

Formation and removal of disinfection by-products in a full scale drinking water treatment plant: supporting information

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Table S1: Information relative to the campaigns performed on the drinking water treatment plant.

Campaigns	A	B	C
Date	10th of April 2018	24th of June 2019	5th of June 2019
Analysis of treated waters	X	X	X
DOC characterization	X	X	X
DBP Formation potential	X	X	
THMs	X	X	X
HAAs			X
Bromide, iodide, iodate	X	X	X
Total iodine		X	

Table S2: Analytical figures of merit for the determination of HAAs and THMs by HS-trap GC-MS in SIM mode.

Compound	Formula	Limit of quantification (ng L ⁻¹)	Retention time (min)	m/z *
Trihalomethanes				
THM4				
Trichloromethane (chloroform)	CHCl ₃	3	1.89	47, <u>83</u> , 85
Bromodichloromethane	CHBrCl ₂	3	2.73	83, <u>85</u> , 129
Dibromochloromethane	CHBr ₂ Cl	3	4.17	127, <u>129</u> , 131
Tribromomethane (bromoform)	CHBr ₃	3	6.18	171, <u>173</u>
I-THMs				
Dichloriodomethane	CHCl ₂ I	0.4	4.75	83, <u>85</u> , 127
Bromochloriodomethane	CHBrClI	1	7.21	<u>127</u> , 129, 131
Dibromiodomethane	CHBr ₂ I	0.2	10.38	171, <u>173</u> , 300
Chlorodiiodomethane	CHClI ₂	0.5	11.42	<u>175</u> , 177, 302
Bromodiiodomethane	CHBrI ₂	0.8	14.66	219, <u>221</u> , 348
Triiodomethane (iodoform)	CHI ₃	2	17.2	140, <u>267</u> , 394
Haloacetic acids				
HAAs				
Chloroacetic acid	ClCH ₂ COOH	50	3.51	<u>108</u> , 79, 59
Bromoacetic acid	BrCH ₂ COOH	25	4.67	<u>152</u> , 93, 95
Dichloroacetic acid	Cl ₂ CHCOOH	10	4.91	<u>85</u> , 83, 59
Dibromoacetic acid	Br ₂ CHCOOH	10	9.97	171, 59, <u>173</u>
Trichloroacetic acid	Cl ₃ CHCOOH	10	6.94	<u>117</u> , 59, 119
Others				
Bromochloroacetic acid	BrClCHCOOH	10	7.16	<u>129</u> , 59, 127
Iodoacetic acid	ICH ₂ COOH	2	7.10	<u>200</u> , 169, 141
Internal standards				
1,2-dibromopropane (for THM analysis)			5.35	93, <u>121</u> , 123
2-Bromopropionic acid (for HAA analysis)			5.38	<u>87</u> , 109, 135

*Mass used for quantification underlined

Table S3: GC conditions for THMs and for HAAs

Parameter	Conditions
Column	ZB-5MS Phenomenex® column (30 m × 0.25 mm 1 µm film thickness)
Inlet conditions	Splitless, 200°C. Column flow rate: controlled by the HS column pressure*
GC temperature program	40 °C for 3 min, 20 °C/min to 60 °C hold 3 min. 5 °C/min to 100 °C, and 25 °C/min to 200 °C hold 5 min
Ion source temperature	250 °C
MS transfer line temperature	290 °C

* The GC-MS was directly connected with the TurboMatrix Headspace 40 Trap, thus bypassing the inlet split of the GC injector. By installing the fused silica tubing in this way, the GC carrier gas is supplied by the HS and the incoming HS sample is not split or diluted in any way.

