

Do persistent organic pollutants stimulate cyanobacterial blooms?

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Abstract

The use of persistent organic pollutants (POPs), such as herbicides, pesticides, pharmaceutical and personal care products (PCPPs), and polycyclic aromatic hydrocarbons (PAHs), has more than doubled since 1950. POPs find their way into aquatic ecosystems through agricultural and industrial runoff, wastewater treatment effluent discharge, and atmospheric deposition. Cyanobacterial harmful algal blooms (CyanoHABs), which can produce toxins potent enough to cause human death, have been increasing in intensity, frequency, and spatial scale throughout the same time period as accelerated POP usage. Here, we provide a meta-analysis and suggest that POP stressors may be significantly aggravating nutrient-driven CyanoHABs by suppressing the growth of competing phytoplankton, and/or by indirectly or directly stimulating cyanobacterial growth.

Key words: cyanobacteria harmful algal blooms (CyanoHABs), herbicide, persistent organic pollutants (POPs), pesticide, pharmaceutical and personal care products (PCPPs)

Introduction

Cyanobacterial harmful algal blooms (CyanoHABs) are a major cause of water quality degradation in rivers, lakes, and estuaries worldwide. CyanoHABs can disrupt food webs and cause significant changes in dissolved oxygen and pH (Paerl 2014). In addition, because many cyanobacterial taxa produce a diverse suite of potent and deadly cyanotoxins (Codd et al. 1999) as well as other cellular metabolites that create taste and odor problems in drinking water supplies (Graham et al. 2010), CyanoHABs can pose significant human and animal health hazards; impair fisheries, drinking water, and irrigation supplies; and result in substantial economic damage (Sharma et al. 2013).

Extensive research has demonstrated that the abundance and toxicity of cyanobacteria is strongly influenced by eutrophication, which is caused by the over-supply of 2 key nutrients, phosphorus (P) and nitrogen (N) to surface waters (Paerl and Otten 2013). N:P stoichiometry also has significant effects on cyanobacterial dominance; in particular, cyanobacterial growth tends to be favored when the N:P ratio is low (Smith 1983, Orihel et al. 2012, Harris et al. 2014). Other environmen-

tal factors also can potentially influence nuisance cyanobacterial growth, including changes in food web structure (Elser 1999, Ekvall et al. 2014) and global warming (Paerl and Huisman 2008, Kosten et al. 2012).

A recent study showed that cyanobacterial blooms have significantly increased globally relative to other phytoplankton taxa since the 1950s, with relatively sharper increases in cyanobacteria biomass noted in low-nutrient alpine systems compared with nutrient-rich lowland systems (Taranu et al. 2015). The cause for this increase in relative cyanobacterial abundance is not yet fully understood, but we hypothesize here that anthropogenic inputs of organic stressors may be a substantial (up to 10% of total biomass; Everaert et al. 2015) under-recognized direct and/or indirect contributor to cyanobacterial proliferation in the world's surface waters.

Persistent organic pollutants

For more than 6 decades, a diverse mix of persistent organic pollutants (POPs) that include more than 400 different herbicides, pesticides, fungicides (Fig. 1) as well as a diverse suite of unaccounted for polycyclic aromatic hydrocarbons (PAHs), pharmaceutical and personal care

products (PPCPs), and polychlorinated biphenyls (PCBs) have been released at accelerating rates into receiving waters via wastewater effluents, agricultural and industrial runoff, and atmospheric deposition (Boyd et al. 2003, Lohmann et al. 2009, Dougherty et al. 2010). Some of these compounds degrade in only a few days or weeks whereas others persist for decades, years, or centuries before being degraded by abiotic and/or biotic processes (US EPA 2014a). POPs can persist in the environment in gas, liquid, or solid phases and can be transported thousands of miles from their sources by atmospheric wind currents and bodily fluid excretion from birds and other migrating animals (Evenset et al. 2007). As a result, POPs frequently co-occur and are environmentally detectable throughout the year in a large proportion of the world's surface waters (Stone et al. 2014), including in relatively pristine Arctic regions (Halsall 2004, Rig  t et al. 2010).

