Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Photochemical interactions between n-Ag_2S and n-TiO_2 amplify their bacterial stress response

Supporting information

Carolyn M. Wilke[1], Claire Petersen[1], Marco A. Alsina[1,2], Jean-François Gaillard[1], and Kimberly A. Gray[1*]*

[1]Department of Civil and Environmental Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL, 60208

[2] Current address: Department of Construction Engineering and Management, University of Talca, Camino Los Niches Km.1, Curicó, Región del Maule, Chile

*Corresponding authors: Kimberly A. Gray and Jean-François Gaillard

Email: k-gray@northwestern.edu, jf-gaillard@northwestern.edu

Phone: (847)-467-4252, (847)-467-1376

Fax: (847)-491-4011, (847)-491-4011

	Chemical components (mM)										
DOC [(a)] (mg L^{-1})	Ca^{2+} [(b)]	Mg^{2+} [(b)]	Na^{+} [(c)]	K^{+} [(c)]	Cl^{-} [(d)]	SO_4^{2-} [(d)]	NO_3^{-} [(d)]	ΣPO_4 [(e)]	Alk [(f)] meq L^{-1}	IS [(g)]	pH[(h)]
2.41 ±0.08	0.76 ±0.07	0.41 ±0.04	0.36 ±0.02	0.035 ±0.001	0.32 ±0.05	0.21 ±0.06	0.022 ±0.009	BDL[(i)]	1.92 ±0.04	5.4 ±0.4	8.1 ±0.1

[(a)] DOC: dissolved organic carbon, measured on high-temperature combustion total organic carbon analyzer (Dohrmann Series Apollo 9000)
[(b)] Ca^{2+}, Mg^{2+} measured by flame atomic absorbance spectroscopy (Perkin Elmer PinAAcle 500)
[(c)] Na^{+}, K^{+} measured by flame atomic emission spectroscopy (GBC 932 AA)
[(d)] Cl^{-}, SO_4^{2-}, NO_3^{-} measured by ion chromatography (Methrom Compact IC pro Unit #881)
[(e)] ΣPO_4, or soluble reactive phosphorus, measured by colorimetry after reaction with molybdate [1, 2], detection limit ~ 1 µM
[(f)] Alk: alkalinity, measured by computerized titration using a MacIntosh ME-10 unit, a Thermo™ Scientific Orion Glass Body ROSS™ Combination Electrode, and 0.1000(+/- 0.0005) N hydrochloric acid.
[(g)] IS: ionic strength on the mM unit basis.
[(h)] measured using a Thermo™ Scientific Orion Glass Body ROSS™ Semi Micro Combination Electrode and an Accumet Research AR20 pH meter using NIST buffer solutions for calibration.
[(i)] BDL: Below detection limit

Table S1: Chemical characteristics of Lake Michigan Water. All measurements were done in triplicate and reported values are average ± standard deviation. This table was published in the ESI of Wilke, et al. (Environ. Sci.: Nano, 2018, **5**, 96-102)[3]

