Supporting Information

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SI Materials and Methods

Chemicals and Standards. All-*trans*-retinoic acid (atRA), 13-*cis*-RA (13cRA), 9-*cis*-RA (9cRA), and acitretin were purchased from Sigma. All-*trans*-4-oxo-RA (at-4-oxo-RA), 13-*cis*-4-oxo-RA (13c-4-oxo-RA), 9-*cis*-4-oxo-RA (9c-4-oxo-RA), and atRA-d_5 were obtained from Toronto Research Chemicals.

Methanol, acetonitrile, ethyl acetate, hexane, methylene chloride, and chloroform were HPLC grade and purchased from Fisher Chemical. HPLC-grade formic acid and acetic acid were provided by Dima Technology. Ultrapure water was obtained by a Milli-Q Synthesis water purification system (Millipore) under a conductivity of 18.2 $\Omega \cdot cm^{-1}$.

Study Area. Taihu Lake (119°54′–120°36′ N, 30°56′–31°33′ E), the third-largest freshwater lake in China (surface area: 2,338 km^2, maximum depth: 2.6 m, average depth: 1.9 m, mean water residence time: 264 d), is located in the highly developed and densely populated Yangtze Delta and serves as an important source of water for irrigation, aquaculture, and industrial waters as well as the primary drinking water source for 30 million residents in the lake basin and Shanghai. Since the 1980s, eutrophication as a consequence of human activities has become an increasingly serious issue in Taihu Lake, and annual lake-wide cyanobacteria blooms have occurred during warm seasons every year.

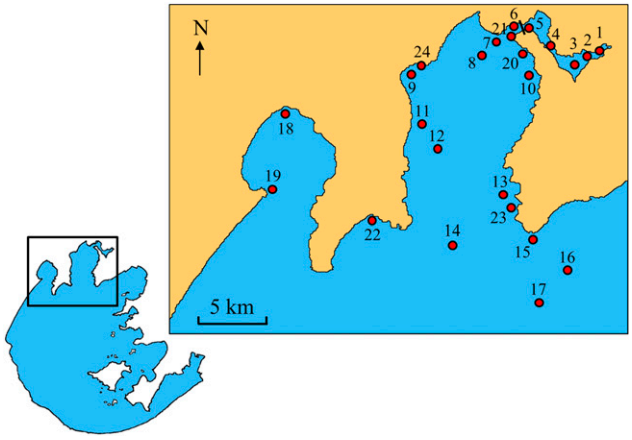

Fig. S1. Sampling sites in Taihu Lake, China.

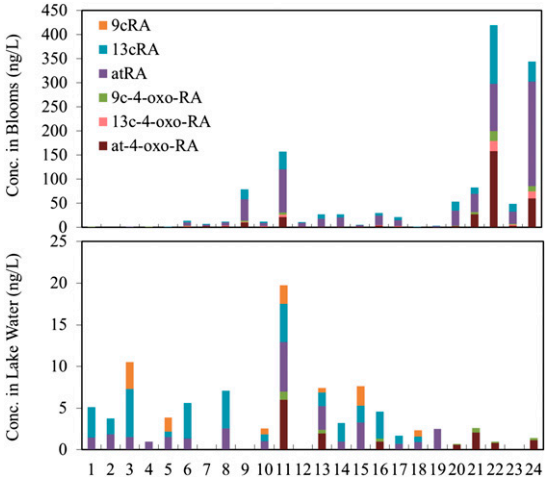

Fig. S2. Concentrations of RAs and 4-oxo-RAs in bloom samples (*Upper*) and water samples (*Lower*) collected from Taihu Lake, China. The *x* axis represents the sampling sites.

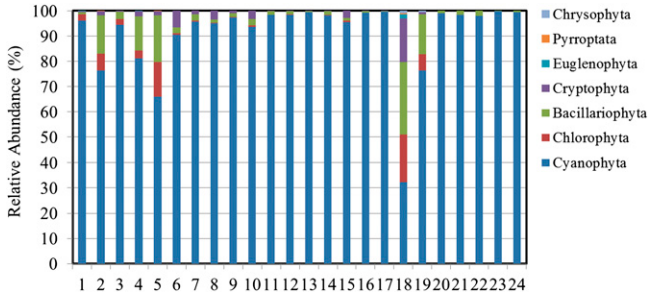

Fig. S3. Composition of phytoplankton biomass in Taihu Lake, China.