Many POPs are known to have potent biological effects, including the taxon-specific modification of population growth in phytoplankton communities. We performed a synthetic review of the ecotoxicology literature to test the hypothesis that the presence of environmentally relevant concentrations of POPs in aquatic ecosystems directly or indirectly favors the growth cyanobacteria relative to other phytoplankton taxa (i.e., the percent composition of cyanobacterial abundance and/or biovolume was higher than eukaryotic taxa in the presence of POPs). Relevant publications from 1980 to 2015 were found by searching Google Scholar and Web of Science for key words, including "cyanobacteria" and the general

chemical classes of POPs, as well as the common and formula names of specific compounds (Supplementary Table S1). References within relevant publications found via Google Scholar or Web of Science were then searched for additional relevant data. We included only experiments that directly evaluated the quantitative response of cyanobacteria and eukaryotic phytoplankton cell counts or biovolume to the presence of POPs. To prevent discrepancies between different publications, the relative taxon-specific responses (or the reported effective concentration values, EC_{50}) for a given suite of cyanobacteria and phytoplankton were only evaluated within a given study. We identified 107 studies that examined 227 individual compounds; 133 of these compounds were distinctly different POPs and included 39 herbicides, 26 pesticides, 11 fungicides, 39 PPCPs, 17 PAHs, and 1 PCB.

Frequency histograms were created to quantify the results of our analysis (Fig. 2, Supplementary Table S2). Each histogram depicts 3 categories that refer to the response of cyanobacteria relative to eukaryotic algae when both were exposed to a specific class of POP. A given POP response was classified as positive if its presence allowed cyanobacteria to become inhibited less by EC_{50} or become dominant by greater abundance in mixed cultures/field experiments relative to all other phytoplankton taxa tested for that specific compound; negative if the quantitative response of cyanobacteria was depressed relative to all the other tested species; and neutral if the response of cyanobacteria was intermediate relative to the other taxa being tested. Within each of the 107 studies examined, an evaluation of response frequency (f) was performed for each individual experiment performed. Thus, if a given study performed multiple experiments that examined the responses of cyanobacteria to multiple POPs, each individual experiment contributed a value of $f = 1$ to one (and only one to avoid double counting) of the 3 different response categories. In cases where multiple studies investigated a single unique POP (e.g., glyphosate), the response observed in each individual study of this POP contributed a value of $f = 1$.

Effects of herbicides on cyanobacterial growth

The 133 different compounds evaluated in our analysis of the POP literature can be broadly grouped into 2 categories: those that have a known mode of action against photosynthetic organisms (i.e., herbicides) and those that do not. Herbicides affect photosynthetic organisms through modes of action that include, but are not limited to: amino acid pathway inhibitors (e.g., glyphosate), photosynthesis inhibitors (e.g., atrazine), growth regulators (e.g., 2-4D), cell membrane disruptors

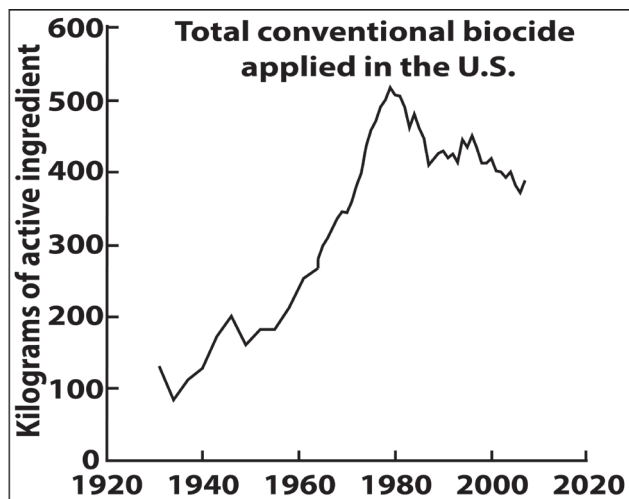


Fig. 1. Total kilograms of active ingredient biocides (herbicides, pesticides, and fungicides) applied to the U.S. landscape from 1931–2007. Note: the data shown represent time trends derived from a merger of multiple published datasets (Donaldson et al. 2002, Aspelin 2003, Grube et al. 2011); these databases overlapped between 1964–2007.

(e.g., paraquat and diquat), and shoot and/or root inhibitors (e.g., alachlor).

Since the introduction of genetically modified glyphosate-resistant crops in 1996, glyphosate (i.e., Roundup) usage in the United States has increased from <15 to >50 million kg yr⁻¹ and has become the most widely used herbicide in the world (Perez et al. 2011). Herbicides containing glyphosate generally inhibit cyanobacterial growth less than the growth of other phytoplankton because cyanobacteria are not sensitive to glyphosate (Forlani et al. 2008, Perez et al. 2011). In the glyphosate–cyanobacteria studies we surveyed, all showed either a positive or neutral effect on cyanobacteria relative to other phytoplankton taxa (Fig. 2). Furthermore, likely with the help of heterotrophic bacteria (Saxton et al. 2011), some species of cyanobacteria can even use the P bound within the glyphosate molecule to support their growth (Bai et al. 2014), allowing these cyanobacteria to have a potential competitive advantage over eukaryotic algal species that cannot use this source of organic P.

