Supplementary material

Correlating fluorescence spectral properties with DOM molecular weight and size distribution in wastewater treatment systems

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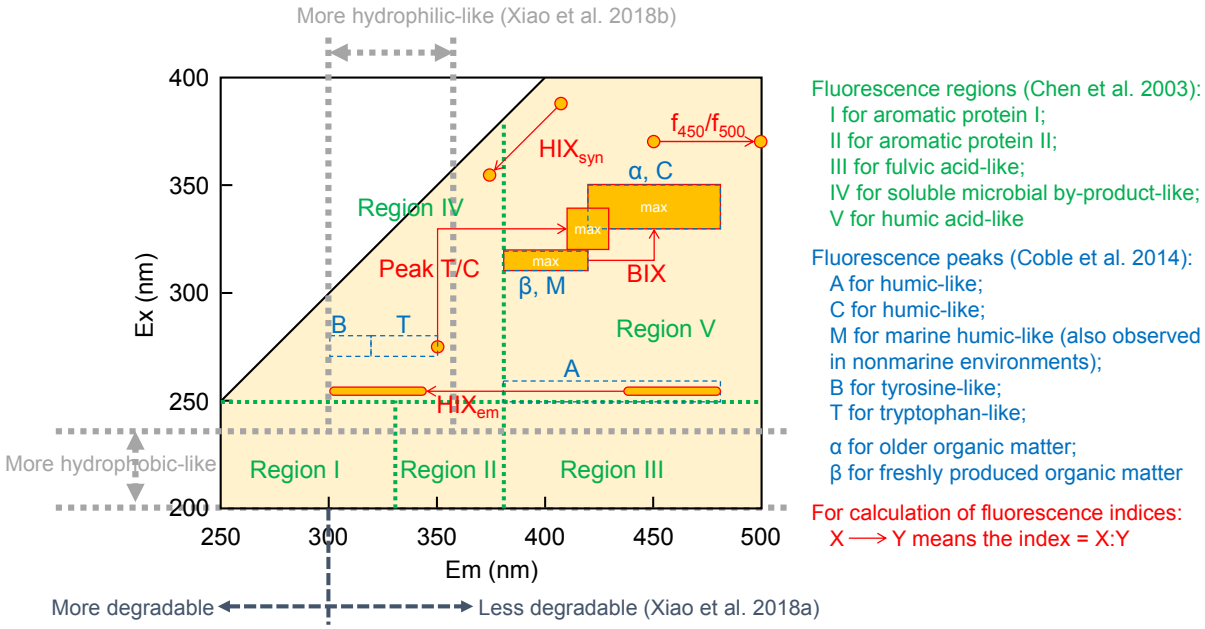

Fig. S1. Illustration of typical fluorescence regions, fluorescence peaks and fluorescence indices, according to the references of:

[1] W. Chen, P. Westerhoff, J. A. Leenheer, et al. Fluorescence excitation-emission matrix regional integration to quantify spectra for dissolved organic matter. *Environ. Sci. Technol.*, 2003, https://doi.org/10.1021/es034354c

[2] P. G. Coble, J. Lead, A. Baker, et al. *Aquatic Organic Matter Fluorescence*, Cambridge University Press, New York, 2014, https://doi.org/10.1017/cbo9781139045452

[3] K. Xiao, S. Liang, A. Xiao, et al. Fluorescence quotient of excitation-emission matrices as a potential indicator of organic matter behavior in membrane bioreactors. *Environ. Sci.: Water Res. Technol.*, 2018a, https://doi.org/10.1039/c7ew00270j

[4] K. Xiao, Y. Shen, S. Liang, et al. Characteristic regions of the fluorescence excitation-emission matrix (EEM) to identify hydrophobic/hydrophilic contents of organic matter in membrane bioreactors. *Environ. Sci. Technol.*, 2018b, https://doi.org/10.1021/acs.est.8b02684