Table S4 : Headspace trap parameters

Parameter	Optimum conditions
Sample volume	10 mL
thermostating	10 min, 60 °C
needle temperature	90 °C
transfer line temperature	100 °C
trap load temperature	42 °C
trap desorption temperature	220 °C
number of cycles	1
pressurization time	1 min
decay time	1.3 min
Dry purge time	4 min
desorption time	0.5 min
trap hold	13 min
column pressure	15,6 psi
vial pressure	40 psi
desorption pressure	15,6 psi

For HAAs, each sample should be analyzed 3.5 hours after preparation (allowing sufficient time to hydrolyze the excess of dimethylsulfate) but no more than 5 hours later, to limit methyl ester hydrolysis.

Table S5: HPLC conditions for iodine and bromine speciation by HPLC-ICP-MS

Injection Volume (μL)	25
Elution flow rate ($\mu\text{L min}^{-1}$)	400
Elution gradient	10 mM NaOH held for 3 min, increased to 20 mM in 1 min, held at 20 mM for 8 min, decreased back to 10 mM in 30 s, held for another 5 minutes for equilibration (total run time : 17.50 minutes).
Targets retention times	IO ₃ ⁻ : 2 min 50 s Br ⁻ : 5 min 20 s I ⁻ : 12 min 10 s

Table S6: THMFP/DOC measured in both raw and treated waters with the same THMFP test in the literature

Chlorination conditions	THMFP/DOC raw waters ($\mu\text{g THM mgC}^{-1}$)	THMFP/DOC treated waters ($\mu\text{g THM mgC}^{-1}$)	
7 days, pH 7, 25 °C 3-5 mg L ⁻¹ free chlorine residual	27.3	21.64-25.53	(Teksoy et al. 2008)
	48.2		(Tubić et al. 2013)
	59-167		(Pifer and Fairey 2014)
	95 (average)	76 (average)	(Yang et al. 2015)
	43-145		(Delpla and Rodriguez 2016)
	149	71	(Golea et al. 2017)

Table S7: Average retention by the activated carbon filtration and standard deviation observed for the 3 campaigns of measurement for THMs and percentage obtained for campaign B for HAAs. Chemical and Physical properties of THMs and HAA when available.

Species	Average removal during GAC filtration (%)	Relative standard deviation (3 campaigns) (%)	MW (g mol ⁻¹)	Solubility (g L ⁻¹)	log K _{ow}
Trihalomethanes					
CHCl ₃	15	17	119.4	8.0	1.97
CHBrCl ₂	18	10	163.8	4.0	2.0
CHBr ₂ Cl	43	9	208.3	2.7	2.16
CHBr ₃	58	15	252.7	3.1	2.4
∑ THM4	31	6			
CHCl ₂ I	77	8	210.8	0.717 (a)	2.03 (a)
CHBrClI	88	6	255.3	0.346 (a)	2.11 (a)
CHBr ₂ I	94	5	299.7	0.162 (a)	2.20 (a)
CHClI ₂	96	2	302.3	0.082 (a)	2.53 (a)
CHBrI ₂	Not present	-	346.7	0.038 (a)	2.62 (a)
CHI ₃	Not present	-	393.7	0.100	3.03 (a)
∑ I-THMs	87	6			
Haloacetic acids					
Chloroacetic acid	91	-	94.5	miscible	0.22
Bromoacetic acid	97	-	138.9		0.41
Dichloroacetic acid	96	-	128.9		0.92
Dibromoacetic acid	97	-	217.8		0.70
Trichloroacetic acid	85	-	163.4		1.33
Bromochloroacetic acid	96	-	173.4		0.61
Iodoacetic acid	>91 (b)	-	185.9		0.85
∑ HAAs	95	-			

References: Pubchem Open database

(a) Environ. Sci. Technol. 2018 52(22): 13047-13056. doi: 10.1021/acs.est.8b04625.