Atrazine and metribuzin herbicides in environmentally relevant concentrations also have been found to favor cyanobacterial growth at the cost of other algal species (Lüring and Roessink 2006, Pannard et al.

2009). For example, Pannard et al. (2009) demonstrated a high sensitivity of multispecies phytoplankton assemblages to long-term herbicide exposure and observed significant effects of atrazine on algal community structure even at herbicide concentrations as low as 0.1 µg L⁻¹. They concluded that cyanobacteria were more tolerant to atrazine than other phytoplankton taxa, particularly under conditions of elevated nutrient supply. Other studies have found that cyanobacteria and/or diatoms are more tolerant to atrazine than chlorophyte phytoplankton taxa (DeLorenzo et al. 1999, Magnusson et al. 2012), suggesting that in cyanobacteria–chlorophyte co-dominated systems, the presence of herbicides like atrazine may have the potential to shift the system to cyanobacterial dominance. Additionally, although most relevant studies in our meta-analysis held nutrient concentrations and temperature constant when comparing cyanobacteria and eukaryotic phytoplankton taxa in the presence of POPs, Bérard et al. (1999) reported that inhibition of cyanobacterial growth by herbicides is reduced at elevated water temperatures, and we thus have concerns that global warming could potentially influence or modify interactions between eutrophication and POP stressors.

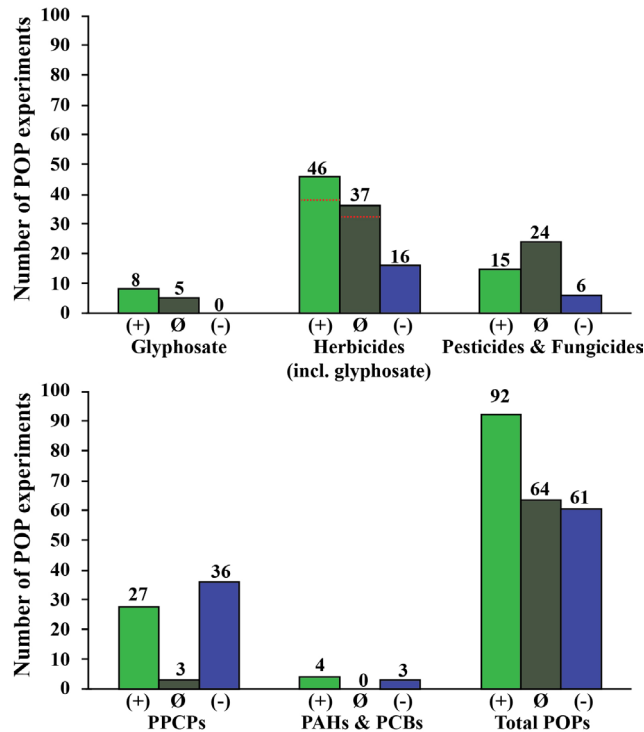


Fig. 2. Histograms showing the response of cyanobacteria relative to eukaryotic phytoplankton taxa in the presence persistent organic pollutants (POPs). The positive (green), neutral (brown), and negative (blue) categories refer to POPs that favored cyanobacteria, showed taxa more and less sensitive than cyanobacteria, and did not favor cyanobacteria relative to eukaryotic taxa, respectively, in multi-phytoplankton species experiments. The herbicide POP category includes glyphosate experiments; dashed red bars indicate the frequency of herbicide POP experiments without glyphosate. Numbers above histogram bars represent the number of POP experiments in each category. PPCPs = pharmaceutical and personal care products (including antibiotics); PAHs and PCBs = polycyclic aromatic hydrocarbons and polychlorinated biphenyls.

Metribuzin and other herbicides have also been shown to favor cyanobacteria relative to other phytoplankton taxa (Fig. 2; Fairchild et al. 1998, Gustavson et al. 2003, Caquet et al. 2005). For example, in a lab-based competition experiment between a cyanobacteria and a chlorophyte alga, cyanobacteria became dominant in the presence of $100 \mu\text{g L}^{-1}$ of metribuzin; in sharp contrast, the chlorophyte alga completely dominated cyanobacteria in mixed cultures that did not contain metribuzin (Lürling and Roessink 2006). This led Lürling and Roessink (2006) to conclude that herbicide-contaminated surface waters potentially may be “on the way to cyanobacterial blooms.”