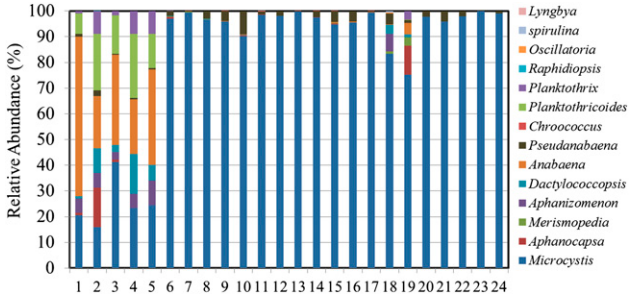

Fig. S4. Composition of cyanobacteria biomass in Taihu Lake, China.

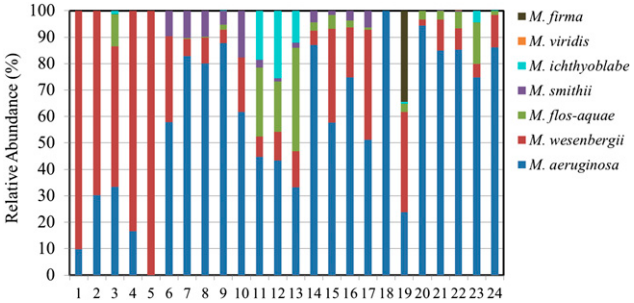

Fig. S5. Composition of *Microcystis* colonies in Taihu Lake, China.

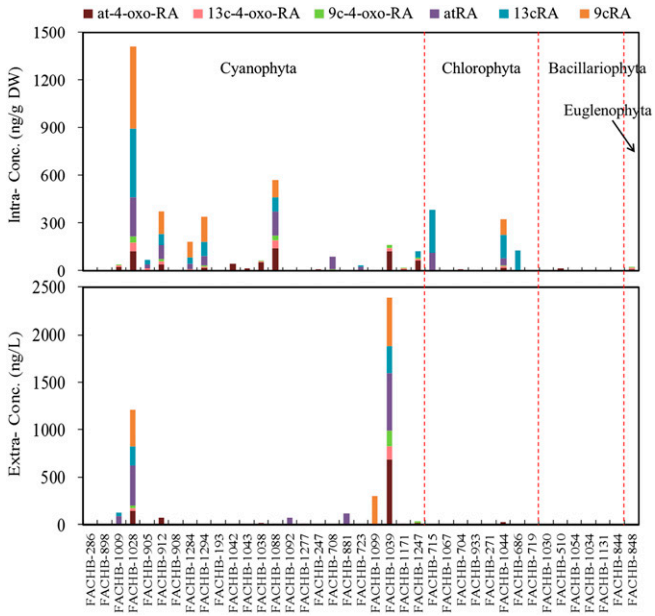

Fig. S6. Intracellular (*Upper*) and extracellular (*Lower*) concentrations of RAs and 4-oxo-RAs in cultured cyanobacteria and algae.

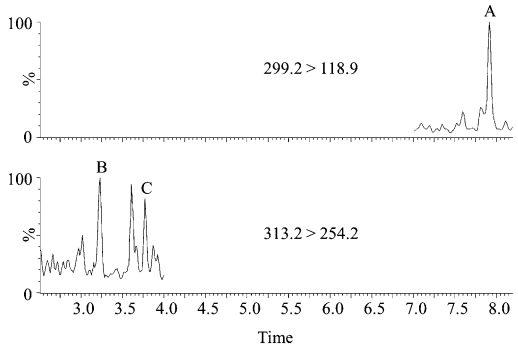

Fig. S7. Ultraperformance liquid chromatography/tandem mass spectrometry (UPLC-MS/MS) chromatograms of intracellular retinoids in axenic strains of *Microcystis aeruginosa* (PCC 7806). *A*, atRA [1.9 ng/g dry weight (DW)]; *B*, at-4-oxo-RA (0.3 ng/g DW); and *C*, 9c-4-oxo-RA (0.3 ng/g DW).