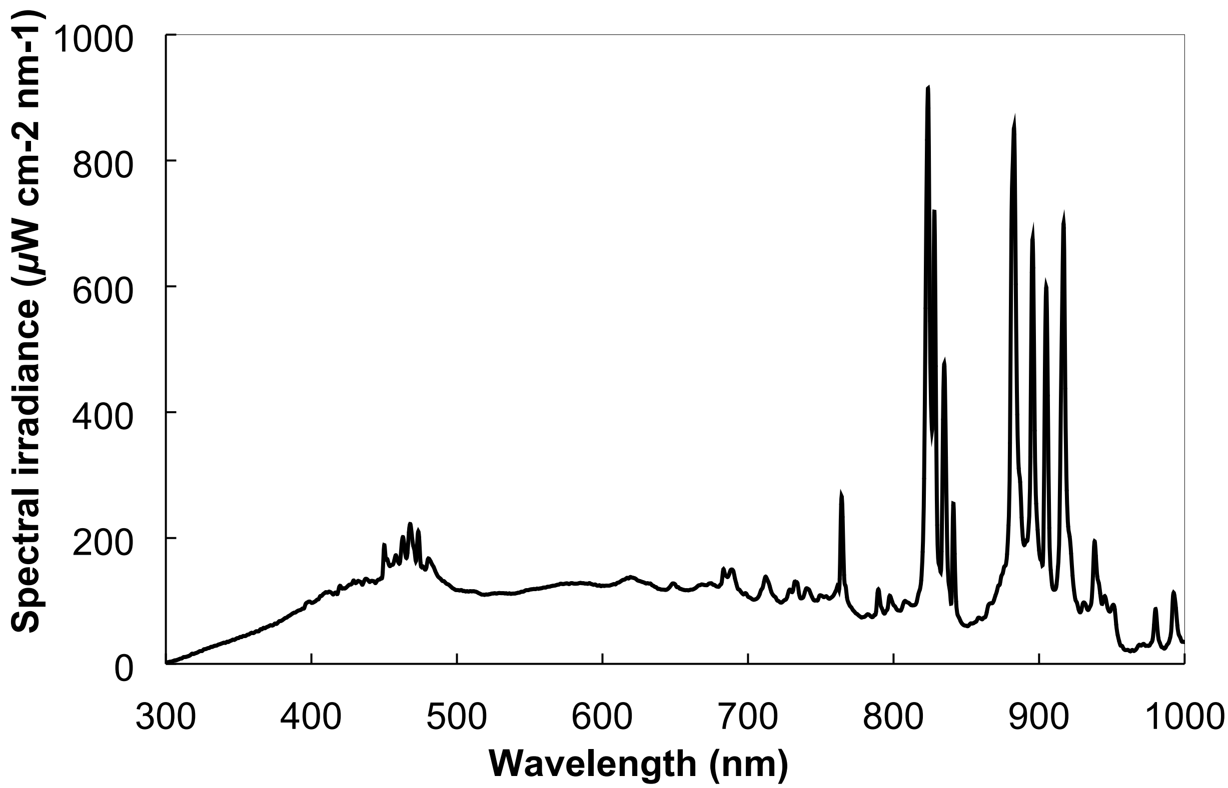

Figure S1: Spectrum of simulated solar irradiation from Xe arc lamp (900W).

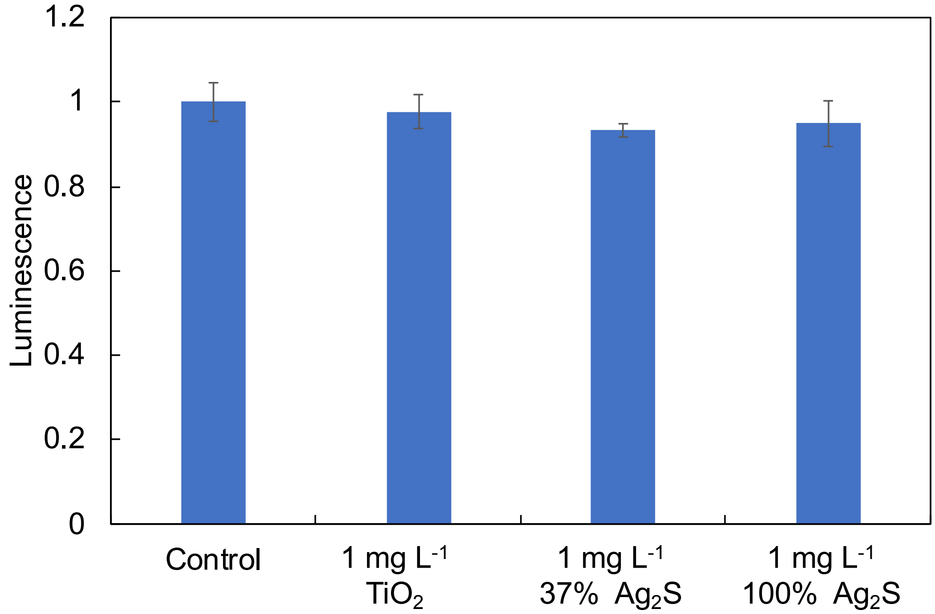

Figure S2: Potential interferences with NMs for the ATP assay. Significant differences were not observed between NMs and the control (based on $p < 0.05$).