(b) Calculated with the limit of quantification

Table S8: Individual LC 50 chronic cytotoxicity (Lethal Concentration for 50% of a population) from Wagner and Plewa, 2017)

Individual cytotoxicity					
Trihalomethanes	LC50 (M)	LC50 ($\mu\text{g L}^{-1}$)	Haloacetic acids	LC50 (M)	LC50 ($\mu\text{g L}^{-1}$)
CHBr_3	3.96×10^{-3}	15.7	Chloroacetic acid	8.10×10^{-4}	8.57
CHBr_2Cl	5.36×10^{-3}	25.7	Bromoacetic acid	9.60×10^{-6}	0.07
CHBrCl_2	1.15×10^{-2}	70.2	Dichloroacetic acid	7.30×10^{-3}	56.6
CHCl_3	9.62×10^{-3}	80.6	Trichloroacetic acid	2.40×10^{-3}	14.7
CHI_3	4.47×10^{-5}	0.11			
CHBrI_2	1.91×10^{-3}	5.5	Dibromoacetic acid	5.90×10^{-4}	2.7
CHClI_2	2.40×10^{-3}	7.9	Iodoacetic acid	2.95×10^{-6}	0.02
CHBr_2I	1.40×10^{-3}	4.7	Bromochloroacetic acid	7.78×10^{-4}	4.5
CHCl_2I	4.13×10^{-3}	19.6			
CHBrClI	2.42×10^{-3}	9.5			

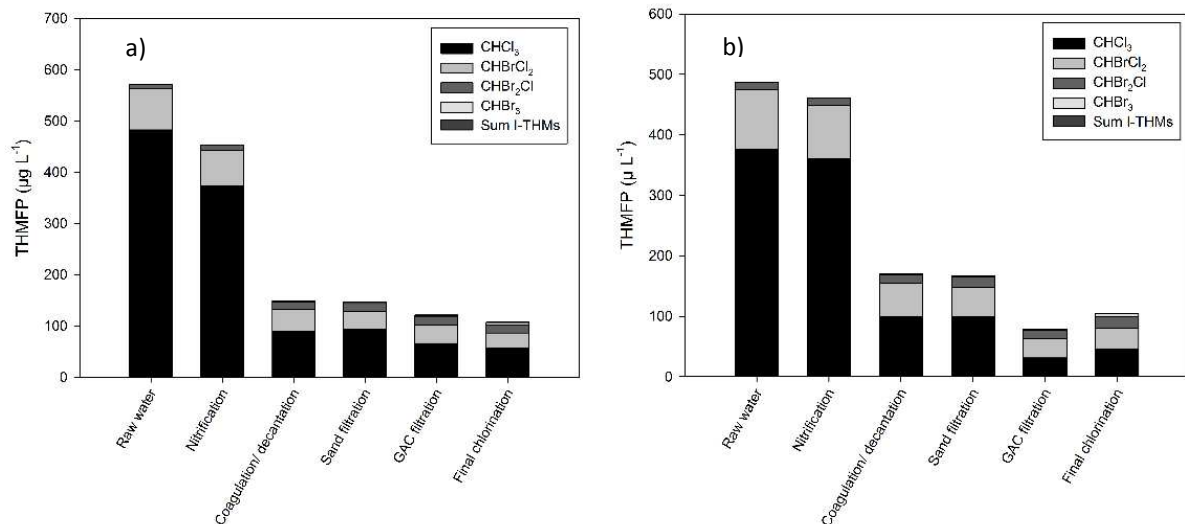


Figure S1: THMFP reduction across the treatment line. a) campaign A and b) campaign B.

