Supporting Information

Experimental details

Sample Sites

Tegeler See is located in the north-west of Berlin (Germany). It covers a surface area of 4.1 km^2 with a maximum depth of 16 m and a theoretical water detention time of 137 days. Tegeler See is eutrophic and influenced by the discharge of a wastewater treatment plant (Schönerlinde). Since 2001 the lake has been diluted with water of the river Havel. Therefore the theoretical water detention time has decreased. For lake water batch tests water was taken from the south-east side of the lake near the bank side.

Wannsee is located in the south-west of Berlin, at a widening of the river Havel of about 1000 m. The surface area is 2.6 km^2, the maximum depth is 10 m. The lake is eutrophic and influenced by the outflow of Tegeler See and in the winter months by the discharge of Berlins largest wastewater treatment plant (Ruhleben). Water was taken from the east bank for surfacewater batch tests.

Both lakes are characterized by a typical algae bloom in late summer (1, 2) and at both lakes raw drinking water is extracted after bank filtration.

Analytical Methods

Adsorbable organic bromine (AOBr)

For the AOBr determination the organic material of the filtered (0.45 μm, cellulose/nitrate, prewashed with 200 mL ultra pure (u.p.) water) and acidified water sample (pH 2; 100 mL) is

enriched on activated carbon (80 mg) with simultaneous displacement of inorganic halides by using a nitrate rich washing solution. For the adsorption a three channel EFU 1000 unit (THERMO INSTRUMENTS, Germany) was used. By combustion of the activated carbon the adsorbed organic halogen compounds are reduced to bromide, chloride and iodide, which are trapped in 5 mL deionized water with a trace of sodium sulfide and then analyzed by a DIONEX DX 100 ion chromatography (see below; (3)). The AOBr detection limit (LOD) is 0.3 µg/L, the quantification limit (LOQ) is 0.5 µg/L. All data provided are mean values based on double or triplicate determinations. The precision is better than 5%.

In case of samples with a high bromide concentration the samples were treated prior enrichment with sulfite to exclude interferences. From iodine chemistry it is known that in the presence of iodide, iodine and polyiodides (I_3^-, I_5^-, I_7^-) are formed under acidic and oxidizing conditions (4). These conditions are produced during sample pretreatment for AOBr analysis and it is expected that analogues bromine species are produced with, could adsorb on the activated carbon (see Figure S3).

Intracellular bromine

A defined volume of the algae suspension was filtered through 1.2 µm filters (cellulose/nitrate membrane filters; prewashed with 200 mL u.p. water); with known filter mass for later mass determination. The filters containing the algae were washed with u.p. water and dried in a desiccator at room temperature over night. Two of these filters were used for dry mass determinations at 105°C and the rest were resuspended in water by ultrasonic treatment. The suspension was concentrated (SPEEDVAC Concentrator A160, SAVANT, THERMO LIFESCIENCE) at 55°C to a small volume and then transferred into a small crucible, dried under nitrogen at 60°C and weighed for the determination of the samples initial volume (calculated through the dry mass concentration). The dry algae were finally used for the

intracellular algae bromide determination by direct combustion as for the AOBr measurement but without preceding enrichment on activated carbon.

Intracellular organic bond bromine

A defined volume of the algae suspension was filtered through a 1.0 µm filter (regenerated cellulose (RC) filter from WHATMAN®, prewashed with 200 mL u.p. water); with known filter mass for later mass determination. The filter containing the algae was washed with u.p. water and dried in a desiccator at room temperature overnight. For the dry weight determination the filter was weight and the dry weight was calculated by subtracting the filter mass. For the determination of the intracellular organic bromine content the biomass on the filter was hydrolyzed under alkaline conditions (30 mL, 5% potassium hydroxide in methanol/u.p. water 8:2 for 2 h at 85°C). The hydrolyzed biomass was filtered through another 1.0 µm RC-filter (washed with 200 mL dichloromethane) and the flask was rinsed with methanol and dichloromethane under ultra sonic treatment. The RC-filter was washed with dichloromethane. The pH of the water phase was adjusted to pH 5 with conc. hydrochloric acid and 0.4 g of sodium chloride was added. The organic phase was separated and the water phase was repeatedly washed with dichloromethane (5 x 10 mL). The dichloromethane extract was concentrated to a small volume (20 mL) with a SpeedVac Concentrator A160 (SAVANT, THERMO LIFESCIENCE, 20°C), dried with sodium sulfate (approx. 15 g, stirred for 2 h), sodium sulfate was filtered off again and the dichloromethane extract was further concentrated (<1.5 mL). The small volume of dichloromethane extract was transferred into a small crucible and dried with nitrogen gas. The concentrated intracellular organic bromine was measured by direct combustion of the dried extract, followed by ion chromatography of the trapped combustion gas and quantification of the detected bromide, just as for the AOBr measurement but without preceding the enrichment.