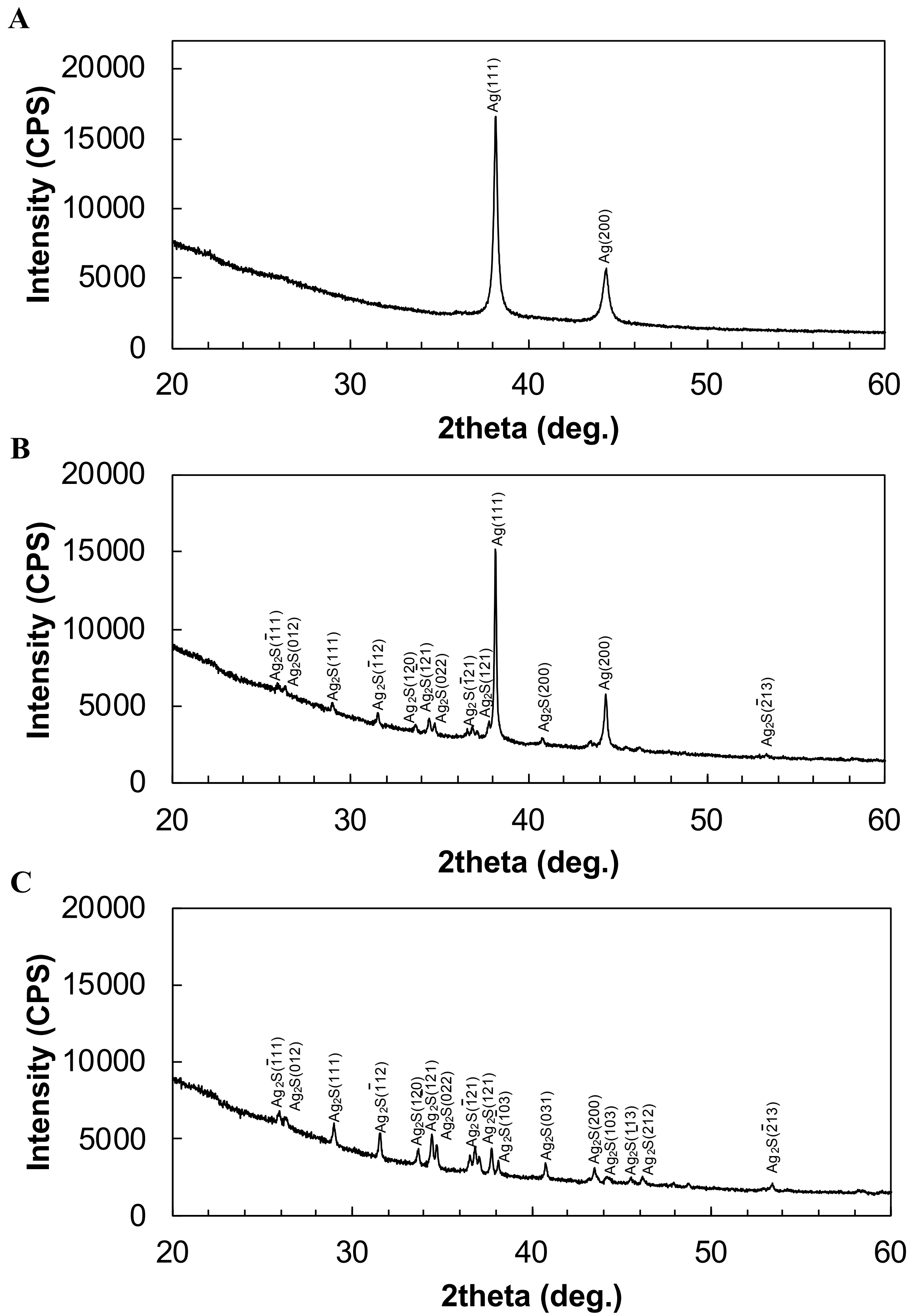

Figure S3: X-ray diffractograms for (A)n-Ag, (B) 37% Ag_2S, and (C) 100% Ag_2S.