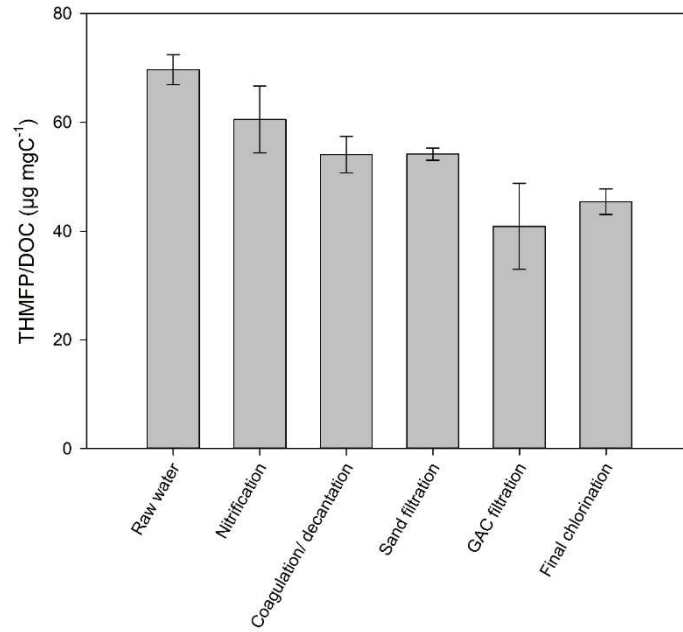


Figure S2: Average evolution of the THMF/DOC across the treatment line for campaigns A and B.

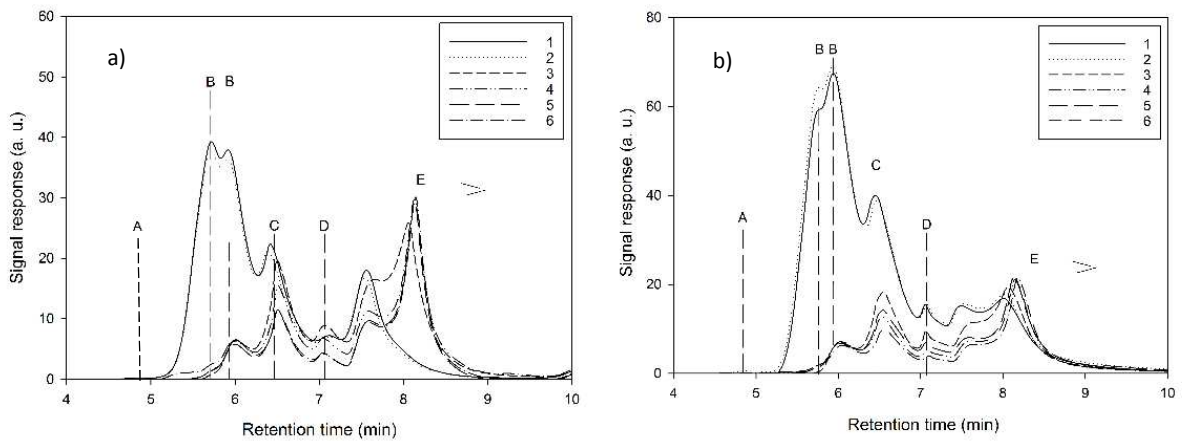


Figure S3: Chromatograms of waters samples obtained by size exclusion chromatography with UV detection at 254 nm. a) campaign C, and b) campaign B. 1: raw water, 2: after nitrification, 3: after coagulation-decantation, 4: after intermediate chlorination and sand filtration, 5: after GAC filtration, 6: after final chlorination. A: biopolymers, B: humic substances, C: building blocks, D: low molecular weight acids, E: low molecular weight neutrals.

