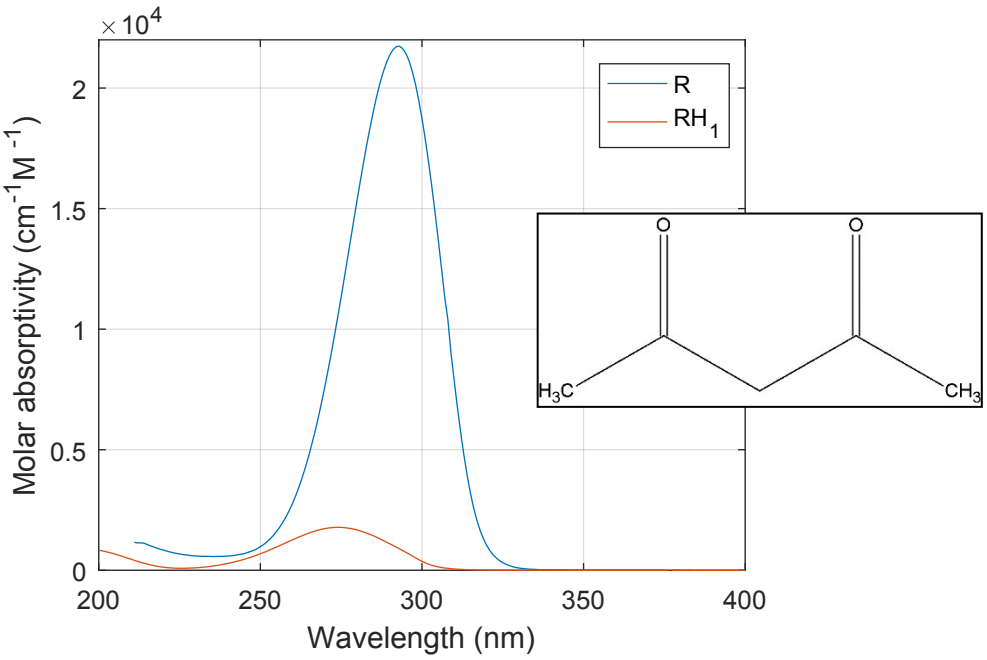

Figure S. 3 : Molar absorptivity spectra of acetylacetone deprotonated species (R) and protonated species(RH1) in nanopure water (Dominant specie sat near neutral pH : RH1).

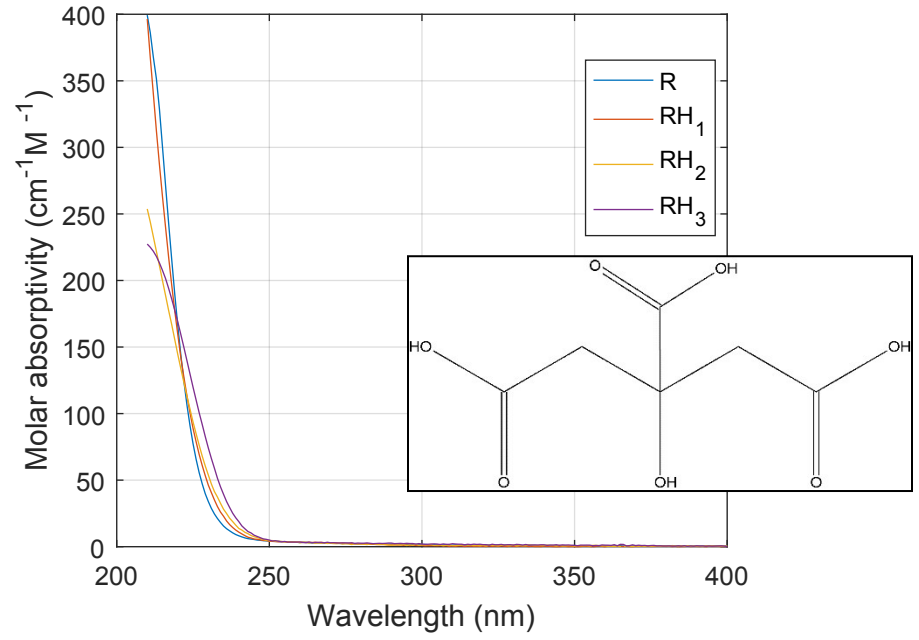

Figure S. 4 : Molar absorptivity spectra of citric acid deprotonated species (R) and protonated species (RH1, RH2, RH3) in nanopure water (Dominant species at near neutral pH : R).