Ion Chromatography

Ion chromatography was carried out with an IONPAC AS9-SC column with AG9-SC pre-column on a DIONEX DX 100 workstation. As eluent $NaHCO_3/Na_2CO_3/H_3BO_3$ (0.75 mM $NaHCO_3$ + 2.2 mM Na_2CO_3 + 3.75 mM boric acid) with a flow of 2 mL/min was used. Bromide was detected by UV absorption at 210 nm.

Chlorophyll-*a*

Chlorophyll-*a* analysis was carried out according to German standard method DIN 38412-16. Briefly, samples were filtered and the filter cakes were extracted with boiling ethanol. Membrane filters (0.45 µm) were used instead of glass fiber filters as in the standard method. The extinction (665 nm) of the extracts were measured and the chlorophyll-*a* concentrations were calculated with the formula given in DIN 38412-16. Because of the light sensitivity of chlorophyll-*a* all steps of the procedure were done in a shaded laboratory.

Hydrogen Peroxide

The N,N-diethyl-p-phenylenediamine (DPD) method for the determination of low hydrogen peroxide concentrations was used (5) with small modifications: 2.7 mL of sample was pipetted into a 4 mL disposable cuvette and mixed with 300 µL buffer (0.5 M Na_2HPO_4, 0.5 M NaH_2PO_4 of pH 6.0). DPD (N,N-diethyl-p-phenylenediamine 5 µL, Merck) and POD (peroxidase product of horseradish, 5 µL, Merck) were added in rapid succession, mixed, and the absorption at 551 nm was measured after 45 s reaction time using a PERKIN-ELMER Photometer Lambda 12 (Überlingen, Germany).

Enzyme activity

The activity of the bromoperoxidase was measured by monitoring the bromination of 0.1 mM monochlorodimedone (MCD) at 290 nm (absorption coefficient 19.9 mM^{-1} cm^{-1}) in 50 mM MES buffer (pH 6.4; 2-morpholinoethanesulfonic acid, Sigma-Aldrich) containing 20 mM (1.6 g/L) KBr and 10 mM (340 mg/L) hydrogen peroxide (6).

Nutrient solution for algae growth (*Microcystis aeruginosa*)

A nutrient solution in u.p. water with following concentrations was prepared (7) and autoclaved (120 °C, 1.1 bar) for approx. 20 minutes.

1: $NaNO_3$	467 mg/L
2: $Ca(NO_3)_2 \times 4\ H_2O$	9 mg/L
3: $K_2HPO_4 \times 3H_2O$	31 mg/L
4: $MgSO_4 \times 7H_2O$	25 mg/L
5: Na_2CO_3	21 mg/L
6: Fe-EDTA complex*	10 mL/L
7: micronutrient solution	0.08 mL/L

Made up of:

H_3BO_3	3.10 g/L
$MnSO_4 \times H_2O$	1.69 g/L
$Na_2WO_4 \times 2H_2O$	33 mg/L
$(NH_4)_6Mo_7O_{24} \times 4\ H_2O$	88 mg/L
KBr	119 mg/L
KI	83 mg/L
$ZnSO_4 \times 7H_2O$	287 mg/L
$Cd(NO_3)_2 \times 4H_2O$	154 mg/L
$Co(NO_3)_2 \times 6H_2O$	146 mg/L
$CuSO_4$	80 mg/L
$NiSO_4 \times 6H_2O$	13,2 mg/L
$(NH_4)_2SO_4$	6,6 mg/L
$Cr(NO_3)_3 \times 9H_2O$	41 mg/L
$Al_2(SO_4)_3K_2SO_4 \times 12H_2O$	32,6 mg/L

*) Preparation of the Fe-EDTA complex: 5 mL of 0.1 M $FeCl_2 \times 4H_2O$ (22.8 g/L) in 0.1 N HCl and 5 mL of a 0.1 M solution of the disodium-salt of EDTA (3.7 g/L Titriplex III, Merck) in u.p. water were combined and filled up to 500 mL with u.p. water.

References

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(5) Bader, H.; Sturzenegger, V.; Hoigne, J. Photometric-Method for the Determination of Low Concentrations of Hydrogen-Peroxide by the Peroxidase Catalyzed Oxidation of N,N-Diethyl-P-Phenylenediamine (Dpd). *Water Res.* **1988**, *22*, 1109-1115.

(6) Rush, C.; Willetts, A.; Davies, G.; Dauter, Z.; Watson, H.; Littlechild, J. Purification, Crystallization and Preliminary-X-Ray Analysis of the Vanadium-Dependent Haloperoxidase from *Corallina-Officinalis*. *FEBS Let.* **1995**, *359*, 244-246.