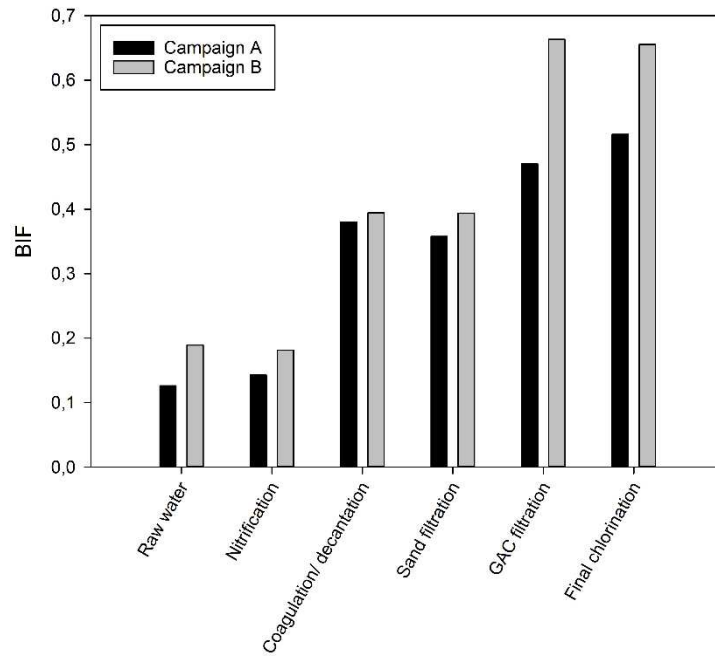


Figure S4: Bromine incorporation factor (BIF) evolution along the treatment line

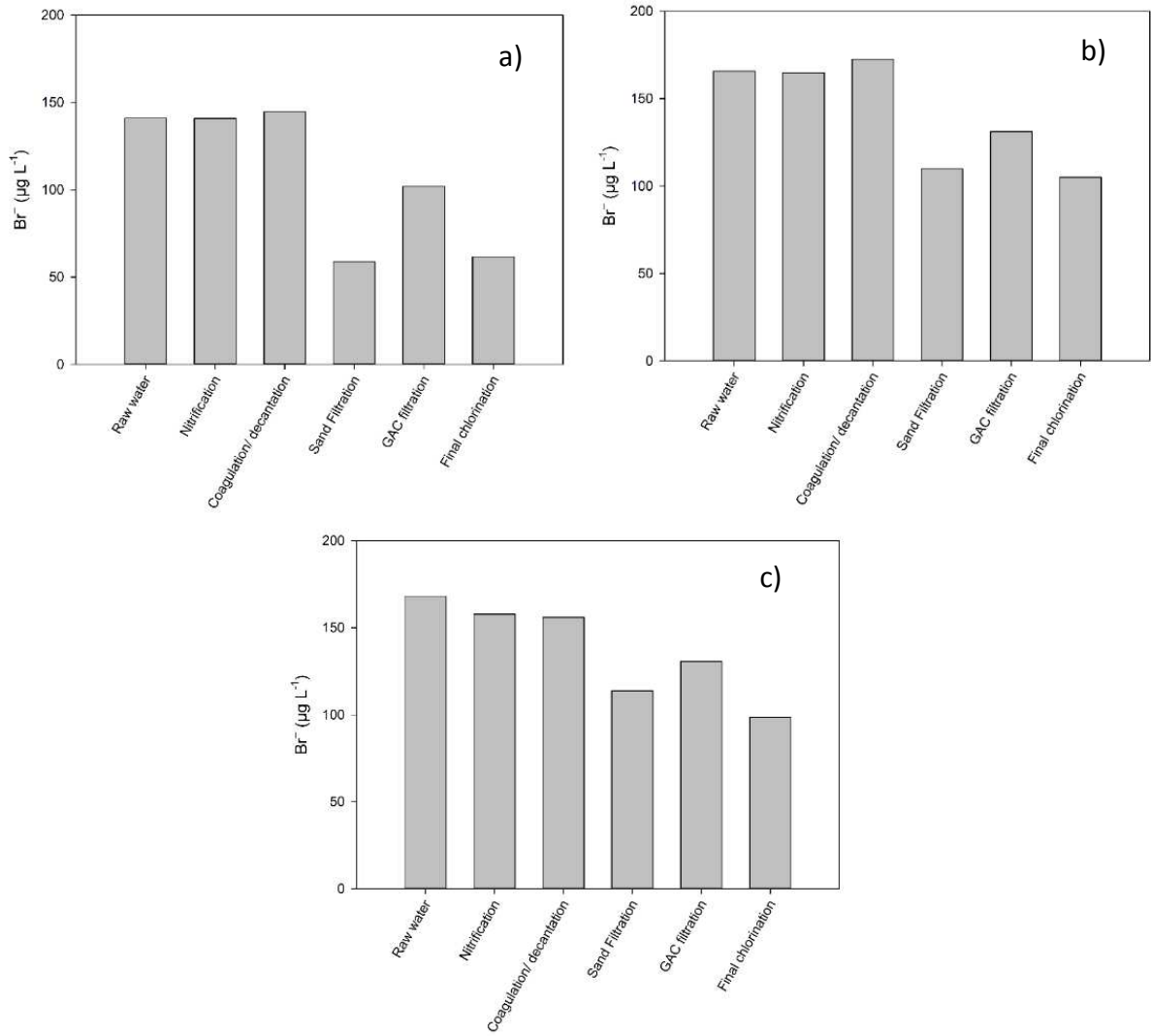


Figure S5: bromide evolution after the different treatment steps. a) campaign A, b) campaign B, c) campaign C.

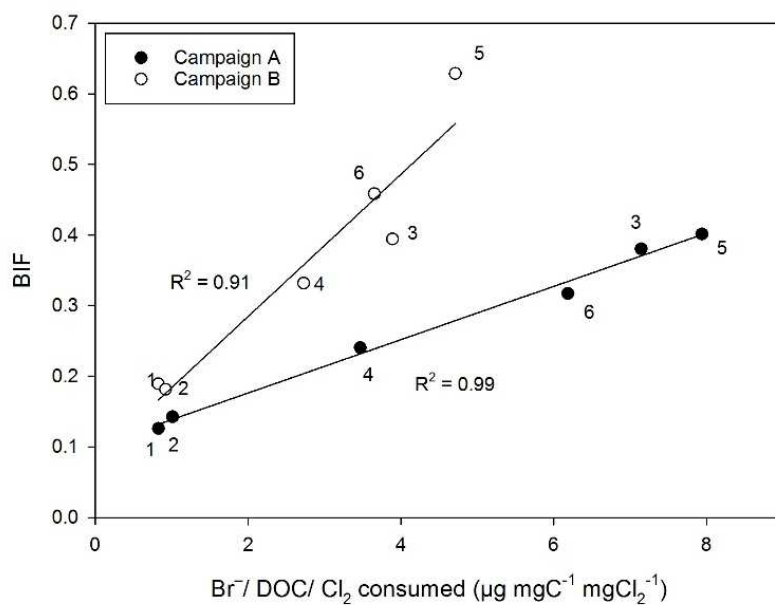


Figure S6: Evolution of the bromine incorporation factor (BIF) for ΔTHMFP as a function of the Br^-/DOC concentration ratio and chlorine consumption. 1: Raw water, 2: after nitrification, 3: after coagulation-decantation, 4: after intermediate chlorination and sand filtration, 5: after GAC filtration, 6: after final chlorination.