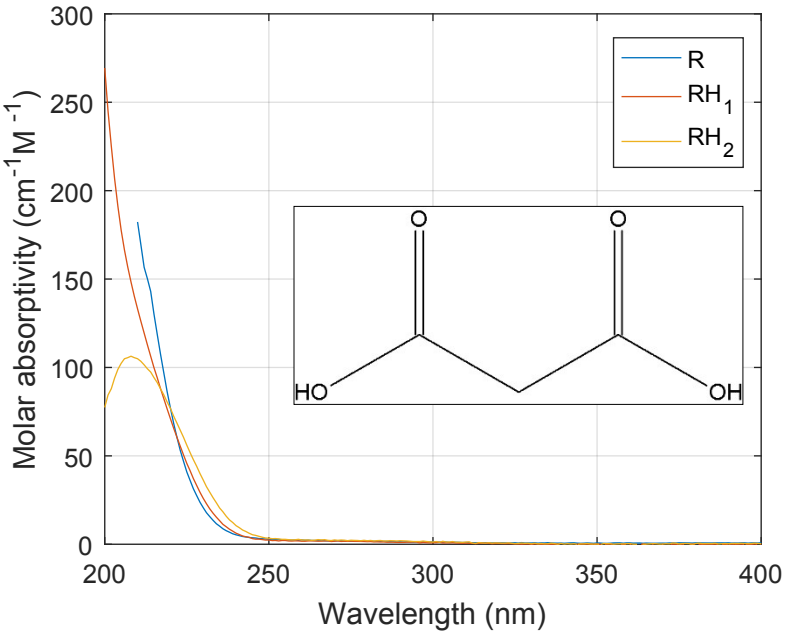

Figure S. 5 : Molar absorptivity spectra of malonic acid deprotonated species (R) and protonated species (RH1, RH2) in nanopure water (Dominant species at near neutral pH : R).

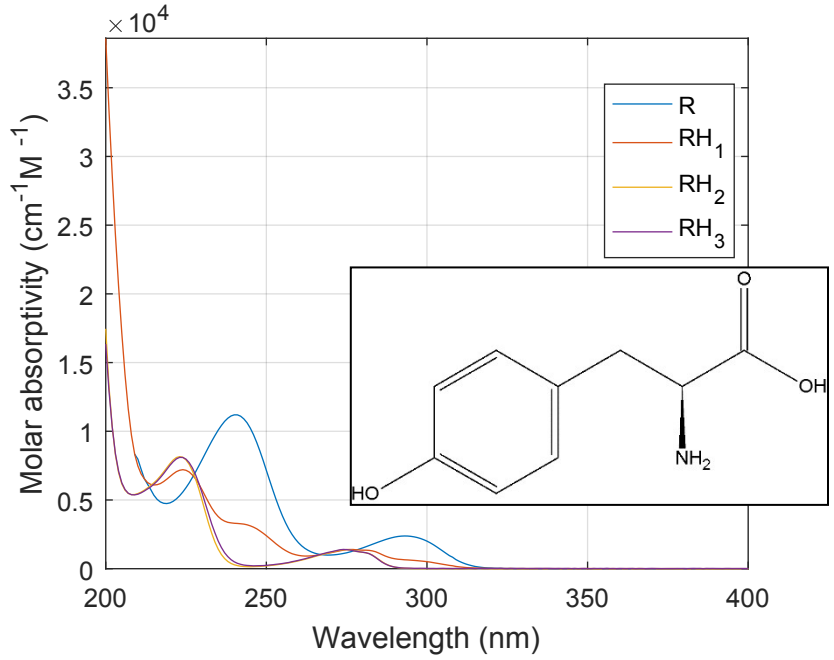

Figure S. 6 : Molar absorptivity spectra of tyrosine deprotonated species (R) and protonated species (RH1, RH2) in nanopure water (Dominant species at near neutral pH : RH2).