Table S1. Information on the cyanobacteria and algae surveyed

Phylum	Genus	Species	Strain no.	Origin
Cyanophyta	*Merismopedia*	*Merismopedia* sp.	FACHB-286	United States
	Synechocystis	*Synechocystis* sp.	FACHB-898	France
	Microcystis	*Microcystis* sp.	FACHB-1009	Dianchi Lake (China)
		M. flos-aquae	FACHB-1028	Taihu Lake (China)
		M. aeruginosa	FACHB-905	Dianchi Lake
		M. aeruginosa	FACHB-912	Taihu Lake
		M. wesenbergii	FACHB-908	Dianchi Lake
		M. viridis	FACHB-1284	Dianchi Lake
		M. ichthyoblabe	FACHB-1294	Taihu Lake
	Chroococcus	*Chroococcus* sp.	FACHB-193	Donghu Lake (China)
	Nostoc	*Nostoc* sp.	FACHB-1042	China
		Nostoc sp.	FACHB-1043	China
	Anabaena	*A. cylindrica*	FACHB-1038	Dianchi Lake
		Anabaena sp.	FACHB-1088	Nanhu Lake (China)
		A. flos-aquae	FACHB-1092	Dianchi Lake
	Pseudanabaena	*Pseudanabaena* sp.	FACHB-1277	Xionghe Reservoir (China)
	Oscillatoria	*O. tenuis*	FACHB-247	United States
		O. planctonica	FACHB-708	Donghu Lake
		O. raciborskii	FACHB-881	Dianchi Lake
	Phormidium	*P. mucicola*	FACHB-723	China
		Phormidium sp.	FACHB-1099	Dianchi Lake
	Aphanizomenon	*Ap. flos-aquae*	FACHB-1039	Dianchi Lake
		Ap. flos-aquae	FACHB-1171	Taihu Lake
		Ap. issatschenkoi	FACHB-1247	Donghu Lake
Chlorophyta	*Chlamydomonas*	*Chlamydomonas* sp.	FACHB-715	Donghu Lake
	Chlorella	*Chlorella* sp.	FACHB-1067	China
	Pediastrum	*Pediastrum* sp.	FACHB-704	China
	Scenedesmus	*Scenedesmus* sp.	FACHB-933	Dianchi Lake
	Selenastrum	*S. capricornutum*	FACHB-271	United States
	Ankistrodesmus	*Ankistrodesmus* sp.	FACHB-1044	Dianchi Lake
	Oedogonium	*Oedogonium* sp.	FACHB-686	China
	Staurastrum	*Staurastrum* sp.	FACHB-719	Taiping Lake (China)
Bacillariophyta	*Cyclotella*	*C. hebeiana*	FACHB-1030	Guanqiao Pond (China)
	Nitzschia	*Nitzschia* sp.	FACHB-510	China
	Navicula	*Navicula* sp.	FACHB-1054	Taihu Lake
	Melosira	*M. varians*	FACHB-1034	Guangzhou (China)
	Synedra	*Synedra* sp.	FACHB-1131	Donghu Lake
	Cymbella	*Cymbella* sp.	FACHB-844	China
Euglenophyta	*Euglena*	*E. gracilis*	FACHB-848	Japan

FACHB, Freshwater Algae Culture Collection of the Institute of Hydrobiology, Chinese Academy of Sciences.

Table S2. Recoveries and limits of quantification (LOQs) for RAs and 4-oxo-RAs in different matrices

Parameter	Sample	Matrix	at-4-oxo-RA	13c-4-oxo-RA	9c-4-oxo-RA	atRA	13cRA	9cRA
Percentage recovery	Natural blooms	Intracellular	62 ± 5	53 ± 9	54 ± 3	61 ± 4	66 ± 7	54 ± 8
		Extracellular	55 ± 6	60 ± 7	59 ± 7	51 ± 9	56 ± 8	59 ± 4
	Cultured algae	Intracellular	70 ± 1	61 ± 7	69 ± 3	56 ± 9	61 ± 7	50 ± 3
		Extracellular	76 ± 3	68 ± 2	59 ± 8	58 ± 5	52 ± 6	63 ± 2
LOQ	Natural blooms	Intracellular	0.1	0.1	0.1	0.3	0.3	0.8
		Extracellular	0.06	0.1	0.1	0.2	0.2	0.4
	Cultured algae	Intracellular	0.5	1.0	1.0	3.0	4.0	6.0
		Extracellular	3.0	4.0	10	8.0	8.0	20

LOQ concentrations are expressed in ng/L except for intracellular cultured algae, which is expressed in ng/g DW.