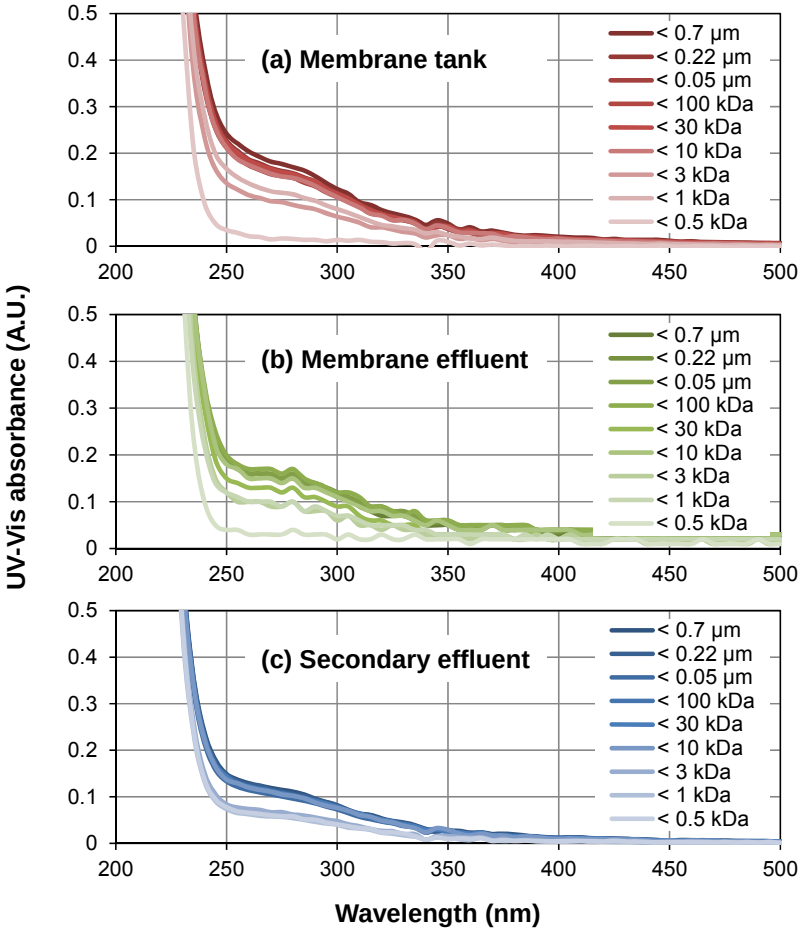

Fig. S2. UV-Vis spectra of DOM with different molecular weight/size levels from (a) membrane tank, (b) membrane effluent, and (c) oxidation ditch secondary effluent.

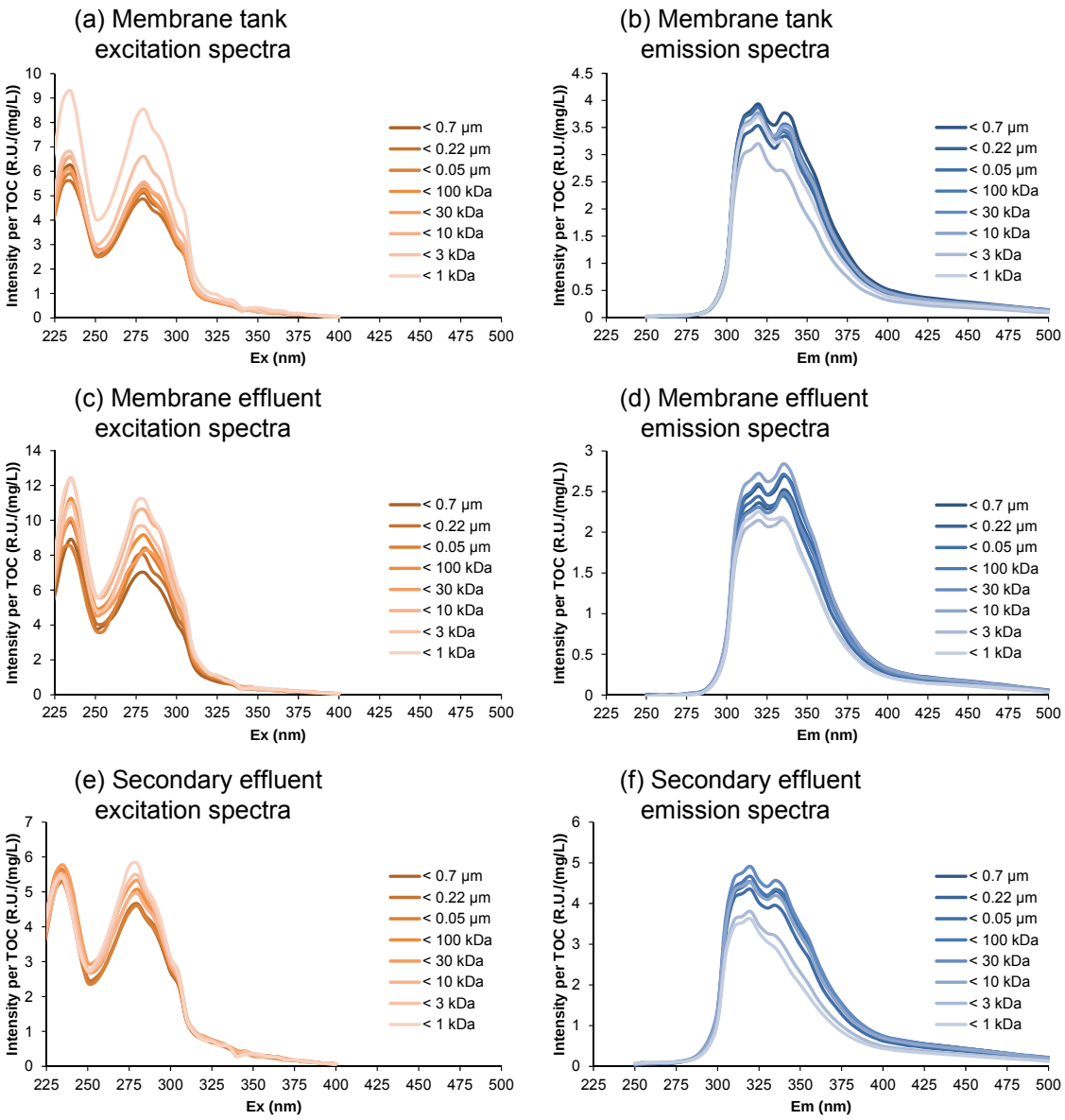

Fig. S3. Fluorescence excitation spectra and emission spectra of the DOM fractions.