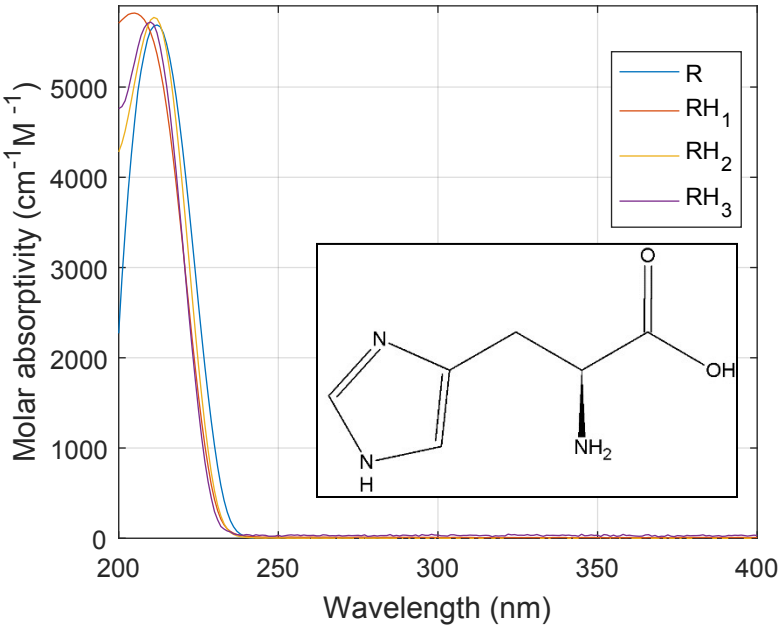

Figure S. 7 : Molar absorptivity spectra of histidine deprotonated species (R) and protonated species (RH1, RH2, RH3) in nanopure water (Dominant species at near neutral pH : RH1).