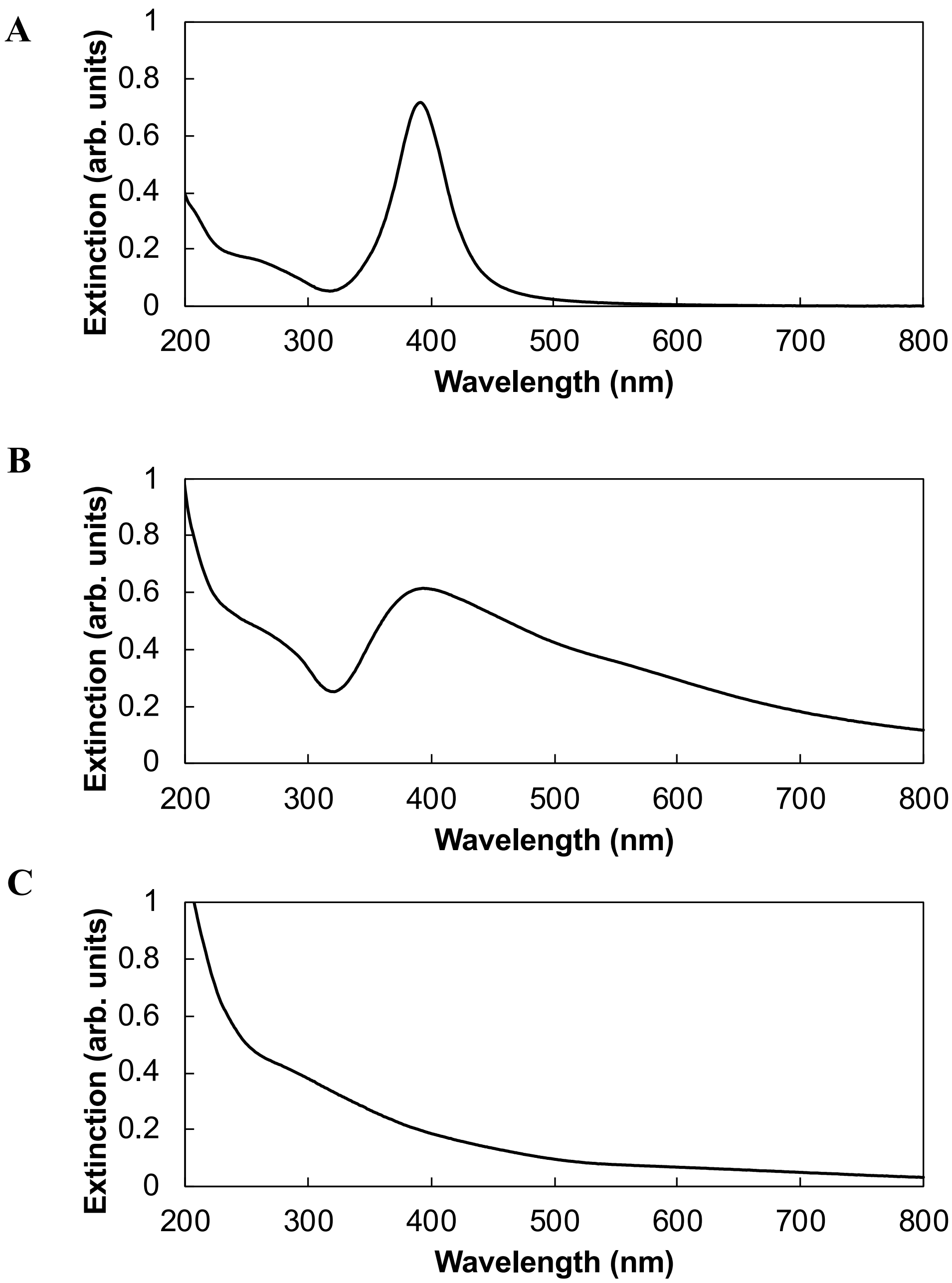

Figure S4: UV-vis extinction spectra of Ag-containing NMs. (A) n-Ag, 40 fold dilution (B) 37% Ag_2S, 10 fold dilution (C) 100% Ag_2S, 10 fold dilution.