(7) Zehnder, A.; Gorham, P. R. Factors Influencing the Growth of *Microcystis aeruginosa* Kutz Emend Elenkin. *Can. J. Microbiol.* **1960**, *6*, 645.

Figures

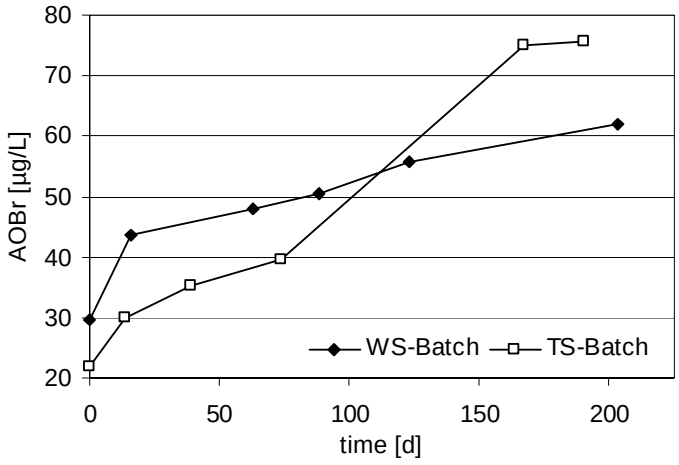

Figure S1: Change of AOBr concentration in two lake water batch tests, irradiated with artificial sunlight at room temperature (ca. 20°C). WS-Batch = Wannsee water, TS-Batch = Tegeler See water.

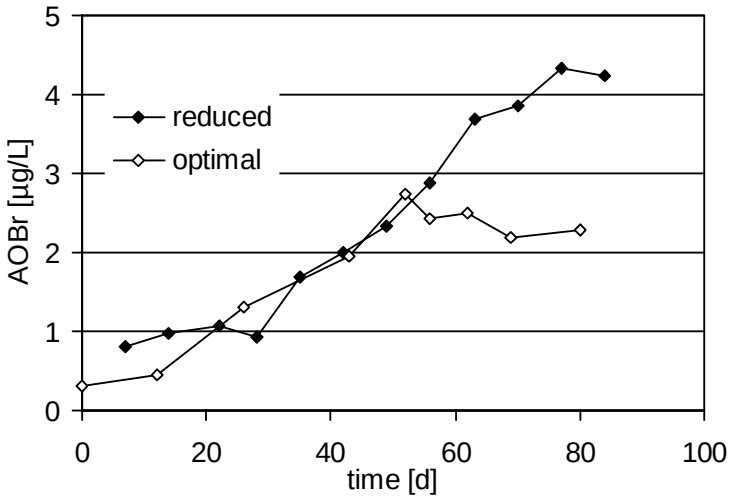

Figure S2: Cyanobacteria (*Mycrocystis aeruginosa*) batch test at 25°C, with aeration and irradiation with artificial sunlight: AOBr concentration for reduced and optimal nutrient supply.

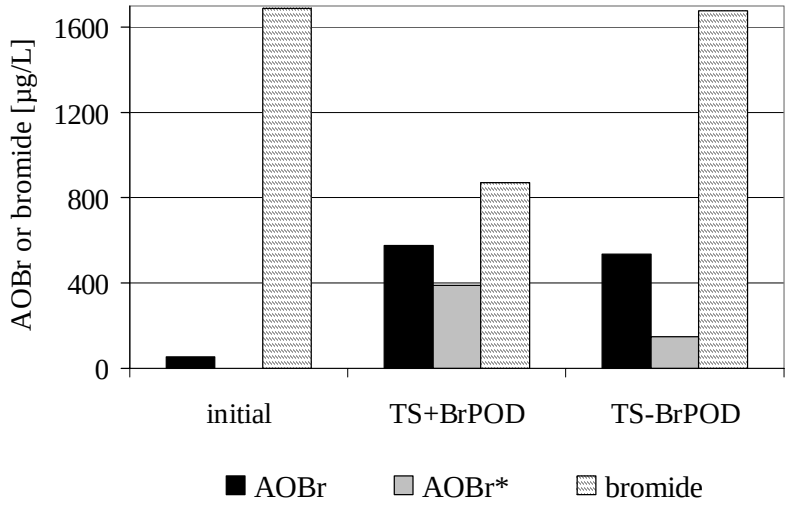

Figure S3: Autoclaved Tegeler See water (TS) tenfold concentrated and spiked with H_2O_2 (10 mM) and bromide (100 µg/L) in 0.5 mM MES buffer (pH 6.4) at 25°C: Initial = TS, TS+BrPOD = TS with adition of BrPOD (20 units/mL), TS-BrPOD = TS without addition of BrPOD. Samples were taken after 49 d, n.d. = not determined. AOBr* = sulfite addition prior enrichment.