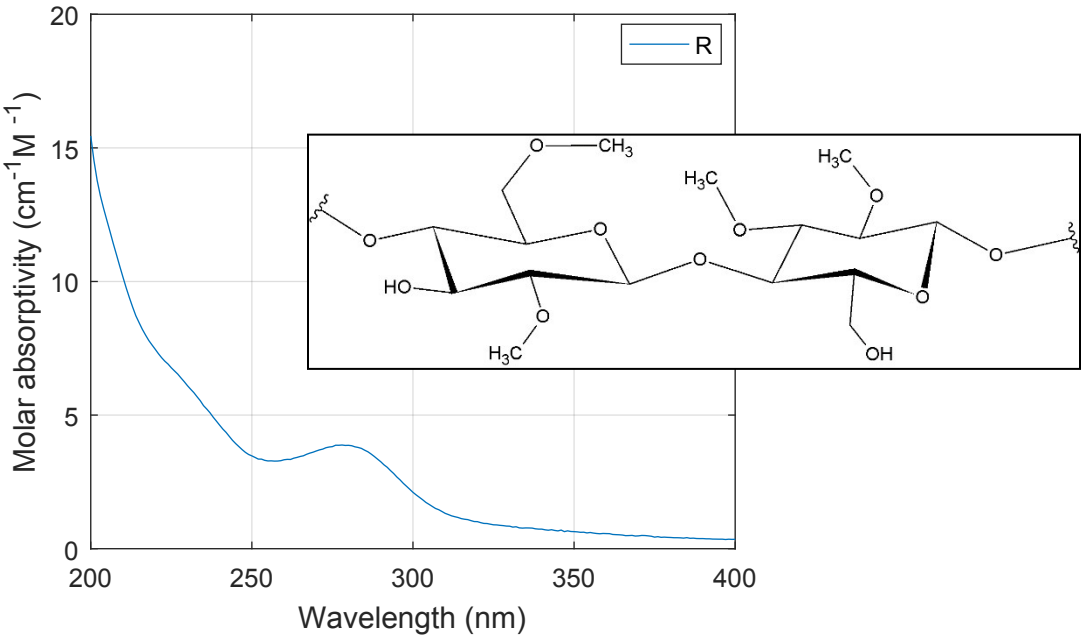

Figure S. 8 : Molar absorptivity spectrum of methylcellulose in nanopure water

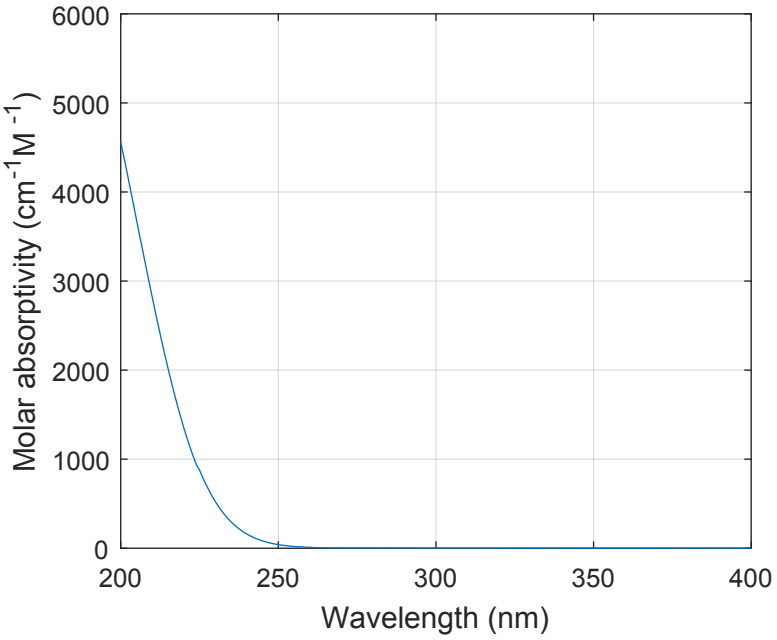

Figure S. 9 : Molar absorptivity spectrum of sodium sulphite in nanopure water

Table S. 2 : DBP formation for all model compounds and for the pretreated water at all reaction times

Compound	Time	THMs	HAAs			HANs		HNMs	HKs	
		TCM	MCAA	DCAA	TCAA	DCAN	TCAN	CPK	DCP	TCP
	h	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Resorcinol	0.5	760	1	5	22	2,55*	< 0.01	< 0.01	0.12	0.01
	1	850	< 1	3	26	3,05*	< 0.01	< 0.01	0.18	0.05
	2	910	< 1	3	33	2,94*	< 0.01	< 0.01	0.09	0.05
	6	950	< 1	2	58	2,15*	< 0.01	< 0.01	0.10	0.04
	24	1010	< 1	3	60	1,84*	< 0.01	< 0.01	< 0.01	0.10
p-cresol	0.5	1	1	2	1	2.19*	< 0.01	< 0.01	4.57	0.1
	1	1	1	2	1	2.10*	< 0.01	< 0.01	10.05	0.18
	2	1	1	2	2	1.35*	< 0.01	< 0.01	4.00	0.29
	6	2	1	2	5	0.86*	< 0.01	< 0.01	2.91	1.68
	24	2	< 1	2	11	0.19*	< 0.01	< 0.01	0.40	4.82
Acetylacetone	0.5	850*	8	6	< 1	< 0.01	< 0.01	< 0.01	> 200.0	> 200.0
	1	380	8	7	< 1	< 0.01	< 0.01	< 0.01	139.4	> 200.0
	2	510	14	14	< 1	< 0.01	< 0.01	< 0.01	137.7	> 200.0
	6	660	27	31	1	< 0.01	< 0.01	< 0.01	55.2	> 200.0
	24	1340	57	127	1	< 0.01	< 0.01	< 0.01	6.1	> 200.0
Citric acid	0.5	3	< 1	4	3	< 0.01	< 0.01	0.02*	0.43	0.34
	1	3	< 1	2	4	0.25*	< 0.01	0.06*	0.68	0.54
	2	4	< 1	2	4	0.14*	< 0.01	0.03*	0.41	0.40
	6	14	< 1	2	12	0.19*	< 0.01	0.07*	0.50	1.07
	24	46	< 1	2	46	0.08*	< 0.01	0.03*	0.17	0.58
Malonic acid	0.5	1	n.a.	n.a.	n.a.	0.10*	< 0.01	0.05*	0.22	0.04
	1	2	n.a.	n.a.	n.a.	< 0.01	< 0.01	< 0.01	0.22	0.13
	2	3	5	17	11	0.12*	< 0.01	< 0.01	0.00	0.18
	6	2	10	73	26	0.22*	< 0.01	< 0.01	0.24	0.10
	24	4	n.a.	303	n.a.	0.39*	< 0.01	0.04*	0.16	0.21
Tyrosine	0.5	13	< 1	5	8	10.13	0.05	< 0.01	0.09	< 0.01
	1	16	< 1	8	18	15.55	0.13	< 0.01	0.06	< 0.01
	2	27	< 1	12	32	19.44	0.20	< 0.01	< 0.01	< 0.01
	6	40	< 1	24	60	22.64	0.38	0.12	0.04	< 0.01
	24	48	< 1	26	54	35.27	0.50	< 0.01	< 0.01	< 0.01