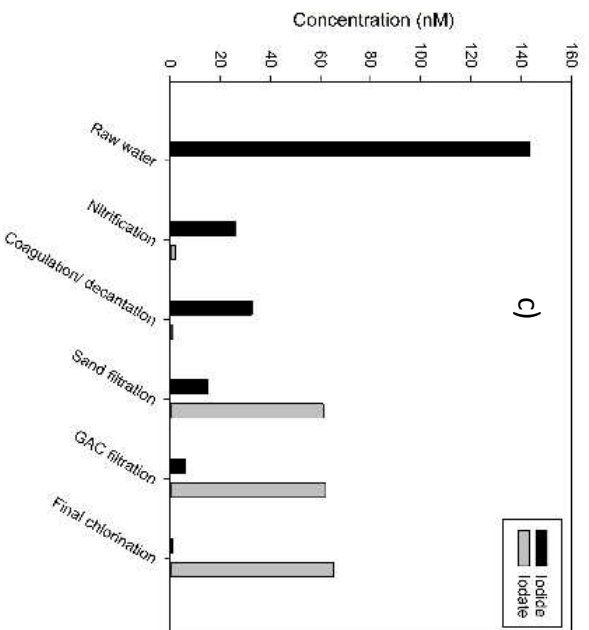
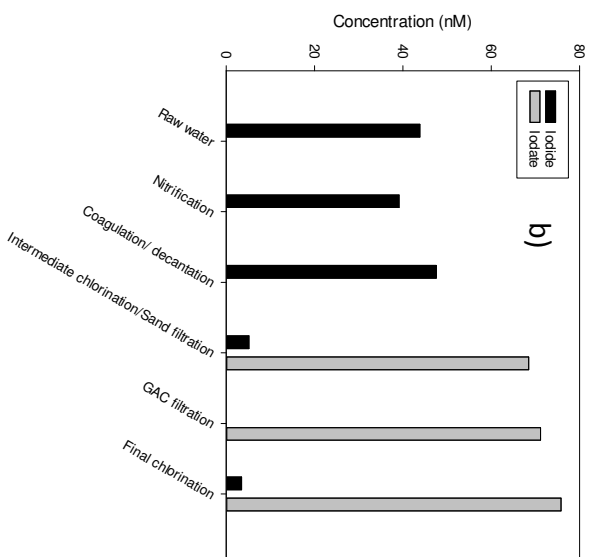
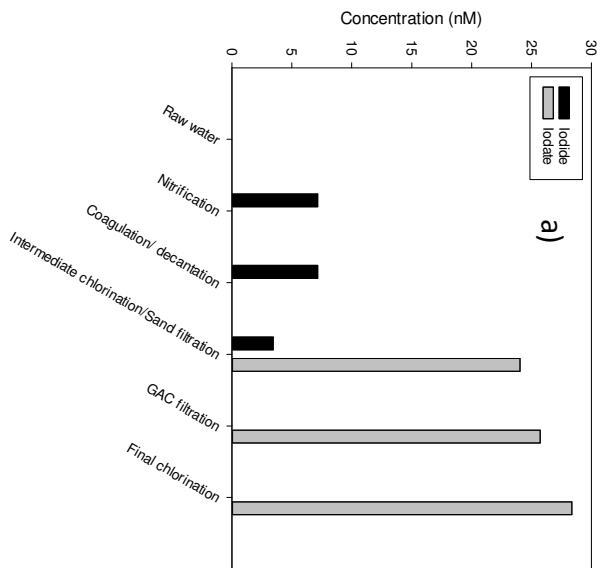


Figure S7: Iodide and iodate evolution across the treatment line. a) campaign A, b) campaign B, c) campaign C.

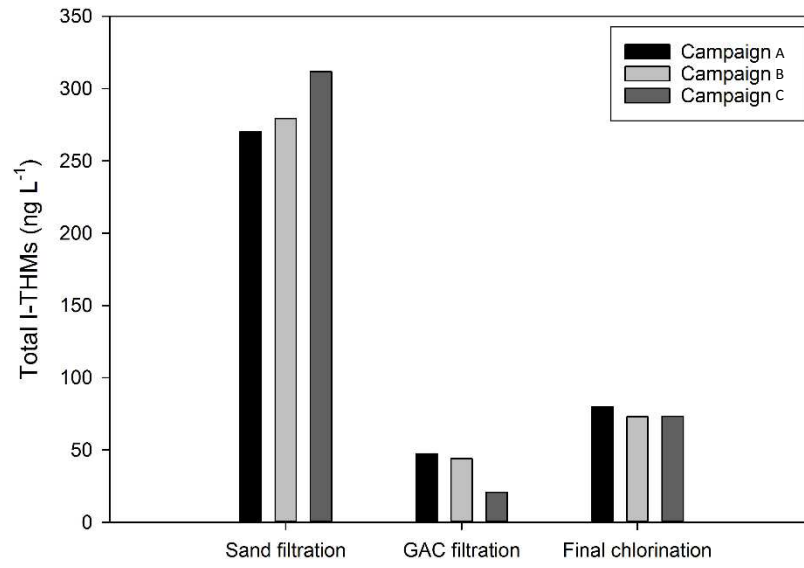


Figure S8: Total I-THMs in the last 3 treatment steps for all 3 campaigns.

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