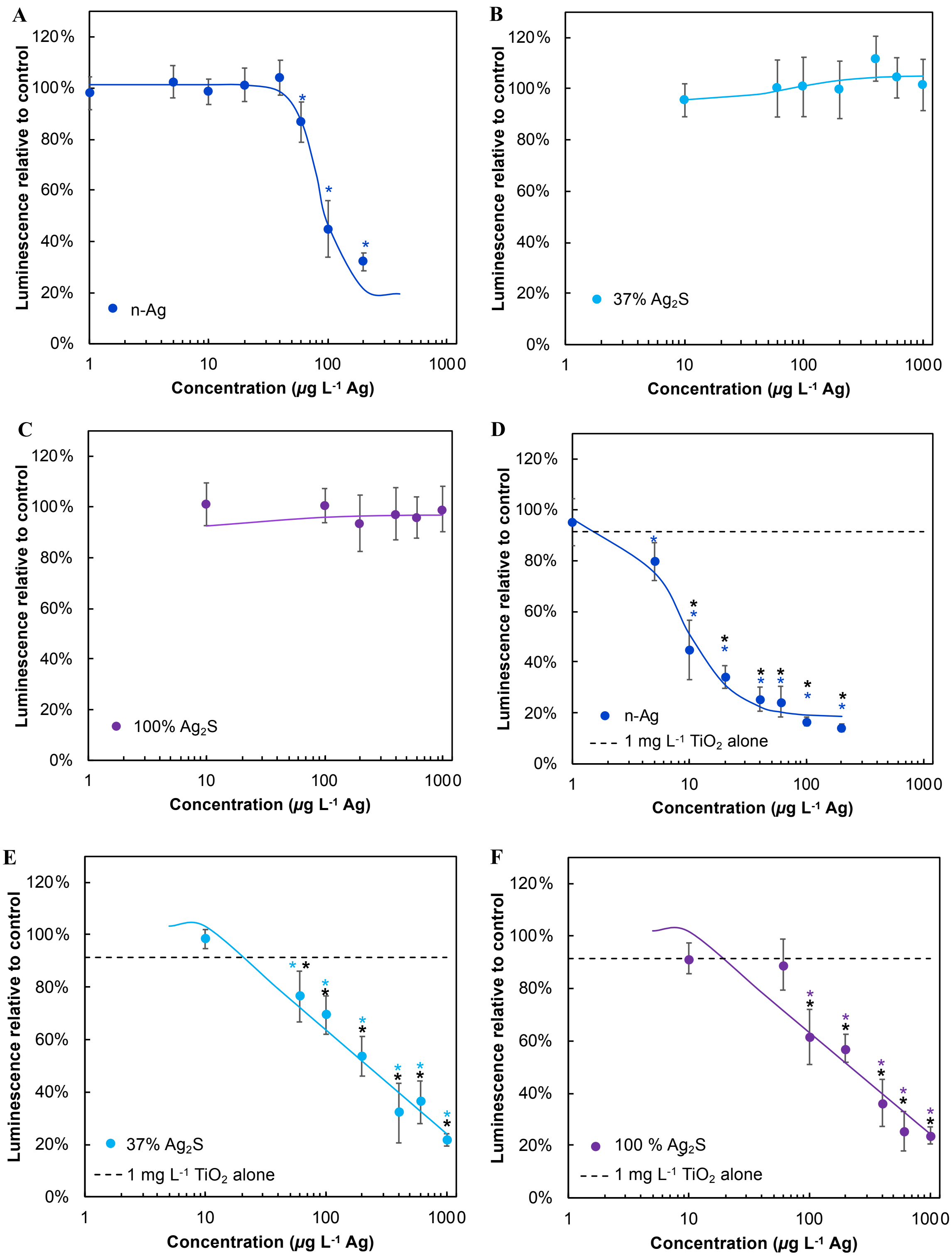

Figure S5: Effect of n-Ag, or partially or fully sulfidized n-Ag on bacterial ATP under simulated solar irradiation reproduced from main text (A-C) without n-TiO_2 or (D-F) with 1 mg/L n-TiO_2 (dashed line shows n-TiO_2 alone for comparison). Statistical significance ($p < 0.05$) for values compared with control is shown by asterisks in same color as dataset. For tests with TiO_2, statistical significance compared with n-TiO_2 alone is shown by black asterisk.

Ag-containing NM	**Concentration of stock (as Ag, ppm)**	**Morphology**	**Primary size (nm)**	**Hydrodynamic diameter (nm)**	**Zeta potential (mV)**
citrate n-Ag	219 ± 6	spherical	13 ± 7	18.3±0.1	-27.0 ± 2.6
37% Ag_2S	160 ± 2	spherical, with bridges formed between particles	38 ±18	40.8 ±0.4	-29.9± 1.2
100% Ag_2S	139 ± 2	spherical, with bridges formed between particles	17 ± 11	55.0± 1.1	-32.8± 3.2

Table S2: Characterization of Ag-containing NMs

References

1. Stainton, M.; Capel, M.; Armstrong, F., Chemical analysis of fresh water. Mar. Serv. Misc. Spec. Pub. #25. **1977**, 166 p.
2. Murphy, J.; Riley, J. P., A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* **1962,** *27*, 31-36.
3. Wilke, C. M.; Gaillard, J.-F.; Gray, K. A., The critical role of light in moderating microbial stress due to mixtures of engineered nanomaterials. *Environ. Sci. Nano.* **2018**.