Compound	Time	THMs	HAAs			HANs		HNMs	HKs	
		TCM	MCAA	DCAA	TCAA	DCAN	TCAN	CPK	DCP	TCP
	h	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Histidine 1	0.5	1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1	1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	2	< 1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	6	2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	24	2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Histidine 2	0.5	n.a.	< 1	< 1	< 1	0.20	< 0.01	< 0.01	0.04*	0.08*
	1	n.a.	< 1	< 1	< 1	0.29	< 0.01	< 0.01	0.02*	0.02*
	2	n.a.	< 1	< 1	< 1	0.64	< 0.01	< 0.01	0.03*	0.03*
	6	n.a.	< 1	< 1	< 1	1.17	< 0.01	< 0.01	0.03*	0.05*
	24	n.a.	< 1	1	1	1.88	< 0.01	< 0.01	0.02*	0.04*
Methylcellulose	6	2	2	2	1	1.14*	< 0.01	< 0.01	0.15	0.07
	24	2	3	2	1	< 0.01	< 0.01	0.03*	0.13	0.10
Pretreated water	0.5	15	< 1	7	6	0.65	0.04	0.16	0.52	0.92
	1	18	< 1	8	8	0.76	0.05	0.16	0.58	1.01
	2	20	< 1	8	10	1.00	0.06	0.18	0.64	1.52
	6	23	< 1	8	10	1.26	0.08	0.20	0.61	1.52
	24	27	< 1	11	17	1.74	0.10	0.20	0.55	2.08
	48	30	< 1	11	17	1.99	0.10	0.22	0.50	2.43

* Probable contamination of the solution or of the analysed sample.

Table S. 3 : DBP molar yield (mmol/mol of compounds) for all model compounds and for the pretreated water (mmol/mol of C) at all reaction times

Compound	Time	THMs	HAAs			HANs		HNMs	HKs	
		TCM	MCAA	DCAA	TCAA	DCAN	TCAN	CPK	DCP	TCP
	h									
Resorcinol	0.5	649	1.4	4.0	13.5	SC*	< LQ**	< LQ	0.10	0.01
	1	724	< LQ	2.4	16.1	SC	< LQ	< LQ	0.14	0.03
	2	772	< LQ	2.0	20.7	SC	< LQ	< LQ	0.07	0.03
	6	812	< LQ	1.6	36.0	SC	< LQ	< LQ	0.08	0.03
	24	862	< LQ	2.5	37.2	SC	< LQ	< LQ	< LQ	0.06
p-cresol	0.5	1.1	1.7	2.2	0.8	SC	< LQ	< LQ	4.53	0.07
	1	1.1	1.4	1.9	0.8	SC	< LQ	< LQ	9.98	0.14
	2	1.2	1.4	1.8	1.4	SC	< LQ	< LQ	3.97	0.23
	6	1.7	1.6	1.7	3.6	SC	< LQ	< LQ	2.89	1.31
	24	2.5	< LQ	1.5	8.5	SC	< LQ	< LQ	0.40	3.77
Acetylacetone	0.5	SC	2.2	1.2	< LQ	< LQ	< LQ	< LQ	> 39.2	> 39.2
	1	79.3	2.2	1.3	< LQ	< LQ	< LQ	< LQ	27.3	> 39.2
	2	107	3.6	2.6	< LQ	< LQ	< LQ	< LQ	27.0	> 39.2
	6	139	7.2	5.9	0.2	< LQ	< LQ	< LQ	10.8	> 39.2
	24	279	15.1	24.6	0.2	< LQ	< LQ	< LQ	1.20	> 39.2
Citric acid	0.5	0.9	< LQ	1.0	0.7	< LQ	< LQ	SC	0,12	0,07
	1	0.9	< LQ	0.6	0.9	SC	< LQ	SC	0,19	0,12
	2	1.0	< LQ	0.5	0.9	SC	< LQ	SC	0,11	0,09
	6	4.1	< LQ	0.5	2.7	SC	< LQ	SC	0,14	0,23
	24	13.7	< LQ	0.7	9.9	SC	< LQ	SC	0,05	0,13
Malonic acid	0.5	0.1	n.a.	n.a.	n.a.	SC	< LQ	SC	0.02	0.00
	1	0.2	n.a.	n.a.	n.a.	< LQ	< LQ	< LQ	0.02	0.01
	2	0.2	0.4	1.2	0.6	SC	< LQ	< LQ	< LQ	0.01
	6	0.1	1.0	5.1	1.4	SC	< LQ	< LQ	0.02	0.01
	24	0.3	n.a.	21.1	n.a.	SC	< LQ	SC	0.01	0.01
Tyrosine	0.5	7.5	< LQ	2.4	3.2	6.17	0.02	< LQ	0.05	< LQ
	1	9.2	< LQ	4.3	7.9	9.47	0.06	< LQ	0.03	< LQ
	2	15.3	< LQ	6.4	13.2	11.84	0.09	< LQ	< LQ	< LQ
	6	22.3	< LQ	12.4	24.7	13.79	0.18	0.05	0.02	< LQ
	24	26.8	< LQ	13.3	21.9	21.48	0.23	< LQ	< LQ	< LQ