Effects of non-herbicide POPs on cyanobacteria

Pesticides and fungicides

POPs that do not have a specific mode of action against photosynthetic organisms include pesticides, fungicides, PPCPs, PAHs, and PCBs. Although pesticides (i.e., insecticides) and fungicides have been found to favor cyanobacteria over other phytoplankton taxa in laboratory studies (Wendt-Rasch et al. 2003, Ma et al. 2008), other mesocosm and laboratory studies have shown mixed results (Fig. 2; DeLorenzo et al. 1999, Le Boulanger et al. 2011). In natural systems, heterotrophic bacteria, zooplankton, and fungi community composition may play a role in the success of cyanobacteria in the presence of POPs compared to other phytoplankton. For example, Saxton et al. (2011) showed that the heterotrophic bacterial community was instrumental in allowing cyanobacteria to use P bound within P-rich POPs, which can serve as a novel potential organic P source that cannot be utilized by other phytoplankton. This microbial interaction may explain why some studies have

shown that organophosphorus pesticides stimulate cyanobacterial growth at environmentally relevant pesticide concentrations (Sun et al. 2013). Thus, POP-specific changes associated within the heterotrophic bacteria, zooplankton, and/or fungi communities could be one reason why mixed results were seen in the pesticide and fungicide frequency histogram (Fig. 2). Given that the current literature shows an ambiguous response of cyanobacteria to organic pesticides and fungicides, more research is needed to determine whether cyanobacteria are directly and/or indirectly favored over other phytoplankton taxa in the presence of pesticide and fungicide POPs.

Pharmaceutical and personal care products (PPCPs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs)

PPCPs include pharmaceutical compounds like prescription antibiotics and anticancer drugs as well as personal care products like over-the-counter antimicrobials, fragrances, and UV blockers (Bernot and Justice 2014). Our analysis suggests that some of these POPs may favor the growth of cyanobacteria (Stoichev et al. 2011, Liu et al. 2012, Nietch et al. 2013, Brezovšek et al. 2014), whereas others, especially antibiotics, seem to favor other phytoplankton taxa over cyanobacteria (Fig. 2; Ebert et al. 2011, Qian et al. 2012, González-Pleiter et al. 2013). An intriguing trend is evident in the literature, however; recent studies have shown that cyanobacteria may be favored in the presence of antibiotics (Fig. 3), contrasting with what past studies have observed. Some recent studies have even found that the presence of antibiotics caused increased production of the cyanobacterial hepatotoxin microcystin (Liu et al. 2015). This observation could reflect differences among the antibiotics used in these experiments or differences in

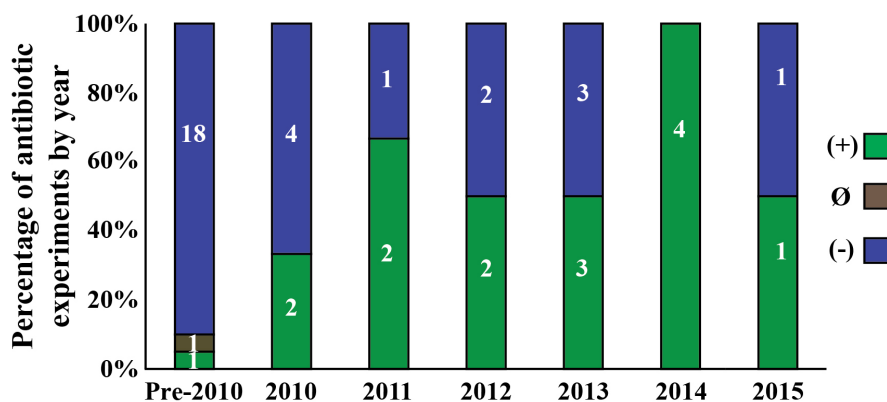


Fig. 3. Percentage of experiments that compared cyanobacteria and eukaryotic phytoplankton in the presence of antibiotics by year, with positive (green), neutral (brown), and negative (blue) categories referring to antibiotics that favored cyanobacteria, showed taxa more and less sensitive than cyanobacteria, and did not favor cyanobacteria relative to eukaryotic taxa, respectively, in multi-phytoplankton species experiments. Numbers inside histogram bars represent the number of experiments comparing cyanobacteria and eukaryotic taxa in the presence of antibiotics each year.

experimental methodology but could also potentially suggest that cyanobacteria may be becoming more tolerant or possibly antibiotic-resistant over ecological and evolutionary time (i.e., pollution-induced community tolerance; Blanck and Wängberg 1988).