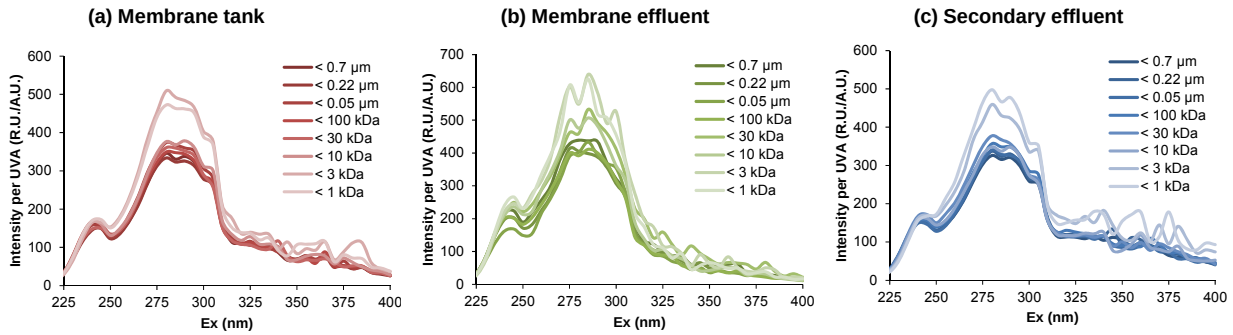

Fig. S4. Fluorescence excitation spectra in terms of fluorescence intensity (R.U.) per excitation UV absorbance (A.U.).

Table S1 Correlation analyses between conventional fluorescence indices and logarithmic molecular size cut-off in the range from 1 kDa to 0.7 μm

	HIX_{syn}	HIX_{em}	BIX	FI	Peak T/C
Spearman's ρ					
Membrane tank	0.833*	0.738*	0.048	-0.071	-0.762*
Membrane effluent	0.238	0.643(*)	-0.214	0.548	-0.548
Secondary effluent	0.690(*)	0.833*	-0.071	-0.405	-0.881**
Pearson's r					
Membrane tank	0.905**	0.659(*)	-0.218	0.023	-0.743*
Membrane effluent	0.121	0.667(*)	-0.228	0.602	-0.343
Secondary effluent	0.793*	0.710*	-0.129	-0.188	-0.818*

Note: The superscript ** denotes highly significant ($p < 0.01$); * denotes significant ($0.01 \leq p < 0.05$); (*) denotes moderately significant ($0.05 \leq p < 0.1$).

Table S2 Correlation analyses between conventional UV spectral indices and logarithmic molecular size cut-off in the range from 1 kDa to 0.7 μm

	E_2:E_3	$S_{275\text{-}295}$	$S_{350\text{-}400}$	S_R
Spearman's ρ				
Membrane tank	-0.738*	0.286	0.333	0.190
Membrane effluent	0.220	0.024	-0.515	-0.143
Secondary effluent	0.167	0.452	0.738*	0.786*
Pearson's r				
Membrane tank	-0.629(*)	0.233	0.412	0.301
Membrane effluent	0.232	0.029	-0.341	-0.287
Secondary effluent	0.085	0.439	0.699(*)	0.697(*)

Note: The superscript ** denotes highly significant ($p < 0.01$); * denotes significant ($0.01 \leq p < 0.05$); (*) denotes moderately significant ($0.05 \leq p < 0.1$).

Table S3 Fluorescence intrinsic lifetimes of the molecular-size fractions and detection of outliers.

	Membrane tank	Membrane effluent	Secondary effluent
Estimated τ_0/ρ_F (ns·g-TOC/mmol-fluorophore)[a]	0.73 ± 0.10	0.52 ± 0.07	0.74 ± 0.05
Outlier according to ordinary least-square regression (Cook's distance >1)[b]	"<0.5 kDa" (0.92)	not found	"<0.5 kDa" (0.63)
Outlier according to Theil's robust regression (residual's modified Z-score > 3.5)[b]	"<0.5 kDa" (0.92); "<1 kDa" (0.53)	"<0.5 kDa" (0.61)	"<0.5 kDa" (0.63)

Note: [a] Averaged over different molecular-size fractions with standard deviation; [b] Outlier marked in double quotes with its τ_0/ρ_F value included in parentheses.