Compound	Time	THMs	HAAs			HANs		HNMs	HKs	
		TCM	MCAA	DCAA	TCAA	DCAN	TCAN	CPK	DCP	TCP
	h									
Histidine 1	0.5	1.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1	1.0	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	2	< LQ	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	6	1.6	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	24	1.9	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Histidine 2	0.5	n.a.	< LQ	< LQ	< LQ	2.24	< LQ	< LQ	SC	SC
	1	n.a.	< LQ	< LQ	< LQ	3.25	< LQ	< LQ	SC	SC
	2	n.a.	< LQ	< LQ	< LQ	7.20	< LQ	< LQ	SC	SC
	6	n.a.	< LQ	< LQ	< LQ	13.29	< LQ	< LQ	SC	SC
	24	n.a.	< LQ	10.8	7.5	21.29	< LQ	< LQ	SC	SC
Methylcellulose	6	0.4	0.6	0.4	0.1	SC	< LQ	< LQ	0.03	0.01
	24	0.4	0.6	0.4	0.1	SC	< LQ	SC	0.02	0.01
Pretreated water	0.5	0.74	< LQ	0.32	0.24	0.036	0.002	0.006	0.025	0.035
(mmol/mol C)	1	0.93	< LQ	0.36	0.30	0.042	0.002	0.006	0.028	0.038
	2	1.00	< LQ	0.39	0.36	0.056	0.003	0.007	0.031	0.058
	6	1.18	< LQ	0.39	0.38	0.070	0.003	0.007	0.030	0.058
	24	1.39	< LQ	0.54	0.62	0.097	0.004	0.008	0.026	0.079
	48	1.51	< LQ	0.54	0.62	0.111	0.004	0.008	0.024	0.092

*SC: Suspected contamination. Molar yield is not calculated.

** < LQ: The DBP concentration is lower than the method quantification limit. Molar yield is not calculated.

Table S. 4 : Comparison of DBP yields at 24 h on a ΔA basis for model compounds and pretreated water

	THMs		HAAs		HANs		HNMs	HKs	
Wavelength	TCM	MCAA	DCAA	TCAA	DCAN	TCAN	CPK	DCP	TCP
(nm)	µg cm/L	µg cm/L	µg cm/L	µg cm/L	µg cm/L	µg cm/L	µg cm/L	µg cm/L	µg cm/L
Resorcinol									
238	49,930	0	159	2,952	91*	0	0	0	4.9
274	-74,907	0	-239	-4,428	-136*	0	0	0	-7.4
290	830,952	0	2,649	49,121	1,509*	0	0	0	82
p-cresol									
246	4,040	1,582	2,943	18,484	320*	0	0	673	8,114
278	-193	-75	-126	-881	-15*	0	0	-32	-387
293	-3,783	-1,482	-2,475	-17,309	-300*	0	0	-631	-7,598
Acetylacetone									
274	-18,634	-794	-1,772	-20	0	0	0	-1924**	n.a.
Citric acid									
No peak	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Malonic acid									
No peak	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Tyrosine									
225	-890	0	-475	-996	-657	-9.3	0	0	0
242	994	0	531	1,113	734	10	0	0	0
290	1,482	0	790	1,658	1,093	15	0	0	0
Histidine									
212	-64	0	n.a.	n.a.	n.a.	0	0	n.a.	n.a.
232	562	0	n.a.	n.a.	n.a.	0	0	n.a.	n.a.
Methylcellulose									
No peak	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Pretreated water									
212	-6,326	0	-2628	-3860	-404	-23	-47	-128	-484
225	-9,067	0	-3767	-5533	-580	-33	-67	-183	-693
242 (for 238/242/246)	-4,250	0	-1766	-2594	-272	-16	-31	-86	-325
276 (for 274/278)	-3,277	0	-1361	-2000	-210	-12	-24	-66	-251
290 (for 290/293)	-4,250	0	-1766	-2594	-272	-16	-31	-86	-325

* Probable contamination of the solution or of the analysed sample.

** After a reaction time of 1h.