Similarly, a diverse set of other kinds of PPCPs has consistently been observed to favor cyanobacteria relative to eukaryotic phytoplankton taxa. For example, Drury et al. (2013) observed a 6-fold increase in the relative abundance of cyanobacteria in the presence of common antimicrobial agents like triclosan. Proia et al. (2013) have recently attributed substantial increases in cyanobacteria and decreases of other algal taxa in a Mediterranean river to the presence of ibuprofen and paracetamol in the water column. Moreover, because PPCP concentrations are in general 3–5 times higher in winter months compared to summer months due to the temperature dependence of their biological degradation (Vieno et al. 2005), winter-time relative cyanobacterial abundance may perhaps increase in surface waters experiencing high PPCP loading, especially in areas where nutrient and light conditions are already favorable for cyanobacterial growth.

PAHs and PCBs also have been observed to stimulate relative cyanobacterial abundance and/or biovolume in experimental laboratory communities. Of the 7 studies we identified in our survey of the literature examining these compounds, 4 indicated that the presence of PAHs and PCBs had a positive effect on cyanobacteria relative to eukaryotic taxa (Fig. 2). Although the manufacturing of PCBs was banned in the United States in 1979 (US EPA 2014b), substantial concentrations of legacy PCBs still remain in marine and freshwater sediments, and their presence could favor the growth and ecological success of cyanobacterial akinetes (resting cells) and/or viable sedimented cyanobacterial cells (Latour et al. 2004) over other phytoplankton taxa. Given that relatively few studies have investigated the relative effects of cyanobacterial abundance in the presence of PAHs and PCBs, much more research is needed to fully understand the relative response of cyanobacteria to PAHs and PCBs as well as other organic stressors such as polybrominated diphenyl ethers (PBDEs).

Conclusions and future research directions

Is our aquatic future thus likely to be increasingly blue-green (Elliott 2012)? Unfortunately, the extensive empirical evidence provided here suggests that the answer to this question may be yes. We conclude that cyanobacteria are in general favored over other phytoplankton taxa when taxon-sensitive POPs are present because cyanobacteria (1) have a higher tolerance (less sensitive) to POPs than other taxa, and (2) in some cases have the ability to use nutrients bound within POPs to stimulate their growth, possibly in conjunction with POP biodegradation by heterotrophic bacteria. Systems

with relatively high POP loading will therefore potentially have higher relative cyanobacterial abundance relative to systems experiencing relatively low POP loading, especially in areas where environmental conditions are already favorable for cyanobacteria bloom development.

Nonetheless, as shown by our survey of the current literature, some studies found that other phytoplankton taxa are favored over cyanobacteria in the presence of POPs (Fig. 2), indicating that ambiguity exists concerning whether cyanobacteria are consistently favored relative to other phytoplankton taxa in the complex chemical mixtures existing in the world's surface waters. Given that most studies in the literature are laboratory based (Supplementary Table S2), we are hopeful that future field-based experimental and empirical studies will quantitatively elucidate whether relative cyanobacterial abundance is actually higher in natural systems exposed to relatively high POP loading. At a minimum, we hope that future studies can answer important new questions raised by our study, including: (1) Do current POP mixtures released into surface waters promote more frequent CyanoHABs? (2) Will inputs of future POPs (e.g., Enlist Duo herbicide) favor cyanobacteria over other phytoplankton taxa? (3) Do sedimented POPs cause cyanobacteria resting cells to outcompete the resting cells of eukaryotic phytoplankton? (4) Have winter-time CyanoHABs increased because of increased POP loading? Or are increases forthcoming? (5) Are cyanobacteria becoming more tolerant or even possibly resistant to common POPs like antibiotics and herbicides over ecological and evolutionary time? (6) Can POPs cause changes within the consumer community, which in turn may lead to consumer-driven nutrient recycling stoichiometry that indirectly promotes CyanoHABs?

We conclude that selective pressures from multiple POPs, in combination with the previously recognized factors of nutrient enrichment and warmer temperatures, will favor increases in the frequency, intensity, and geographical extent of nuisance cyanobacterial blooms in the world's surface waters. We therefore hypothesize that aquatic ecosystems receiving significant inputs of POPs may exhibit a greater probability of experiencing CyanoHABs than nearby ecosystems that have a similar nutrient content but low POP loading. Because the formation of cyanobacterial blooms is multifactorial in nature, we strongly suggest that future water quality management efforts must focus on more than nutrient loading control alone to fully combat the expansion of undesirable CyanoHABs in the world's surface waters.

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Supplementary Material

Supplementary Material is available for download via the Inland Waters website, <https://www.fba.org.uk/journals/index.php/IW/article/viewFile/887>

Supplementary Tables 1 & 2